Table V. Properties of 2-Aryl-2-norbornyl and 2-Aryl-2-camphenilyl *p*-Nitrobenzoates

Substituent	System	Isomer	Mp, °C	Anal.
p-CH_3O	N	Exo[a]	91–91.5	C, H
	N	Endo[b]	115 dec	C, H, N
	C	Exo[a]	127.5–128.5	C, H
	C	Endo[c]	133.8–134.8	
p-CH_3	N	Exo	112 dec	C, H, N
	N	Endo	142–144 dec	C, H, N
p-H	N	Exo[d]	107.5	
	N	Endo[d]	137	
	C	Exo	124 dec	C, H, N
	C	Endo	144.8–145.3	C, H, N
p-CF_3	N	Exo	127.5–128	C, H, N, F
	N	Endo	135–135.5	C, H, N, F
	C	Exo	156.5–157	C, H, N
	C	Endo	137.8–138.5	C, H, N
3,5-$(CF_3)_2$	N	Exo	150.5–151	C, H, N, F
	N	Endo	136–136.5	C, H, N, F

[a] Benzoate. [b] Lit. mp 90–105 °C. D. C. Kleinfelter, Ph.D. Thesis, Princeton University, 1960. [c] Lit. mp 129.5–135 °C. P. D. Bartlett et al., *Justus Liebigs Ann. Chem.*, **623**, 217 (1959). [d] D. L. Vander Jagt, Ph.D. Thesis, Purdue University, 1967.

matography over alumina and eluted with pentane, $n^{20}D$ 1.5472. The products from the *p*-methoxy derivative were separated by preparative GLC. The ^1H NMR spectra of the trapping products from the *p*-H and *p*-CF_3 derivatives were taken for neat samples. The exo:endo ratio was calculated by measuring the peak area exhibited by the C_2 protons. The exo proton appeared in these derivatives at δ 3.1–3.2 ppm and the endo protons at δ 2.6–2.7. The exo:endo product ratios in the trapping 2-arylnorbornanes are summarized in Table II.

Products of Solvolysis in 2-Aryl-2-camphenilyl *p*-Nitrobenzoates. The procedure was described earlier.[5] One millimole of *p*-nitrobenzoate was solvolyzed in 25 mL of 0.08 M solution of sodium acetate or sodium bicarbonate in 80% acetone for 10 half-lives. The products were analyzed by ^1H NMR by comparing the heights of methyl signals appearing at δ 0.44 -0.48 (endo OH) and 0.74–0.80 (exo OH). The results are summarized in Table III.

Kinetic Measurements. The rate constants for the solvolysis of 2-aryl-2-norbornyl and 2-aryl-2-camphenilyl derivatives were measured in 80% aqueous acetone following the titrimetric procedure described earlier.[12,30]

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Synthesis of Tricyclo[3.1.1.$0^{3,6}$]heptan-6-yl Derivatives[1a]

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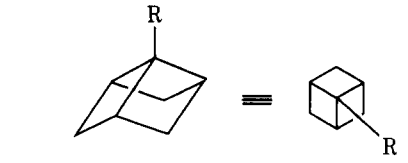
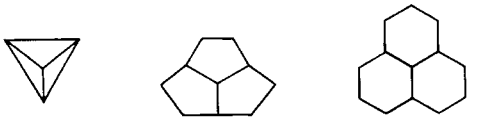
Abstract: Semibenzylic acid ring contraction of 6-halotricyclo[3.2.1.$0^{3,6}$]octan-7-one (**6**) furnished tricyclo[3.1.1.$0^{3,6}$]heptane-6-carboxylic acid (**1**), a novel, new ring system characterized by three cyclobutane rings fused to a common carbon atom. Tricyclic halo ketone **6** was prepared by base-catalyzed intramolecular cyclization of *exo,exo*-7-halobicyclo[3.2.1]octan-6-on-3-yl mesylate (**7**) which was derived from bicyclo[3.2.1]oct-6-en-3-one by reduction with sodium in ethanol, mesylation, and then oxidative chlorination with chromyl chloride or from the ketal of bicyclo[3.2.1]oct-2-(and -3-) en-6-one by regio- and stereoselective hydroboration/oxidation, mesylation, hydrolysis, and bromination. Curtius acid rearrangement of acid **1** produced the 6-acetamide derivative **2**. The ^1H and ^{13}C NMR spectra of this novel ring system are reported.

