TABLE VI

PROPERTIES OF CHLOROMETHYLATED DODECYLBENZENES

Phenyldodecane	Bp, °C (1 mm)	Cl, % (calcd)
I	158–162	11.9 (12.0)
II	145–148	11.6 (12.0)
III	138–142	11.5 (12.0)

tion ratio of the *para* derivative becomes great, but the compositions of chloromethylated dodecylbenzenes for the insertion reaction cannot be determined by ir, nmr, or glpc. The yields of chloromethylated dodecylbenzenes are low[20] in every case; so raw dodecylbenzenes must be treated repeatedly to obtain chloromethylated compounds. Their properties are shown in Table VI.

Reactions of Chloromethylated Dodecylbenzenes.—The procedure was similar to the case of benzyl chloride, except for the reaction time, 3 hr, and the reactant ratio, dodecylbenzyl chloride:$ZnCl_2$:DMA = 10:1:10 by weight. The properties of the insertion products are shown in Table IV.

Registry No.—Ethylene oxide, 75-21-8; benzyl chloride, 100-44-7; *p*-methylbenzyl chloride, 104-82-5; *p*-chlorobenzyl chloride, 104-83-6; *p*-methoxybenzyl chloride, 824-94-2; *o*-methylbenzyl chloride, 552-45-4; *m*-methylbenzyl chloride, 620-19-9; *p*-nitrobenzyl chloride, 100-14-1.

Acknowledgment.—The authors wish to thank Professor D. Swern, Temple University, for advice and helpful discussion.

Bridged Polycyclic Compounds. LXI. Synthesis and Some Properties of Tribenzobicyclo[3.2.2]nonatriene (Homotriptycene) and Derivatives[1]

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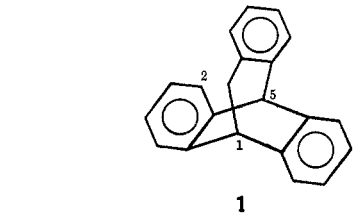
A preparation of homotriptycene (1) was conducted *via* ring expansion of tribenzobicyclo[2.2.2]octatrienylcarbinyl cation. Alkyl cations from 1 (*i.e.*, 2 and 7) do not rearrange to each other, but the 2-tribenzobicyclo[3.2.2]nonatrienyl cation (2) is an intermediate whose degeneracy was demonstrated with the aid of deuterium labeling. Pmr spectra of some homotriptycenes and triptycenes are recorded.

A natural extension of work in this laboratory on bridged polycyclic systems centered about tribenzobicyclo[3.2.2]nonatriene (**1**) and some of its derivatives, in particular, the carbonium ion **2**. For reasons of simplicity **1** will be referred to as homotriptycene, as it



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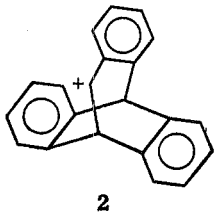

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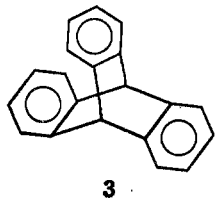

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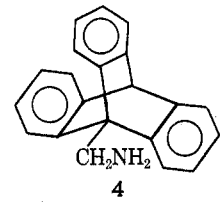
is the next higher homolog of 9,10-dihydro-9,10-*o*-benzenoanthracene, or triptycene (**3**). Within the last few years syntheses of bicyclo[3.2.2]nonatriene[2] and one of its mono-[3] and both of its dibenzo-substituted[4] derivatives have been described. We now describe another member of this bicyclic family, tribenzobicyclo[3.2.2]-nonatriene.

The key to the synthesis of the homotriptycene ring system appeared to us to be a ring expansion reaction of some derivative of 1-methyltriptycene. As 1-aminomethyltriptycene (**4**) was known,[5] this appeared to be a very reasonable precursor. In accord with our expectations, nitrous acid in glacial acetic acid converted **4** into a mixture representing a 42% yield of 1-tribenzobicyclo[3.2.2]nonatrienol (**5**-OH) and a 56%



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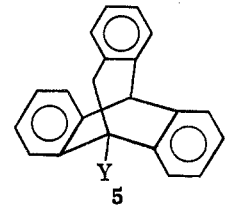

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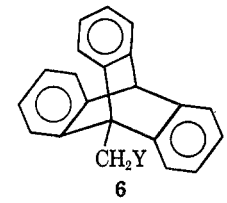


6

yield of the corresponding acetate (**5**-OAc).[6] We did not find any alcohol or acetate with unrearranged carbon skeleton (*i.e.*, **6**-OH or **6**-OAc). Neither **5**-OH nor **5**-OAc seemed to be an ideal precursor of **1**, as **5**-OH

(1) Paper LX: S. J. Cristol, M. A. Imhoff, and D. C. Lewis, *J. Org. Chem.*, **35**, 1722 (1970).

(2) (a) M. J. Goldstein and A. H. Gevirtz, *Tetrahedron Lett.*, 4413 (1965); (b) M. Jones, Jr., and S. D. Reich, *J. Amer. Chem. Soc.*, **89**, 3935 (1967); (c) M. J. Goldstein and B. G. Odell, *ibid.*, **89**, 6356 (1967).

(3) J. Ciabattoni, J. E. Crowley, and A. S. Kende, *ibid.*, **89**, 2778 (1967).

