products similar to those obtained from the reaction of 1 with phosphoric acid were also obtained. Neither the possible alkylation product, 1-phenyl-3-(p-t-butylphenyl)propane, nor its dealkylated form, 1,3-diphenylpropane, were produced.

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Bridged Polycyclic Compounds. LIX. Stereochemistry of Rearrangements in Dibenzobicyclo[2.2.2]octadienyl and Dibenzobicyclo[3.2.1]octadienyl Systems and of Additions to Dibenzobicyclo[2.2.2]octatriene¹

STANLEY J. CRISTOL, RONALD J. BOPP, AND A. EARL JOHNSON

Department of Chemistry, University of Colorado, Boulder, Colorado 80302

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cis-3-Deuteriodibenzo-2-bicyclo[2.2.2]octadienyl p-toluenesulfonate (6) is converted stereospecifically upon acetolysis into syn-8-deuteriodibenzo-exo-2-bicyclo[3.2.1]octadienyl acetate (7). In perchloric acid-acetic acid this exo acetate is rapidly transformed to an equilibrium mixture with its endo epimer and is then stereospecifically rearranged to cis-3-deuteriodibenzo-2-bicyclo[2.2.2]octadienyl acetate (8). The results are discussed in terms of a single classical cationic intermediate (12). Addition of acetic acid to dibenzobicyclo[2.2.2]octatriene (3) gives dibenzo-2-bicyclo[2.2.2]octadienyl acetate (11). This reaction is substantially slower than the rearrangement of either endo- or exo-dibenzo-2-bicyclo[3.2.1]octadienyl acetates (9 and 10) to dibenzo-2-bicyclo[2.2.2]octadienyl acetate (11), so that their intermediacy cannot be ascertained. Addition of deuterioacetic acid leads to both cis- and trans-3-deuteriodibenzobicyclo[2.2.2]octadienyl acetates (8 and 15), but most (and perhaps all) of the trans product arises from acid-catalyzed isomerization of the cis-addition product 8. Similar results obtain with trifluoroacetic acid and deuteriotrifluoroacetic acid.

In previous work, largely in this laboratory, it has been shown that dibenzobicyclo [2.2.2] octadiene derivatives (1) undergo Wagner-Meerwein rearrangements to dibenzobicyclo [3.2.1] octadiene derivatives (2), and vice versa. The reactions which occurred were generally stereospecific, at least with respect to the carbon skeletal migration.^{2,3} In all of the cases heretofore



reported, substituents were present as Y or Z in 1 or 2 and we were therefore interested in extending our knowledge about stereochemistry with Y or Z labeled only with deuterium. In these experiments, we were aided by our previous work on pmr spectra of dibenzobicyclooctadienes,^{4,5} where large differences in couplings were observed for diastereoisomers, so that we had available simple means for studying the steric course of rearrangements.

(1) Paper LVIII: S. J. Cristol and G. O. Mayo, J. Org. Chem., 34, 1762 (1969).

- (2) S. J. Cristol, F. P. Parungo, and D. E. Plorde, J. Amer. Chem. Soc., 87. 2870 (1965). (3) S. J. Cristol, F. P. Parungo, D. E. Plorde, and K. Schwarzenbach, ibid.,
- 87, 2879 (1965). (4) S. J. Cristol, T. W. Russell, J. R. Mohrig, and D. E. Plorde, J. Org.
- Chem., 31, 581 (1966).

(5) S. J. Cristol, J. R. Mohrig, and D. E. Plorde, ibid., 30, 1956 (1965).

In conjunction with this work, we began a study of the course of addition of protic species to dibenzobicyclo [2.2.2] octatriene (3). Earlier work^{2,6} had shown that the electrophilic additions of halogens or of halogenlike species (bromine in acetic acid, Prévost reagent) to 3 gave syn, exo products 4. Study of addition of protic and deuterated species to this bicyclooctatriene system seemed an interesting extension of our previous work on similar additions to bicycloheptadiene and bicycloheptene systems.⁷⁻¹¹

The desired deuterium-labeled compounds were prepared from 3 by treatment with deuteriodiborane followed by oxidation. Comparison of the pmr spectrum of the product (5) with the analyzed⁴ spectrum of the undeuterated analog showed that the product had the anticipated¹² cis stereochemistry. Acetolysis of the



(6) S. J. Cristol, R. P. Arganbright, and D. D. Tanner, ibid., 28, 1374 (1963).
(7) S. J. Cristol, T. C. Morrill, and R. A. Sanchez, *ibid.*, **31**, 2719 (1966);

ibid., 31, 2726 (1966); ibid., 31, 2733 (1966).

