60° (bath temperature) (10 mm) and the distillate was collected at −78°. Gas chromatographic analysis and separation on a 10 ft × 0.25 in. 5% OV-17 column at 110° showed **7** and **8** to be present in a ratio of 1:4.5. There was collected 90 mg of **7** and 410 mg of **8**.

For **7**: *Anal.* Calcd for C_8H_{12}: C, 88.81; H, 11.19. Found: C, 88.52; H, 11.29. For **8**: Found: C, 88.70; H, 11.45.

Reduction of 7.—A vigorously stirred solution of 54 mg (0.50 mmol) of **7** and 3.88 g (20 mmol) of dipotassium azodicarboxylate in 6 ml of methanol was treated dropwise during 30 min with 3.0 g (50 mmol) of acetic acid. Stirring was continued until the yellow color had faded, and the reaction mixture was poured onto 25 ml of water and 25 ml of pentane. The water layer was extracted with pentane (10 ml) and the combined organic phases were shaken with saturated sodium bicarbonate solution and dried. The majority of the solvent was removed by careful distillation at atmospheric pressure, and the product (10 mg) was collected on the OV-17 column at 110°. The nmr sample of the hydrocarbon was identical with that of an authentic sample of *exo*-7-methylbicyclo[4.1.0]heptane (**9**).[10,11,17]

Reduction of 8.—Like treatment of **8** resulted in the formation of *endo*-7-methylbicyclo[4.1.0]heptane (**10**), whose pmr spectrum was identical in all respects with that of an authentic sample.[17]

***endo*-1,7-Dimethylbicyclo[4.1.0]hept-2-ene (12).**—When a solution of 1.0 g (10.6 mmol) of 2-methyl-1,3-cyclohexadiene (**11**) and 1.6 ml (15 mmol) of diethylzinc in 5 ml of dry pentane was treated dropwise under nitrogen with 5.65 g (20 mmol) of 1,1-diiodoethane dissolved in 3 ml of pentane in the predescribed manner, there was produced a single substance (190 mg isolated after preparative vpc purification on the OV-17 column at 110°) identified as **12**.

Anal. Calcd for C_9H_{14}: C, 88.45; H, 11.55. Found: C, 88.46; H, 11.55.

Magnesium Bromide Catalyzed Isomerization of 13.—To a solution of freshly prepared magnesium bromide in anhydrous ether [2 ml of a solution (bottom layer) prepared from magnesium turnings (excess) and 1,2-dibromoethane (18.8 g, 0.10 mol) in 100 ml of ether] diluted with 6 ml of dry benzene was added 0.44 g (3.6 mmol) of **13**. After 2.5 hr at 50°, the reaction mixture was cooled in ice water and 10 ml of water was cautiously introduced. The organic layer was removed and the aqueous phase was extracted with pentane. The combined organic phases were dried and carefully concentrated at atmospheric pressure. The remaining material was distilled at 60° (bath temperature) (1 mm) and the volatiles were collected at −78°. The lone product was purified by preparative vpc on the OV-17 column at 110° and identified as **14** (21 mg).

Anal. Calcd for C_9H_{14}: C, 88.45; H, 11.55. Found: C, 88.25; H, 11.71.

Registry No.—**1**, 2566-57-6; **5**, 36601-89-5; **7**, 36601-90-8; **8**, 36601-91-9; **12**, 36601-92-0; **14**, 36601-93-1; **16**, 33375-20-1.

Acknowledgment.—This work was supported in part with funds provided by the donors of the Petroleum Research Fund, administered by the American Chemical Society.

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[17] We thank Professor R. M. Magid for kindly providing us with the requisite pmr spectra.

Rearrangements Attending Attempts to Form the 1-Dibenzosemibullvalenylcarbinyl (1-Dibenzotricyclo[3.3.0.$0^{2,8}$]octadienylcarbinyl) Cation[1]

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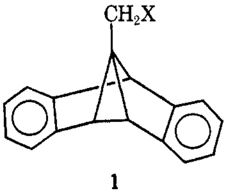
Received July 25, 1972

Silver acetate promoted acetolysis of 1-bromomethyl-3,6-dibenzotricyclo[3.3.0.$0^{2,8}$]octadiene (**1**-Br) and deamination of 1-aminomethyl-3,6-dibenzotricyclo[3.3.0.$0^{2,8}$]octadiene (**1**-NH_2) have been studied. Solvolysis leads only to the rearranged acetates **2**, **3**, **4**, and **5**, along with benzofluorene **6**; "normal" deamination in acetic acid gives, besides **6**, unrearranged acetate **1**-OAc and alcohol **1**-OH and exo products **2** (acetate and alcohol); and "aprotic" deamination gives **6**, **1**-OAc, and **2**-OAc. Mechanistic rationalizations of these differing sets of results are offered.

Each of our groups has developed interest in carbonium-ion rearrangements in bridged polycyclic compounds and, in particular, in the question of multiplicity of carbonium-ion intermediates, as well as in the study of dibenzosemibullvalene and its derivatives.[4] These interests overlapped in work on the rearrangements attending treatment of 1-bromomethyl-3,6-dibenzotricyclo[3.3.0.$0^{2,8}$]octadiene (1-bromomethyldibenzosemibullvalene, **1**-Br) with silver acetate in acetic acid (Colorado group) and of the corresponding deamination of **1**-NH_2 (Ohio State group). This paper describes the results of those experiments.