(4) (a) S. J. Cristol, R. M. Sequeira, and C. H. DePuy, *ibid.*, **87**, 4007 (1965); (b) S. J. Cristol, R. M. Sequeira, and G. O. Mayo, *ibid.*, **90**, 5564 (1968); (c) S. J. Cristol, G. O. Mayo, and G. A. Lee, *ibid.*, **91**, 214 (1969).

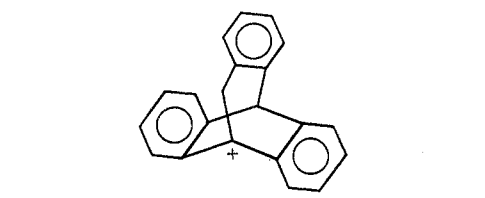
(5) E. C. Kornfeld, P. Barney, J. Blankley, and W. Faul, *J. Med. Chem.*, **8**, 342 (1965).

(6) The presence of large amounts of alcohols from diazotization reactions in acetic acid has been noted before.[7]

(7) (a) J. H. Ridd, *Quart. Rev.* (London), **15**, 418 (1961); (b) P. S. Bailey and J. G. Burr, Jr., *J. Amer. Chem. Soc.*, **75**, 2951 (1953); (c) A. Streitwieser, Jr., *J. Org. Chem.*, **22**, 861 (1957); (d) H. Felkin, *Bull. Soc. Chim. Fr.*, 1582 (1960); (e) J. R. Mohrig, Ph.D. Thesis, University of Colorado, 1963; (f) G. T. Tiedeman, Ph.D. Thesis, University of Colorado, 1964.

was converted only extremely slowly with thionyl chloride to **5**-Cl. However, the nitrous acid experiment suggested that the Demjanov ring expansion was useful for entry into the homotriptycene ring system.

Use of nitrosyl chloride[8] in methylene chloride with **4** gave rearranged (**5**-Cl) and unrearranged (**6**-Cl) chlorides in yields of 66 and 12%, respectively. The isolation of **6**-Cl in this experiment and the absence of **6**-OH and **6**-OAc in the acetic acid deamination described above raise some interesting questions. There is the possibility that at least a portion of the nitrosyl chloride reaction proceeds by a noncarbonium ion process, not utilized in the other deamination. Alternatively, chloride ion may trap some other carbonium ion precursor faster than it rearranges to **7**. This precursor may be the primary cation **8** or the ion **9**. Note that geometric requirements make **9** σ bonded, rather than a phenonium ion. Our data do not enable a choice to be made among these possibilities.



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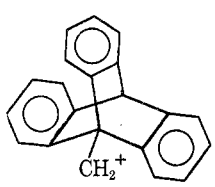

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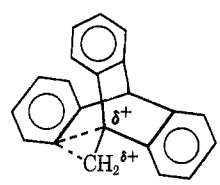


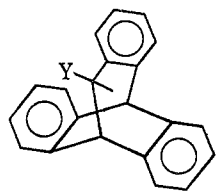
9

Nitrosyl chloride and nitrous acid deaminations are susceptible to modifications to give a wide variety of substituents at the bridgehead (C-1 of **1**). As an example, when ethanol was a cosolvent with dichloromethane during nitrosyl chloride treatment of **4**, large amounts of ethyl 1-tribenzobicyclo[3.2.2]nonatrienyl ether (**5**-OEt) were formed. Proper choice of solvent or solute–solvent systems could supply many different bridgehead derivatives of **5**.

The success of the deamination procedure from **4** as the ring-expansion process was fortunate, as other **6** compounds did not react readily. For example, **6**-OAc was recovered unchanged after 2 hr of refluxing in 1 *M* $HClO_4$ in acetic acid and **6**-Cl was recovered unchanged after treatment with silver acetate in acetic acid at 210° for 24 hr.

Reduction of **6**-Cl with sodium in *t*-butyl alcohol gave 1-methyltriptycene (**6**-H).[9] In similar fashion, homotriptycene (**1**) was obtained from **5**-Cl.

1 was transformed to a monobromo derivative (**10**-Br) by light-promoted treatment with N-bromosuccinimide. Chlorohomotriptycene (**5**-Cl) gave a similar reaction. Treatment of **1** with 2 mol of NBS gave the dibromo compound **11**-Br. Solvolyses of **10**-Br in 1:1 methanol–benzene and 1:1 ethanol–benzene at reflux were complete in less than 1 hr and gave the methyl (**10**-OCH_3) and ethyl (**10**-OEt) ethers, respectively and quantitatively. Silver acetate in acetic acid gave **10**-OAc quantitatively. Thus, in these experiments, ion **2** does not isomerize to **7**.