Tricyclo[3.1.1.$0^{3,6}$]heptane (**1**, R = H) represents a novel carbon skeleton characterized structurally by a chair cyclohexane ring in which the three alternate axial bonds are connected to a single bridging carbon atom. Herein we wish to describe the full details[2] of the synthesis and characterization of the first known examples[3] of this ring system, tricyclo[3.1.1.$0^{3,6}$]heptane-6-carboxylic acid (**1**) and the 6-acetamide derivative **2**. This symmetrical tricycloheptane skeleton[4] is the smallest isolated member of the general family of molecules characterized by the symmetrical spanning of a ring perimeter by a single bridging carbon atom. Other members of this class include the elusive tetrahedrane (**3**)[6] and the well-documented



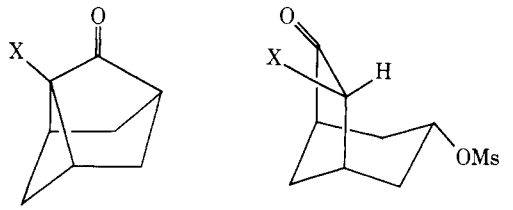
1, R = COOH
2, R = $NHCOCH_3$



3 4 5

triquinacine (**4**)[7] and phenalene (**5**)[8] systems. Alternatively, **1** and **2** can be considered as trisnoradamantane derivatives.

An examination of the structure of acid **1** reveals that a rational synthesis of this molecule must incorporate the construction of three four-membered rings fused about a *common* carbon atom bearing a carboxylic acid substituent. The synthesis enumerated below involves, in retrosynthetic order, the following key features: generation of the last two cyclobutane rings by a base-induced semibenzilic acid ring contraction of 6-halotricyclo[3.2.1.$0^{3,6}$]octan-7-one **6**; formation of the initial

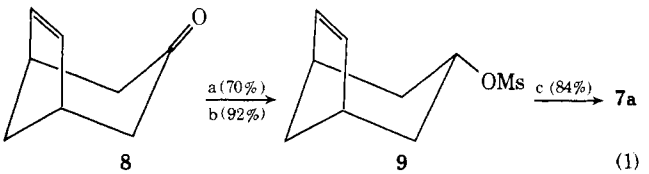


6a, X = Cl
b, X = Br

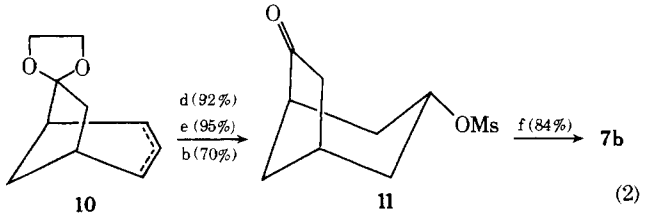
7a, X = Cl
b, X = Br

four-membered ring by intramolecular ring closure of 7-halobicyclo[3.2.1]octanone **7** to yield **6**; and regio- and stereoselective synthesis of the exo-C_3-substituted bicyclo-[3.2.1]octan-6-one skeleton **7**.

The two halo ketones **7** were prepared from the 3-keto olefin **8** and the 6-keto olefin derivatives **10** as shown in eq 1 and 2. In the chloro ketone sequence (eq 1), the required exo-C_3-oxygen atom stereochemistry was established by a dissolving metal reduction of **8** to give the more stable equatorial (exo) alcohol.[9] In the bromo ketone series (eq 2) introduction of the exo-C_3-oxygen substituent with both the required regio- and stereoselectivity was accomplished via hydroboration/oxidation of ketal olefins **10**.[10]



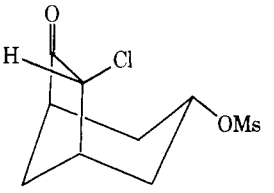
8 **9** (1)



10 **11** (2)

a, Na, EtOH, Δ; b, MsCl, Et_3N, CH_2Cl_2, 0 °C; c, CrO_2Cl_2, acetone, −76 to 25 °C, aqueous $NaHSO_3$; d, disiamylborane or di-α-pinocamphenylborane, THF, 0 °C; aqueous NaOH, H_2O_2; e, acetone, *p*-TsOH (catalyst); f, Br_2, $CHCl_3$, 25 °C.

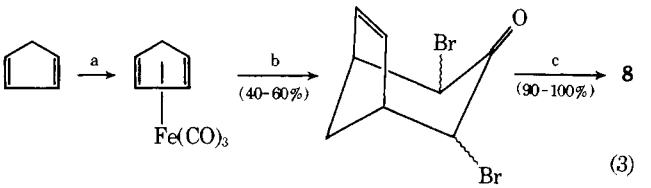
The desired 7-halobicyclo ketones **7** were prepared by chromyl chloride oxidation[11] of olefin **9** to give **7a** and by bromination of ketone **11** to give **7b**. In both cases a *single* stereoisomer of **7** was obtained and, as depicted in formulas **7a** and **7b**, the halogen atom stereochemistry was tentatively assigned as exo on the basis of attack from the less hindered face of the bicyclo[3.2.1]octane skeleton.[12] This assignment was supported by the observed coupling constant for the C_7 proton, $J_{1,7}$ = 2.5 Hz, for both halo ketones **7**. Pyrrolidine-catalyzed isomerization of **7a** furnished the isomeric endo-C_7 chloro ketone **12** in which the C_7 proton coupling constant was



12

$J_{1,7}$ = 6 Hz. The smaller coupling constant, J = 2.5 Hz, is in accord with that expected[13] for **7**, e.g., the endo-C_7-C_1 proton–proton dihedral angle is ca. 85°; and the larger value, J = 6 Hz, for **12** in which the exo-C_7-C_1 proton–proton dihedral angle is ca. 25°.