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When **1**-Br was treated in acetic acid with silver acetate, either at room temperature or at approximately 100°, ready reaction occurred with the formation of four acetate products (**2**-OAc, **3**-OAc, **4**-OAc, and **5**-OAc) and one hydrocarbon, 3,4-benzofluorene (**6**). Pmr analysis indicated that the reaction mixture comprised 30% **2**-OAc, 6% **3**-OAc, 24% **4**-OAc, 23% **5**-OAc, and 16% **6**. No unrearranged **1**-OAc was detectible in the reaction mixture, nor was there any evidence for ring opening to the benzohydryl acetate **7**. That the reaction mixture is the result of kinetic, rather than thermodynamic, control was demonstrated by treatment of a mixture of the four acetates with 0.5 *M* $HClO_4$ in acetic acid at room temperature. The mixture was converted cleanly to **4**-OAc. Treatment with 0.02 *M* $HClO_4$ demonstrated that *endo*-**3**-OAc was more

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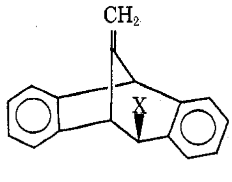
[1] Paper LXXIV in series Bridged Polycyclic Compounds of the University of Colorado group. Paper LXIII: S. J. Cristol, J. R. Mohrig, and G. T. Tiedeman, *J. Org. Chem.*, **37**, 3239 (1972).

[2] University of Colorado. G. C. S. gratefully acknowledges support *via* a NASA fellowship.

[3] The Ohio State University.

[4] See, for example, (a) S. J. Cristol, R. M. Sequeira, and G. O. Mayo, *J. Amer. Chem. Soc.*, **90**, 5564 (1968); (b) S. J. Cristol, W. Y. Lim, and A. R. Dahl, *ibid.*, **92**, 4013 (1970); (c) L. A. Paquette and G. H. Birnberg, *ibid.*, **94**, 164 (1972); (d) L. A. Paquette and G. V. Meehan, *ibid.*, **92**, 3039 (1970).

stable than exo isomer **2**, a result consistent with similar properties of the demethylene compounds **8** and their derivatives.[5] **1**-OAc was also readily converted to **4**-OAc by acid catalysis.



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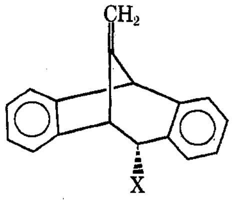

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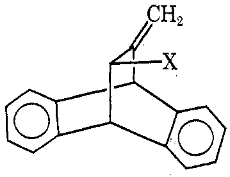

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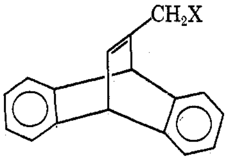

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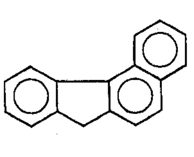

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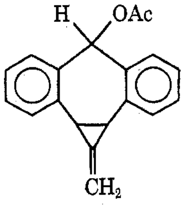

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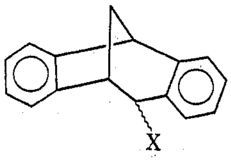
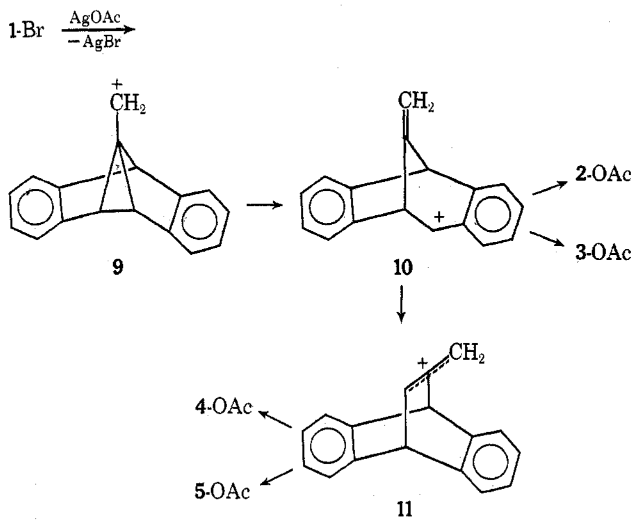


8

The product mixture from treatment of **1**-NH$_2$ with sodium nitrite in acetic acid was substantially different from that produced by acetolysis of **1**-Br. It comprised 16% unrearranged acetate **1**-OAc, 12% the corresponding alcohol **1**-OH, 24% exo acetate **2**-OAc, 40% exo alcohol **2**-OH, and 8% **6**. None of the endo isomers **3** or of the [2.2.2] products **4** and **5** were found. Deamination of **1**-NH$_2$ with isoamyl nitrite in diglyme containing an equivalent of acetic acid led to a mixture containing 33% **1**-OAc, 51% **2**-OAc, and 16% **6**. Again, no endo product **3**-OAc or [2.2.2] products **4** and **5** were noted.