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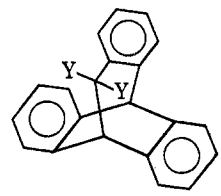

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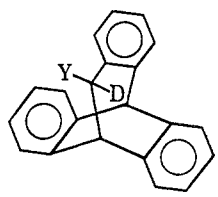

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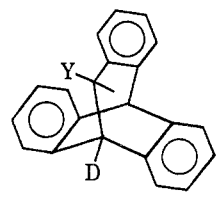
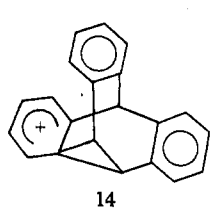


13

Ion **2**, if a classical ion, is triply degenerate (*via* Wagner–Meerwein rearrangement) and should demonstrate scrambling of one of the bridgehead atoms and the cationic carbon atom. To test this, **1** was converted with potassium *t*-butoxide and DMSO-d_6 to dideuteriohomotriptycene (**11**-D) and bromination of this led to **12**-Br. The pmr spectrum of **12**-Br indicated that no rearrangement occurred in the radical bromination. When **12**-Br was solvolyzed in methanol in the absence of base or in the presence of 0.02, 0.38, or 3.8 *M* sodium methoxide, it was converted cleanly to a mixture of methyl ethers (**12**-OCH_3 and **13**-OCH_3), which in each case appeared (by pmr analysis) to be an equimolar mixture. Thus, complete scrambling occurs in 2-homotriptycyl ion (**2**) before capture.

An alternative to the classical structure **2** for the ionic intermediate is the phenonium ion structure **14** which would also rationalize the observed scrambling. The completely delocalized structure for the unsubstituted bicyclo[3.2.2]nonatrienyl cation has been rejected by Goldstein and Odell,[10] and their objections would probably pertain as well to our system. A distinction could be made between **2** and **14**, if **14** is stable toward interconversion by Wagner shifts, by appropriate ring labeling. Possibly Olah's method[11] would also be applicable.



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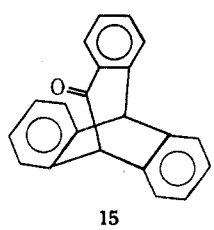

15

Hydrolysis of the dibromide **11**-Br with aqueous sodium acetate gave the ketone **15**. This was also prepared by oxidation of **1** and was readily reduced to the alcohol **10**-OH with lithium aluminum hydride and in analogous fashion to the deuterio analog **12**-OH.

Attempts to interconvert ions **2** and **7** were not successful. Both **5**-OAc and **10**-OAc were stable to 1–2 hr of refluxing in 1 *M* $HClO_4$ in acetic acid. While

(8) P. A. S. Smith, D. R. Baer, and S. N. Ege, *J. Amer. Chem. Soc.*, **76**, 4564 (1954).

(9) W. Theilacker, U. Berger-Brone, and K. H. Beyer, *Chem. Ber.*, **93**, 1658 (1960).

(10) M. J. Goldstein and B. G. Odell, *J. Amer. Chem. Soc.*, **89**, 6356 (1967); M. J. Goldstein, *ibid.*, **89**, 6357 (1967).

(11) G. M. Olah and A. M. White, *ibid.*, **91**, 3954, 3956 (1969).

it is possible that **7** was not in fact formed from **5**-OAc by this treatment, it is obvious that **10**-OAc gives **2** readily under these conditions. It seems certain[12] that treatment of **5**-OH with thionyl chloride, which leads to **5**-Cl, proceeds *via* **7**, and rearrangement did not occur in this experiment, nor did any **10** species form in the deamination of **4** which led to **5** species. Although **7** must be a highly unstable ion,[13] it seems clear that it must be substantially more stable than the primary ion **8**.

The lack of interconversion between **7** and **2** by a 1,2 hydride shift is reasonably rationalized on geometric grounds.[15] The carbon–hydrogen bonds which would be involved in migration are nearly orthogonal to the p orbital of the cationic center, and the energy barrier to such a migration must therefore be significantly greater than those for capture of each ion by nucleophile.

Structure and Pmr Spectra.—The structures of the compounds described above were generally ascertained by consideration of the interconversions among them and by pmr spectra. Like triptycene,[16] the 1-substituted triptycenes had bridgehead absorption in the τ 4.5–4.7 range, and had two distinct aromatic absorption bands, each representing six protons, presumably reflecting the shielding and deshielding effects of the aromatic rings. The homotriptycenes had broad aromatic absorptions but were generally not readily separable into low- and high-field bands on the 60-Mc instrument. With chlorine, hydroxy, and ethoxy at C-1 in homotriptycene (compounds **5**), two aromatic protons, presumably those *syn periplanar*, were significantly deshielded, and, with compound **15**, the hydrogen *ortho* to the keto group was, as expected,[17] significantly deshielded. Details of the pmr spectra are given in the Experimental Section.

Experimental Section

Elemental microanalyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn. Melting points are corrected. Except where otherwise stated, pmr spectra were taken in $CDCl_3$ on a Varian Associates Model A-60 spectrometer.

Deamination of 1-Aminomethyltriptycene (4) with Nitrous Acid–Acetic Acid.—Dry sodium nitrite, 2.12 g (31 mmol), was added to a solution of 1.02 g (3.1 mmol) of the hydrochloride of **4**[5] in 60 ml of anhydrous acetic acid (distilled from acetyl borate[18]) over a 1-hr period at 18–20°. On the next day the mixture was added to 50 ml of benzene and 50 ml of water. The water layer was separated and washed with three 25-ml portions of benzene. The combined benzene layers were washed with water, aqueous $NaHCO_3$, and saturated aqueous NaCl and dried ($MgSO_4$). After evaporation, the residue was crystallized from methanol to give 910 mg of a mixture; analysis (pmr) showed 530 mg (56%) of **5**-OAc and 380 mg (42%) of **5**-OH.

