Bridged Polycyclic Compounds. L.[1] Synthesis, Rearrangements, and Reactions of Some Dibenzobicyclo[3.2.2]nonatrienes and Dibenzotricyclo[3.3.1.$0^{2,8}$]nonadienes

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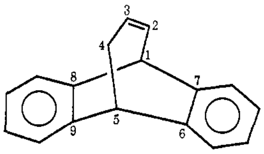
Abstract: Addition of the dichlorocarbene precursor phenyl(trichloromethyl)mercury to dibenzobicyclo[2.2.2]-octatriene (**1**) leads to 3,3-dichloro-6,7;8,9-dibenzotricyclo[3.2.2.$0^{2,4}$]nonadiene (**2**). Thermal rearrangement of **2** gives 3,4-dichloro-6,7;8,9-dibenzobicyclo[3.2.2]nona-2,6,8-triene (**3**). Rearrangements between this system (derivatives of A), the 2,3;8,9-dibenzobicyclo[3.2.2]nona-2,6,8-triene system (derivatives of B), and the 3,4;6,7-dibenzotricyclo[3.3.1,$0^{2,8}$]nona-3,6-diene (derivatives of C) system have been studied in a preliminary fashion. The rearrangements available in these systems involve allylic, Wagner–Meerwein, and homoallyl–cyclopropylcarbinyl, and our results appear consistent with classical cation intermediates. Pmr spectral correlations and synthetic procedures for a number of new compounds are reported.

In the course of our work on bridged polycyclic compounds, we were interested in the preparation and reactions of examples of the two dibenzobicyclo[3.2.2]-nonatriene systems, the 9,10-propeno-9,10-dihydroanthracenes (A) and the ethenodibenzocycloheptadienes (B). This paper reports some of our first work on the chemistry of these systems.



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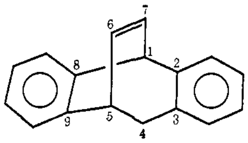

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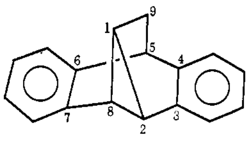
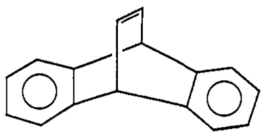


C

In a preliminary communication,[2] we described our initial work with these systems, and subsequently there have been a number of communications in which derivatives of bicyclo[3.2.2]nonatriene[3a–c] and benzobicyclo[3.2.2]nonatriene[3d] have been described. Work has also been conducted in our laboratory on tribenzobicyclo[3.2.2]nonatriene.[3e]

The key to the production of the dibenzononatrienes was the addition of dichlorocarbene to dibenzobicyclo-[2.2.2]octatriene (**1**) to give the cyclopropane **2**. When the reaction of **1** with chloroform and bases[4] (potassium *t*-butoxide or *n*-butyllithium) was attempted, the olefin was recovered unchanged. Similarly, **2** was not produced by decarboxylation of sodium trichloroacetate[5] in the presence of **1**.[6] The desired cyclopropane, 3,3-dichlorodibenzotricyclo[3.2.2.$0^{2,4}$]nonadiene (**2**), was, however, prepared in fair yield through the use of phenyl(trichloromethyl)mercury.[7,8]



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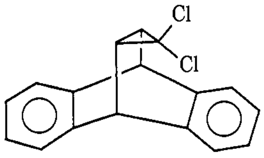

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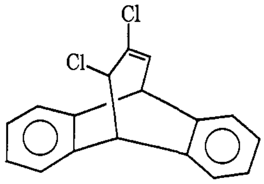
The thermal rearrangement of dihalocyclopropanes formed from the addition of dihalocarbenes to olefins has become a general procedure for ring expansion.[9] As expected, heating **2** at 200° in the absence of solvent gave dichloro compound **3**.[10] In addition to dichloride **3**, an isomer, **4**, was sometimes obtained in the thermolysis. Both dichlorides **3** and **4** were stable thermally. Each survived virtually unchanged a 3-hr exposure to



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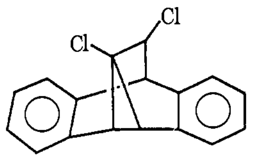

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(1) Previous paper in series: S. J. Cristol and G. C. Fusco, *J. Org. Chem.*, **33**, 106 (1968).

(2) S. J. Cristol, R. M. Sequeira, and C. H. DePuy, *J. Amer. Chem. Soc.*, **87**, 4007 (1965).

(3) (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); (d) J. Ciabattoni, J. E. Crowley, and A. S. Kende, *ibid.*, **89**, 2778 (1967); (e) D. K. Pennelle, Ph.D. Thesis, University of Colorado, 1968.

(4) W. E. Doering and A. K. Hoffman, *J. Amer. Chem. Soc.*, 76, 6162 (1954).

(5) (a) L. F. Fieser and D. H. Sachs, *J. Org. Chem.*, **29**, 1113 (1964); (b) A. Winston, J. P. M. Bederka, W. G. Isner, P. C. Juliano, and J. C. Sharp, *ibid.*, 30, 2784 (1965).

(6) The failure of these normal syntheses may be due to the fact that olefin 1, which is a solid, cannot be used as solvent in the reactions producing dichlorocarbene. Thus, the concentration of 1 in solution in an inert solvent is low; this increases the probability that the carbene undergoes decomposition by other routes.

(7) D. Seyferth, J. M. Burlitch, and J. K. Heeren, *J. Org. Chem.*, 27, 1491 (1962).

(8) T. J. Logan, *Org. Syn.*, **48**, 98 (1966).

(9) See, among others: (a) W. E. Parham and H. E. Reiff, *J. Amer. Chem. Soc.*, 77, 1177 (1955); (b) P. S. Skell and S. R. Sandler, *ibid.*, **80**, 2024 (1958); (c) E. E. Schweizer and W. E. Parham, *ibid.*, **82**, 4085 (1960); (d) W. R. Moore and H. R. Ward, *Chem. Ind.* (London), 594 (1961); (e) S. Winstein and J. Sonnenberg, *J. Org. Chem.*, **27**, 748 (1962); (f) W. R. Moore, W. R. Moser, and J. E. LaPrade, *ibid.*, **28**, 2200 (1963); (g) R. C. DeSelms and C. M. Combs, *ibid.*, **28**, 2206 (1963); (h) E. Bergman, *ibid.*, **28**, 2210 (1963); (i) C. W. Jefford, S. Mahajan, J. Gunsher, and B. Waegell, *Tetrahedron Lett.*, **28**, 2333 (1965).

(10) The proofs of structures of compounds reported in this manuscript are discussed later in the section on nuclear magnetic resonance spectra.

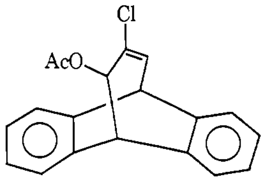
Table I. Silver Acetate–Acetic Acid Solvolysis of Dichlorides at Reflux

Dichloride (mmol)	AgOAc, mmol	HOAc, ml	Time, hr (min)	Recovered chloride,[a] %	Product composition acetates, % 6a	6b	5
2 (0.728)	0.749	10	1	30	69	21	11
2 (0.711)	0.731	10	1	28	69	21	11
2 (6.75)	7.2	10	3	0	67	23	10
3 (0.693)	0.719	10	(66)	0	68	21	11
3 (0.679)	0.701	10	(26)	4	67	22	12
4 (0.275)	0.285	5	1	30	71	21	7

[a] The recovered chlorides were unrearranged.

