of the original *exo*-6-deuterium of Ia migrated during the rearrangement Ia → IIa.

The structure of compound IV was confirmed by its nmr spectrum. A signal at 4.00 ppm is due to the *endo*-2-hydrogen. Splittings of 4.2 and 1.9 cps result from couplings with the *exo*-3 and *anti*-7-hydrogens,[10] respectively. The *anti*-7-hydrogen gives a doublet of components at 1.38 ppm, and double irradiation at this position removes the splitting of 1.9 cps exhibited by the *endo*-2-hydrogen (4.00 ppm). A broadened doublet, J_{gem} = 10.1 cps, for the *syn*-7-hydrogen appears at 2.06 ppm. The downfield shift of this signal is attributed to the anisotropic effect of the *exo*-2-chlorine. The appearance of the *exo*-3-hydrogen at 3.44 ppm as a triplet is expected from the almost equal $J_{4,exo\text{-}3}$ and $J_{endo\text{-}2,\, exo\text{-}3}$.[11] In the spectrum of IVa the signal for the *endo*-2-hydrogen is a simple doublet, $J_{2,3}$ = 4.2 cps, the signal for the *syn*-7-hydrogen is collapsed to a single line, and the doublet at 1.38 ppm for the *anti*-7-hydrogen is absent.

Finally, additional quantitative evidence for the *exo*-5-deuterium in IIa is found in the nmr spectrum of Va (see also ref 5). The *syn*-7 proton of V gives a multiplet centered at δ = 1.51 ppm, whereas the signals for the *exo*-5 and *exo*-6 protons are centered at 1.71 ppm. Comparison of pertinent integration areas of V and Va confirms that at least 95–96% of the deuterium originally in the *exo*-6 position of Ia resides in the *exo*-6 position of Va.

[10] J. Meinwald and Y. C. Meinwald, *J. Am. Chem. Soc.*, **85**, 2514 (1963).

[11] If a Wagner–Meerwein rearrangement had taken place during treatment of III with PCl_5, the formation of 7-*anti*-phenyl-2-*exo*-norbornyl chloride might be expected. Its nmr spectrum should be considerably different from that observed for IV.

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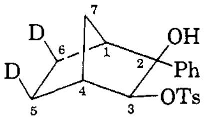
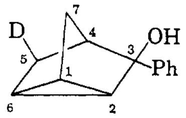
Stereospecific Elimination and Migration of Deuterium during Hydrolysis of a Substituted Norbornyl Tosylate[1]

Sir:

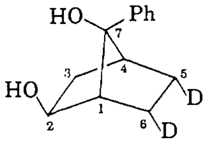
Hydride shifts (6,1 and 6,2)[2] occur during solvolyses of 2-*exo*-norbornyl derivatives. We recently established the intramolecularity and stereochemistry of one of these shifts.[3,4] During hydrolysis of the dideuterated[5] tosylate **1a** we now report (1) a stereospecific elimination and (2) a stereospecific 5,4 migration, respectively, of the 5-*exo* deuterium. Hydrolysis of **1a** in aqueous acetone (containing sodium carbonate), led to the quantitative production of compounds **2a**, **3a**, and **4a** with deuterium in the positions shown. The three products were easily separated by chromatography on alumina in yields of 25, 60, and 15%, respectively. Traces of another diol have been detected.



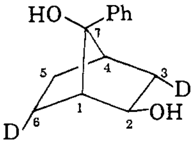
1a



2a



3a



4a

The structures of compounds **2**, **3**, and **4** (without deuterium) were established through their nmr and infrared spectra and by their chemical reactions.[6] In addition, **2** was independently synthesized by reaction of nortricyclenone with phenylmagnesium bromide. Compounds **3** and **4** were also prepared by solvolysis of **1** which contained a deuterium in the *endo*-3 position, and each, as expected, contained one atom of deuterium per mole in the 1 (bridgehead) position. Deuterium contents in all cases were determined by integration of the appropriate signals of the nmr spectra.

Most of the signals in the nmr spectrum of **2** are well separated, and can be assigned on the basis of expected inductive and anisotropic effects. In addition to five aromatic hydrogens and one exchangeable hydrogen (OH), the following are observed: (1) a one-proton doublet, J = 10.1 cps at 2.13 ppm, due to the *syn*-7-hydrogen. It is deshielded by the hydroxyl and therefore appears at lowest field. The latter doublet is reciprocated by a doublet at 1.29 ppm (7-*anti*-H); (2) a one-proton (4 H) broadened signal at 1.73 ppm; and (3) signals for the remaining five hydrogens in two bands at 1.23 ppm (3 H) and at 1.07 ppm (2 H).