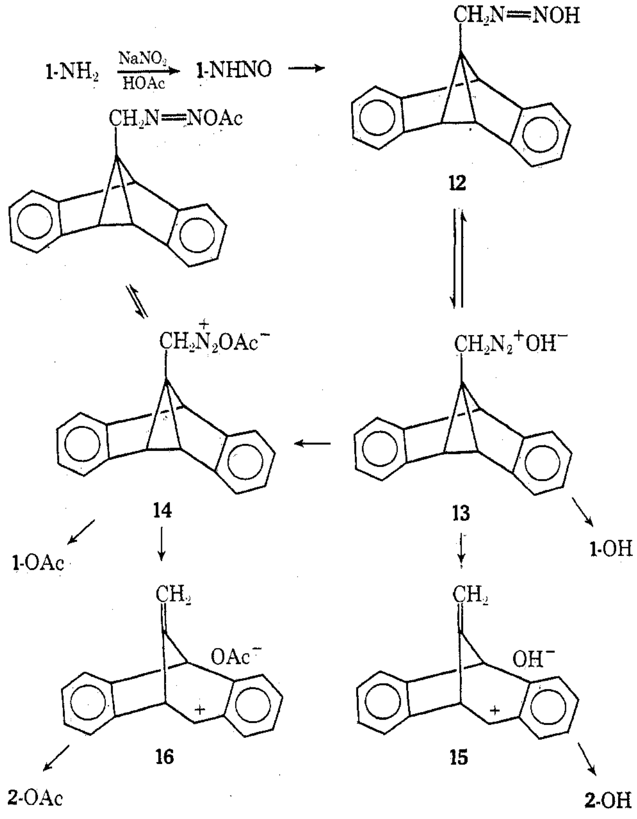
The acetate products of the solvolysis experiments with **1**-Br can be readily rationalized by the reactions in Scheme I. We have chosen to write classical ion intermediates, rather than nonclassical ones, in these systems for several reasons. First, there is no evidence for the latter, and indeed there is contrary evidence in similar systems where similarly highly stabilized classical ions intervene.[4a,5] Finally, the formation of both exo and endo acetates **2**-OAc and **3**-OAc can be most readily accommodated to the capture of **10** from either side (with exo capture predominating, as anticipated[5]), although nonclassical intermediates could be devised to accommodate these results. Apparently there is no solvent participation (*i.e.*, direct displacement) in an S$_N$2-like process to give **1**-OAc nor is ion **9** captured to give **1**-OAc products before rearrangement. Although ion **9** is a cyclopropylcarbinyl cation, it does not appear to be stable enough to resist rearrangement to its allylcarbinyl isomer, the benzylic ion **10**, and indeed it seems likely that it is completely by-passed in the reaction process (*e.g.*, **1**-Br goes directly to **10**; see below).

SCHEME I



The deamination results and rationalizations are outlined in Scheme II. Available evidence suggests that deamination proceeds through unstable diazohydroxides,[6] which are generally assumed to decay to products, often through ion-pair intermediates. The timing of carbon–nitrogen and nitrogen–oxygen heterolytic bond cleavages is markedly dependent upon structure.[1] When the diazonium ion is long lived, sol-

SCHEME II



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[5] (a) S. J. Cristol and D. D. Tanner, *J. Amer. Chem. Soc.*, **86**, 3122 (1964); (b) S. J. Cristol, F. P. Parungo, D. E. Plorde, and K. Schwarzenbach, *ibid.*, **87**, 2879 (1965); (c) S. J. Cristol, R. J. Bopp, and A. E. Johnson, *J. Org. Chem.*, **34**, 3574 (1969).

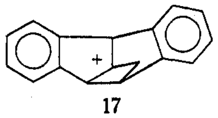
[6] (a) H. Zollinger, "Azo and Diazo Chemistry," Wiley-Interscience, New York, N. Y., 1961, pp 123–136; (b) R. A. M. O'Ferrall, *Advan. Phys. Org. Chem.*, **5**, 362 (1967); (c) E. H. White and D. J. Woodcock in "The Chemistry of the Amino Group," S. Patai, Ed., Wiley-Interscience, New York, N. Y., 1968, pp 440–483; (d) L. Friedman in "Carbonium Ions," Vol. II, G. A. Olah and P. v. R. Schleyer, Ed., Wiley-Interscience, New York, N. Y., 1970, pp 655–713; (e) C. J. Collins, *Accounts Chem. Res.*, **4**, 315 (1971).

vent exchange occurs, and the product is largely that involving solvent (*e.g.*, acetate ester in acetic acid). On the other hand, it has been proposed[1] that, when the carbonium ion resulting from the loss of nitrogen from the diazonium ion is a very stable one, its formation is either coincident with breaking of the nitrogen–oxygen bond or follows it very shortly, so that there is much capture by the geminate[1] hydroxide ion to give alcohol, often with substantial retention in the alcohol product.[7]

Our results permit us to suggest that the diazonium ion which is produced from **1**-NH_2 is of medium longevity. We propose that it either reacts with its geminate hydroxide ion to yield the alcohol **1**-OH coincident with loss of nitrogen,[8] or that this ion pair exchanges with solvent to give the acetate ion pair **14**. As proposed in Scheme II, either ion pair **13** or **14** can lose nitrogen to give (possibly directly) ion pairs **15** and **16**, respectively. If these ion pairs collapse to products before relaxation (that is, epimeric migration of the counterion), they will yield the exo isomers **2** without the endo isomers. Assuming that isomerization of ion **10** to **11** is slow compared with collapse of **15** and **16**, we can also accommodate the fact that the tight ion pairs **15** and **16** lead by rapid collapse to species **2**, while the solvent-separated ion pairs involved in the solvolysis reactions outlined in Scheme I permit equilibration of **10** and **11** before coordination capture by external solvent species or by counterions.[10]

Thus it seems possible to explain the product differences observed here in the two methods for formation of the carbonium-ion system.