A solution of 1.34 g of a similar mixture (4.3 mmol) in 200 ml of anhydrous ether was added slowly to a solution of 1.0 g (26 mmol) of $LiAlH_4$ in 100 ml of anhydrous ether. The mixture was heated at reflux for 1 hr, cooled to 0°, and *cautiously*(!) decomposed with water. The ethereal layer was filtered, washed with dilute aqueous HCl, $NaHCO_3$, and saturated NaCl solution and dried ($MgSO_4$). The residue from solvent evaporation was recrystallized from benzene–Skellysolve B (petroleum ether, bp 60–70°) to give 1.22 g (85%) of **1-tribenzobicyclo[3.2.2]-nonatrienol** (**5**-OH), as small prisms, mp 150.5–151°; pmr (in CD_3COCD_3) τ 2.2 m, (2 aromatic H), 2.8 m, (10 aromatic H), 4.93, s (2, OH, H-5), and 6.66 s (2, H-2).

Anal. Calcd for $C_{21}H_{16}O$: C, 88.70; H, 5.67. Found: C, 88.45; H, 5.69.

This alcohol (200 mg, 0.70 mmol) was acetylated with acetyl chloride in N,N-dimethylaniline and chloroform using a standard procedure[19] to give, after recrystallization from aqueous methanol, 201 mg (88%) of **1-tribenzobicyclo[3.2.2]nonatrienyl acetate** (**5**-OAc), mp 153–154°; pmr τ 2.8 m (12 aromatic H), 5.13 s (1, H-5), 6.60 s (2, H-2), and 7.61 s (3, $OCOCH_3$).

Anal. Calcd for $C_{23}H_{18}O_2$: C, 84.64; H, 5.56. Found: C, 84.47; H, 5.68.

Preparation of 1-Chloro-tribenzobicyclo[3.2.2]nonatriene (5-Cl) and 1-Chloromethyltriptycene (6-Cl).—Gaseous nitrosyl chloride (5-ml liquid equiv at 0°) was passed over an ice–water-cooled solution of 5.00 g (0.0176 mol) of **4** in 100 ml of reagent grade dichloromethane until the yellow-brown nitrosyl chloride was no longer decolorized, following the general procedure of Smith.[8] Initial reaction produced a precipitate, gas evolution, and warming of the reaction mixture. Further addition led to less gas evolution and promoted solution of the earlier formed solid. After 2 hr of stirring, the solvent was removed by rotary evaporation; the residual solid was chromatographed on Merck 71707 neutral alumina. Elution with Skellysolve B gave 3.50 g (66%) of **5**-Cl; 25% benzene in Skellysolve B eluted 0.645 g (12%) of 1-chloromethyltriptycene (**6**-Cl), mp 231–232° (lit.[5] 229.5–236.5°); 75% benzene in Skellysolve B yielded 0.150 g of an unknown material, mp 180–182° (decomposition and gas evolution), which was not investigated.

Recrystallization of **5**-Cl from benzene–Skellysolve B deposited white needles: mp 157–157.5°; pmr τ 2.3 m (2 aromatic H), 2.8 m (10 aromatic H), 5.14 s (H-5), and 6.70 s (2, H-2).

Anal. Calcd for $C_{21}H_{15}Cl$: C, 83.30; H, 4.99. Found: C, 83.19; H, 5.02.

For **6**-Cl, the pmr spectrum was τ 2.6 m (6 aromatic H), 3.0 m (6 aromatic H), 4.64 s (H-5), 4.96 s (2, H-2).

Ethyl 1-tribenzobicyclo[3.2.2]nonatrienyl ether (**5**-OEt) was obtained in a nitrosyl chloride deamination of **4** as a side product when absolute ethanol was added to the methylene chloride solution before addition of NOCl. Recrystallization gave impure **5**-OEt, mp 152.5–158.5°; pmr τ 2.5 m (2 aromatic H), 2.9 m (10 aromatic H), 5.20 s (H-5), 6.22 q (2, J = 7.5 Hz, OCH_2CH_3), 6.73 s (H-2), and 8.66 t (3, J = 7.5 Hz, OCH_2CH_3).

Reduction of 6-Cl to 1-Methyltriptycene (6-H).—A solution of 156 mg (0.582 mmol) of **6**-Cl in 150 ml of *t*-butyl alcohol was treated with 7 g (0.3 g-atom) of sodium shot for 24 hr. Water was added (*caution!*) until solution was complete. Extraction with benzene, washing of the benzene layer with water, dilute HCl, and saturated NaCl, and drying (Na_2SO_4) gave, after evaporation of the benzene, chromatography on Merck 71707 alumina, and elution with Skellysolve B, 135 mg (97%) of **6**-H, mp (petroleum ether recrystallization) 258–259° (lit.[9] 253–254°); pmr τ 2.6 m (6 aromatic H), 3.0 m (6 aromatic H), 4.62 s (H-5), and 7.64 s (3, CH_3).

Reaction of 5-OH with Thionyl Chloride.—A solution of approximately 200 mg of **5**-OH in 10 ml of reagent grade thionyl chloride was heated at gentle reflux. After 15 hr the reagent-solvent was removed by distillation. Water (2 or 3 drops) was added to hydrolyze unreacted chlorosulfinate ester and the mixture was taken up in acetone. This solution was dried (Na_2SO_4) and the solvent removed by evaporation. Carbon tetrachloride was added to the residual solid and removed by evaporation. Integration of the peaks of the pmr spectrum showed that about 18% of the homotriptycene material was **5**-Cl.