Although several routes to the starting keto olefin **8** are available,[14] a modification of the [4 + 3] cycloaddition route[14c] using in situ generated cyclopentadieniron tricarbonyl[15] provided a convenient source of **8** in 40–60% overall yield (see eq 3).



(3)

a, $Fe_2(CO)_9$, Et_2O, Δ; b, Br_2CH-C=O-$CHBr_2$; c, Zn/Cu, NH_4Cl, MeOH, H_2O.

Intramolecular ring closure of bicyclic halo ketones **7** was effected initially by treatment with freshly sublimed potassium *tert*-butoxide in benzene at 50 °C to furnish tricyclic halo ketones **6** in modest yield (13–25%). Subsequently it was observed that an improved yield (40%) of tricyclic chloro ketone **6a** could be obtained from **7a** by using sodium bis(trimethylsilyl)amide in benzene at 50 °C. The spectral properties of these tricyclic materials are in complete accord with the proposed structures (see Experimental Section for details). In particular, the carbonyl group absorption in the infrared for ketones **6a** and **6b** (1785, 1780 cm^{-1}, respectively) is ca. 20 cm^{-1} higher frequency than that of the parent ketone **7**, X = H (1763 cm^{-1}).[10] This shift is characteristic of ketones containing a coplanar α-halogen substituent.[16]

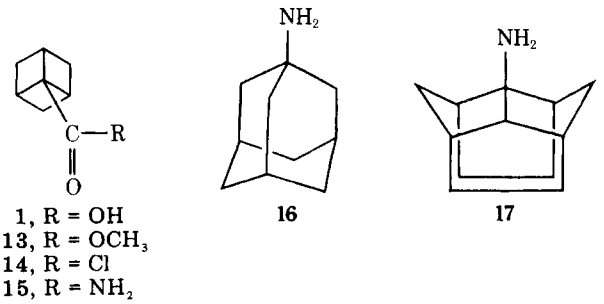
Semibenzilic acid ring contraction[17] of both tricyclic halo ketones **6** occurred smoothly upon exposure to hot 50% aqueous potassium hydroxide to give crystalline tricyclo[3.1.1.$0^{3,6}$]-heptane-6-carboxylic acid (**1**) in good yield (75–90%); facile ring contraction of **6** to **1** undoubtedly reflects the optimal trans, antiparallel disposition of the migrating C_1 carbon atom and the C_6 halogen atom leaving group in **6**. Alternatively, acid **1** could be obtained directly from bicyclic chloro ketone **7a** in ca. 45% overall yield by sequential treatment with sodium bis(trimethylsilyl)amide and then aqueous base.

The structure of acid **1** was determined unequivocally by examination of the ^1H and ^{13}C NMR spectra of the corresponding methyl ester **13**. The ^1H NMR spectrum of **13** showed ($CDCl_3$) δ at 3.67 (s, 3, OCH_3), 2.80–3.20 (m, 6, C_1 H, exo C_2 H), and 2.25 ppm (d, 3, J = 12 Hz, endo C_2 H). In the presence of 1 molar equiv of Eu(fod)$_3$ the 6 H multiplet was

resolved into two signals at δ 6.85 (broad, t, 3, J = 8 Hz, C_1 H) and 4.40 ppm (broadened d of t, 3, J = 12, 8 Hz, exo C_2 H). These chemical shift data confirm the presence of three different ring skeleton protons in **13** and the observed coupling constants are in complete accord with those expected for the C_1 and C_2 protons, e.g. the exo-C_2-C_1 proton-proton dihedral angle is ca. 27° and the endo-C_2-C_1 proton-proton dihedral angle is ca. 97°. The proton noise-decoupled ^{13}C NMR spectrum[18] of **13** showed signals for the three different ring nucleus carbon atoms as singlets at δ 35.7 ($C_{2,4,7}$), 39.1 ($C_{1,3,5}$), and 56.6 ppm (C_6) downfield from internal Me_4Si.

