NMR (300 MHz, $CDCl_3$) δ 2.12 (s, 3 H), 2.15-2.52 (m, 4 H), 3.82 (s, 3 H), 3.86 (s, 3 H), 4.81 (t, 1 H, J = 8.7 Hz), and 5.14 (s, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 19.2, 20.2, 29.7, 52.2, 52.4, 65.0, 84.1, 97.8, 133.3, 148.6, 160.4, 161.9, 172.1, and 196.6; HRMS for $C_{14}H_{15}NO_7$, calcd 309.0848, found 309.0844.

Another fraction that was also isolated from the column was assigned as 1-acetyl-5-(hydroxyacetyl)-2-pyrrolidone (8%): mp 122-123 °C; IR (neat) 3450, 1745, 1692, 1290, and 1242 cm^{-1}; NMR (300 MHz, $CDCl_3$) δ 2.16 (dddd, 1 H, J = 13.4, 9.5, 4.0, and 3.2 Hz), 2.29 (dddd, 1 H, J = 13.4, 9.6, 9.4, and 9.3 Hz), 2.52 (s, 3 H), 2.60 (ddd, 1 H, J = 17.9, 9.3, and 4.0 Hz), 2.73 (ddd, 1 H, J = 17.9, 9.4, and 9.5 Hz), 3.18 (br s, 1 H), 4.44 (d, 1 H, J = 19.2 Hz), 4.51 (d, 1 H, J = 19.2 Hz), and 4.92 (dd, 1 H, J = 9.6 and 3.2 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) 19.3, 23.8, 31.4, 58.6, 66.0, 170.1, 173.8, and 206.6. Anal. Calcd for $C_8H_{11}NO_4$: C, 51.87, H, 5.99, N, 7.57. Found: C, 51.74, H, 5.81, N, 7.48.

Treatment of **52** with 1.2 equiv of dimethyl fumarate according to the standard procedure afforded a mixture of two cycloadducts. Chromatography of the crude reaction mixture using a 10-40% ethyl acetate-hexane mixture as the eluent afforded 6(*endo*),7(*exo*)-dicarbomethoxy-5-methyl-1,2,3,6,7,8,9,9a-octahydro-5*H*-pyrrolo[1,2-*a*]azepine-3,9-dione (**55**) as a colorless oil (30% yield): IR (neat) 1730, 1680, 1380, 1268, and 1177 cm^{-1}; NMR (300 MHz, $CDCl_3$) δ 1.81 (s, 3 H), 2.04-2.59 (m, 4 H), 3.65 (s, 3 H), 3.80 (s, 3 H), 3.98 (d, 1 H, J = 3.5 Hz), 4.07 (dd, 1 H, J = 9.4 and 3.5 Hz), 4.35 (dd, 1 H, J = 9.0 and 6.3 Hz), and 4.86 (d, 1 H, J = 9.4 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 17.8, 18.9, 30.4, 49.9, 52.0, 52.2, 53.2, 58.3, 82.0, 96.3, 170.2, 170.4, 173.4, and 205.4; HRMS for $C_{14}H_{17}NO_7$, calcd 311.1005, found 311.1006.

The second cycloadduct isolated from the column was assigned as 6(*exo*),7(*endo*)-dicarbomethoxy-5-methyl-1,2,3,6,7,8,9,9a-octahydro-5*H*-pyrrolo[1,2-*a*]azepine-3,9-dione (**56**) (12%): IR (neat) 1738, 1696, 1380, 1260, and 1174 cm^{-1}; NMR (300 MHz, $CDCl_3$) δ 2.10 (s, 3 H), 2.22-2.56 (m, 4 H), 3.34 (d, 1 H, J = 6.7 Hz), 3.46 (dd, 1 H, J = 6.7 and 2.3 Hz), 3.74 (s, 3 H), 3.77 (s, 3 H), 4.41 (dd, 1 H, J = 8.9 and 7.9 Hz), and 4.89 (d, 1 H, J = 2.3 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 19.6, 20.5, 30.8, 49.3, 52.3, 52.5, 56.2, 59.7, 82.0, 95.6, 168.6, 170.3, 172.6, and 204.8. Anal. Calcd for $C_{14}H_{17}NO_7$: C, 54.01, H, 5.51, N, 4.50. Found: C, 53.85, H, 5.36, N, 4.24.

Preparation and Rhodium-Catalyzed Reaction of *N*-Carbomethoxy-2-(2-diazoacetyl)indole (57). To a suspension containing 1.6 g of sodium hydride (50% mineral oil) in 40 mL of tetrahydrofuran was slowly added 3.2 g of indole-2-carboxylic acid. The resulting suspension was allowed to stir at room temperature for 3 h until no more hydrogen had evolved and the reaction mixture had become clear. To this mixture was added 3.2 mL of methyl chloroformate. The resulting solution was washed with a 1.0 N hydrochloric acid solution, dried over sodium sulfate, and concentrated under reduced pressure. The residue was treated with a diazomethane ether solution and after workup gave (diazoacetyl)indole **57** as a yellow solid in 65% yield: mp 101-102 °C; IR (KBr) 2100, 1750, 1610, 1545, 1455, 1400, and 1320 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 3.96 (s, 3 H), 5.74 (s, 1 H), 6.89 (s, 1 H), 7.22 (t, 1 H, J = 7.8 Hz), 7.37 (t, 1 H, J = 7.8 Hz), 7.52 (d, 1 H, J = 7.8 Hz), and 8.00 (d, 1 H, J = 7.8 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 53.7, 55.9, 113.1, 114.2, 121.6, 123.0, 126.4, 126.9, 135.7, 137.1, 150.8, and 179.0. Anal. Calcd for $C_{12}H_9N_3O_3$: C, 59.26; H, 3.73; N, 17.28. Found: C, 59.27; H, 3.76; N, 17.22.

Treatment of a 500-mg sample of diazo keto amide **57** in 5 mL of chloroform with a catalytic amount of rhodium acetate dimer in either the presence (1.2 equiv) or absence of dimethyl acetylenedicarboxylate gave rise to 1,2-dihydro-4',4'-dimethoxy-1,4-dioxo-2,1'-bi(4*H*-[1,3]oxazino[3,4-*a*]indole) (**58**) (56%): mp 145-146 °C; IR (neat) 1740, 1690, 1535, 1450, 910, and 750 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 3.99 (s, 3 H), 4.02 (s, 3 H), 5.46 (s, 1 H), 6.83 (s, 1 H), 6.95 (s, 1 H), 7.11-7.26 (m, 3 H), 7.39 (s, 1 H), 7.40-7.51 (m, 2 H), 7.69 (d, 1 H, J = 8.1 Hz), 7.92 (d, 1 H, J = 8.5 Hz), and 7.97 (d, 1 H, J = 8.1 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 52.6, 53.1, 82.5, 93.5, 109.8, 109.9, 110.7, 113.0, 115.0, 119.8, 121.7, 122.7, 122.9, 123.9, 126.3, 127.0, 128.9, 130.1, 132.2, 134.3, 135.0, 146.7, 151.9, and 180.2. Anal. Calcd for $C_{24}H_{18}N_2O_6$: C, 66.97; H, 4.22; N, 6.50. Found: C, 67.00; H, 4.25; N, 6.48.

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Supplementary Material Available: Final positional and thermal parameters (Tables I-X) for the X-ray crystal structures of compounds **18** and **20** (6 pages). Ordering information is given on any current masthead page.

Toward a Molecular-Size "Tinkertoy" Construction Set. Preparation of Terminally Functionalized [*n*]Staffanes from [1.1.1]Propellane

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Abstract: A facile but low-yield synthesis of [*n*]staffanes (the oligomers of [1.1.1]propellane **1**, n = 1-5) functionalized on one or both ends is described, and their properties are summarized. The substituents are $-COOCH_3$, $-n-C_4H_9$, $-C_6H_5$, -Br, -I, and $-SCOCH_3$, and their conversion to others, such as -COOH, $-COCH_3$ and -SH, is demonstrated. It is proposed that these rod-shaped molecules will be useful in the development of a molecular-size civil engineering construction set analogous to children's toy construction sets.

In preliminary communications[2,3] we identified the development of a molecular-size civil engineering construction set, analogous to the children's "Tinkertoy"[4] play set, as a long-term goal worthy of pursuit. The Tinkertoy set consists of straight rods and spoollike connectors (Figure 1). Its molecular analogue would offer a

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(2) (a) Kaszynski, P.; Michl, J. *J. Am. Chem. Soc.* **1988**, *110*, 5225. (b) Kaszynski, P.; Friedli, A. C.; Michl, J. The Third Chemical Congress of North America, Toronto, Canada, June 4-10, 1988, Book of Abstracts, ORGN 218, American Chemical Society: Washington, D.C., 1988. (c) The carbon atoms in each bicyclo[1.1.1]pentane cage of an [*n*]staffane are numbered in the usual way and primes are used to distinguish the individual cages.[3] For instance, the methylene positions in the terminal cages of [3]staffane are 2, 4, 5, 2'', 4'', and 5''; those on the internal cage are 2', 4', and 5'. A general position characterized by k primes is indicated by $2^{(k)}$, $4^{(k)}$, etc., following the usage common in mathematics, where a first derivative is labeled f', a second derivative f'', and an kth derivative, $f^{(k)}$.

(3) Michl, J.; Kaszynski, P.; Friedli, A. C.; Murthy, G. S.; Yang, H.-C.; Robinson, R. E.; McMurdie, N. D.; Kim, T. In *Strain and Its Implications in Organic Chemistry*; de Meijere, A., Blechert, S., Eds.; NATO ASI Series, Vol. 273; Kluwer: Dordrecht, 1989; p 463.

(4) Tinkertoy is a trademark of Playskool, Inc., Pawtucket, RI 02862, and designates a children's toy construction set consisting of straight wooden sticks and other simple elements insertable into spool-like connectors. The assembly of triangular trinuclear metal cluster units into polyhedra and stacks has been referred to as "Tinker-Toy" construction: Underwood, D. J.; Hoffmann, R.; Tatsumi, K.; Nakamura, A.; Yamamoto, Y. *J. Am. Chem. Soc.* **1985**, *107*, 5968. We use the expression in a related but different sense.

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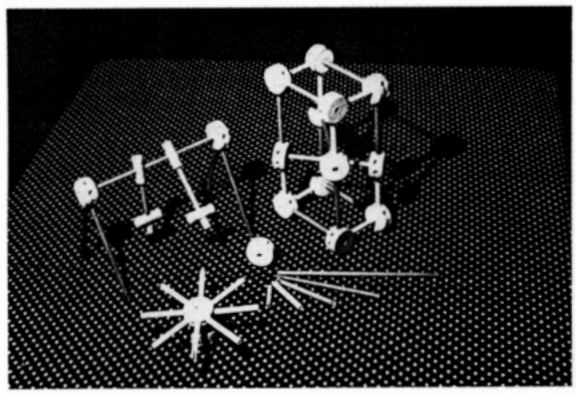

Figure 1. The rods and spools of the Tinkertoy[4] construction set.

versatile approach to the assembly of miniature engineering structures, free-floating or anchored to a surface. If a selection of sticks with arbitrary lateral substituents were available, a lattice derived from ordinary crystallographic lattices by insertion of spacers between lattice points could be prepared and would represent a macroscopic "designer solid", a controlled spatial array of preselected active groups at preselected points in space, carried by an inert covalent scaffolding. The active groups could be charged, polarizable, magnetic, light-absorbing and emitting, phototransformable, rigid or mobile, and they could act as electron donors or acceptors, etc., offering a wide range of applications for the resulting solids. The solid could be periodic in only two dimensions and of an aperiodic design in the direction normal to a base surface, totally controlled by a Merrifield-type layer-by-layer synthesis. Such material could resemble the aerogels[5] in its extremely low density, but, unlike these, it would possess a regular and controlled structure. Mechanical strength could be enhanced by filling with a suitable monomer followed by polymerization. Controlled aperiodic composition in two or even three dimensions could possibly be accomplished by construction starting with a line or a point instead of a surface. We see no reason why far more complex structures and moving machinery could not be assembled from the same construction elements eventually, and it does not take much imagination to foresee a surface covered with molecular-size swings or windmills generating electromagnetic radiation in response to a jet of gas ("molecular mobiles").

Civil[6] and electrical[7] engineering with individual molecules ("nanotechnology"[8]) have been the subjects of intense speculation but so far have not progressed very far in practice.[9] One of the many difficulties has been the unavailability of suitable molecular building blocks. We now provide full details of our synthesis of a set of end-functionalized straight construction elements based on the radical oligomerization of [1.1.1]propellane (**1**) to the oligo[1.1.1]propellane structures [*n*]**1**, for which we have introduced[2] the name [*n*]staffanes. Preliminary reports of some of our preparations of functionalized[2,3,10-12] and the parent[13] staffanes have already appeared.

Although we are not aware of prior attempts to make available closely controlled molecular "chestnut and toothpick" construction sets of the kind we have begun to develop, certainly chemists have been interested in rigid-rod molecules as well as in the design and control of molecular interactions and solid structures for a long time. Without any claim to completeness, we list a few of the conspicuous publications on the former[14-18] and the latter[19-22] subjects. Some of the recent crystal engineering work[19,22] is particularly kindred in spirit to our own efforts,[2,3] except that we are primarily interested in building intricate objects on a nanometer scale and solids that are aperiodic in at least one direction, rather than crystals with extensive three-dimensional periodicity.

The oligomers of propellanes are an obvious first choice for molecular Tinkertoy rods. [1.1.1]Propellane (**1**), [2.2.2]propellane (**2**), and 1,4-didehydrocubane (**3**) can be viewed as the parents of the oligomeric series named [*n*]staffanes [*n*]**1**, [*n*]rodanes [*n*]**2** (in adaptation of Zimmerman's original proposal[14]), and polycubyls [*n*]**3**, respectively. Like two other obvious choices, the carbynes [*n*]**0** and the polyarylenes exemplified by [*n*]**4**, these structures are intrinsically linear, including the end substituents. Unlike [*n*]**0** and [*n*]**4**, they are formally saturated and transparent in the visible and UV regions, thus facilitating the anticipated communication with the active groups in designer solids, and are far more likely to be electrically insulating. Also unlike [*n*]**0** but like [*n*]**4**, they are more likely to be relatively inert to oxidation and thermally stable. They offer good opportunities for the attachment of side substituents. The high strain-energy content of the structures [*n*]**1** and [*n*]**3**, about a dozen kcal/mol per C–C bond, adds additional interest to the exploration of their chemistry. Many mixed series of cooligomers such as [*l*,*m*,*n*]**5** and [*l*,*m*,*n*]**6** can also be envisaged, offering a finer gradation of lengths. We realize that any advanced construction set should also contain flat elements characteristic of children's "Lego" construction sets,[23] but we initially restrict our attention to simple rods.

The advantages offered by oligopropellanes as molecular spacers have not escaped attention and indeed [*n*]**2**, $n = 1$ and $n = 2$, have seen past use in studies of energy and electron transfer.[14,24] Higher

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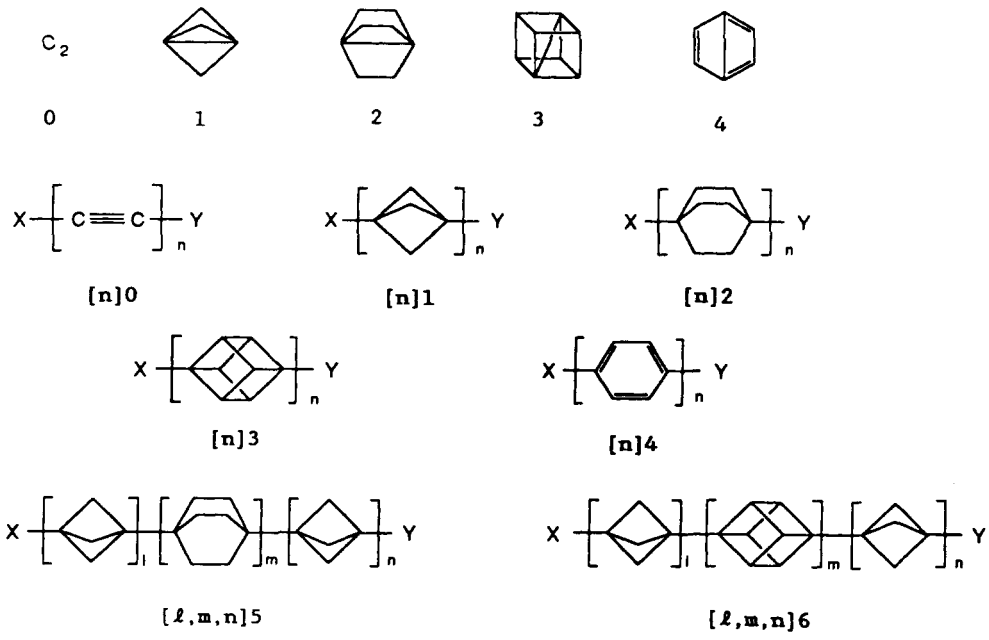
Chart I



	X	Y
a:	H	COOH
b:	H	COOMe
c:	H	CHMeOEt
d:	COOMe	COOMe
e:	COCl	COOMe
f:	COPh	COPh
g:	COOH	COOH
h:	COPh	COOMe
i:	OCOPh	OCOPh
j:	COMe	COMe
k:	*n*-Bu	I
l:	*n*-Bu	COMe
m:	*n*-Bu	COOH
n:	Ph	I
o:	Ph	COMe
p:	Ph	COOH
q:	Ph	COOMe
r:	COOH	COOMe

	X	Y
s:	I	I
t:	CN	Br
u:	Br	Br
v:	*t*-Bu	Br
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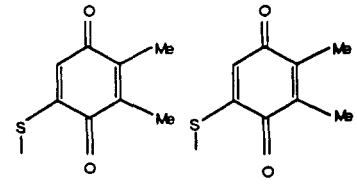
cc:		
dd:	H	H
ee:	H	CCl_3

members of the series [*n*]**2** have not been reported in the literature but have been synthesized in Zimmerman's laboratory.[25] The first report of a member of the polycubyl series [**2**]**3**, carrying a single substituent, has appeared,[26] and work on higher members of the series is underway in Eaton's laboratory.[27] Elsewhere, we reported our own efforts to prepare **3** and also the syntheses of a singly functionalized member of the series [*n*]**3**[28] and of some

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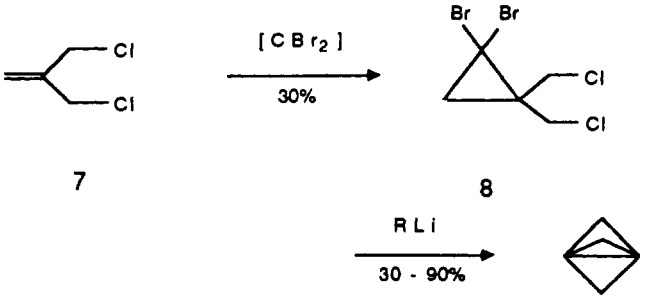
members of the mixed series [*l*,*m*,*n*]**5** and [*l*,*m*,*n*]**6**.[29]

Although not a high-yield process, the synthesis of the [*n*]staffane derivatives [*n*]**1** is short and facile. In contrast to **2** and **3**, Wiberg and Walker's[30] simplest propellane **1** is accessible from a cheap commercially available material in two easy steps developed in the laboratory of Szeimies.[31,32] Addition of dibromocarbene to methallyl dichloride (**7**) yields the tetrahalide **8** and this is converted with alkyllithium to **1**. This synthesis lends itself to scale-up.[33,34]



7 8 1

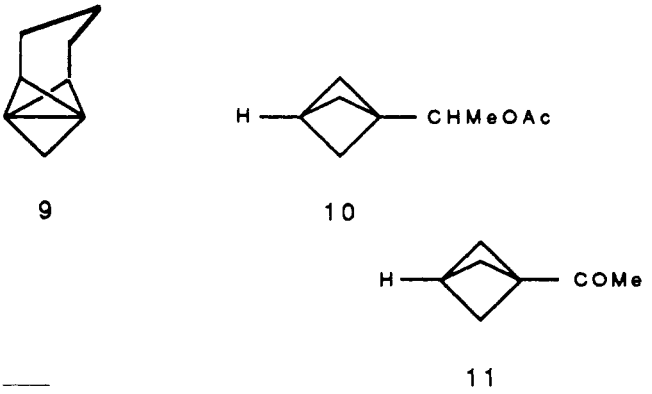
The feasibility of radical addition across the central bond of **1** was noted soon after its initial preparation, and, in a reaction with cyanogen bromide, the first formation of a dimer and a trimer was observed.[35,36] This particular reaction partner has not been of preparative value on a larger scale in our hands so far, but we have found that other radical telomerizing reagents provide better overall yields of purified products.

Presently, we describe additions across C–H, C–C, C–I, C–Br, and S–S bonds. Usually no single oligomer dominates, but this is not detrimental at this time as long as they can be separated, since all of them are desired. The overall yields of the purified oligomers are low, and considerable improvement may be possible by use of high-performance liquid chromatography. However, even the small amounts of products presently available are useful for a variety of purposes, and we believe that the intrinsic interest of the new compounds warrants a publication at this time.

Several oligomers [*n*]**1**, X = Y = SR and SO_2R, have also been independently isolated and characterized in the laboratory of Szeimies.[32,37] To our knowledge, the first claimed [*n*]staffane derivative was 3,3′-diphenyl[2]staffane, prepared by a different route.[38a] When we repeated this work in $CHCl_3$, we obtained 1-phenylbicyclo[1.1.1]pentane instead. The spectral properties of independently prepared 3,3′-diphenyl[2]staffane[38b] differed from those reported.[38a]

We have also reported the anion-induced and radical-induced formation of an insoluble polymer from the parent propellane **1** and its structure and properties.[2] More recently, Schlüter has reported that a polymer of identical properties also results from spontaneous polymerization of neat **1**,[39] and methods for production of a polymer with terminal hydrogens have been developed in our laboratory.[13,40] The formation and isolation of oligomers, up to *n* = 3, from a more complicated [1.1.1]propellane **9**[41] and its anion-induced polymerization[42] have also been reported.

The feasibility of organolithium-induced polymerization, and of addition of Grignard reagents[32] across the strained central bond to yield monomeric adducts, suggests nucleophile-induced oligomerization as a viable alternative to radical-induced conversion of **1** into functionalized [*n*]staffanes ([*n*]**1**). Unfortunately, a closer examination revealed that such nucleophile-induced oligomerization is quite complex, as will be reported separately.[43]



9 10 11

Results and Discussion

Synthesis of End-Functionalized [n]Staffanes by Radical-Induced Oligomerization. **[1.1.1]Propellane (1).** The procedure[33] we use for the preparation of ether-containing solutions of this starting material is a scaled-up version of that originally reported by Szeimies[31,32] and modified by Wiberg,[36] who introduced the use of methyllithium in the second step.

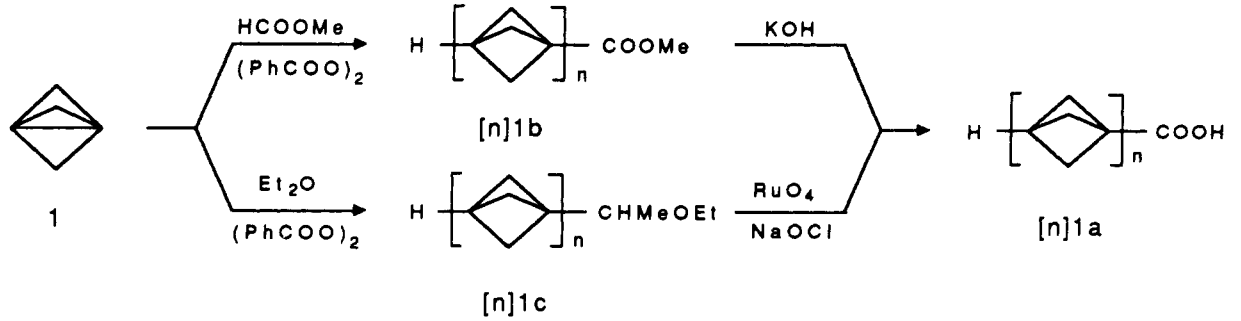
In some of the radical addition reactions, the presence of diethyl ether is detrimental. However, in the absence of a complexing agent, the reaction of **8** with alkyllithium reagents does not give acceptable yields of **1**. Since it is difficult to separate diethyl ether from **1** by distillation completely, we have developed a variant of the Szeimies synthesis of **1** in which ether is replaced by *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TMEDA),[2] and we now provide a detailed description. An alternative procedure has been recently reported from the laboratory of Szeimies.[34] In all of our synthetic work, solutions of **1**, from 0.1 M up to about 3 M in concentration, were used for further steps without isolation.