225° temperatures. However, when either **3** or **4** was heated at 200° for 1 min in the presence of a trace of ferric chloride, a mixture containing approximately 60% **4** and 40% **3** resulted. It seems likely, therefore, that those cases where **4** was obtained in the thermolyses had adventitious amounts of Lewis acid present.[11]

When the dichlorocyclopropane **2** was solvolyzed in acetic acid containing silver acetate, displacement of one atom of chlorine occurred. Pmr analysis of the product indicated the presence of three acetates, **5**, **6a**, and **6b**. Acetate **5** was present in the smallest amount and **6a** was the most abundant one.



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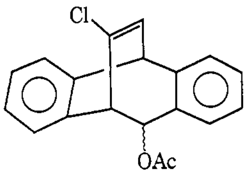
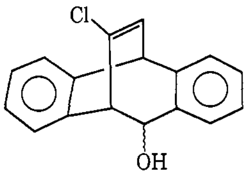
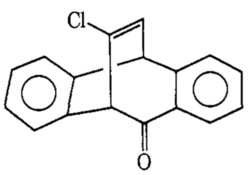


6a (*exo*)
b (*endo*)

6a was saponified to alcohol **7a**. **7a** was oxidized to the chloro ketone **8**. When **8** was treated with lithium aluminum hydride, a mixture of the epimeric chloro alcohols **7a** and **7b** was produced (reduction of ketone **8** with lithium aluminum deuteride made it possible to determine that the alcohols were produced in a ratio of seven parts of *exo* to eight parts of *endo*). The mixture was acetylated with acetic anhydride in pyridine to convert the alcohols into their respective acetates, **6a** and **6b**. These acetates were identical with those produced in the solvolysis of **3**.



7a (*exo*)
b (*endo*)



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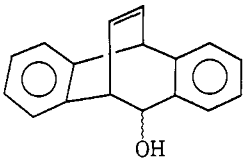
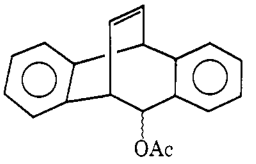
In the [3.2.2] system (B) to which **6** and **7** belong, the notation *exo*-4 has been arbitrarily assigned to the group on C-4 which is *syn* to the ethylene bridge, and the *endo*-4 notation to that which is *anti* to the ethylene bridge. As the coupling constants for the *endo* and *exo* protons at C-4 in the acetoxy compounds **6a** and **6b** were very similar, it was impossible to assign structures directly to these compounds. Accordingly, we dechlorinated **6** and **7** with sodium biphenyl radical anion in dimethoxyethane. The resulting epimeric alcohols **9** were not isolated but were acetylated directly to give the epimeric acetates **10**.



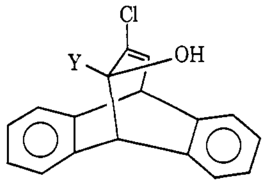
9a (*exo*)
b (*endo*)



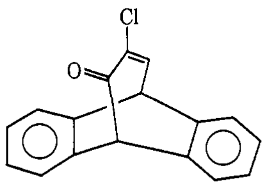
10a (*exo*)
b (*endo*)

We then considered the result of dechlorination upon the chemical shifts of the acetate **6a** and **10a**, and **6b** and **10b**. The *exo* proton was assigned to that compound, **6b** and **10b**, in which the chemical shift effect was greater. This is described in detail in the section on pmr spectra.

The alcohol **11a** produced by the saponification of **5** was oxidized to ketone **12**. As anticipated from its structure, reduction of ketone **12** with lithium aluminum deuteride led to only one alcohol, **11b**.



11a, Y = H
b, Y = D



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Dichlorides **3** and **4** were also solvolyzed in acetic acid with the aid of silver acetate. The results of these solvolyses, along with comparable ones with the cyclopropane **2**, are summarized in Table I.

It may be noted from Table I that the dichlorocyclopropane **2** and the cyclopropylcarbinyl isomer **4** are significantly less reactive than the allylic chloride **3**. It may also be noted that the products are sometimes isomerized slowly in the silver acetate–silver chloride–acetic acid medium.[12] This leads to some uncertainty as to the precise nature of the kinetically formed product. However, it is clear that the initial kinetic mixture contains a small amount of acetate **5**, and largely comprises **6a** and **6b** with the *exo* isomer **6a** predominating in a ratio of about 3:1. It may also be surmised from the data in Table I that the kinetic product mixtures are suggestively similar, and may be identical, from all of the three substances. Thus, it is clear that removal of a chloride ion from each of the three isomers leads to a rapidly rearranging set of cations which equili-

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[11] Goldstein and Odell[3c] report a similar rearrangement of bicyclo-[3.2.2]nona-3,6,8-trien-2-ol to tricyclo[3.3.1.$0^{2,8}$]nona-3,6-dien-9-ol.

[12] We have noted in the course of our work on similar systems that the silver ion present as silver acetate or as precipitated silver chloride often has a slight catalytic effect on the rearrangement of acetate esters.

brate faster than they coordinate with acetic acid or with acetate ion under the conditions of the solvolysis.

The kinetically controlled product mixtures containing largely acetate in the B series of [3.2.2] compounds, *i.e.*, compounds **6a** and **b**, were converted by a dilute solution of perchloric acid in acetic acid to the A series, that is, to **5**. The results of these experiments are summarized in Table II. When a very dilute perchloric acid (0.001 *M*) solution was used, it was possible to determine the equilibrium ratio of *exo-* to *endo*-acetates (**6a**:**6b**) during the rearrangement, and it appeared that the ratio was approximately 1.3.

Table II. The Perchloric Acid Catalyzed Acetolysis of Alcohol **7a** and Acetates **6a** and **6b**

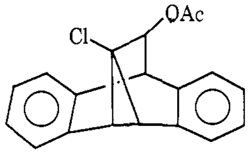
Substrate	[Substrate], *M*	[HClO$_4$], *M*	Temp, °C	Time, min	Product composition, % 6a	6b	5
7a	0.066	0.017	82	10	73	23	4
7a	0.063	0.017	80	60	42	29	29
7a	0.065	0.017	100	60	4	4	92
6b	0.056	0.017	84	10	48	26	26
6a	0.055	0.017	81	10	58	28	14
a	0.047	0.001	100	20	46	37	18
b	0.041	0.001	100	30	47	34	19

[a] A mixture containing 31% of **6a**, 52% of **6b**, and 17% of **5**. A mixture containing 46% of **6a**, 37% of **6b**, and 18% of **5**.