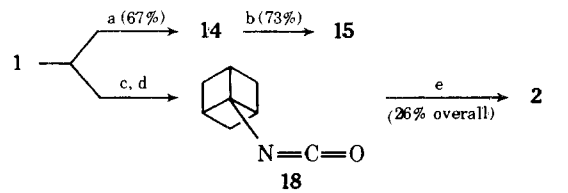
Although ester **13** contains three cyclobutane rings fused about a single carbon atom, treatment of **13** with $AgBF_4$ in acetone (25 °C, 21 h) gave no reaction. This result suggests that the σ-bond strain in the tricyclo[3.1.1.$0^{3,6}$]heptane nucleus is not sufficient to facilitate a Ag(I)-catalyzed rearrangement characteristic of other strained cage systems.[20]

In view of the considerable interest in the antiviral activity of caged systems such as adamantamine (**16**),[2] and the caged derivative **17**,[22] acid **1** was converted into the nitrogen derivatives **15** and **2** as shown below. Attempts to isolate the Curtius rearrangement product, isocyanate **18**, led to apparent decomposition of the tricyclo[3.1.1.$0^{3,6}$]heptane system to give unidentified materials. Direct treatment of crude isocyanate **18** (present by IR) with methyllithium,[23] however, furnished the desired 6-acetamide derivative **2** in 26% overall yield from acid **1**. The biological activity of these substances has not been established yet.



1, R = OH
13, R = OCH_3
14, R = Cl
15, R = NH_2

16 **17**



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a, $SOCl_2$, 25 °C, 12 h; b, NH_3 (anhydrous), C_6H_6, 25 °C; c, EtOCOCl, Et_3N, NaN_3, acetone-H_2O (1:1); d, C_6H_6, Δ, 1 h; e, MeLi, Et_2O, 0 °C.

Experimental Section

Melting points were determined on a Mel-Temp apparatus and are uncorrected. Nuclear magnetic resonance spectra were obtained on a Varian Associates Model A-60, HA-100, or Perkin-Elmer Model R-12 spectrometer; infrared spectra were measured on a Perkin-Elmer Model 237B grating infrared spectrometer. Low-resolution mass spectra were obtained on a Du Pont Model 21-491 mass spectrometer, and high-resolution mass spectra were obtained using a CEC Model 21-100 mass spectrometer. The microanalytical determinations were made by Chemalytics, Inc., Tempe, Ariz. Organic solutions were routinely dried over anhydrous $MgSO_4$ prior to evaporation.

Bicyclo[3.2.1]oct-6-en-3-one (8). A stirred mixture of freshly cracked cyclopentadiene (8.0 g, 0.121 mol) and $Fe_2(CO)_9$ (10 g, 0.027 mol) were heated at reflux in ether (75 mL) for 1.5 h under N_2 during which time the solution turned brown, and a brown precipitate was observed.[15] Tetrabromoacetone (10.1 g, 0.027 mol) in ether (10 mL) was added dropwise, resulting in evolution of gas. The reaction mixture was stirred at room temperature for 14 h, then filtered through Celite and washed with H_2O. The solution was dried, the solvent was evaporated, and the dark residue was chromatographed (Al_2O_3-benzene) to give 5.0 g (64%) of crude 2,4-dibromobicyclo[3.2.1]oct-6-en-3-one. This crude dibromo ketone (5.0 g, 0.014 mol), freshly prepared Zn/Cu couple[24] (9 g, 0.14 g-atom), and NH_4Cl (5 g) were stirred in absolute methanol (95 mL) for 18 h under nitrogen. This mixture was filtered, H_2O (15 mL) was added, and ceric ammonium nitrate was added until gas evolution ceased. The bulk of the solvent was evaporated, and the residue was extracted with ether. After drying, the solvent was evaporated to give 1.85 g (56% from $Fe_2(CO)_9$) of ketone **8** which could be purified by sublimation (80–85 °C at 22 mm) to give crystalline material: mp 96–100 °C (lit.[14a] mp 99–100.5 °C); IR (CCl_4) 1704 cm^{-1}; NMR (CCl_4) δ 1.60–2.45 (m, 6), 2.75–3.05 (m, 2), and 6.00 ppm (s, 2).

***exo*-Bicyclo[3.2.1]oct-6-en-3-yl Methanesulfonate (9).** Using the procedure of LeBel and Maxwell,[9] ketone **8** was converted into *exo*-bicyclo[3.2.1]oct-6-en-3-ol in 70% yield: mp 98–100 °C (lit.[9] mp 90.5–92 °C); NMR ($CDCl_3$) δ 1.20 (d,d,d, 2, J = 2.5, 10, and 13 Hz, endo-$C_{2,4}$ H), 1.35 (br d, 1, J = 12 Hz, endo-C_8 H), 1.60–2.15 (m, 3), 2.65 (m, 2), 3.28 (br, s, 1, OH), 3.75 (t,t, 1, J = 6.5, 10 Hz, endo-C_3 H), and 5.83 ppm (q, 2, J = 1 Hz, vinyl H). Treatment of this alcohol with methanesulfonyl chloride, Et_3N, and CH_2Cl_2 as described by Crossland and Servis[25] yielded mesylate **9** in 92% yield: mp 55–56 °C; NMR ($CDCl_3$) δ 1.30–2.34 (m, 6), 2.60–2.90 (m, 2), 4.67 (t,t, 1, J = 7, 10.5 Hz, endo-C_3 H), and 5.90 ppm (br, s, 2); mass spectrum *m/e* (rel intensity) 202 (3, molecular ion), 107 (7), 106 (19), 90 (34), 79 (55), and 66 (100).

