indicating only a weak interaction between the two ends of the ligand. The log β (and hence $\Delta G°$) for the Fe_2L_3 complex of **5** is only slightly greater than twice that of the FeL_3 complex of **11** (log β = 25.6).[1] In order to account for the effect of proton competition in ligand strength comparisons, we rank the relative iron-binding ability of ligand by the pM value, defined as $-\log [Fe^{3+}]$ of a pH 7.4 solution that is 10^{-5} M in total ligand and 10^{-6} M in total iron. The pM for **5** is 21.7, almost the same as the value of 21.9 for rhodotorulic acid (**6**), although 4–14 units less than the pM for siderophores containing *three* bidentate catechol or hydroxamate groups.[5] The corresponding pM for transferrin is 23.6[2] (assuming $[HCO_3^-]$ = 0.024 M), so that neither **5** nor **6** is expected to be (thermodynamically) effective of in vivo iron removal from transferrin at low (10 μM) concentrations. At higher concentrations of ligand, the equilibrium will shift to favor the Fe_2L_3 species, and indeed, **5** removes iron from transferrin at approximately millimolar concentrations. The rate of removal by 0.2 mM ligand is somewhat slower for **5** than for the tricatecholate ligands enterobactin, MECAM, and 3,4-LICAMS. These four ligands remove 2%, 6%, 10%, and 6%, respectively, of the iron from transferrin in 30 min.[33] At 1.6 mM the rate of removal by **5** is nearly the same as the rate interpolated for the sulfonated synthetic tricatechol ligand 3,4-LICAMS.[33] Thus at millimolar concentrations, **5** is a viable agent for iron removal from transferrin. Ligands incorporating three hydroxypyridinone groups should be equally effective at removing iron from transferrin at even lower concentration.

(33) Carrano, C. J.; Raymond, K. N. *J. Am. Chem. Soc.* **1979**, *101*, 5401–4.

Conclusions

The diprotic, tetradentate ligand 1,5-bis[(1,2-dihydro-1-hydroxy-2-oxopyridin-6-yl)carbonyl]-1,5-diazapentane (**5**) reacts with ferric ion to form a Fe_2L_3 complex. In the solid state this complex has the triply-bridged structure **7**, (Figure 1). The iron-complexing ability of **5** at neutral pH resembles that of the dihydroxamate siderophore rhodotorulic acid (**6**). Unlike rhodotorulic acid or other hydroxamate ligands (including desferrioxamine B, the current therapeutic agent for human iron overload), **5** is kinetically competent to remove iron from transferrin in vitro at millimolar concentrations.

Acknowledgment. We thank Dr. Fred Hollander of the U.C. Berkeley CHEXRAY Diffraction Facility (supported in part by the National Science Foundation) for his assistance with various technical aspects of the X-ray diffraction work. An NSF graduate fellowship to R.C.S. is gratefully acknowledged. This work was supported by NIH Grant AM-32999.

Registry No. 5, 97570-39-3; $Fe_2(C_{15}H_{14}N_4O_6)_3 \cdot H_2O \cdot 2CH_3OH$, 97570-38-2; Fe, 7439-89-6.

Supplementary Material Available: Tables S1–S4, containing anisotropic thermal parameters, hydrogen atom positions, observed and calculated structure factors, and bond lengths and angles (53 pages). Ordering information is given on any current masthead page.

Pericyclynes of Order [5], [6], [7], and [8]. Simple Convergent Syntheses and Chemical Reactions of the First Homoconjugated Cyclic Polyacetylenes[1]

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Abstract: Convergent syntheses are reported for the fully methylated derivatives of [5]-, [6]-, [7]-, and [8]pericyclyne (**23**, **26**, **29**, and **32**). All the carbon atoms in each of these homoconjugated cyclic polyacetylenes were derived from the same five-carbon starting material, 2-methyl-3-butyn-2-ol. An octamethyl derivative of [5]pericyclyne with a CH_2 group at one corner has also been prepared (**36**); however, attempts to synthesize derivatives of [3]- and [4]pericyclyne were not successful. A cyclic oligomerization approach to the synthesis of pericyclynes unexpectedly gave octamethylcyclododeca-1,3,7,9-tetrayne (**39**), an isomer of octamethyl[4]pericyclyne which also has four acetylenes in a 12-membered ring. Physical and spectroscopic properties of these new cyclic polyacetylenes are discussed. Decamethyl[5]pericyclyne (**23**) forms an isolable complex with silver triflate and reacts with $Co_2(CO)_8$ to give both mono- and bis-$Co_2(CO)_6$ complexes. The latter is formed with surprisingly high chemiselectivity. Similar chemistry is seen with dodecamethyl[6]pericyclyne (**26**). The free pericyclynes can be recovered from their silver complexes by treatment with aqueous ammonia and from their cobalt complexes by oxidation with Ce(IV). Various other chemical reactions of these unusual new compounds are also reported.

Rings of atoms containing one or more —C≡C— units ("cyclynes") have aroused the curiosity of organic chemists for many years;[2,3] however, surprisingly little attention has been accorded those rings comprised entirely of —C≡C— units and CH_2 groups joined together in alternation around the perimeter, e.g., **1**, **2**, and **3**. For this intriguing class of molecules, we have


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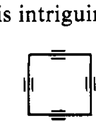
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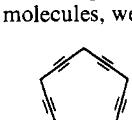
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suggested the name "pericyclynes", an appellation which connotes the presence of alkyne functionality on every side of the ring.[4]

(1) Part 4 in the series on "Cyclynes". For part 3, see ref 4; for part 5, see ref 27.
(2) Meier, H. *Synthesis* **1972**, 235–253.
(3) Nakagawa, M. In "The Chemistry of the Carbon–Carbon Triple Bond"; Patai, S., Ed.; Wiley-Interscience: New York, 1978; Vol. 2, pp 635–712.

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A numeral prefix, [*N*], is used to indicate both the number of corners (CH_2 groups) and the number of sides (—C≡C— units) that constitute a particular pericyclyne. Such compounds are expected to display a variety of interesting properties.

Valance tatuomerization of [3]pericyclyne by a symmetry-allowed intramolecular [2 + 2 + 2] cycloaddition,[5] for example, would give *tris*-cyclopropabenzene (**4**), the ultimate small ring annelated benzene. Years of research on molecules of this latter

4a

4b

4c

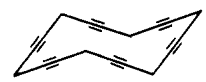
type[6] have led to syntheses of benzene rings with three fused cyclobutane rings[7] and to benzene rings annelated with two cyclobutanes and one cyclopropane,[8] but no compounds have yet been characterized with three, or even two, cyclopropanes fused to the same benzene ring. If **4** can exist, will its structure be better represented by one of the two bond-localized forms **4a** or **4b** or by the bond convergent hybrid **4c**? Will [3]pericyclyne have its —C≡C— units bowed out? Which valence tautomer will be the favored one? Will there even be a barrier on the C_9H_6 energy surface between **1** and **4**? It is possible, of course, that the energy minimum may lie somewhere between the two extremes, i.e., an "arrested transition state" for the pericyclic reaction. The name "pericyclyne" was chosen partly also to suggest this possibility. Analogous valence tautomerizations can be envisioned for the pericyclynes of higher order.

Simple group additivity calculations[9] suggest that the strain energy associated with the three-membered rings in **4**, and in the "closed" valence tautomers of other pericyclynes, will probably outweigh whatever stabilization[10] would be gained by formation of an aromatic $4N + 2$ annulene, so it seems unlikely that any of the pericyclynes will suffer irreversible thermal valence tautomerization to a polycyclopropaannulene. Nevertheless, the pericyclynes themselves should be characterized by unusual orbital interactions of a cyclic homoconjugative nature.

Homoconjugation and homoaromaticity were first recognized in cationic systems many years ago, principally through the pioneering work of Winstein,[11] and the importance of homoconjugation in neutral hydrocarbon systems has now likewise been established.[12] Some controversy still exists, however, as to whether or not neutral hydrocarbon systems can exhibit *aromatic* character arising from cyclic homoconjugation, i.e., homoaromaticity.[13,14] Pericyclynes, especially the smaller ones, offer an excellent opportunity to study this question.

The p orbitals in [3]pericyclyne can be divided into two sets, one in-plane and one out-of-plane. All six out-of-plane p orbitals line up perfectly parallel to one another and comprise a π system much like that in benzene, only with three homoconjugative interruptions. Orthogonal to this, the six in-plane p orbitals form a cyclic array in the center of the ring.[15] Each set contains six electrons, thus making [3]pericyclyne a double-barreled *tris*-homobenzene.[16] In [4]pericyclyne, each set contains eight electrons, whereas in [5]pericyclyne two $4N + 2$ systems are again found.

Higher pericyclynes, obviously, need not remain planar. The conformational possibilities available to [6]pericyclyne, for example, parallel those of its more diminutive cousin, cyclohexane. Thus, chair, boat, and twist-boat conformations (**5**, **6**, and **7**, respectively) should all be accessible. In this respect, pericyclynes



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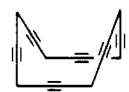

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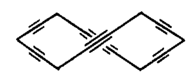

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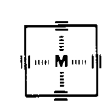
can be viewed as "exploded cycloalkanes" obtained formally from the parent system by inserting a —C≡C— unit between every pair of originally bonded carbon atoms.

Two significant differences can be anticipated, however, between the conformational properties of pericyclynes and those of cycloalkanes. The first derives from the fact that torsional effects and transannular van der Waals repulsions should virtually disappear in the pericyclynes, since the dimensions of the ring will be greatly magnified while the substituents at the corners will remain unchanged in size. Consequently, conformations **5**, **6**, and **7**, each of which can be constructed without angle strain, should differ in energy from one another hardly at all. By comparison, cyclohexane exists >99% in the chair form at room temperature.[17]

The other novel conformational property of pericyclynes concerns their flexibility. The ease with which C—C≡C bond angles can be deformed from linearity and the large number of sp carbon atoms over which angle strain can be spread will practically eliminate the barriers to conformational interconversions in the pericyclynes. Thus, the barrier separating **5** from **6** and/or **7** should be only a small fraction of the 11 kcal/mol required for the same conformational change in cyclohexane.[17]

Finally, the potentially interesting chemical properties of the pericyclynes should not be overlooked. In this regard, [4]pericyclyne might serve as a tetradentate ligand, analogous to a porphyrin **8**. Related complexes involving higher members of the series can likewise be envisioned, e.g., **9** and **10**.



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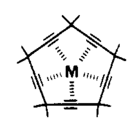

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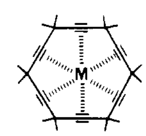


10

All of the above considerations prompted us to synthesize the first representatives of this intriguing family of compounds. Sakurai and his group in Japan have recently begun research on silicon analogues of the pericyclynes.[5]

Syntheses

Our pathway to pericyclynes relies on the cyclization of linear precursors which already contain all of the requisite —C≡C— units. This strategy offers several advantages over alternative approaches that introduce the triple bonds after formation of the large ring. Foremost among these is the entropy advantage gained in the cyclization step by reducing the conformational flexibility

(4) Scott, L. T.; DeCicco, G. J.; Hyun, J. L.; Reinhardt, G. *J. Am. Chem. Soc.* **1983**, *105*, 7760–7761.

(5) See, for example, Sakurai, H.; Eriyama, Y.; Hosomi, A.; Nakadaira, Y. *Chem. Lett.* **1984**, 595. Cyclododeca-1,5,9-triyne was once suspected of undergoing an intramolecular "acetylene trimerization"; however, labeling studies have revealed that it does not: Dower, W. V.; Vollhardt, K. P. C. *J. Am. Chem. Soc.* **1982**, *104*, 6878–6879.

(6) Thummel, R. P. *Isr. J. Chem.* **1982**, *22*, 11–18 and references cited therein.