In our hands, large-scale synthesis of the tetrahalide precursor **8** from methallyl dichloride **7** proceeds in only about 30% yield of pure material, and we have not been able to reproduce the originally reported[31] 45% yield. Our results are more consistent with the more recent report of 35%.[34] On the basis of the yields of isolated final products, the yields of **1** from **8** are about 70% in the presence of ether, in agreement with literature,[37] and only about 30–35% in its absence. This difference is very important for the overall yields of the desired staffane derivatives, at least until a higher yield access to pure ether-free **1** is developed. We state explicitly for each oligomerization reaction below whether the presence of ether is tolerated.

[*n*]Staffane-3-carboxylic Acids [*n*]1a. The acids were obtained first, by the reaction of **1** with methyl formate in the absence of ether to yield the esters [*n*]**1b**, followed by hydrolysis,[2] and, more recently, by the reaction with diethyl ether to yield [*n*]**1c**, followed by oxidation. The oligomers can be separated either before or after the oxidation. Yields of the acids in this synthesis vary from

(28) Hassenrück, K.; Radziszewski, J. G.; Balaji, V.; Murthy, G. S.; McKinley, A. J.; David, D. E.; Lynch, V. M.; Martin, H.-D.; Michl, J. *J. Am. Chem. Soc.* **1990**, *112*, 873.
(29) Hassenrück, K.; Murthy, G. S.; Lynch, V. M.; Michl, J. *J. Org. Chem.* **1990**, *55*, 1013.
(30) Wiberg, K. B.; Walker, F. H. *J. Am. Chem. Soc.* **1982**, *104*, 5239. Wiberg, K. B. *Chem. Rev.* **1989**, *89*, 975.
(31) Semmler, K.; Szeimies, G.; Belzner, J. *J. Am. Chem. Soc.* **1985**, *107*, 6410.
(32) Szeimies, G. In *Strain and Its Implications in Organic Chemistry*; de Meijere, A., Blechert, S., Eds.; NATO ASI Series, Vol. 273; Kluwer: Dordrecht, 1989; p 361.
(33) Kaszynski, P.; Michl, J. *J. Org. Chem.* **1988**, *53*, 4593.
(34) Belzner, J.; Bunz, U.; Semmler, K.; Szeimies, G.; Opitz, K.; Schlüter, A.-D. *Chem. Ber.* **1989**, *122*, 397.
(35) Wiberg, K. B.; Waddell, S. T.; Laidig, K. *Tetrahedron Lett.* **1986**, *27*, 1553.
(36) Wiberg, K. B.; Waddell, S. T. *J. Am. Chem. Soc.* **1990**, *112*, 2194.
(37) Bunz, U.; Polborn, K.; Wagner, H.-U.; Szeimies, G. *Chem. Ber.* **1988**, *121*, 1785.
(38) (a) Patrick, T. B.; Johri, K. K.; White, D. H.; Bertrand, W. S.; Mokhtar, R.; Kilbourn, M. R.; Welch, M. J. *Can. J. Chem.* **1986**, *64*, 138. (b) ^{1}H NMR δ 1.93 (s, 12 H), 7.21–7.32 (m, 10 H); EIMS; *m*/*z* 286 (M, 1); HRMS, *m*/*z* (calcd for $C_{22}H_{21}$ 285.1643) 285.1650; mp 221–222 °C. Friedli, A. C. Ph.D. Dissertation, University of Texas, 1992.
(39) Schlüter, A.-D. *Polymer Commun.* **1989**, *30*, 34.
(40) Murthy, G. S.; Hassenrück, K.; Lynch, V. M.; Michl, J., unpublished results.
(41) Belzner, J.; Szeimies, G. *Tetrahedron Lett.* **1987**, *28*, 3099.
(42) Schlüter, A.-D. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 296. Schlüter, A.-D. *Macromolecules* **1988**, *21*, 1208.
(43) Morrison, R. W.; Michl, J., unpublished results.

Scheme I



run to run. The highest overall multistep yield of materials of better than 99% purity was 16% of **[1]1a**, 11% of **[2]1a**, 4.5% of **[3]1a**, 3% of **[4]1a**, and 1.5% of **[5]1a**, based on **8**.

The oxidation of the ether adducts **[*n*]1c** to the acids **[*n*]1a** can be carried out as a one-pot reaction or with intermediate isolation of a crude mixture of acetates and methyl ketones (formed in an about 1:2 ratio). In the case of $n = 1$ these intermediates, **10** and **11**, have been isolated.

In the presence of 20% of diethyl ether, the reaction with methyl formate produces a mixture of both series of oligomers, the diethyl ether adducts **[*n*]1c** and the methyl formate adducts **[*n*]1b**, in a ratio of about 2:1.

In both oligomerization reactions, a significant amount of unseparated higher oligomers remains as an insoluble residue. To optimize the yield of the lower oligomeric ether adducts, quite dilute ethereal solutions were used. The relatively low-molecular weight highly crystalline "polymer" was identified[2a] as poly-[1.1.1]propellane by CP MAS ^{13}C NMR.

The first five acids **[*n*]1a** and esters **[*n*]1b** ($n = 1$–5) and the first two diethyl ether adduct intermediates **[*n*]1c** ($n = 1, 2$) were isolated in pure state by taking advantage of the decreasing volatility and solubility with increasing degree of oligomerization.

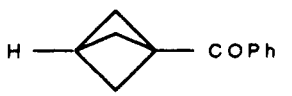
Dimethyl [*n*]Staffane-3,3$^{(n-1)}$-dicarboxylates [*n*]1d via Chlorocarbonylation of Methyl [*n*]Staffane-3-carboxylates. Double end-functionalization was achieved by photochemical chlorocarbonylation of the monoesters **[*n*]1b** with oxalyl chloride,[2] inspired by the previously reported[44] chlorocarbonylation of bicyclo[1.1.1]pentane. Subsequent reaction with methanol converted the ester chlorides **[*n*]1e** to the diesters **[*n*]1d**.

Typically, several regioisomers are formed. In the lower oligomers, the chlorocarbonylation occurs preferentially at the free bridgehead position, and **[2]1d** was readily isolated in 10% yield as the major product from **[2]1b**. However, as the ratio of methylene to methine groups increases upon going to the higher oligomers, the relative yield of the doubly end-functionalized diester **[*n*]1d** drops, and the separation of the regioisomers becomes more difficult. Thus, **[3]1b** was converted to a ~2:1 mixture of **[3]1d** with other isomers, and the process appears impractical for the higher members of the series. An attempt to increase the regioselectivity by the use of oxalyl bromide failed due to its insufficient reactivity.

Our efforts to achieve photochemical functionalization of the methyl esters **[2]1b** with biacetyl under conditions described for the acetylation of adamantane and its derivatives[45] gave only unreacted starting material. Also the attempted coupling reaction[46] of two molecules of **[2]1b** using *tert*-butyl peroxide failed. All of these results are in line with the report[47] that the bridgehead hydrogen atoms of bicyclo[1.1.1]pentane are very difficult to abstract, more so than those of cyclopropane, and that hydrogen abstraction from the bridges is harder still.

Dimethyl [*n*]Staffane-3,3$^{(n-1)}$-dicarboxylates [*n*]1d via Addition of Benzil to 1. A more general route to doubly end-functionalized diacids resulted from an investigation[33,48] of the reactivity of bicyclo[1.1.1]pent-1-yl radicals with carbonyl compounds. We now find that the addition of benzil to **1** produces low yields of >99% pure 3,3$^{(n-1)}$-dibenzoyl[*n*]staffanes **[*n*]1f**, even in the presence of ether (1.7–4.5%, 2.3–3.8%, 0.5–0.7%, and 0.1% based on **8**, for $n = 1, 2, 3$, and 4, respectively). The low yields are due at least in part to a rapid buildup of an insoluble film on the walls of the immersion photochemical apparatus used and contain no correction for the 20–80% of unreacted **1** which can be recovered and reused. The reaction presumably proceeds by the mechanism proposed[33] for the addition of biacetyl to **1**.

Compounds **12** and **13** were isolated as byproducts of the oligomerization. The thermal decomposition product from **12** has been isolated and identified as **14**.



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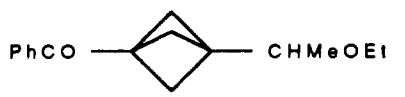
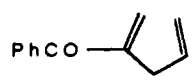


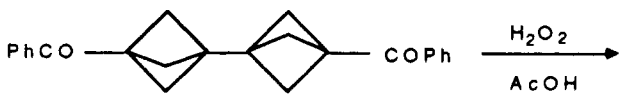
13



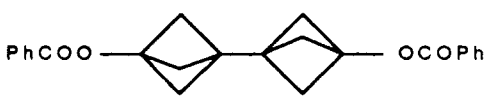
14

The diketones **[*n*]1f** were oxidized with RuO_4/NaOCl to the diacids **[*n*]1g**, which were converted to their dimethyl esters **[*n*]1d** with diazomethane. The oxidation is slow, offering access to the intermediate keto acids. This was demonstrated on the second member of the keto acid series, isolated as the methyl ester **[2]1h**.

Baeyer–Villiger oxidation of **[2]1f** yielded the dibenzoate **[2]1i** smoothly, indicating that the diketones will also serve as precursors for [*n*]staffane-3,3$^{(n-1)}$-diols.



[2]1f

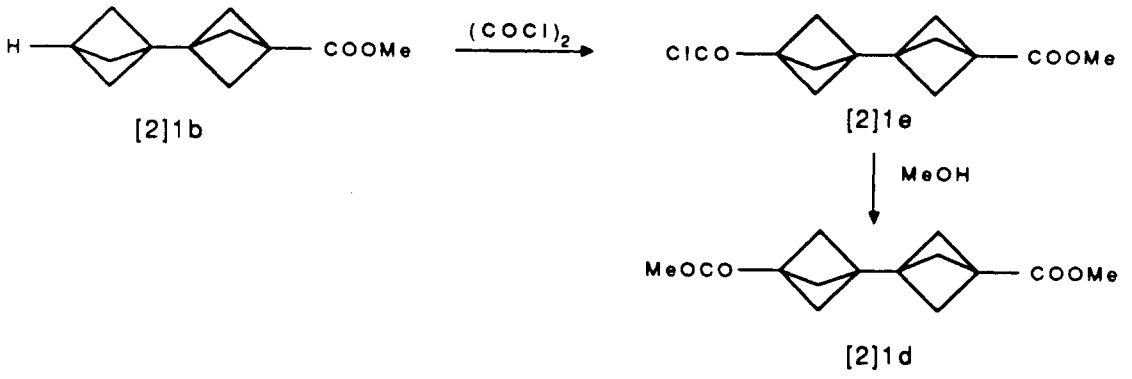


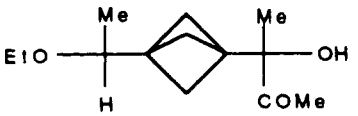
[2]1i

The orientation of the oxidation is noteworthy since a dibenzoylcubane derivative has been reported to yield a derivative of a diphenyl cubanedicarboxylate.[49] Sterically, and with respect to hybridization, the bridgehead carbon atom of cubane and bicyclo[1.1.1]pentane are very similar.

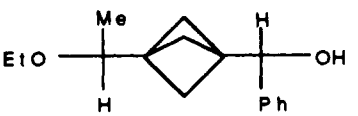
(44) Wiberg, K. B.; Williams, V. Z., Jr. *J. Org. Chem.* **1970**, *35*, 369.
(45) Fukunishi, K.; Kohno, A.; Kojo, S. *J. Org. Chem.* **1988**, *53*, 4369, and references therein.
(46) Johnston, K. M.; Williams, G. H. *J. Chem. Soc.* **1960**, 1168.
(47) Maillard, B.; Walton, J. C. *J. Chem. Soc., Chem. Commun.* **1983**, 900.
(48) Kaszynski, P.; McMurdie, N. D.; Michl, J. *J. Org. Chem.* **1991**, *56*, 307.
(49) Eaton, P. E.; Higuchi, H.; Millikan, R. *Tetrahedron Lett.* **1987**, *28*, 1055.

Scheme II

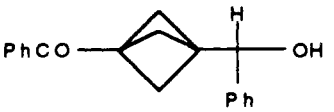




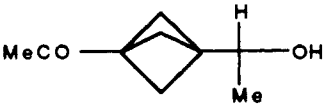
17



18

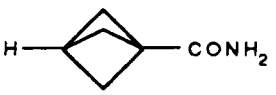


19



20

Bauer–Haller degradation of **12** with sodium amide yielded the carboxamide **15** as the only product in fair yield, suggesting an alternative route from the diketones [*n*]**1f** to the diacids [*n*]**1g** if the regioselectivity of the cleavage is general.



15

16

Reactions of other carbonyl compounds with **1** were investigated briefly. 1-Phenylpropane-1,2-dione reacted with **1** to give the expected statistical mixture of the three products [**1**]**1f**, **16**, and [**1**]**1j**. It is already known[33] that [**1**]**1j** is the sole product from addition of biacetyl to **1**. Reaction of methyl pyruvate with **1** in ether gave exclusively the product **17**, where the bridgehead substituents arise from methyl pyruvate and diethyl ether.

Aldehydes that contain less activated carbonyl groups also reacted with **1** and gave products in which the bridgehead substituents were derived either from the carbonyl compound alone or both from the carbonyl compound and a third reaction partner. For instance, benzaldehyde gives both types of products, **18** and **19**, in diethyl ether or only **19**[36] in its absence, whereas acetaldehyde produces only **20**.[33,35,36]

These results suggest the mechanism outlined in Scheme IV. The initially formed oxy radical **21** can react via one of two routes depending on (i) its fragmentation propensity, (ii) the hydrogen atom donor strength of the carbonyl compound, and (iii) the hydrogen atom donor strength of the solvent. Examples of products resulting from the first route (A) are **17** and **18**, (RH = solvent) as well as **19** and **20** (RH = carbonyl reagent). An example of a product from the second route (B) is [**1**]**1j**. The relatively high nucleophilicity of the bridgehead bicyclo[1.1.1]-pent-1-yl radical has been used in synthesis of other derivatives of bicyclo[1.1.1]pentane.[12,48]

Aliphatic aldehydes other than acetaldehyde did not react with **1** under our conditions. However, pivalaldehyde and isobutyraldehyde have been reported[36] to react with neat **1**, giving complex mixtures of products. Carbonyl compounds such as esters, thioesters, or amides are apparently not electrophilic enough and did not react with bicyclo[1.1.1]pent-1-yl radicals under our conditions.

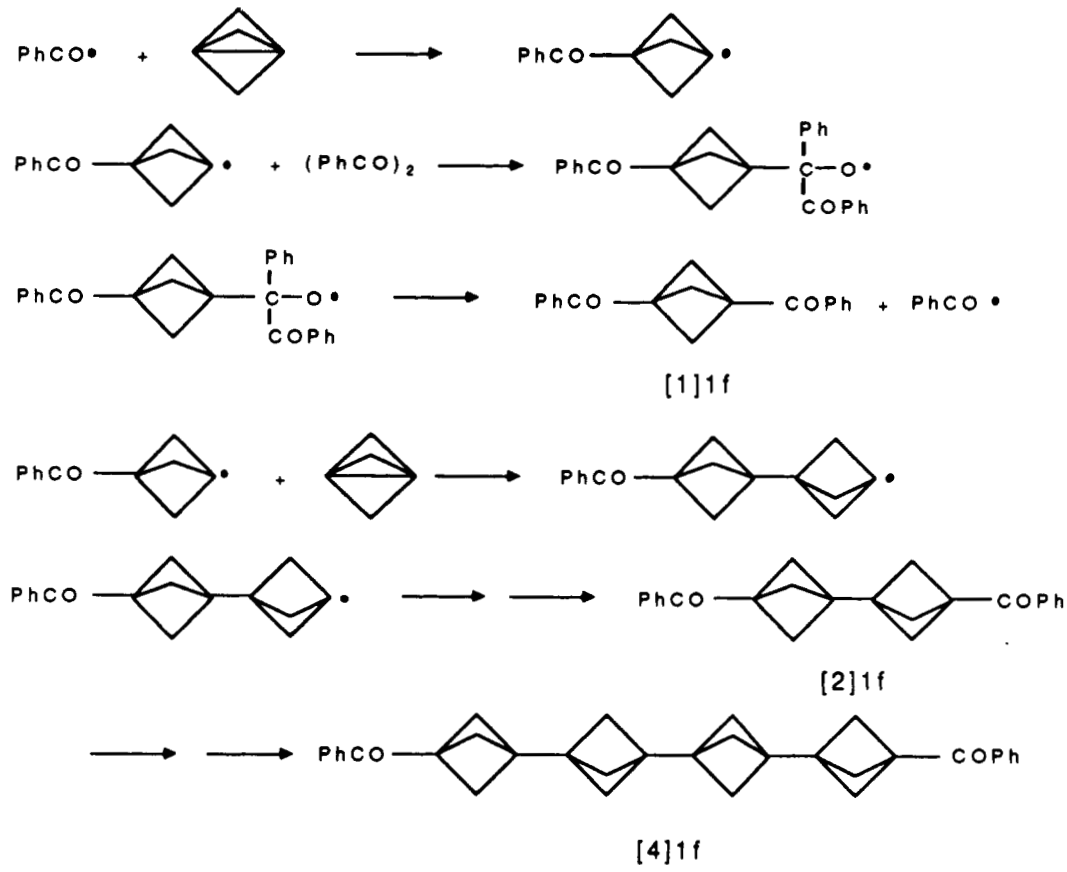
Photoinduced Oligomerizing Addition of [1.1.1]Propellane to Organic Halides. Iodides. Thermal additions of **9** to methyl and ethyl iodides[41] as well as photochemically induced reactions of **1** with other alkyl C–I bonds in ether solvent[48] yield monomeric adducts. A few additional examples of reactions that yielded monomeric products are described in the Experimental Section. The addition, coupled with radical-induced transformations[48] of the bridgehead iodides, constitutes a general synthetic method for the insertion of an [*n*]staffane unit between an alkyl group and a fragment derived from an electron-deficient double bond (e.g., a Michael acceptor and an activated carbonyl compound). In this sense, **1** acts as a synthetic equivalent of the [*n*]staffane-3,3$^{(n-1)}$-diyl dianion **22**, in a generalization of a claim previously made[48] for the case of $n = 1$.

22

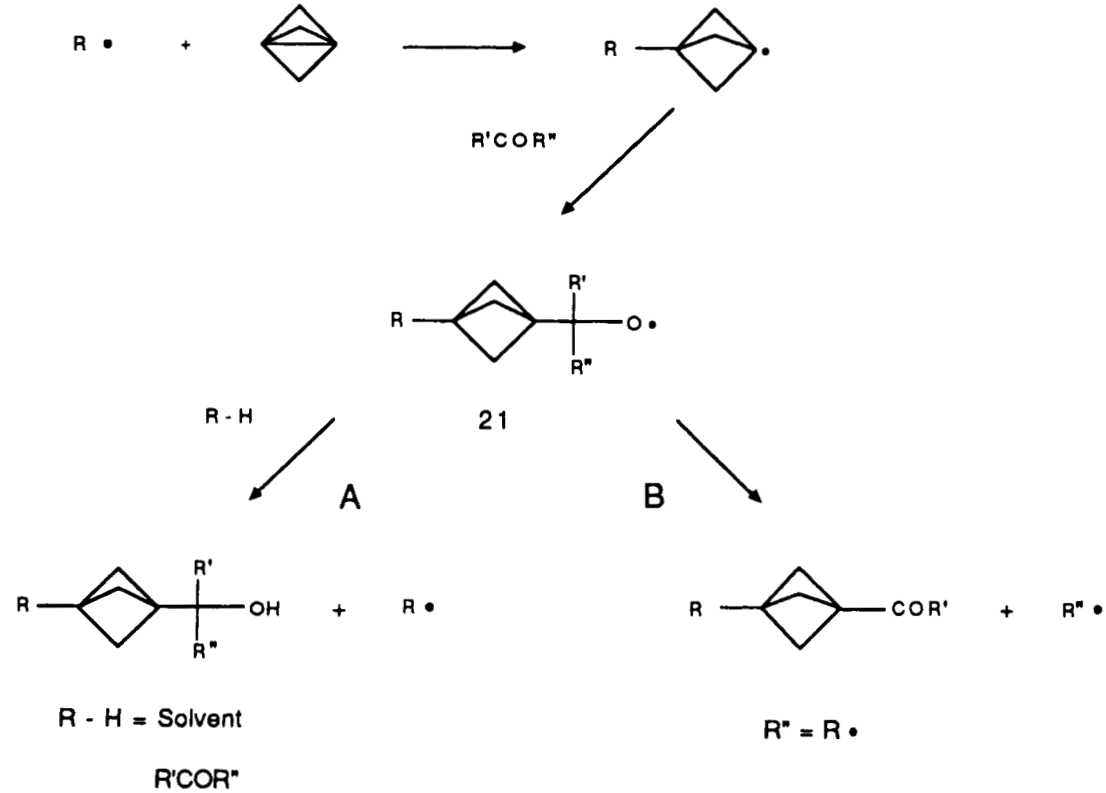
The relatively unstable bridgehead iodides [*n*]**1k** obtained by photochemical addition of **1** to *n*-butyl iodide in pentane have been converted to the methyl ketones [*n*]**1l**, and the first five ketones have been separated. The overall multistep yields were 4.3% of [**1**]**1l**, 5.3% of [**2**]**1l**, 2.7% of [**3**]**1l**, 1.3% of [**4**]**1l**, and 0.2% of [**5**]**1l** based on **8** (Scheme V). Formation of some oligomers has been observed even in ethereal solutions at higher concentrations of **1**, using less than 1 equiv of butyl iodide.[43] The first three ketones have been oxidized to 3$^{(n-1)}$-*n*-butyl[*n*]staffane-3-carboxylic acids [*n*]**1m**, of interest as liquid crystals and surfactants.[12,50]

(50) Liquid crystals: Kaszynski, P.; Otteson, D.; Michl, J., 13th International Liquid Crystals Conference, Vancouver, B. C., July 22–27, 1990. Book of Abstracts SYN-46. Surfactants: Friberg, S. E.; Kayali, I.; Kaszynski, P.; Michl, J. *Langmuir*, in press.

Scheme III



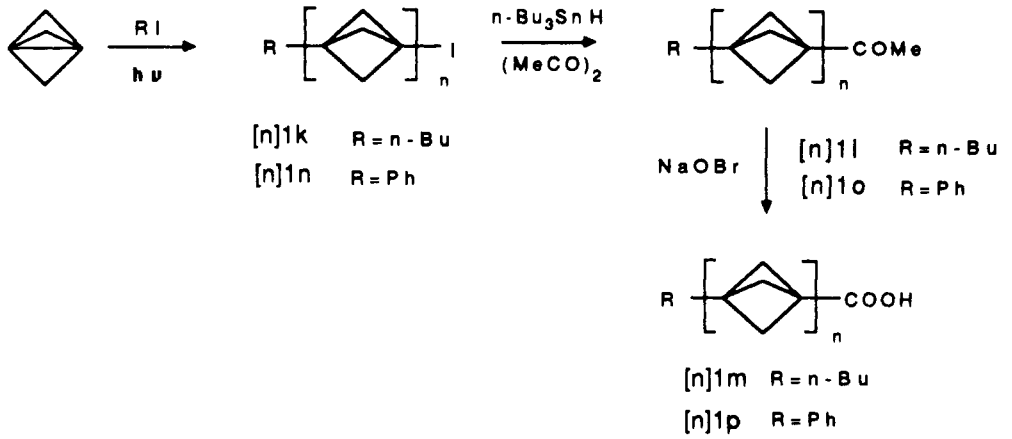
Scheme IV



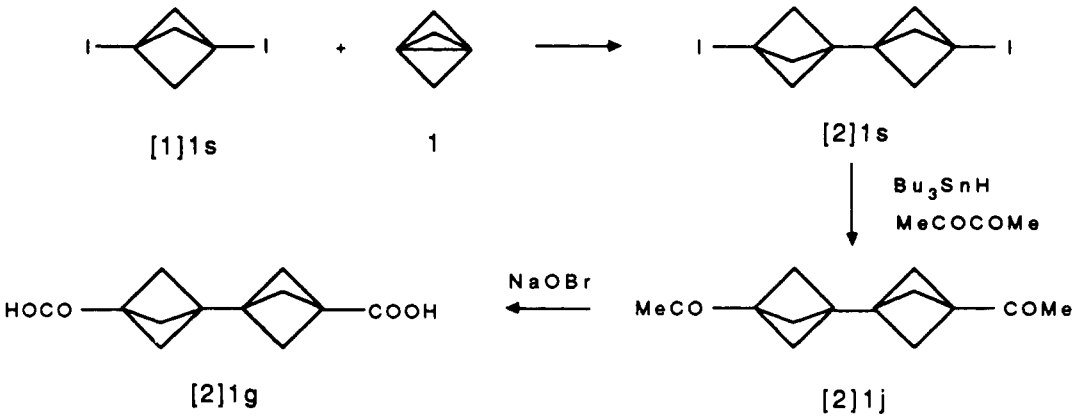
Aryl iodides are less well suited for the [*n*]staffane insertion reaction. Several were tried, but only iodobenzene in pentane yielded an oligomeric series at all.[12] This low-yield reaction provides access to an interesting group of [*n*]staffane derivatives. However, it requires the use of high propellane concentrations and is subject to the same problem with polymer film buildup as the reaction of **1** with benzil.