(8) S. J. Cristol and R. Caple, ibid., 31, 2741 (1966).

(9) S. J. Cristol and G. C. Fusco, ibid., 33, 106 (1968)

- (10) S. J. Cristol, W. K. Seifert, D. W. Johnson, and J. B. Jurale, J. Amer. Chem. Soc., 84, 3918 (1962)
- (11) S. J. Cristol, L. K. Gaston, and D. W. Johnson, Tetrahedron Lett., 185 (1963).
- (12) H. C. Brown, "Hydroboration," W. A. Benjamin, Inc., New York, N. Y., 1962, Chapter 8.



cis-deuterio p-toluenesulfonate 6 gave syn-8-deuterioexo-2-dibenzobicyclo [3.2.1]octadienyl acetate (7) (structure demonstrated by comparison of the pmr spectrum with that of the known undeuterated acetate).⁵ Thus the stereospecific Wagner-Meerwein rearrangement which occurred in the solvolysis of 6 to 7 involved the migration of the bond *anti* to the leaving p-toluenesulfonate group.

When 7 was treated with 1 M perchloric acid in acetic acid at room temperature for 160 min it rearranged to the thermodynamically more stable [2.2.2] acetate. The pmr spectrum of the product was identical with that of an authentic sample of *cis*-3deuteriodibenzo-2-bicyclo[2.2.2]octadienyl acetate (8) prepared from acetylation of the *cis*-deuterio alcohol 5. Thus the acid-catalyzed rearrangement from the [3.2.1] system to the [2.2.2] system was also stereospecific.

Closer scrutiny of the reaction indicated that the acid-catalyzed rearrangement of the [3.2.1] system to the [2.2.2] system followed the path of Scheme I. In 1 M perchloric acid in acetic acid the *exo* acetate 9 was found to equilibrate rapidly (<5 min) to a 58:42 mixture of *exo* and *endo* acetates 9 and 10, respectively, before any substantial rearrangement to the [2.2.2] system had taken place. The [3.2.1] acetates were converted into the [2.2.2] acetate 11 in approximately 90 min.¹³

This system is then analogous to the systems described earlier.^{2,3} exo [3.2.1] product is produced by kinetic control, and with stereospecific anti migration from the [2.2.2] system. This is then converted rapidly into the equilibrium mixture of exo and endo [3.2.1] isomers and more slowly converted (again stereospecifically) into the [2.2.2] isomer. Intervention of the classical cation 13 is interdicted by the clean stereospecificity of the [3.2.1] \rightleftharpoons [2.2.2] rearrangements, and the unimportance of consideration of the delocalized nonclassical ion 14 is measured by the rapid exo-endo interconversion.¹⁴ As before, it is possible to accommodate the initial formation of exo (pseudoaxial) products by the assumption of stereoelectronic factors^{2,3,16}

(13) S. J. Cristol, R. Kellman, and C. G. McCarty, unpublished work.

(14) Winstein and his collaborators¹⁵ have recently described the cation equivalent to 14, but with double bonds rather than fused benzene rings, as anti homoaromatic. This description would fit our earlier suggestion²⁺³ that 14 and its analogs do not intervene in the reactions we have been studying, but that the classical benzylic cation 12 and its analogs are the sole intermediates required.

(15) S. Winstein, Mechanisms Conference, Brandeis University, June 1968. favoring the formation and cleavage of quasiaxial over quasiequatorial bonds, or by the assumption of torsional strain effects.^{17,18}



Geitonodesmic¹⁹ attack on 12 with *anti* migration of the carbon-carbon bond from C-1 to C-2 leads (with appropriate stereochemistry) to the [2.2.2] acetate. The rapid and stereospecific transformation of 7 to 8 and of 9 and 10 to 11 lend credence to the assumption made previously³ that failure of *syn*-8-chloro or -bromo derivatives (2, Y = H; Z = Cl, Br) to rearrange to [2.2.2] isomers 1 is a steric (or field effect) problem.

Dibenzobicyclooctatriene (3) is not a highly reactive olefin, and did not add measurable amounts of acetic acid under uncatalyzed conditions at 110° in a month. However, addition was accomplished by heating the reactants in a sealed tube at 200° for one month. Even under these conditions, the addition was only about 50% complete. The product of this addition was shown to be the [2.2.2] acetate 11. The pseudo-first-order rate constant was estimated to be 2×10^{-8} sec⁻¹ at 200°.