Discussion of Results

We have discussed the solvolysis rearrangement of the dichlorocyclopropane **2** to the mixture of acetates **6** in a previous communication.[2] The fact that **2** reacted rapidly with silver acetate in acetic acid at reflux to give **6**, while the monochloro compound, *anti*-3-chlorodibenzotricyclo$[3.2.2.0^{2,4}]$nonadiene (**14**), was inert, was rationalized on the assumption that the leaving chloride ion must be *trans* to the hydrogens at the cyclopropano ring junction.[13] This strikingly favored stereochemistry made it clear that the solvolysis did not proceed *via* the cyclopropyl cation **15**, but rather proceeded directly from **2** to the allyl cation **16**.[14–18]

It is of interest that while the thermolysis of **2** gives the allylic chloride **3** anticipated from the many previous examples in the literature,[9] the silver acetate assisted solvolysis of **2** does not yield the corresponding acetate **5** as principal product, but rather leads to a mixture containing a few per cent of **5** with the epimeric Wagner–Meerwein isomers of **5**, that is, with **6a** and **6b** (see Table I). This mixture was similar to those produced (also by kinetic control) from **3** and from **4**, and this suggests that equilibration of cations **16**, **17**, and **20** competes favorably with coordination with acetic acid. There appears to be no compelling reason not to assume that structures **16**, **17**, and **20** represent real species rather than canonical forms contributing to mesomeric structures, and indeed the formation of both *exo-* and *endo*-acetates **6a** and **6b** in the solvolysis is most readily explained using classical ions as intermediates.



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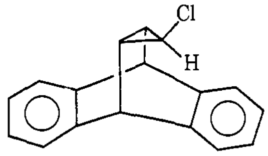

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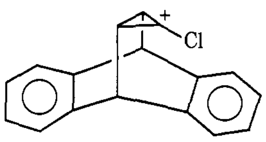

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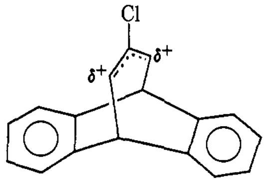

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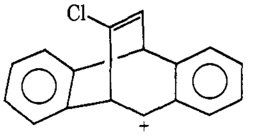

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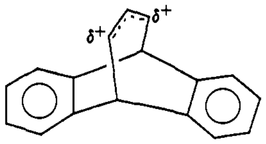

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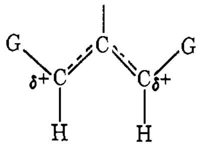

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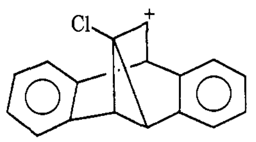

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Our results could also be interpreted as involving equilibration between nonclassical cations **21** and **22** or between **21** and **23**, where **21** could lead to **3**, **5**, and *exo*-**6a**, and **22** or **23** could lead to **4**, **13** (not yet observed), or *endo*-**6b**. However, whenever two or more nonclassical cations have been formulated to explain stereochemical differences between reactions of epimers, there appear to be fairly large energy barriers between them, so that they do not equilibrate rapidly, compared with solvent coordination.[19–24]

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(13) These hypotheses were confirmed[2] by study of 7,7-dichloronorcarane (reactive toward silver acetate) and the epimeric 7-chloronorcaranes (the *syn* isomer was reactive; the *anti* isomer was inert).

(14) This work, combined with that described in ref 13, was offered[2] as evidence supporting a concept[15] concerning the stereochemical basis of electrocyclic transformations, in which it was adduced that the groups *trans* to the leaving group in the cyclopropane ring opening should move outward, while the *cis* groups should move inward. The relative reactivities of **2** and **14** are consistent with the idea that such a concerted disrotatory process is possible with **2** going directly to cation **16** (if the *syn*-chlorine is lost as chloride ion), while **14** cannot go directly to **18** by such a process, but would instead have to proceed either to a cyclopropyl cation or to an allylic cation **19** in which the bridgehead atoms of the bicyclic system would have the locations denoted as G (a substantially impossible situation due to the constraint of the bicyclic system).[16] The rates of solvolysis of a variety of cyclopropyl *p*-toluenesulfonates have been shown to be consistent with the concept of simultaneous ionization and ring opening.[17] On the other hand, it has been suggested that cyclopropyl cations intervene in the decomposition of cyclopropanediazonium ions.[18]

(15) (a) C. H. DePuy, L. G. Schnack, J. W. Hausser, and W. Wiedemann, *J. Amer. Chem. Soc.*, **87**, 4006 (1965); (b) R. B. Woodward and R. Hoffmann, *ibid.*, **87**, 395 (1965).

(16) See also L. Ghosez, P. Laroche, and G. Slinckx, *Tetrahedron Lett.*, 2767 (1967).

(17) (a) P. von R. Schleyer, G. W. Van Dine, U. Schöllkopf, and J. Paust, *J. Amer. Chem. Soc.*, **88**, 2868 (1966); (b) P. von R. Schleyer, Abstracts of the Twentieth National Organic Symposium, Burlington, Vt., June 1967, p 7.

(18) W. Kirmse and H. Schutte, *J. Amer. Chem. Soc.*, **89**, 1284 (1967).

(19) S. Winstein, M. Shatavsky, C. Norton, and R. B. Woodward, *ibid.*, **77**, 4183 (1955).

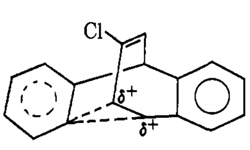
(20) S. Winstein and E. T. Stafford, *ibid.*, **79**, 505 (1957).

(21) E. T. Van Tamelen and C. I. Judd, *ibid.*, **80**, 6035 (1958).

(22) C. H. DePuy, I. A. Ogawa, and J. C. McDaniels, *ibid.*, **82**, 2397 (1960); **83**, 1668 (1961).

(23) S. J. Cristol, J. R. Mohrig, F. P. Parungo, D. E. Plorde, and K. Schwarzenbach, *ibid.*, **85**, 2675 (1963).

(24) H. D. Tanida, T. Tsuji, and T. Irie, *J. Org. Chem.*, **31**, 3941 (1966).



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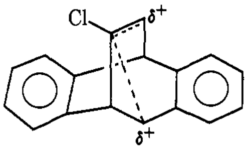

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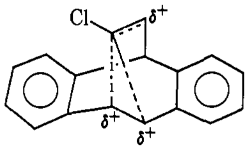

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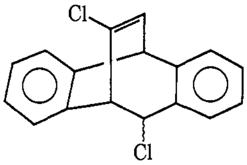


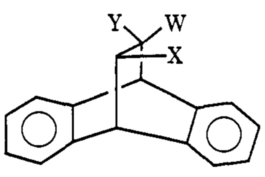
24a (*exo*)
b (*endo*)

When (Table II) the acetate **6a** or **6b** (or the corresponding alcohols which are converted in the reaction mixture to **6a** and **6b**) was warmed in acetic acid containing perchloric acid, there resulted a mixture containing small amounts of **6a** and **6b** (in approximately equal amounts) and over 90% of **5**. The epimerization between **6a** and **6b** was somewhat faster than the isomerization to **5**. These results suggest that the formation of **3** by thermolysis of **2** probably proceeds *via* the **24** isomers, but that these isomerize to **3** rapidly under the conditions of their formation.