The formation of benzofluorene (**6**) represents a more deep-seated rearrangement than those of the other products. It is of especial interest that **6** is produced only when the carbonium-ion system is entered from **1**-X species, and that it is not produced in the solvolyses of **2**-Br, **3**-Br, **4**-Br, or **5**-Br, although all of the acetates (except for **1**-OAc) are produced in these solvolyses.[11] It therefore must be assumed that the first stage in the formation of **6** is a rearrangement concerted with the loss of nucleofuge[12] and using a path not involving ion **10**. Several pathways appear possible for this rearrangement, assuming classical cations. If the 1,2 (or 1,8) bond migrates, the cyclobutyl cation **17** would form. Cyclobutyl–homoallyl interconversion yields ion **18**, which has the correct carbon skeleton but requires hydride shifts followed by proton loss (or proton loss followed by double-bond isomerization) for aromatization to **6**. Alternatively migration of the 2,8 bond gives the ion **19** which is the cyclopropylcarbinyl isomer of **17**. Also a third alternative involves migration of the benzo ring (a 1,3-aryl migration[4d]) to give **20** followed by cyclopropyl cation to allyl cation rearrangement (it seems likely that these steps would be telescoped) would give **21** which would lose a proton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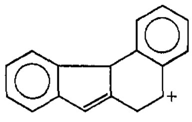
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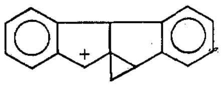
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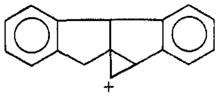
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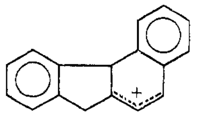
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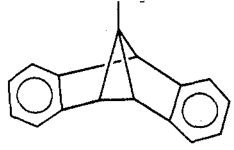
to give **6**. Each of these proposed routes has at least one less than attractive feature, and we have no labeling experiments to distinguish among the several possibilities, so that these suggestions are speculative, at best.

The reaction of **1**-NH_2 with isoamyl nitrite in diglyme containing an equivalent of acetic acid deserves further comment. This procedure, which Friedman and Bayless[13] have termed "aprotic diazotization," has been suggested by them to proceed *via* diazo esters produced by addition of acetic acid to the diazoalkanes formed by deprotonation of the diazonium ions in the aprotic solvent system. Our failure to find the alcohols **2**-OH or **3**-OH in the "aprotic" system would appear to confirm that suggestion, and comparison of results in this system with that in glacial acetic acid, where more than half of the alcohol–acetate fraction is alcohol, provides the beginning of an insight into solvent effects on relative rate constants for the various processes involved.

Preparation of Reagents and Identification of Products.—Compounds with the skeleton represented by **1** were derived from 1-carboethoxydibenzotricyclo[3.3.0.0^{2,8}]octadiene (**22**-Et) or its methyl ester analog (**22**-Me). These compounds are readily available by



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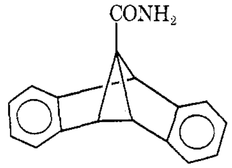

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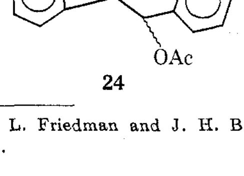

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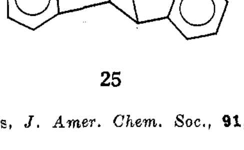

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[7] (a) R. A. Moss, A. W. Fritz, and E. M. Emery, *J. Org. Chem.*, **36**, 3881 (1971); (b) H. Felkin, *C. R. Acad. Sci.*, **236**, 298 (1953); (c) R. Huisgen and C. Rüchardt, *Justus Liebigs Ann. Chem.*, **601**, 21 (1956).

[8] A number of investigators have suggested direct displacement of nucleophiles upon diazonium ions.[9]

[9] (a) J. A. Berson and D. A. Ben-Efraim, *J. Amer. Chem. Soc.*, **81**, 4094 (1959); (b) J. A. Berson and A. Remanick, *ibid.*, **86**, 1749 (1964); (c) J. G. Traynham and M. T. Yang, *ibid.*, **87**, 2394 (1965); (d) R. D. Guthrie, *ibid.*, **89**, 6718 (1967); (e) J. H. Bayless, A. T. Jurewicz, and L. Friedman, *ibid.*, **90**, 4466 (1968); (f) W. J. Albery, J. E. C. Hutchins, R. M. Hyde, and R. H. Johnson, *J. Chem. Soc. B*, 219 (1968).

[10] We have looked[11] into the solvolysis of the bromides **2**, **3**, **4**, and **5** (which will be reported later) and have data consistent with the idea that **10** and **11** do equilibrate but that their rates of equilibration are competitive with their rates of capture by solvent.

[11] G. C. Schloemer, Ph.D. Thesis, University of Colorado.

