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Bridged Polycyclic Compounds. LXXX. Rearrangements in the Dibenzobicyclooctadiene Systems. Higher Energy Carbocations[1]

Stanley J. Cristol* and Ronald J. Bopp

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

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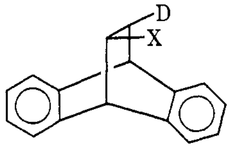
Treatment of 2-deuterio-2-dibenzobicyclo[2.2.2]octadienyl acetate (**9**) with acetic acid–sulfuric acid leads to equilibration with 1-deuterio-2-dibenzobicyclo[2.2.2]octadienol (**10**). Similar treatment of 1,*cis*-3-dideuterio-2-dibenzobicyclo[2.2.2]octadienyl acetate (**13**) gives both 1,*trans*-3-dideuterio-2-dibenzobicyclo[2.2.2]octadienyl acetate (**14**) and the 2,*trans*-3-dideuterio ester (**15**), with the former being produced two or three times as fast as the latter. These results demonstrate the existence of 2-dibenzobicyclo[2.2.2]octadienyl cation (**6**) and 1-protonated dibenzotricyclo[3.3.0.0^{2,8}]octadiene (**7**) as high-energy carbocations available in such rearranging systems.

Some time ago[2] we reported that acetolysis of the *p*-toluenesulfonate of *cis*-3-deuterio-2-dibenzobicyclo[2.2.2]octadienol (**1**-OTs) led stereospecifically (*i.e.*, with clean anti migration) to *syn*-8-deuterio-*exo*-2-dibenzobicyclo[3.2.1]octadienyl acetate (**2**-OAc), which was in turn cleanly transformed (through the endo epimer of **2**-OAc) in acetic acid containing perchloric acid to *cis*-3-deuterio-2-dibenzobicyclo[2.2.2]octadienyl acetate (**1**-OAc). The *trans*-3-deuterio acetate **3**-OAc was absent from the latter reaction mixture.



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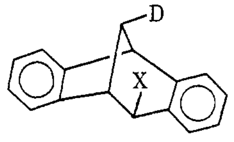

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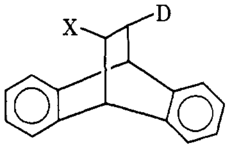

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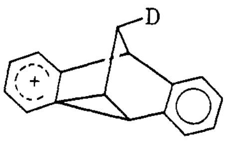

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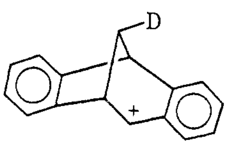

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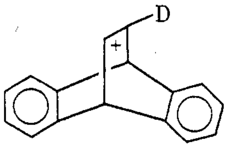

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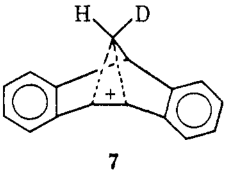

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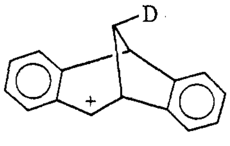

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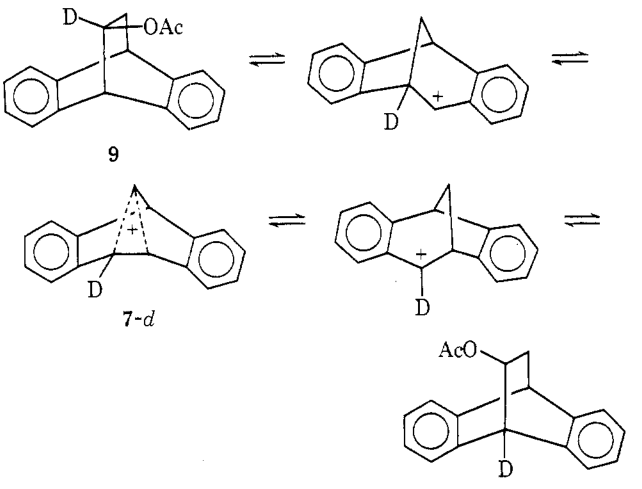
These data were consistent with the intervention of some combination of the phenyl-bridged nonclassical ion (**4**) or some variant thereof[2,3] and that of the benzylic ion **5** or with that of the latter alone, including a geitonodesmic reaction.[3,4] The absence of **3**-OAc made it clear that neither 2-dibenzobicyclo[2.2.2]octadienyl cation (**6**) nor the bridged ion **7** (1-deuterated dibenzotricyclo[3.3.0.0^{2,8}]octadiene) intervenes in these reactions (**7** could be an intermediate or a transition state on the reaction coordinate between **5** and **8**). Thus **6** and **7** are obviously of higher energy than **4** and/or **5**, and the lower energy pathways involving the latter ions (or analogs) are transversed in these and in many similar reactions.[5] Species analogous to **7** have been shown to be involved as *low-energy* intermediates in reactions of bicyclo[3.2.1]octanyl systems,[6] but as discussed earlier,[7] geometric constraints not present in the latter system are present in **7**.