It is of some interest that in the time required for the equilibrations of the **6** ⇄ **5** acetates reported in Table II, the acetate **13** with the cyclopropylcarbinyl system was not formed, even though, as described above, the chlorides **3** and **4** are present in almost equal amounts at equilibrium. The failure to produce the acetate **13** in this study would appear the result of the actual lack of reaching the **5** ⇄ **13** equilibrium. It would appear, from the data of Table I, that the chloride **3** is considerably more reactive in yielding cations than the chloride **4**. It may be presumed that similarly acetate **5** will yield cations faster than **13**. As it may be anticipated that the acetates, like the chlorides, are present in approximately equal amounts at true equilibrium, it is therefore necessary that the acetate **13** must be produced from equilibrating cations at a considerably lesser rate than **5**.

Certain aspects of these isomerizations appear to us to be of interest enough to warrant discussion, although the discussion must be somewhat speculative at this stage of our knowledge. The results in these [3.2.2] systems can be compared with the interconversion between [3.2.1]- and [2.2.2]dibenzobicyclooctadiene systems.[25] In those rearrangements, the formations of [3.2.1] compounds **26** from [2.2.2] systems **25** are highly stereospecific, as are the reverse. Thus, for example, the silver ion assisted solvolysis of the *trans*-dichloride **29** yields only the *anti*-8-chloro acetates (largely, if not entirely, **30a**) without any *syn*-8-chloro compounds **31**.[25d]

Epimerization of **30a** and **30b** and their transformations to the [2.2.2] isomer give only the *trans*-acetoxy chloride **32**, without any *syn* or *cis* isomers being formed.[25e]



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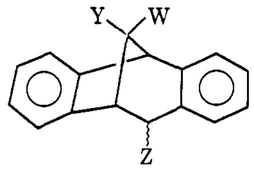
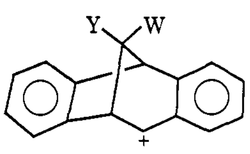


26a (*exo*)
b (*endo*)



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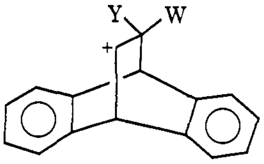

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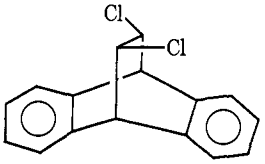

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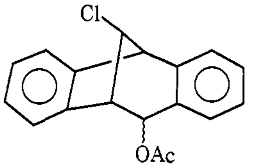
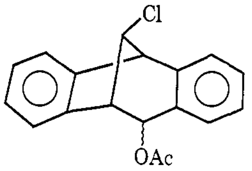
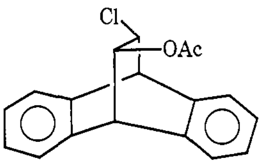


30a (*exo*)
b (*endo*)

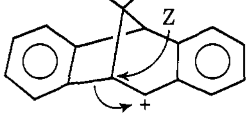


31a (*exo*)
b (*endo*)



32

Similar transformations have been observed in the *cis-syn* series, including the case Y = H, W = D.[26] The results in the [3.2.1] ⇄ [2.2.2] transformations have been accommodated[25e] by the assumption that [2.2.2] ions **28** do not intervene in the transformations but that the sole cationic intermediates are the classical [3.2.1] ions **27**. These react with nucleophiles most rapidly (and reversibly) from the *exo* (*quasi-axial*) direction to give the stereoselectivity generally shown in kinetic control. *exo* departure of nucleofuge also is rapid to return to **27** ions and *endo* attack on **27** gives the *endo* products **26b**. As the existence of the [2.2.2] ions **28** is generally proscribed by the stereospecificity of the rearrangements, it was suggested that the [2.2.2] products **25** were the result of attack of nucleophile at the position vicinal to the benzylic cationic center in **27** with coincident migration of the *anti* carbon–carbon bond to the cationic center (see **33**). This process was dubbed[25e] "geitonodesmic."



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The results on the [2.2.2]-[3.2.1]dibenzobicyclooctadiene system are quite different from those of the dibenzobicyclononatriene and dibenzotricyclononadiene systems discussed in this paper where, as mentioned above, several cationic intermediates are seen to intervene in the solvolysis and rearrangements studies.

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(25) See, *inter alia:* (a) S. J. Cristol and R. K. Bly, *J. Amer. Chem. Soc.*, **82**, 6155 (1960); (b) S. J. Cristol, R. P. Arganbright, and D. D. Tanner, *J. Org. Chem.*, **28**, 1374 (1963); (c) S. J. Cristol and D. D. Tanner, *J. Amer. Chem. Soc.*, **86**, 3122 (1964); (d) S. J. Cristol, F. P. Parungo, and D. E. Plorde, *ibid.*, **87**, 2870 (1965); (e) S. J. Cristol, F. P. Parungo, D. E. Plorde, and K. Schwarzenbach, *ibid.*, **87**, 2879 (1965).

(26) A. E. Johnson, Ph.D. Thesis, University of Colorado, 1965.

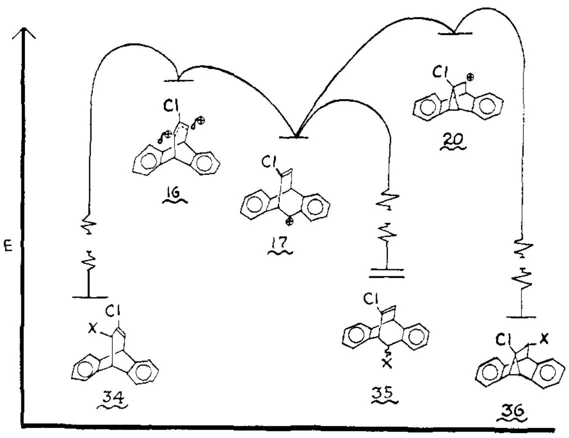
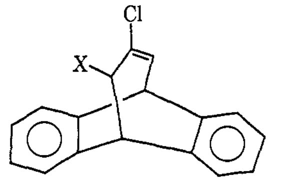


Figure 1. Energy diagram demonstrating the relative stabilities of cations **16**, **17**, and **20**, and compounds **34**, **35**, and **36**, and possible reaction pathways between them.



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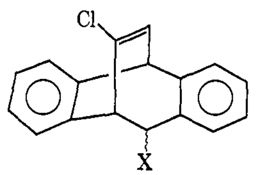

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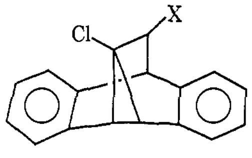

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These, at the present state of our work, appear best to be considered as the classical ions **16**, **17**, and **20**. If we assume that kinetic control is the result of coordination of nucleophile with the *most stable* cationic species in the system (*i.e.*, that with the greatest population),[27,28] we can construct an energy diagram on which these three cations appear (see Figure 1). The relative stabilities of the three cations are reasonable, as **16** and **17** are allylic and benzylic, respectively, with **16** being relatively destabilized by an α rather than a β chlorine atom. The position of the cyclopropylcarbinyl cation **20** on the energy diagram is also consistent with destabilization by the α chlorine atom.[29] Furthermore, its location is prescribed by the fact that **3** and **4** are of almost equal thermodynamic stability, while **3** is considerably more rapidly ionized than is **4** (see Table I). If we now make the necessary assumption that the free energies of activation for coordination with nucleophile of **16**, **17**, and **20** are greater than that for rearrangement of **16** to **17** (and possibly *vice versa*) and of **20** to **17** (but not *vice versa*), we can readily accommodate all of the facts delineated above. Halides **2**, **3**, and **4** will all lead to a mixture of cations containing largely **17**, some **16**, and only traces of **20**. The rates of coordination *vs.* rearrangement will then accommodate the formation of **35** isomers largely (with small amounts of **34**) by kinetic control, largely **34** by partial equilibration, and mixtures composed largely of **34** and **36** by thermodynamic control. The whole situation is mapped in Figure 1.

