

5. Both **7** and **8** were shown to be 1:1 adducts by mass spectrometry.⁸

The structure of **7** was established on the basis of both spectroscopic and chemical evidence. This major product showed no trans double bond absorption in the infrared, while exhibiting a strong cis double bond absorption at 14.05μ .⁹ Nmr spectroscopy showed two vinylic C-H resonances at τ 3.98 (d of d, $J = 3.0$ and 1.8 Hz) and 4.01 (br s). The bridgehead protons appeared as complex multiplets centered at τ 6.49 and 6.97 . The peak at τ 6.97 is presumably due to the interior bridgehead proton which should feel the deshielding effects of the double bonds less than the external bridgehead proton. The remaining 16 protons appear as part of a complex pattern extending from τ 7.72 to 8.80 .⁹ The uv spectrum of **7** showed strong end absorption with a shoulder appearing at $\lambda_{\text{max}}^{\text{isooctane}}$ 233 nm (ϵ 1370) consistent with a nonconjugated interaction between adjacent double bonds.⁹

The mass spectral cracking pattern provided strong evidence for the proposed structure. The cleavage of the eight-membered bridge could be clearly detected and major peaks were observed corresponding to stepwise loss of each of the eight methylene units. The loss of the eight-carbon bridge gave *o*-ditrifluoromethylbenzene (**9**), m/e 214, as a major fragment. The subsequent fragmentation of this portion of the molecule corresponded to that of an authentic sample of **9** and to that observed below m/e 214 for 2,3-ditrifluoromethylbicyclo[2.2.2]octadiene (**10**).¹⁰

Finally, the proximity of the two double bonds could be demonstrated by the facile photochemical conversion of **7** into a saturated isomer (exact mass = 326.1466). In view of the well-established photochemical conversion of bicyclo[2.2.1]heptadiene into quadricyclane,¹¹ and of **10** into 1,6-ditrifluoromethyltetracyclo[4.2.0.2.8.0^{5,7}]octane,¹⁰ this photoisomer of **7** has tentatively been assigned structure **11**. The mass spectral cracking pattern of **11** differed considerably from that of **7**. In particular, the formation of **9** as a major fragmentation product was no longer observed.

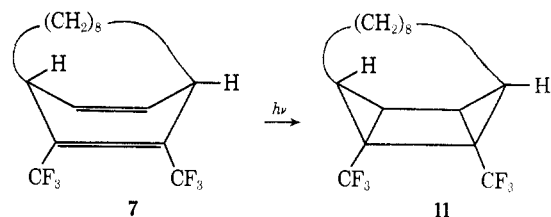
The structural assignment for the minor product **8** was based on a combination of ir, uv, nmr, and mass

(8) The exact mass of **7** was found to be 326.1466 (calcd m/e 326.1469), and that of **8** was 326.1474.

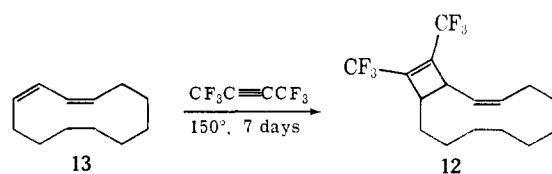
(9) 2,3-Ditrifluoromethylbicyclo[2.2.2]octadiene (**10**)¹⁰ served as a useful model for spectral comparison purposes: ir 14.20μ ; nmr τ 3.56 (vinylic protons, d of d), 5.91 (bridgehead protons, br m); uv, shoulder at $\lambda_{\text{max}}^{\text{acetone}} 234 \text{ nm}$ (ϵ 950).

(10) R. S. H. Liu, *Tetrahedron Lett.*, 1409 (1969).

(11) F. I. Sonntag and R. Srinivasan, *Org. Photochem. Syn.*, **1**, 97 (1971), and references contained therein.



spectral methods. The ir spectrum showed only cis double bond absorption, while the uv spectrum showed no long-wavelength maximum similar to those observed for **7** and **10**.¹⁰ The nmr spectrum of **8**, which was quite complex, also was consistent with the structure. The mass spectrum showed systematic loss of seven methylene units, but essentially no loss of the eighth methylene. This is consistent with the formation of a stable allylic species from **8**. More convincing evidence was obtained through comparison of the mass spectral cracking pattern of **8** with that of **12** (obtained as the only identifiable product from the reaction of **13** with perfluoro-2-butyne).¹² The cracking patterns of **8** and **12** were almost identical.