Addition of acetic acid to 3 to give 11 readily occurred when the reaction was catalyzed with either 1 Mperchloric acid or with 1 M sulfuric acid. The rates of addition in 1 M perchloric acid in acetic acid were studied from 29–72°. The rates obtained are given in Table I. The rate of addition in 1 M sulfuric acid in acetic acid at 84.5° was found to be $3 \times 10^{-4} \text{ sec}^{-1}$.

Neither 9 nor 10 could be detected in samples taken during the course of either catalyzed or uncatalyzed

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

- (17) P. R. Schleyer, ibid., 89, 701 (1967).
- (18) S. J. Cristol, R. M. Sequeira, and G. O. Mayo, *ibid.*, **90**, 5564 (1968).
 (19) A geitonodesmic reaction has been defined^{*} as one in which a reagent attacks a cation at an atom neighboring the cationic center with coincident migration of the *anti* bond to the cationic center.

RATES OF ADDITION OF ACETIC ACID TO
DIBENZOBICYCLO $[2.2.2]$ OCTATRIENE IN 1 M
PERCHLORIC ACID IN ACETIC ACID ^a

Temp, °C	k, sec ⁻¹	<i>t</i> 1/2, hr
72	1.1×10^{-3}	0.18
	0.9×10^{-3}	0.21
48.5	$7.9 imes 10^{-5}$	2.4
-0.2	7.0×10^{-5}	2.8
37.8	1.7×10^{-5}	11.3
28.8	$5.7 imes 10^{-6}$	33.7
$E_{\rm act} = 25$ kcal.	/mol.	

reactions, although they might be anticipated as the kinetic product and intermediate product, respectively, if one assumes that the addition follows the normal carbonium-ion mechanism, in analogy to other electrophilic additions to $3^{2,6}$ However, a comparison of the addition rates to 3 (Table I) with the rearrangement rates of 9 and 10 to 11 discussed earlier shows that the [3.2.1] acetates would not accumulate in measurable amounts during the addition reaction, were they in fact intermediates. In 1 *M* perchloric acid in acetic acid, the half-life for the addition reaction at 29° is 34 hr, but that for rearrangement of 10 and 11 to 12 under the same conditions is approximately 30 min.¹³

Additional information on the addition was obtained by using deuterated solvent. Treatment of **3** with acetic acid- d_4 , 1 *M* in sulfuric acid- d_2 , at 86° for 10 hr (essentially complete reaction) gave a 70:30 mixture of *cis*- and *trans*-3-deuteriodibenzo-2-bicyclo[2.2.2]octadienyl acetates (8 and 15), respectively. When we carried out the addition to about 10% disappearance of **9**, the ratio of *cis/trans* was increased to 86:14. Obviously *cis* addition is preferred over *trans*, and the results reflect the fairly ready isomerization of **8** toward its equilibrium mixture with 15.

The predominant *cis* addition observed can be accommodated by either (or both) of two reaction paths, one involving the carbonium ion 12 which under reaction conditions gives 7 and its *endo* epimer rapidly and reversibly and 8 via geitonodesmic attack less rapidly, as discussed above for the rearrangement of 9 and 10 to 11. Unfortunately the data do not permit us to choose between this carbonium-ion process and a *cis* molecular addition in which no intermediates are involved. Again, it is clear, however, that the symmetrical ion 13 (or its deuterated analog) cannot accommodate the data, just as was the case in solvolysis.²⁰

As it is $known^{21}$ that trifluoroacetic acid adds readily to olefins at moderate temperatures, we hoped that isolation of one or both of the dibenzobicyclo-[3.2.1]octadienyl trifluoroacetate (16) epimers might be possible. When addition of neat trifluoroacetic acid to **3** was attempted at 25°, no identifiable products could be isolated. However, when the addition was carried out in benzene at 50°, dibenzobicyclo[2.2.2]octadienyl trifluoroacetate (17) was formed. The product was hydrolyzed and isolated as the alcohol. As with acetic acid, no [3.2.1] products were observed. The trifluoroacetate ester of the deuterio-labeled alcohol 18 rearranged rapidly and stereospecifically to the trifluoroacetate 19. The half-life for the rearrangement at



 50° in benzene-trifluoroacetic acid (3.3:1) mixture was about 4 hr, while that for addition to 3 was about 72 hr. *cis-trans* equilibration of 19 was not noted in 96 hr at 50° , within the limits of pmr analysis.

Addition of deuteriotrifluoroacetic acid to **3** was investigated briefly. The product was largely the *cis*-**19**, produced with at least 80% stereospecificity based on pmr analysis. Unfortunately, during the course of the reaction, the deuterium content of the acid reagent decreased from >99%-92%, so that the pmr analysis of the product was confused by coincident addition of protiotrifluoroacetic acid.

