(ether = methyl, ethyl, methyl *n*-propyl, methyl isopropyl).[17] A 1:3 complex, $(C_2H_5)_2O{\cdot}3BF_3$, has also been reported.[17] In all these cases the structure of the complex was not established. The only kinetic study that might be seen as supportive of fluorine bridges between boron atoms is that of Clayton & Eastham, who found BF_3–methanol catalysis in the isomerization of *cis*- and *trans*-2-butenes to be first order in free BF_3 in solution as well as first order in BF_3 CH_3OH.[18]

Acknowledgment. This work was supported by a Penta Corporation Grant of Research Corp. and by the National Science Foundation (Grant CHE 79-15122).

Registry No. BF_3, 7637-07-2; H_2O, 7732-18-5; benzyl chloride, 100-44-7; benzene, 71-43-2; toluene, 108-88-3.

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(15) Brown, H. C.; Stehle, P. F.; Tierney, P. A. *J. Am. Chem. Soc.* **1957**, *79*, 2020–2021.

(16) Martin, D. R.; Hicks, W. B. *J. Phys. Chem.* **1946**, *50*, 422–427.

(17) Wirth, H. E.; Jackson, M. J.; Griffiths, H. W. *J. Phys. Chem.* **1958**, *62*, 871–872.

(18) Clayton, J. M.; Eastham, A. M. *Can. J. Chem.* **1961**, *39*, 138–143. See also Clayton, J. M.; Eastham, A. M. *J. Chem. Soc.* **1963**, 1636–1643.

Photochemical Transformations. 47. Direct Irradiation in Acetic Acid of 1-(Bromomethyl)dibenzosemibullvalene [1-(Bromomethyl)-3,4:6,7-dibenzotricyclo[3.3.0.0^{2,8}]octa-3,6-diene][1]

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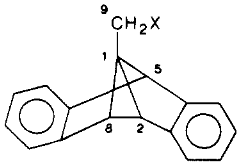
Received July 28, 1988

Treatment of 1-Br with silver acetate in acetic acid or deamination of 1-NH_2 in acetic acid has been shown[2] to lead to the hydrocarbon 3,4-benzofluorene (**2**), in addition to a mixture of acetates. Paquette and Meehan earlier reported[3] that base-induced decomposition of the *p*-toluenesulfonylhydrazone of dibenzosemibullvalene-1-carboxaldehyde (**3**) also gave **2**, and they also reported a mechanistic interpretation of that result, on the basis of deuterium-labeling experiments. More recently,[4] we noted that direct irradiation of **4**-Cl in acetic acid led to a mixture of acetates and to about 15% of **2**, along with some 1-methylfluoroanthene.



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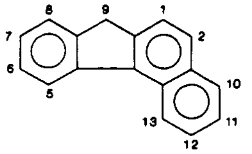

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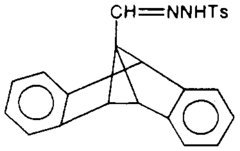
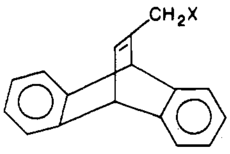


3

As it is known[4] that **4**-OAc gives **1**-OAc upon irradiation in acetic acid or in benzene (via a di-π-methane process), it seemed likely that **4**-Cl might similarly give **1**-Cl and that **1**-Cl might be the source of **2** in the irradiation. As preliminary attempts to prepare **1**-Cl from **1**-OH failed, rearranged chlorides being obtained instead, and as **1**-Br is readily prepared,[2] we decided to study its photoreactions.

Compound **1**-Br is inert to triplet acetone photosensitization.[4] Direct irradiation of **1**-Br in acetic acid with 254-nm light gave **2** as sole product, consistent with the idea suggested above. It is of interest that no acetates were formed, although they are the major products of the ground-state reactions with silver acetate of **1**-Br and of the homoallylic isomers (**5**) of **1** and are also products of ground- and excited-state reactions of **4**-Cl, **4**-Br, and their allylic isomers **6**. It is similarly of interest that **2** arises, although in much poorer yields, from the ground-state reactions[2] of **1** species and not from the isomeric **4**, **5**, or **6** species. It was assumed that the acetate mixture arose from rearrangement (migration of the C-1, C-2 bond to C-9) in $\mathbf{1}^+$, or in a process concerted with loss of nucleofuge from **1**-X, to give the benzylic cation $\mathbf{5}^+$ (cyclopropylcarbinyl to homoallyl cation rearrangement). Cation $\mathbf{5}^+$ is known[2] to equilibrate rapidly with its Wagner–Meerwein rearrangement allylic isomer $\mathbf{4}^+ \leftrightarrow \mathbf{6}^+$; failure to see products from $\mathbf{1}^+$ in the reactions of **4**, **5**, and **6** species suggests that $\mathbf{1}^+$ is much less stable than $\mathbf{5}^+$.