The existence of classical ion **17** as a reaction intermediate is consistent with the formation of both *exo*-**6a** and *endo*-**6b** from the kinetically controlled acetolyses (**6a**:**6b** 3:1, Table I) and with the observation that equilibration leads to a mixture containing approximately equal amounts of **6a** and **6b** faster than these rearrange to **5**. The kinetically controlled results may be compared to those from the [3.2.1] ion **27** where *exo* coordination ordinarily is favored over *endo*.[25c,e] The [3.2.1] results were rationalized, as were similar ones in bicyclo[3.2.1]octenyl systems,[30] on the assumption of stereoelectronic favoring of formation and cleavage of *quasi-axial* over *quasi-equatorial* bonds. When the one-carbon bridge in the [3.2.1] cation **27** is changed to the two-carbon double-bond bridge in **17**, the *axial–equatorial* nature of the *exo–endo* bonds becomes less pronounced, and stereoelectronic preference would be correspondingly less important.[31] The suggestion made recently[32] that the preferred stereochemistry of formation and cleavage of epimeric bonds is due to torsional strain effects offers an alternative explanation to the same observation, with bridge length having the same effects.

Nothing in the data presently available permits us to consider the stereochemistry of coordination of nucleophile with the allyl cation **16** (nor indeed whether one end of the allylic cation is favored over the other). If, in fact, as we have suggested, **16** is an intermediate, it may be expected to react equally well from the direction from which it was formed from **17** and from the opposite direction and at either end (appropriate labeling in or resolution of the substrates will obviously be required). We hope to carry out experiments to test this, as the results will be of considerable interest no matter what is observed. Resolution or other labeling may be of interest in the question of the intermediacy of ion **20**, which (in the absence of an important gegenion interaction) would be racemic. **20** may lie on a path by which **17** could racemize, and the question of whether **20** is formed from **4** or whether **4** goes directly with rearrangement to **17** is an important one in cyclopropylcarbinyl–homoallyl cation rearrangements.

Pmr Spectra and Structure Proofs. The pmr absorbance spectra of the aliphatic protons of the dibenzobicyclo[3.2.2]nonatrienes and the dibenzotricyclononadienes described in this work are listed in Table III.

The numbering systems used are those shown in structures A, B, and C and are self-consistent although not always strictly in accord with IUPAC rules. The coupling constants are the observed, not the calculated, values.

The pmr spectrum of dichloride **2** exhibited triplets at τ 5.37 and 7.84 with apparent coupling constants of

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(27) S. J. Cristol and R. V. Barbour, *J. Amer. Chem. Soc.*, **88**, 4262 (1966).

(28) This argument assumes that the activation free energies for coordination of each of the ions with nucleophile are not significantly different, or that the energies are lesser for reaction with the more stable ion.

(29) The relative positions of the cations corresponding to 16, 17, and 20, but without chlorine substituents, are not so easily deduced; work on these systems is in progress. See, however, ref 11.

(30) H. L. Goering and D. L. Towns, *J. Amer. Chem. Soc.*, **85**, 2295 (1963).

(31) An interesting extension of the concept that the length of the two bridges (benzo of 1.39 Å and others of variable length) controls the *exo*:*endo* ratio predicts that saturation of the etheno bridge in 17 would favor *endo* attack over *exo*. This will be tested in our future work.

(32) P. von R. Schleyer, *J. Amer. Chem. Soc.*, **89**, 701 (1967).

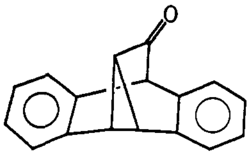
Table III

Compd	τ values[a] H-1	H-2	H-4	H-5	H-6	H-7	Others	Solvent	J, cps
2	5.33 (3)	7.82 (3)	. . .	. . .	. . .	. . .	. . .	$CDCl_3$	$J_{12} = J_{14} = 2.6$
3	5.65 (2)	3.28 (4)	5.23 (4)	5.52 (2)	. . .	. . .	. . .	$CDCl_3$	$J_{12} = 9.4$ $J_{45} = 4.2$ $J_{24} = 0.7$
5	5.68 (2)	3.20 (4)	4.51 (4)	5.53 (2)	. . .	. . .	Acetate 7.93 (1)	CCl_4	$J_{12} = 9.3$ $J_{45} = 4.2$ $J_{24} = 0.6$
11	5.70 (2)	3.33 (2)	5.5 (mult)	5.58 (2)	. . .	. . .	Hydroxyl 7.99 (2)	$CDCl_3$	$J_{12} = 9$ $J_{4,OH} = 7$
12	5.28 (2)	2.32 (2)	. . .	4.75 (1)	. . .	. . .	. . .	$CDCl_3$	$J_{12} = 9.3$
4	. . .	6.78 (1)	. . .	5.80 (2)	. . .	. . .	H-9 5.32 (2)	$CDCl_3$	$J_{59} = 3.5$
6a	5.75 (2)	. . .	4.22 (2)	5.85 (4)	. . .	3.23 (4)	Acetate 7.90 (1)	CCl_4	$J_{17} = 7.5$ $J_{45} = 4.6$ $J_{57} = 2.2$
6b	5.72 (2)	. . .	3.72 (2)	5.97 (4)	. . .	3.10 (4)	Acetate 8.00 (1)	CCl_4	$J_{17} = 7.3$ $J_{45} = 4.2$ $J_{57} = 1.9$
7a	5.75 (2)	. . .	5.44 (4)	5.90 (4)	. . .	3.18 (4)	Hydroxyl 7.65 (2)	$CDCl_3$	$J_{17} = 7.4$ $J_{45} = 4.4$ $J_{57} = 2.2$ $J_{4,OH} = 10$
7b	5.78 (2)	. . .	5.13 (2)	6.21 (4)	. . .	3.22 (4)	Hydroxyl not obsd	$CDCl_3$	$J_{17} = 7.4$ $J_{45} = 4.3$ $J_{57} = 2.2$
8	5.50 (2)	. . .	. . .	5.29 (2)	. . .	3.11 (4)	Mult at τ 2.00	CCl_4	$J_{17} = 7.3$ $J_{57} = 2.1$
9a	5.84 (4)	. . .	5.51 (2)	6.08 (8)	3.73 (8)	3.17 mult	Hydroxyl not obsd	CCl_4	$J_{17} = 6.4$ $J_{67} = \sim 9$ $J_{45} = 4.8$
9b	5.82 (4)	. . .	5.45 (2)	6.30	3.62 (8)	3.21 mult	Hydroxyl not obsd	CCl_4	$J_{67} = \sim 8$ $J_{17} = 6.2$ $J_{45} = \sim 4$
10a	5.77 (4)	. . .	4.16 (2)	5.97 (8)	3.67 (8)	3.17 mult	Acetate 7.96 (1)	CCl_4	$J_{45} = 4.2$ $J_{67} = \sim 6$
10b	5.72 (4)	. . .	3.96 (2)	6.00 (8)	3.52 (8)	3.02 mult	Acetate 8.02 (1)	CCl_4	$J_{17} = 6.6$ $J_{16} = 1.4$ $J_{45} = 4.5$ $J_{56} = 7.0$ $J_{67} = 8.8$ $J_{57} = 1.2$

[a] Numbers in parentheses refer to multiplicities.