The importance of the latter reaction was confirmed by mass spectral analysis of the trimethylsilyl derivatives of the crude alcohols obtained by hydrolysis of the trifluoroacetate addition product. Neither the acetate 11 nor its alcohol gave a large enough molecularion peak for useful isotopic composition information. The principal peak in these spectra was the anthracene cation radical peak (retro-Diels-Alder reaction). However, the trimethylsilyl ether of the alcohol gave an M - 15 peak (loss of methyl)²² which was useful to our purpose. The mass spectral analysis indicated that the sample of alcohols had only 90% of deuterium incorporation including about 3% on the benzo rings. This 10% protonic content appears to be the major source of the cis proton observed in the pmr spectrum of the alcohol mixture, which would, of course, analyze by pmr for trans-deuterio compound. It would appear, then, that addition of trifluoroacetic acid has a predominant cis stereochemistry, like that of acetic acid.

Experimental Section

Purified anhydrous acetic acid was prepared according to the procedure described by Fieser.²³

Pmr spectra were taken on Varian A-60 and Varian A-60A nuclear magnetic resonance spectrometers. All chemical shifts are relative to internal TMS. The mass spectra were obtained on a CEC 21-103C mass spectrometer operating at 70 eV.

Addition of Acetic Acid to Dibenzobicyclo [2.2.2] octatriene (3). —Anhydrous acetic acid (10 ml) and 200 mg (1.0 mmol) of the olefin 3^2 were sealed in a heavy-walled Pyrex tube and heated at 200° for 30 days. The reaction mixture was poured into 50 ml of 3 *M* NaOH and extracted with ether. The ethereal extracts were combined, dried (MgSO₄), and concentrated. The pmr spectrum of the addition product in CCl₄ was identical with that

⁽²⁰⁾ At the suggestion of one of the referees, we are deferring discussion of the *cis-trans* isomerization $\mathbf{s} \rightleftharpoons \mathbf{15}$ to a later paper.

⁽²¹⁾ P. E. Peterson, C. Casey, E. V. P. Tao, A. Agtarap, and G. Thompson, J. Amer. Chem. Soc., 87, 5163 (1965).

⁽²²⁾ J. H. Beynon, "Mass Spectrometry and its Applications to Organic Chemistry," Elsevier Publishing Co., New York, N. Y., 1960, pp 353-354.

⁽²³⁾ L. F. Fieser, "Experiments in Organic Chemistry," 3rd ed, D. C. Heath and Co., Boston, Mass., 1955, p 281.

previously reported⁴ for dibenzo-2-bicyclo[2.2.2] octadienyl acetate 11. Integration of the bridgehead protons of **3** and 11 at τ 5.03 and τ 5.60, 5.87, respectively, showed that only 50% reaction had occurred. The proton α to the acetate in 11 overlaps with the bridgehead protons of **3** and was accounted for in the calculation.

Perchloric Acid Catalyzed Addition of Acetic Acid to Dibenzobicyclo [2.2.2] octatriene (3). A. Catalyzed Addition with 1 MPerchloric Acid in Acetic Acid.—A solution of 300 mg (1.5 mmol) of 3 in 10 ml of 1 M perchloric acid in acetic acid was held at 24°. Aliquots (5 ml) were taken after 6 hr and 47.5 hr. Each aliquot was poured into 50 ml of 6 M NaOH, and followed by two extractions with 25-ml portions of CCl₄. The extracts were dried (MgSO₄), then evaporated to dryness. Pmr analysis as described above indicated that the 6-hr sample contained about 5% 11 and the 47.5-hr sample contained about 50% acetate 11.

B. Catalyzed Addition with 0.1 M Perchloric Acid in Acetic Acid.—The procedure was the same as described above. Pmr analysis of a 167-hr product mixture showed that 2-6% acetate addition had occurred.

Perchloric Acid Catalyzed Additions of Acetic Acid to Dibenzobicyclo [2.2.2] octatriene (3). Kinetic Runs.—A solution approximately 0.1 M in 3 was prepared by adding 50 ml of 1 Mperchloric acid, equilibrated in a constant-temperature bath, to a 100-ml flask containing 1.0-1.4 g of 3. The flask was stoppered and shaken vigorously (while still in the rate bath) to dissolve the olefin. Aliquots (5.0 ml) were quenched with aqueous NaOH and extracted with benzene. The combined benzene extracts were concentrated and the residue analyzed by pmr spectrometry. The disappearance of the peak at τ 5.03 (bridgehead protons from 3) was used to determine the extents of reaction. First-order rate constants are given in Table I.