In summary, we have developed a simple, high-yield method for the synthesis of inside-outside bicyclics. The process outlined should be general, and should make these unusual bicyclic molecules readily available for further study. We are currently involved in a detailed study of the chemical properties of these molecules. In addition, we are investigating 2 + 4 cycloadditions to 1,3-*trans*,*trans*-cycloalkadienes as a route to inside-inside bicyclics.

Acknowledgment. We are indebted to the National Science Foundation for a grant which supported this investigation.

(12) Models indicate that the cisoid configuration of the butadiene moiety of **13** would require a significantly strained distortion of the whole molecule. Thus, **13** would not be expected to readily yield a Diels-Alder type product.

(13) The Ohio State University Postdoctoral Fellow, 1971-1972.

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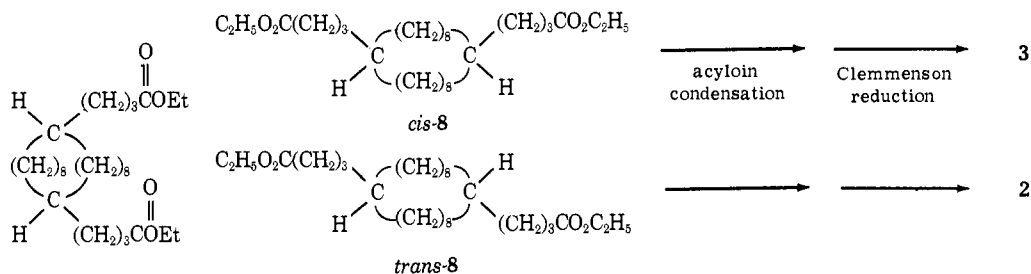
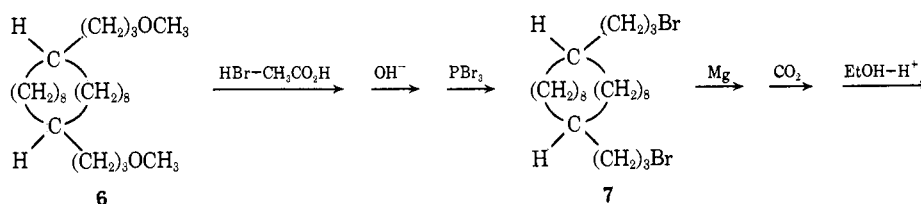
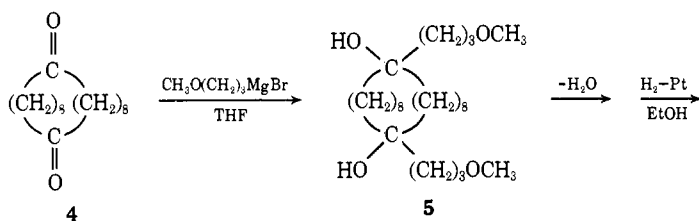
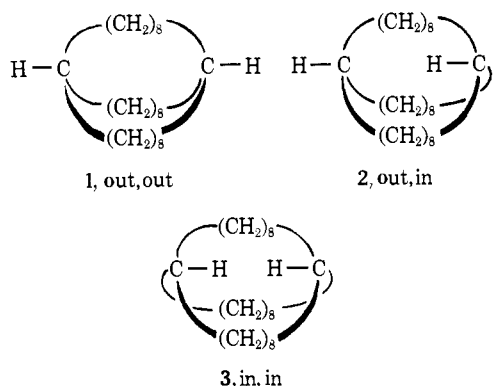
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Bicyclo[8.8.8]hexacosane. Out,In Isomerism

Sir:

Bridgehead protons in small bicyclic molecules, such as bicyclo[2.2.2]octane, occupy space exclusively outside the hydrocarbon cavity of the ring system. Relative to the three methylene chains, the bridgehead carbon atoms are of an opposite spatial sense. Isomers which have one or both of the bridgehead protons located inside of the cavity would be exceedingly unstable as a result of intolerable bond angle deformation and nonbonded interactions.¹ These structural restrictions are, however, relaxed as soon as the constituent rings

(1) K. Mislow, "Introduction to Stereochemistry," W. A. Benjamin, New York, N. Y., 1966, p 102.



become large enough to accommodate the bridgehead protons within the cavity. Such isomerism (out,in) involving nitrogen bridgeheads has been demonstrated earlier in the ammonium ions of 1,($k + 2$)-diazabicyclo[$k.l.m$]alkanes.²