2.6 cps. This is an example of a four-spin A_2X_2 system which is not amenable to simple first-order analysis.[33]

Dichloride **4** has a very simple pmr spectrum. The chemical shift of the two cyclopropane protons (τ 6.78) compares with those of similar protons in compounds **37**[34] (τ 6.98) and **38**[35] (τ 7.10).



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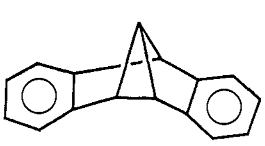

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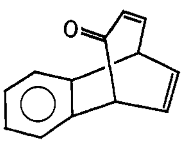
The outstanding features of the pmr spectra of the **A** series of dibenzobicyclononatrienes include (1) a coupling of the vinyl proton with the adjacent bridgehead proton with $J \sim 9$ cps; (2) a long-range coupling of the vinyl proton with H-4, $J < 1$ cps; (3) a coupling (J = 4) between H-4 and the adjacent bridgehead proton (H-5); and (4) a downfield tail on the aromatic proton area.

The vinylic proton in ketone **12** has been shifted so far downfield by the conjugated carbonyl group that it appears at lower field than the aromatic protons. Similar phenomena have also been observed for compounds **39**[3d] and **40**.[36]



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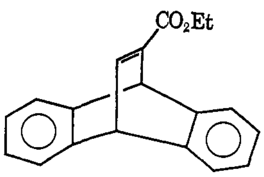

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The major features of the spectra of compounds belonging to the **B** series include (1) a coupling between the vinylic proton and the adjacent bridgehead proton of 7.3 cps; (2) a long-range coupling of 2 cps between the vinylic proton and H-5; (3) a coupling of approximately 4 cps between H-5 and either H-4_{exo} or H-4_{endo};

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(33) For an analysis of the A_2X_2 case, see K. B. Wiberg and B. J. Nist, "The Interpretation of NMR Spectra," W. A. Benjamin, Inc., New York, N. Y., 1962, p 309. However, such spectra have lately been analyzed by weak double irradiation: E. Lustig, E. P. Ragelis, N. Duy, and J. A. Ferretti, *J. Amer. Chem. Soc.*, **89**, 3953 (1967).

(34) V. Ioan, M. Popovici, and C. D. Nenitzescu, *Tetrahedron Lett.* **38**, 3383 (1965).

(35) G. F. Emerson, L. Watts, and R. Pettit, *J. Amer. Chem. Soc.*, 87, 131 (1965).

(36) P. K. Shenoy, Ph.D. Thesis, University of Arizona, 1966.

and (4) the appearance of H-4$_{exo}$ at lower field than H-4$_{endo}$ in all cases.

A distinguishing feature of the spectrum of ketone **8** was the marked downfield shift of one aromatic proton due to the adjacent carbonyl group.[37]

The assignment of the *exo–endo* configuration about carbon **4** in compounds **6** and **7** was accomplished by removing the vinylic chlorine atom and comparing the chemical shifts of H-4 in compounds **9** and **10** with those of H-4 in compounds **6** and **7**.

The proton at C-4 in acetate **6a** absorbs at τ 4.22 while the same proton in the chlorine-free acetate **10a** (derived from **6a**) absorbs at τ 4.16. The protons in the analogous alcohols, **7a** and **9a**, absorb at τ 5.44 and 5.51, respectively. Hence the presence of a chlorine atom in this series has little effect on the chemical shift of H-4.

The proton at C-4 in acetate **6b** absorbs at τ 3.72, and in the related chlorine-free acetate **10b** at τ 3.96. In the analogous alcohols, **7b** and **9b**, the H-4 absorptions occur at τ 5.13 and 5.45, respectively. Here the chlorine atom has much more effect on the chemical shift of H-4. We have therefore tentatively assigned the *exo* configuration to acetate **6a** and its related compounds, **7a**, **9a**, and **10a** (where the hydrogen at C-4 is *endo*), and the *endo* configuration to acetate **6b** and its related compounds, **7b**, **9b**, and **10b**.

Experimental Section

Proton magnetic resonance spectra were obtained using a Varian Associates Model A-60 spectrometer. Infrared spectra were were measured on a Beckman IR-5 infrared spectrometer in 1-mm matched cells in carbon tetrachloride at a concentration of 10 mg/ml. Microanalyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn. Melting points are corrected.

Preparation of 3,3-Dichlorodibenzotricyclo[3.2.2.0^{2,4}]nonadiene (2). A solution of 3.5 g (17 mmol) of dibenzobicyclo[2.2.2]octatriene (**1**)[25d] and 14 g (35 mmol) of phenyl(trichloromethyl)mercury[8] in 100 ml of dry thiophene-free benzene was heated at reflux under nitrogen for 1 week. The solution was allowed to cool to room temperature and the precipitate of phenylmercuric chloride was filtered. Evaporation of the benzene from the filtrate left a yellow oil which was dissolved in carbon tetrachloride and chromatographed over Merck 71707 neutral alumina. Elution with petroleum ether (bp 60–70°) gave 3.9 g of a clear oil. The oil was taken up in ethanol, and 1.9 g (39%) of 3,3-dichlorodibenzotricyclo[3.2.2.0^{2,4}]nonadiene (**2**), mp 152–154°, was obtained upon careful crystallization.

Anal. Calcd for $C_{17}H_{12}Cl_2$: C, 71.09; H, 4.21; Cl, 24.69. Found: C, 71.23; H, 4.34; Cl, 24.62.

The mother liquors contained unreacted **1**.

The Thermal Isomerization of 3,3-Dichlorodibenzotricyclo[3.2.2.0^{2,4}]nonadiene (2) to 3,4-Dichloro-6,7;8,9-dibenzobicyclo[3.2.2]nona-2,6,8-triene (3). Dichloride **2**, 250 mg, was heated in a small tube at 200° for 50 min. The tube was cooled and the contents were taken up in carbon tetrachloride and subjected to pmr analysis. The spectrum indicated that 3,4-dichloro-6,7;8,9-dibenzobicyclo[3.2.2.]nona-2,6,8-triene (**3**) was present and that none of **2** remained. An analytical sample, mp 184–185.5°, was crystallized from ethanol.

Anal. Calcd for $C_{17}H_{12}Cl_2$: C, 71.09; H, 4.21; Cl, 24.69. Found: C, 71.19; H, 4.04; Cl, 24.41.

Occasionally dichloride **4**, 1,9-dichlorodibenzotricyclo[3.3.1.0^{2,8}]nonadiene, was also detected in the reaction product. Dichlorides **3** and **4** were separated with difficulty by fractional crystallization. After the mixture was adsorbed on Merck 71707 neutral alumina, petroleum ether (bp 60–70°) eluted fractions rich in dichloride **3** first followed by fractions rich in dichloride **4**. Dichloride **4** was recrystallized from ethanol, mp 193.5–194.5°.