[12] (a) This term for describing a group leaving with an electron pair has been used in Europe for some time.[12b,c] We recommend its further acceptance. (b) J. Mathieu, A. Allais, and J. Valls, *Angew. Chem.*, **72**, 71 (1960); (c) C. A. Grob and P. W. Schiess, *Angew. Chem. Int. Ed. Engl.*, **6**, 1 (1967).

[13] L. Friedman and J. H. Bayless, *J. Amer. Chem. Soc.*, **91**, 1790 (1969).

Ciganek's elegant photochemical procedure.[14] Reduction of **22** with lithium aluminum hydride gave **1-OH**[15] which gave **1-OAc** with acetic anhydride in pyridine. Treatment of **1-OH** with phosphorus tribromide and pyridine in benzene gave **1-Br**.

Treatment of **22-Me** with methanolic sodium hydroxide gave, after acidification, **22-H**, which upon treatment first with thionyl chloride and then with ammonia gave the amide **23**. Diborane reduction of **23** gave **1-NH$_2$**.

The product mixtures from the solvolyses were analyzed by pmr techniques before and after treatment with lithium aluminum hydride to convert the acetates to alcohols, and those from the deamination without lithium aluminum hydride treatment (**4-OH** and **5-OH** are more readily distinguishable than their acetates).

A pure sample of **5-OH** was prepared by lithium aluminum hydride–aluminum chloride reduction[16] of 7-carboethoxydibenzobicyclo[2.2.2]octatriene as described by Shenoy.[17] As reported by Shenoy, omission of aluminum chloride gave the saturated alcohol. **5-OAc** was also prepared from propargyl acetate and anthracene,[15] although the Shenoy procedure for **5-OH** is simpler. Treatment of **5-OAc** (or **2-** or **3-OAc**) with perchloric acid in acetic acid gave **4-OAc**. Pure samples of **2-OAc** or **3-OAc** were not obtained, but mixtures of the two can be readily characterized by the different coupling constants of the carbinyl (C-4) proton with the bridgehead proton.[18] A mixture or **2-OAc** and **3-OAc** was prepared by a Wittig reaction on **24** which was prepared by oxidation of **25**. **25** was prepared by treatment of epoxydibenzobicyclo[2.2.2]octadiene[19] with acetic acid. Compound **6** is known.[20]

Experimental Section

Pmr spectra were determined on Varian A-60A and HA-100 spectrometers.

1-Hydroxymethyldibenzotricyclo[3.3.0.0^{2,8}]octadiene (1-OH).[15] —A solution of 3.11 g (11.2 mmol) of 1-carboethoxytricyclo-[3.3.0.0^{2,8}]octadiene (**22-Et**)[14] and 800 mg of lithium aluminum hydride in 60 ml of tetrahydrofuran was heated at reflux for 24 hr. Work-up in the usual way gave, after treatment with charcoal and recrystallization from petroleum ether (bp 60–70°), 1.60 g (63%) of **1-OH**: mp 147–148° (lit,[4d] mp 146–147°); pmr ($CDCl_3$) τ 2.5–3.0 (8 H, m, aromatic H), 5.57 (1 H, s, H-5), 6.17 (2 H, s, H-9), 7.01 (2 H, s, H-2, H-8), 8.10 (1 H, s, OH).

1-Acetoxymethyldibenzotricyclo[3.3.0.0^{2,8}]octadiene (1-OAc). —Treatment of **1-OH** with acetic anhydride in pyridine gave **1-OAc**, mp 144.2–145.5°, after recrystallization from isopropyl alcohol: pmr ($CDCl_3$) τ 2.6–3.2 (m, 8, aromatic H), 5.56 (s, 3, H-2, H-5, H-8), 6.90 (s, 2, CH_2O), 8.08 (s, 3, CH_3CO); pmr (C_6D_6), the τ 5.56 singlet divides into τ 5.68 (s, 1, H-5) and τ 5.78 (s, 2, H-2, H-8).

Anal. Calcd for $C_{19}H_{16}O_2$: C, 82.58; H, 5.80. Found: C, 82.72; H, 5.67.

1-Bromomethyldibenzotricyclo[3.3.0.0^{2,8}]octadiene (1-Br).—A stirred solution of 250 mg (1.07 mmol) of **1-OH** in 25 ml of reagent grade benzene containing 1 ml of phosphorus tribromide (2.8 g, 10.3 mmol) and 1 ml of pyridine was heated to 60° for 45 min. The reaction mixture was then poured into 50 ml of water and extracted with several 25-ml portions of benzene. The benzene layers were washed with water and sodium bicarbonate solution and dried ($MgSO_4$). Removal of the solvent and recrystallization (charcoal) from petroleum ether (bp 60–70°) gave 166 mg (52%) of **1-Br**: mp 132.5–135°; pmr ($CDCl_3$) τ 2.5–3.0 (8 H, aromatic H), 5.51 (1 H, s, H-5), 6.20 (2 H, s, H-9), 6.84 (2 H, s, H-2, H-8).

Anal. Calcd for $C_{17}H_{13}Br$: C, 68.70; H, 4.41. Found: C, 69.07; H, 4.52.