Anal. Calcd for $C_9H_{14}O_3S$: C, 53.45; H, 6.98. Found: C, 53.18; H, 6.98.

***exo*-Bicyclo[3.2.1]octan-6-on-3-yl Mesylate (11).** Using the general procedures described previously[10] ketal olefins **10** were converted by sequential hydroboration/oxidation (disiamylborane, 99%; di-α-pinocamphenylborane, 92%) and then TsOH/acetone transketalization (90–95%) into a mixture of ketal alcohols, bp 110–113 °C (0.7 mm). VPC analysis on 5% FFAP, Chromosorb W, 10 ft × ⅛ in. at 180 °C of the corresponding acetates (Ac_2O, pyridine, 77%) showed three components (15:10:75) in order of increasing retention time. The major isomer was identified as the desired exo-C_3 derivative by comparison with a sample prepared from authentic alcohol.[10] The minor components were not further characterized. Crystallization of a sample of the crude alcohol mixture (n-Bu_2O/Et_2O) yielded pure *exo*-bicyclo[3.2.1]octan-3-ol-6-one, mp 149–151 °C (lit.[10] mp 150–151 °C). Using the procedure of Crossland and Servis,[25] the mixture of crude alcohols was converted into the corresponding mesylates. Crystallization from benzene-pentane yielded pure **11** in 70% yield: mp 93.5–95.5 °C; IR ($CHCl_3$) 1748 cm^{-1}; NMR ($CDCl_3$) δ 1.55–2.95 (m, 16), 3.03 (s, 3), and 4.81 ppm (tt, 1, J = 6.5 and 11 Hz, C*H*OMs).

Anal. Calcd for $C_9H_{14}O_4S$: C, 49.52; H, 6.47; S, 14.69. Found: C, 49.54; H, 6.51; S, 14.38.

***exo,exo*-7-Chlorobicyclo[3.2.1]octan-6-on-3-yl Mesylate (7a).** Chromyl chloride (23.0 g, 0.148 mol) was added dropwise to a stirred solution of keto olefin **8** (7.7 g, 0.038 mol) in acetone (500 mL) cooled to −76 °C under nitrogen. The dark red-brown solution was stirred for 1 h at −76 °C and 2 h at room temperature, then poured into a solution of $NaHSO_3$ (150 g) in ice water (2 L). The layers were separated, and the aqueous phase was extracted with CH_2Cl_2. The combined organic layers were dried, the solvent was evaporated, and the resulting dark residue was dissolved in $CHCl_3$ and filtered through silica gel. After solvent evaporation, the residue was crystallized from benzene to yield 8.0 g of pure mesylate **7a** (84%): mp[26] 128.7–130.2 °C; IR ($CHCl_3$), 1760 cm^{-1}; NMR ($CDCl_3$) δ 1.57–2.95 (m, 8), 3.01 (s, 3), 4.08 (d, 1, J = 2.5 Hz, CHCl), and 4.74 ppm (tt, 1, J = 6, 11 Hz); mass spectrum *m/e* (rel intensity) 252, 254 (1, 0.3, molecular ions), 183, 185 (9, 3), 156, 158 (82, 29), 149 (46), 121 (28), 93 (100), 79 (96).

Anal. Calcd for $C_9H_{13}O_4ClS$: C, 42.77; H, 5.18; S, 12.68. Found: C, 42.89; H, 5.15; S, 12.39.

***endo,exo*-7-Chlorobicyclo[3.2.1]octan-6-on-3-yl Mesylate (12).** Exo chloro ketone **7a** (180 mg, 0.7 mmol) and pyrrolidine (0.07 g, 1 mmol) were stirred at reflux in toluene (10 mL) for 14 h under nitrogen. The solvent was evaporated in vacuo, and the residue was stirred with 25% aqueous HCl for 1 h at room temperature. The reaction mixture was extracted with ether, and the combined extracts were washed with saturated $NaHCO_3$ and dried. The solvent was evaporated and the residue was crystallized from benzene to give 80 mg of endo chloro ketone **12** (44%): mp 117.6–119.0 °C; IR ($CHCl_3$) 1763 cm^{-1}; NMR

($CDCl_3$) δ 1.80–2.95 (m, 8), 2.98 (s, 3), 4.36 (d, 1, J = 7 Hz, CHCl), and 4.78 ppm (tt, J = 6, 11 Hz, C*H*OMs); mass spectrum *m/e* (rel intensity) 252, 254 (1, 0.3, molecular ion), 183, 185, (6, 3), 156, 158 (44, 16), 149 (39), 128 (34), 121 (24), 93 (100), 79 (99). High-resolution mass spectrum, calcd for $C_9H_{13}O_4{}^{35}Cl{}^{32}S$, 252.0223; found, 252.0220.