(7) Natakul, W.; Thummel, R. P.; Taggard, A. D. *J. Am. Chem. Soc.* **1979**, *101*, 770–771.

(8) Billups, W. E.; Arney, B. E., Jr.; Lin, L.-J. *J. Org. Chem.* **1984**, *49*, 3436–3437.

(9) Benson, S. I. "Thermochemical Kinetics"; Wiley-Interscience: New York, 1976.

(10) Dewar, M. J. S. "The Molecular Orbital Theory of Organic Chemistry"; McGraw-Hill: New York, 1969; Chapter 5.

(11) Winstein, S. *Q. Rev.* **1969**, *23*, 141–176. Warner, P. M. In "Tropics in Nonbenzenoid Aromatic Chemistry"; Hirokawa Publishing Co.: Tokyo, 1977; Vol. II, p 283.

(12) See for example: Martin, H.-D.; Mayer, B. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 283–314. And: Houk, K. N.; Rondan, N. G.; Paddon-Row, M. N.; Jefford, C. W.; Huy, P. T.; Burrow, P. D.; Jordan, K. D. *J. Am. Chem. Soc.* **1983**, *105*, 5563–5569 and references cited therein. And: Scott, L. T. *Pure Appl. Chem.*, in press.

(13) Houk, K. N.; Gandour, R. W.; Strozier, R. W.; Rondan, N. G.; Paquette, L. A. *J. Am. Chem. Soc.* **1979**, *101*, 6797–6802.

(14) Paquette, L. A.; Snow, R. A.; Muthard, J. L.; Cynkowski, T. *J. Am. Chem. Soc.* **1979**, *101*, 6991–6996.

(15) The C_{16} hexaquinacene molecule of Paquette has a similar "in-plane" cycle of six p orbitals.[14] See also: McMurry, J. E.; Haley, G. J.; Matz, J. R.; Clardy, J. C.; Van Duyne, G.; Gleiter, R.; Schäfer, W.; White, D. H. *J. Am. Chem. Soc.* **1984**, *106*, 5018–5019.

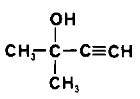
(16) The "double aromaticity" proposed by Schleyer et al. has some of these same features: Chandrasekhar, J.; Jemmis, E. D.; Schleyer, P. v. R. *Tetrahedron Lett.* **1979**, 3707–3710.

(17) Anet, F. A. L.; Bourn, A. J. R. *J. Am. Chem. Soc.* **1967**, *89*, 760–768.

of the long-chain molecules; a —C—C≡C—C— unit has no more rotational degrees of freedom than does a —C—C— unit. In addition, this approach permits the use of preformed (commerically available) alkynes, thus obviating the need for multiple elimination reactions. Finally, this approach lends itself to the development of general homologation procedures to yield precursors for many pericyclynes of differing sizes.

From the outset, we were concerned about the well-known[18] propensity of "skipped diynes" (—C≡C—CH_2—C≡C—) to suffer prototropic rearrangments under mild conditions, e.g., NaOH. To avoid such problems, therefore, we chose to replace all the propargylic hydrogens with immobile CH_3 groups. It seemed improbable that methyl substituents would alter the electronic or conformational properties of the pericyclynes to any large extent. Furthermore, the presence of *gem*-dimethyl groups at several points in the acyclic chain might even help in the final cyclization step.

Thus, we began with 2-methyl-3-butyn-2-ol (**11**), the commercially available adduct of acetone and acetylene. By standard procedures,[19-21] **11** can be transformed easily on a large scale into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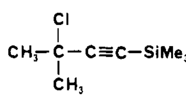
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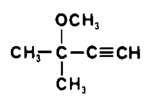
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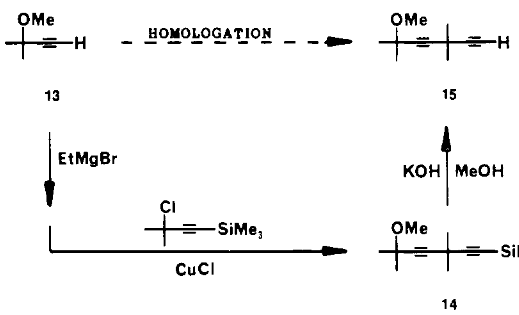
compounds **12** and **13**, the two principal building blocks used in all of the syntheses which follow.

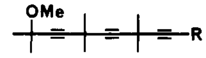
Decamethyl[5]pericyclyne. An homologation procedure based on the alkylation of terminal acetylenes with the tertiary propargylic chloride **12** was found to provide ready access to a whole family of acyclic homoconjugated polyacetylenes.[22] The first step involves deprotonation of **13** with EtMgBr followed by CuCl-catalyzed coupling[23] with **12** to give the diacetylene **14**. Subsequent desilylation of **14** with potassium hydroxide in methanol then yields **15**, a simple homologue of **13** (eq 1).



(1)

Careful spectroscopic examination of the material obtained from this coupling reaction reveals the occasional formation of small amounts (<10%) of an allene, the formal S_N2' product, which is isomeric with **14**. Allenes often represent the major products from the reactions of propargylic halides with nucleophiles, but the bulky trimethylsilyl group on **12** hinders S_N2' attack in this case. The copper may also play a role in determining the regioselectivity of this reaction.[23] Removal of the unwanted allene is most easily accomplished by distillation after the desilylation step, for only the trimethylsilyl group of the acetylenic isomer **14** is cleaved under the conditions used.

Repetition of the homologation sequence illustrated in eq 1, starting now from **15**, gives **16**, the next higher member of the series. Another cycle gives **17**, and another gives **18**. The coupling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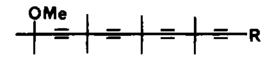
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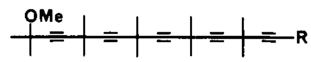

18

a) R = $SiMe_3$
b) R = H

steps all proceed in ca. 65% yield with very little allene formation, and the desilylations are nearly quantitative.

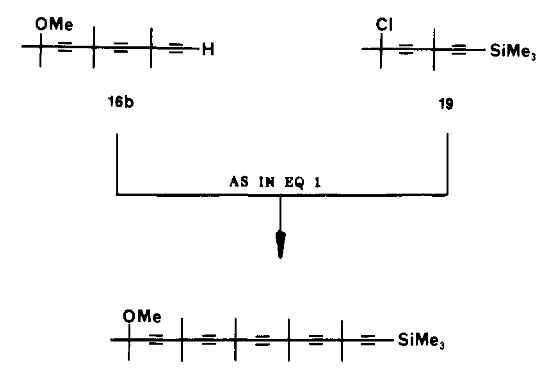
To quell ennui arising from this method of preparing **18** (and still higher homologues, see below), we devised an alternative, more efficient synthesis. Coupling of one diacetylenic unit with one triacetylenic unit clearly represents a more convergent strategy than the stepwise homologation route described above. Accordingly, a diacetylenic alkylating agent was prepared from **14** by exchanging the methoxy group for a chloride as shown in eq 2.

(2)

14 **19**

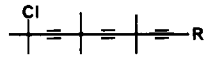
Though hardly a reaction of great generality, this ether cleavage with acetyl chloride proceeds very smoothly at room temperature in the present case (82% yield). Presumably the first step entails acylation of the ether oxygen to form an oxonium ion; loss of methyl acetate (the observable byproduct) followed by capture of chloride ion in an S_N1 reaction then completes the transformation.[24] Lewis acids have an accelerating effect but are not essential. The same reaction can also be effected with dry HCl and $ZnCl_2$.

Coupling of **16b** with **19**, the homologue of **12**, gives pentayne **18a** directly (eq 3).



(3)

The conversion of propargylic ether **14** to the corresponding chloride **19** (eq 2) was easily extended to the synthesis of higher homologues (**20**–**22**).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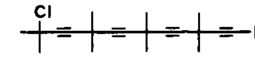
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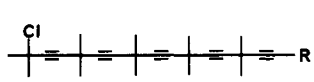

22

a) R = $SiMe_3$
b) R = H

(18) Mathai, I. M.; Taniguchi, H.; Miller, S. I. *J. Am. Chem. Soc.* **1967**, *89*, 115–120 and references cited therein.

(19) Shostakovskii, M. F.; Shikhiev, I. A.; Komarov, N. V. *Izv. Akad. Nauk. SSSR, Ser. Khim.* **1956**, 1271; *Chem. Abstr.* **1957**, *51*, 5690a.

(20) Hennion, G. F.; Sheehan, J. J.; Maloney, D. E. *J. Am. Chem. Soc.* **1950**, *72*, 3542–3545.

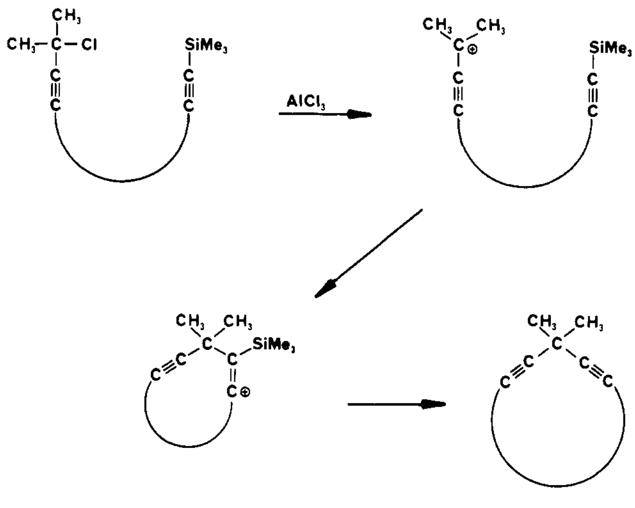
(21) Corey, E. J.; Floyd, D.; Lipshutz, B. H. *J. Org. Chem.* **1978**, 3418–3420.

(22) Alkylations of terminal acetylenes with tertiary alkyl chlorides has previously been reported by: Zimmerman, H.; Pincock, J. A. *J. Am. Chem. Soc.* **1973**, *95*, 3246–3250.

(23) Although the coupling step of this sequence qualifies formally as nucleophilic substitution at a tertiary carbon atom, the reaction almost certainly does not follow a classical S_N2 mechanism. More likely it is mediated by the copper. In the absence of CuCl, the coupling fails completely.

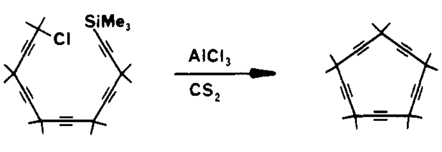
(24) For related reactions, see: Karger, M. H.; Mazur, Y. *J. Am. Chem. Soc.* **1968**, *90*, 3378–3379.

Scheme I



Initial attempts to prepare decamethyl[5]pericyclyne (**23**) were modeled after the anionic coupling reactions used to build up the acyclic precursors **15–18** (e.g., eq 1 and 3). After some experimentation, it was found that deprotonation of **22b** could be accomplished, without disturbing the chloride, by the action of *n*-BuLi at −78 °C; however, no conditions could be found to cyclize the intermediate anion to **23**. Catalysis by CuCl and other transition-metal species was explored at various temperatures without success. Consequently, efforts were turned to the development of a cationic cyclization reaction.