7-Acetoxymethyldibenzobicyclo[2.2.2]octatriene (5-OAc), mp 104–105°, was prepared by a diene synthesis between anthracene and propargyl acetate:[15] pmr ($CDCl_3$) τ 2.0–3.0 (9 H, m, H-8, aromatic H), 5.00 (1 H, s, H-4), 5.10 (1 H, d, H-1, J = 3.3 Hz), 5.33 (2 H, d, H-9, J = 1.3 Hz), 8.19 (3 H, s, acetate). It was converted to **5-OH** by hydrolysis. **7-Hydroxymethyldibenzobicyclo[2.2.2]octatriene (5-OH)** was also prepared by the lithium aluminum hydride–aluminum chloride reduction[16] of 7-carboethoxydibenzobicyclo[2.2.2]octatriene, as described by Shenoy.[17] It melted at 126–127° and had pmr ($CDCl_3$) τ 2.3–3.0 (8 H, m, aromatic H), 3.35 (1 H, d of d, H-8, J = 1.5, J = 5.0 Hz), 4.98 (1 H, s, H-4), 4.98 (1 H, d, H-1, J = 5.0 Hz), 5.83 (2 H, d, H-9, J = 1.5 Hz), 8.52 (1 H, s, OH).

4-*exo*-Acetoxy-8-*syn*-hydroxydibenzobicyclo[3.2.1]octadiene (25).—A solution of 16.2 g (73 mmol) of epoxydibenzobicyclo-[2.2.2]octadiene[19] in 200 ml of glacial acetic acid was heated at 50° for 12 hr. Addition of 500 ml of cold water was followed by extraction with several 100-ml portions of ether. The combined ether extracts were washed with water and aqueous sodium bicarbonate and dried ($MgSO_4$). Evaporation of the ether left an oil, which was chromatographed on Merck 71707 alumina and eluted with benzene. The crude **25** weighed 9.2 g (45%) and was recrystallized from benzene: mp 124.5–126°; pmr ($CDCl_3$) τ 2.5–3.0 (8 H, m, aromatic H), 4.21 (1 H, d, H-4, J = 2.0 Hz), 5.40 (1 H, m, H-8, J = 4.0, J = 4.5, J = 10 Hz), 6.11 (1 H, d, H-1, J = 4.0 Hz), 6.57 (1 H, d of d, H-5, J = 2.0, J = 4.5 Hz), 7.44 (1 H, d, OH, J = 10 Hz), 7.92 (3 H, s, acetate).

Anal. Calcd for $C_{18}H_{16}O_3$: C, 77.13; H, 5.75. Found: C, 77.03; H, 5.75.

4-Acetoxy-8-methylenedibenzobicyclo[3.2.1]octadiene (*exo*-**2-OAc**, *endo*-**3-OAc**).—Solid sodium dichromate (11.5 g, 39 mmol) was added to a stirred solution of 10.0 g (36 mmol) of **25** in 200 ml of glacial acetic acid at room temperature, after which stirring was continued for 45 min. The reaction mixture was poured into water and extracted with ether. The ethereal extracts were washed with water and aqueous sodium bicarbonate and then dried ($MgSO_4$). Evaporation of the solvent left an oil which appeared (pmr) to be mainly **24**. This was not purified but used directly in the Wittig reaction.

A 53% dispersion (446 mg) of sodium hydride (10 mmol) was placed in a flask under a nitrogen atmosphere and washed with pentane several times to remove the mineral oil. The flask was placed in a bath at 75° and 10 ml of dimethyl sulfoxide (DMSO) was added. Reaction proceeded with hydrogen evolution, and, when this stopped, 3.5 g (10 mmol) of methyltriphenylphosphonium bromide[21] dissolved in 30 ml of DMSO was added to the ice-cold solution. After 20 min, 4 g of impure **24** dissolved in 15 ml of DMSO was added. The reaction mixture was stirred overnight. Addition of water was followed by extraction with ether. The ether layer was dried ($MgSO_4$), and evaporation left an oil which upon alumina chromatography and benzene elution gave 400 mg (10%) of a mixture of **2-OAc** and **3-OAc** (~90% **2-OAc**). Although this mixture was not separated, the following pmr absorbances ($CDCl_3$) can be confidently[18] assigned: **2-OAc**, τ 2.5–3.0 (8 H, m, aromatic H), 4.05 (1 H, d, H-4, J = 2.0 Hz), 4.95 (1 H, s, H-9), 5.03 (1 H, s, H-9), 5.68 (1 H, s, H-1), 6.12 (1 H, d, H-5, J = 2.0 Hz), 7.76 (3 H, s, acetate); **3-OAc**, τ 2.5–3.0 (8 H, m, aromatic H), 3.75 (1 H, d, H-4, J = 6 Hz), ~4.90 (1 H, s, H-9), ~5.00 (1 H, s, H-9), 6.00 (1 H, d, H-5, J = 6 Hz), 7.76 (3 H, s, acetate). The mixture was reduced with lithium aluminum hydride to give a mixture of **2-OH** and **3-OH**. Pmr data: **2-OH** ($CDCl_3$), τ 2.5–3.0 (8 H, m, aromatic H), 4.92 (1 H, s, H-9), 4.98 (1 H, s, H-9), 5.25 (1 H, d, H-4, J = 2 Hz), 5.74 (1 H, s, H-1), 6.16 (1 H, d, H-5, J = 2 Hz); **3-OH** (CCl_4), τ 2.5–3.0 (8 H, m, aromatic H), 5.10 (1 H, s, H-9), 5.10 (1 H, d, H-4, J = 5.5 Hz), 5.11 (1 H, s, H-9), 5.80 (1 H, s, H-1), and 6.08 (1 H, d, H-5, J = 5.5 Hz).