The above sample was resubjected to the same treatment with

(12) D. J. Cram, *J. Amer. Chem. Soc.*, **75**, 332 (1953); E. S. Lewis and C. E. Boozer, *ibid.*, **74**, 308 (1952); **75**, 3182 (1953).

(13) The relative instability of this bridgehead ion **7** may be inferred from the slow transformation with thionyl chloride of **5**-OH *via* **5**-OSOCl to **5**-Cl (half-life about 4 days) compared with the saturated analog 1-bicyclo-[3.2.2]nonanol, which is converted to its chloride in 1 hr.[14]

(14) C. A. Grob, M. Ohata, E. Renk, and A. Weiss, *Helv. Chim. Acta*, **41**, 1191 (1958).

(15) (a) J. S. Meek and W. R. Benson, private communication, have rationalized the lack of rearrangement,[15b] when 1-aminodibenzobicyclo-[2.2.2]octadiene is deaminated, on similar grounds: (b) W. R. Benson, Ph.D. Thesis, University of Colorado, 1958. (c) Similarly the 2-adamantyl cation does not rearrange[15d] to the more stable[15e] 1-adamantyl cation on acetolysis. (d) P. von R. Schleyer and R. D. Nicholas, *J. Amer. Chem. Soc.*, **83**, 182 (1961): (e) *ibid.*, **83**, 2700 (1961).

(16) W. B. Smith and B. A. Shoulders, *J. Phys. Chem.*, **69**, 2022 (1965).

(17) L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press, London, 1959, p 111.

(18) A. Pictet and A. Geleznoff, *Chem. Ber.*, **36**, 2219 (1903).

(19) R. Chittaran, "Organic Syntheses," Coll. Vol. IV, John Wiley & Sons, New York, N. Y., 1963, p 263.

thionyl chloride. After 70 hr (85 hr total) the isolated material was 50% **5**-OH and 50% **5**-Cl.

In a parallel experiment approximately 200 mg of **5**-OH was set in refluxing thionyl chloride for 14 days. After work-up, a mixture of 17% **5**-OH and 83% **5**-Cl was separated by column chromatography, using Merck 71707 alumina and petroleum ether, to give **5**-Cl, mp and mmp 155.5–156.5°.

Reduction of 5-Cl to Homotriptycene (Tribenzobicyclo[3.2.2]-nonatriene) (1).—A mixture of 3.63 g (0.0116 mol) of **5**-Cl and 100 ml of dry *t*-butyl alcohol was stirred in a 250-ml round-bottom flask fitted with a condenser and drying tube. Enough benzene, 30 ml, was added to promote solution and 8.0 g (0.35 g-atom) of sodium metal shot was added in three portions, with dissolution of the sodium occurring between additions. After the sodium metal was completely consumed, the mixture was added to 150 ml of water. The benzene extract (two 150-ml portions) was dried (Na_2SO_4) and the solvent removed to give, after recrystallization from ethanol, 2.89 g (93%) of **1**, mp 205.0–205.5°; pmr τ 2.8 m (12 aromatic H), 5.25 s (H-5), 5.82 t, (J = 3.8 Hz, H-1), and 6.80 d (2, H-2).

Anal. Calcd for $C_{21}H_{16}$: C, 93.99; H, 6.01. Found: C, 93.92; H, 6.08.

Preparation of 2-Bromotribenzobicyclo[3.2.2]nonatriene (10-Br).—A mixture of 2.46 g (0.00811 mol) of **1** and 1.44 g (0.00811 mol) of N-bromosuccinimide (NBS) in 150 ml of carbon tetrachloride was set under an unfrosted, 100-W tungsten bulb for 2 hr.[20] The flask and bulb were insulated in order to permit reflux. When the reaction mixture cooled, it was set into a refrigerator at −20° to allow complete crystallization of succinimide, which was removed by filtration. The solvent was distilled *in vacuo*. Four recrystallizations of the initially red-brown residue in benzene–petroleum ether deposited 2.93 g (92%) of **10**-Br as thick prisms, mp 192–193.5°; pmr τ 2.8 m (12 aromatic H), 4.20 d (J = 4.5 Hz, H-2), 5.20 s (H-5), and 5.42 d (H-1).

Anal. Calcd for $C_{21}H_{15}Br$: C, 72.63; H, 4.35. Found: C, 72.85; H, 4.45.

In an alternate procedure the imide-free carbon tetrachloride product solution was passed through a pad of activated charcoal. Only one recrystallization was then needed.

Preparation of 2,2-Dibromotribenzobicyclo[3.2.2]nonatriene (11-Br).—Approximately 100 ml of carbon tetrachloride containing 212 mg (0.789 mmol) of **1** and 281 mg (1.58 mmol) of NBS was set under reaction conditions described for the synthesis of **10**-Br. The resulting yellow solution was cooled and filtered through a pad of activated charcoal. Evaporation of the colorless solution yielded 248 mg (74%) of **11**-Br, mp 217–220°; pmr τ 2.0 m (1 aromatic H), 2.4 m (2 aromatic H), 2.8 m (9 aromatic H), 4.79 s (H-1), and 5.22 s (H-5).

Anal. Calcd for $C_{21}H_{14}Br_2$: C, 59.19; H, 3.31. Found: C, 59.33; H, 3.22.