When tetradeuterioacetic acid was added to dibenzobicyclooctatriene at 86° (catalyzed by 1 *M* D_2SO_4), the predominant kinetic product was the cis deuterio ester **1**-OAc-d_3,[2] but the trans epimer **3** was also formed. Thus, when 10% of the olefin had been consumed, the ratio of **1**-OAc-d_3 to **3**-OAc-d_3 was approximately 86:14. By the time (10 hr) the addition was essentially complete, the ratio of **1** to **3** had dropped to 7:3. The isomerization of **1** to **3** obviously utilized one or both of the higher energy reaction channels described above (**6** or **7**), and it seemed of interest to determine which was utilized. We report now that processes involving both **6** and **7** occur at competitive rates.

Our first experiment was designed to test for the possible intervention of **7**. To this end, we prepared 2-deuterio-2-dibenzobicyclo[2.2.2]octadienyl acetate (**9**). If **6** were the sole intermediate between **1**-OAc and **3**-OAc, then, in the time for the $1 \rightleftarrows 3$ equilibration, *dl*-**9** would act as if it were inert, as its equivalent rearrangement would be degenerate. On the other hand, intervention of **7** (as either an intermediate or a transition state) would lead to scrambling of deuterium between C-2 and C-1, a process readily followed by pmr intensity measurements. (The C-1 proton absorbs at δ 4.50 and that at C-2 at δ 5.05.) This process is shown in Scheme I (in which we have omitted the intermediate phenyl-bridged cations analogous to **4**). Bridge migration *via* **7**, in the **1** to **3** rearrangement, is thus analogous to that *via* **7**-*d* in the **9** to **10** rearrangement.

When **9** was heated in a 1.4 *M* sulfuric acid solution in acetic acid at 85°, it was found to rearrange toward its

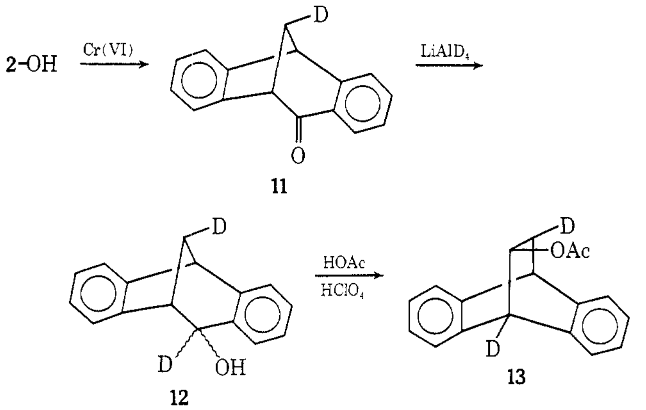
Scheme I



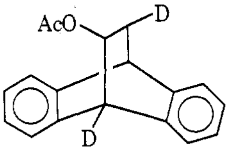
equilibrium mixture with **10**. Thus, after 28 hr, the ratio of **9** to **10** was 72:28, while after 74 hr, it was 61:39. While these results clearly implicated the cation **7**, comparative studies with **1**-OAc rearranging to **3**-OAc under similar conditions indicated that cis–trans equilibration is almost complete (52:48) after only about 30 hr. Thus the possibility of the competition of the open secondary cation **6** with **7** in these rearrangements still remained.

To investigate this possibility, we prepared the doubly labeled compound **13** as shown in Scheme II. With this compound it is possible to note cis–trans isomerization *via* the open secondary cation **6**, which would lead to **14**, as well as that *via* cation **7** (a process analogous to that of Scheme I), which would give **15**, The reaction can be followed by watching the doublet intensity at δ 5.05 (J = 9 Hz) due to the C-2 proton in compound **13** change on the one hand to a doublet (J = 3 Hz) at the same frequency for the simple cis–trans isomerization giving **14**, or reduce in total intensity at δ 5.05 to give a new singlet at δ 4.50 (C-1 proton in**15**). Accompanying the **13** → **14** or **15** transformation is a reduction in the δ 2.25 intensity and appearance of a new multiplet at δ 1.42 as the proton trans to the acetoxy group is transformed to one cis to the acetoxy group.[2,8] The formation of **16** from **14** *via* Scheme I would complicate the arithmetic in any precise treatment of data, but cause no interference in our interpretations.