7-Acetoxy-8-methylenedibenzobicyclo[2.2.2]octadiene (4-OAc). —The acetate mixture from the solvolysis of **1-Br** (4.6 g, 16.6 mmol) (see below) was dissolved in 50 ml of 0.5 *M* perchloric acid in acetic acid. After 40 hr at room temperature, the solution

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was poured into 250 ml of cold water and extracted several times with ether. The ether extracts were combined and washed with water and aqueous sodium bicarbonate. Drying ($MgSO_4$), solvent evaporation, and chromatography on Merck 71707 alumina with benzene elution gave 4.35 g (95%) of **4**-OAc, mp 97–98°, after recrystallization from benzene: pmr ($CDCl_3$) τ 2.5–3.0 (8 H, m, aromatic H), 4.57 (1 H, m, H-7, J = 3.5, J = 1.8, J = 2.0 Hz), 4.78 (1 H, d, H-9, J = 2.0 Hz), 5.07 (1 H, d, H-9, J = 1.8 Hz), 5.31 (1 H, s, H-4), 5.43 (1 H, d, H-1, J = 3.5 Hz), 8.05 (3 H, s, acetate).

Anal. Calcd for $C_{19}H_{16}O_2$: C, 82.58; H, 5.80. Found: C, 82.89; H, 6.05.

Lithium aluminum hydride reduction of **4**-OAc gave 8-methylene-7-dibenzobicyclo[2.2.2]octadienol (**4**-OH): mp 148–149° after recrystallization from petroleum ether; bp 60–70°; pmr ($CDCl_3$) τ 2.5–3.0 (8 H, m, aromatic H), 4.75 (1 H, broad s, H-9), 4.90 (1 H, d, H-9, J = 1 Hz), 5.48 (1 H, s, H-4), 5.62 (2 H, unresolved m, H-1, H-7), 8.20 (1 H, broad s, OH).

Anal. Calcd for $C_{17}H_{14}O$: C, 87.15; H, 6.02. Found: C, 87.29; H, 6.20.

Silver-Assisted Acetolysis of 1-Br.—A solution of 100 mg (0.338 mmol) of **1**-Br and 100 mg (0.60 mmol) of silver acetate in 30 ml of glacial acetic acid was heated at 90° for 45 min. The cooled solution was filtered and the filtrate diluted with 300 ml of water. Ether extraction, washing with water and aqueous sodium bicarbonate, drying ($MgSO_4$), and solvent evaporation left 95 mg (100%) of an oil which by pmr analysis comprised 30% **2**-OAc, 5% **3**-OAc, 21% **5**-OAc, 24% **4**-OAc, and 18% **6**. The pmr analysis was done on a solution in deuteriochloroform. Acetate methyl peaks at τ 8.05 for **4**-OAc, 8.00 for **5**-OAc, and 7.76 for **2**-OAc and **3**-OAc gave preliminary data. The C-4 proton absorbances at τ 4.05 for **2**-OAc and at 3.75 for **3**-OAc were used to determine the **2**:**3** ratio. The acetate mixture was reduced to an alcohol mixture with lithium aluminum hydride and the ratio of **5**-OH to **4**-OH was obtained by integration of the absorbances at τ 5.22 and 4.7 for **5**-OH and τ 5.83 and 3.41 for **4**-OH. Benzofluorene was analyzed by integration of the absorbance at τ 6.05.

Separation of Alcohols from Solvolysis Mixtures.—The acetate mixture from the solvolysis was reduced with lithium aluminum hydride in ether and the oil which resulted was subjected to chromatography on Merck 71707 alumina with elution with 5% ether in benzene. **4**-OH, mp 147–148° after recrystallization from petroleum ether, was eluted first, followed by mixtures of **2**-OH and **3**-OH contaminated by **4**-OH. We did not succeed in separating **2**-OH and **3**-OH. The last fractions contained **5**-OH, mp 123–123.5° after recrystallization from petroleum ether.

Dibenzotricyclo[3.3.0.0^{2,8}]octadiene-1-carboxylic Acid (22-H).—A solution of 2.00 g (7.6 mmol) of **22**-Et[14] in 50 ml of 40% aqueous sodium hydroxide and sufficient methanol to cause dissolution was refluxed overnight. The solution was cooled in an ice bath while 20% sulfuric acid was added dropwise with stirring to effect neutralization. The resulting white precipitate was separated by filtration, washed with water, and dried to yield 1.5 g (79%) of the acid. Recrystallization from isopropyl alcohol afforded white needles: mp 229–231°; pmr ($CDCl_3$) τ −0.57 (s, 1, COOH), 2.5–3.1 (m, 8, aromatic H), 5.03 (s, 1, H-5), 6.14 (s, 2, H-2, H-8).

Anal. Calcd for $C_{17}H_{12}O_2$: C, 82.24; H, 4.87. Found: C, 82.06; H, 4.88.