2-Bromo-1-chlorotribenzobicyclo[3.2.2]nonatriene was prepared from 500 mg (1.65 mmol) of **5**-Cl and 332 mg (1.86 mmol) of NBS in 100 ml of CCl_4 as described for **10**-Br. The product, after recrystallization from CCl_4, weighed 579 mg (92%), mp 182–185°; pmr τ 1.9 m (2 aromatic H), 2.8 m (10 aromatic H), 4.11 s (H-2), and 5.20 s (H-5).

Anal. Calcd for $C_{21}H_{14}ClBr$: C, 66.00; H, 3.70. Found: C, 66.00; H, 3.61.

Preparation of Methyl 2-Tribenzobicyclo[3.2.2]nonatrienyl Ether (10-OCH_3).—A solution of 106 mg (0.55 mmol) of **10**-Br in 10 ml of 1:1 benzene–methanol was heated at reflux for 1 hr. Solvents were removed by rotary evaporation after charcoal filtration, giving 91 mg (100%) of **10**-OCH_3, mp 210–214°, mp (after recrystallization from benzene–petroleum ether) 215–216°; pmr τ 2.8 m (12 aromatic H), 5.22 s (H-5), 5.42 d, 5.57 d (J = 4.5 Hz, H-1, H-2), and 6.30 s (3, CH_3).

Anal. Calcd for $C_{22}H_{18}O$: C, 88.56; H, 6.08. Found: C, 88.72; H, 5.91.

Preparation of Ethyl 2-Tribenzobicyclo[3.2.2]nonatrienyl Ether (10-OEt).—Treatment of the crude reaction product from 2.45 g (0.91 mmol) of **1** with 1.62 g (0.91 mmol) of NBS with ethanol gave 2.85 g (100%) of **10**-OEt, mp 169–171°; pmr τ 2.8 m (12 aromatic H), 5.21 s (H-5), 5.42 s (2, H-1 and H-2), 6.01 q (2, OCH_2, J = 7.5 Hz), and 8.67 t (3, CH_3).

Anal. Calcd for $C_{23}H_{20}O$: C, 88.43; H, 6.45. Found: C, 88.26; H, 6.38.

This ether was readily converted to **10**-Br by treatment with 50% aqueous HBr at reflux.

Preparation of 2-Tribenzobicyclo[3.2.2]nonatrienone (15).—After a 14-hr reflux, a solution of 213 mg (0.499 mmol) of dibromide **11**-Br and 100 mg (1.22 mmol) of anhydrous sodium acetate in 16 ml of 80 vol % aqueous acetic acid was poured into 100 ml of cold water. Ether extraction was followed by washing with water, dilute aqueous Na_2CO_3, and saturated NaCl solutions and evaporation of the ether to give 169 mg of a yellow oil which deposited cubic prisms, 121 mg (86%) of **15**, mp 175.5–176.0°, after washing with petroleum ether–benzene; pmr τ 2.0 m (1 aromatic H), 2.7 m (11 aromatic H), 4.77 s, and 4.95 s (H-1 and H-5).

Anal. Calcd for $C_{21}H_{14}O$: C, 89.34; H, 5.00. Found: C, 89.20; H, 5.03.

Preparation of 2-Tribenzobicyclo[3.2.2]nonatrienol (10-OH).—Lithium aluminum hydride (45 mg, 1.1 mmol) in 50 ml of absolute ether was cooled and stirred under a nitrogen blanket as 203 mg (0.723 mmol) of **15** in 100 ml of absolute ether was slowly (0.5 hr) added. After reflux for 1 hr, the reaction mixture was cooled and kept cool during the dropwise addition of water-saturated ether. When the gray solid had completely whitened, the ether solution was filtered.

Recrystallization from cyclohexane of the solid obtained from the above solution by solvent evaporation gave, in two crops, transparent prisms with occluded solvent. Vacuum desiccation for 24 hr was needed to bring the solid to constant weight, 199 mg (97%). Loss of solvent destroyed the prisms and left an opaque solid, mp 162–163°. Prior to the melting point this material liquefied and resolidified at approximately 100°. When the temperature was elevated slowly to 100°, liquefication was substituted by a softening with resolidification; pmr τ 2.8 m (12 aromatic H), 5.15 d (J = 4.5 Hz, H-2), 5.20 s (H-5), and 5.60 d (H-1).

Anal. Calcd for $C_{21}H_{16}O$: C, 88.70; H, 5.67. Found: C, 88.48; H, 5.54.

2-Tribenzobicyclo[3.2.2]nonatrienol-2-*d* (12-OH) was prepared in a similar manner with lithium aluminum deuteride and had initial mp 99–105° and mp 161–162°; pmr (in CCl_4) τ 2.8 m (12 aromatic H), 5.32 s (H-5), and 5.78 s (H-1).

Preparation of 4,4-Dideuteriotribenzobicyclo[3.2.2]nonatriene (11-D).—A pmr tube which contained 546 mg (2.03 mmol) of **1** and 1.5 ml of dimethyl sulfoxide-d_6 (99.5% D, Strohler Isotope Chemicals, Azusa, Calif.) was heated to 90° (variable-temperature controller) in the pmr cavity to maintain solution. After the spectrum of **1** was recorded, 10 mg (0.1 mmol) of potassium *t*-butoxide was added. Vigorous mixing was followed by development of a dark pink color. Deuteration at C-2 reached a constant level, 96%, after 4 hr.