The oligomeric addition products of iodobenzene, **[*n*]1n**, have been converted into the methyl ketones **[*n*]1o**, which have been isolated individually but more commonly were oxidized to the acids

Scheme V

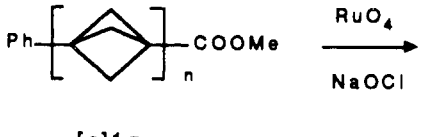


Scheme VI



[*n*]**1p**, and these were isolated individually in the form of the methyl esters [*n*]**1q**. In a typical case, overall multistep yields of high-purity products were 3.9% of [**1**]**1q**, 1.8% of [**2**]**1q**, 0.2% of [**3**]**1q**, plus about 0.04% of slightly impure [**4**]**1q**, all based on **8** and corrected for recovered **1** in pentane. Sometimes, the yields of oligomers were up to twice higher.

Lithiation, followed by carboxylation[51] of [**1**]**1n** provides a viable alternative preparation of [*n*]**1p**. Ruthenium tetroxide oxidation[52] of the phenyl substituent in [*n*]**1q** to a second carboxyl group in [*n*]**1r** is surprisingly difficult for $n > 1$, and the route to the diacid [**2**]**1g** via the diiodide [**2**]**1s** described below is distinctly superior.



The insertion of **1** into a C–I bond at the bridgehead position of bicyclo[1.1.1]pentane cage in effect constitutes an extension of an [*n*]staffane into an [*n*+1]staffane. Unfortunately, it appears to be less general than the insertion of **1** into the C–I bonds of ordinary alkyl iodides. For instance, [**1**]**1s** has been converted cleanly to the diiodide [**2**]**1s** by irradiation with an excess of **1** in pentane,[53] but no further conversion to [**3**]**1s** is observed. The diiodide was converted to the diketone [**2**]**1j** by reaction with biacetyl in the presence of tri-*n*-butyltin hydride and further into the diacid [**2**]**1g** in an overall yield of 8% based on **8**. Basic hydrolysis of the dimethyl ester provides the monoacid [**2**]**1r**, easily isolated in a 52% yield.

Irradiation of **1** in the presence of the bridgehead iodide [**1**]**1k** provided an oligomeric series of iodides [*n*]**1k** isolated as the ketones [*n*]**1l** after reaction with biacetyl, in the following yields based on [**1**]**1**: 27% of [**1**]**1l**, 12% of [**2**]**1l**, 4.7% of [**3**]**1l**, and 1.4% of [**4**]**1l**.

Under similar experimental conditions, oligomerization of **1** in the presence of the iodide [**1**]**1n** produced a very low yield of the series of iodides [*n*]**1n**, which were converted to a mixture of the ketones [*n*]**1o** in an approximate ratio of 20:7:3:1 as determined by GC analysis.

Bromides. With the single exception of cyanogen bromide, which yields the oligomeric series [*n*]**1t**,[35,36] the previously known reactions of bromides with **1**[35,36,48,54] or **9**[41] involve the insertion of a single bicyclo[1.1.1]pentane cage. Our search[2,3] for conditions that lead to oligomerization initially produced some monomeric adducts, and, in the cases of benzyl bromide and, particularly, allyl bromide,[48] the dimer[3,53,54] [**2**]**1u**.

We now find that *tert*-butyl bromide reacts with **1** in ether to form the series [*n*]**1v** up to $n = 5$. Due to the fragility of the higher oligomers, only the first two members were isolated. An oligomeric series [*n*]**1w** also resulted from the reaction of **1** in pentane with ethyl bromoacetate, which was previously reported[48] to form only the monomeric adduct in diethyl ether in good yield. The products were reduced with tri-*n*-butyltin hydride and the first three esters

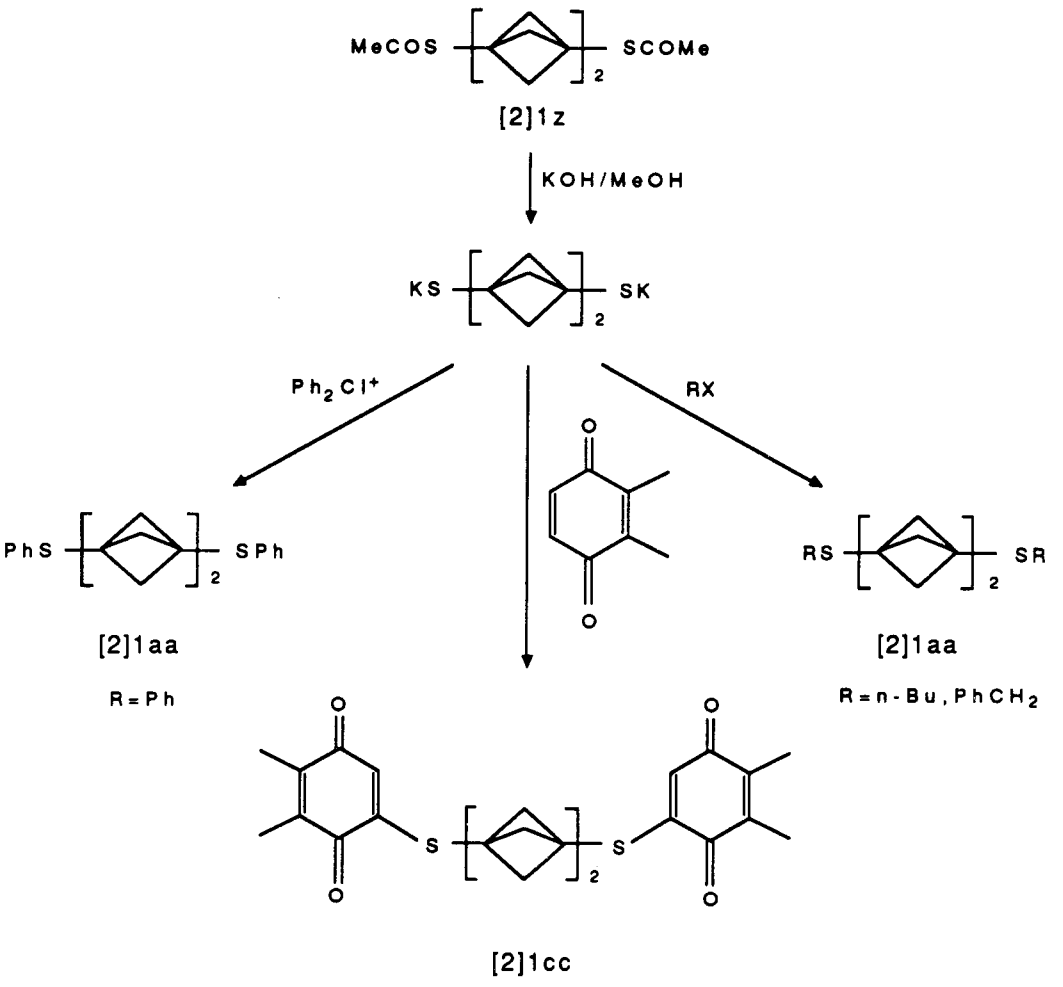
(51) Della, E. W.; Hemakanthi, G.; Pigou, P. E. *J. Org. Chem.* **1988**, *53*, 592.

(52) Applequist, D. E.; Renken, T. L.; Wheeler, J. W. *J. Org. Chem.* **1982**, *47*, 4985.

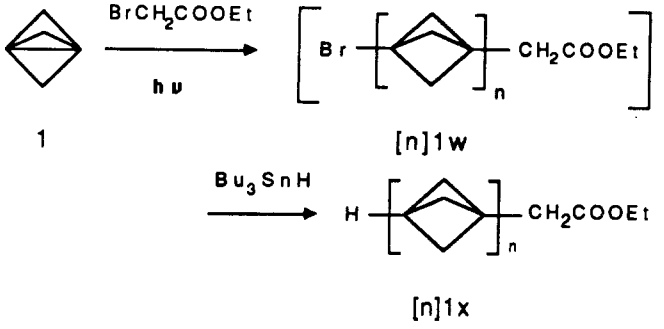
(53) Blokhin, A. V.; Tyurekhodzhaeva, M. A.; Sadovaya, N. K.; Zefirov, N. S. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1989**, 1933.

(54) Gleiter, R.; Pfeifer, K.-H.; Szeimies, G.; Bunz, U. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 413.

Scheme VII



[*n*]**1x** were isolated. The overall multistep yields were 2.7% of [**1**]**1x**, 4.4% of [**2**]**1x**, and 2.0% of [**3**]**1x**, based on **8**.



The reactivity of the bridgehead bromides is more limited than that of bridgehead iodides, and thus they are not suitable for preparation of doubly end-functionalized [*n*]staffanes. Only reduction with tri-*n*-butyltin hydride[48] and lithiation with *tert*-butyllithium[51] followed by carboxylation have been reported.

Chlorides. Oligomerizations of **1** with 1,1,1-trichloroethane[55] and carbon tetrachloride[35,36,41,56] gave adducts up to $n = 3$, but *tert*-butyl hypochlorite[35,36] formed only a monomer. The addition of sulfonyl chlorides to **1** in ether represents a relatively high-yield path to [**1**]**1y** and [**2**]**1y**.[3,57] In general, however, the bridgehead chlorides are too inert to be of much synthetic use.[48]

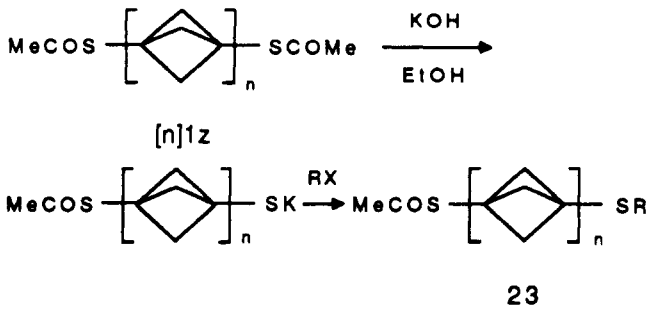
3,3$^{(n-1)}$-Bis(acetylthio)[*n*]staffanes [*n*]1z. As described in preliminary reports,[2,3,10-12] the addition of **1** to diacetyl disulfide yields a readily separable mixture of at least five oligomers [*n*]**1z** and proceeds cleanly even in the presence of diethyl ether and methyl bromide. The overall multistep yields of adducts of better than 99% purity were 2.7% of [**1**]**1z**, 14.4% of [**2**]**1z**, 2.6% of [**3**]**1z**, 0.3% of [**4**]**1z**, and 0.05% of [**5**]**1z**, based on **8**. At low concentrations of diacetyl disulfide, the ether adducts [*n*]**1c** are formed as well but are readily separated since they are much more soluble in alcohol.

Hydrolysis of [*n*]**1z** to the dithiols [*n*]**1aa** (R = H) is essentially quantitative. Their subsequent synthetic manipulation is straightforward, and several examples are given in Scheme VII. These steps can be performed either before or after oligomer separation.

The bisalkylthio derivatives [*n*]**1aa** (R = alkyl) can be obtained in a one-pot procedure from [*n*]**1z** by hydrolysis and alkylation. Some have been also obtained directly by addition of dialkyl disulfides to **1**.[3,10,11] Interestingly, sterically hindered disulfides such as di-*tert*-butyl disulfide and dipivaloyl disulfide did not react at all under our conditions, and neither did sulfones or sulfides. The disulfide oligomerization process was independently reported from the laboratory of Szeimies,[32,37] who also converted the first two bismethylthio compounds, [**1**]**1aa** and [**2**]**1aa**, (R = Me), to disulfones [*n*]**1bb** by oxidation and to the parent dithiols [*n*]**1aa** (R = H) by reduction with lithium in ethylamine. Since this is a relatively low-yield procedure, the synthesis of the dithiols via the bisacetylthio compounds [*n*]**1z**[11] is preferable. It also permits a facile differentiation of the two ends of the molecules (e.g., **23**).

The phenylation of the dithiols with the diphenylchloronium cation is another example of a smooth one-pot process starting with [*n*]**1z**. The first two members of the bisphenylthio series, [**1**]**1aa**[32,35-37] and [**2**]**1aa**[32,37] (R = Ph), were previously synthesized by addition of diphenyl disulfide to **1**, but the higher oligomers were not formed. Since 1-(phenylthio)bicyclo[1.1.1]pentane has

(55) Bunz, U.; Szeimies, G. *Tetrahedron Lett.* **1989**, *30*, 2087.
(56) Zefirov, N. S.; Sadovaya, N. K.; Surmina, L. S.; Godunov, I. A.; Koz'min, A. S.; Potekhin, K. A.; Maleev, A. V.; Struchkov, Y. T. *Izv. Akad. Nauk. SSSR, Ser. Khim.* **1988**, 2648.



been converted into 1-lithiobicyclo[1.1.1]pentane,[58] the 3,3(n-1)-bis(phenylthio)[n]staffanes [n]1aa (R = Ph) promise to provide an entry to doubly end-lithiated [n]staffanes and thus an alternative synthesis of [n]1g.

The addition of 2,3-dimethyl-1,4-benzoquinone to [2]staffane-3,3′-dithiol yielded the bisquinone [2]1cc.

Phosphorus Compounds. Tetraethyl hypophosphite produced the monomeric adduct **24** as well as an alternating cooligomer **25** expected to result from a subsequent addition of the bridgehead radical **26** to **24**, presumably by the mechanism outlined in Scheme VIII. Before isolation, products **24** and **25** were air-oxidized to stable compounds **27** and **28**, respectively.

The nucleophilic radical displacement of the ethyl radical from an ethoxy group on phosphorus is a well-established process.[59] Addition of hypophosphite across electron-deficient olefins has been reported.[60] The closely related tetraalkyldiphosphines are also known to react with alkenes by a mechanism analogous to that shown in Scheme VIII.[61] Since potential propagation sites are continuously present at both ends of the molecule, the length of the alternating oligomer is limited by delivery of the bicyclopentyl radical **26**, but we have made no attempt to direct the reaction to the higher oligomers or a polymer.

Properties of End-Functionalized [n]Staffanes. **Thermal Behavior.** Considering their very high expected ring strain energy (~14 kcal/mol per ring carbon[62]), the [n]staffane derivatives described presently possess remarkable thermal stability. Most of them begin to decompose only near 300 °C, even in air.

Differential scanning calorimetry yielded the approximate heats of fusion and decomposition listed in Table I. [n]Staffanes with $-OCOC_6H_5$, –COOH, and $-SC_4H_9$ substituents are stable up to 290 °C, and their decomposition maxima appear around 340 °C. Those with $-SCOCH_3$ and –COOMe substituents are a little less stable and start to decompose at about 280 °C. Those with $-COC_6H_5$ substituents begin to decompose at about 225 °C, with a maximum near 290 °C. The heat of decomposition ranges from 30 to 43 kcal/mol per bicyclic cage, depending on substitution. The behavior of [1]1f is exceptional in that it exhibits two exotherms, at 290 and 350 °C, with heats of decomposition roughly in a 2:1 ratio for the two stages.

The melting points of the staffane derivatives are much higher than those of *n*-alkanes with the same number of carbons and similar functionalities, presumably reflecting very efficient crystal packing and a low entropy of melting for the rigid rods relative to flexible chains. They do not alternate as *n* increases, in keeping with the expected[63] difference between the packing of straight and zigzag chains. The bisacetylthio derivatives [n]1z as well as some of the alkylation products [n]1aa and other derivatives ([n]1l) have liquid crystalline properties when $n \geq 3$.[10]

Solubility. The quite high melting points of the higher [n]staffane derivatives suggest that there may be a problem with their solubility. This is indeed so for the terminal dicarboxylic acids [n]1g and to a lesser degree, terminal monocarboxylic acids [n]1a, but, in general, low solubility has not been enough of a problem to hinder synthetic work. Solubility generally increases with (i) decreasing *n*, (ii) the number of substituents (except for COOH), and (iii) the floppiness of the substituents. A few representative examples of approximate solubilities are collected in Table II.

Structure. Reports of single-crystal X-ray structures for molecules described here, [2]1b,[2a,3,64] [2]1z,[3,64] [3]1z,[2a,3,10,11,64] [4]1z,[64] [2]1u,[3,64] as well as reports of the related structures [3]1dd,[13,40] [4]1dd,[13,40] [2]1ee,[40] [2]1bb,[37] and [2]1aa (R = Me)[37] have already appeared. A review of known structures of substituted bicyclo[1.1.1]pentanes and staffanes as well as a discussion of molecular structure and crystal packing is provided in ref 64.

Here, we merely point out a few of the most salient features: the [n]staffane skeletons are all perfectly or nearly perfectly linear arrays of staggered bicyclo[1.1.1]pentane cages, whose dimensions are quite similar to those of simple bicyclo[1.1.1]pentanes.[3,64-66]

Table I. Approximate Heats of Fusion (H_m) and Decomposition (H_{dec}) of [n]Staffane Derivatives

			decomposition mp (°C)			
compd	mp	ΔH_m[a]	start	max	end	$\Delta H_{dec}/n$[b]
[4]1b	233	6	280	325	370	36
[1]1f	125	6	225	290		18
				355	395	11
[2]1f	160	7	225	290	350	43
[2]1g	c	c	290	340	370	31
[3]1g	c	c	290	325	360	34
[2]1i	215	9	293	343	375	39
[3]1z	137	2.0[d]				
	167	3.3[d]				
	192	0.2[d]	275	330	375	35

[a] Kcal/mol. [b] Kcal/mol; *n* is the number of bicyclo[1.1.1]pentane units in the molecule. [c] No melting before decomposition. [d] Reference 10.

Table II. Approximate Solubilities of [n]Staffane Derivatives in Water, Ethanol, and Chloroform[a]

compd	H_2O	compd	$CHCl_3$
[1]1a	b	[1]1a	910
[2]1a	40	[2]1a	90
[3]1a	c	[3]1a	14
[1]1a[d]	b	[4]1a	c
[2]1a[d]	200	[1]1b	b
[3]1a[d]	10	[2]1b	840
[4]1a[d]	c	[3]1b	380
[1]1g	33	[4]1b	50
[2]1g	c	[5]1b	30
	EtOH	[1]1d	610
[1]1z	210	[2]1d	320
[2]1z	150	[3]1d	30
[3]1z	13	[4]1d	c
[4]1z	6	[1]1z	b
[5]1z	c	[2]1z	950
		[3]1z	330
		[4]1z	50

[a] g/L. [b] >1000 g/L. [c] <1 g/L. [d] Potassium salt (0.5 M KOH).

Table III. First Ionization Potentials of [n]Staffanes

compd	IP[a] (eV)	ref
[1]1dd	10.72	54, 71
[2]1dd	9.78	54, 71
[3]1dd	9.18	71
[4]1dd	8.86	71
[5]1dd	8.74	71

[a] Vertical ionization potential.

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(58) Wiberg, K. B.; Waddell, S. T. *Tetrahedron Lett.* **1988**, *29*, 289.
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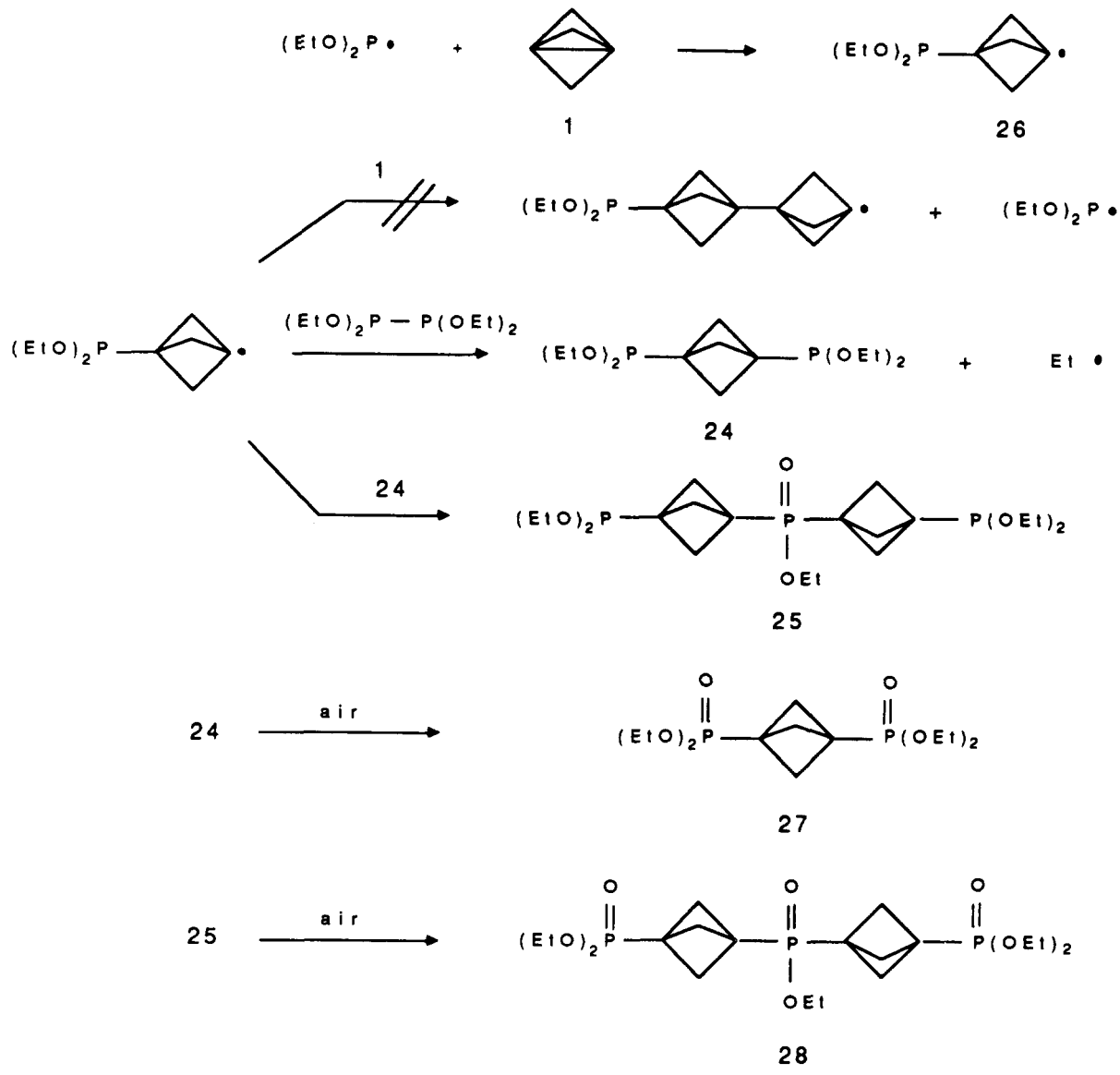
(64) Friedli, A. C.; Lynch, V. M.; Kaszynski, P.; Michl, J. *Acta Cryst. B* **1990**, *46*, 377.
(65) Padwa, A.; Shefter, E.; Alexander, E. *J. Am. Chem. Soc.* **1968**, *90*, 3717.

Scheme VIII



The intercage C–C bonds are remarkably short, ~1.47 Å, as would be expected from simple hybridization arguments (Bent's rules[67]). The transannular interbridgehead distance is ~1.86 Å, and the length increment is about $3^1/_3$ Å. The longer staffs tend to pack with their axes parallel and separated by about 5–5.5 Å.

None of the X-ray work located the positions of hydrogen atoms accurately enough to contribute to the resolution of the controversy[66] concerning the symmetry of bicyclo[1.1.1]pentane: if the hydrogen atoms are coplanar with the bridge carbon atoms, it is D_{3h}; if the CH_2 groups are twisted, it is D_{3d}. Ab initio calculations[68,69] and NMR measurements[70] in a liquid crystal suggest that the former is correct.

Spectroscopic Properties. The [n]staffane skeleton is transparent in the UV region, and all absorptions above 200 nm are attributable to the end substituents. They provide little if any evidence for the expected significant interactions across the saturated skeletons. Thus, the absorption spectra of **[1]1f** and **[2]1f** are virtually identical and have twice the intensity of that of **12**, which is similar to that of pivalophenone.

The photoelectron spectra of several substituted bicyclo[1.1.1]pentanes, [2]staffane, and 3,3′-dibromo[2]staffane have been reported.[54] The spectra of the first five hydrocarbons and several of their substituted derivatives have been measured.[71] The first ionization potential of the hydrocarbons drops regularly as *n* increases and appears to converge to about 8.5 eV (Table III).