Cognizant of the ease with which tertiary propargylic cations can be generated (cf. eq 2) and of the "Friedel–Crafts-like" reactivity of alkynylsilanes,[25] we added the silylated pentayne chloride **22a** dropwise to a hot solution of $AlCl_3$ in CS_2.[26] This reaction gave the desired pericyclyne **23** in 35% yield (eq 4). The



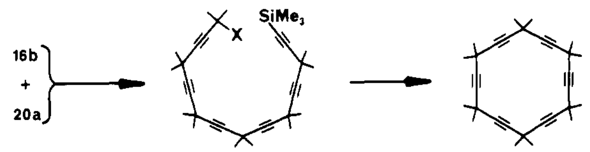
(4)

22a **23**

physical and spectroscopic properties of **23**, as well as those of the other pericyclynes described below, are collected together in a later section of this paper. The paper which follows contains (inter alia) an X-ray crystal structure of **23**, the photoelectron spectrum and the electron transmission spectrum of **23**, plus extensive calculations on pericyclynes in general.[27]

We have no direct evidence on the mechanism of the novel reaction in eq 4; however, the steps depicted in Scheme I appear entirely reasonable. The vinyl cation intermediate would be stabilized by the β-silyl group[28] and would reside in a large enough ring to retain its linear geometry. Alternatively, electrophilic attack by the initial tertiary cation on the Si–C bond could give the product directly. Other catalysts ($SnCl_4$ and $FeCl_3$) and other solvents (CH_2Cl_2 and CH_3NO_2) gave inferior yields. Extension of this reaction to the synthesis of higher pericyclynes proved to be straightforward.

Dodecamethyl[6]pericyclyne. In keeping with a convergent strategy, the triyne ether **16b** and the triyne chloride **20a** were coupled by the standard procedure to give the hexayne ether **24**. Conversion to the corresponding chloride **25** and cyclization to dodecamethyl[6]pericyclyne **26** presented no difficulties (eq 5). The yield in the cylization step was 22%.

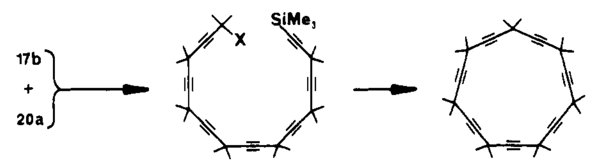


(5)

24 X = OMe **26**

25 X = Cl

Tetradecamethyl[7]pericyclyne. The heptayne ether **27** was prepared by coupling the tetrayne ether **17b** with the triyne chloride **20a**. At this time, the stepwise homologation route described earlier for preparation of tetrayne ether **17b** was replaced by a more convergent coupling of diyne ether **15** with diyne chloride **19**. Conversion of heptayne ether **27** to the corresponding chloride **28** and cyclization to tetradecamethyl[7]pericyclyne **29** was achieved by the usual procedure (eq 6); however, the yield in the cyclization step dropped to 6.2%.

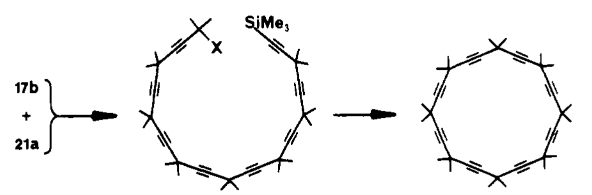


(6)

27 X = OMe **29**

28 X = Cl

Hexadecamethyl[8]pericyclyne. The two tetraynes **17b** and **21a** were coupled to give the octayne ether **30**. The yield in this coupling reaction (54%), although somewhat below those in all the previous couplings, was still quite acceptable. Cyclization of the corresponding chloride **31** to the 24-membered ring of hexadecamethyl[8]pericyclyne **32** by the normal method was accomplished in 1.5% yield (eq 7).



(7)

30 X = OMe **32**

31 X = Cl

Octamethyl[5]pericyclyne. For a variety of reasons, we considered it important to prepare at least one pericyclyne which was not fully methylated. Any unusual electronic properties resulting from the cyclic homoconjugation ought to have a greater effect on the ^1H NMR signal of a hydrogen attached directly to the ring, for example, than on that of a more remote methyl hydrogen. A CH_2 group at one corner of a pericyclyne would also provide a handle for the preparation of additional species of interest, e.g., the corresponding ketone, fulvene, anion, cation, radical, carbene, etc.

Toward this end, tetrayne ether **17b** was coupled with the propargylic bromide **33**. The resulting pentayne (**34**), our first "skipped diyne" with a CH_2 group sandwiched between two acetylenes, proved unstable on standing in air and was therefore used immediately in the next reaction. The corresponding chloride (also unstable) was prepared in the usual manner and cyclized to octamethyl[5]pericyclyne **36** (eq 8). In crystalline form, the

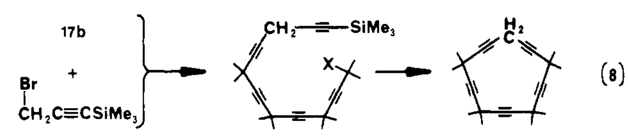
(25) Weber, W. P. "Silicon Reagents for Organic Synthesis"; Springer-Verlag: New York, 1983; Chapter 9.

(26) Cf. the intramolecular *acylations* of alkynylsilanes that give macrocyclic ketones: Utimoto, K.; Tanaka, M.; Kitai, M.; Nozaki, H. *Tetrahedron Lett.* **1978**, 2301–2304.

(27) Houk, K. N.; Scott, L. T.; Rondan, N. G.; Reinhardt, G.; Hyun, J. L.; DeCicco, G. J.; Weiss, R.; Chen, M. H. M.; Bass, L. S.; Clardy, J.; Jorgensen, F. S.; Sarkozi, V.; Petit, C.; Ng, L.; Jordan, K. D. *J. Am. Chem. Soc.*, following paper in this issue. Semiempirical calculations have also been carried out on [3]-, [4]-, and [5]pericyclyne by: Dewar, M. J. S.; Holloway, M. K. *J. Chem. Soc., Chem. Commun.* **1984**, 1188–1191.

(28) Wierschke, S. G.; Chandrasekhar, J.; Jorgensen, W. L. *J. Am. Chem. Soc.* **1985**, *107*, 1496–1500.

final product is reasonably stable.

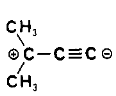


33 34 X = OMe 36

35 X = Cl

Attempted Syntheses of Octamethyl[4]pericyclyne and Hexamethyl[3]pericyclyne. Qualitative considerations suggest that these two compounds should be perfectly viable if synthetic routes could be found to make them. Unfortunately, we have been unsuccessful to date in all attempts to cyclize **20a** and **21a** under high-dilution conditions as in eq 4–8. Anionic cyclizations of **20b** and **21b**, with or without transition-metal catalysis, have likewise failed in our hands. Apparently, angle strain in the transition state raises the activation energies for these cyclizations enough for polymerization to dominate completely. We are therefore investigating alternative routes to these most interesting pericyclynes.

Attempted One-Pot Syntheses of Pericyclynes. In a formal sense, all the methylated pericyclynes can be viewed as cyclic oligomers of the propargylide zwitterion **37**. The alluring possibility that pericyclynes might actually be accessible in the laboratory by a polymerization approach prompted us to search for low molecular weight products from the decomposition of species such as **38**. Transient intermediates formed by γ eliminations had previously been trapped (as allenylidenes),[29] but to our knowledge their modes of polymerization had not been investigated. In the absence of trapping agents, the chloro compound (**38**, X = Cl) gave only high molecular weight products, and the methoxy compound (**38**, X = OMe) survived unchanged even in refluxing THF. The tetrahydropyranyl ether (**38**, X = OTHP) and the acetate (**38**, X = OAc), however, on warming with CuCl, both gave isolable amounts of a cyclic tetramer.[30] Unfortunately, the $C_{20}H_{24}$ hydrocarbon formed was not octamethyl[4]pericyclyne but proved instead to have the structure **39** (X-ray crystal structure in the following paper). A proposal for the mechanism of for-



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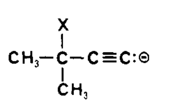

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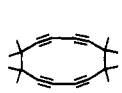


39

X = Cl, OAc, OTHP, OMe

mation of **39** from **38** was advanced in our preliminary communication of these results[30] and need not be repeated here; in the present context, it is sufficient simply to note that this route to pericyclynes has not yet been realized. A cationic polymerization route based on the chemistry illustrated in Scheme I, starting with the difunctional monomer **12**, was likewise tried without success.

Physical and Spectroscopic Properties

The fully methylated pericyclynes reported here (**23**, **26**, **29**, and **32**) are all colorless, highly crystalline, air-stable solids. The two smaller ones sublime readily in the open air, and all four exhibit sharp melting behavior without decomposition in closed capillaries (Table I). The highest-melting member of the family, dodecamethyl[6]pericyclyne (mp 249–250 °C), dissolves well in THF but is only moderately soluble in benzene and has very low solubility in chloroform, hexane, and pentane. The other three compounds all dissolve well in most common organic solvents. Octamethyl[5]pericyclyne (**36**), the only pericyclyne with a CH_2 group in the ring, melts at 125–127 °C with decomposition to a yellow oil.

Table I. Selected Properties of Several Pericyclynes

	23	26	29	32
mp, °C	201–202	249–250	173–174	189–190
^{1}H NMR[a]	1.45	1.45	1.48	1.45
^{13}C NMR[a]	82.85	83.58	83.68	83.19
	31.29	31.97	31.87	31.53
	26.17	26.03	26.12	25.59

[a] Chemical shifts in ppm downfield from tetramethylsilane. [5], [6], and [7] in C_6D_6; [8] in $CDCl_3$

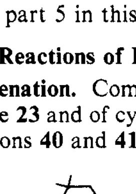
Not surprisingly, IR spectroscopy shows no —C≡C— stretching bands, even for the least symmetrical of our pericyclynes (**36**). The Raman spectrum of decamethyl[5]pericyclyne (**23**), on the other hand, was found to have several closely spaced bands at 2276 (s), 2256 (w), 2244 (w), and 2230 (s) cm^{-1}. No attempt has been made to analyze these data in detail; however, the observation of more than one band presumably indicates that the actylene stretching modes are coupled. We have not recorded the Raman spectra of any other pericyclynes. Mass spectra of these compounds are dominated by peaks corresponding to the expected sequential loss of methyl groups.

The ^{13}C NMR spectra of pericyclynes **23**, **26**, **29**, and **32** are unexceptional and virtually superimposable on one another (Table I). The same is true for their ^{1}H NMR spectra (Table I), which show no evidence for ring currents resulting from cyclic homoconjugation. In all four compounds, the CH_3 protons resonate at ca. δ 1.45; no difference is seen between the 4N and the 4N + 2 series. Even in octamethyl[5]pericyclyne (**36**), the protons attached directly to the ring resonate at a perfectly normal chemical shift for CH_2 protons flanked by two acetylenes (δ 3.08). These results, though superficially disappointing, in fact conform to the modern view of ring currents. It is well-known from annulene chemistry that any deviation from "bond convergence" (equivalent bond lengths) around a conjugated cycle reduces the ring current associated with that cycle.[31] In the pericyclynes, the distance between p orbitals on a particular acetylenic unit is very much shorter than that between p orbitals across a homoconjugation gap, and this leads to a highly "bond alternate" cycle for which little or no ring current should be expected. The absence of a ring current, however, must not be mistaken for evidence that these pericyclynes are totally devoid of cyclic homoconjugative interactions!

Neither the UV nor the MCD spectrum of decamethyl[5]pericyclyne (**23**) shows any prominent peaks above 200 nm that would correspond to low-energy electronic transitions.[32] The former is characterized by strong end absorption (ϵ 1000 at 200 nm), however, and a small shoulder at 230 nm (ϵ 30), but the best evidence for a strong, cyclic, homoconjugative interaction in these compounds comes from photoelectron spectroscopy and electron transmission spectroscopy. These gas-phase spectroscopic studies, together with extensive theoretical calculations on the pericyclynes, have been carried out in collaboration with Prof. K. N. Houk and K. D. Jordan at the University of Pittsburgh and constitute a portion of part 5 in this series of papers.[27]

Chemical Reactions of Pericyclynes and of Cyclyne 39

Hydrogenation. Complete hydrogenation of decamethyl[5]pericyclyne **23** and of cyclyne **39** to the corresponding saturated hydrocarbons **40** and **41** could be achieved only with difficulty.