Anal. Calcd for $C_{17}H_{12}Cl_2$: C, 71.09; H, 4.21; Cl, 24.69. Found: C, 71.16; H, 4.30; Cl, 24.48.

Silver Ion Assisted Acetolyses of Dichlorides 2, 3, and 4. Dichlorocyclopropane **2**, 1.93 g (6.75 mmol), and 1.2 g (7.2 mmol) of silver acetate were heated at reflux in 10 ml of glacial acetic acid for 3 hr. The solution was cooled and poured into water, and the resulting slurry was extracted with ether. The organic extract was washed well with water and with saturated aqueous sodium carbonate and was then dried over anhydrous magnesium sulfate. The ether was removed by rotary evaporation leaving 2.20 g of a yellow oil. The oil was crystallized from ethanol yielding 1.23 g (58%) of 6-chloro-2,3;8,9-dibenzobicyclo[3.2.2]nona-2,6,8-trien-*exo*-4-ol acetate (**6a**), mp 143–145°, which had a carbonyl absorption at 5.78 μ. The pmr spectrum of the residue, 0.90 g (42%), indicated that it contained 21% (0.19 g) of acetate **6a**, 55% (0.50 g) of 6-chloro-2,3;8,9-dibenzobicyclo[3.2.2]nona-2,6,8-trien-*endo*-4-ol acetate (**6b**), and 24% (0.21 g) of 3-chloro-6,7;8,9-dibenzobicyclo[3.2.2]nona-2,6,8-trien-4-ol acetate (**5**).

Anal. Calcd for $C_{19}H_{15}O_2Cl$: C, 73.43; H, 4.86; Cl, 11.41. Found (for **6a**): C, 73.01; H, 4.84; Cl, 11.18.

The acetate mixture was partially separated by chromatography on Merck 71695 alumina which had been conditioned by washing with ethyl acetate and then with several portions of carbon tetrachloride and dried overnight at 150°. The first fraction eluted by petroleum ether (bp 60–70°) contained the *endo*-acetate **6b** only. This acetate was further purified by short-path distillation, bp 120° (0.4 mm), mp 55–60°.

Anal. Calcd for $C_{19}H_{15}O_2Cl$: C, 73.43; H, 4.87. Found (for **6b**): C, 73.21; H, 4.95.

Other solvolyses of dichlorides **2**, **3**, and **4** were carried out in the manner described above. The results are summarized in Table I.

Saponification of 6-Chloro-2,3;8,9-dibenzobicyclo[3.2.2]nona-2,6,8-trien-*exo*-4-ol Acetate (6a) to 7a, and -*endo*-4-ol Acetate (6b) to 7b. *exo*-Acetate **6a**, 1.23 g (4.00 mmol), was dissolved in 10 ml of ethanol. Aqueous potassium hydroxide (5 ml of 1 *N*) was added, and the solution was warmed on the steam bath for 20 hr. The ethanol was removed by rotary evaporation, and the residue was extracted from water with chloroform. The chloroform extract was washed with water and dried over anhydrous magnesium sulfate. Removal of the solvent by rotary evaporation provided 1.3 g of 6-chloro-2,3;8,9-dibenzobicyclo[3.2.2]nona-2,6,8-trien-*exo*-4-ol (**7a**), a clear colorless oil.

Crystallization of the oil from petroleum ether (bp 60–70°) yielded 986 mg (92%) of pure alcohol, mp 145–146°.

Anal. Calcd for $C_{17}H_{13}OCl$: C, 75.98; H, 4.87; Cl, 13.20. Found: C, 75.80; H, 4.77; Cl, 13.09.

The *p*-nitrobenzoate had mp 158–160°.

Anal. Calcd for $C_{24}H_{16}NO_4Cl$: C, 68.98; H, 3.86. Found: C, 68.73; H, 3.96.

When the *endo*-acetate **6b** was treated in the same fashion, an oil was obtained whose pmr spectrum was consistent with that anticipated for **7b** (6-chloro-2,3;8,9-dibenzobicyclo[3.2.2]nona-2,6,8-trien-*endo*-4-ol). We did not succeed in crystallizing it. The *p*-nitrobenzoate melted at 103–105°.

Anal. Calcd for $C_{24}H_{16}NO_4Cl$: C, 68.98; H, 3.86. Found: C, 68.94; H, 4.07.

The Chromic Acid Oxidation of 6-Chloro-2,3;8,9-dibenzobicyclo[3.2.2]nona-2,6,8-trien-*exo*-4-ol (7a). Alcohol **7a**, 1.31 g (4.9 mmol), was dissolved in 75 ml of reagent grade ether. A 12-ml sample of a dichromate solution[38] (5.00 g of sodium dichromate dihydrate and 3.75 ml of 95% sulfuric acid diluted to 25 ml with water) was added and the reaction mixture was stirred at room temperature overnight. Water was added and the green aqueous layer was removed and extracted with ether. The combined ether layers were washed with water and saturated aqueous sodium carbonate and dried over anhydrous magnesium sulfate. Evaporation of the ether left a yellow oil whose pmr spectrum indicated that it was mainly 6-chloro-2,3;8,9-dibenzobicyclo[3.2.2]nona-2,6,8-trien-4-one (**8**). The oil was taken up in ethanol, decolorized with activated charcoal, and crystallized from ethanol, yielding a total of 1.09 g (84%) of ketone **8**, mp 157.0–158.5°.

Anal. Calcd for $C_{17}H_{11}OCl$: C, 76.54; H, 4.16; Cl, 13.29. Found: C, 76.62; H, 4.04; Cl, 13.49.

The Lithium Aluminum Hydride Reduction of Ketone 8. A solution of 241 mg (0.904 mmol) of **8** and 400 mg (10.5 mmol) of lithium aluminum hydride in 50 ml of absolute ether was stirred at room temperature for 3 hr. The excess lithium aluminum hydride was

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(37) L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press, Oxford, 1959, pp 122–123.

(38) A variation of the method of H. C. Brown and C. P. Garg, *J. Amer. Chem. Soc.*, **83**, 2952 (1961).

destroyed by the cautious addition of ethyl acetate, followed by the addition of 6 *M* hydrochloric acid to dissolve the inorganic salts. The solution was extracted with ether and the ether extract was washed with water and saturated aqueous sodium carbonate. The organic extract was dried over anhydrous magnesium sufate and the ether was removed by rotary evaporation leaving 226 mg (93%) of an oil whose pmr spectrum indicated that it was a mixture of alcohols **7a** and **7b**. The crude product was acetylated directly by dissolving it in 25 ml of a 1:1 benzene–pyridine mixture containing 2 ml of acetic anhydride. The mixture was stirred at room temperature for 22 hr and was then poured into an ice–hydrochloric acid mixture. The resulting suspension was extracted with ether and the ether extract was washed with water and saturated aqueous sodium carbonate, and was dried over anhydrous magnesium sulfate. The ether was removed by rotary evaporation leaving 253 mg (90% over-all) of an oil whose pmr spectrum indicated it was a mixture of approximately equal parts of acetates **6a** and **6b**.