***exo,exo*-7-Bromobicyclo[3.2.1]octan-6-on-3-yl Mesylate (7b).** Bromine (21.0 g, 0.131 mol) was added dropwise to keto mesylate **11** (27.5 g, 0.126 mol) in $CHCl_3$ (250 mL). The solution was stirred for 12 h at room temperature, then washed with cold H_2O and dried. The solvent was evaporated, and the residue was crystallized from benzene to give 31.3 g of exo bromo ketone **7b** (84%): mp[26] 138.5–140 °C; IR (CH_2Cl_2) 1753 cm^{-1}; NMR ($CDCl_3$) δ 1.60–2.95 (m, 8), 3.00 (s, 3), 4.20 (d, 1, J = 3 Hz, CHBr), and, 4.73 ppm (tt, 1, J = 6, 11.5 Hz, C*H*OMs); mass spectrum *m/e* (rel intensity) 296, 298 (1, molecular ions), 200, 202, (26), 171, 173 (9), 149 (19), 121 (44), 93 (100).

Anal. Calcd for $C_9H_{13}O_4BrS$: C, 36.39; H, 4.41; Br, 26.90; S, 10.79. Found: C, 36.31; H, 4.50; Br, 26.42; S, 11.01.

6-Chlorotricyclo[3.2.1.$0^{3,6}$]octan-7-one (6a). A. Freshly sublimed potassium *tert*-butoxide (1.12 g, 0.01 mol) was added to a stirred solution of exo chloro ketone **7a** (2.52 g, 0.01 mol) in dry benzene (50 mL) at 30 °C under nitrogen. The solution was stirred at 30 °C for 50 min, then H_2O (0.18 g, 0.01 mol) was added. The solution was dried, and the solvent was evaporated. Chromatography (SiO_2–CCl_4) of the crude residue gave 400 mg of pure **6a** (25%): mp 75.8–79.5 °C; IR (CCl_4) 1785 cm^{-1}; NMR (CCl_4) δ 1.78 (d, 1, J = 10 Hz, endo-C_4 H), 2.03 (br, d, 2, J = 10 Hz, endo-$C_{2,8}$ H), 2.15–2.90 (m, 4), 2.90–3.43 (m, 1, C_1 H); mass spectrum *m/e* (rel intensity) 156, 158 (88, 29, molecular ion), 128, 130 (34, 12), 121 (84), 102, 104 (83, 25), 93 (78), 91 (100), 77 (99), 39 (98).

Anal. Calcd for C_8H_9OCl: C, 61.35; H, 5.79. Found: C, 61.49; H, 6.03.

B. Exo chloro ketone **7a** (210 mg, 0.8 mmol) and sodium bis(trimethylsilyl)amide[27] (180 mg, 1 mmol) were stirred in benzene (10 mL) for 1.5 h at 50 °C under nitrogen, then H_2O (2 mL) was added. The organic phase was separated and dried, and the solvent was evaporated. The residue was sublimed (80 °C, 1 mm) to give 50 mg of crystalline product **6a** (40%), mp 76–79 °C, which was identical by IR and NMR with that prepared by procedure A.

6-Bromotricyclo[3.2.1.$0^{3,6}$]octan-7-one (6b). Exo bromo ketone **7b** (100 mg, 0.34 mmol) was dissolved in benzene (5 mL), and the solution was heated to 50 °C with stirring under nitrogen. Freshly sublimed potassium *tert*-butoxide (0.04 g, 0.34 mmol) was added in four portions over a 1.5 h period, and the solution was stirred for an additional 0.5 h at 50 °C. The solvent was evaporated, and the residue was chromatographed (SiO_2–CCl_4) to give 12 mg of crystalline product **7b** (13%): mp 77.5–79.2 °C; IR (CCl_4) 1780 cm^{-1}; NMR ($CDCl_3$) δ 1.78 (d, 1, J = 10 Hz, endo-C_4 H), 2.08 (br d, 2, J = 12 Hz, endo-$C_{2,8}$ H), 2.35 (m, 3, exo-$C_{2,4,8}$ H), 2.72 (br d, t, J = 2, 7 Hz, $C_{3,5}$ H), and 3.20 ppm (m, 1, C_1 H); mass spectrum *m/e* (rel intensity) 200, 202 (9, molecular ion), 185, 187 (3), 172, 174 (7), 159, 161 (15), 146, 148 (35), 131, 133 (12), 121 (100). High-resolution mass spectrum, calcd for $C_9H_8O^{79}Br$, 199.9842; found, 199.9837.