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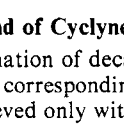


41

In both cases, the initial uptake of hydrogen was rapid, but the

(29) Hartzler, H. D. In "Carbenes"; Moss, R. A.; Jones, M., Jr., Eds.; Wiley-Interscience: New York, 1975; Vol. II, Chapter 2.
(30) Scott, L. T.; DeCicco, G. J. *Tetrahedron Lett.* **1976**, 2663–2666.
(31) For a theoretical treatment, see: Pople, J. A.; Untch, K. G. *J. Am. Chem. Soc.* **1966**, *88*, 4811–4815.
(32) We thank Prof. J. Michl (Utah) for recording MCD spectra.

reactions slowed markedly in the later stages. Repeated addition of fresh catalyst and resumption of the hydrogenation served to drive the reduction of **23** nearly to completion. A small amount of bromine was then added to consume residual olefinic material before isolation and purification of **40**. Several atmospheres of pressure were required to effect complete hydrogenation of **39** to **41**. Presumably the unsaturated centers in the partially reduced intermediates derived from **23** and **39** become buried among the ubiquitous methyl groups and lose their ability to interact with the catalyst. An attempt to semireduce **23** to the corresponding pentaene with Lindlar's catalyst was not successful.

Medium- and large-ring carbocycles with one or more sets of *gem*-dimethyl groups have attracted considerable attention over the years as subjects for conformational analysis studies.[33] Customarily, such compounds have been prepared from relatively saturated precursors; however, the syntheses described here for the previously unknown hydrocarbons **40** and **41** demonstrate the potential value of alternative approaches based on cyclyne chemistry. The room-temperature NMR spectra of **40** and **41** reveal a high degree of conformational flexibility in both compounds. We have not examined their NMR spectra at low temperatures.

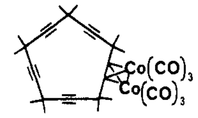
Transition-Metal Complexation. The C—C≡C—C distance of 4.15 Å in pericyclyne **23** gives the cavity in this compound exceptionally large dimensions.[27] In a *planar* conformation of **23** with straight sides 4.15 Å long, the distance from the center of the ring to the center of each —C≡C— unit measures nearly 2.9 Å. This is somewhat further than the distance from the center of 18-crown-6 to the oxygen atoms lining the perimeter of its cavity[34] and is substantially larger than the 1.9–2.0-Å metal-to-acetylene distance found in most transition-metal complexes of carbon–carbon triple bonds.[35] Thus, the cavity in **23** appears too large for simultaneous bonding of all five acetylenes to a circumvallated metal atom or ion.

Electronic considerations likewise offer little encouragement that a guest might be found to occupy the hole in **23**. We know of no atom or ion with low-lying vacant orbitals of the proper symmetry to accommodate five convergent electron pairs in a common plane. Nevertheless, guided more by hope than by theory, we exposed pentayne **23** to a variety of potential complexing agents and were rewarded by the discovery of a stable silver triflate complex. Dodecamethyl[6]pericyclyne, **26**, the next higher member in the pericyclyne family, likewise forms an isolable complex with silver triflate.

These complexes are most conveniently prepared by warming a dilute solution of silver triflate in tetrahydrofuran (THF) with an excess of the pericyclyne. Concentration of the homogeneous reaction mixture to a small volume and dilution with chloroform then precipitates the relatively insoluble complex as fine, white crystals, leaving the excess pericyclyne in solution. Both complexes dissolve well in THF and sparingly in benzene, but neither shows appreciable solubility in other common organic solvents. Attempts to grow crystals suitable for X-ray analysis, unfortunately, have not yet been successful. On silica gel, these complexes do not release the free hydrocarbon ligands; however, treatment with aqueous ammonia permits quantitative recovery of the original pericyclynes.

As expected for structures with the silver in the center of the ring (**9** and **10**), these pericyclyne complexes give ^{1}H NMR spectra comprised of just a single line and ^{13}C NMR spectra with only three signals. Silver ions chelated by three connected benzene rings have previously been found in the cyclophane field.[36] The simultaneous bonding of silver triflate to both acetylenes in cyclotetradeca-1,8-diyne and to all three double bonds in cyclododeca-1,5,9-triene has also been reported.[37] Of course, rapid interconversions of less symmetrical structures, either directly or via the free pericyclynes, cannot be ruled out as the explanation for our NMR results.

Treatment of pentayne **23** with 1 equiv of $Co_2(CO)_8$ gives the expected[38] $Co_2(CO)_6$ complex **42** together with the bis-$Co_2(CO)_6$ complex **43** and recovered **23**. Formation of **43** under these



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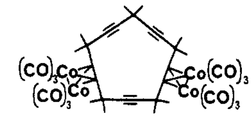

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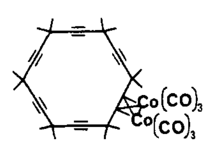
conditions indicates that the initial product (**42**) and the starting material (**23**) react with $Co_2(CO)_8$ at comparable rates. Two equivalents of $Co_2(CO)_8$ convert **23** to **43** in 68% isolated yield. Both complexes are stable in crystalline form when protected from air, but both decompose somewhat in solution.

It is interesting to note that the second $Co_2(CO)_6$ group does not become attached to an acetylene which is proximal to the first but coordinates instead to one of the distal acetylenes. NMR spectroscopy leaves no doubt as to which of the two isomeric bis-$Co_2(CO)_6$ complexes is formed. In the ^{1}H NMR spectrum of **42**, the singlet for the methyl groups flanking the coordinated acetylene is shifted downfield by 0.21 ppm, while the other methyl singlets remain at approximately the same chemical shift as the signal for the methyl groups in **23**. In the ^{1}H NMR spectrum of **43**, both of the 12-hydrogen singlets are shifted downfield while the 6-hydrogen singlet remains unshifted; thus, the unique *gem*-dimethyl group must lie *away* from the two $Co_2(CO)_6$ groups rather than between them. Apparently, the first $Co_2(CO)_6$ group deactivates the adjacent acetylenes toward complexation.

Dodecamethyl[6]pericyclyne **26** forms the analogous mono- and bis-$Co_2(CO)_6$ complexes **44** and **45**, respectively. The ^{1}H NMR spectrum of **45** has a 12-hydrogen singlet shifted 0.31 ppm downfield, another 12-hydrogen singlet shifted 0.16 ppm downfield, and a third 12-hydrogen singlet which is essentially unshifted relative to the singlet of the starting hydrocarbon. Only the



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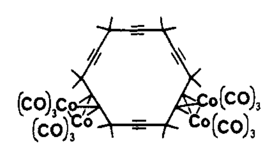

45

"meta" isomer fits this spectrum. The "ortho" isomer would give four singlets in a ratio of 6:12:12:6, whereas the "para" isomer would give only two singlets in a ratio of 12:24. The absence of the ortho isomer conforms with expectations based on the chemistry of **23**, but formation of the meta isomer (74% isolated yield) in preference to the para isomer (none detected) is difficult to understand.

The uncomplexed pericyclynes can be recovered quantitatively from **43** and **45** by oxidation of the cobalt with ceric ammonium nitrate.

Other Reactions. Both cyclynes **23** and **39** are quite stable to heat and air, and neither suffers any change upon irradiation through Pyrex with a 450-W medium-pressure mercury lamp. On the other hand, direct irradiation through quartz destroys both compounds; unfortunately, no low molecular weight products could be isolated. Tetrayne **39** reacts rapidly with bromine and with trifluoroacetic acid, giving a large number of products in each case. Surprisingly, tetracyanoethylene does not attack either **23** or **39**; both hydrocarbons can be recovered unchanged even after several hours at 60 °C. Oxidation of **39** with $NaIO_4/RuCl_3$ gives tetramethylsuccinic acid. We are continuing to explore the chemical properties of these unusual new compounds.

(33) Dale, J. "Stereochemistry and Conformational Analysis"; Verlag Chemie: New York, 1978.

(34) Hiraoka, M. "Crown Compounds"; Elsevier: New York, 1982.

(35) Ittel, S. D.; Ibers, J. A. *Adv. Organomet. Chem.* **1976**, *14*, 55.

(36) Cohen-Addad, C.; Baret, P.; Chautemps, P.; Pierre, J.-L. *Acta Crystallogr., Sect. C* **1983**, *C39*, 1346–1349. Kang, H. C.; Hanson, A. W.; Eaton, B.; Boekelheide, V. *J. Am. Chem. Soc.* **1985**, *107*, 1979–1985.

(37) Lewandos, G. S.; Gregston, D. K.; Nelson, F. R. *J. Organomet. Chem.* **1976**, *118*, 363–374.

(38) For a review of acetylene–$Co_2(CO)_6$ complexes, see Dickson, R. S.; Fraser, P. J. *Adv. Organomet. Chem.* **1974**, *12*, 323.

Experimental Section

General. Tetrahydrofuran (THF) and ether were dried by distillation under nitrogen from the sodium ketyl of benzophenone immediately prior to use. Dimethylformamide (DMF) was dried by distillation under nitrogen from magnesium sulfate. Anhydrous cuprous chloride was prepared according to the procedure in "Inorganic Syntheses".[39] Baker silica gel 60–200 was used for all column chromatography, and Woelm silica gel F was used for preparative-layer chromatography. All ^{13}C NMR spectra were recorded at 25 MHz on a JEOL FX100 instrument; ^{1}H NMR spectra were recorded on the same instrument (100 MHz) or on an Hitachi Perkin-Elmer R24B spectrometer (60 MHz); chemical shifts are reported in parts per million (ppm) downfield from tetramethylsilane. Mass spectra were recorded on an AEI MS-9 instrument with an ionization voltage of 70 eV. Combustion analyses were performed by Spang, Eagle Harbor, MI, and high-resolution mass spectra were recorded at the Midwest Center for Mass Spectrometry, Lincoln, NE (NSF Regional Facility). Melting points are uncorrected.

3-Chloro-3-methyl-1-(trimethylsilyl)-1-butyne (12).[19,20] To 1.0 mol of *n*-butyllithium in hexane (2.3 M) cooled to −78 °C was added 42.5 g (0.51 mol) of 2-methyl-3-butyn-2-ol (**11**) in 300 mL of dry THF over a 30-min period with stirring. On those occasions when the mixture set into a gel, more THF was added to keep it fluid. The light-yellow solution was then stirred at −78 °C for 1 h more. To this solution was added 1.05 g (4.45 mmol) of mercurous chloride, 0.58 g (5.9 mmol) of anhydrous cuprous chloride,[39] and then 110 g (1.01 mol) of chlorotrimethylsilane dissolved in 300 mL of dry THF. The dark-gray–green reaction mixture was allowed to warm to room temperature and was then brought to reflux for 5.5 h. The resulting heterogeneous mixture was cooled to room temperature and diluted with 400 mL of 10% aqueous hydrochloric acid. The aqueous layer was separated and extracted with 100 mL of ether. The combined organic layers were dried over magnesium sulfate and concentrated under reduced pressure. Vacuum distillation gave 71–73 g (90–92%) of colorless 2-methyl-4-(trimethylsilyl)-3-butyn-2-ol: bp 69–72 °C/15 torr [lit.[19] 71 °C/18 torr]. Care must be taken during the distillation to prevent the product from crystallizing (mp 42 °C) before it reaches the receiver. A 10.4-g (67 mmol) sample of this material was added to 30 mL of concentrated hydrochloric acid which was kept below 10 °C by means of an ice bath. To this mixture was added a trace of copper powder and 5.5 g (50 mmol) of anhydrous calcium chloride.[20] The reaction mixture was then placed in a room-temperature water bath and stirred until NMR analysis of the organic layer indicated completion of the reaction (ca. 16 h). The milky organic layer was separated, washed with 2 × 20 mL of 5% aqueous sodium bicarbonate, stirred over anhydrous potassium carbonate at room temperature for 24 h, filtered, and concentrated under reduced pressure to give 11.0–11.6 g (95–100%) of crude product. Vacuum distillation gave 10.1–10.5 g (87–90%) of pure 3-chloro-3-methyl-1-(trimethylsilyl)-1-butyne (**12**) as a colorless liquid: bp 46 °C/14 torr [lit.[19] 49 °C/14 torr].