Sulfuric Acid Catalyzed Addition of Acetic Acid to Dibenzobicyclo [2.2.2] octatriene (3).—An experiment similar to those described for HClO₄ was conducted with 1 M H₂SO₄ at 84.5°. The first-order constant was 3×10^{-4} sec⁻¹.

Sulfuric Acid- d_2 Catalyzed Addition of Acetic Acid- d_4 to Dibenzobicyclo[2.2.2]octatriene (3).—A solution of 759 mg (3.2 mmol) of 3, 1.71 g (17.1 mmol) of 98% sulfuric acid- d_2 , and 15.5 g (71 mmol) of acetic acid was held at 86° for 10 hr (essentially complete reaction). The reaction mixture was then worked up as described above. The pmr spectrum of the resulting product acetate mixture (753 mg, 78% yield, mp 95–98°) showed peaks at τ 7.81 and 8.82 (protons assigned *trans* and *cis* to the acetoxyl group in the undeuterated acetate 11)^{3,4} in the ratio 7:3. The pmr spectrum of pure *cis* acetate **8** is discussed below. By following the reaction by pmr, it was determined that after 10% reaction the ratio of the peaks at τ 7.81 and 8.82 was approximately 86:14. This analysis is probably reliable to $\pm 6\%$.

Preparation of Trifluoroacetic Acid-*d*.—Phosphorus pentoxide (10 g) was added to 150 g of trifluoroacetic anhydride. The mixture was first heated at reflux and then distilled into a predried 250-ml three-neck flask fitted with an inlet port covered with a rubber syringe cap. A total of 112.5 g (0.54 mol) of anhydride was collected. To the anhydride was added 10.7 g (0.54 mol) of deuterium oxide (99.5% isotopically pure) via a syringe, through the septum. The reaction flask was cooled in an ice-water bath during the addition. The percentage of hydrogen in the freshly prepared deuterated acid was determined to be 0.7 (quantitative pmr spectrum).

Addition of Trifluoroacetic Acid to Dibenzobicyclo[2.2.2]octatriene (3) in Benzene as Solvent.—To a solution of 30 ml of benzene and 9 ml of trifluoroacetic acid, which was 0.1 M in added sodium trifluoroacetate, was added 3.0 g (15 mmol) of 3. The mixture was allowed to react at 50° for 3 days, after which it was neutralized with sodium hydroxide and extracted with benzene. The benzene extracts were combined, dried $(MgSO_4)$ and concentrated. The pmr spectrum of the oil showed that the product was dibenzo-2-bicyclo[2.2.2]octadienyl trifluoroacetate This assignment was based on comparison of the pmr (17). spectrum with that of the trifluoroacetate obtained upon dissolving the parent alcohol²⁴ in trifluoroacetic acid [peaks at τ 4.83 (m, 1, H₂), 5.45 (d, 1, J = 3.5 Hz, bridgehead H₁), 5.87 (t, 1, $J = \sim 3.0$ Hz, bridgehead H₄), 7.82 (two quartets, 1, $J = \sim 3.0, 9, 14$ Hz, H₃ trans to trifluoroacetate), 8.53 (d of t, 1, $J = \sim 3$, 14 Hz, H_s cis to trifluoroacetate)]. The pmr spectrum of the oil indicated that 50% reaction (determined by integration of the bridgehead protons of 3 and 17) had occurred.

(24) K. Alder and H. F. Rickert, Ann., 543, 1 (1939).

This oil was separated into its components as described in the next paragraph. A total of 1.2 g (75% yield based on reacted 3) of the alcohol (mp 138-140°, lit.²⁴ 140-142°) was obtained from hydrolysis of the 17 preparation. The pmr spectrum of the alcohol was identical with that previously reported.⁴

Addition of Trifluoroacetic Acid-d to Dibenzobicyclo[2.2.2]octatriene (3).—Trifluoroacetic acid-d (23 g, 0.20 mol), which was 0.1 M in added sodium trifluoroacetate, 50 ml of dry benzene and 5.0 g (0.024 mol) of 3 were sealed in a 100-ml round-bottom flask and held at 50° for 74 hr (\sim 30 ± 5% reaction). Pmr spectra of the mixture, before and after reaction, showed that the fraction of prototrifluoroacetic acid in the deuterated mixture increased from 1 to 8% during the reaction. The reaction mix-ture was quenched with water and extracted with ether. The ether extracts were combined and washed with saturated sodium bicarbonate until neutral. The ether-benzene extract was dried (MgSO₄) and concentrated. The resulting oil was chro-matographed on 60 g of alumina. Unreacted **3** was eluted with 500 ml of petroleum ether (bp 60-70°) and the addition product was eluted with 500 ml of chloroform. The addition product isolated by this procedure was the alcohol; the trifluoroacetate addition product was hydrolyzed to the alcohol during chromatog-The alcohol was recrystallized several times from raphy. ethanol-water to give 1.0 g (60% yield based on 30% reaction), mp 138-139.° The pmr spectrum of the alcohol showed that trifluoroacetic acid-d added to 3 to give the trifluoroacetate of 5 with at least 80% stereospecificity. The pmr spectrum of pure 5 is reported elsewhere in this paper. A broad unresolved absorption between τ 8.5 and 9.0 (H₃ cis to the hydroxyl function in the isolated alcohol product) integrated to $20 \pm 5\%$ of the total area for the H_8 cis and trans protons. This may be due to contamination with the epimer of 5 or with undeuterated alcohol. (See below.)