The vibrations of the [n]staffane skeleton are very characteristic.[3,13,72] The four features most worthy of note are a very intense long-axis polarized CH_2 wag at ~1210 cm^{-1}, an unusually high frequency "accordion" motion associated with the short intercage C–C bonds (~1370 cm^{-1}), a calculated but not yet observed low-frequency staff bending motion (below 100 cm^{-1}, decreasing with *n*), and a very low calculated barrier to internal rotation (<2 kcal/mol).

It has already been noted that the ^1H and ^{13}C NMR spectra of the [n]staffanes[13] and their end-substituted derivatives[2a,3,11] show simple regularities, which permitted the development of an empirical increment method for the prediction of chemical shifts.[73]

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(70) Orendt, A.; Grant, D. M.; Kaszynski, P.; Michl, J., unpublished results. The NMR spectrum is compatible with a D_{3h} structure perturbed by thermally induced CH_2 twist vibrations.
(71) David, D. E.; Murthy, G. S.; Hassenrück, K.; Friedli, A. C.; Kaszynski, P., unpublished results.
(72) Murthy, G. S.; Hassenrück, K.; Balaji, V.; Michl, J., unpublished results.

Conclusions

The effort required to produce designer solids, surface mobiles, and similar structures can be separated into three phases: (i) synthesis and characterization of sticks, (ii) production of connector spools, and (iii) development of specific assembly techniques for the construction of the desired complex nanostructures. The present paper contributes to the solution of the simplest problem, the synthesis of laterally unadorned but end-functionalized sticks.

The [*n*]staffanes that have been developed for this purpose appear to meet the obvious requirements: their structures are straight, the length increment is small ($3^1/_3$ Å, and with the use of cooligomers,[29] ~1 Å), and they contain axially attached versatile substituents at each terminus and offer opportunities for attachment of others along their length (see ref 74 for bridge chlorination). They are transparent to UV and visible light, stable to heat, air, and common solvents, and readily available in three steps from commercial materials, albeit in only low yields. Since only minute amounts of material are required for the intended use, the low yields are not a serious concern at present. The solubility of most doubly end-substituted derivatives is quite satisfactory up to $n = 5$, but the higher monocarboxylic and dicarboxylic acids and esters ($n = 4, 5$) are poorly soluble.

Finally, we expect the [*n*]staffane skeleton to be an electrical insulator, but do not yet have definitive information on the rate of electron and energy transfer through this spacer. Initial results from the measurement of intramolecular charge-transfer bands of Ru(II)–Ru(III) mixed-valence complexes derived from **[1]1aa** and **[2]1aa** (R = Me) indicate electron-transfer rates comparable to those found earlier for the more flexible spacers consisting of a series of spiro-linked cyclobutanes, with comparable through-bond Ru–Ru distances.[75]

The preparation of other series of straight staffs providing access to other overall lengths and the preparation of straight staffs provided with additional functionalities along their length, permitting the attachment of arbitrary groups at preselected points as well as efforts to improve the synthetic yields, are underway now in an attempt to reach a conclusion of the first phase. The second phase represents the next challenge; for preliminary reports of initial steps toward the development of suitable spools, see refs 3 and 76.

Experimental Section

Boiling points are uncorrected. Melting points were determined using a Boetius PHMK05 apparatus with microscope attachment at a warmup rate of 4 °C/min or in a sealed capillary and are uncorrected. NMR spectra were run at 360 MHz in $CDCl_3$ using a Nicolet NT-360 instrument, unless specified otherwise. The 500-MHz spectra were run in $CDCl_3$ using a General Electric QE-500 instrument. Infrared spectra were recorded in $CHCl_3$, using a Nicolet 60SXR FTIR instrument unless specified otherwise. Ultraviolet spectra were measured in spectral grade *n*-hexane using a Varian CARY 2300 spectrophotometer. Chemical ionization (CI) and electron impact (EI) mass spectra were obtained using Bell & Howell 21-491 and VG ZAB-2E spectrometers. High-resolution fast atom bombardment (HR FAB) mass spectra were measured at the Midwest Center for Mass Spectroscopy, Department of Chemistry, University of Nebraska—Lincoln, Lincoln, NE. Photoelectron spectra (HeI) were measured using a homebuilt spectrometer with a nominal resolution of 30 meV (FWHM). Elemental analyses were performed at Atlantic Microlabs, Norcross, GA. Differential scanning calorimetry was done using a Perkin-Elmer TAS 7 instrument. The samples were contained in sealed aluminum pans and heated at a rate of 20 °C/min. Preparative gas chromatography was performed using a 6 ft SE-30 20% on Chromosorb column. Solubilities were established by preparing a saturated solution of the desired compound in a pure solvent at ambient temperature, sonicating for 1 min, centrifuging to remove suspended solids, and evaporating an aliquot of known volume to a constant weight. Each reported solubility determination is an average of at least two measurements.

Solutions of methyllithium in ether (1.4 M, halide free), butyllithium in pentane (2.0 M) or butyllithium in hexanes (10 M), bromoform (96% purity), 3-chloro-2-chloromethyl-1-propene (94% purity), and anhydrous methyl formate were purchased from Aldrich Chemical Co. and used without further purification.

Organization of the Synthetic Procedures. The following description is arranged alphabetically by the oligomer end groups according to the formula labels: staffanecarboxylic acids ([*n*]**1a**), staffanedicarboxylic acids ([*n*]**1g**), butylstaffanecarboxylic acids ([*n*]**1m**), phenylstaffanecarboxylic acids ([*n*]**1p**), and staffanedithiols ([*n*]**1aa**, R = H). Finally, experimentals for miscellaneous oligomers such as [*n*]**1y** and for monomers are given.

1,1-Bis(chloromethyl)-2,2-dibromocyclopropane (8). A 50% solution of sodium hydroxide (1000 mL) is added in 10–15 min to a vigorously stirred mixture of bromoform (370 mL, 4.24 mol), 3-chloro-2-chloromethyl-1-propene (**7**, 250 g, 2.0 mol), benzyltriethylammonium chloride (10 g), ethanol (8 mL), and methylene chloride (200 mL). The temperature during the addition as well as later is kept between 25 and 35 °C, using an ice bath as necessary. After overnight stirring, the thick black mixture is allowed to separate into layers. The top aqueous layer is removed, and the bottom layer is gently washed with two 500-mL portions of water. Water (1 L) and hexanes (2 L, Skelly B) are then added. The mixture is well shaken and filtered through Celite. The yellow-brown organic layer is separated, the aqueous layer is washed with Skelly B, and the combined organic extracts are dried over $MgSO_4$ and filtered through Celite. Concentration and vacuum distillation gives 350–380 g of a mixture of starting materials and a black-brown residue which is distilled on a Kugelrohr giving 315–350 g of a semicrystalline fraction (65 °C/0.45 mmHg up to 115 °C/0.9 mmHg), containing about 70% of the product **8** (by GC). Crystallization from 400 mL of pentane in a dry ice–acetone bath gives 205–215 g of wet white crystals (mp 38–41 °C). The crude product is dissolved in 400 mL of pentane, treated with 7.5 g of silica gel, and filtered. A second low-temperature crystallization yields 171–182 g of product which melts at 44–46 °C. A third crystallization from 400 mL of pentane gives 164–175 g of pure **8** (29–31% yield based on 94% pure olefin **7**): mp 47 °C (lit.[34] 45–46 °C); ^{1}H NMR δ 1.82 (s, 2 H), 3.95 and 3.98 (AB, d, J = 11.9 Hz, 4 H); ^{13}C NMR δ 32.07, 34.07, 35.35, 47.67.

[1.1.1]Propellane (1) in Diethyl Ether. From 0.1 mol of **8**, 210 mL of ethereal solution of [1.1.1]propellane is obtained according to the published procedure.[33] ^{1}H NMR in Et_2O–C_6D_6 (~1:4) δ 1.73 (s) and in Et_2O–$CDCl_3$ (~1:4) δ 1.97 (s). After separation of **1** by preparative GC, in $CDCl_3$ solvent, δ 2.04 (s) [lit.[30] δ 2.06 (s)]. We assign the peak at δ 1.97 (s) in Et_2O–C_6D_6 solution, and at δ 2.58 (s) in the Et_2O–$CDCl_3$ solution, to CH_3Br by comparison with an authentic sample. These results suggest that the ^{1}H NMR peak at δ 2.57, recently assigned as due to **1**,[34] may actually be due to methyl bromide. On the basis of the ^{1}H NMR spectrum, the molar proportions of solution components are approximately 100:8:4:12 of ether, methyl bromide, **1**, and pentane. The concentration of **1** is about 3% by weight, and its yield is about 70%.

[1.1.1]Propellane (1) in Ether-Free Pentane Solution. In order to prepare an ether-free solution of **1**, 1,1-bis(chloromethyl)-2,2-dibromocyclopropane (**8**, 59.5 g, 0.2 mol), *N,N,N',N'*-tetramethylethylenediamine (TMEDA, 50 mL) and pentane (50 mL) are placed under argon in a 500-mL four-necked flask equipped with a mechanical stirrer, septum, low-temperature thermometer, and a side-arm connector to a cold trap. The mixture is cooled to −50 °C, and *n*-BuLi in pentane (250 mL of a 2.0 M solution) or *n*-BuLi in hexanes (44 mL of a 10 M solution diluted with at least 100 mL of pentane) is added over a period of 45–60 min, keeping the temperature between −35 and −25 °C. When the addition is complete, the black reaction mixture is stirred for 0.5 h at −30 °C and quenched by addition of 5 mL of water. Vacuum transfer (40 mmHg) to a dry ice–acetone trap at 0–10 °C gives about 300 mL of a clear solution of crude **1**. This solution contains an about 42% yield of **1** and is further purified by careful fractional distillation. The fraction boiling at 25–38 °C gives a solution of **1** free of traces of TMEDA and butyl bromide. When analyzed by ^{1}H NMR, the ratio of the singlet at 1.78 ppm due to **1** to the signal of the added internal standard, typically benzene, provides an estimate of the concentration and yield of **1**. Yields are consistently 30–35% but usually decrease when less than 150 mL total pentane volume is used.

[*n*]Staffane-3-carboxylic Acids ([*n*]1a) from Methyl Formate Adducts [*n*]1b

Methyl [*n*]Staffane-3-carboxylates ([*n*]1b) by Reaction of 1 with Methyl Formate. The crude propellane solution obtained above is mixed

(73) Friedli, A. C.; Kaszynski, P.; Downing, J. W.; Michl, J., unpublished results.

(74) Robinson, R. E.; Michl, J. *J. Org. Chem.* **1989**, *54*, 2051.

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(76) Michl, J.; Ibrahim, A. M. 200th National Meeting of the American Chemical Society Washington, D. C., August 27–31, 1990. Book of Abstracts ORGN 0124.

with methyl formate (800 mL) and benzoyl peroxide (0.4 g). The resulting mixture is irradiated in a Pyrex photochemical apparatus with a 450-W medium pressure mercury immersion lamp for 12 h. Excess methyl formate is carefully distilled off, and the residue is distilled on a Kugelrohr (65–85 °C/45 mmHg) to give 1.60 g of **[1]1b**. Careful stepwise sublimation of the solid residue gives the higher oligomers separately in approximately 95% purity. Analytical samples are obtained either by redistillation or resublimation in a gradient sublimer. A brownish insoluble polymeric residue (~0.9 g) remains after sublimation. Thermally programmed evaporation of this residue from a direct insertion probe yielded CIMS corresponding to spectra expected for oligomers longer than $n = 6$ by extrapolation from those of the higher individually isolated oligomers (66 additional mass units per bicyclic cage).

Methyl [1]Staffane-3-carboxylate ([1]1b). Bp 75–76 °C/65 mmHg; yield 6.3% based on **8**; mp −42 to −40 °C; ^{1}H NMR δ 2.07 (s, 6 H), 2.41 (s, 1 H), 3.64 (s, 3 H); ^{13}C NMR δ 27.82, 42.66, 51.33, 51.61, 169.91; IR (neat) 2978, 1739 (C=O), 1321, 1215 (CH_2 wag), 1142 cm^{-1}; EIMS, m/z 125 (M − H, 10), 111 (38), 95 (47), 67 (100), 66 (75), 65 (58). Anal. Calcd for $C_7H_{10}O_2$: C, 66.64; H, 7.99. Found: C, 66.65; H, 8.05.

Methyl [2]Staffane-3-carboxylate ([2]1b). Sublimation 65 °C/45 mmHg; yield 5.6% based on **8**; mp 71.5–72.5 °C; ^{1}H NMR δ 1.64 (s, 6 H), 1.85 (s, 6 H), 2.39 (s, 1 H), 3.64 (s, 3 H); ^{13}C NMR δ 26.59, 36.67, 39.74, 44.48, 49.23, 50.63, 51.40, 170.91; IR 1724 (C=O), 1314, 1137 cm^{-1}; EIMS, m/z 131 (19), 117 (44), 105 (39), 93 (29), 91 (100), 77 (35); CIMS (CH_4), m/z 193 (MH, 100). Anal. Calcd for $C_{12}H_{16}O_2$: C, 74.96; H, 8.39. Found: C, 74.97; H, 8.41.

Methyl [3]Staffane-3-carboxylate ([3]1b). Sublimation 95 °C/45 mmHg; yield 2.7% based on **8**; mp 153 °C; ^{1}H NMR δ 1.42 (s, 6 H), 1.59 (s, 6 H), 1.84 (s, 6 H), 2.37 (s, 1 H), 3.65 (s, 3 H); ^{13}C NMR δ 26.43, 36.73, 37.40, 38.46, 39.63, 45.13, 47.94, 49.15, 50.55, 51.41, 170.95; IR 2966, 1726 (C=O), 1314, 1135 cm^{-1}; EIMS, m/z 157 (25), 143 (27), 142 (28), 131 (36), 129 (42), 117 (46), 115 (27), 105 (41), 91 (100), 79 (36), 77 (39), 65 (30); CIMS (CH_4), m/z 260 (MH + 1, 17), 259 (MH, 100). Anal. Calcd for $C_{17}H_{22}O_2$: C, 79.03; H, 8.59. Found: C, 79.00; H, 8.60.

Methyl [4]Staffane-3-carboxylate ([4]1b). Sublimation 130 °C/45 mmHg; yield 1.0% based on **8**; mp 224–226 °C (sealed tube); ^{1}H NMR δ 1.37 (s, 6 H), 1.40 (s, 6 H), 1.58 (s, 6 H), 1.83 (s, 6 H), 2.36 (s, 1 H), 3.64 (s, 3 H); ^{13}C NMR (500 MHz) δ 26.38, 36.65, 37.41, 37.82, 38.22, 38.27, 39.59, 45.19, 47.75, 47.78, 49.06, 50.46, 51.45, 170.99; IR 2965, 1727 (C=O), 1314 cm^{-1}; CIMS (CH_4), m/z 326 (MH + 1, 14), 325 (MH, 100). Anal. Calcd for $C_{22}H_{28}O_2$: C, 81.44; H, 8.70. Found: C, 81.19; H, 8.72.

Methyl [5]Staffane-3-carboxylate ([5]1b). Sublimation 175 °C/45 mmHg or 130 °C/0.2 mmHg; yield 0.3% based on **8**; mp dec >300 °C (sealed tube); ^{1}H NMR δ 1.35 (s, 6 H), 1.36 (s, 6 H), 1.40 (s, 6 H), 1.58 (s, 6 H), 1.83 (s, 6 H), 2.36 (s, 1 H), 3.65 (s, 3 H); ^{13}C NMR (500 MHz) δ 26.39, 36.67, 37.42, 37.89, 37.96, 38.08, 38.21, 38.31, 39.62, 45.28, 47.68, 47.74, 47.78, 49.08, 50.48, 51.51, 171.07; IR 2965, 1720 (C=O), 1313 cm^{-1}; CIMS (CH_4), m/z 392 (MH + 1, 20), 391 (MH, 100); HRMS, m/z (calcd for $C_{27}H_{34}O_2$ 390.2559) 390.2564.

[n]Staffane-3-carboxylic Acids ([n]1a) by Hydrolysis of Esters [n]1b. In a typical experiment the ester **[n]1b** (50 mg) is refluxed in 2 mL of a 5% solution of KOH in ethanol (**[1]1b**, **[2]1b**, and **[3]1b**) or 2-propanol (**[4]1b** and **[5]1b**). The solvent is evaporated to dryness and water (3 mL) is added to the residue. Potassium salts of acids **[1]1a** and **[2]1a** form homogeneous solutions, while the salts of the higher homologues are very poorly soluble. The resulting solutions are washed with chloroform, and the aqueous phases are acidified with hydrochloric acid. In the case of **[3]1b**, **[4]1b**, and **[5]1b** the potassium salts are filtered off, washed with warm chloroform, and refluxed for 3 h in 15% hydrochloric acid. The acids are extracted with ethyl ether (**[1]1a**) or filtered off. The crude products are further purified by vacuum distillation (**[1]1a**) or sublimation ($n > 1$).

[1]Staffane-3-carboxylic Acid ([1]1a).[44] Bp 125–127 °C/45 mmHg; mp 59–60 °C (lit.[44] mp 59–59.7 °C); ^{1}H NMR δ 2.11 (s, 6 H), 2.44 (s, 1 H); ^{13}C NMR δ 27.82, 42.48, 51.56, 175.54; IR 1700 (C=O) cm^{-1}; EIMS, m/z 111 (M − 1, 20), 69 (25), 67 (100), 66 (75), 65 (34).

[2]Staffane-3-carboxylic Acid ([2]1a). Sublimation 115 °C/0.5 mmHg; mp 206–207 °C (sealed tube); ^{1}H NMR δ 1.65 (s, 6 H), 1.89 (s, 6 H), 2.40 (s, 1 H); ^{13}C NMR δ 26.62, 36.52, 39.71, 44.31, 49.17, 50.57, 176.15; IR 2973, 1701 (C=O) cm^{-1}; EIMS, m/z 178 (M, 2), 145 (16), 133 (30), 131 (62), 119 (43), 118 (47), 117 (87), 115 (60), 105 (81), 103 (51), 93 (78), 92 (60), 91 (100), 79 (65), 77 (81), 65 (61); CIMS (CH_4), m/z 180 (MH + 1, 4.7), 179 (MH, 51), 123 (100), 105 (30). Anal. Calcd for $C_{11}H_{14}O_2$: C, 74.13; H, 7.92. Found: C, 74.14; H, 7.97.

[3]Staffane-3-carboxylic Acid ([3]1a). Sublimation 130 °C/0.5 mmHg; mp 266–269 °C (sealed tube); ^{1}H NMR δ 1.42 (s, 6 H), 1.59 (s, 6 H), 1.86 (s, 6 H), 2.37 (s, 1 H); ^{13}C NMR δ 26.44, 36.60, 37.35, 38.50, 39.65, 45.10, 47.93, 49.16, 50.55, 176.04; IR 2965, 1701 (C=O) cm^{-1}; EIMS, m/z 157 (12), 143 (18), 142 (20), 131 (31), 129 (41), 117 (52), 115 (30), 105 (40), 91 (100), 79 (36), 77 (48), 67 (26), 65 (34); CIMS (CH_4), m/z 245 (MH, 100), 143 (13). Anal. Calcd for $C_{16}H_{20}O_2$: C, 78.65; H, 8.25. Found: C, 78.72; H, 8.26.

[4]Staffane-3-carboxylic Acid ([4]1a). Sublimation 140 °C/0.2 mmHg; mp >300 °C dec without melting; ^{1}H NMR δ 1.37 (s, 6 H), 1.41 (s, 6 H), 1.58 (s, 6 H), 1.88 (s, 6 H), 2.36 (s, 1 H); IR (KBr) 2965, 1695 (C=O), 1217 (CH_2 wag) cm^{-1}; CIMS (CH_4), m/z 312 (MH + 1, 12), 311 (MH, 100). Anal. Calcd for $C_{21}H_{26}O_2$: C, 81.25; H, 8.44. Found: C, 81.14; H, 8.48.

[5]Staffane-3-carboxylic Acid ([5]1a). Sublimation 165 °C/0.5 mmHg; mp > 300 °C dec without melting; IR (KBr) 2963, 1699 (C=O), 1211 (CH_2 wag); CIMS, m/z 378 (MH + 1, 15), 377 (MH, 100); CI HRMS, m/z (calcd for $C_{26}H_{33}O_2$: 377.2481) 377.2472.

[n]Staffane-3-carboxylic Acids ([n]1a) from Ether Adducts [n]1c

3-(1-Ethoxyethyl)[n]Staffanes ([n]1c). A solution of **1** in diethyl ether, prepared from 0.1 mol of **8** as described above, is diluted with an equal volume of anhydrous diethyl ether, a few grains of benzoyl peroxide are added, and the mixture is irradiated for 5 h in a Pyrex flask. Gas chromatographic analysis shows the peaks of the first six ether adducts **[n]1c** in decreasing amounts. The first two were isolated by preparative GC as volatile liquids with a characteristic aroma, in yields of roughly 20 and 15%, respectively, based on **8**.

3-(1-Ethoxyethyl)[1]staffane ([1]1c). ^{1}H NMR δ 1.00 (d, J = 6.6 Hz, 3 H), 1.13 (t, J = 6.9 Hz, 3 H), 1.66 and 1.70 (AB, dd, J_1 = 9.5 Hz, J_2 = 1.4 Hz, 6 H), 2.44 (s, 1 H), 3.27 (q, J = 6.6 Hz, 1 H), 3.44–3.51 (m, 2 H); ^{13}C NMR δ 15.61, 16.94, 27.18, 48.13, 48.64, 64.61, 74.19; IR (neat) 2972, 1204 and 1196 (CH_2 wag), 1107 cm^{-1}; EIMS, m/z 125 (M − Me, 3), 79 (44), 73 (32), 71 (70), 45 (100), 41 (50); CIMS (CH_4), m/z 139 (M − 1, 3), 125 (4), 95 (100). Anal. Calcd for $C_9H_{16}O$: C, 77.09; H, 11.50. Found: C, 77.12; H, 11.55.

3-(1-Ethoxyethyl)[2]staffane ([2]1c). ^{1}H NMR δ 1.02 (d, J = 6.6 Hz, 3 H), 1.15 (t, J = 6.9 Hz, 3 H), 1.47 and 1.51 (AB, dd, J_1 = 9.4 Hz, J_2 = 1.1 Hz, 6 H), 1.62 (s, 6 H), 2.38 (s, 1 H), 3.33 (q, J = 6.6 Hz, 1 H), 3.45–3.52 (m, 2 H); ^{13}C NMR δ 15.69, 17.12, 26.47, 39.19, 41.12, 45.23, 47.46, 49.19, 64.67, 74.13; IR (neat) 2967, 1211 (CH_2 wag), 1105 cm^{-1}; EIMS, m/z 145 (22), 131 (26), 119 (48), 117 (40), 105 (56), 93 (35), 91 (95), 79 (31), 73 (38), 71 (32), 45 (100), 43 (60), 41 (35); CIMS (CH_4), m/z 205 (M − 1, 6), 177 (5), 161 (31), 159 (32), 133 (52), 119 (100), 105 (64). Anal. Calcd for $C_{14}H_{22}O$: C, 81.49; H, 10.75. Found: C, 81.48; H, 10.78.

[n]Staffane-3-carboxylic Acids ([n]1a) by Oxidation of Ether Adducts [n]1c. Dry ether (210 mL) and benzoyl peroxide (0.25 g) are added to an ethereal solution of **1** prepared from **8** (29.7 g, 0.10 mol). The mixture is stirred and irradiated in a Pyrex flask for 8 h, and the progress of the reaction is monitored by GC. The solvent is evaporated, and the white gluey residue is dissolved in carbon tetrachloride (50 mL) and added to a well stirred Chlorox solution (750 mL) containing ruthenium dioxide (0.25 g). Stirring is continued until GC shows the absence of the starting material and the organic layer has turned black.

At this point, it is possible to continue the oxidation of the higher acetates and ketones without isolation. Additional Chlorox (1 L) is added, and CCl_4 along with RuO_4 and some **10** and **11** is distilled off from the reaction mixture under water aspirator vacuum. Sodium hydroxide (25 g) in water (50 mL) is added, and the stirring is continued for 24 h at room temperature and 3 h at 50 °C. The workup procedure is as described below.