3-Methoxy-3-methyl-1-butyne (13).[21] A slurry of 72 g (1.5 mol) of sodium hydride (50% in oil) in 1 L of dry DMF was cooled to 0 °C. This mixture was stirred while 84 g (1.0 mol) of 2-methyl-3-butyn-2-ol (**11**) in 150 mL of DMF was added over a period of 2 h, and stirring was continued for 1 h more at 0 °C. Then 190 g (1.5 mol) of dimethyl sulfate was added over a period of 1 h, and the reaction mixture was stirred at room temperature for an additional hour. Excess sodium hydride was destroyed by the slow addition of 100 mL of glacial acetic acid. The product was distilled directly from the reaction mixture with an oil bath at 150–160 °C. The crude material was washed with aqueous sodium bicarbonate and aqueous sodium chloride, dried over magnesium sulfate, and distilled to give 78.5 g (80%) of 3-methoxy-3-methyl-1-butyne (**13**) as a colorless liquid: bp 78–80 °C [lit.[21] 81 °C].

Coupling Reactions. General Procedure.[22] Under a nitrogen atmosphere, the acetylenic ether (**13**, **15**, **16b**, or **17b**) in dry THF was added dropwise to a solution of ethylmagnesium bromide in THF (1.4 M, 10% excess) at 0 °C. On those occasions when crystals began to form during the addition, the reaction mixture was warmed to room temperature and then cooled back to 0 °C. At the end of the addition, the gray solution was heated to 50 °C for 30 min and then cooled back to room temperature. A catalytic amount of anhydrous cuprous chloride[39] was added. The alkylating agent (**12**, **19**, **20a**, or **21a**) in dry THF was then added over a 5–15-min period, depending on the scale of the reaction. The solution was stirred for 2 h at 50–55 °C and overnight at room temperature, during which time the magnesium salt precipitated. The reaction mixture was quenched with 10% aqueous sulfuric acid, and the layers were separated. The aqueous layer was extracted with ether. The combined organic layers were washed with aqueous sodium bicarbonate and aqueous ammonium chloride, dried over magnesium sulfate, and concentrated under reduced pressure. The crude product was purified either by distillation or by column chromatography.

6-Methoxy-3,3,6-trimethyl-1-(trimethylsilyl)-1,4-heptadiyne (14). This material was prepared according to the general procedure described above for coupling reactions using 57.0 g (582 mmol) of monoyne ether **13** in 100 mL of THF, 2.0 g of cuprous chloride,[39] and 102.0 g (585 mmol) of monoyne chloride **12** in 100 mL of THF. Distillation gave 113.5 g (83%) of 6-methoxy-3,3,6-trimethyl-1-(trimethylsilyl)-1,4-heptadiyne (**14**) as a colorless oil: bp 60–68 °C/1.0 torr; ^{1}H NMR (CCl_4) δ 3.17 (s, 3), 1.47 (s, 6), 1.33 (s, 6), 0.15 (s, 9); MS, *m/z* (rel intensity) no M^+, 222 (12), 221 (100), 191 (11), 103 (18), 97 (22), 89 (30), 73 (100), 59 (28), 43 (31). Anal. Calcd for $C_{14}H_{24}OSi$: C, 71.12; H, 10.23. Found: C, 71.28; H, 10.14.

Removal of Trimethylsilyl Groups. General Procedure. A methanol solution of the trimethylsilylalkyne (**14**, **16a**, or **17a**) was cooled to 0 °C. A solution of potassium hydroxide in methanol was added, and the reaction mixture was stirred for 16 h. Then 200 mL of water was added, and the mixture was extracted with 5 × 50 mL of pentane. The combined organic layers were washed with water, dried over magnesium sulfate, and concentrated under reduced pressure. The crude product was either distilled, chromatographed, or used without further purification.

6-Methoxy-3,3,6-trimethyl-1,4-heptadiyne (15). This material was prepared according to the general procedure described above for the removal of trimethylsilyl groups using 40.0 g (169 mmol) of diyne ether **14** and 28.0 g (500 mmol) of potassium hydroxide in 250 mL of methanol. Distillation of the crude product gave 22.3 g (80%) of 6-methoxy-3,3,6-trimethyl-1,4-heptadiyne (**15**) as a colorless oil: bp 62–63 °C/15 torr; ^{1}H NMR (CCl_4) δ 3.15 (s, 3), 1.95 (s, 1), 1.45 (s, 6), 1.33 (s, 6); MS, *m/z* (rel intensity) 164 (M^+, <1), 150 (12), 149 (100), 117 (13), 115 (14), 105 (13), 91 (41), 77 (21), 51 (29), 43 (79). Anal. Calcd for $C_{11}H_{16}O$: C, 80.44; H, 9.82. Found: C, 80.10; H, 8.78.

9-Methoxy-3,3,6,6,9-pentamethyl-1-(trimethylsilyl)-1,4,7-decatriyne (16a). This material was prepared according to the general procedure described above for coupling reactions using 24.0 g (146 mmol) of diyne ether **15** in 50 mL of THF, 0.5 g of cuprous chloride,[39] and 28.0 g (160 mmol) of monoyne chloride **12** in 50 mL of THF. Distillation gave 27.3 g (62%) of 9-methoxy-3,3,6,6,9-pentamethyl-1-(trimethylsilyl)-1,4,7-decatriyne (**16**) as a colorless oil: bp 85–87 °C/0.1 torr; ^{1}H NMR (CCl_4) δ 3.20 (s, 3), 1.43 (s, 12), 1.33 (s, 6), 0.13 (s, 9). This material was not purified further before removal of the trimethylsilyl group.

9-Methoxy-3,3,6,6,9-pentamethyl-1,4,7-decatriyne (16b). This material was prepared according to the general procedure described above for the removal of trimethylsilyl groups using 32.0 (106 mmol) of triyne ether **16a** and 25.0 g (446 mmol) of potassium hydroxide in 300 mL of methanol. Distillation of the crude product gave 18.8 g (77%) of 9-methoxy-3,3,6,6,9-pentamethyl-1,4,7-decatriyne (**16b**) as a colorless oil: bp 68–71 °C/0.1 torr; ^{1}H NMR ($CDCl_3$) δ 3.20 (s, 3), 2.01 (s, 1), 1.47 (s, 12), 1.33 (s, 6); MS, *m/z* (rel intensity) no M^+, 216 (12), 215 (100), 185 (12), 169 (10), 142 (10), 59 (36), 43 (28). Anal. Calcd for $C_{16}H_{22}O$: C, 83.42; H, 9.63. Found: C, 83.36; H, 9.47.

12-Methoxy-3,3,6,6,9,9,12-heptamethyl-1-(trimethylsilyl)-1,4,7,10-tridecatetrayne (17a). This material was prepared according to the general procedure described above for coupling reactions using 20.5 g (125 mmol) of diyne ether **15** in 50 mL of THF, 1.2 g of cuprous chloride,[39] and 32.0 g (133 mmol) of diyne chloride **19** in 50 mL of THF. Distillation gave 31.9 g (69%) of 12-methoxy-3,3,6,6,9,9,12-heptamethyl-1-(trimethylsilyl)-1,4,7,10-tridecatetrayne (**17a**) as a colorless oil: bp 124 °C/0.2 torr; ^{1}H NMR (CCl_4) δ 3.15 (s, 3), 1.43 (s, 18), 1.33 (s, 6), 0.15 (s, 9). This material was not purified further before removal of the trimethylsilyl group.

12-Methoxy-3,3,6,6,9,9,12-heptamethyl-1,4,7,10-tridecatetrayne (17b). This material was prepared according to the general procedure described above for the removal of trimethylsilyl groups using 11.0 g (30 mmol) of tetrayne ether **17a** and 6.0 g (107 mmol) of potassium hydroxide in 60 mL of methanol. Workup gave 8.85 g (100%) of reasonably pure 12-methoxy-3,3,6,6,9,9,12-heptamethyl-1,4,7,10-tridecatetrayne (**17b**) as a pale yellow oil. An analytically pure sample was prepared (76% yield) by distillation: bp 80–82 °C/0.05 torr; ^{1}H NMR (CCl_4) δ 3.15 (s, 3), 1.93 (s, 1), 1.43 (s, 18), 1.33 (s, 6); GC/MS, *m/z* (rel intensity) no M^+, 282 (12), 281 (100), 251 (12), 219 (12), 193 (11), 106 (20), 105 (22), 97 (13), 91 (16), 85 (31), 84 (55), 77 (31), 73 (24). Anal. Calcd for $C_{21}H_{28}O$: C, 85.08; H, 9.52. Found: C, 84.95; H, 9.48.

15-Methoxy-3,3,6,6,9,9,12,12,15-nonamethyl-1-trimethylsilyl-1,4,7,10,13-hexadecapentayne (18a). This material was prepared according to the general procedure described above for coupling reactions using 10.25 g (44.6 mmol) of triyne ether **16b** in 20 mL of THF, 0.3 g of cuprous chloride,[39] and 11.60 g (48.2 mmol) of diyne chloride **19** in 20 mL of THF. Chromatography on silica gel with 30:1 hexane/ethyl acetate gave 12.57 g (65%) of 15-methoxy-3,3,6,6,9,9,12,12,15-nona-

(39) Anhydrous cuprous chloride is a colorless powder: Keller, R. N.; Wycoff, H. D. *Inorg. Synth.* **1946**, *2*, 1. Commercially available cuprous chloride is often contaminated with cupric chloride hydrate (green).

methyl-1-(trimethylsilyl)-1,4,7,10,13-hexadecapentayne (**18a**) as colorless crystals: mp 70–71 °C; ^{1}H NMR (CCl_4) δ 3.15 (s, 3), 1.44 (s, 24), 1.35 (s, 6), 0.17 (s, 9). Anal. Calcd for $C_{29}H_{42}OSi$: C, 80.12; H, 9.74. Found: C, 80.31; H, 9.68.

15-Methoxy-3,3,6,6,9,9,12,12,15-nonamethyl-1,4,7,10,13-hexadecapentayne (18b). This material was prepared according to the general procedure described above for the removal of trimethylsilyl groups using 20.0 g (46 mmol) of pentayne ether **18a** and 5.6 g (100 mmol) of potassium hydroxide in 400 mL of methanol. Chromatography of the crude product on 100 g of silica oil with 3% ethyl acetate/hexane gave 16.3 g (98%) of 15-methoxy-3,3,6,6,9,9,12,12,15-nonamethyl-1,4,7,10,13-hexadecapentayne (**18b**) as colorless crystals: mp 40–41 °C; ^{1}H NMR (CCl_4) δ 3.12 (s, 3), 1.92 (s, 1), 1.40 (s, 24), 1.30 (s, 6).

Polyacetylenic Chlorides from Polyacetylenic Ethers. General Procedure. A solution of the acetylenic ether (**14**, **16a**, **17a**, **18a**, **24**, **27**, or **30**) and acetyl chloride in dry dichloromethane was stirred at 0 °C. Four drops of stannic chloride were added. The reaction mixture turned black immediately, and the temperature rose to 10–15 °C. Stirring was continued for 15 min, then the mixture was diluted with ice–water. The two layers were separated, and the aqueous layer was extracted with methylene chloride. The combined organic layers were washed with water and aqueous sodium bicarbonate, dried over sodium sulfate, and concentrated under reduced pressure. The crude product was purified by distillation, recrystallization, or sublimation.