Stability of cis-3-Deuteriodibenzo-2-bicyclo[2.2.2]octadienol (5) in Trifluoroacetic Acid-Benzene Mixture.—A solution of 5 (200 mg, 1.7 mmol), trifluoroacetic acid (0.6 ml), and benzene (2 ml) was allowed to stand at 50° for 4 days. A pmr spectrum verified that 19 was formed. The reaction mixture was neutralized with 1 M aqueous sodium hydroxide and stirred overnight. This was sufficient to cause hydrolysis of 19. Work-up as described above gave 90 mg (45% recovery) of alcohol, mp 138-139°. A pmr spectrum of the alcohol was identical with that of pure 5.

Preparation of cis-3-Deuteriodibenzo-2-bicyclo[2.2.2] octadienol (5).-A 100-ml three-neck flask was equipped with a gas inlet, 50 ml pressure compensated dropping funnel, condenser, and a gas outlet connected to a bubble trap containing 50 ml of anhydrous ether. To the predried apparatus was added 5.0 g (24 mmol) of 3, 0.40 g (9.3 mmol) of lithium aluminum deuteride, and 40 ml of anhydrous ether. A mixture of 40 ml of anhydrous ether and 1.08 ml (7.20 mmol) of freshly distilled boron trifluoride etherate was added dropwise. The mixture was heated at reflux for 24 hr. The reaction was quenched by adding wet ether. After addition of 10 ml of 3 M NaOH, 10 ml of 30%hydrogen peroxide was added dropwise. This mixture was stirred and heated at reflux for 24 hr. The reaction mixture was extracted with ether. The ether extract was dried (MgSO₄) and concentrated. The pmr spectrum of the crude product indicated that 10-15% of unreacted **3** remained. The reaction mixture was chromatographed on 50 g of neutral alumina. The **3** was eluted with 500 ml of petroleum ether (bp 60-70°), and the reremaining material was eluted with 500 ml of chloroform. The remaining material was educed with 500 ml of chlorobini. The alcohol was recrystallized from ethanol-water to give 4.12 g (75% yield) of product, mp 142-143°. The pmr spectra in CDCl₃ follow: τ 2.54-3.22 (m, 8, aromatic), 5.73 (d, 1, J = 3.0 Hz, bridgehead H₁), 5.85 (d, 1, J = 3.0 Hz, bridgehead H₄), 5.95 (d of d, 1, J = 2.8, 8.5 Hz, H₂), 7.83 (broad d, 1, J = 0.6 Hz, the constant of H₃ trans to OH), 8.68 (s, 1, OH). No peak at τ 8.82, attributed to proton H₃ cis to the hydroxyl in the nondeuterated analog,⁴ was present in the spectrum. Thus addition occurred 100% stereospecifically to give cis-3-deuteriodibenzo-2-bicyclo[2.2.2]octadienol (5).

Anal. Calcd for C₁₆H₁₃DO: C, 86.10; H (D), 6.73. Found: C, 86.38; H (D), 6.82.

Preparation of *cis*-3-Deuteriodibenzo-2-bicyclo[2.2.2]octadienyl *p*-Toluenesulfonate (6).—*p*-Toluenesulfonyl chloride (0.21 g, 1.1 mmol), 3 ml of anhydrous pyridine, and 5 (0.24 g, 1.1 mmol) were placed in a 10-ml erlenmeyer flask; the flask was stoppered and allowed to stand at room temperature for 24 hr. Crystals of pyridine hydrochloride formed in the flask within 2 hr; the next morning hexagonal crystals were also present in the reaction mixture. These hexagonal crystals were large enough to be picked from the reaction mixture. The crystals were washed with petroleum ether (bp 60-70°) and dried, mp 127-128° dec. Other samples melted as high as 159-161° dec, with melting points varying from 100 to 161° depending upon rate of heating and upon unknown variables (impurities), as well as upon water washing. The pmr spectra in carbon tetrachloride of all of these samples were similar: τ 5.11 (two d, 1, J = 3.3, 8.7 Hz, H₂), 5.51 (d, 1, J = 3.3 Hz, bridgehead H₁), 5.84 (d, 1, J = 2.8 Hz, bridgehead H₄), 7.63 (s, 3, CH₃), 7.89 (broad d, 1, J = 8.7 Hz, H₃ trans to sulfonate), 2.10-3.05 (m, 8, aromatic). Anal. Calcd for C₂₃H₁₉O₃DS: C, 73.18; H (D), 5.61. Found: C, 73.35; H (D), 5.87.