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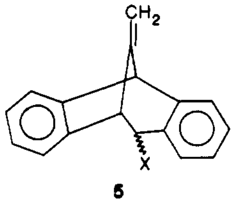

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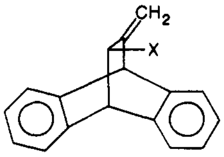
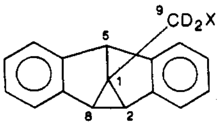


6

Three reaction paths were suggested[2] for the formation of **2**. One involved migration (note the projection **7** of dideuterio-**1**) of C-2 or C-8 from C-1 to C-9, which would give the cyclobutyl cation **8**. (In this discussion, we assume labeling at C-9 of **1**.) Cyclobutyl–homoallyl interconversion leads to ion **9**, which has the correct carbon skeleton but requires hydride shifts followed by proton loss (or proton loss followed by double-bond isomerization) for aromatization to benzofluorene. The key initial step is a 1,2-Wagner–Meerwein shift. A second possible pathway involves migration of C-2 from C-8 to C-9 (a 1,3-shift) to give **10**, the cyclopropylcarbinyl isomer of **8** and **9**. The third path proposed involves migration of the benzo ring from C-8 to C-9 (also a 1,3-migration) to give the cyclopropyl



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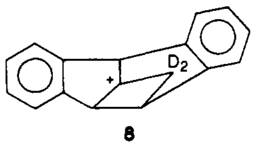

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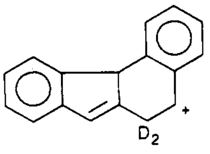

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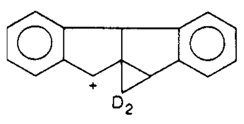
(1) Previous paper in series: Cristol, S. J.; Aeling, E. O.; Strickler, S. J.; Ito, R. D. *J. Am. Chem. Soc.* **1987**, *109*, 7101.

(2) Cristol, S. J.; Schloemer, G. C.; James, D. R.; Paquette, L. A. *J. Org. Chem.* **1972**, *37*, 3852.

(3) Paquette, L. A.; Meehan, G. V. *J. Am. Chem. Soc.* **1970**. *92*, 3039.

(4) Cristol, S. J.; Braun, D.; Schloemer, G. C.; Vanden Plas, B. J. *Can. J. Chem.* **1986**, *64*, 1081.

0022-3263/89/1954-1209$01.50/0



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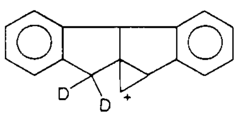

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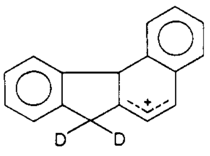
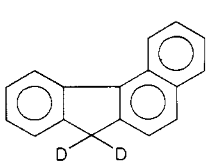


12

cation 11, whose conversion to the allyl cation 12 might be concerted with its formation. Loss of a proton from 12 would give benzofluorene. We have noted in structures 7–12 the fate of deuterium initially at C-9 in 1 (or 7). Thus benzo migration would lead to benzofluorene labeled with two deuterium atoms at the methylene (C-9) carbon atom as in 13, while the other two processes would lead to monolabeling at C-1 (as in 14). In our experience,[5] fluorenes exchange hydrogens photochemically (and also with basic catalysis[3]) at C-9, but not at other positions, so that formation of 13 might be compromised in our photochemical experiments by having fewer than two deuterium atoms in the product. This should not be the case in silver-ion-promoted reactions. The ^{1}H NMR spectrum of 3,4-dibenzofluorene has been analyzed[6] so that the location of the deuterons on each of the aromatic positions and the methylene position can readily be determined.



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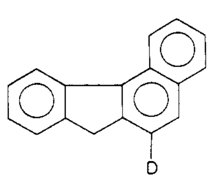

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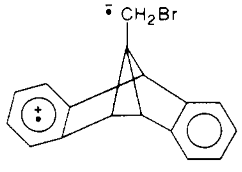

15

Accordingly, we subjected 7-Br, the dideuterio analogue of 1-Br, to both silver-ion-promoted and irradiation-promoted reactions. In each experiment, the 3,4-benzofluorene was isolated and was shown, by high-resolution mass spectrometry, to be monodeuterated. Comparison of the ^{1}H NMR spectra, which were identical from both sources, with the Mathews' analysis[6] showed that both products were 1-deuterio-3,4-benzofluorene (14). Thus the slightly broad doublet centered at δ 7.52 for H-1 in 2 was missing, and that somewhat downfield (approximately δ 7.66) for H-2 was replaced by a broad singlet, as anticipated for ortho-deuterium coupling. The two-proton singlet resonance at δ 4.02 for the methylene protons in 2 was unaffected in the samples of 14.