6-Chloro-3,3,6-trimethyl-1-(trimethylsilyl)-1,4-heptadiyne (19). This material was prepared according to the general procedure described above for the conversion of polyacetylenic ethers to polyacetylenic chloride using 60 g (254 mmol) of diyne ether **14** and 30 g (382 mmol) of acetyl chloride in 75 mL of dichloromethane. Distillation gave 50.3 g (82%) of 6-chloro-3,3,6-trimethyl-1-(trimethylsilyl)-1,4-heptadiyne (**19**) as a colorless oil: bp 62–64 °C/0.6 torr [lit.[40] 78–79 °C/3 torr]; ^{1}H NMR ($CDCl_3$) δ 1.73 (s, 6), 1.40 (s, 6), 0.10 (s, 9); MS, m/z (rel intensity) no M^+, 205 (16), 204 (47), 189 (66), 168 (30), 147 (44), 133 (29), 132 (30), 131 (26), 117 (24), 97 (32), 93 (41), 91 (26), 73 (100), 59 (20).

9-Chloro-3,3,6,6,9-pentamethyl-1-(trimethylsilyl)-1,4,7-decatriyne (20a). This material was prepared according to the general procedure described above for the conversion of polyacetylenic ethers to polyacetylenic chlorides using 11.6 g (38.4 mmol) of triyne ether **16a** and 10.0 g (127 mmol) of acetyl chloride in 25 mL of dichloromethane. Recrystallization of the crude product from pentane gave 10.4 g (88%) of 9-chloro-3,3,6,6,9-pentamethyl-1-(trimethylsilyl)-1,4,7-decadiyne (**20a**) as colorless needles: mp 34–35 °C; ^{1}H NMR (CCl_4) δ 1.75 (s, 6), 1.43 (s, 12), 0.11 (s, 9). Anal. Calcd for $C_{18}H_{27}ClSi$: C, 70.43; H, 8.87. Found: C, 70.25; H, 8.73.

9-Chloro-3,3,6,6,9-pentamethyl-1,4,7-decatriyne (20b). To a suspension of 222 mg (1.63 mmol) of powdered anhydrous zinc chloride in 25 mL of dry methylene chloride was added 500 mg (2.17 mmol) of triyne ether **16b**, and dry hydrogen chloride gas was bubbled through the rapidly stirred mixture for 40 min. The reaction was quenched by the cautious addition of powdered anhydrous potassium carbonate in small portions with stirring until the solution no longer changed color. The solution was filtered and concentrated under reduced pressure. Sublimation of the crude product (30 °C/0.1 torr) gave 448 mg (88%) of 9-chloro-3,3,6,6,9-pentamethyl-1,4,7-decatriyne (**20b**) as a colorless solid: mp 34–36 °C; ^{1}H NMR ($CDCl_3$) δ 2.14 (s, 1), 1.83 (s, 6), 1.49 (s, 6), 1.46 (s, 6); MS m/z (rel intensity) no M^+, 219 (19), 199 (18), 198 (15), 183 (52), 169 (63), 168 (51), 167 (64), 153 (90), 142 (65), 129 (42), 128 (52), 120 (36), 119 (48), 115 (50), 105 (27), 91 (100). Anal. Calcd for $C_{15}H_{19}Cl$: C, 76.74; H, 8.16; Cl, 15.10. Found: C, 76.83; H, 8.27; Cl, 15.06.

12-Chloro-3,3,6,6,9,9,12-heptamethyl-1-(trimethylsilyl)-1,4,7,10-tridecatetrayne (21a). This material was prepared according to the general procedure described above for the conversion of polyacetylenic ethers to polyacetylenic chlorides using 20.0 g (54 mmol) of tetrayne ether **17a** and 17.0 g (217 mmol) of acetyl chloride in 50 mL of dichloromethane. Sublimation of the crude product (40 °C/0.2 torr) gave 17.2 g (85%) of 12-chloro-3,3,6,6,9,9,12-heptamethyl-1-(trimethylsilyl)-1,4,7,10-tridecatetrayne (**21a**) as colorless crystals: mp 54–56 °C; ^{1}H NMR (CCl_4) δ 1.73 (s, 6), 1.42 (s, 18), 0.17 (s, 9). Anal. Calcd for $C_{23}H_{33}ClSi$: C, 74.05; H, 8.82. Found: C, 74.00; H, 8.83.

12-Chloro-3,3,6,6,9,9,12-heptamethyl-1,4,7,10-tridecatetrayne (21b). To a suspension of 0.612 g (4.49 mmol) of powdered anhydrous zinc chloride in 50 mL of dry methylene chloride was added 1.78 g (6.01 mmol) of tetrayne ether **17b**, and dry hydrogen chloride gas was bubbled through the rapidly stirred mixture for 20 min. The reaction was quenched by the cautious addition of powdered anhydrous potassium carbonate in small portions with stirring until the solution no longer changed color. The solution was filtered and concentrated under reduced pressure. Sublimation of the crude product (75 °C/50 torr) gave 1.48 g (82%) of 12-chloro-3,3,6,6,9,9,12-heptamethyl-1,4,7,10-tridecatetrayne (**21b**) as a colorless solid: mp 41.5–43.5 °C; ^{1}H NMR ($CDCl_3$) δ 2.14 (s, 1), 1.81 (s, 6), 1.49 (s, 6), 1.44 (s, 12); MS, m/z (rel intensity) 300 (4, M^+), 249 (39), 234 (43), 219 (100), 204 (38), 193 (50), 179 (41), 165 (39). An analytically pure sample was prepared by recrystallization from pentane at −78 °C: mp 46.5–47 °C. Anal. Calcd for $C_{20}H_{25}Cl$: C, 79.84; H, 8.38; Cl, 11.79. Found: C, 79.58; H, 8.19; Cl, 11.81.

15-Chloro-3,3,6,6,9,9,12,12,15-nonamethyl-1-(trimethylsilyl)-1,4,7,10,13-hexadecapentayne (22a). This material was prepared according to the general procedure described above for the conversion of polyacetylenic ethers to polyacetylenic chlorides using 10.0 g (23 mmol) of pentayne ether **18a** and 14.0 g (178 mmol) of acetyl chloride in 20 mL of dichloromethane. Sublimation of the crude product (105 °C/0.1 torr) gave 8.3 g (82%) of 15-chloro-3,3,6,6,9,9,12,12,15-nonamethyl-1-(trimethylsilyl)-1,4,7,10,13-hexadecapentayne (**22a**) as colorless crystals: mp 76–77 °C; ^{1}H NMR (CCl_4) δ 1.75 (s, 6), 1.40 (s, 24), 0.13 (s, 9). Anal. Calcd for $C_{28}H_{39}ClSi$: C, 76.58; H, 8.95. Found: C, 76.68; H, 8.95.

15-Chloro-3,3,6,6,9,9,12,12,15-nonamethyl-1,4,7,10,13-hexadecapentayne (22b). To a room-temperature solution of 0.5 g (1.38 mmol) of pentayne ether **18b** in 1 mL of dry methylene chloride were added 5 mL of acetyl chloride and 1 drop of stannic chloride. After 10 min, the reaction mixture was diluted with 10 mL of pentane and 10 mL of water. The organic layer was separated, dried over magnesium sulfate, and concentrated under reduced pressure. Recrystallization of the crude product from pentane at −78 °C gave 0.225 g (45%) of 15-chloro-3,3,6,6,9,9,12,12,15-nonamethyl-1,4,7,10,13-hexadecapentayne (**22b**) as a colorless powder: mp 71–72 °C; ^{1}H NMR (CCl_4) δ 1.95 (s, 1), 1.75 (s, 6), 1.43 (s, 24).

Cyclization Reactions. General Procedure. A solution of the acetylenic chloride (**22a**, **25**, **28**, **31**, or **35**) in 150 mL of carbon disulfide[41] was added dropwise with stirring over a period of 6 h to a refluxing solution of aluminum chloride (anhydrous, powdered) in 1.0 L of carbon disulfide[41] by using a high-dilution apparatus.[42] The black reaction mixture was kept at reflux for 30 min more, cooled to room temperature, and then quenched with 300 mL of dilute hydrochloric acid. The mixture and residue were extracted with dichloromethane. The combined organic layers were washed with aqueous sodium bicarbonate and aqueous sodium chloride, dried over magnesium sulfate, and concentrated under reduced pressure. The dark red semicrystalline crude product was purified by chromatoraphy on silica gel with 1:1 benzene/hexane followed by recrystallization.

Decamethyl[5]pericyclyne (23). This material was prepared according to the general procedure described above for cyclization reactions using 1.5 g (3.4 mmol) of the pentayne chloride **22a** and 1.6 g (12 mmol) of aluminum chloride. Chromatography and recrystallization from hexane gave 316–390 mg (28–35%) of decamethyl[5]pericyclyne (**23**) as large colorless needles: mp 201–202 °C; ^{1}H NMR (C_6D_6) δ 1.45; ^{13}C NMR (C_6D_6) δ 82.9, 31.3, 26.2; IR (KBr) 2980 (vs), 2930 (s), 2860 (w), 1465 (w), 1450 (w), 1435 (w), 1373 (w), 1355 (s), 1255 (vs), 1125 (s), 1090 (s, br), 1015 (s, br), 795 (s), 642 (s), 528 (sh), 515 cm^{-1} (s); Raman (crystal) 2276 (s), 2256 (w), 2244 (m), 2230 cm^{-1} (s); UV (pentane) end absorption (ϵ at 200 nm = 1000), no max > 200 nm, shoulder 230 nm (ϵ 30); MS (42 eV), m/z (rel intensity) 330 (M^+, 24), 315 (100), 300 (7), 285 (30), 270 (12), 257 (17), 255 (11); MS M^+ calcd for $C_{25}H_{30}$ 330.2348, found 330.2346. Anal. Calcd for $C_{25}H_{30}$: C, 90.85; H, 9.15. Found: C, 90.69; H, 9.27.

18-Methoxy-3,3,6,6,9,9,12,12,15,15,18-undecamethyl-1-(trimethylsilyl)-1,4,7,10,13,16-nonadecahexayne (24). This material was prepared according to the general procedure described above for coupling reactions using 7.3 g (31.7 mmol) of triyne ether **16b** in 25 mL of THF, 0.4 g of cuprous chloride,[39] and 11.5 g (37.5 mmol) of triyne chloride **20a** in 25 mL of THF. Chromatography on silica gel with 30:1 hexane/ethyl acetate gave 10.2 g (64%) of 18-methoxy-3,3,6,6,9,9,12,12,15,15,18-undecamethyl-1-(trimethylsilyl)-1,4,7,10,13,16-nonadecahexayne (**24**) as colorless crystals: mp 59–60 °C; ^{1}H NMR ($CDCl_3$) δ 3.27 (s, 3), 1.44 (s, 30), 1.40 (s, 6), 0.17 (s, 9). Anal. Calcd for $C_{34}H_{48}OSi$: C, 81.54;

(40) Shostakovskii, M. F.; Komarov, N. V.; Kuznetsova, V. P.; Igonina, I. I.; Semenova, N. V. *Izv. Okad. Nauk. SSSR, Otdel. Khim. Nauk.* **1962**, 510; *Chem. Abstr.* **1962**, *57*, 15138*d*.

(41) Reagent grade carbon disulfide was used directly from the bottle for these cyclization reactions. In scrupulously dried carbon disulfide, $AlCl_3$ is too reactive a catalyst, and these cyclizations fail. In scrupulously dried carbon disulfide with $EtAlCl_2$ as the catalyst, cyclization occurs in acceptable yield. Apparently, $AlCl_3$ is fortuitously deactivated by impurities (water?) in reagent-grade carbon disulfide, which results in a catalyst comparable to $EtAlCl_2$.

(42) Vogtle, F.; Wittig, G. *J. Chem. Educ.* **1973**, *50*, 650.

H, 9.66. Found: C, 81.68; H, 9.62.