Preparation of cis-3-Deuteriodibenzo-2-bicyclo[2.2.2] octadienyl Acetate (8).—Anhydrous sodium acetate (1.50 g, 18.3 mmol) 196 mg (0.88 mmol) of alcohol 5 and 15 ml (0.16 mol) of acetic anhydride were heated at reflux for 90 min, then poured into 300 ml of water. The resulting mixture was extracted with ether and the ether extracts were combined and washed with aqueous NaHCO₃ until neutral. The ether layer was dried (MgSO₄) and concentrated to yield 228 mg (97% yield) of 8: mp 98-99°; pmr (CCl₄) τ 2.5-3.2 (m, 8, aromatic), 4.98 (two d, 1, J = 2.5, 9.0 Hz, H₂), 5.50 (d, 1, J = 2.5 Hz, bridgehead H₁), 5.79 (d, 1, J = 3.0 Hz, bridgehead H₄), 7.73 (broad d, 1, J = 9.0 Hz, H₃ trans to acetate), 8.18 (s, 3, acetate methyl). The pmr spectrum was similar to that of the nondeuterated acetate,⁴ except that the peak at τ 8.59 attributed to the C₃ proton cis to the acetate function in the nondeuterated alcohol was absent in the deuterated analog.

Anal. Calcd for C₁₈H₁₅O₂D: C, 81.48; H (D), 6.46. Found: C, 81.25; H (D), 6.76.

Acetolysis of *cis*-3-Deuteriodibenzo-2-bicyclo[2.2.2]octadienyl p-Toluenesulfonate (6).—A solution of 6 (258 mg, 0.685 mmol) in 10 ml of anhydrous acetic acid, 1 *M* in sodium acetate, was stirred at 38.6° for 115 hr. The reaction was quenched by adding 25 ml of water, and the resulting mixture was extracted with three 15-ml portions of pentane. The pentane extracts were combined, dried (K_2CO_3), and evaporated to dryness. The residue (170 mg, 90% yield) had, after drying under vacuum, mp 86-89°; pmr (CCl₄) τ 2.6-3.2 (m, 8, aromatic), 4.20 (d, 1, J = 2.0 Hz, H₂), 6.20 (d, 1, J = 4.5 Hz, bridgehead H₅), 6.54 (d of d, 1, J = 2.0 Hz, 5.0, bridgehead H₁), 7.67 (t, 1, J = 4.8 Hz, H₈), 8.50 (s, 3, acetate methyl). Based on comparison of the pmr spectrum with that reported⁶ for the analogous undeuterated compound² the product was identified as *syn*-8-deuteriodibenzo-*exo*-2-bicyclo[3.2.1]octadienyl acetate (7).

Anal. Calcd for C₁₈H₁₅DO₂: C, 81.48; H (D), 6.46. Found: C, 81.65; H (D), 7.07.

Rearrangement of syn-8-Deuteriodibenzo-exo-2-bicyclo[3.2.1]octadienyl acetate (7) in Perchloric Acid-Acetic Acid.—Acetate 7 (150 mg, 0.56 mmol), obtained from acetolysis of 6, was dissolved in 10 ml of 1 M perchloric acid in acetic acid and allowed to stand at 24° for 160 min. Water (50 ml) was added and the mixture was extracted with pentane. The combined pentane extracts were dried (K₂CO₃) and concentrated. The pmr spectrum of the residue (ca. 90 mg, 50%, mp 98-99.2°) was identical with that of the authentic sample of 8 described above.

Anal. Calcd for $\hat{C}_{18}H_{18}O_2D$: C, 81.48; H (D), 6.46. Found: C, 81.18; H (D), 6.76.