When the higher acetates and ketones are to be isolated, the organic layer is separated, treated with Na_2SO_3, and filtered through silica gel. The filtrate is carefully evaporated, and the mixture of acetates and ketones is dissolved in methanol (50 mL) containing NaOH (10 g) and stirred overnight at room temperature. The mixture is evaporated, Chlorox (1.5 L) and NaOH (20 g) are added to the residue, and the mixture is stirred at room temperature overnight and then at 50 °C overnight. The reaction mixture is filtered and the solid washed with warm chloroform to give 1.78 g of sodium salts of **[n]1a**, $n \geq 3$. The filtrate is extracted with chloroform, acidified with hydrochloric acid, and filtered to give **[2]1a** (0.99 g, 11.1% yield of 98% pure material, based on **8**). The filtrate is extracted with ether to give 90% pure **[1]1a**. Kugelrohr distillation (120 °C/10 mmHg) gives 1.77 g (15.8% yield, based on **8**) of **[1]1a**. The sodium salts are decomposed by refluxing with 10% HCl for 3 h to give 1.23 g of free acids **[n]1a**, $n \geq 3$. A sample of 100 mg is separated by gradient sublimation into the individual oligomers **[3]1a**, **[4]1a**, and **[5]1a** in approximately 90% purity. The yields based on **8** are 4.5%, 3.0%, and 1.5%, respectively. Analytical samples were prepared by hydrolysis of the methyl esters **[n]1b** obtained by treatment of crude acids **[n]1a** with diazomethane and purified by preparative GC.

Compounds **10** and **11** were isolated by preparative GC from the intermediate mixture after the first step of the oxidation of [*n*]**1c** with RuO_4.

1-(1-Acetoxyethyl)bicyclo[1.1.1]pentane (10). ^1H NMR δ 1.12 (d, J = 6.5 Hz, 3 H), 1.68 and 1.71 (AB, dd, J_1 = 9.3 Hz, J_2 = 1.3 Hz, 6 H), 2.03 (s, 3 H), 2.48 (s, 1 H), 4.85 (q, J = 6.5 Hz, 1 H); ^{13}C NMR δ 16.45, 21.16, 27.05, 46.58, 48.32, 69.51, 170.68; IR (neat) 2973, 1744 (C=O), 1245 cm^{-1}; EIMS, m/z 93 (5), 79 (53), 43 (100); HRMS, m/z (calcd for $C_9H_{14}O_2$ 154.0994) 154.0998. Anal. Calcd for $C_9H_{14}O_2$: C, 70.10; H, 9.15. Found: C, 70.15; H, 9.18.

1-Acetylbicyclo[1.1.1]pentane (11). ^1H NMR δ 2.03 (s, 6 H), 2.07 (s, 3 H), 2.45 (s, 1 H); ^{13}C NMR δ 25.90, 27.12, 49.61, 51.10, 206.14; IR (neat) 1706 (C=O), 1209 (CH_2 wag) cm^{-1}; EIMS, m/z 109 (M - 1, 4), 95 (14), 67 (54), 43 (100); HRMS, m/z (calcd for C_7H_9O 109.0653) 109.0655.

Dimethyl [*n*]Staffane-3,3$^{(n-1)}$-dicarboxylates ([*n*]1d) from Monocarboxylates [*n*]1b

Dimethyl [2]Staffane-3,3′-dicarboxylate ([2]1d) by Chlorocarbonylation of [2]1b. A mixture of [2]**1b** (182 mg, 1.0 mmol), oxalyl chloride (0.13 mL), and Freon 11 ($CFCl_3$, 0.15 mL) is irradiated in a quartz tube for 5 h. The thick, reddish mixture is treated with methanol, and the resulting mixture of methyl esters is sublimed. The first fraction (50–60 °C/10 mmHg) gives the starting [2]**1b** (16 mg), and the second fraction (110 °C/10 mmHg) gives 80 mg of semicrystalline white product containing 80% (by GC) of the diester [2]**1d**. Crystallization from ethanol gives 25 mg (10% yield) of pure product: mp 194.5–195 °C sublimation; ^1H NMR δ 1.89 (s, 12 H), 3.66 (s, 6 H); ^{13}C NMR δ 36.83, 38.95, 50.60, 51.51, 170.54; IR 1725 (C=O), 1308 cm^{-1}; EIMS, m/z 219 (M - MeO, 0.6), 159 (12), 131 (79), 91 (100), 59 (52); CIMS (CH_4), m/z 252 (MH + 1, 14.8), 251 (MH, 100), 131 (28). Anal. Calcd for $C_{14}H_{18}O_4$: C, 67.18; H, 7.25. Found: C, 66.93; H, 7.33.

Hydrolysis of the crude mixture (80 mg) with KOH in methanol followed by esterification of the crude diacid [2]**1g** with diazomethane and sublimation gives the same yield of [2]**1d**.

Dimethyl [3]Staffane-3,3″-dicarboxylate ([3]1d) by Chlorocarbonylation of [3]1b. A mixture of [3]**1b** (180 mg), oxalyl chloride (0.20 mL), and $CFCl_2CF_2Cl$ (0.30 mL) are irradiated for 10 h in a quartz tube. At this point the conversion to product is 70%, and the tube walls are coated. The mixture is transferred to another quartz tube and irradiated for additional 10 h. The thick red liquid is poured into methanol. Several milligrams of the product are isolated by preparative GC as a white solid: mp 239–240 °C (sealed tube); ^1H NMR δ 1.46 (s, 6 H), 1.85 (s, 12 H), 3.65 (s, 6 H); ^{13}C NMR δ 36.73, 37.70, 39.46, 47.97, 50.54, 51.45, 170.86; IR 1726 (C=O), 1308 cm^{-1}; EIMS, m/z 285 (M - MeO, 0.1), 181 (6), 157 (47), 142 (40), 129 (41), 117 (26), 115 (35), 105 (30), 91 (100), 79 (33), 77 (44), 65 (47), 59 (69); CIMS (CH_4), m/z 318 (MH + 1, 20.6), 317 (MH, 100). Anal. Calcd for $C_{19}H_{24}O_4$: C, 72.13; H, 7.65. Found: C, 72.14; H, 7.68.

3,3$^{(n-1)}$-[*n*]Staffanedicarboxylic Acids ([*n*]1g) via Benzil Adducts [*n*]1f

3,3$^{(n-1)}$-Dibenzoyl[*n*]staffanes ([*n*]1f). A solution of benzil (5.50 g, 26 mmol) in an ethereal solution of propellane (210 mL, made from 0.10 mol of **8**) is stirred and irradiated for 5 h in an immersion photochemical apparatus. The solvent is removed on a rotary evaporator, and the semicrystalline yellow residue (12 g) is passed through a silica gel column. The resulting mixture (7 g) is short-path distilled (up to 120 °C/0.5 mmHg) to give 2.0 g of a mixture of **12** and 1-benzoyl-3-(1-ethoxyethyl)bicyclo[1.1.1]pentane (**13**). The cold trap contains about 0.3 g of a mixture of ethers [1]**1c** and [2]**1c**. Semicrystalline residue (4.3 g) is separated on silica gel column using benzene as an eluent to give 1.9 g of yellowish crystalline product. ^1H NMR analysis of this mixture shows signals attributable to [*n*]**1f**: δ. 2.79, [1]**1f**; δ 2.19, [2]**1f**; δ 2.11 (s, 12 H) and 1.56 (s, 6 H), [3]**1f**; 2.09 (s, 12 H) and 1.48 (s, 12 H), [4]**1f**, in 12:19:4:1 molar proportions. The mixture can be separated into individual oligomers on a silica gel column using a mixture of hexane–ethyl acetate as an eluent. The first three members ([1]**1f** through [3]**1f**) have been fully characterized.

1,3-Dibenzoyl[1]staffane ([1]1f). Sublimation 110–115 °C/0.1 mmHg; yield 2% based on **8**; mp 122–123 °C (needles, aqueous MeOH); ^1H NMR δ 2.79 (s, 6 H), 7.45–7.50 (m, 4 H), 7.57–7.61 (m, 2 H), 8.01–8.03 (m, 4 H); ^{13}C NMR δ 44.45, 56.15, 128.61, 128.84, 133.12, 136.42, 196.73; IR 1663 (C=O), 1288 cm^{-1}; UV, λ_{max} nm (log ϵ_{max}), 244 (4.44), 280 (3.28), 337 (2.11); EIMS, m/z 275 (M - 1, 3), 171 (43), 105 (100), 77 (69); HRMS, m/z (calcd for $C_{19}H_{16}O_2$ 276.1150) 276.1155, (calcd for $C_{19}H_{15}O_2$ 275.1072) 275.1073. Anal. Calcd for $C_{19}H_{16}O_2$: C, 82.58; H, 5.84. Found: C, 82.61; H, 5.84.

3,3′-Dibenzoyl[2]staffane ([2]1f). Yield 5.5% based on **8**; mp 161–163 °C (plates, MeOH); ^1H NMR δ 2.19 (s, 12 H), 7.42–7.46 (m, 4 H), 7.52–7.57 (m, 2 H), 7.98–8.01 (m, 4 H); ^{13}C NMR δ 39.66, 43.20, 52.36, 128.43, 128.86, 132.78, 136.70, 197.47; IR 1665 (C=O), 1324 cm^{-1}; UV, λ_{max} nm (log ϵ_{max}), 242 (4.43), 279 (3.25), 337 (2.06); EIMS, m/z 341 (M - 1, 1), 237 (5), 131 (4), 105 (100), 91 (8), 77 (40); HRMS, m/z (calcd for $C_{24}H_{22}O_2$ 342.1620) 342.1622. Anal. Calcd for $C_{24}H_{22}O_2$: C, 84.12; H, 6.48. Found: C, 84.04; H, 6.49.

3,3″-Dibenzoyl[3]staffane ([3]1f). Mp 200 °C; ^1H NMR δ 1.55 (s, 6 H), 2.11 (s, 12 H), 7.41–7.46 (m, 4 H), 7.50–7.55 (m, 2 H), 7.98 (d, J = 7.6 Hz, 4 H); ^{13}C NMR δ 37.80, 39.95, 43.03, 47.91, 52.21, 128.30, 128.77, 132.64, 136.63, 197.86; IR 2978, 1661 (C=O), 1319, 1296 cm^{-1}; EIMS, m/z 263 (4), 157 (3), 143 (5), 129 (5), 117 (3), 115 (3), 105 (100), 91 (7), 77 (35). Anal. Calcd for $C_{29}H_{28}O_2$: C, 85.26; H, 6.91. Found: C, 85.01; H, 6.93.

1-Benzoyl[1]staffane (12). Bp 79–80 °C/0.3 mmHg; ^1H NMR δ 2.31 (s, 6 H), 2.55 (s, 1 H), 7.40–7.44 (m, 2 H), 7.50–7.54 (m, 1 H), 7.98–8.03 (m, 2 H); ^{13}C NMR δ 28.36, 49.30, 53.27, 128.30, 128.80, 132.65, 136.45, 197.08; IR (neat) 1668 (C=O), 1323, 1215 (CH_2 wag) cm^{-1}; UV, λ_{max} nm (log ϵ_{max}), 242 (4.10), 279 (2.88), 338 (1.73); EIMS, m/z 171 (M - 1, 19), 105 (100), 77 (61); HRMS, m/z (calcd for $C_{12}H_{11}O$ 171.0810) 171.0814. Anal. Calcd for $C_{12}H_{12}O$: C, 83.68; H, 7.03. Found: C, 83.75; H, 7.06.

1-Benzoyl-3-(1-ethoxyethyl)bicyclo[1.1.1]pentane (13). ^1H NMR δ 1.11 (d, J = 6.4 Hz, 3 H), 1.19 (t, J = 7.0 Hz, 3 H), 2.18 and 2.22 (AB, dd, J_1 = 9.5 Hz, J_2 = 1.4 Hz, 6 H), 3.45 (q, J = 6.4 Hz, 1 H), 3.50–3.59 (m, 2 H), 7.40–7.45 (m, 2 H), 7.51–7.55 (m, 1 H), 7.99–8.02 (m, 2 H); ^{13}C NMR δ 15.56, 16.75, 43.04, 43.76, 51.55, 64.74, 73.39, 128.28, 128.75, 132.65, 136.50, 197.57; IR (neat) 1667 (C=O), 1322, 1205 (CH_2 wag), 1105 cm^{-1}; EIMS, m/z 229 (M - Me, 5), 197 (17), 105 (100), 77 (47), 45 (30); HRMS, m/z (calcd for $C_{15}H_{17}O_2$ 229.1229) 229.1225. Anal. Calcd for $C_{16}H_{20}O_2$: C, 78.65; H, 8.25. Found: C, 78.71; H, 8.26.

2-Benzoyl-1,4-pentadiene (14). Purification of **12** using preparative GC resulted in conversion of approximately one-third of the sample into **14**: ^1H NMR δ 3.21 (d, J = 6.2 Hz, 2 H), 5.07–5.17 (m, 2 H), 5.67 (s, 1 H), 5.80–6.00 (m, 2 H), 7.42–7.46 (m, 2 H), 7.52–7.56 (m, 1 H), 7.74–7.77 (m, 2 H); ^{13}C NMR δ 36.21, 117.16, 126.43, 128.18, 129.48, 132.16, 134.93, 137.70, 146.40, 197.66; IR (neat) 1658 (C=O) cm^{-1}; EIMS, m/z 172 (M, 39), 171 (M - 1, 24), 105 (100), 77 (55); HRMS, m/z (calcd for $C_{12}H_{12}O$ 172.0888) 172.0893. The compound polymerizes easily and was not submitted for combustion analysis.

Dimethyl [*n*]Staffane-3,3$^{(n-1)}$-dicarboxylates ([*n*]1d) via Oxidation of 3,3$^{(n-1)}$-Dibenzoyl[*n*]staffanes ([*n*]1f). The crude mixture (35.5 g) obtained by benzil addition to **1** on a 0.3 mol scale as described above is dissolved in carbon tetrachloride (250 mL) and added to a solution of Chlorox (500 mL) containing ruthenium dioxide (0.4 g). The reaction mixture is stirred at room temperature and every few hours a portion of a solution of sodium hypochlorite prepared from NaOH (500 g), water (1.2 L), and chlorine (408 g) is added. After 72 h total a solution of sodium hydroxide (30 g) and Chlorox (25 mL) are added, and the mixture is stirred for 15 min and filtered. The solid is washed with CCl_4, suspended in water (200 mL), and acidified with hydrochloric acid. The precipitate is filtered off, dried, and washed with warm chloroform to give 1.65 g of a mixture of acids. The aqueous phase is washed with carbon tetrachloride (to remove all the ruthenium as RuO_4) and acidified with hydrochloric acid (50 mL). The well-chilled suspension is filtered to give white crude [2]**1g** (1.50 g). The filtrate is extracted with ether (3×), the extract dried, and the solvent evaporated. The semicrystalline residue (6.5 g) is washed with warm chloroform to give crude [1]**1g** (2.8 g), which is converted to the dimethyl ester and distilled (135 °C/25 mmHg) to give [1]**1d** (2.5 g, 4.5% yield based on **8**). The chloroform extracts are evaporated, and the residue is distilled (130 °C/22 mmHg) to give 80% pure [1]**1a** (1.9 g). The crude [2]**1g** is converted to [2]**1d** by diazomethane and sublimed (105 °C/10 mmHg) to give pure diester [2]**1d** (0.86 g, 2.7% yield based on **8**). The crude mixture of [3]**1g** and [4]**1g** containing some [2]**1g** is treated with diazomethane and sublimed (up to 180 °C/1 mmHg) to give a white mixture of diesters (0.50 g). Preparative GC separation gives [2]**1d** (60 mg), [3]**1d** (214 mg, 0.7% yield based on **8**), and [4]**1d** (40 mg, 0.1% yield based on **8**). The relative yields of the four diesters differ somewhat from run to run.

Dimethyl [4]Staffane-3,3‴-dicarboxylate ([4]1d). Sublimation 150 °C/20 mmHg; yield 40 mg, 0.1% based on **8**; mp 279–281 °C; ^1H NMR δ 1.41 (s, 12 H), 1.83 (s, 12 H), 3.65 (s, 6 H); ^{13}C NMR δ 36.68, 37.46, 38.14, 39.56, 47.80, 50.48, 51.50, 171.00; IR 2967, 1721 (C=O), 1314 cm^{-1}; EIMS, m/z 223 (6), 195 (12), 157 (42), 155 (33), 143 (36), 142 (34), 131 (40), 129 (52), 128 (33), 117 (42), 115 (35), 105 (51), 91 (100), 77 (38), 59 (43); CIMS (CH_4), m/z 384 (MH + 1, 19), 383 (MH, 100); FAB HRMS, m/z (calcd for $C_{24}H_{31}O_4$ 383.2222) 383.2218. Anal. Calcd for $C_{24}H_{30}O_4$: C, 75.36; H, 7.91. Found: C, 75.32; H, 7.92.

Methyl 3′-Benzoyl[2]staffane-3-carboxylate ([2]1h). Mp 116–118 °C; ^1H NMR δ 1.94 (s, 6 H), 2.14 (s, 6 H), 3.67 (s, 3 H), 7.42–7.48 (m, 2

H), 7.52–7.56 (m, 1 H), 7.97–7.99 (m, 2 H); ^{13}C NMR (500 MHz) δ 36.86, 39.04, 39.47, 43.15, 50.57, 51.63, 52.31, 128.41, 128.85, 132.86, 136.49, 170.66, 197.67; IR 1726 (C=O), 1663 (C=O) cm^{-1}; EIMS, *m/z* 295 (M − 1, 1), 159 (11), 131 (46), 105 (100), 91 (48), 77 (59); CIMS (CH_4), *m/z* 298 (MH + 1, 29), 297 (MH, 100), 237 (43), 219 (70); CI HRMS, *m/z* (calcd for $C_{19}H_{21}O_3$ 297.1491) 297.1495. Anal. Calcd for $C_{19}H_{20}O_3$: C, 77.00; H, 6.80. Found: C, 76.73; H, 6.74.

3,3′-Dibenzoyloxy[2]staffane ([2]1i). A mixture of 3,3′-dibenzoyl-[2]staffane ([2]**1f**, 136 mg, 0.5 mmol), 30% hydrogen peroxide (1.0 mL), and 3.0 mL of acetic acid is stirred at 65 °C for 8 h[77] and cooled in an ice bath, and the white precipitate is filtered off to give [2]**1i** (148 mg, 98%). Recrystallization from an ethanol–chloroform mixture gives white plates: mp 222–224 °C; ^{1}H NMR δ 2.19 (s, 12 H), 7.41–7.45 (m, 4 H), 7.53–7.57 (m, 2 H), 8.01–8.03 (m, 4 H); ^{13}C NMR δ 32.52, 53.35, 63.42, 128.31, 129.63, 130.36, 132.97, 165.93; IR 1722 (C=O), 1286 cm^{-1}; EIMS, *m/z* 105 (100), 77 (39); CIMS (CH_4), *m/z* 375 (MH, 5.6), 374 (M, 14.8), 253 (72), 105 (100). Anal. Calcd for $C_{24}H_{22}O_4$: C, 76.98; H, 5.92. Found: C, 76.83; H, 5.92.

Bicyclo[1.1.1]pentane-1-carboxamide (15).[78] 1-Benzoylbicyclo-[1.1.1]pentane **12** (138 mg, 0.8 mmol) and sodium amide (130 mg, 3.3 mmol) are refluxed for 4 h in dry benzene (2 mL) under an atmosphere of dry argon. The reaction mixture is poured into ice water, and the organic products are quickly extracted with chloroform and dried over sodium sulfate. Evaporation of the solvents leaves a crude product (55 mg) which after crystallization from benzene and sublimation (50 °C/0.2 mmHg) gives 41 mg (45% yield) of the amide: mp 205–207 °C (sealed tube; lit.[78] 202–203 °C); ^{1}H NMR δ 2.06 (s, 6 H), 2.47 (s, 1 H), 5.50–5.90 (br, 2 H); ^{13}C NMR δ 26.88, 44.13, 51.16, 172.31; IR (KBr) 3337 and 3166 (N–H), 1663 and 1635 (C=O), 1436, 1228 (CH_2 wag) cm^{-1}; EIMS, *m/z* 111 (M, 3), 110 (25), 67 (100), 66 (33), 44 (61), 41 (53); HRMS, *m/z* (calcd for C_6H_8NO 110.0606) 110.0603. No benzamide was detected by GCMS, using an authentic sample for reference.

[*n*]Staffane-3,3$^{(n-1)}$-dicarboxylic Acids ([*n*]1g) by Hydrolysis of Dimethyl Esters [*n*]1d. The diester [*n*]**1d** (50 mg) is refluxed in methanol (3 mL) containing KOH (0.20 g) for 1 h. The solvent is evaporated, and the residue is dissolved in water (3 mL), refluxed for 15 min, filtered, and acidified with hydrochloric acid. The precipitated product is filtered off, washed with water and chloroform, and dried to give about a 90% yield of white diacid.

[2]Staffane-3,3′-dicarboxylic Acid ([2]1g). Mp > 300 °C dec; ^{1}H NMR (0.6 M KOH in D_2O; ref to dioxane) δ 1.56 (s); ^{13}C NMR (0.6 M KOH in D_2O; reference to dioxane) δ 37.47, 38.79, 49.73, 66.50 (dioxane), 180.80; IR (KBr) 1695 (C=O) cm^{-1}; EIMS, *m/z* 131 (46), 91 (100), 77 (38), 43 (39), 41 (52); CIMS (CH_4), *m/z* 223 (MH, 62), 205 (24), 159 (49), 133 (14), 131 (100); CI HRMS, *m/z* (calcd for $C_{12}H_{15}O_4$ 223.0970) 223.0972.

[3]Staffane-3,3″-dicarboxylic Acid ([3]1g). Mp > 300 °C dec; ^{1}H NMR (0.6 M KOH in D_2O; reference to dioxane) δ 1.24 (s, 6 H), 1.53 (s, 12 H); ^{13}C NMR (0.6 M KOH in D_2O; reference to dioxane) δ 37.21, 37.84, 38.73, 47.12, 49.75, 66.50 (dioxane), 180.94; IR (KBr) 1697 (C=O), 1215 (CH_2 wag) cm^{-1}; EIMS, *m/z* 169 (8), 157 (51), 143 (34), 142 (48), 131 (34), 129 (56), 128 (33), 117 (50), 115 (32), 105 (39), 91 (100), 79 (38), 77 (46), 65 (40); CIMS (CH_4), *m/z* 290 (MH + 1, 15), 289 (MH, 100); FAB HRMS, *m/z* (calcd for $C_{17}H_{19}O_4$ 287.1283) 287.1288.

[4]Staffane-3,3‴-dicarboxylic Acid ([4]1g). Mp > 300 °C dec; ^{1}H NMR (0.6 M KOH in D_2O; reference to dioxane) δ 1.22 (s, 12 H), 1.53 (s, 12 H); IR (KBr) 1698 (C=O), 1216 (CH_2 wag) cm^{-1}; EIMS, *m/z* 118 (54), 105 (28), 77 (12); FABMS, *m/z* 354 (M, 28), 353 (M − 1, 100), 309 (71); FAB HRMS, *m/z* (calcd for $C_{22}H_{25}O_4$ 353.1753) 353.1743.

[2]Staffane-3,3′-dicarboxylic Acid ([2]1g) via Diiodide [2]1s

1,3-Diiodobicyclo[1.1.1]pentane ([1]1s). Sublimed iodine (15.0 g, 59 mmol) dissolved in dry ether (100 mL) is added dropwise to a magnetically stirred solution of **1** prepared from 0.10 mol of **8**. Heptane (25 mL) is added to the resulting solution, and the solvents are evaporated. The slightly colored crystals are recrystallized from heptane to give 13.5 g (42% yield based on **8**) of white crystals of the diiodide: mp 153 °C dec (sealed tube; lit.[79] mp 147–148 °C); ^{1}H NMR δ 2.67 (s) [lit.[36] δ 2.66 (s)]; ^{13}C NMR δ −1.80, 68.25; IR 1186, 840 cm^{-1}; UV, λ_{max} nm (log ϵ_{max}), 203 (4.71), 260 (3.74); EIMS, *m/z* 320 (M, 5), 193 (40), 128 (35), 127 (43), 66 (100), 65 (70). Anal. Calcd for $C_5H_6I_2$: C, 18.77; H, 1.89; I, 79.34. Found: C, 18.84; H, 1.90; I, 79.24. A reaction of iodine with **1** in ether/cyclohexane (generated from **8** and phenyllithium[43]) or **1** in pentane gives [1]**1s** in 49.5% and 30% yields based on **8**, respectively.