In the spectrum of **2a** the band at 1.07 ppm had an intensity of only one hydrogen. The relative intensities of all other lines were the same. Thus at least 95–96% of a deuterium atom was lost during the reactions **1a** → **2a**. In addition, the signal for the C-4 hydrogen of **2a** exhibits a width at half-height of 4.6 cps, whereas the same signal for **2** has a width of 5.2 cps, and the deuterium atom in **2a** results in the removal of one coupling constant. Double irradiation shows that the C-4 hydrogen of **2** is weakly spin coupled to hydrogens, contributing to the signals at 1.23 and 1.07 ppm. The latter are assigned to the methylene hydrogens at C-5. Double irradiation of the one-proton signal at 1.07 ppm had no effect upon the signal for the C-4 hydrogen of **2a**. The deuterium atom in **2a** is thus located at C-5 and *anti* to the phenyl substituent at C-3.

The spectra of **3** and **4** both exhibit one-proton signals appearing as X parts of ABX systems. The pattern is characteristic for an *endo*-hydrogen of an H–C–O group.[7] The signal is centered at 3.64 ppm for compound **3** and at 3.56 ppm for compound **4**. In the upfield region of the spectrum of **3** there are two bands at 1.39 and at 1.21 ppm, assigned to the *exo*-5- and -6-hydrogens and confirmed through spin decoupling from the 1- and 4-hydrogens at 2.24 and 2.47 ppm. Two bands at 0.99 and at 0.82 ppm are assigned to the 5- and 6-*endo*-hydrogens. The *exo* and *endo* protons at C-3 appear at 1.89 ppm, and these were spin decoupled

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[1] Research sponsored by the U. S. Atomic Energy Commission under contract with the Union Carbide Corporation.

[2] J. Berson, "Molecular Rearrangements," Vol. 1, P. de Mayo, Ed., Interscience Publishers, Inc., New York, N. Y., 1963, pp 138–155.

[3] B. M. Benjamin and C. J. Collins, *J. Am. Chem. Soc.*, **87**, 1556 (1965).

[4] See also J. A. Berson and P. W. Grubb, *ibid.*, **87**, 4016 (1965).

[5] Not more than 3% *endo* deuteration took place (see ref 3).

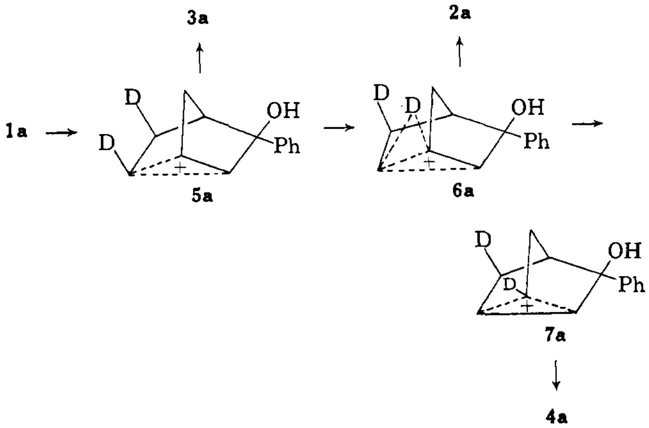
[6] All gave satisfactory carbon and hydrogen analyses, performed by Huffman Microanalytical Laboratories, Wheatridge, Colo.

[7] T. J. Flautt and W. F. Erman, *J. Am. Chem. Soc.*, **85**, 3212 (1963).

from the *endo* hydrogen at C-2 (3.64 ppm). In **3a** the signals for the 5- and 6-*endo*-hydrogens (0.99 and 0.82 ppm) are absent and the pair of signals for the 5- and 6-*exo*-hydrogens is collapsed into a single broadened peak centered at 1.25 ppm. None of the other spectral features is altered. Neither of the two deuterium atoms originally at the 5- and 6-*exo* positions of **1a** migrated, and they now appear at the 5- and 6-*endo* positions of **3a**.

Integration of the spectrum of **4a** shows the molecule contains two deuterium atoms. The signal of **4** which appears at 3.56 ppm is a well-resolved quartet. Separation of the outer peaks is 12.2 cps and that of the inner peaks is 4.4 cps. The same signal for **4a** appears as a doublet while a set of sharp signals centered at 1.68 ppm originally due to the *endo*-3 proton of **4** is now absent. The doublet of **4a** at 3.56 ppm represents the smaller coupling constant (J_{ax} = 3.5 cps) of the ABX system. The two coupled hydrogens are therefore in a *trans* configuration, and placement of one deuterium atom at C-3 and *endo* is confirmed. A pair of signals at 1.21 and at 1.08 ppm is due to the 5- and 6-*endo*-hydrogens. Their intensity in **4a** is half that of **4**, and therefore there is one *endo*-deuterium in these positions. From these data we cannot rigidly exclude deuterium from the *endo*-5 position. Integration of the signals for the hydrogens (of **4a**) at C-1 (2.42 ppm) and C-2 (3.56 ppm) shows that neither of these positions contains a measurable amount of deuterium. Thus at least 97% of the deuterium originally *exo*-5 in **1a** has left that position, and a discrete 5,4 shift of deuterium has taken place. Any rational mechanism producing an *endo*-5-deuterium should also affect the *endo*-3 label; we conclude our assignment of an *endo*-6-deuterium is correct.