Reductive Cleavage of syn-8-Deuteriodibenzo-exo-2-bicyclo-[3.2.1]octadienyl Acetate (7).—To a solution of acetate 7 (940 mg, 3.54 mmol) in 50 ml of anhydrous ether was added a solution of 310 mg (8.2 mmol) of lithium aluminum hydride in 100 ml of anhydrous ether. The mixture was then heated at reflux for 5 hr. A 50:50 mixture of hydrochloric acid-water was added slowly (caution!) until most of the salts had disappeared. Ether extraction, drying (MgSO₄), and solvent removal gave 700 mg, 90% yield, of product alcohol: mp 115-118°, lit.² (for undeuterated) mp 117-119°; pmr (CDCl₃) τ 2.6-3.3 (m, 8, aromatic), 5.52 (d, 1, J = 2.0 Hz, H₂), 6.21 (d, 1, J = 4.5 Hz, bridgehead H₈), 6.69 (d of d, 1, J = 5.0, 2.0 Hz, H₁), 6.80 (s, 1, OH), 7.68 (t, 1, J = 5.0 Hz, H₈ anti). Based on comparison of the pmr spectrum with that reported⁶ for the undeuterated analog² the compound was identified as syn-8-deuteriodibenzo-exo-2-bicyclo-[3.2.1]octadienol (18).

Rearrangement of syn-8-Deuteriodibenzo-exo-2-bicyclo[3.2.1]octadienol (18) in Trifluoroacetic Acid.—The alcohol 18 (193 mg, 0.87 mmol) was dissolved in 1.93 ml of benzene and 0.6 ml of trifluoroacetic acid which was 0.1 M in sodium trifluoroacetate. Reaction proceeded for 26 hr at 50°. Water (20 ml) was added to the cooled reaction mixture, and this was followed by extraction with ether. The ether extracts were combined, dried (Mg-SO₄), and concentrated. The residual yellow oil was chromatographed on 50 g of neutral alumina. No material was eluted with 500 ml of petroleum ether (bp 60-70°). The product alcohol was eluted with 500 ml of chloroform. The trifluoroacetate product 19 was apparently hydrolyzed to the corresponding alcohol during chromatography. Recrystallization from ethanol-water gave 110 mg (63% yield) of alcohol, mp 139-140°. The pmr spectrum of the product was identical with that of authentic alcohol 5 discussed previously.

Trimethylsilylation of cis-3-Deuteriodibenzo-2-bicyclo[2.2.2]octadienol (5) and of Dibenzo-2-bicyclo [2.2.2] octadienol.-To 500 mg (2.25 mmol) of the undeuterated alcohol was added 900 mg (4.42 mmol) of bis(trimethylsilyl)acetamide and 3 ml of dry benzene. The reaction mixture was allowed to react for 24 hr, after which the solvent and excess silating agent were evaporated on a rotary evaporation apparatus. The remaining solid was recrystallized from hexane (ca. 100 mg, 15% yield): mp 93-95°; pmr (CDCl₃) $\tau 2.5$ -3.1 (m, 8, aromatic), 5.68-5.98 (m, 3, H_1 , H_2 , and H_4), 7.54-8.0 (m, 1, H_3 trans to trimethylsilyl group), 8.63 (d of t, 1, $J = \sim 2.8$, 12.5 Hz, H₃ cis to trimethylsilyl group), 9.93 (s, 9, SiCH₃). This sample was used to obtain the mass spectrogram of the alcohol. The same reaction was run on 200 mg of the deuterated alcohol (mixture from addition of trifluoroacetic acid to 3) to give ca. 50 mg (19% yield) of silyl ether, mp 93-94°. The mass spectrum of the undeuterated silyl ether (70 eV) m/e (rel intensity) 278 (0), 279 (565), 280 (153), 281 (40); for the silvl ether of the deuterio alcoholic mixture 278 (0), 279 (28), 280 (288), 281 (89), 282 (24). The ratio of m/e 279:280 for the silvl ether of deuterated alcohol obtained from trifluoroacetic acid addition to 3 was 28:280 (corrected). Thus 10% of the alcohol mixture contains hydrogen rather than deuterium. Also in the mass spectrum of the silvl ether the base peak was the anthracene molecular ion m/e (relative area) 178 (30,600), (m + 1)/e (relative area) 179 (4870), while the corresponding ratio from the deuterated silvl ether mixture was 178 (30,600), 179 (5900). Thus (5900 - 4870)/31,600 (corrected) = 1030/31,600 = 3.2% deuterium in the anthracene portion of the molecule.

Registry No.—3, 2734-13-6; 5, 21438-85-7; 5 trimethylsilyl ether, 21438-86-8; 6, 6669-80-3; 7, 21438-88-0; 8, 6372-64-1; 17, 21438-90-4; 18, 21438-91-5; dibenzo-2-bicyclo[2.2.2]octadienol trimethylsilyl ether, 21438-92-6.

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