Scheme II



Compound **13** was heated at 85° for 30 hr in an acetic acid solution containing 1 M sulfuric acid, and the acetate was recovered. The pmr spectrum of the product was considerably changed from that of **13**. The ratio of the δ 2.25 to 1.42 peak intensities in the product was 53:47, indicating that the cis–trans isomerization was over 90% complete (*ca.* 4 half-lives). On the other hand, the ratio of intensities at δ 5.05 and 4.50 was 71:29 (approximately 1 half-life for the deuterium scrambling between C-2 and C-1). Accompanying these phenomena was a decline in the J = 9 Hz doublet at δ 5.05 and a buildup of a doublet with J = 3 Hz at δ 5.05 as anticipated;[9] the δ 4.17 doublet remained unchanged in the experiment.



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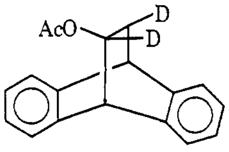

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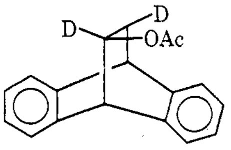

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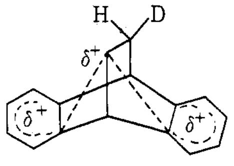
After 75 hr, the transformation measured by δ 5.05 to 4.50 peak intensities was 56:44 (*ca.* 3 half-lives) while those of the J = 9 to 3 and δ 2.25 to 1.42 were 50:50, to the best of our ability to estimate them.[9]

Recognizing that mechanisms involving either **6** or **7** lead to cis–trans isomerization, while only that involving **7** leads to proton–deuteron scrambling, we find the interesting result that these processes occur at quite similar rates, the secondary cation **6** being formed perhaps two or three times as rapidly as the bridged cation **7**. Although these cations are needed to explain the results described in this paper, we emphasize that they are in fact higher energy species than those (**4** and **5**) utilized[4] in the normal interconversion of [2.2.2] and [3.2.1] systems. They are nevertheless formed under conditions where repeated ionizations are caused to occur. While it is practicable to conduct experiments in which the rates of ionization to **4** or **5** could be measured by labeled acetate exchange and compared with cis–trans isomerization rates, in order to get a measure of the energy difference between **4** and/or **5** and **6** and **7**, we do not now contemplate such experiments.

A referee has noted that the simple cis to trans isomerization, which we have proposed is due to the intermediacy of **6**, may equally well be explained by assuming that the phenonium ion **4** is "inverted" to its mirror image by displacement of the electron pair at the spiro carbon atom by an electron pair from the π system of the opposed benzene ring. The "inverted" **4** would have the same relationship to **3** that **4** has to **1**.[10] The transition state **17** for this interconversion differs conceptually from **6** in that σ bonding is assumed in **17**, while the cationic center in **6** would interact with the benzene rings only by π interaction. It is not clear to us how **6** and **17** can be distinguished experimentally.



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The referee has also objected to our conclusion that **6** and **7** are higher in energy than **4** and **5**. He points out that this conclusion may be incorrect if they are *intermediates* which lie in a deep energy well surrounded by high energy barriers separating them from **4** and/or **5**. We see no reason to assume that this is more valid than the usual assumption[11] that reactive cationic intermediates are not significantly different in energy content from the transition states which separate them from their products.