1-Dibenzotricyclo[3.3.0.0^{2,8}]octadienecarboxamide (23).—To a suspension of 5.15 g (20.8 mmol) of **19**-H in 60 ml of dry benzene was added 4.84 g (41 mmol) of freshly distilled thionyl chloride and 1.65 g (20 mmol) of dry pyridine. This mixture was refluxed for 1.5 hr. The solvent and excess thionyl chloride were removed *in vacuo* and the residual oil was treated with ~200 ml of ether saturated with ammonia. After standing for 30 min, the ether solution was washed with an equal volume of water and the water layer was reextracted with methylene chloride. The combined organic phases were dried, filtered, and evaporated to give 4.94 g (96%) of **23** as fine white needles: mp 208–209° from hexane–benzene; pmr ($CDCl_3$) τ 2.5–3.1 (m, 8, aromatic H), 4.29 (br, 2, NH_2), 5.25 (s, 1, H-5), 6.25 (s, 2, H-2, H-8).

Anal. Calcd for $C_{17}H_{13}NO$: C, 82.57; H, 5.30; N, 5.66. Found: C, 82.60; H, 5.18; N, 5.55.

1-Aminomethyldibenzotricyclo[3.3.0.0^{2,8}]octadiene (1-NH$_2$).—To 40 ml of diborane in tetrahydrofuran (~1 M, 40.0 mmol) was added dropwise under nitrogen a solution of 1.66 g (6.73 mmol) of **23** in 60 ml of anhydrous tetrahydrofuran. The solution was refluxed for 8 hr, stirred at room temperature overnight, treated with 6 N hydrochloric acid (~10 ml) until gas evolution was complete, and freed of tetrahydrofuran *in vacuo*. The aqueous emulsion so produced was saturated with sodium hydroxide pellets and extracted with six portions of methylene chloride. The usual work-up furnished 1.41 g (90.4%) of **1**-NH_2 as a fluffy white powder: mp 180.5–182.5° dec from isopropyl alcohol; pmr ($CDCl_3$) τ 2.5–3.2 (m, 8, aromatic H), 5.58 (s, 1, H-5), 6.89 (s, 2, H-9), 7.00 (s, 2, H-2, H-8), 8.91 (s, 2, $-NH_2$).

Anal. Calcd for $C_{17}H_{15}N$: C, 87.51; H, 6.48. Found: C, 87.74; H, 6.63.

Protic Deamination of 1-NH$_2$.—To a solution of 1.5 g (6.44 mmol) of **1**-NH_2 in 50 ml of glacial acetic acid was added 3.54 g (51.3 mmol) of sodium nitrite in small portions. After the solid dissolved and evolution of nitrogen ceased, the orange solution was poured into a mixture of 75 ml of benzene and 75 ml of water. The water layer was extracted with benzene (8 × 50 ml) and the combined benzene layers were washed with saturated sodium bicarbonate solution (5 × 50 ml), dried, and evaporated. Chromatography on silica served to separate the mixture of acetates from 3,4-benzofluorene (**6**, 42.2 mg), white plates, mp 124–125° (lit.[4d] mp 125.5–126.5°). The composition of the acetate–alcohol mixture was determined by careful integration of the pmr spectrum. Preparative thick layer chromatographic separation of the mixture led to the isolation of the following components: **2**-OAc (171.4 mg), **1**-OAc (111.7 mg), **2**-OH (239.6 mg), and **1**-OH (68.6 mg). The total recovery of products based on starting material was 39%.

Aprotic Deamination of 1-NH$_2$.—To a solution of 102 mg (0.44 mmol) of **1**-NH_2 in 20 ml of anhydrous diglyme (distilled from sodium) was added under nitrogen 26.2 mg (25 μl, 0.44 mmol) of anhydrous acetic acid and 62.8 mg (72 μl, 0.545 mmol) of freshly distilled isoamyl nitrite and the mixture was heated rapidly to 130° by immersing the flask in a preheated oil bath. After 15 min, the orange solution was cooled, poured into 50 ml of water, and extracted with ether (2 × 50 ml). The ether was washed with saturated sodium bicarbonate solution (50 ml) and water (100 ml), dried, and evaporated. Analysis was by pmr. Preparative thin layer chromatography on silica gel (elution with 20% ether in hexane) gave 8.9 mg (15.7%) of **6**, 37.1 mg (51.4%) of **2**-OAc, and 23.8 mg (32.9%) of **1**-OAc. The overall recovery of products was 59%.

Acid-Catalyzed Rearrangement of 1-OAc.—**1**-OAc (50 mg, 0.18 mmol) was dissolved in 10 ml of 0.027 M perchloric acid in acetic acid and this solution was stirred with exclusion of moisture for 9 hr at room temperature. The contents were poured into 10 ml of water and extracted with ether (2 × 25 ml). The customary work-up gave an orange oil, the pmr spectrum of which was superimposable upon that of authentic **4**-OAc.

Registry No.—**1**-Br, 28545-62-2; **1**-NH_2, 34131-53-8; **1**-OH, 28545-61-1; **1**-OAc, 36481-82-0; **2**-OAc, 36357-95-6; **2**-OH, 36357-96-7; **3**-OH, 36357-97-8; **4**-OAc, 36357-98-9; **4**-OH, 36357-99-0; **5**-OAc, 36358-00-6; **5**-OH, 27651-43-9; **22**-H, 10589-07-8; **23**, 28889-08-9; **25**, 36358-02-8.