Clearly then, any process in which the benzo group migrates to give 11 is excluded. We are unable to exclude either of the other two reaction paths. The process involving 8 has the advantage of 1,2-vs 1,3-migration; that involving 10 has the advantage of a more stable intermediate.

It is of interest that Paquette and Meehan[3] labeled 3 with deuterium at the aldehydo carbon atom (C-9) and showed that the deuterium was located in their product at the methylene carbon atom. They proposed from this result that a carbene intermediate was involved in the rearrangement, rather than a carbocation. Our results support that conclusion.

Members of our research group have proposed[1,7] that photoreactions of β-arylethyl halides (and analogous compounds) involving Wagner–Meerwein or analogous rearrangements have, as the key step, the transformation of the π,π^* excited state of the compound by an intramolecular electron transfer to a σ^* orbital to give a zwitterionic biradical. In the case of 1-Br, the resulting species would be 15. It has been noted that such photoexcited species do not decay by processes identical with those of ground-state reactions of unexcited species. The present results are consistent with such differences. Species 15 leads entirely to 2, while the ground-state reaction of 1-Br gives 2 only as a minor product, with the cyclopropylcarbinyl to homoallyl rearrangement (C-1, C-2 bond migration to C-9) to give cation 5^+ being the principal mode of reaction. The factors that control these choices are not clear, but may be related to the preference for syn migration in photoreactions and anti migration in ground-state reactions.[8]

Experimental Section

General Procedures. Melting points were determined with a Thomas-Hoover Unimelt apparatus. ^{1}H NMR spectra were determined on either a Varian EM-390 (90 MHz) or Bruker WM-250 (FT, 250 MHz) nuclear magnetic resonance spectrometer. Chemical shift values reported are in ppm downfield from tetramethylsilane (TMS). Chloroform-*d* was used as solvent. TMS was used as an internal standard with the EM-390, and the residual proton resonance of chloroform-*d* was used as an internal standard on the Fourier transform instrument. ^{2}H NMR spectra were measured by Martin Ashley on the Bruker instrument with an external D_2O reference and CH_2Cl_2 as solvent. Mass spectra were obtained on a VG Analytical 7070 instrument.

Preparation of 1-(Dideuteriobromomethyl)-3,4:6,7-dibenzotricyclo[3.3.0.0^{2,8}]octa-3,6-diene (7-Br). Compound 7-Br was prepared from 7-OH[3] with PBr_3 and pyridine in benzene as described[2] for the preparation of 1-Br from 1-OH. Our experiment gave a reduced yield of 7-Br, and ^{1}H NMR analysis of the crude product (isolated after the organic solvent was evaporated and after separation and extraction) showed that about 50% was thermally rearranged bromides.[9] The reaction mixture was crystallized from hexanes to give white crystals of 7-Br: mp 133–135 °C (lit.[9] mp for 1-Br 132.5–135 °C); ^{1}H NMR δ 7.5–7.0 (m, 8 H, aromatic protons), 4.49 (s, 1 H, H-5), 3.16 (s, 2 H, H-2, H-8). The peak[9] at δ 3.8 for H-9 in 1-Br was absent: ^{2}H NMR δ 3.84 (br s, H-9); MS, *m/e* calcd for $C_{17}H_{11}D_2{}^{79}Br$ 298.0326, found 298.0320.

Silver-Ion-Assisted Solvolysis of 7-Br. A solution of 204 mg (0.67 mmol) of 7-Br and 100 mg (1.2 mmol) of AgOAc in 30 mL of glacial HOAc was heated at 90 °C for 50 min. The cooled solution was filtered and diluted with 500 mL of water. Ether extraction, washing with water, brine, and aqueous $NaHCO_3$, drying ($MgSO_4$), and solvent removal under reduced pressure left 200 mg of an oil. This oil, by ^{1}H NMR analysis, had substantially the same ratio of products reported[2] for similar treatment of 1-Br. Chromatography on silica gel (60–200 mesh) of the oil, with hexane elution, gave 24 mg of 1-deuterio-3,4-benzofluorene (14): mp 124–126 °C (lit.[3] mp for 2 125.5–126.5 °C); ^{1}H NMR δ 8.87 (br d, 1 H, H-13, $J_{12,13}$ = 8 Hz), 8.48 (br d, 1 H, H-5, $J_{5,6}$ = 8 Hz), 8.1–7.2 (m, 7 H, aromatic protons), 4.02 (s, 2 H, H-9); ^{2}H NMR

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[5] Cristol, S. J.; Ali, M. Z. Unpublished work.