Experimental Section

Preparation of 2-Deuterio-2-dibenzobicyclo[2.2.2]octadienol. 2-Dibenzobicyclo[2.2.2]octadienone[12] (440 mg, 2.0 mmol) in 10 ml of ether was added dropwise to 58.4 mg (1.4 mmol) of lithium aluminum deuteride in 30 ml of ether. The mixture was heated at reflux overnight. Water (5 ml) was added slowly and then 6 M hydrochloric acid was added to dissolve the precipitated salts. The mixture was extracted with ether. The ether layer was washed with aqueous sodium bicarbonate until neutral, dried (magnesium sulfate), and concentrated. The resulting solid (430 mg, 95% yield) was shown by pmr to be the desired deuterated alcohol, mp 138–140° (lit.[12] undeuterated mp 140–141°). The pmr spectrum (deuteriochloroform) exhibited peaks at δ 4.25 (s, 1 H, H-1), 4.14 (t, 1 H, J = 2.5 Hz, H-4), 2.17 (d of d, 1 H, J = 2.5, 13.0 Hz, H-3 trans to OH), 1.20 (d of d, 1 H, J = 2.5, 13.0 Hz, H-3 cis to OH), 6.8–7.4 (m, 8 H, aromatic), 1.52 (s, 1 H, hydroxyl proton). The pmr spectrum was consistent with that previously reported[8] for the undeuterated analog.

Equilibration of 2-Deuterio-2-dibenzobicyclo[2.2.2]octadienol with 1.4 *M* Sulfuric Acid in Acetic Acid. 2-Deuterio-2-dibenzobicyclo[2.2.2]octadienol (150 mg, 0.67 mmol) was dissolved in 2.7 ml of acetic acid which contained 0.2 ml of sulfuric acid (1.4 M). Transformation to **9** occurs in a very short time under these conditions. The mixture was allowed to react for 28 hr at 85 ± 1°. The mixture was poured into 15 ml of water and extracted with ether. The ether layer was washed with aqueous sodium bicarbonate until neutral, dried over anhydrous magnesium sulfate, and concentrated. The pmr spectrum (deuteriochloroform) of the resulting oil (*ca.* 120 mg, 71%) showed a ratio of intensity at δ 4.5 (H at C-1) to that at δ 5.0 (H at C-2) of 71:29. When the reaction was run for 74 hr (278 mg of alcohol, 5 ml of acetic acid, and 0.37 ml of sulfuric acid), the per cent of protium at C-2 was 39 ± 5%. Note that 50% exchange is complete equilibration. The triplet at δ 4.1–4.2 (H at C-4) did not change character or intensity.

Preparation of *syn*-8-Deuterio-2-dibenzobicyclo[3.2.1]octadienone (11). *syn*-8-Deuterio-2-dibenzobicyclo[3.2.1]octadienol (2-OH,[2] 1.95 g, 8.7 mmol) in 30 ml of ether was added to 14 ml of 0.6 M chromic acid and allowed to react for 12 hr at room temperature. The chromic acid solution was prepared by dissolving 50 g of sodium dichromate dihydrate in 37.5 ml of concentrated sulfuric acid and diluting to 250 ml with water. The mixture was extracted with ether. The ether was washed with aqueous sodium bicarbonate until neutral, treated with charcoal, dried ($MgSO_4$), and concentrated. The solid was recrystallized from methanol to give 1.17 g (62%) of **11**, mp 112–115°, mmp with authentic[13] undeuterated ketone 114–115°. The pmr spectrum was consistent with that reported[14] for the undeuterated analog, with absorption by the syn proton absent.

Reduction of *syn*-8-Deuterio-2-dibenzobicyclo[3.2.1]octadienone with Lithium Aluminum Deuteride. *syn*-8-Deuterio-2-dibenzobicyclo[3.2.1]octadienone (**11**, 1.14 g, 5.0 mmol) in 20 ml of ether was added dropwise to 108 mg (2.57 mmol) of lithium aluminum deuteride in 20 ml of ether. The mixture was allowed to stand for 12 hr, after which 5 ml of water was added, followed by 6 M hydrochloric acid to dissolve the salts. The mixture was extracted with ether. The ether extract was dried ($MgSO_4$) and concentrated. The remaining solid, 1.16 g (100%), had a broad melting point range from 80 to 140°, with the majority of material melting at 131–132°. The ir (carbon tetrachloride) showed an alcohol band at 3550 cm^{-1}. The pmr spectrum was consistent with that of a mixture of *endo-* and *exo*-2,*syn*-8-dideuterio-2-dibenzobicyclo[3.2.1]octadienols (**12**). The pmr spectrum (carbon tetrachloride) exhibited major peaks at δ 6.90–7.45 (m, 8 H, aromatic), 3.99 (d, 1 H, J = 4.5 Hz, H-5), 3.47 (d, ~1 H, J = 5.0 Hz, H-1), 2.57 (t, ~1 H, J = 5.0 Hz, H-8 anti), and 1.70 (s, 1 H, hydroxyl), all attributable to the endo isomer. The exo isomer differed only by having H-1 absorbance at δ 3.29 and H-8 anti at δ 2.34. By integration of the 3.29 and 3.47 peaks the exo:endo ratio was estimated to be 12:88. No peak at δ 4.48 (proton H-2 in the undeuterated alcohol) was present in this spectrum.