Tricyclo[3.1.1.$0^{3,6}$]heptane-6-carboxylic Acid (1). A. 7-Chlorotricyclo ketone **6a** (300 mg, 1.9 mmol) was added to 33% aqueous KOH (10 mL) and the mixture was heated at reflux for 24 h. The reaction mixture was cooled, acidified with concentrated HCl, and extracted with CH_2Cl_2. After drying, the solvent was evaporated and the residue was crystallized from pentane to yield 210 mg of pure acid **1** (85%): mp 94–96.5 °C; IR ($CHCl_3$) 1685 cm^{-1}; NMR ($CDCl_3$) δ 2.24 (br d, 3, J = 11 Hz), 2.75–3.33 (m, 6), and 11.40 ppm (s, 1, OH); mass spectrum *m/e* (rel intensity) 138 (5, molecular ion), 121 (5), 93 (100), 91 (90).

Anal. Calcd for $C_8H_{10}O_2$: C, 69.54; H, 7.30. Found: C, 69.45; H, 7.39.

Treatment of 7-bromotricyclo ketone **6b** under similar conditions furnished acid **1** in 90% yield.

B. A solution of sodium bis(trimethylsilyl)amide[27] (1.0 g, 3.4 mmol) in benzene (15 mL) was added rapidly but dropwise to a stirred solution of chloro ketone **7a** (600 mg, 3.4 mmol) in benzene (10 mL) heated to 70 °C under N_2. After an additional 0.5 h, the benzene was evaporated in vacuo and 33% aqueous KOH (10 mL) was added. The resulting mixture was heated at reflux for 16 h under N_2, then cooled, acidified with 4 N HCl, and extracted with CH_2Cl_2. The combined extracts were dried, filtered, concentrated, and then cooled to yield 200 mg of acid **1** (41%), mp 94–96 °C.

Treatment of acid **1** with excess diazomethane in ether (4 h, 25 °C) followed by evaporation of solvent and microdistillation (80–90 °C at 20 mm) of the residue, furnished the liquid methyl ester **13** in ca. quantitative yield: IR (CCl_4) 1725 cm^{-1}; ^1H and ^{13}C NMR spectra, see text, $-OCH_3$ group at 51.3 ppm; mass spectrum *m/e* (rel intensity) 152 (2, molecular ion), 137 (8), 121 (10), 93 (97), 91 (100), 65 (38).

Tricyclo[3.1.1.$0^{3,6}$]heptane-6-carboxylic Acid Amide (15). Acid **1** (450 mg, 3.3 mmol) was stirred with $SOCl_2$ (15 g, 120 mmol) for 20 h under nitrogen. The excess $SOCl_2$ was evaporated in vacuo, and the residue was distilled to give 350 mg of acid chloride **14** (67%), bp 90–92 °C (20 mm), which solidified on standing: mp 43–46 °C; IR ($CHCl_3$) 1775, 1715, and 1690 cm^{-1}. Without further purification, acid chloride **14** (130 mg, 0.8 mmol) was dissolved in a mixture of ether (5 mL) and benzene (15 mL) and excess dry ammonia was slowly bubbled through the solution until no further precipitation occurred (2 h). Ethyl acetate (60 mL) was added, and the mixture was heated to 70 °C, filtered, and then cooled to give 80 mg of crystalline amine **15** (73%): mp 211–213.5 °C; IR ($CHCl_3$) 3500, 3380, and 1660 cm^{-1}; NMR not recorded; amide **15** is insoluble in CCl_4, $CDCl_3$, benzene-d_6, acetone-d_6, and pyridine-d_5.

Anal. Calcd for $C_8H_{11}NO$: C, 70.04; H, 8.08; N, 10.21. Found: C, 69.79; H, 7.87; N, 9.96.

***N*-Tricyclo[3.1.1.$0^{3,6}$]heptane-3-yl Acetamide (2).** Acid **1** (163 mg, 1.2 mmol) was reacted with triethylamine (150 mg, 1.5 mmol) and ethyl chloroformate (180 mg, 1.7 mmol) followed by aqueous NaN_3 (140 mg, 2 mmol) using the procedure of Weinstock.[28] The resulting crude crystalline acid azide [IR ($CHCl_3$) 2135, 1700 cm^{-1}] was dissolved in dry benzene (5 mL), the solution was heated at reflux under N_2 for 1 h, then the solvent was evaporated to give isocyanate **18** as a yellow oil, IR ($CHCl_3$) 2275 cm^{-1}. This material was then dissolved in dry ether (2 mL) and added dropwise to a solution of methyllithium (1.7 M, 1.25 mL, 2.6 mmol) in ether (5 mL) cooled to 0 °C under N_2. The resulting solution was allowed to warm to 25 °C, stirred for 2 h, acidified with 0.5 N HCl (10 mL), and extracted with ether. The combined extracts were dried, filtered, and concentrated. The crude product was sublimed (75 °C, 0.2 mm) to yield acetamide **2** (47 mg, 26%): mp 132–135 dec: IR ($CHCl_3$) 3500–3100, 1665 cm^{-1}; NMR ($CDCl_3$) δ 1.90–2.40 (m, 3), 2.00 (s, 3, $-CH_3$), 2.68–3.05 (m, 6).