18-Chloro-3,3,6,6,9,9,12,12,15,15,18-undecamethyl-1-(trimethylsilyl)-1,4,7,10,13,16-nonadecahexayne (25). This material was prepared according to the general procedure described above for the conversion of polyacetylenic ethers to polyacetylenic chlorides using 8.0 g (16 mmol) of hexayne ether **24** and 5.0 g (64 mmol) of acetyl chloride in 25 mL of dichloromethane. Recrystallization of the crude product from pentane followed by sublimation (110 °C/0.1 torr) gave 7.5 g (93%) of 18-chloro-3,3,6,6,9,9,12,12,15,15,18-undecamethyl-1-(trimethylsilyl)-1,4,7,10,13,16-nonadecahexayne (**25**) as colorless crystals: mp 91–92 °C; ^{1}H NMR ($CDCl_3$) δ 1.79 (s, 6), 1.43 (s, 30), 0.15 (s, 9). Anal. Calcd for $C_{33}H_{45}ClSi$: C, 78.44; H, 8.98. Found: C, 78.41; H, 8.90.

Dodecamethyl[6]pericyclyne (26). This material was prepared according to the general procedure described above for cyclization reactions using 1.5 g (3.0 mmol) of the hexayne chloride **25** and 1.2 g (9.0 mmol) of aluminum chloride. Chromatography and recrystallization from THF gave 200–256 mg (17–22%) of dodecamethyl[6]pericyclyne (**26**) as colorless thin leafs: mp 249–250 °C; ^{1}H NMR (C_6D_6) δ 1.45; ^{13}C NMR (C_6D_6) δ 83.6, 32.0, 26.0; IR (KBr) 2985 (vs), 2935 (s), 2875 (w), 1360 (s), 1270 (vs), 1125 (s), 995 (w), 630 cm^{-1} (s). Anal. Calcd for $C_{30}H_{36}$: C, 90.85; H, 9.15. Found: C, 90.78; H, 9.14.

21-Methoxy-3,3,6,6,9,9,12,12,15,15,18,18,21-tridecamethyl-1-(trimethylsilyl)-1,4,7,10,13,16,19-docosaheptayne (27). This material was prepared according to the general procedure outlined above for coupling reactions using 13.8 g (46.6 mmol) of tetrayne ether **17b** in 50 mL of THF, 0.4 g of cuprous chloride,[39] and 15.5 g (50.6 mmol) of triyne chloride **20a** in 50 mL of THF. Chromatography on silica gel with 30:1 hexane/ethyl acetate gave 16.75 g (63%) of 21-methoxy-3,3,6,6,9,9,12,12,15,15,18,18,21-tridecamethyl-1-(trimethylsiiyl)-1,4,7,10,13,16,19-docosaheptayne (**27**) as colorless crystals: mp 78–80 °C; ^{1}H NMR ($CDCl_3$) δ 3.21 (s, 3), 1.41 (s, 36), 1.31 (s, 6), 0.16 (s, 9). Anal. Calcd for $C_{39}H_{54}OSi$: C, 82.62; H, 9.60. Found: C, 82.72; H, 9.67.

21-Chloro-3,3,6,6,9,9,12,12,15,15,18,18,21-tridecamethyl-1-(trimethylsilyl)-1,4,7,10,13,19-docosaheptayne (28). This material was prepared according to the general procedure described above for the conversion of polyacetylenic ethers to polyacetylenic chlorides using 9.8 g (17.3 mmol) of heptayne ether **27** and 9.0 g (115 mmol) of acetyl chloride in 25 mL of dichloromethane. Sublimation of the crude product (120 °C/0.1 torr) gave 8.45 g (86%) of 21-chloro-3,3,6,6,9,9,12,12,15,15,18,18,21-tridecamethyl-1-(trimethylsilyl)-1,4,7,10,13,16,19-docosaheptayne (**28**) as colorless crystals: mp 94–95 °C; ^{1}H NMR ($CDCl_3$) δ 1.79 (s, 6), 1.43 (s, 36), 0.16 (s, 9). Anal. Calcd for $C_{38}H_{51}ClSi$: C, 79.88; H, 9.00. Found: C, 79.91; H, 8.91.

Tetradecamethyl[7]pericyclyne (29). This material was prepared according to the general procedure described above for cyclization reactions using 1.5 g (2.6 mmol) of the heptayne chloride **28** and 0.9 g (6.7 mmol) of aluminum chloride. Chromatography and recrystallization from hexane gave 75 mg (6.2%) of tetradecamethyl[7]pericyclyne (**29**) as very long, slender, colorless needles, resembling glass wool: mp 173–174 °C; ^{1}H NMR (C_6D_6) δ 1.48; ^{13}C NMR (C_6D_6) δ 83.7, 31.9, 26.1; IR (KBr) 2985 (vs), 2935 (s), 2870 (w), 1470 (w), 1440 (w), 1360 (w), 1270 (vs), 1130 cm^{-1} (w). Anal. Calcd for $C_{35}H_{42}$: C, 90.85; H, 9.15. Found: C, 90.97; H, 9.24.

24-Methoxy-3,3,6,6,9,9,12,12,15,15,18,18,21,21,24-pentadecamethyl-1-(trimethylsilyl)-1,4,7,10,13,16,19,22-pentacosaoctayne (30). This material was prepared according to the general procedure described above for coupling reaction using 7.0 g (23.6 mmol) of tetrayne ether **17b** in 50 mL of THF, 0.3 g of cuprous chloride,[39] and 9.1 g (24.4 mmol) of tetrayne chloride **22a** in 50 mL of THF. Chromatography on silica gel with 30:1 hexane/ethyl acetate gave 8.01 g (54%) of 24-methoxy-3,3,6,6,9,9,12,12,15,15,18,18,21,21,24-pentadecamethyl-1-(trimethylsilyl)-1,4,7,10,13,16,19,22-pentacosaoctayne (**30**) as colorless crystals: mp 92–93 °C; ^{1}H NMR ($CDCl_3$) δ 3.25 (s, 3), 1.39 (s, 42), 1.35 (s, 6), 0.15 (s, 9). Anal. Calcd for $C_{44}H_{60}OSi$: C, 83.48; H, 9.55. Found: C, 83.52; H, 9.60.

24-Chloro-3,3,6,9,9,12,12,15,15,18,18,21,21,24-pentadecamethyl-1-(trimethylsilyl)-1,4,7,10,13,16,19,22-pentacosaoctayne (31). This material was prepared according to the general procedure described above for the conversion of polyacetylenic ethers to polyacetylenic chlorides using 2.0 g (3.2 mmol) of octayne ether **30** and 1.7 g (22 mmol) of acetyl chloride in 20 mL of dichloromethane. Sublimation of the crude product (150 °C/0.1 torr) gave 1.70 g (86%) of 24-chloro-3,3,6,6,9,9,12,12,15,15,18,18,21,21,24-pentadecamethyl-1-(trimethylsilyl)-1,4,7,10,13,16,19,22-pentacosaoctayne (**31**) as colorless crystals: mp 113.5–114.5 °C; ^{1}H NMR ($CDCl_3$) δ 1.79 (s, 6), 1.43 (s, 42), 0.16 (s, 9). Anal. Calcd for $C_{43}H_{57}ClSi$: C, 81.02; H, 9.01. Found: C, 81.26; H, 8.98.

Hexadecamethyl[8]pericyclyne (32). This material was prepared according to the general procedure described above for cyclization reactions using 1.1 g (1.7 mmol) of the octayne chloride **31** and 1.0 g (7.5 mmol) of aluminum chloride. Chromatography and recrystallization from hexane gave 14 mg (1.5%) of hexadecamethyl[8]pericyclyne (**32**) as short colorless needles: mp 189–190 °C; ^{1}H NMR ($CDCl_3$) δ 1.45; ^{13}C NMR ($CDCl_3$) δ 83.2, 31.5, 25.6. MS, M$^+$ calcd for $C_{40}H_{48}$ 528.3756, found 528.3765.

15-Methoxy-6,6,9,9,12,12,15-heptamethyl-1-(trimethylsilyl)-1,4,7,10,13-hexadecapentayne (34). This material was prepared according to the general procedure described above for coupling reactions using 8.8 g (30 mmol) of tetrayne ether **17b** in 25 mL of THF, 0.2 g of cuprous chloride,[39] and 8.0 g (42 mmol) of 3-bromo-1-(trimethylsilyl)-propyne (**33**)[43] in 25 mL of THF. Chromatography on silica gel with 30:1 hexane/ethyl acetate gave 7.2 g (60%) of 15-methoxy-6,6,9,9,12,12,15-heptamethyl-1-(trimethylsilyl)-1,4,7,10,13-hexadecapentayne (**34**) as an unstable colorless oil: ^{1}H NMR ($CDCl_3$) δ 3.22 (s, 3), 3.07 (s, 2), 1.43 (s, 24), 0.14 (s, 9).

15-Chloro-6,6,9,9,12,12,15-heptamethyl-1-(trimethylsilyl)-1,4,7,10,13-hexadecapentayne (35). This material was prepared according to the general procedure described above for the conversion of polyacetylenic ethers to polyacetylenic chlorides using 3.5 g (8.6 mmol) of pentayne ether **34** and 2.0 g (25 mmol) of acetyl chloride in 20 mL of dichloromethane. Workup in the usual manner gave 3.2 g (90%) of 15-chloro-6,6,9,9,12,12,15-heptamethyl-1-(trimethylsilyl)-1,4,7,10,13-hexadecapentayne (**35**) as an unstable pale yellow oil: ^{1}H NMR ($CDCl_3$) δ 3.09 (s, 2), 1.76 (s, 6), 1.41 (s, 18), 0.16 (s, 9).

Octamethyl[5]pericyclyne (36). This material was prepared according to the general procedure described above for cyclization reactions using 1.5 g (3.7 mmol) of the pentayne chloride **35** and 1.2 g (9 mmol) of aluminum chloride. Chromatography gave 149 mg (13.5%) of crude octamethyl[5]pericyclyne (**36**) as pale yellow needles. Recrystallization twice from pentane gave large colorless crystals: mp 125–127 °C (dec to a yellow oil); ^{1}H NMR ($CDCl_3$) δ 3.08 (s, 2), 1.42 (narrow doublet, 24); ^{13}C NMR ($CDCl_3$) δ 84.0, 82.6, 82.3, 82.1, 72.4, 31.1, 30.8, 25.7, 25.5, 9.9; IR (KBr) 2980 (vs), 2935 (s), 2865 (w), 1455 (s), 1355 (s), 1310 (s), 1270 (vs), 1255 (vs), 1135 (s), 670 (s), 625 cm^{-1} (s); MS, M$^+$ calcd for $C_{23}H_{26}$ 302.2035, found 302.2057.