Consideration of a symmetrical three-stranded hydrocarbon with tetrahedral bridgeheads shows that two topologically distinct structures can exist: one in which the bridgehead carbons have the same spatial sense and the other in which their spatial sense is opposite. In the latter instance the topological structure can be further refined such that two isomers (atropisomers) are capable of independent existence if the methylene chains are of critical lengths. In the bicyclic ammonium ions, the atropisomer with both bridgehead protons outside the molecular cavity is the familiar variety, but when each chain contains at least seven methylenes, the bridgehead hydrogens can be located inside the molecular cavity.² When some of the methylene groups are replaced by ether linkages, thus reducing the interchain nonbonded interactions, even structures with five-membered chains can exist as in,in ammonium ions.³ The interconversion of such

atropisomers (e.g., $\mathbf{1} \rightleftharpoons \mathbf{3}$), which can be called homeomorphic isomerization, is feasible based on model considerations when the chains contain about ten methylenes but has not been demonstrated experimentally in ammonium or quaternary ammonium ions of the 1,($k + 2$)-diazabicyclo[$k.l.m$]alkanes containing chains of up to 14 methylenes.^{2,4} The topological structure with bridgehead carbons of similar spatial orientation constitutes a third distinct isomer (e.g., $\mathbf{2}$), but in this case homeomorphic isomerization leads to no further atropisomer unless a chain contains a label, since on "turning inside out" the sense of each bridgehead is simply exchanged.

We now wish to report examples of such topological structures and their atropisomers involving carbon bridgeheads. Of the three possible isomeric bicyclo[8.8.8]hexacosanes ($\mathbf{1}$, $\mathbf{2}$, and $\mathbf{3}$), $\mathbf{2}$ and $\mathbf{3}$ have been synthesized and characterized. The sequence of reactions used is outlined below, starting from 1,10-cyclooctadecadione.⁵ Each step occurred in excellent yield which resulted in an overall yield of ca. 20%. Intermediates $\mathbf{5}$ and $\mathbf{6}$ were obtained as cis-trans mixtures which were not readily separated by conventional techniques. The dibromides *cis*- and *trans*- $\mathbf{7}$ were separated by fractional recrystallization from *n*-hexane, and their stereochemistry was unambiguously assigned on the basis of their subsequent transformation to the bicyclic hydrocarbons. The *trans* isomer (mp 73–76°) was less soluble in *n*-hexane than the *cis* isomer (oil). The isomers *cis*- and *trans*- $\mathbf{7}$ were individually converted to the esters *cis*- and *trans*- $\mathbf{8}$ which were cyclized by the acyloin condensation under high dilution conditions. The resulting acyloins were converted to the

(3) (a) B. Dietrich, J.-M. Lehn, and J. P. Sauvage, *Tetrahedron Lett.*, 2885 (1969); (b) J. Cheney and J. M. Lehn, *J. Chem. Soc., Chem. Commun.*, 487 (1972).

(4) Unpublished results of C. H. Park and M. F. Habibi.

(5) K. Ziegler and R. Aurnhammer, *Justus Liebigs Ann. Chem.*, 513, 43 (1934).

(2) H. E. Simmons and C. H. Park, *J. Amer. Chem. Soc.*, 90, 2428, 2429, 2431 (1968).

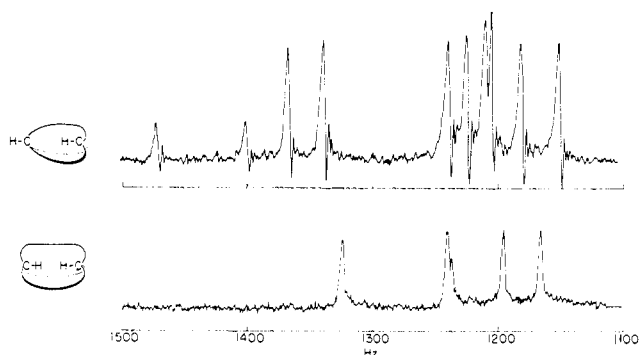


Figure 1. ^{13}C spectra of **2** and **3** in carbon tetrachloride. Chemical shifts are from external methyl iodide at 25.1 MHz.

hydrocarbons by Clemmenson reduction. All new compounds gave satisfactory elemental analyses and molecular weights by mass spectra. The 220-MHz pmr spectra of the bicyclic hydrocarbons did not aid in their structural assignment since the absorptions due to the bridgehead protons are obscured.

The diester *trans*-**8** can give only the out,in hydrocarbon **2**, but the diester *cis*-**8** can lead to both out,out-**1** and in,in-**3**. In the former case a single hydrocarbon product was observed, the assignment of whose stereochemistry was based on its ^{13}C nmr spectrum which showed ten peaks of appropriate intensity (Figure 1). The assignment of stereochemistry of hydrocarbon derived from the diester *cis*-**8** was based on the following considerations. Theoretical calculations to be published later show that the order of thermodynamic stability of the hydrocarbons is $3 > 1 > 2$. If this order is reflected in the cyclization $7 \rightarrow 8$, the single observed product is predicted to be in,in-**3**. The ^{13}C spectrum of this product shows five peaks of appropriate intensity but does not readily differentiate between the out,out and in,in atropisomers.