[6] Jones, D. W.; Matthews, R. S.; Bartle, K. D. *Spectrochimica Acta* **1972**, *28A*, 2053.

[7] Cristol, S. J.; Bindel, T. H.; Hoffmann, D.; Aeling, E. O. *J. Org. Chem.* **1984**, *49*, 2368 and other papers in this series.

[8] Cristol, S. J.; Opitz, R. J. *J. Org. Chem.* **1985**, *50*, 4558.

[9] Cristol, S. J.; Schloemer, G. C.; Braun, D.; Mayo, G. O. *Can. J. Chem.* **1986**, *64*, 1077.

δ 7.6 (br s, H-1); MS, *m/e* calcd for $C_{17}H_{11}D$ 217.1002, found 217.1015.

General Photochemistry. For photochemical reactions, a Rayonet Srinivasan-Griffin Photochemical Reactor (Southern New England Ultraviolet Co.), equipped with a merry-go-round apparatus and 254-nm (RPR-2537*P*) lamps, was used. All irradiations were done in quartz tubes. The tubes were sealed with serum stoppers secured with copper wire, and the solutions were deoxygenated by bubbling N_2 through them for 25 min.

Direct Irradiation of 1-(Bromomethyl)-3,4:6,7-dibenzotricyclo[3.3.0.0^{2,8}]octa-3,6-diene (1-Br) in HOAc. Two matched quartz tubes were charged with 12.5 mL of a 0.062 M solution of 1-Br in glacial HOAc (prepared by dissolving 473 mg (1.6 mmol) of 1-Br in 25 mL of HOAc). After being sealed and deoxygenated, tube 1 was masked with aluminum foil to block out light to check for any possible ground-state reaction. Tube 2, similarly treated, was left unmasked. Both tubes were placed on the merry-go-round of the Rayonet. The tubes were irradiated for 30 min.

After irradiation, each tube was opened and the contents poured into 100 mL of ether and extracted with 100 mL of saturated brine. The brine layer was then extracted twice with 50 mL of ether. The ether fractions were combined and extracted twice with 100 mL of water, twice with 100 mL of brine, thrice with 100-mL portions of aqueous $NaHCO_3$, and twice with 100 mL of brine. The solution was then dried ($MgSO_4$) and filtered, and the ether was removed under reduced pressure.

^1H NMR analysis of the reaction mixture in tube 1 showed only 1-Br present. ^1H NMR analysis of tube 2 showed a mixture of about 20% of 3,4-benzofluorene (**2**) and 80% of 1-Br. No other products were seen. Column chromatography with hexanes on silica gel (60–200 mesh) gave 35 mg (0.16 mmol, 21% conversion based on starting amount of 1-Br) of **2**: mp 125–127 °C; ^1H NMR δ 8.85 (br d, 1 H, H-13, $J_{12,13}$ = 8 Hz), 8.46 (br d, 1 H, H-5, $J_{5,6}$ = 8 Hz), 8.1–7.2 (m, 8 H, aromatic protons), 4.01 (s, 2 H, H-9).

Direct Irradiation of 7-Br in HOAc. A solution of 205 mg (0.67 mmol) of **7**-Br in 12.5 mL of HOAc was deoxygenated and then irradiated for 1 h with 254-nm light in the Rayonet.

After irradiation, the tube was opened, and the contents were poured into 100 mL of ether and worked up as described for the 1-Br photoreaction. Workup as above gave 49.2 mg (0.23 mmol, 34% conversion) of **14**: mp 125–126.5 °C; ^1H NMR δ 8.85 (br d, 1 H, H-13, $J_{12,13}$ = 8 Hz), 8.45 (br d, 1 H, H-5, $J_{5,6}$ = 8 Hz), 8.1–7.2 (m, 7 H, aromatic protons), 4.02 (s, 2 H, H-9); ^2H NMR δ 7.74 (br s, H-1). The locus of the deuterium atom was determined by ^2H NMR analysis and comparison of the ^1H NMR spectrum with that reported[6] for **2**: MS, *m/e* calcd for $C_{17}H_{11}D$ 217.1002, found 217.1015.