5,5,6,6,11,11,12,12-Octamethyl-1,3,7,9-cyclododecatetrayne (39). A solution of 50.4 g (0.3 mol) of the tetrahydropyranyl ether of 2-methyl-3-butyn-2-ol (**38**, X = OTHP)[44] in 300 mL of dry THF was cooled to −78 °C under a nitrogen atmosphere. To this solution were added 120 mL (0.3 mol) of *n*-butyllithium in hexane (2.5 M) dropwise over a 45-min period with stirring. Stirring was continued at this temperature for 1 h more, 3.0 g of freshly prepared (colorless) anhydrous cuprous chloride[39] was then added, and the cold bath was replaced with a water bath maintained at +50 °C. The reaction mixture was stirred at this temperature for an additional 22 h. The reaction mixture was cooled to room temperature and acidified (to litmus paper) with 5% aqueous hydrochloric acid. The aqueous layer was separated and extracted with ether. These washings were combined with the original organic layer and then washed with saturated aqueous sodium chloride until the washings were neutral to litmus paper, dried over magnesium sulfate, and concentrated under reduced pressure. The viscous residue was partially dissolved in pentane and filtered through silica gel to remove polymeric material. Concentration to dryness under reduced pressure left a solid residue which was recrystallized from absolute ethanol to give 0.5–0.6 g (ca. 3%) of reasonably pure product. Sublimation under reduced pressure followed by one more recrystallization gave analytically pure 5,5,6,6,11,11,12,12-octamethyl-1,3,7,9-cyclododecatetrayne (**39**) as colorless needles: mp 150 °C (dec); ^{1}H NMR ($CDCl_3$) δ 1.18; ^{13}C NMR (C_6D_6) δ 90.4, 70.5, 42.6, 23.5; IR (KBr) 2250, 1450, 1395, 1365 cm^{-1}; Raman (crystal) 2234 cm^{-1}; UV (ethanol) 263 (ε 510), 248 (770), 236 nm (720); MW (osmometric) calcd for $C_{20}H_{24}$ 264, found 260 ± 10; MS (70 eV), *m/z* (rel intensity) 264 (M$^+$, 30), 249 (4), 234 (5), 219 (9), 181 (15), 180 (86), 165 (6), 133 (12), 132 (100), 117 (16), 91 (11); MS M$^+$ calcd for $C_{20}H_{24}$ 264.1878, found 264.1880. Anal. Calcd for $C_{20}H_{24}$: C, 90.85; H, 9.15. Found: C, 90.57; H, 9.45.

Hydrogenation of Decamethylcyclopentadeca-1,4,7,10,13-pentayne (23) to 1,1,4,4,7,7,10,10,13,13-Decamethylcyclopentadecane (40). To a solution of 33 mg of decamethyl[5]pericyclyne (**23**) in 10 mL of ethyl acetate was added 10 mg of PtO_2, and the resulting mixture was stirred at room temperature under 1 atm of hydrogen gas for 16 h. The catalyst was then removed by filtration and washed with 15 mL of ethyl acetate. Removal of the solvent under reduced pressure gave the crude product. NMR analysis at this point indicated the presence of olefinic material, so the reaction was continued with fresh catalyst for an additional 16 h. This procedure was repeated 5 times. To consume the last traces of olefinic material, 1 drop of bromine was added. Sublimation (80 °C, 0.1

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torr) gave 25 mg (71%) of the saturated hydrocarbon **40** as colorless needles: mp 70–71 °C; ^{1}H NMR ($CDCl_3$) δ 1.10 (s, 20, CH_2), 0.80 (s, 30, CH_3); ^{13}C NMR ($CDCl_3$) δ 35.2 (CH_2), 32.2 (quat C), 28.0 (CH_3); MS, M^+ calcd for $C_{25}H_{50}$ 350.3913, found 350.3901.

Hydrogenation of Octamethylcyclododeca-1,3,7,9-tetrayne (39) to 1,1,2,2,7,7,8,8-Octamethylcyclododecane (41). To a solution of 19.2 mg of cyclyne **39** in 8 mL of ethyl acetate was added 21.0 mg of 5% Rh/alumina, and the resulting mixture was shaken at room temperature under 3 atm of hydrogen gas in a Parr apparatus for 2 h. The catalyst was then removed by filtration and washed with ethyl acetate. Removal of the solvent under reduced pressure followed by sublimation (80 °C, 1.0 torr) gave 16.1 mg (79%) of the saturated hydrocarbon (**41**) as colorless crystals: mp 54–56 °C; ^{1}H NMR ($CDCl_3$) δ 1.36 (s, 16, CH_2), 0.83 (s, 24, CH_3); MS (70 eV), *m/z* 280 (M^+). Anal. Calcd for $C_{20}H_{40}$: C, 85.63; H, 14.37. Found: C, 85.73; H, 14.14.

Silver Triflate Complex of Decamethylcyclopentadeca-1,4,7,10,13-pentayne (23). Under a nitrogen atmosphere, 34 mg (0.1 mmol) of decamethyl[5]pericyclyne (**23**) and 24 mg (0.09 mmol) of silver trifluoromethanesulfonate (triflate) were stirred in 3 mL of dry THF at 65 °C for 30 min. The solution was cooled to room temperature, concentrated to 1 mL, and then diluted with 3 mL of chloroform. The silver complex precipitated as fine white crystals. Recrystallization from THF/hexane gave 45 mg (74%) of the silver complex as fine white crystals which were stable only in the absence of light and moisture: mp 219 °C (dec to a black oil); ^{1}H NMR (C_6D_6) δ 1.45 (s); ^{13}C NMR (C_6D_6) δ 82.1 (C≡C), 31.2 (quat C), 26.2 (CH_3); IR (KBr) 2985 (s), 2970 (s), 2935 (m), 2860 (w), 1260 (vs), 1175 (s), 1065 (vs), 655 (s), 645 cm^{-1} (s).

Silver Triflate Complex of Dodecamethylcyclooctadeca-1,4,7,10,13,16-hexayne (26). Under a nitrogen atmosphere, 29 mg (0.073 mmol) of dodecamethyl[6]pericyclyne (**26**) and 17 mg (0.066 mmol) of silver triflate were stirred in 3 mL of dry THF at 65 °C for 30 min. The solution was cooled to room temperature, concentrated to 1 mL, and then diluted with 3 mL of chloroform. The silver complex precipitated as fine white crystals. Recrystallization from THF/hexane gave 36 mg (75%) of the silver complex as fine white crystals which were stable only in the absence of light and moisture: mp 200 °C (dec to a black oil), ^{1}H NMR (C_6D_6) δ 1.45 (s); ^{13}C NMR (C_6D_6) δ 83.6 (C≡C), 32.0 (quat C), 26.0 (CH_3); IR (KBr) 2980 (vs), 2935 (s), 2860 (w), 1268 (vs), 1030 (s), 650 (s), 640 cm^{-1} (s); MS, M^+ calcd for $C_{30}H_{36}Ag$ 503.1878, found 503.1867.

Regeneration of Pericyclynes from Their Silver Triflate Complexes. The silver triflate complex of decamethyl[5]pericyclyne (10.0 mg) was stirred in a two-phase mixture of pentane (5 mL) and concentrated aqueous ammonia (5 mL) at room temperature for 10 min. The pentane layer was separated, dried over magnesium sulfate, and concentrated under reduced pressure to give 5.6 mg (100%) of decamethyl[5]pericyclyne (**23**) which was identical in all respects with the original hydrocarbon. Dodecamethyl[6]pericyclyne **26** was likewise regenerated from its silver triflate complex in quantitative yield.

$Co_2(CO)_6$ Complexes (42 and 43) of Decamethylcyclopentadeca-1,4,7,10,13-pentayne (23). Under a nitrogen atmosphere, 136 mg (0.4 mmol) of Co_2CO_8 was added to a solution of 66 mg (0.2 mmol) of decamethyl[5]pericyclyne (**23**) in 10 mL of dry ether, and the resulting dark red solution was stirred at room temperature. Thin-layer chromatography (silica gel, hexane) was used to monitor the progress of the reaction. After 5 min, the Co_2CO_6 complex (**42**, see below) constituted the main product (R_f = 0.2). As the reaction proceeded, however, the bis-Co_2CO_6 complex **43** began to appear (R_f = 0.5) at the expense of the initial product, even before all the starting pericyclyne was consumed. After 2.5 h, the reaction was complete. Filtration of the reaction mixture and concentration of the filtrate under reduced pressure gave a crude product that was chromatographed (silica gel, hexane) to give 122 mg (68%) of **43** as dark-red plates: mp 185–188 °C, ^{1}H NMR (C_6D_6) δ 1.63 (s, 12), 1.53 (s, 12), 1.43 (s, 6); ^{13}C NMR (C_6D_6) δ 107.9, 107.8, 86.7, 85.4, 85.1, 34.2, 33.6, 31.1, 26.3; IR (KBr) 2980 (s), 2930 (s), 2860 (w), 2085 (vs), 2040 (vs), 2015 (vs), 1980 (sh), 1580 cm^{-1} (w). By interrupting this reaction during the first 30 min or by using less than 1 M equiv of Co_2CO_8, it is possible to isolate (chromatographically) the mono-Co_2CO_6 complex **42** as bright red needles: mp 160–162 °C, ^{1}H NMR (C_6D_6) δ 1.66 (s, 12), 1.46 (s, 12), 1.41 (s, 6); ^{13}C NMR (C_6D_6) δ 107.5, 86.5, 86.2, 84.9, 84.7, 35.0, 33.3, 31.2, 30.3, 26.6; IR (KBr) 2980 (s), 2940 (s), 2865 (w), 2085 (vs), 2040 (vs), 2005 (vs), 1980 (sh), 1965 (sh), 1595 (s), 1260 cm^{-1} (s).

$Co_2(CO)_6$ Complexes (44 and 45) of Dodecamethylcyclopentadeca-1,4,7,10,13,16-hexayne (26). Under a nitrogen atmosphere, 70 mg (0.2 mmol) of Co_2CO_8 was added to a solution of 40 mg (0.1 mmol) of dodecamethyl[6]pericyclyne (**26**) in 20 mL of dry ether, and the resulting dark-red solution was stirred at room temperature. Thin-layer chromatography (silica gel, hexane) was used to monitor the progress of the reaction. After 10 min, the Co_2CO_6 complex **44** constituted the main product (R_f = 0.2), although the bis-Co_2CO_6 complex **45** had already begun to appear (R_f = 0.5). No attempt was made to isolate and characterize the mono-Co_2CO_6 complex **44**. As the reaction proceeded, the amount of bis-Co_2CO_6 complex **45** increased at the expense of **44**. After 1 h, the reaction was complete. Filtration of the reaction mixture and concentration of the filtrate under reduced pressure gave a crude product that was chromatographed (silica gel, hexane) to give 72 mg (74%) of **45** as red crystals: mp 193–195 °C, ^{1}H NMR (C_6D_6) δ 1.76 (s, 12), 1.61 (s, 12), 1.46 (s, 12); ^{13}C NMR (C_6D_6) δ 200.3 (w, br), 108.5 107.7, 87.6, 85.8, 85.0, 83.3, 34.7, 34.2, 33.2, 32.6, 31.8, 26.0; IR (KBr) (2985 (s), 2935 (s), 2860 (w), 2095 (vs), 2060 (vs), 2020 (vs), 1970 (sh), 1582 (w), 1455 (s), 1380 (s), 1355 (s), 1275 (s), 1255 (s), 730 (s), 670 (s), 650 (s), 610 cm^{-1} (s).

Regeneration of Pericyclynes from Their $Co_2(CO)_6$ Complexes. A 10-mg sample of the bis-Co_2CO_6 complex **43** was added to a solution of 1.0 g of ceric ammonium nitrate in 5 mL of acetone. The reaction mixture was stirred at room temperature for 30 min, diluted with water, and extracted with pentane. The pentane layer was washed with aqueous sodium chloride, dried over magnesium sulfate, and concentrated under reduced pressure to give 5.4 mg (100%) of decamethyl[5]pericyclyne (**23**) which was identical in all respects with the original hydrocarbon. Dodecamethyl[6]pericyclyne (**26**) was likewise regenerated from **45** in quantitative yield.

Oxidation of Octamethylcyclododeca-1,3,7,9-tetrayne (39). To a solution of 20.0 mg (0.08 mmol) of tetrayne **39** in 5 mL of *tert*-butyl alcohol and 1 mL of water were added 0.6 g (2.80 mmol) of $NaIO_4$ and a catalytic amount of $RuCl_3$. The reaction mixture was stirred at room temperature for 20 h. Then 10 mL of water and 1 mL of concentrated HCl were added, and the mixture was extracted with three 10-mL portions of ether. The organic layers were combined, dried over magnesium sulfate, and concentrated under reduced pressure. Esterification of the crude product mixture with excess diazomethane in THF followed by GC separation gave the dimethyl ester of tetramethylsuccinic acid (17%), identified by NMR, GC, and MS comparison with an authentic sample.

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