The out,in atropisomer **2** reacts readily with bromine under ionic conditions⁶ to give a hexabromide which on catalytic reduction ($\text{H}_2/\text{Ra-Ni}$) regenerates the hydrocarbon **2**. On the other hand, the atropisomer derived from *cis*-**8** is inert to bromination under the same conditions. Since tertiary hydrogens in normal environments are rapidly attacked by bromine under these conditions,⁶ this suggests that the isomer derived from *cis*-**8** is the in,in atropisomer whose tertiary bridgehead protons must be abnormally shielded from attack by reagents. Experiments to clarify these observations are under way.

(6) R. C. Fort, Jr., and P. v. R. Schleyer, *Chem. Rev.*, **64**, 277 (1964).

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Carborundanes. II. Derivative Chemistry of a Very Reluctantly Reactive Bridgehead Silicon Center

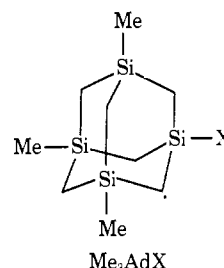
Sir:

In a recent communication¹ a facile synthesis of the 1,3,5,7-tetrasiladadamantane cage system (*i.e.*, the car-

(1) C. L. Frye, J. M. Klosowski, and D. R. Weyenberg, *J. Amer. Chem. Soc.*, **92**, 6379 (1970).

borundanes) was described. As noted previously,^{1,2} nucleophilic displacements at such silicon sites are markedly retarded. We now report some of the more interesting derivative chemistry of this reluctantly reactive tricyclo cage system, including the first example of a silylamine which is sufficiently robust to be recovered from solution in hydrochloric acid with the Si-N bond still intact!

We have found it convenient to regard this silylmethylene cage as a large nucleus, Ad, with four tetrahedrally disposed valences (*i.e.*, the apical valences of the four bridgehead silicon sites). The work described herein employed the monofunctional cage, Me_3AdX ; the



various derivatives were isolated, identified, and characterized by appropriate combinations of glc, ir, nmr, and mass spectroscopy (Table I).

Our initial attempt to hydrolyze the chlorosilane, Me_3AdCl , although unsuccessful, does illustrate the solvolytic stability of this material. After 1 month under ambient conditions in a 10% aqueous acetone solution containing Et_3N , this chlorosilane had undergone no detectable reaction. The analogous bromosilane, Me_3AdBr , underwent 75% conversion to the desired silanol, Me_3AdOH , in 9 days under similar conditions. The chloride was subsequently converted to the silanol, but under much more forcing conditions. Thus, Me_3AdCl (1.0 g, 0.0040 mol) was dissolved in moist *tert*-amyl alcohol (9 ml) to which were added $\text{Bu}_4\text{N}^+\text{Cl}^-$ (1.13 g, 0.0040 mol) and KOH (0.184 g, 0.0040 mol). After 30 min at 80° , glc assay indicated almost complete consumption of the starting chlorosilane. Addition of water and extraction with hexane afforded an almost quantitative yield of Me_3AdOH . This same compound was also prepared by heating the silane hydride, Me_3AdH (0.25 g, 8×10^{-4} mol), in dioxane (2 ml) containing water (1.0 g, 0.05 mol) and palladium on carbon³ (0.5 g of 5% Pd/C) at reflux for 3 days.

The preparation of the silane hydride itself also illustrates the sluggish nature of these displacements. Excess LiAlH_4 (0.5 g, 1.3×10^{-2} mol) was added to a mixture of Me_3AdCl and Me_3AdBr (0.5 g total, $\sim 8 \times 10^{-4}$ mol) in ether (100 ml). After 24 hr at reflux, 75 ml of ether was distilled from the system which was then refluxed for an additional 2 hr. Conventional work-up followed by mass spectral assay indicated almost no reduction of the chloride and consumption of only half the bromide. This partially reduced mixture was then refluxed with another 0.5 g of LiAlH_4 in ether for 3 days, whereupon the ether was distilled and the residue was baked on a steam bath for 30 min. The residue was then taken up with ether, acetone was cautiously added to decompose the excess LiAlH_4 ,

(2) A. L. Smith and H. A. Clark, *ibid.*, **83**, 3345 (1961).

(3) G. H. Barnes, Jr., and N. E. Daughenbaugh, *J. Org. Chem.*, **31**, 885 (1966).