3,3′-Diiodo[2]staffane ([2]1s). 1,3-Diiodobicyclo[1.1.1]pentane ([1]**1s**, 9.75 g, 30.5 mmol) is irradiated in a rapidly stirred solution of **1** in pentane (65 mmol, 190 mL). The diiodide is added in two portions (6 g at first, then the remainder after 1 h). The reaction appears to proceed rapidly as judged by product precipitation, but ^{1}H NMR monitoring shows that it takes about 8 h before the solution is practically free of the starting diiodide [1]**1s**. Pentane solution of **1** is then recovered by distillation directly from the reaction vessel (162 mL, 0.22 M, 35.6 mmol), and the residue is vacuum dried to give 11.46 g (97% yield based on [1]**1s**) of crystalline [2]**1s**: mp 120 °C dec (lit.[53] mp 116–124 °C dec); ^{1}H NMR δ 2.18 (s); ^{13}C NMR δ 6.35, 47.49, 59.73; IR 1203, 1083, 882, 815 cm^{-1}; UV, λ_{max} nm (log ϵ_{max}), 195 (4.73), 254 (3.46); EIMS, *m/z* 179 (38), 163 (40), 131 (99), 129 (49), 115 (32), 91 (100); CIMS (CH_4), *m/z* 132 (100), 131 (77), 117 (95), 91 (33). Anal. Calcd for $C_{10}H_{12}I_2$: C, 31.12; H, 3.13; I, 65.75. Found: C, 31.16; H, 3.16; I, 65.62.

3,3′-Diacetyl[2]staffane ([2]1j). A mixture of diiodide [2]**1s** (11.46 g, 29.7 mmol), dry benzene (200 mL), and biacetyl (8.4 mL, 96 mmol), and tri-*n*-butyltin hydride (25.8 mL, 96 mmol) is rapidly stirred and irradiated for 6 h. The starting material does not completely dissolve until after 3 h of irradiation. Benzene is removed, and the residue is recrystallized twice from hexanes (200 mL) to give a yellowish [2]**1j** (3.52 g). The filtrate is evaporated, and then eluted with 20% ethyl acetate/hexanes through a silica gel column to give another 0.65 g of [2]**1j**. Combined fractions are recrystallized from heptane to give a total of 3.77 g (65% yield) of [2]**1j**: mp 134–135 °C; ^{1}H NMR δ 1.87 (s, 12 H), 2.10 (s, 6 H); ^{13}C NMR δ 25.97, 38.33, 43.32, 50.05, 206.25; IR 3021, 2982, 1697 (C=O), 1360 cm^{-1}; EIMS, *m/z* 175 (M − Me, 3), 157 (6), 142 (5), 133 (9), 131 (6), 105 (11), 91 (16), 77 (5), 43 (100); CIMS, *m/z* 219 (M + 1, 3), 201 (16), 175 (M − 43, 13), 159 (100), 143 (62), 131 (27); CI HRMS, *m/z* (calcd for $C_{12}H_{15}O$ 175.1123) 175.1124. Anal. Calcd for $C_{14}H_{18}O_2$: C, 77.03; H, 8.31. Found: C, 77.15; H, 8.32.

Dimethyl[2]staffane-3,3′-dicarboxylate ([2]1d) from Oxidation of Diketone [2]1j. A solution of sodium hypobromite was generated as described[33] from sodium hydroxide (17.3 g, 43.2 mmol) in water (150 mL) and bromine (7.9 mL, 15.4 mmol) at 0 °C. 3,3′-Diacetyl[2]staffane ([2]**1j**, 3.77 g, 17.3 mmol) in dioxane (150 mL) is added dropwise to the hypobromite over 1 h to produce a milky yellow solution. After 3 h stirring at ambient temperature and 1 h at 40 °C, water (150 mL) is added, and the solution becomes clear. Extraction with ether (2 × 100 mL) and then acidification of the aqueous layer with concentrated hydrochloric acid gives a fine precipitate. Filtration, washing with water and chloroform, and then vacuum drying yields 3.78 g (88% yield) of >98% pure diacid [2]**1g**. Yield based on **8**, excluding **1** used in the formation of [2]**1s** is 28%, and including **1** used and not recovered, 8%. Treatment of a sample of diacid [2]**1g** with diazomethane gives a nearly quantitative yield of clear crystals of [2]**1d**, mp 193–194 °C (sealed tube). Conversion to diester on a larger scale is accomplished by reflux with freshly distilled thionyl chloride, followed by reflux with anhydrous methanol. Thus [2]**1g** (1.10 g, 5 mmol) produces [2]**1d** (1.17 g, 94% yield) after bulb-to-bulb sublimation (145–150 °C/0.6 mmHg).

3′-(Methoxycarbonyl)[2]staffane-3-carboxylic Acid ([2]1r). Dimethyl [2]staffane-3,3′-dicarboxylate [2]**1d** (0.75 g, 3.0 mmol) is dissolved in refluxing methanol (30 mL). A solution of sodium hydroxide (122 mg, 3 mmol) in methanol (10 mL) is added over 1 h, and the reflux continued for 1 h. Methanol is then evaporated, and the salts vacuum dried. The products are dissolved in water (30 mL) and methylene chloride (30 mL), $NaHCO_3$ solution is added to pH 8, and the layers are separated. The aqueous layer is extracted with methylene chloride (2 × 10 mL). The dried (Na_2SO_4) and evaporated organic layer contained [2]**1d** (116 mg, 22% yield). Methylene chloride (30 mL) is added to the aqueous layer, and the mixture is carefully acidified with concentrated hydrochloric acid and then filtered to yield diacid [2]**1g** (115 mg, 17% yield). The organic layer from the filtrate is separated and dried with sodium sulfate, and the solvent is evaporated to give [2]**1r** (366 mg, 52% yield): sublimation 115 °C/0.6 mmHg; mp 243.5–244.5 °C; ^{1}H NMR δ 1.89 (s, 6 H), 1.92 (s, 6 H), 3.66 (s, 3 H); ^{13}C NMR δ 36.70, 36.86, 38.93, 39.02, 50.63 (two cages), 51.56, 170.52, 175.19; IR 2988, 2919, 2882, 1728 (C=O), 1694 (C=O), 1221, 1140 cm^{-1}; EIMS, *m/z* 203 (2), 159 (17), 131 (100), 117 (21), 91 (92), 59 (19). Anal. Calcd for $C_{13}H_{16}O_4$: C, 66.09; H, 6.83. Found C, 66.07; H, 6.87.

3$^{(n-1)}$-*n*-Butyl[*n*]staffane-3-carboxylic Acids ([*n*]1m) from Butyl Iodide Adduct [*n*]1k

3-Acetyl-3$^{(n-1)}$-*n*-butyl[*n*]staffanes ([*n*]1l) by Reaction of 1 with 1-Iodobutane and Radical Acetylation. A pentane solution (240 mL) of propellane (0.10 mol) and 1-iodobutane (6.4 g, 35 mmol) are irradiated at room temperature through a Pyrex filter for 6 h. An example of isolation of the resulting bridgehead iodide [1]**1k** appears below, but, presently, no isolation is needed. The solvent is evaporated, the viscous

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residue is dissolved in dry benzene (140 mL), and biacetyl (7.0 mL, 80 mmol) is added, followed by tri-*n*-butyltin hydride (11 mL, 41 mmol). The mixture is irradiated in an immersion photochemical apparatus for 4 h. The solution is stirred over saturated potassium fluoride, diluted with water, and filtered through Celite. The organic phase is separated and dried over sodium sulfate, and the solvents are evaporated to leave a crude mixture of the ketones (9 g). The mixture is passed through a silica gel column using hexanes and then ethyl acetate/hexanes (1:5) as eluents. The ketone fraction is fractionally distilled. The first fraction is collected up to 60 °C/0.7 mmHg and the second from 60 to 95 °C/0.7 mmHg. The first fraction is redistilled (99–101 °C/22 mmHg) to give **[1]1l** as a colorless oil (2.66 g, 16% yield based on **1**). The redistillation (89–91 °C/0.65 mmHg) of the second fraction gives pure **[2]1l** as a colorless viscous oil (1.20 g, 10% yield based on **1**).

The residue is recrystallized from ethanol to give a waxy solid (1.21 g) containing mostly **[4]1l** and **[5]1l**. The filtrate containing mostly **[3]1l** and some **[4]1l** is concentrated and slowly sublimed overnight (95 °C/0.6 mmHg), with the cold tip of the sublimer held about half an inch above the surface of the hot bath. The collected material is recrystallized from methanol to give 96% pure **[3]1l** (0.9 g), which after resublimation gives >98% pure **[3]1l** (0.70 g). The combined residues from both sublimations are sublimed further to give an intermediate fraction containing **[3]1l** and **[4]1l** (0.4 g). The temperature of 130–135 °C is maintained overnight allowing collection of 95% pure **[4]1l**, which after recrystallization from ethanol–chloroform mixture and resublimation gives 99% pure ketone (0.30 g). Now the temperature of the bath is raised to 175 °C. The collected product is boiled with ethanol, cooled down, and filtered off to give 150 mg of a mixture which is separated by preparative GC, to give **[5]1l** (60 mg) and **[4]1l** (50 mg). Combined intermediate fractions and filtrates are recrystallized from methanol to give 0.60 g of a mixture containing mostly **[3]1l**. The mixture is purified by careful stepwise sublimation as described above. The ketones **[*n*]1l** are isolated in at least 98% purity. Analytical samples were obtained by preparative GC. The ketones have also been separated by reverse-phase HPLC using methanol or acetonitrile as eluent.

1-Acetyl-3-*n*-butyl[1]staffane ([1]1l). Yield 2.66 g (4.8% based on **8**); ^{1}H NMR δ 0.87 (t, J = 7.1 Hz, 3 H), 1.18–1.34 (m, 4 H), 1.43 (t, J = 7.7 Hz, 2 H), 1.83 (s, 6 H), 2.08 (s, 3 H); ^{13}C NMR δ 13.96, 22.73, 26.04, 28.42, 31.10, 39.56, 44.41, 51.10, 206.92; IR (neat) 2965, 2920, 2873, 1705 (C=O), 1360, 1172 cm^{-1}; EIMS, m/z 166 (M, 4), 123 (54), 81 (28), 43 (100). Anal. Calcd for $C_{11}H_{18}O$: C, 79.46; H, 10.91. Found: C, 79.43; H, 10.94.

3-Acetyl-3′-*n*-butyl[2]staffane ([2]1l). Yield 1.20 g (3.1% based on **8**); ^{1}H NMR δ 0.86 (t, J = 7.2 Hz, 3 H), 1.16–1.31 (m, 4 H), 1.38 (t, J = 7.7 Hz, 2 H), 1.43 (s, 6 H), 1.81 (s, 6 H), 2.09 (s, 3 H); ^{13}C NMR δ 14.07, 22.82, 26.06, 28.77, 31.55, 38.47, 38.89 (2C), 43.34, 48.91, 50.06, 207.25; IR (neat) 2959, 2908, 2869, 1706 (C=O), 1357, 1209 cm^{-1}; EIMS, m/z 232 (M, 1), 189 (5), 171 (31), 157 (30), 131 (20), 105 (35), 31 (51), 43 (100). Anal. Calcd for $C_{16}H_{24}O$: C, 82.70; H, 10.41. Found: C, 82.48; H, 10.38.

3-Acetyl-3″-*n*-butyl[3]staffane ([3]1l). Yield 1.10 g (3.3% based on **8**); mp K 67 A 134 I °C; ^{1}H NMR δ 0.86 (t, J = 7.1 Hz, 3 H), 1.18–1.31 (m, 4 H), 1.37–1.43 (m with maxima at 1.39 and 1.41, 14 H), 1.81 (s, 6 H), 2.09 (s, 3 H); ^{13}C NMR δ 14.09, 22.86, 26.07, 28.84, 31.69, 37.49, 38.29, 38.68, 38.93 (2C), 43.33, 47.78, 48.90, 50.03, 207.23; IR 2962, 2907, 2873, 1695 cm^{-1}; EIMS, m/z 183 (4), 171 (6), 157 (16), 143 (25), 131 (25), 129 (23), 119 (19), 117 (31), 105 (40), 93 (29), 91 (70), 79 (33), 55 (26), 43 (100). Anal. Calcd for $C_{21}H_{30}O$: C, 84.51; H, 10.13. Found: C, 84.35; H, 10.14.

3-Acetyl-3‴-*n*-butyl[4]staffane ([4]1l). Yield 0.40 g (1.3% based on **8**); ^{1}H NMR δ 0.86 (t, J = 7.1 Hz, 3 H), 1.18–1.32 (m, 4 H), 1.37–1.43 (m with maxima at 1.36, 1.37, and 1.40, 20 H), 1.80 (s, 6 H), 2.08 (s, 3 H); ^{13}C NMR δ 14.07, 22.84, 26.01, 28.83, 31.70, 37.49, 37.88, 38.08, 38.33, 38.62, 38.91, 39.03, 43.32, 47.74 (two rings), 48.91, 50.02, 207.07; IR 2963, 2907, 2873, 1695 cm^{-1}; EIMS, m/z 251 (1), 224 (4), 169 (13), 157 (22), 131 (26), 117 (25), 105 (37), 93 (32), 91 (42), 79 (24), 55 (24), 43 (100). Anal. Calcd for $C_{26}H_{36}O$: C, 85.66; H, 9.95. Found: C, 85.46; H, 9.90.

3-Acetyl-3⁗-*n*-butyl[5]staffane ([5]1l). Yield 60 mg (0.2% based on **8**) of the crude ketone was obtained and not purified further; mp >300 °C dec; ^{1}H NMR δ 0.86 (t, J = 7.1 Hz, 3 H), 1.18–1.33 (m, 4 H), 1.37–1.43 (m with maxima at 1.35, 1.37, and 1.40, 26 H), 1.80 (s, 6 H), 2.09 (s, 3 H); ^{13}C NMR δ 14.09, 22.86, 26.04, 28.86, 31.73, 37.49, 37.89, 38.01, 38.05, 38.14, 38.35, 38.62, 38.91, 39.08, 43.33, 47.73 (three rings), 48.91, 50.04, 207.14; IR 2966, 2906, 2873, 1696 cm^{-1}; EIMS, m/z 185 (4), 169 (5), 149 (10), 129 (10), 128 (13), 117 (15), 105 (23), 91 (29), 81 (25), 69 (29), 57 (28), 55 (50), 43 (100), 41 (66).

Haloform Oxidation of the Ketones [*n*]1l to the Acids [*n*]1m. The ketone (0.50 g) is dissolved in dioxane (15 mL) and slowly added to well-stirred Chlorox (20 mL) containing sodium hydroxide (1 g) at room temperature. The mixture is stirred overnight at room temperature and then at 50 °C for additional 3 h. The progress of the reaction is monitored by GC. The sodium salts are filtered off (except for the sodium salt of **[1]1l** which is water soluble), washed with water and decomposed with dilute hydrochloric acid. The free acid is dried, sublimed, and recrystallized giving pure product in an average yield of 80%.

3-*n*-Butyl[1]staffane-1-carboxylic Acid ([1]1m). Sublimation 70 °C/0.5 mmHg and recrystallized from hexanes; mp 90–91 °C; ^{1}H NMR δ 0.88 (t, J = 7.1 Hz, 3 H), 1.20–1.34 (m, 4 H), 1.44 (t, J = 7.7 Hz, 2 H), 1.91 (s, 6 H), 10.7 (br s, 1 H); ^{13}C NMR δ 13.97, 22.73, 28.45, 30.90, 37.56, 40.30, 51.54, 176.59; IR 1698 (C=O) cm^{-1}; EIMS, m/z 126 (20), 125 (53), 111 (4), 93 (47), 83 (100), 81 (5), 80 (33), 79 (50), 67 (48), 55 (87), 41 (65). Anal. Calcd for $C_{10}H_{16}O_2$: C, 71.39; H, 9.59. Found: C, 71.38; H, 9.55.

3′-*n*-Butyl[2]staffane-3-carboxylic Acid ([2]1m). Sublimation 100 °C/0.5 mmHg and recrystallized from pentane at −78 °C; mp 186–187 °C; ^{1}H NMR δ 0.87 (t, J = 7.1 Hz, 3 H), 1.18–1.31 (m, 4 H), 1.38 (t, J = 7.7 Hz, 2 H), 1.43 (s, 6 H), 1.88 (s, 6 H), 10.5 (br s, 1 H); ^{13}C NMR δ 14.03, 22.82, 28.77, 31.56, 36.60, 38.37, 38.94, 39.63, 49.03, 50.57, 176.45; IR 2963, 2991, 2870, 1700 (C=O) cm^{-1}; EIMS, m/z 189 (M − COOH, 2), 131 (100), 105 (38), 93 (54), 91 (2), 79 (34), 41 (32). Anal. Calcd for $C_{15}H_{22}O_2$: C, 76.88; H, 9.47. Found: C, 76.93; H, 9.48.

3″-*n*-Butyl[3]staffane-3-carboxylic Acid ([3]1m). Sublimation 110 °C/0.5 mmHg and recrystallized from chloroform; mp 269–271 °C (sealed tube); ^{1}H NMR δ 0.86 (t, J = 7.1 Hz, 3 H), 1.18–1.35 (m, 4 H), 1.37 (t, J = 7.7 Hz, 2 H), 1.38 (s, 6 H), 1.41 (s, 6 H), 1.87 (s, 6 H), 10.5 (br s, 1 H); ^{13}C NMR δ 14.05, 22.85, 28.84, 31.69, 36.53, 37.36, 38.34, 38.0, 38.91, 39.71, 47.88, 48.95, 50.54, 176.45; IR 2960, 2907, 2872, 1702 (C=O) cm^{-1}; EIMS, m/z 217 (19), 189 (22), 159 (44), 147 (46), 133 (48), 131 (65), 119 (58), 105 (76), 93 (47), 91 (100), 79 (48), 55 (58), 41 (47). Anal. Calcd for $C_{20}H_{28}O_2$: C, 79.95; H, 9.39. Found: C, 79.74; H, 9.34.

Oligomerization of 1-*n*-Butyl-3-iodobicyclo[1.1.1]pentane ([1]1k) with 1. A pentane solution (8 mL) of **1** (3.3 mmol) and 1-*n*-butyl-3-iodobicyclo[1.1.1]pentane (**[1]1k**, 490 mg, 2 mmol) are irradiated in a Pyrex test tube for 5 h. The yellowish mixture is evaporated, the residue is dissolved in dry benzene (5 mL), and biacetyl (0.8 mL) is added, followed by tri-*n*-butyltin hydride (1 mL). The mixture is irradiated for 3 h at room temperature. The yellow solution is stirred overnight over a saturated solution of potassium fluoride, diluted with water and filtered through Celite. The organic phase is separated, dried over sodium sulfate, and evaporated to give 840 mg of a crude mixture. The mixture is passed through a silica gel column using hexanes, then a mixture of ethyl acetate with hexanes (1:5) to elute side products first, and then a mixture of the ketones (330 mg). The ketones are separated on preparative GC to give **[1]1l** (90 mg, 27% yield), **[2]1l** (55 mg, 12% yield), **[3]1l** (28 mg, 4.7% yield), **[4]1l** (10 mg, 1.4% yield), and **[5]1l** (4 mg, 0.5% yield), where all the yields are based on **[1]1k**. The total yield is 46% based on the iodide **[1]1k** and 26% based on propellane **1**.

Methyl 3$^{(n-1)}$-Phenyl[*n*]staffane-3-carboxylates [*n*]1q from Iodobenzene Adducts [*n*]1n

3-Acetyl-3$^{(n-1)}$-phenyl[*n*]staffanes ([*n*]1o) by Reaction of 1 with Iodobenzene and Radical Acetylation. A solution of propellane (60 mmol) in pentane (120 mL) from the reaction of **8** (59.4 g, 0.2 mol) with 10 M BuLi in pentane is cannulated into a quartz immersion apparatus[80] containing iodobenzene (2.2 mL, 20 mmol) and irradiated for 8 h. The unreacted **1** is removed by distillation as a pentane solution directly out of the immersion flask (bath temperature up to 50 °C, 30–50% of **1** recovered, as established by ^{1}H NMR with added benzene as internal standard). The mixture of crude iodides **[*n*]1n** is mixed with biacetyl (2.6 mL, 30 mmol) and tri-*n*-butyltin hydride (8.1 mL, 30 mmol) in dry benzene (100 mL) and stirred and irradiated through Pyrex for 6 h. The resulting thick yellow solution is stirred over aqueous potassium fluoride for 3 h, the polymer is filtered off and washed with methylene chloride, and the layers are separated. The concentrated organic layer is flashed down a silica column with hexane to remove tin-containing fractions and unreacted iodides and then with 10% ethyl acetate in hexane used to elute a mixture of the ketones **[*n*]1o**. The yields are variable and typically 3.5–6 g of the mixture of ketones **[*n*]1o** is obtained. This is used for preparation of esters **[*n*]1q** without further separation.

(79) Zefirov, N. S.; Surmina, L. S.; Sadovaya, N. K.; Koz'min, A. S. *Izv. Akad. Nauk. SSSR, Ser. Khim.* **1987**, 2871.

(80) The procedure works best when the space between the inner and outer lamp housing is no larger than two centimeters. When the concentration of **1** is high and that of iodobenzene low, oligomeric material quickly builds up on the inner housing wall, absorbing the majority of the emission and halting the polymerization process; the surface of the reaction vessel should be scratched periodically under N_2 to remove the oligomers coating the walls.

A small sample of the ketone mixture was separated on a silica gel column with 3% ethyl acetate in hexanes or reverse-phase preparative HPLC with 70% methanol/water or 70% acetonitrile/water.

1-Acetyl-3-phenyl[1]staffane ([1]1o). Bp 80–90 °C/0.5 mmHg (Kugelrohr); ^{1}H NMR δ 2.19 (s, 3 H), 2.29 (s, 6 H), 7.22–7.35 (m, 5 H); ^{13}C NMR δ 26.25, 41.94, 43.52, 52.92, 125.99, 126.94, 128.27, 139.74, 206.54; IR (neat) 2975, 1703 (C=O), 1366, 1190 cm^{-1}; EIMS, *m/z* 186 (M, 28), 171 (52), 143 (100), 128 (91), 115 (59), 103 (55), 77 (51), 43 (62); HRMS, *m/z* (calcd for $C_{13}H_{14}O$ 186.0966) 186.0962. Anal. Calcd for $C_{13}H_{14}O$: C, 83.83; H, 7.58. Found: C, 83.75; H, 7.63.

3-Acetyl-3′-phenyl[2]staffane ([2]1o). Mp 124–125 °C; ^{1}H NMR δ 1.84 (s, 6 H), 1.85 (s, 6 H), 2.12 (s, 3 H), 7.19–7.32 (m, 5 H); ^{13}C NMR δ 26.09, 37.83, 38.73, 40.76, 43.42, 50.19, 50.95, 125.96, 126.37, 129.10, 141.08, 206.94; IR 1693 (C=O), 1433, 1309, 1216, 751 cm^{-1}; EIMS, *m/z* 251 (Me), 237 (M − H, 7), 209, 169 (29), 141 (23), 128 (26), 115 (26), 91 (72), 77 (27), 43 (100); HRMS, *m/z* (calcd for $C_{16}H_{17}$ 209.1330) 209.1340. Anal. Calcd for $C_{18}H_{20}O$: C, 85.67; H, 7.99. Found: C, 85.58; H, 8.05.

3-Acetyl-3″-phenyl[3]staffane ([3]1o). Mp 175–176 °C; ^{1}H NMR δ 1.50 (s, 6 H), 1.84 (s, 6 H), 1.85 (s, 6 H), 2.10 (s, 3 H), 7.18–7.31 (m, 5 H); ^{13}C NMR δ 26.08, 37.68, 38.16, 38.25, 38.88, 40.59, 43.36, 47.92, 50.06, 50.94, 125.99, 126.23, 128.06, 141.49, 207.13; IR 2979, 2973, 2908, 2874, 1695 (C=O), 1135, 894 cm^{-1}; EIMS, *m/z* 303 (M − 15, 4), 167 (62), 141 (68), 129 (78), 128 (88), 115 (77), 91 (100), 77 (67), 43 (85); HRMS, *m/z* (calcd for $C_{22}H_{23}O$ 303.1758) 303.1749. Anal. Calcd for $C_{23}H_{26}O$: C, 86.75; H, 8.23. Found: C, 86.66; H, 8.25.

3-Acetyl-3‴-phenyl[4]staffane ([4]1o). Mp 258–260 °C dec; ^{1}H NMR δ 1.44 (s, 6 H), 1.45 (s, 6 H), 1.82 (s, 6 H), 1.84 (s, 6 H), 2.09 (s, 3 H), 7.19–7.28 (m, 5 H); ^{13}C NMR (500 MHz) δ 26.10, 37.53, 37.93, 38.08, 38.29, 38.34, 38.91, 40.53, 43.34, 47.74, 47.85, 50.02, 50.92, 125.98, 126.17, 128.04, 141.61, 207.30; IR 2909, 2875, 1690 (C=O), 1120 cm^{-1}; EIMS, *m/z* 195 (89), 131 (97), 130 (53), 129 (62), 116 (40), 115 (39), 91 (100), 85 (34), 53 (58); CIMS, *m/z* 383 (M − 1, 8); HRMS, *m/z* (calcd for $C_{28}H_{32}O$ 384.2453) 384.2445.