All of the results are nicely rationalized by the sequences **1a** → **5a** → **3a**; **1a** → **5a** → **6a** → **2a**; and **1a** → **5a** → **6a** → **7a** → **4a**. The intermediate (or transition-state) **6a** can lose a deuterium to yield the phenylnortricyclanol **2a**, or it can proceed to **7a** with completion of the 5,4 shift. Structure **6a** is similar to that proposed earlier by Aboderin and Baird.[8] An alternate explanation involving a homo-E2 elimination will be shown later to be untenable.



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(8) A. A. Aboderin and R. L. Baird, *J. Am. Chem. Soc.*, **86**, 252 (1964).

(9) Research Participant of the Oak Ridge Institute of Nuclear Studies from the University of Alabama.

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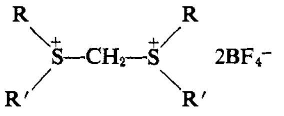
Methylenebis(dialkylsulfonium) Salts

Sir:

Treatment of bis(methylthio)methane and bis(ethylthio)methane with triethyl- or trimethyloxonium fluoroborates produces the methylenebis(dialkylsulfonium) fluoroborates **1**–**3**.[1,2] These bissulfonium salts are precipitated from aqueous solution by the slow addition of ethanol as glistening white crystals: **1**, mp 190–195° (99% yield); **2**, mp 131–133° (76%);[3] and **3**, mp 152–158° (68%). Methylenebis(diethylsulfonium) difluoroborate (**3**) is typical of these salts. It is soluble in water and acetone but insoluble in ethanol and solvents less polar than acetone. Its nmr spectrum in trifluoroacetic acid is consistent with structure **3**: τ 4.80[4] (singlet, two protons), 6.12 (quartet, eight protons), and 8.27 (triplet, 12 protons). An aqueous solution of **3** rapidly decolorizes potassium permanganate and bromine water. The rate of permanganate consumption is noticeably slowed at low pH.



1, R = R′ = methyl
2, R = methyl, R′ = ethyl
3, R = R = ethyl

These bissulfonium salts behave as monobasic acids in aqueous solution. Potentiometric titration with alkali in dilute aqueous solution yielded the following data: **1**, $\mathrm{p}K_a$ = 9.00 ± 0.10, equiv wt, 313, 323 (calcd, 312); **2**, $\mathrm{p}K_a$ = 8.35 ± 0.04, equiv wt, 342, 342 (calcd, 340); **3**, $\mathrm{p}K_a$ = 7.43 ± 0.03, equiv wt, 366, 359 (calcd, 368). This neutralization reaction can be followed in the ultraviolet spectra of the bissulfonium salts. A 10^{-3} *M* solution of methylenebis(diethylsulfonium) difluoroborate (**3**) in methanol exhibits an absorption maximum at 214 mμ (ϵ ~1000).[5] Addition of small amounts of hydrogen chloride to this solution reduces the absorption at 214 mμ to zero, while addition of 1 equiv of sodium methoxide results in greatly enhanced absorption (λ_{max}^{MeOH} 215 mμ (ϵ 10,000, 10^{-4} *M* solution)). These changes are reversible, and along with the titration data suggest the formation of the bis(dialkylsulfonium)methylides **4**–**6**, similar to those reported in the case of the closely related methylenebis(triphenylphos-

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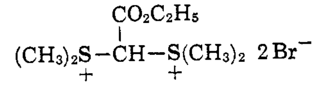
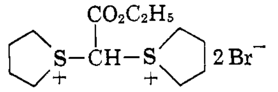
(1) Satisfactory analyses were obtained for all three bissulfonium salts reported.

(2) The only previous report of compounds having the methylenebissulfonium structure is that of the two substituted compounds, i and ii, by H. Böhme and E. Böll, *Ber.*, **90**, 2013 (1957). These authors did not report on the chemistry of i and ii.



$$(\mathrm{CH_3})_2\underset{+}{\mathrm{S}}-\overset{\mathrm{CO_2C_2H_5}}{\overset{|}{\mathrm{CH}}}-\underset{+}{\mathrm{S}}(\mathrm{CH_3})_2\ 2\mathrm{Br}^-$$

i



ii

(3) This compound was prepared by treating bis(methylthio)methane with triethyloxonium fluoroborate.

(4) Tetramethylsilane was employed as an internal standard.

(5) The bissulfonium salts do not obey Beer's law, and we have not been able to account for the deviations solely in terms of their dissociation as weak acids. Similar Beer's law deviations have been reported for trimethylenebissulfonium salts by D. C. Nicholson, E. Rothstein, R. W. Saville, and R. Whitley, *J. Chem. Soc.*, 4019 (1953).