Preparation of 1,*cis*-3-Dideuterio-2-dibenzobicyclo[2.2.2]octadienyl Acetate (13). The mixture of alcohols **12** (613 mg, 2.74 mmol) was dissolved in 35 ml of 1 M perchloric acid in acetic acid and allowed to stand for 12 hr at 22°. The mixture was poured into 100 ml of water and extracted with ether. The ether layer was washed three times with 50-ml portions of water and with aqueous sodium bicarbonate until neutral, dried ($MgSO_4$), treated with charcoal, and concentrated. The resulting solid had a melting point of 95–99°. After recrystallization from petroleum ether (bp 60–80°), 560 mg (77%) of product was obtained, mp 98–100°, mmp with authentic undeuterated acetate 98–100°. The pmr spectrum (carbon tetrachloride) was consistent with the structure 1,*cis*-3-dideuterio-2-dibenzobicyclo[2.2.2]octadienyl acetate (**13**) and exhibited peaks at δ 6.90–7.35 (m, 8 H, aromatic), 5.02 (d, 1 H, J = 9.0 Hz, H-2), 4.17 (d, 1 H, J = 2.5 Hz, H-4), 2.23 (d of d, 1 H, J = 2.5, 9.0 Hz, H-3 trans to acetate), and 1.75 (s, 3 H, acetate methyl).

Equilibration of 1,*cis*-3-Dideuterio-2-dibenzobicyclo[2.2.2]octadienyl Acetate (13) with 1 *M* Sulfuric Acid in Acetic Acid. A portion of the sample of **13** described above (252 mg, 0.95 mmol) was dissolved in 10 ml of 1 M sulfuric acid in acetic acid and allowed to stand at 85.5 ± 0.1° for 30 hr. The solution was poured into 75 ml of water and extracted with ether. The ether layer was washed several times with 50-ml portions of water, washed with aqueous sodium bicarbonate until neutral, dried ($MgSO_4$), treated three times with charcoal, and concentrated. The pmr spectrum of the resulting oil is described in the discussion section, as is that of a sample allowed to react for 75 hr.

Acknowledgment. The authors are indebted to the National Science Foundation for generous support of this research.

Registry No.—2-OH, 21438-91-5; **11**, 50894-30-9; *endo*-**12**, 50894-31-0; *exo*-**12**, 50894-32-1; **13**, 50640-89-6; 2-deuterio-2-dibenzobicyclo[2.2.2]octadienol, 50641-11-7; 2-dibenzobicyclo[2.2.2]octadienone, 6372-63-0.

References and Notes

(1) Paper LXXIX: S. J. Cristol and H. W. Mueller, *J. Amer. Chem. Soc.*, **95**, 8489 (1973).

(2) S. J. Cristol, R. J. Bopp, and A. E Johnson, *J. Org. Chem.*, **34**, 3574 (1969).

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(4) We are accumulating evidence for the intervention of both **4** and **5** cations in these reactions (R. S. Beckley, Ph.D. Thesis, University of Colorado, 1970; M. C. Kochansky, Ph.D. Thesis, University of Colorado, 1971).

(5) See references listed in ref 2.

(6) (a) H. L. Goering and M. F. Sloan, *J. Amer. Chem. Soc.*, **83**, 1397 (1961); (b) J. A. Berson and P. Reynolds-Warnhoff, *ibid.*, **84**, 682 (1962); **86**, 595 (1964).

(7) See footnote 15 in ref 3.

(8) S. J. Cristol, T. W. Russell, J. R. Mohrig, and K. Schwarzenbach, *J. Org. Chem.*, **31**, 581 (1966).

(9) At the time this work was carried out, our nmr capabilities were not good enough for complete resolution of these peaks for instrumental integrations. Inspection of the traces suggests that the center doublet was somewhat less intense than the outside doublet. Similarly, integrations on other peak intensities are only reproducible to ±5% and thus the half-life estimates given are quite approximate.

(10) For a similar proposal of nonclassical ion–nonclassical ion rearrangement, see T. Svensson and S. Winstein, *J. Amer. Chem. Soc.*, **94**, 2336 (1972).

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