Small samples of the iodides **[1]1n** and **[2]1n** were isolated from the mixture of crude iodides **[*n*]1n** by removal of iodobenzene (25–40 °C/0.5 mmHg), followed by sublimation and recrystallization of **[1]1n** (pentane, −78 °C) and **[2]1n** (washed with pentane). Heating the iodides above 100 °C causes a rapid exothermic decomposition of the remaining oligomers.

1-Iodo-3-phenyl[1]staffane ([1]1n). Sublimation 40 °C/0.5 mmHg; mp 64–65 °C; ^{1}H NMR δ 2.60 (s, 6 H), 7.12–7.14 (m, 2 H), 7.24–7.31 (m, 3 H); ^{13}C NMR δ 6.82, 50.48, 62.01, 125.97, 127.04, 128.39, 138.43; IR 3002, 1076 cm^{-1}; EIMS, *m/z* 188 (2), 187 (3), 143 (M − I, 100), 128 (75), 115 (33), 103 (72), 77 (54). Anal. Calcd for $C_{11}H_{11}I$: C, 48.91; H, 4.10. Found: C, 48.89; H, 4.15.

3-Iodo-3′-phenyl[2]staffane ([2]1n). Sublimation 60 °C/0.5 mmHg; ^{1}H NMR δ 1.90 (s, 6 H), 2.24 (s, 6 H), 7.17–7.31 (m, 5 H); ^{13}C NMR δ 8.02, 38.01, 41.08, 48.35, 51.60, 59.68, 125.97, 126.49, 128.16, 140.68; EIMS, *m/z* 259 (1), 131 (79), 117 (100), 104 (51), 91 (89), 65 (35), 39 (48); CIMS, *m/z* 335 (M − H, 1), 209 (100), 167 (47), 132 (21), 131 (39), 117 (38), 91 (22).

Oligomerization of 1-Iodo-3-phenyl[1]staffane ([1]1n) with 1. A pentane solution (10 mL) of **1** (4.0 mmol) and 1-iodo-3-phenylbicyclo-[1.1.1]pentane (**[1]1n**, 380 mg, 1.2 mmol) is irradiated in quartz test tube for 6 h. The yellowish mixture is evaporated, the residue is dissolved in dry benzene (5 mL), and biacetyl (150 μL) is added, followed by tri-*n*-butyltin hydride (450 μL). The mixture is irradiated for 3 h at room temperature. The mixture is passed through a silica gel column using hexanes and then a mixture of ethyl acetate with hexanes (1:5) to elute side products first and then a mixture of the crude ketones (440 mg). The ratio of **[1]1n**:**[2]1n**:**[3]1n**:**[4]1n** is 20:7:3:1, as determined by analytical GC.

Methyl 3$^{(n-1)}$-Phenyl[*n*]staffane-3-carboxylates ([*n*]1q) via Oxidation of 3-Acetyl-3$^{(n-1)}$-phenyl[*n*]staffanes ([*n*]1o). The crude mixture of ketones **[*n*]1o** obtained above (3.5 g) is dissolved in dioxane (200 mL) and added over 0.5 h to a solution of sodium hypobromite, prepared from sodium hydroxide (24.0 g) and bromine (11.0 mL) in 100 mL of water at 0 °C. After warming to room temperature overnight and then at 40 °C for 3 h, sodium bisulfite is added, and NaOH is added if the pH is not above 8. The mixture is filtered to give a solid containing predominantly the sodium salts of **[3]1p** and **[4]1p** and some tin-containing products. Multiple extraction of the filtrate with ether precipitates a solid between layers which is filtered off to give mainly sodium salts of **[2]1p**. Acidification of the aqueous layer with concentrated hydrochloric acid (50 mL) precipitates 3-phenylbicyclo[1.1.1]pentane-1-carboxylic acid (**[1]1p**), which is filtered off and dried. The crude acid **[1]1p** is recrystallized from cold heptane and/or sublimed (110 °C/1 mmHg) to give 0.93 g (3.9% yield based on **8**) of the pure acid, which is converted to its methyl ester **[1]1q** by reaction with diazomethane. The fraction containing the salt of **[2]1p** is acidified, dried, treated with diazomethane in ether, and sublimed (95 °C/0.5 mmHg) to give **[2]1q** (0.25 g, 1.8% yield based on **8**). The fraction containing the higher oligomers is sonicated with hydrochloric acid, filtered off, and dried. Treatment with diazomethane gives a mixture of **[3]1q** and **[4]1q** containing some **[2]1q**. This is separated on preparative GC to give **[3]1q** (24 mg, 0.2%, based on **8**) and partially thermally decomposed **[4]1q** (~5 mg) which is purified on a silica gel column with 10% ethyl acetate in hexanes.

When less iodobenzene (1/5 equiv) is used, the relative yields of higher oligomers are greater. In one case, the reaction of **1** (60 mmol) with iodobenzene (12 mmol) gave the esters **[*n*]1q** in overall yields: **[2]1q** (81 mg, 0.5%), **[3]1q** (121 mg, 0.8%), and **[4]1q** (90 mg, 0.7%, partially decomposed). All yields are based on **8** and corrected for recovered **1**.

Methyl 3-Phenyl[1]staffane-1-carboxylate ([1]1q). Bp 102 °C/0.5 mmHg (lit.[52] bp 85–90 °C/0.4 mmHg); ^{1}H NMR δ 2.23 (s, 6 H), 3.71 (s, 3 H), 7.19–7.33 (m, 5 H); ^{13}C NMR δ 36.92, 41.77, 51.63, 126.01, 126.88, 128.23, 139.61, 170.68; EIMS, *m/z* 202 (M, 1), 143 (M − COOMe, 100), 141 (30), 128 (54), 115 (30), 103 (23), 77 (23).

Methyl 3′-Phenyl[2]staffane-3-carboxylate ([2]1q). Mp 150–151 °C; ^{1}H NMR δ 1.89 (s, 6 H), 1.93 (s, 6 H), 3.67 (s, 3 H), 7.19–7.32 (m, 5 H); ^{13}C NMR δ 36.80, 37.75, 39.42, 40.74, 50.66, 51.01, 51.46, 125.94, 126.33, 128.09, 141.11, 170.81; IR 2974, 2872, 1727 (C=O), 1301, 1216, 1118 cm^{-1}; EIMS, *m/z* 209 (M − COOMe, 8), 193 (28), 178 (28), 169 (100), 167 (45), 141 (44), 131 (18), 103 (24), 91 (93); HRMS, *m/z* (calcd for $C_{18}H_{20}O_2$ 268.1385) 268.1429. Anal. Calcd for $C_{18}H_{20}O_2$: C, 80.56; H, 7.52. Found: C, 80.44; H, 7.56.

Methyl 3″-Phenyl[3]staffane-3-carboxylate ([3]1q). Mp 208 °C; ^{1}H NMR δ 1.50 (s, 6 H), 1.84 (s, 6 H), 1.87 (s, 6 H), 3.66 (s, 3 H), 7.17–7.30 (m, 5 H); ^{13}C NMR δ 36.72, 37.53, 38.15, 38.25, 39.59, 40.58, 47.99, 50.53, 50.95, 51.49, 125.98, 126.22, 128.05, 141.52, 170.98; IR 2965, 2905, 2870, 1731 (C=O), 1303, 1212 cm^{-1}; EIMS, *m/z* 167 (15), 129 (29), 128 (33), 115 (38), 91 (100), 77 (44), 65 (27); CIMS, *m/z* 336 (MH + 1, 23), 335 (MH, 100), 197 (26); CI HRMS, *m/z* (calcd for $C_{23}H_{27}O_2$ 335.2011) 335.2002. Anal. Calcd for $C_{23}H_{26}O_2$: C, 82.60; H, 7.84. Found: C, 82.43; H, 7.88.

Methyl 3‴-Phenyl[4]staffane-3-carboxylate ([4]1q). Mp > 252 °C dec; ^{1}H NMR δ 1.43 (s, 6 H), 1.45 (s, 6 H), 1.83 (s, 6 H), 1.85 (s, 6 H), 3.65 (s, 3 H), 7.15–7.30 (m, 5 H); ^{13}C NMR δ 36.68, 37.45, 37.93, 38.07, 38.28, 38.35, 39.61, 40.53, 47.81, 47.84, 50.48, 50.92, 51.53, 125.98, 126.17, 128.04, 141.62, 171.07; IR 2955, 2924, 1733 (C=O), 1212 cm^{-1}; EIMS, *m/z* 235 (2), 193 (7), 167 (19), 141 (25), 128 (34), 115 (41), 91 (100), 77 (40), 65 (41); CI HRMS, *m/z* (calcd for $C_{28}H_{33}O_2$ 401.2475) 401.2481.

3-Phenylbicyclo[1.1.1]pentane-1-carboxylic Acid ([*n*]1p) via Lithiation of [1]1n. The method of Della[51] is followed. 1-Iodo-3-phenylbicyclo-[1.1.1]pentane (**[1]1n**, 100 mg, 0.37 mmol) is dissolved in dry ether (2 mL), and 1.7 M *tert*-butyllithium (550 μL, 0.935 mmol) is added dropwise at −78 °C. The solution is stirred for 1 h at −50 °C, and then CO_2 is bubbled through for 15 min. The product is dissolved in water and washed with ether, and then the aqueous layer is acidified. Extraction with methylene chloride, drying with Na_2SO_4, removal of solvent, and sublimation, (80 °C/0.25 mmHg) gives 56 mg (52% yield) of white crystalline **[1]1p**: mp 176 °C (lit.[52] mp 174–176 °C); ^{1}H NMR δ 2.37 (s, 6 H), 7.21–7.35 (m, 5 H); ^{13}C NMR δ 36.90, 41.91, 53.42, 126.04, 128.39, 139.47, 175.81; EIMS, *m/z* 187 (M − 1, 1), 143 (100), 128 (53), 103 (66), 77 (80), 51 (88).

Attempted Oxidation of Methyl 3$^{(n-1)}$-Phenyl[*n*]staffane-3-carboxylates [2]1q and [3]1q. An attempt to oxidize methyl 3′-phenyl[2]staffane-3-carboxylate (**[2]1q**) with ruthenium tetroxide was made according to the Applequist procedure for the conversion of **[1]1q** to **[1]1r**.[52] The oxidation is surprisingly slow and even after 2 days, only half of the starting **[2]1q** reacted to give **[2]1r**. No conversion of **[3]1q** to **[3]1r** was achieved under the same conditions.

Ethyl [*n*]Staffane-3-acetates ([*n*]1x) from Ethyl Bromoacetate Adducts [*n*]1w

Oligomerization of Ethyl Bromoacetate with 1 and Preparation of Ethyl [*n*]Staffane-3-acetates ([*n*]1x). Ethyl bromoacetate (206 μL, 2 mmol) is added to a solution of **1** in pentane (10 mL, 4 mmol) and irradiated in a quartz test tube for 6 h. The mixture of oligomers is concentrated, and tri-*n*-butyltin hydride (570 μL, 2.1 mmol), benzene (1.5 mL), and AIBN (2 mg) are added.[48] After 3 h reflux, the mixture

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is stirred over potassium fluoride for 3 h and filtered. The resulting esters are separated by preparative GC to give [1]1x, (56 mg, 2.7% yield based on 8), [2]1x (65 mg, 4.4% yield based on 8), and [3]1x (19 mg, 1.6% yield based on 8).

Ethyl [1]staffane-1-acetate ([1]1x). ^{1}H NMR δ 1.25 (t, J = 7.4 Hz, 3 H), 1.79 (s, 6 H), 2.45 (s, 1 H), 2.47 (s, 2 H), 4.12 (q, J = 7.4 Hz, 2 H); ^{13}C NMR δ 14.29, 27.86, 38.43, 41.06, 51.22, 59.99, 171.26; IR (neat) 2972, 1738 (C=O), 1285, 1257, 1210, 1199, 1184, 1098, 1034 cm^{-1}; EIMS, m/z 125 (M - OEt, 13), 97 (47), 79 (100). Anal. Calcd for $C_9H_{14}O_2$: C, 70.10; H, 9.15. Found: C, 70.16; H, 9.18.

Ethyl [2]Staffane-3-acetate ([2]1x). ^{1}H NMR δ 1.25 (t, J = 7.4 Hz, 3 H), 1.57 (s, 6 H), 1.61 (s, 6 H), 2.38 (s, 1 H), 2.45 (s, 2 H), 4.11 (q, J = 7.4 Hz, 2 H); ^{13}C NMR δ 14.35, 26.48, 34.73, 38.02, 39.99, 44.89, 49.25, 50.11, 60.04, 171.49; IR (neat) 2982, 1739 (C=O), 1279, 1214, 1042 cm^{-1}; EIMS, m/z 175 (M - OEt, 11), 131 (46), 117 (54), 105 (77), 91 (100). Anal. Calcd for $C_{14}H_{20}O_2$: C, 76.33; H, 9.15. Found: C, 76.22; H, 9.12.

Ethyl [3]Staffane-3-acetate ([3]1x). Mp 69.5–70 °C; ^{1}H NMR δ 1.25 (t, J = 7.3 Hz, 3 H), 1.39 (s, 6 H), 1.54 (s, 6 H), 1.58 (s, 6 H), 2.36 (s, 2 H), 2.44 (s, 1 H), 4.11 (q, J = 7.4 Hz, 2 H); ^{13}C NMR δ 14.35, 26.39, 34.78, 37.65, 38.04, 38.34, 39.80, 45.28, 47.93, 49.15, 50.05, 60.06, 171.55; IR 2965, 1726 (C=O), 1447, 1369, 1280, 1093, 1046, 1028 cm^{-1}; EIMS, m/z 241 (M - OEt, 8), 141 (23), 131 (51), 117 (52), 105 (69), 91 (100). Anal. Calcd for $C_{19}H_{26}O_2$: C, 79.68; H, 9.15. Found: C, 79.60; H, 9.16.

Sulfonyl Chloride Adducts [n]1y

1-Chloro-3-(methanesulfonyl)bicyclo[1.1.1]pentane ([1]1y, R = Me) and 3-Chloro-3′-(methanesulfonyl)[2]staffane ([2]1y, R = Me). A solution of 1 prepared from 0.1 mol of 8 is photolyzed in a round-bottomed flask with magnetic stirring for 3 h at 0 °C in the presence of methanesulfonyl chloride (1.95 mL, 25 mmol) and benzoyl peroxide (50 mg). The resulting suspension is immediately filtered to give 4.3 g (35% yield based on 8) of white powdery solid of [2]1y (R = Me), which is recrystallized from a heptane–chloroform mixture: mp 185–193 °C dec (lit.[57] mp 184–185 dec); ^{1}H NMR δ 2.06 (s, 6 H), 2.08 (s, 6 H), 2.81 (s, 3 H); ^{13}C NMR δ 36.26, 36.94, 37.37, 48.06, 50.16, 50.24, 56.17; IR 1328, 1326, 1200, 857 cm^{-1}; EIMS, m/z 131 (23), 116 (25), 91 (100); CIMS (CH_4), m/z 249 (MH, 10), 247 (MH, 26), 131 (100). Anal. Calcd for $C_{11}H_{15}ClO_2S$: C, 53.54; H, 6.13; Cl, 14.37; S, 12.99. Found: C, 53.45; H, 6.18; Cl, 14.38; S, 13.03.

The second product [1]1y (R = Me), obtained in 3.2% yield based on 8 by Kugelrohr distillation (90 °C/22 mmHg) of the concentrated filtrate, is recrystallized from heptane to give white crystals: mp 113–114.5 °C (lit.[57] 112–113 °C); ^{1}H NMR δ 2.54 (s, 6 H), 2.86 (s, 3 H); ^{13}C NMR δ 38.50, 47.54, 48.83, 57.10; IR 1316, 1147, 1139, 935 cm^{-1}; EIMS, m/z 145 (M - Cl, 13), 100 (38), 81 (40), 65 (100). Anal. Calcd for $C_6H_9ClO_2S$: C, 39.89; H, 5.02; Cl, 19.62; S, 17.75. Found: C, 39.96; H, 5.01; Cl, 19.56; S, 17.71.

1-(Benzenesulfonyl)-3-chlorobicyclo[1.1.1]pentane ([1]1y, R = Ph). A solution of 1, prepared from 25 mmol of 8, benzenesulfonyl chloride (6.4 mL, 50 mmol), and benzoyl peroxide is irradiated for 6 h. After removing the solvents and distilling off the starting material on a Kugelrohr (up to 90 °C/0.5 mmHg), the crude yellow product is treated with silica gel, washed with heptane (20 mL), and recrystallized from a heptane–toluene mixture to yield 3.1 g (51% yield based on 8) of colorless plates: mp 122–123 °C; ^{1}H NMR δ 2.40 (s, 6 H), 7.56–7.67 (m, 2 H), 7.69–7.71 (m, 1 H), 7.84–7.87 (m, 2 H); ^{13}C NMR δ 48.43, 49.68, 57.07, 128.46, 129.32, 134.09, 136.91; IR 2978, 1520, 1447, 1152, 929, 613 cm^{-1}; EIMS, m/z 207 (M - Cl, 7), 143 (25), 125 (22), 77 (50), 65 (100); HRMS, m/z (calcd for $C_{11}H_{11}O_2S$ 207.0480) 207.0483. Anal. Calcd for $C_{11}H_{11}ClO_2S$: C, 54.43; H, 4.57; Cl, 14.61; S, 13.21. Found: C, 54.49; H, 4.61; Cl, 14.58; S, 13.26. GCMS shows that a small amount of [2]1y is formed, but this product was not isolated.

3,3$^{(n-1)}$-[n]Staffane Thioethers from Adducts of Diacetyl Disulfide [n]1z

3,3$^{(n-1)}$-Bis(acetylthio)[n]staffanes ([n]1z). Diacetyl disulfide (15.0 g, 100 mmol) is added to a solution of propellane in ether (600 mL, made from 0.3 mol of 8). The diacetyl disulfide was prepared in 86% yield by iodine oxidation of sodium thiolacetate [bp 52–57 °C/0.5 mmHg (lit.[81] 60–61 °C/1.0 mmHg); ^{1}H NMR δ 2.49 (s); ^{13}C NMR δ 29.04, 189.73]. The solution is irradiated in a round-bottomed flask for 6 h. Evaporation of solvent to yield 28.8 g of a crude mixture and refrigeration overnight produced 0.59 g of [3]1z and [4]1z after vacuum filtration and wash with cold ethanol. Short-path distillation of the remaining viscous liquid (25–60 °C/0.2 mmHg) typically recovered one-fourth of the starting diacetyl disulfide, and continued distillation (88–90 °C/0.15 mmHg) gave [1]1z. Dilution of the pot residue with an equal volume of ethanol and cooling in an ice-bath gave a yellowish solid containing mostly [2]1z. The remaining dark orange residue was eluted down a large silica column with 10% ethyl acetate in hexanes, and the yellowish purified solid was added to the fraction containing mostly [2]1z. Slow sublimation, a recrystallization, and a final sublimation to eliminate all [3]1z produced 6.1 g of pure [2]1z.

The residue of higher oligomers from the purification of [2]1z as well as the 0.59 g of a mixture of [3]1z and [4]1z were combined and separated by slow fractional sublimation. One run on a 0.3 mol scale produced 10 mg of [5]1z after separation as above and gradient sublimation of the higher oligomer mixture.

1,3-Bis(acetylthio)[1]staffane ([1]1z). Yield 1.76 g, 2.7% based on 8, recrystallized from ethanol/water; mp 57 °C; ^{1}H NMR δ 2.27 (s, 6 H), 2.52 (s, 6 H); ^{13}C NMR δ 31.01, 40.42, 57.84, 195.56; IR 2980, 1693 and 1685 (C=O), 1351, 1119, 1107, 956, 927 cm^{-1}; UV, λ_{max} nm (log ϵ_{max}), 235 (3.86); EIMS, m/z 173 (M-MeCO, 1), 58 (5), 43 (100); CIMS (CH_4), m/z 217 (MH, 85), 141 (100), 99 (47); HRMS, m/z (calcd for $C_8H_9O_2S_2$ 201.0440) 201.0465. Anal. Calcd for $C_9H_{12}O_2S_2$: C, 49.97; H, 5.59; S, 29.64. Found: C, 50.06; H, 5.62; S, 29.59.

3,3′-Bis(acetylthio)[2]staffane ([2]1z). Sublimation 85 °C/0.2 mmHg; yield 6.12 g, 14.4% based on 8; mp 99–100 °C; ^{1}H NMR δ 2.03 (s, 12 H), 2.26 (s, 6 H); ^{13}C NMR δ 31.16, 37.99, 42.84, 53.59, 196.18; IR 2977, 1699 (C=O), 1116, 628 cm^{-1}; UV, λ_{max} nm (log ϵ_{max}), 235 (3.91); EIMS, m/z 239 (M - MeCO, 0.5), 91 (5), 43 (100); CIMS (CH_4), m/z 283 (MH, 26), 165 (53), 131 (100); HRMS, m/z (calcd for $C_{13}H_{15}O_2S_2$ 267.0515) 267.0510. Anal. Calcd for $C_{14}H_{18}O_2S_2$: C, 59.54; H, 6.42; S, 22.70. Found: C, 59.43; H, 6.45; S, 22.61.

3,3″-Bis(acetylthio)[3]staffane ([3]1z). Sublimation 125 °C/0.2 mmHg; yield 0.92 g, 2.8% based on 8; mp K 137 A 192 I;[10] ^{1}H NMR δ 1.47 (s, 6 H), 1.97 (s, 12 H), 2.25 (s, 6 H); ^{13}C NMR δ 31.12, 37.62, 37.83, 43.52, 48.38, 53.26, 196.20; IR 2972, 1700 (C=O), 1118, 629 cm^{-1}; UV, λ_{max} nm (log ϵ_{max}), 235 (3.92); EIMS, m/z 91 (5), 43 (100); CIMS (CH_4), m/z 350 (MH + 1, 20), 349 (MH, 69), 197 (100); HRMS, m/z (calcd for $C_{17}H_{21}OS_2$ 305.1034) 305.1041. Anal. Calcd for $C_{19}H_{24}O_2S_2$: C, 65.48; H, 6.94; S, 18.40. Found: C, 65.37; H, 6.98; S, 18.47.

3,3‴-Bis(acetylthio)[4]staffane ([4]1z). Yield 0.16 g, 0.3% based on 8; mp K 107 A 280 I dec;[10] ^{1}H NMR δ 1.41 (s, 12 H), 1.96 (s, 12 H), 2.25 (s, 6 H); ^{13}C NMR δ 31.22, 37.43, 37.95, 38.25, 43.81, 48.12, 53.39, 196.51; IR 2968, 1698 (C=O), 1118, 628 cm^{-1}; EIMS, m/z 91 (10), 43 (100); CIMS (CH_4), m/z 416 (MH + 1, 22), 415 (MH, 89), 263 (67), 223 (35), 207 (43), 171 (46), 157 (85), 131 (98), 125 (48), 119 (50), 107 (100). Anal. Calcd for $C_{24}H_{30}O_2S_2$: C, 69.52; H, 7.29; S, 15.46. Found: C, 69.60; H, 7.32; S, 15.37.

3,3⁗-Bis(acetylthio)[5]staffane ([5]1z). Yield, 10 mg, 0.03% based on 8; mp > 280 °C dec; ^{1}H NMR δ 1.36 (s, 6 H), 1.40 (s, 12 H), 1.96 (s, 12 H), 2.25 (s, 6 H); ^{13}C NMR δ 31.28, 37.42, 37.98 (two carbons), 38.43, 43.90, 47.78, 48.13, 53.42, 196.59; IR 2966, 1698 (C=O), 1118, 629 cm^{-1}; EIMS, m/z 91 (12), 43 (100); CIMS (CH_4), m/z 481 (MH, 100), 157 (62), 131 (56), 105 (51); CI HRMS, m/z (calcd for $C_{29}H_{37}O_2S_2$ 481.2235) 481.2207.

General Procedure for Base Hydrolysis and Nucleophilic Substitution of 3,3$^{(n-1)}$-Bis(acetylthio)[n]staffanes: Alkylation, Arylation, and Michael Addition. Ethanolic [n]1z (1 equiv) is added dropwise to a solution of KOH (2 equiv) in ethanol (1 mL per 10 mg of the staffane). After 10 min of stirring, GC analysis shows that no starting material remains. Two equivalents of electrophile are then added neat, or as a solution in ethanol or THF, and stirred for 30 min. Workup consists of solvent evaporation, water wash, extraction with methylene chloride, drying with $MgSO_4$, and thorough solvent removal under reduced pressure. Analytically pure materials are obtained by column chromatography and/or sublimation or distillation. Exceptions to this general procedure are noted below.