The Lithium Aluminum Deuteride Reduction of Ketone 8. Ketone **8**, 260 mg (0.976 mmol), was reduced by 413 mg (9.85 mmol) of lithium aluminum deuteride (97% isotopic purity) using the procedure for reduction by lithium aluminum hydride. The pmr spectrum indicated that the alcohols were deuterated at C-4 and that the ratio of *exo*-alcohol **7a** to *endo*-alcohol **7b** was about 7:8 (based on relative integrations of H-5 protons which appear as simple doublets in the absence of the H-4 absorbances).

Treatment of Acetates 6a and 6b and Alcohol 7a with Perchloric Acid and Acetic Acid. In a typical experiment alcohol **7a** (106 mg, 0.395 mmol) was dissolved in 5.0 ml of glacial acetic acid in a 50-ml round-bottom flask equipped with a reflux condenser. The flask was placed in an oil bath held at 82°. After the flask had come to temperature equilibrium (about 5 min) 1.0 ml of a 0.1 *M* solution of perchloric acid in acetic acid was added by pipet. In 600 sec the flask was removed from the oil bath and the reaction was quenched by addition of water.

The slurry was extracted with ether and the ether extracts were washed with water and then aqueous sodium bicarbonate solution and finally dried over anhydrous magnesium sulfate. The ether was removed by rotary evaporation and the residue was examined by pmr spectroscopy. The results of these experiments are summarized in Table II. The acetates did not rearrange measurably in acetic acid at reflux in 8 days in the absence of mineral acid.

Preparation of 3-Chloro-6,7;8,9-dibenzobicyclo[3.2.2]nona-2,6,8-trien-4-ol Acetate (5) and 3-Chloro-6,7;8,9-dibenzobicyclo[3.2.2]-nona-2,6,8-trien-4-ol (11a). The acetate **5** was produced on a preparative scale by heating a mixture of acetates **6a**, **6b**, and **5** (1.54 g, 5.0 mmol) in 10 ml of glacial acetic acid and 0.5 ml of a 1 *M* solution of perchloric acid in acetic acid at reflux for 0.5 hr. Acetate **5** resisted attempts at crystallization and so the crude oily acetate was dissolved in 25 ml of 95% ethanol. Aqueous potassium hydroxide solution (8.0 ml of a 1 *M* solution) was added and the mixture was heated at reflux overnight on a steam bath. The ethanol was removed by rotary evaporation and the residue was extracted with chloroform. After the organic layer was washed with water and dried over anhydrous magnesium sulfate, the solvent was removed by rotary evaporation and the residual solid was crystallized from ethanol (charcoal). The yield of alcohol **11a** was 950 mg (62% over-all), mp 187–189°. Further recrystallizations from ethanol raised the melting point to 191–192°.

Anal. Calcd for $C_{17}H_{13}OCl$: C, 75.98; H, 4.87; Cl, 13.20. Found: C, 76.06; H, 5.01; Cl, 12.93.

The *p*-nitrobenzoate of **11a** was prepared and crystallized from ethanol, mp 108–110°.

Anal. Calcd for $C_{24}H_{16}NO_4Cl$: C, 68.98; H, 3.86. Found: C, 69.10; H, 3.95.

A mixture melting point of the *p*-nitrobenzoates of alcohols **7b** and **11a** was depressed.

3-Chloro-6,7;8,9-dibenzobicyclo[3.2.2]nona-2,6,8-trien-4-one (12) was prepared by the procedure described for ketone **8** using 569 mg (2.12 mmol) of **11a** in 50 ml of ether and 5.0 ml of the oxidizing solution. The product was crystallized from ethanol to give 485 mg (86%) of chloro ketone **12**, mp 228–229°.

Anal. Calcd for $C_{17}H_{11}OCl$: C, 76.54; H, 4.16; Cl, 13.29. Found: C, 76.36; H, 4.36; Cl, 13.49.

3-Chloro-4-deuterio-6,7;8,9-dibenzobicyclo[3.2.2]nona-2,6,8-trien-4-ol (11b). Lithium aluminum deuteride, 596 mg (14.2 mmol, 97% isotopic purity), was added in one portion to a stirred solution of ketone **12** (479 mg, 1.80 mmol) in 50 ml of absolute ether. After 24 hr, ethyl acetate was added to destroy the excess reducing agent; then water and dilute acid (10% HNO_3) were added and the mixture was extracted with ether. The ether extracts were washed with water and sodium bicarbonate solution and dried over anhydrous magnesium sulfate. The ether was removed by rotary evaporation.

Pmr analysis of the residue indicated that only one compound, **11b**, was present. The mixture melting point of the deuterated alcohol **11b** and the undeuterated alcohol **11a** was undepressed.

Reduction of Acetate 6a by Sodium Biphenyl Radical Anion. A solution of 684 mg (2.20 mmol) of *exo*-acetate **6a** in 3 ml of dry dimethoxyethane was prepared in a small flask sealed with a rubber septum. An approximately 1 *M* solution of sodium biphenyl radical anion in dimethoxyethane[39] was injected into the acetate solution with swirling until the blue-green color persisted momentarily (about 12 ml). The flask was opened, a few drops of ethanol were added, and then water was added. The slurry was extracted with ether, and the ethereal extracts were washed with water until the extracts were neutral, and then dried over magnesium sulfate. The ether was removed on a rotary evaporator and the residue (2.24 g) was chromatographed on Merck 71707 alumina. Biphenyl (1.63 g) was eluted by petroleum ether (bp 60–70°). Elution with 10% chloroform in carbon tetrachloride removed the alcohol **9a** (538 mg) in an impure state. The yellow color was not removed by treatment with charcoal in petroleum solvents or ethanol, nor by further chromatography. Therefore in another experiment the crude alcohol **9a** was acetylated with acetic anhydride in benzene–pyridine solution. The crude acetate **10a** was chromatographed on Merck 71695 alumina (washed first with ethyl acetate and carbon tetrachloride as described earlier). Elution with 5% carbon tetrachloride in petroleum ether (bp 60–70°) removed the acetate **10a**, dibenzo-2,3;8,9-bicyclo[3.2.2]nona-2,6,8-trien-*exo*-4-ol acetate, as a colorless oil which eluded attempts at crystallization. An analytical sample was prepared by sublimation at 130–140° (0.5 mm), mp 37–42°.

Anal. Calcd for $C_{19}H_{16}O_2$: C, 82.58; H, 5.84. Found: C, 82.60; H, 5.94.

Reduction of Alcohol 7b by Sodium Biphenyl Radical Anion. *endo*-Alcohol **7b**, 412 mg (1.53 mmol), was reduced by sodium biphenyl radical anion in a manner similar to that described for acetate **6a**. However, chromatographic separation of the alcohol **9b** from sodium biphenyl was omitted. The mixture was acetylated and the acetate **10b**, dibenzo-2,3:8,9-bicyclo[3.2.2]nona-2,6,8-trien-*endo*-4-ol acetate, was separated from biphenyl on pretreated Merck 71695 alumina. The acetate, an oil, was purified by short-path distillation at 120–130° (0.7 mm).

Anal. Calcd for $C_{19}H_{16}O_2$: C, 82.58; H, 5.84. Found: C, 82.72; H, 5.94.

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(39) L. M. Liggett, *Anal. Chem.*, 26, 748 (1954).