Anal. Calcd for $C_9H_{13}NO$: C, 71.49; H, 8.67; N, 9.26. Found: C, 71.38; H, 8.65; N, 9.45.

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$(CH)_{10}$ Transformations. Evidence for Competing Concerted and Stepwise Mechanistic Processes in the Photochemical Reactions of *syn*-Tricyclo[4.4.0.0^{2,5}]deca-3,7,9-triene

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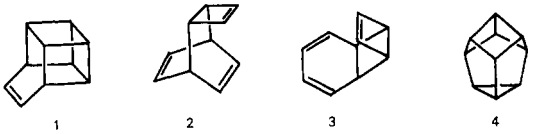
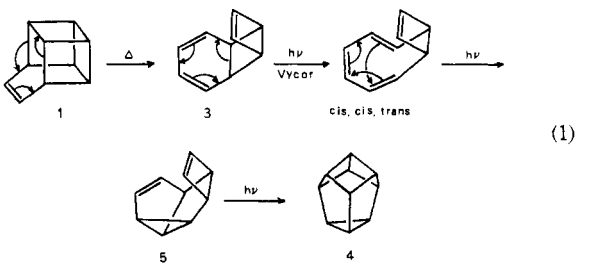
Abstract: The photochemical behavior of *syn*-tricyclo[4.4.0.0^{2,5}]deca-3,7,9-triene (**3**) in Pyrex with 3000-Å light has been examined. Nenitzescu's hydrocarbon (**2**), tetracyclo[5.3.0.0^{2,10}.0^{3,6}]deca-4,8-diene (**5**), benzene (**7**), cyclooctatetraene (**8**), and tricyclo[4.2.0.0^{2,5}]octa-3,7-diene (**9**) were observed as products. This result and investigation with two different specifically deuterium labeled reactants, **3a**-d_2 and **3b**-d_2, show that the photochemical reaction and rearrangement involves a remarkable variety of closely competing mechanistic processes. Analysis of deuterium scrambling indicates that the minimum set of reaction pathways for the **3** → **2** rearrangement consists of a discrete concerted [1,3] sigmatropic shift and the separate formation of a stabilized bis-allylic diradical intermediate **10** which closes to product and also gives degenerate rearrangement (**3** → **3**). Plausible mechanistic paths for formation of **7** and **9** are dissociation of diradical **10** or a concerted [2 + 2] cycloreversion of **3** to **7** and cyclobutadiene.

For over a decade the $(CH)_{10}$ family of compounds with their remarkable propensity for thermal and photochemical transformation has surprised and fascinated chemists.[1] Because the variety of $(CH)_{10}$ structures[2] and the range of accessible reaction pathways are so great,[1] this research field has become important for increasing our understanding of mechanistic processes and for the discovery of new theoretical concepts. For these reasons, interest in the $(CH)_{10}$ hydrocarbons has continued to be high.[3-8]

An ongoing interest in better understanding the roles of structure, bonding, and reactivity and energy in chemical transformations has attracted us to this area. We now have undertaken work aimed at investigating the $(CH)_{10}$ thermal and photochemical energy surfaces. Our initial effort[4b] arose from an interest in seeing if concurrent thermolysis and photolysis of $(CH)_{10}$ compounds would produce new isomers and lead to discovery of novel reaction pathways. In this connection, basketene (**1**) appeared to be a system of choice for study. Other work[8] had recently indicated that thermolysis of **1** produced **2** via the intermediacy of **3.** We found[4b] that modification of the conditions to include heating of **1** with accompanying irradiation through Vycor gave a significant amount of hexacyclic compound **4** along with **2.** Isomer **4,** which was previously unknown, represents a new facet of $(CH)_{10}$ chemistry.

The question of the nature of the reaction process(es) which leads from **1** to **4** is of particular interest since there is an obvious intrinsic need for other $(CH)_{10}$ intermediates in effecting the transformation. Using orbital symmetry rules and the principle of "precedent" it is possible to formulate a simple, straightforward mechanistic scheme which relates **1** and **4** as shown in eq 1. The considerations pertaining to this were outlined in the preliminary report.[4b] More recently, we discovered that heating and irradiating **1** in Pyrex stopped formation of **4** but produced the proposed intermediate **5** (eq 1) and also gave **2.**





(1)

As a test of the adequacy of the mechanistic description in eq 1, we carried out scouting experiments with deuterium la-