3,3′-Bis(butylthio)[2]staffane ([2]1aa, R = Bu) is obtained in quantitative yield using 1-bromobutane as the electrophile: bp 85–90 °C/0.35 mmHg; mp 8 °C; ^{1}H NMR δ 0.90 (t, J = 7.3 Hz, 6 H), 1.35–1.41 (m, 4 H), 1.53–1.58 (m, 4 H), 1.77 (s, 12 H), 2.50 (t, J = 7.4 Hz, 4 H); ^{13}C NMR δ 12.93, 21.46, 30.34, 32.06, 39.51, 39.73, 52.62; IR (neat) 2960, 1210 (CH_2 wag) cm^{-1}; EIMS, m/z 310 (M, 0.5), 253 (M - Bu, 25), 163 (42), 131 (100), 130 (30), 105 (24), 91 (73), 57 (45); HRMS, m/z (calcd for $C_{14}H_{21}S_2$ 253.1085) 253.1076. Anal. Calcd for $C_{18}H_{30}S_2$: C, 69.61; H, 9.74; S, 20.65. Found: C, 69.54; H, 9.77; S, 20.60.

3,3″-Bis(butylthio)[3]staffane ([3]1aa, R = Bu). The product is obtained in a quantitative yield of a white solid: sublimation 110 °C/0.5 mmHg; mp K 54.5 A 95 I;[10] ^{1}H NMR δ 0.90 (t, J = 7.3 Hz, 6 H), 1.33–1.42 (m, 4 H), 1.43 (s, 6 H), 1.51–1.59 (m, 4 H), 1.73 (s, 12 H), 2.49 (t, J = 7.4 Hz, 4 H); ^{13}C NMR δ 13.64, 22.07, 30.85, 32.58, 37.75, 39.78, 40.65, 48.33, 52.66; IR 2961, 1190 cm^{-1}; EIMS, m/z 319 (M - Bu, 1), 129 (30), 91 (100), 79 (38), 65 (45), 57 (76); HRMS, m/z (calcd for $C_{19}H_{27}S$ 287.1834) 287.1834. Anal. Calcd for $C_{23}H_{36}S_2$: C, 73.34; H, 9.64, S, 17.02. Found: C, 73.35, H, 9.68; S, 17.11.

3,3‴-Bis(butylthio)[4]staffane ([4]1aa, R = Bu). The product is obtained in quantitative yield: mp K 81 A 233 I;[10] ^{1}H NMR δ 0.90 (t, J = 7.3 Hz, 6 H), 1.39 (s, 12 H), 1.34–1.42 (m, 4 H), 1.51–1.59 (m, 4 H), 1.72 (s, 12 H); 2.48 (t, J = 7.4 Hz, 4 H); ^{13}C NMR δ 13.64, 22.07, 30.83, 32.58, 37.53, 38.19, 39.76, 40.78, 48.05, 52.66; IR 2958, 2954, 1198 cm^{-1}; EIMS, m/z 385 (M − Bu, 12), 157 (34), 143(33), 141 (33), 131 (36), 129 (50), 125 (70), 117 (37), 115 (34), 105 (57), 91 (100), 79 (39), 77 (35), 59 (30), 57 (41), 55 (37), 43 (39), 41 (73); CIMS (CH_4), m/z 443 (MH, 62), 441 (M − 1, 21), 263 (73), 223 (62), 157 (100), 143 (71), 131 (96), 119 (70), 117 (68), 107 (91), 105 (86), 93 (66), 91 (82); HRMS, m/z (calcd for $C_{28}H_{42}S_2$ 442.2728) 442.2764.

3,3′-Bis(phenylthio)[2]staffane ([2]1aa, R = Ph) is obtained in a 41% yield from 100 mg (0.35 mmol) of **[2]1z** using either a crude aqueous solution of diphenylchloronium salts[82] (~5 mmol) with added chloroform (~10 mL) or isolated diphenylchloronium tetraphenylborate[83] in boiling ethanol: mp 140–141 °C (lit.[37] mp 140–141 °C); ^{1}H NMR δ 1.73 (s, 12 H), 7.27–7.30 (m, 4 H), 7.39–7.42 (m, 6 H); ^{13}C NMR δ 40.13, 41.40, 53.16, 127.53, 128.72, 133.63, 133.85; IR 2984, 1475 and 1439 (C═C), 1145, 891 cm^{-1}.

3,3′-Bis(5,6-dimethyl-1,4-benzoquinonylthio)[2]staffane ([2]1cc). The general procedure is modified by neutralization of the initially produced thiolate salts with dilute acetic acid and extraction into methylene chloride. The organic layer is dried, and the solvent is removed. Following a general procedure,[84] 2 equiv of 2,3-dimethyl-1,4-benzoquinone (obtained from 2,3-dimethyl-1,4-hydroquinone by oxidation with chromic acid) are added to an ethanolic solution of the crude dithiol and refluxed 1 h, producing an orange suspension of the product. Evaporation of the solvent followed by column chromatography (chloroform) yields 49% of the bisquinone **[2]1cc** as an orange powder: mp 238 °C dec; ^{1}H NMR δ 2.01 (s, 12 H), 2.09 (s, 12 H), 6.62 (s, 2 H); ^{13}C NMR δ 12.36, 12.44, 38.34, 42.79, 53.13, 127.01, 140.78, 141.62, 151.36, 184.05, 184.19; IR 1654, 1644, 1624, 1576, 1308, 1132, 867 cm^{-1}; EIMS, m/z 468 (MH_2, 3), 195 (74), 169 (52), 131 (71), 130 (28), 129 (42), 116 (33), 115 (33), 91 (100), 85 (29), 53 (39); HRMS, m/z (calcd for $C_{26}H_{28}O_4S_2$ 468.1429) 468.1426.

Differentiation of [2]Staffane-3,3′-dithiol Termini. A solution of **[2]1z** (100 mg, 0.18 mmol) in ethanol (10 mL) is half hydrolyzed by slowly dropping in a solution of KOH (38 mg, 87% purity) in ethanol (5 mL). After 10 min, benzyl bromide (45 μL, 0.18 mmol) is added. Standard workup yields 98 mg of crystalline solid containing the starting material, **23** (R = $PhCH_2$), and doubly benzylated **[2]1aa** (R = $PhCH_2$). These are separated with column chromatography using 3% ethyl acetate/hexanes eluent to give 30 mg (26% yield) of **23** (R = $PhCH_2$) and 24 mg (18% yield) of **[2]1aa** (R = $PhCH_2$).

3-(Acetylthio)-3′-(benzylthio)[2]staffane (23, R = $PhCH_2$). Mp 106–106.5 °C; ^{1}H NMR δ 1.72 (s, 6 H), 1.97 (s, 6 H), 2.24 (s, 3 H), 3.74 (s, 2 H), 7.23–7.34 (m, 5 H); ^{13}C NMR δ 31.20, 35.77, 38.01, 40.16, 40.25, 43.00, 52.95, 53.58, 126.87, 128.40, 128.70, 138.75, 196.14; IR 1690 (C═O), 1120 cm^{-1}; EIMS, m/z 286 (M − MeCO, 1), 255 (M − Ph, 17), 163 (12), 129 (13), 105 (10), 92 (11), 91 (100), 65 (12), 43 (54). Anal. Calcd for $C_{19}H_{22}OS_2$: C, 69.05; H, 6.71; S, 19.40. Found: C, 68.91; H, 6.77; S, 19.53.

3,3′-Bis(benzylthio)[2]staffane ([2]1aa, R = $PhCH_2$). Mp 156–158 °C; ^{1}H NMR δ 1.71 (s, 12 H), 3.76 (s, 4 H), 7.23–7.37 (m, 10 H); ^{13}C NMR δ 35.72, 40.02, 40.28, 52.80, 126.82, 128.37, 128.64, 138.68; IR 2984, 1475, 1439, 1146 cm^{-1}; EIMS, m/z 287 (M − $PhCH_2$, 2), 195 (16), 131 (12), 91 (100), 65 (11); FABMS, m/z 379 (MH, 5), 307 (59), 181 (61), 107 (100); FAB HRMS, m/z (calcd for $C_{24}H_{25}S_2$ 377.1396) 377.1396.

Miscellaneous Monomeric Adducts

Reaction of 1-Phenylpropane-1,2-dione with 1. Ethereal solution of 1-phenylpropane-1,2-dione (0.47 g, 3.2 mmol) and **1** prepared from 3 mmol of **8** is irradiated for 3 h, and the solvent is evaporated. The semicrystalline residue is separated on a silica gel column using ethyl acetate–benzene (1:4) mixture as an eluent to give three products: 1,3-dibenzoylbicyclo[1.1.1]pentane (**[1]1f**, 89 mg, 11% yield based on **8**), 1,3-diacetylbicyclo[1.1.1]pentane[33] (**[1]1j**, 55 mg, 12% yield based on **8**), and 1-acetyl-3-benzoylbicyclo[1.1.1]pentane (**16**, 151 mg, 24% yield based on **8**): sublimation 65 °C/0.1 mmHg; mp 61–63 °C; ^{1}H NMR δ 2.15 (s, 3 H), 2.49 (s, 6 H), 7.43–7.47 (m, 2 H), 7.54–7.58 (m, 1 H), 7.95–7.98 (m, 2 H); ^{13}C NMR δ 26.08, 43.07, 44.59, 54.03, 128.55, 128.74, 133.11, 136.21, 196.74, 205.28; IR 1702 (C═O), 1665 (C═O), 1283, 1179 cm^{-1}; EIMS, m/z 214 (M, 1), 171 (M − MeCO, 16), 105 (99), 77 (100). Anal. Calcd for $C_{14}H_{14}O_2$: C, 78.48; H, 6.59. Found: C, 78.46; H, 6.63.

Methyl 2-[3-(1-Ethoxyethyl)bicyclo[1.1.1]pent-1-yl]-2-hydroxypropionate (17). Ethereal solution of methyl pyruvate (1.02 g, 10 mmol) and **1** prepared from 10 mmol of **8** is irradiated in a Pyrex flask for 3 h. Evaporation of the solvent followed by vacuum distillation (70–73 °C/0.1 mmHg) gives 1.16 g (48% yield based on **8**) of colorless oily diastereoisomeric mixture, which was not purified further: ^{1}H NMR δ 0.99 (d, J = 6.4 Hz, 3 H), 1.10 (t, J = 7.1 Hz, 3 H), 1.29 (s, 3 H), 1.46–1.60 (m, 6 H), 3.01 (br s, 1 H), 3.33 (q, J = 6.4 Hz, 1 H), 3.44 (q, J = 7.1 Hz, 2 H), 3.71 (s, 3 H); ^{13}C NMR δ 15.50, 16.88, 20.93, 40.23, 43.45, 46.07, 52.17, 64.59, 73.49, 73.60, 175.56; IR (neat) 3512 (O–H), 1735 (C═O), 1258, 1171 cm^{-1}; EIMS, m/z 181 (22), 137 (100), 121 (37), 99 (63), 95 (59), 93 (51), 73 (57), 71 (59), 55 (31), 45 (61), 43 (84); CIMS, m/z 243 (21), 179 (100), 165 (52), 151 (44), 137 (84); CI HRMS m/z (calcd for $C_{13}H_{23}O_4$ 243.1596) 243.1601.

[3-(1-Ethoxyethyl)bicyclo[1.1.1]pent-1-yl]phenylmethanol (18) and (3-Benzoylbicyclo[1.1.1]pent-1-yl)phenylmethanol (19) by Reaction of Benzaldehyde with 1 in the Presence of Diethyl Ether. Freshly distilled benzaldehyde (1.59 g, 15 mmol) is added to 7 mL of ethereal solution of **1** (equivalent of generation of propellane from 3 mmol of **8**) and irradiated for 1.5 h. The reaction mixture is concentrated, and the oily residue is separated on neutral alumina column using hexanes and ethyl acetate in a 5:1 mixture as an eluent. The first fraction contains mostly benzaldehyde, and the second is consistent with **18**: ^{1}H NMR δ 1.01 (dd, J_1 = 6.4 Hz, J_2 = 1.2 Hz, 3 H), 1.13 (t, J = 7.0 Hz, 3 H), 1.45–1.59 (m, 6 H), 2.06 (br s, 1 H), 3.36 (q, J = 6.4 Hz, 1 H), 3.48 (q, J = 7.0 Hz, 2 H), 4.71 (br s, 1 H), 7.28–7.37 (m, 5 H); ^{13}C NMR δ 15.59, 16.99, 42.71, 42.76, 46.31, 64.66, 73.91 (2C), 125.92, 127.24, 128.05, 141.82; EIMS, m/z 228 (M − H_2O, 6), 200 (8), 185 (19), 167 (23), 129 (31), 128 (30), 115 (40), 105 (100), 91 (76), 79 (70), 77 (99), 73 (51), 71 (35); HRMS m/z (calcd for $C_{16}H_{20}O$ 228.1514) 228.1519.

The third fraction contains **19**: ^{1}H NMR δ 2.08 and 2.12 (AB, d, J = 9.4 Hz, 6 H), 2.73 (s, 1 H), 4.74 (s, 1 H), 7.24–7.51 (m, 8 H), 7.90 (d, J = 7.5 Hz, 2 H); ^{13}C NMR δ 43.59, 44.29, 51.08, 73.26, 125.79, 127.43, 128.16, 128.29, 128.71, 132.74, 136.36, 141.23, 197.69; IR (neat) 3455 (br), 2979, 2876, 1663, 1332, 1206 cm^{-1}; EIMS, m/z 171 (19), 105 (100), 77 (52).

1-*n*-Butyl-3-iodobicyclo[1.1.1]pentane ([1]1k). Ethereal solution of propellane **1** (prepared from 50 mmol of **8**) and 1-iodobutane (7 mL, 53 mmol) is irradiated in a round-bottomed flask until GC monitoring reveals no further progress (5 h). Solvents are evaporated and the yellowish residue is distilled (54–55 °C/0.8 mmHg) to give 4.2 g (34% yield based on **8**) of colorless liquid which gradually turns brown upon standing: ^{1}H NMR δ 0.87 (t, J = 7.1 Hz, 3 H), 1.16–1.33 (m, 4 H), 1.49 (t, J = 7.7 Hz, 2 H), 2.18 (s, 6 H); ^{13}C NMR δ 7.8, 13.86, 22.49, 28.91, 31.76, 48.56, 60.64; IR (neat) 837, 1173 cm^{-1}; EIMS, m/z 123 (68), 91 (30), 81 (100), 79 (37), 67 (47); HRMS, m/z (calcd for C_9H_{15} 123.1174) 123.1172. Anal. Calcd for $C_9H_{15}I$: C, 43.22; H, 6.05; I, 50.74. Found: C, 43.06; H, 6.07; I, 50.95.

1-Iodo-3-(1-methylpropyl)bicyclo[1.1.1]pentane. Starting from 2-iodobutane, the procedure given for **[1]1k** provided 4.0 g (32% yield based on **8**) of a slightly brownish liquid (bp 51–52 °C/0.8 mmHg) which becomes brown upon standing: ^{1}H NMR δ 0.79 (d, J = 6.7 Hz, 3 H), 0.85 (t, J = 7.2 Hz, 3 H), 0.93–1.03 (m, 1 H), 1.34–1.41 (m, 1 H), 1.47–1.53 (m, 1 H); 2.16 (s, 6 H); ^{13}C NMR δ 8.29, 11.86, 15.89, 26.48, 36.57, 52.92, 58.91; IR (neat) 1177, 847, 829 cm^{-1}; EIMS, m/z 128 (30), 127 (20), 123 (18), 81 (100), 79 (30), 77 (25), 67 (45), 55 (43); HRMS, m/z (calcd for C_9H_{15} 123.1174) 123.1171. Anal. Calcd for $C_9H_{15}I$: C, 43.22; H, 6.05; I, 50.74. Found: C, 42.99; H, 6.05; I, 51.00.

1,3-Dibromobicyclo[1.1.1]pentane ([1]1u). Bromine (12.8 g, 0.08 mol), freshly distilled from P_2O_5, is added dropwise to a stirred solution of **1** prepared from **8** (0.1 mol). The resulting mixture is evaporated, and the oily yellow residue crystallized from pentane at low temperature (−78 °C) giving 2.9 g (13% yield based on **8**) of white crystals (mp 110–115 °C). Recrystallization yields pure 1,3-dibromobicyclo[1.1.1]pentane (**[1]1u**): mp 122 °C (sealed tube, lit.[30] mp 119.5–120.5 °C); ^{1}H NMR δ 2.57 (s); ^{13}C NMR δ 30.46, 64.72; IR 1200, 873 cm^{-1}; EIMS, m/z 147 (57), 145 (58), 66 (77), 65 (100).

Addition of Benzyl Bromide to Propellane. Ethereal solution of **1** (prepared from 50 mmol of **8**), benzyl bromide (7 mL), and benzoyl peroxide (0.3 g) is irradiated in a round-bottomed flask for 10 h. Solvents are evaporated, excess benzyl bromide is distilled off (4.5 g, 40–43 °C/0.9 mmHg), and the residue is short-path distilled (100 °C/0.6 mmHg) giving 4.9 g of a semicrystalline fraction. Crystallization from pentane yields 3,3′-dibromo[2]staffane (**[2]1u**, 0.63 g, 9% yield based on **8**), which after sublimation (90 °C/1.0 mmHg) gives an analytical sample: mp 175 °C (dec sealed tube to a brown liquid at 203 °C, lit.[53] mp 185–195 °C); ^{1}H NMR δ 2.11 (s); ^{13}C NMR δ 36.30, 40.18, 57.90; IR 1206, 1111, 891, 825 cm^{-1}; EIMS, m/z 131 (19), 117 (39), 91 (100); CIMS (CH_4), m/z 213 (M − Br, 1), 211 (M − Br, 1), 132 (36), 131 (100), 91 (41). Anal. Calcd for $C_{10}H_{12}Br_2$: C, 41.13; H, 4.13; Br, 54.73. Found: C, 41.17; H, 4.18; Br, 54.64.

The filtrate is concentrated to give 90% pure 1-benzyl-3-bromobicyclo[1.1.1]pentane: ^{1}H NMR (major peaks) δ 2.06 (s, 6 H), 2.83 (s, 2 H), 7.04–7.08 (m, 2 H), 7.18–7.31 (m, 3 H); ^{13}C NMR (major peaks)

δ 37.59, 38.03, 41.55, 58.45, 126.29, 128.38, 128.70, 138.33; EIMS, *m/z* 157 (62), 129 (100), 128 (36), 117 (59), 116 (55), 115 (94), 91 (93), 65 (40), 39 (35); HRMS, *m/z* (calcd for $C_{12}H_{13}$: 157.1017) 157.1022. Minor products were identified by GCMS as bibenzyl and remaining [2]**1u**. Attempts at purification of 1-benzyl-3-bromobicyclo[1.1.1]pentane by low temperature recrystallization were unsuccessful.

1-Bromo-3-*tert*-butylbicyclo[1.1.1]pentane ([1]1v). A solution of **1** prepared from 50 mmol of **8** in pentane, *tert*-butyl bromide (35 mL), and benzoyl peroxide (0.1 g) is irradiated in a round-bottomed flask for 10 h. Evaporation of the solvent and excess *tert*-butyl bromide followed by short-path vacuum distillation gives 3.1 g of a semicrystalline fraction. Low-temperature crystallization from pentane gives 1.67 g (16% yield based on **8**) of white crystals: mp 80.5–81.0 °C; ^{1}H NMR δ 0.84 (s, 9 H), 2.03 (s, 6 H); ^{13}C NMR δ 26.45, 31.02, 37.62, 49.65, 55.48; IR 2963, 1199, 1148, 850 cm^{-1}; EIMS *m/z* 205 (2), 123 (12), 107 (28), 91 (62); HRMS *m/z* (calcd for C_9H_{15} 123.1174) 123.1178. Anal. Calcd for $C_9H_{15}Br$: C, 53.21; H, 7.44; Br, 39.34. Found: C, 53.15; H, 7.44; Br, 39.25.

Preparative GC isolation of higher oligomers from a fraction of the residue (1.25 g) from the distillation was attempted. Crude [2]**1v** was recrystallized from pentane at −78 °C: ^{1}H NMR δ 0.80 (s, 9 H), 1.41 (s, 6 H), 2.07 (s, 6 H); ^{13}C NMR δ 25.85, 29.38, 35.52, 37.63, 41.63, 46.03, 47.23, 57.22; IR 2962, 2869, 1361, 1135, 835 cm^{-1}.

Preparation of 27 and 28 by Reaction of Tetraethyl Hypophosphite with 1. An ethereal solution of tetraethyl hypophosphite[85] (6.4 g, 26 mmol) and **1**, prepared from 35 mmol of **8**, is irradiated for 8 h. When no further reaction is observed by GC monitoring, the flask containing the adducts is opened to the air and stirred at room temperature overnight. The resulting viscous yellow oil is passed through a silica gel column (200 g). Elution with ethyl acetate gives 2.0 g of low molecular weight side products not containing the bicyclo[1.1.1]pentane moiety, as determined by NMR and GCMS. Change of the eluent to acetone/ethyl acetate (7:3) permits the collection of a wide band of yellowish product (2.0 g), which after short-path distillation (170 °C/0.1 mmHg) gives 1.64 g (19% yield based on **8**) of 1,3-bis(diethoxyphosphoryl)bicyclo[1.1.1]-pentane (**27**) as a colorless oil: ^{1}H NMR δ 1.22 (td, J_1 = 7.1 Hz, J_2 = 1.1 Hz, 12 H), 2.21–2.22 (m, 6 H), 3.95–4.05 (m, 8 H); ^{13}C NMR δ 16.31 (d, J = 2.3 Hz), 36.52 (A_2X), 51.54, 61.73 (t, J = 3.0 Hz); ^{31}P NMR (H_3PO_4) δ 15.9; IR (neat) 1244, 1220, 1050, 1027, 968 cm^{-1}; EIMS, *m/z* 340 (2), 339 (2), 203 (100), 175 (38), 147 (72); CIMS (CH_4), *m/z* 342 (13), 341 (100); CI HRMS, *m/z* (calcd for $C_{13}H_{26}O_6P_2$ 341.1283) 341.1283. Anal. Calcd for $C_{13}H_{26}O_6P_2$: C, 45.88; H, 7.70; P, 18.20. Found: C, 45.93; H, 7.89; P, 18.02.

Further elution with methanol gave an oily yellow fraction which after drying in vacuum (200 °C/0.1 mmHg) yielded 3.80 g of crude ethyl *P,P*-bis(3-diethoxyphosphorylbicyclo[1.1.1]pent-1-yl)phosphinate (**28**). This byproduct was not purified further: ^{1}H NMR (major peaks) δ 1.20–1.30 (m, 15 H), 2.20–2.22 (m, 12 H), 3.91–4.05 (m, 10 H); ^{13}C NMR (major peaks) δ 16.23 (d, J = 3.3 Hz, 4C), 16.53 (d, J = 4.1 Hz), 37.43 (dd, J_1 = 155.8 Hz, J_2 = 30.0 Hz), 38.09 (dd, J_1 = 91.7 Hz, J_2 = 32.3 Hz), 51.81 (3C), 60.63 (d, J_1 = 6.3 Hz), 61.84 (d, J = 6.7 Hz, 4C); EIMS, *m/z* 497 (2), 405 (9), 361 (32), 295 (100), 211 (46), 203 (76), 175 (40), 173 (71), 147 (96), 143 (58), 129 (34), 65 (41); CIMS, *m/z* 500 (8), 499 (40), 339 (25), 311 (100); CI HRMS, *m/z* (calcd for $C_{20}H_{38}O_8P_3$ 499.1780) 499.1772.

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Multiple Behaviors in the Cleavage of Aryl Alkanoates by α- and β-Cyclodextrins. Processes Involving Two Molecules of Cyclodextrin

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Abstract: The kinetics of ester cleavage of 4-carboxy-2-nitrophenyl alkanoates (**1**) (C2–C8) and of 2-carboxy-4-nitrophenyl alkanoates (**2**) (C2, C4, C6, C8) in an aqueous phosphate buffer (pH 11.7) containing α- or β-cyclodextrin (α- or β-CD) show various types of behavior. Depending on the ester, its acyl chain, and the CD, the kinetics show acceleration (with or without saturation), retardation, acceleration and retardation, retardation and acceleration, or two kinds of acceleration. However, this diversity can be rationalized with simple reaction schemes. Short-chain esters mainly react conventionally through binary CD–ester complexes. For longer chains, some ester/CD combinations exhibit nonproductive 2:1 (CD:ester) binding, whereas other combinations show a cleavage process involving two CD molecules. The latter is most likely due to the attack of a CD (anion) on the 1:1 CD–ester complex *or* to reaction within a weak 2:1 complex. Modes of transition-state binding are probed using the pseudoequilibrium constants (K_{TS}) introduced in earlier work (*Carbohydr. Res.* **1989**, *192*, 181).

Introduction

The cleavage of aryl esters in the presence of cyclodextrins[1] (CDs) in basic aqueous solution has been studied extensively.[1-12] Various types of esters have been employed, and the dependencies of the rate accelerations (or retardations) on structure have been

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