Acetic acid-d_4 (2 drops) was used to neutralize the base. When the solution was added to 50 ml of water, a precipitate formed which was collected by filtration and washed with water. This solid was dried by vacuum desiccation and then dissolved in dichloromethane. The pale yellow solution was decolorized by activated charcoal filtration. Rotary evaporation yielded small prisms (546 mg, 99%). A small portion of this solid was recrystallized from absolute ethanol, mp 205.0–205.5°; pmr τ 2.8 m (12 aromatic H), 5.23 s (H-5), and 5.82 s (H-1).

Preparation of 2-Bromotribenzobicyclo[3.2.2]nonatriene-2-*d* (12-Br).—Bromination of **11**-D was performed according to the procedure described for the synthesis of **10**-Br. The reaction of 302 mg (1.12 mmol) of **11**-D and 199 mg (1.12 mmol) of NBS produced 374 mg (95%) of **12**-Br, mp 190–191.5°; pmr τ 2.8 m (12 aromatic H), 5.22 (H-5), and 5.44 (H-1).

Methanolysis of 12-Br.—When 171 mg (0.491 mmol) of **12**-Br in 100 ml of absolute methanol was heated at reflux for 2 hr, a slight yellow color developed. The methanol was replaced by dichloromethane and this solution was filtered through activated carbon. Solids recovered from this solution, a 1:1 mixture (pmr) of 2-*d* (**12**-OCH_3) and 1-*d* (**13**-OCH_3), methyl 2-tribenzobicyclo-[3.2.2]nonatrienyl ether, were recrystallized from absolute methanol. The first crop, mp 212–213.5°, weighed 77 mg (53%). Subsequent crops totaled 44 mg (30%).

The following methanolyses with added base were also heated at reflux for 2 hr: 48.6 mg (0.140 mmol) of **12**-Br in 100 ml of 0.02 M sodium methoxide in absolute methanol, 30.8 mg (0.089 mmol) of **12**-Br in 100 ml of 0.001 M sodium methoxide in absolute methanol, 36.8 mg (0.106 mmol) of **12**-Br in 20 ml of 0.38 M sodium methoxide in absolute methanol, and 36.8 mg (0.106

(20) This is based upon a general procedure described by I. Koten and R. J. Sauer, *Org. Syn.*, **42**, 26 (1962).

mmol) of 12-Br in 20 ml of 3.8 *M* sodium methoxide in absolute methanol.

The samples were treated in the manner described for the neutral methanolysis, but the recovered ethers were not recrystallized. Because the 3.8 *M* methoxide solution contained large amounts of dissolved solids, the solution was poured into water which was then extracted with dichloromethane. After the solution was dried over anhydrous magnesium sulfate, the ethers were isolated by vacuum evaporation. All products were 1:1 12-OCH_3 and 13-OCH_3 by pmr analysis. The pmr spectrum had absorbances at τ 2.8 m (12 aromatic H), 5.25 s (H-5), 5.45 s, and 5.57 s (0.5 proton each, H-1 and H-2).

Silver Ion Assisted Acetolysis of 10-Br.—Compound 10-Br (200 mg, 0.575 mmol) was added to 10 ml of glacial acetic acid which contained 111 mg (0.664 mmol) of silver acetate. The mixture was stirred and heated for 10 min. The reaction flask was cooled; silver bromide was collected by filtration and washed with several portions of ether. The combined filtrates were washed with water, 10% sodium carbonate solution, and saturated sodium chloride. The ether solution was dried ($MgSO_4$) and the ether evaporated to give 186 mg (99%) of 2-tribenzobicyclo[3.2.2]nonatrienyl acetate (10-OAc), mp 177–178°, after recrystallization from benzene–petroleum ether; pmr τ 2.8 m (12 aromatic H), 3.83 d (J = 4.5 Hz, H-2), 5.17 s (H-5) 5.44 d (H-1), and 7.93 s (3, $OCOCH_3$).

Anal. Calcd for $C_{23}H_{18}O_2$: C, 84.64; H, 5.56. Found: C, 84.83; H, 5.73.

Attempted Silver Ion Assisted Acetolysis of 5-Cl and 6-Cl.—A mixture of 202 mg (0.666 mmol) of 5-Cl and 120 mg (0.720 mmol) of silver acetate in 10 ml of glacial acetic acid was set under reflux for 50 hr. The organic solids were isolated according to the procedure outlined above. Only starting chloride was obtained. When the reaction was repeated at 210° for 48 hr, in a sealed tube, starting material was again isolated. Similar experiments with 6-Cl also led to recovery of starting material.

Treatment of Acetates with Perchloric Acid in Acetic Acid.—A solution of 100 mg of 10-OAc in 1 *M* perchloric acid in glacial acetic acid was heated at reflux for 1 hr. Work-up gave only recovered 10-OAc. When the experiment was conducted for 26 hr, the acetate was destroyed and no material could be recovered. Similar treatments of 5-OAc and 6-OAc for 2 hr gave recovery of starting materials.