Acknowledgment. We are indebted to the National Science Foundation for support of this work under Grant CHE-85-03422.

Registry No. 1-Br, 28545-62-2; **2**, 205-12-9; **7**-OH, 118418-32-9; **7**-Br, 118418-33-0; **14**, 118418-34-1.

2,5-Dihydroxythiophene

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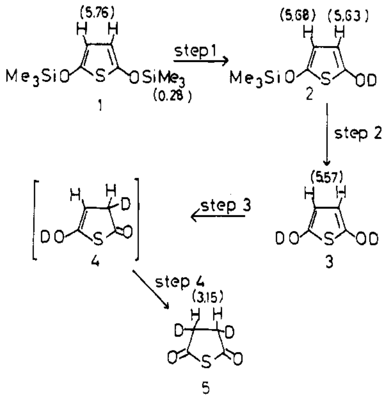
Received July 12, 1988

2,5-Dihydroxythiophene is the diene–diol tautomer of thiosuccinic anhydride. That the latter is the stable form was demonstrated by NMR and IR spectroscopy.[1] Recently we have shown that unstable enolic tautomers of heterocyclic compounds may be generated in solution by careful hydrolysis of their trimethylsilyl derivatives[2-4] and the ready availability of 2,5-bis[(trimethylsilyl)oxy]thiophene[5] led us to attempt to use this as a precursor for the generation of 2,5-dihydroxythiophene.

Scheme I



The ^1H NMR spectrum of 2,5-bis[(trimethylsilyl)oxy]thiophene in DMSO-d_6 at 30 °C shows two signals at δ = 0.28 and 5.76 (assigned as shown in Scheme I). This spectrum also shows that a small amount of hydrolysis has occurred as three small signals at δ = 5.55–5.7 are present. On addition of 1% of 7 × 10^{-4} M DCl in D_2O the two signals of the precursor almost completely disappeared immediately, but there was only a small signal at δ = 3.15, the chemical shift of the protons of thiosuccinic anhydride. Instead there were two small signals at δ = 5.68 and 5.63 and a larger signals at δ = 5.57. After 8 min the two small signal had disappeared completely but the singlet at δ = 5.57 remained, and over the course of 1 h this also disappeared with concurrent growth of the broad singlet of the deuterated thiosuccinic anhydride at δ = 3.15.

We suggest that these results can be explained by the reactions shown in Scheme I. The two signals at δ = 5.68 and δ = 5.63 were ascribed to the O-deuterated monohydroxythiophene (**2**). The ring protons should be a tightly coupled AB pair, so the signals at δ = 5.68 and 5.63 would be the large inner signals of the expected quartet. The signals presumably never became very large because the rates of removal of the two trimethylsilyl groups (steps 1 and 2 Scheme I are similar). The signal at δ = 5.57 was ascribed to the O-deuterated dihydroxy compound (**3**). Now the two ring protons are equivalent so that this signal is a singlet. There is no signal at δ = 0.28, showing that all the trimethylsilyl groups have been hydrolyzed and the chemical shift of the ring protons is slightly upfield as compared to the starting material. This is normally what happens to the chemical shift of the β-protons when a trimethylsilyl derivative is converted into its parent enol.[2-4] The species that is formed is clearly an intermediate on the conversion of **1** into the deuterated thiosuccinic anhydride (**5**), which is formed over the course of 1 h, and there seems to be no alternative structure to **3**. The monoenol **4** would be expected to be an intermediate in the conversion of **3** into **5**, but this was not detected. Unlike **3**, **4** is not aromatic and so would be expected to ketonize much more rapidly.

A similar series of experiments was carried out with 2,5-bis[(trimethylsilyl)oxy]furan[6] in an attempt to generate O-deuterated 2,5-dihydroxyfuran, but the results were not

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(1) Jakobsen, H. J.; Larsen, E. H.; Lawesson, S. O. *Tetrahedron* **1963**, *19*, 1877.

(2) Capon, B.; Kwok, F. C. *Tetrahedron Lett.* **1986**, *27*, 3275.

(3) Capon, B.; Guo, B. Z.; Kwok, F. C.; Wu, Z. P. *Pure Appl. Chem.* **1987**, *59*, 1577.

(4) Capon, B.; Guo, B. Z.; Kwok, F. C.; Siddhanta, A. K.; Zucco, C. *Acc. Chem. Res.* **1988**, *21*, 135.

(5) Lozzi, L.; Ricci, A.; Taddei, M. *J. Org. Chem.* **1984**, *49*, 3408.

(6) Brownbridge, P.; Chen, T. H. *Tetrahedron Lett.* **1980**, *21*, 3424.