Pmr Spectra of Some Triptycenes.—Some triptycene derivatives were prepared as synthetic intermediates and it seems reasonable to record their pmr spectra here. The spectrum of triptycene (3)itself has been recorded[16] and our data are consistent: τ 2.7 m (6 aromatic H), 3.1 m (6 aromatic H), and 4.62 s (2, H-9, H-10). New data include: **1-aminomethyltriptycene** (4),[5] τ 2.6 m (6 aromatic H), 3.1 (6 aromatic H), 4.64 s (H-10), and 5.69 broad s, (2, CH_2); **1-triptycenecarboxaldehyde**,[5] τ 2.5 m (6 aromatic H), 3.1 m (6 aromatic H), and 4.66 s (H-10); **1-hydroxymethyltriptycene**[5] (6-OH), τ 2.5 m (6 aromatic H), 3.1 m (6 aromatic H), 4.54 s (H-10), 4.82 d (2, J = 4 Hz, CH_2), and 5.61 t (OH); **1-acetoxymethyltriptycene** (6-OAc), mp 218–221°, prepared from 6-OH with acetic anhydride in pyridine, pmr τ 2.7 m (6 aromatic H), 3.1 m (6 aromatic H), 4.37 s (2, CH_2), 4.64 s (10-H), and 7.85 s ($OCOCH_3$) (*Anal.* Calcd for $C_{23}H_{18}O_2$: C, 84.64; H, 5.56. Found: C, 84.40; H, 5.58.); **1-ethylenedioxymethyltriptycene**,[5] τ 2.5 m (6 aromatic H), 3.0 m (6 aromatic H), 3.73 s (CH(–O)–O), 4.69 s (H-10), and 5.75 m (4, CH_2CH_2); **1-dimethoxymethyltriptycene**,[5] τ 2.6 m (6 aromatic H), 2.9 m (6 aromatic H), 4.14 s (CH(–O)–O), 4.64 s (H-10), and 5.92 s (6, OCH_3).

Registry No.—**1**, 24098-00-8; **4**, 4423-42-1; **5**-OH, 24098-02-0; **5**-OAc, 24098-03-1; **5**-Cl, 24098-04-2; **5**-OEt, 24098-05-3; **6**-Cl, 1469-58-5; **6**-H, 793-39-5; **6**-OH, 1469-57-4; **6**-OAc, 24098-09-7; **10**-Br, 24098-10-0; **10**-OCH_3, 24098-11-1; **10**-OEt, 24098-12-2; **10**-OH, 24098-13-3; **10**-OAc, 24098-14-4; **11**-Br, 24098-15-5; **11**-D, 24098-16-6; **12**-OH, 24098-17-7; **12**-Br, 24098-18-8; **12**-OCH_3, 24098-19-9; **13**-OCH_3, 24098-20-2; **15**, 24098-21-3; 2-bromo-1-chlorotribenzobicyclo[3.2.2]nonatriene, 24098-22-4; 1-triptycenecarboxaldehyde, 1469-54-1; 1-ethylenedioxymethyltriptycene, 1469-55-2; 1-dimethoxymethyltriptycene, 1469-56-3.

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Transition-State Conformations in the Reductive Opening of Cyclopropyl Methyl Ketones[1]

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The transition-state conformations in the lithium–ammonia reduction of three cyclopropyl methyl ketones, **1–3**, were determined through trapping of the enolates formed in the process. In the ketones studied, the cisoid conformer was found to predominate in the transition-state population distribution. The conformer population is more cisoid if the cyclopropane ring is unsubstituted or substituted in the 2 position than if it is substituted in the 1 position. The enolate trapping experiments show a similarity between ground-state (as calculated from nmr spectral data) and transition-state conformations in the lithium–ammonia reduction of cyclopropyl methyl ketones.

The importance of transition-state conformational preferences in photochemical excitation[2–4] or lithium–ammonia reductions[5–8] of various conjugated cyclopropyl ketones has been well documented. In the photochemical excitation or the lithium–ammonia reduction of fused-ring conjugated cyclopropyl ketones, fragmentation occurs with the cyclopropane bond that has the better orbital overlap with the adjacent carbonyl π system. The conformational geometry of these ring systems is fixed by the fusion of the two rings.

In acyclic conjugated cyclopropyl alkyl ketones the conformational restraints are removed and the ketone carbonyl is allowed to rotate freely over both bonds of the cyclopropane ring. The lithium–ammonia reduction of acyclic cyclopropyl ketones has also been shown to be a highly selective process[7,8] where the cyclopropane bond that cleaves is controlled by both steric and electronic factors. In the reductive cleavage of *cis*- and *trans*-2-methylcyclopropyl methyl ketone, rupture of the C-1–C-3 bond gives rise to a more thermody-

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(2) W. G. Dauben and G. W. Shaffer, *Tetrahedron Lett.*, 4415 (1967).

(3) L. D. Hess and J. N. Pitts, Jr., *J. Amer. Chem. Soc.*, **89**, 1973 (1967).

(4) W. G. Dauben, L. Schutte, R. E. Wolf, and E. J. Deviny, *J. Org. Chem.*, **34**, 2512 (1969).

(5) T. Norin, *Acta Chem. Scand.*, **19**, 1289 (1965).

(6) W. G. Dauben and E. J. Deviny, *J. Org. Chem.*, **31**, 3794 (1966).

(7) R. Fraise-Jullien and C. Frejaville, *Bull. Soc. Chim. Fr.*, 4449 (1968).

(8) W. G. Dauben and R. E. Wolf, *J. Org. Chem.*, **35**, 374 (1970).