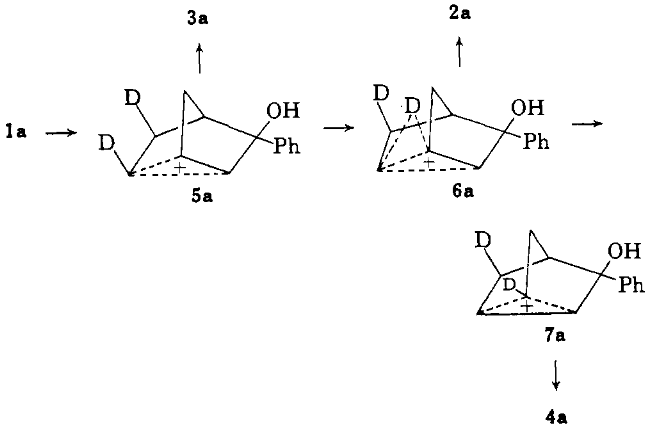
from the *endo* hydrogen at C-2 (3.64 ppm). In **3a** the signals for the 5- and 6-*endo*-hydrogens (0.99 and 0.82 ppm) are absent and the pair of signals for the 5- and 6-*exo*-hydrogens is collapsed into a single broadened peak centered at 1.25 ppm. None of the other spectral features is altered. Neither 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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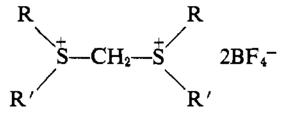
Received October 22, 1965

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**, pK_a = 9.00 ± 0.10, equiv wt, 313, 323 (calcd, 312); **2**, pK_a = 8.35 ± 0.04, equiv wt, 342, 342 (calcd, 340); **3**, pK_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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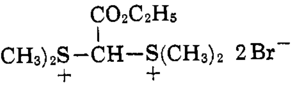
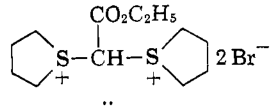
[1] Satisfactory analyses were obtained for all three bissulfonium salts reported.

[2] The only previous report of compounds having the methylenebissulfonium structure is that of the two substituted compounds, i and



$$(CH_3)_2\overset{+}{S}-\overset{CO_2C_2H_5}{\overset{|}{C}H}-\overset{+}{S}(CH_3)_2\ \ 2Br^-$$

i



ii

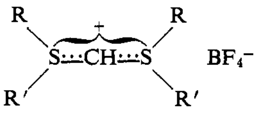
ii, by H. Böhme and E. Böll, *Ber.*, **90**, 2013 (1957). These authors did not report on the chemistry of i and ii.

[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).

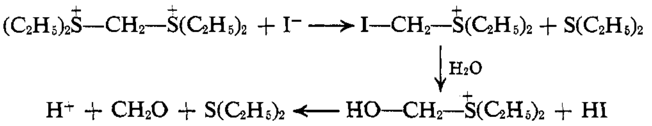
phonium) salts.[6,7] These ylides are discussed in more detail in the following communication.



4, R = R′ = methyl
5, R = methyl, R′ = ethyl
6, R = R′ = ethyl

The bissulfonium salts are hydrolyzed slowly in aqueous solution at ambient temperature. Hydrolysis of **3** was complete in 72 hr and produced formaldehyde (35% as the 2,4-dinitrophenylhydrazone) and diethyl sulfide (identified by nmr spectroscopy), among other products. The addition of a small amount of iodide ion to an aqueous solution of **3** greatly accelerates the hydrolysis. Catalysis by iodide ion can be accounted for by the mechanism proposed in Scheme I, and experiments to test this mechanism are planned.

Scheme I



$$(C_2H_5)_2\overset{+}{S}-CH_2-\overset{+}{S}(C_2H_5)_2 + I^- \longrightarrow I-CH_2-\overset{+}{S}(C_2H_5)_2 + S(C_2H_5)_2$$

$$\Big\downarrow{\scriptstyle H_2O}$$

$$H^+ + CH_2O + S(C_2H_5)_2 \longleftarrow HO-CH_2-\overset{+}{S}(C_2H_5)_2 + HI$$

The preparation of methylenebis(diethylsulfonium) difluoroborate (**3**), a typical case, is described below. Bis(ethylthio)methane[7] (9.8 g, 0.07 mole) was added to 38 g (0.20 mole) of triethyloxonium fluoroborate,[8] and the resulting slurry was stirred in a nitrogen atmosphere at room temperature for 48 hr. The product, a light tan solid, was washed with several portions of ether and finally with methylene chloride to give 20.9 g of a white powder. The crude product was dissolved in the minimum volume of deionized water and precipitated by slow addition of absolute ethanol to the stirring solution. Three precipitations produced 18.1 g (68%) of glistening white crystals, mp 152–158°. *Anal.* Calcd: C, 29.37; H, 6.03; S, 17.43. Found: C, 29.37; H, 5.64; S, 17.34.

Acknowledgments. We wish to thank the research council of the University of Massachusetts for a grant in support of this work. The help of Dr. O. T. Zajicek in obtaining the potentiometric titration data is also gratefully acknowledged.

[6] F. Ramirez, N. B. Desai, B. Hansen, and N. McKelvie, *J. Am. Chem. Soc.*, **83**, 3539 (1961); C. N. Matthews, J. S. Driscoll, and R. J. Wineman, *ibid.*, **83**, 4349 (1962); J. S. Driscoll, D. W. Grisley, Jr., J. V. Pustinger, J. E. Harris, and C. N. Matthews, *J. Org. Chem.*, **29**, 2427 (1964).

[7] H. Böhme and R. Marx, *Ber.*, **74**, 1667 (1941).

[8] H. Meerwein, E. Battenberg, H. Gold, E. Pfeil, and G. Willang, *J. Prakt. Chem.*, **154**, 83 (1939).

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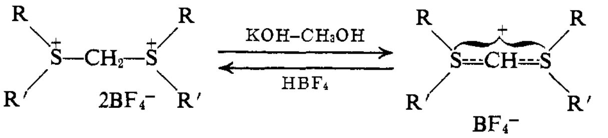
Received February 9, 1966

Bis(dialkylsulfonium)methylides

Sir:

Evidence cited in the preceding communication[1] points to the existence of strikingly stable bis(dialkylsulfonium)methylides. These ylides, **4–6**, have been prepared by treatment of the corresponding methylenebis(dialkylsulfonium) difluoroborates **1–3** with 1 equiv of potassium hydroxide in methanol. They represent the first case of an isolable sulfonium ylide in which the negative charge is stabilized only by sulfonium groups.[2]



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

4, R = R′ = methyl
5, R = methyl, R′ = ethyl
6, R = R′ = ethyl

Ylide **4** is a white solid, mp 104–105°, while ylides **5** and **6** are clear oils at room temperature. Treatment of aqueous solutions of the ylide **4–6** with sodium tetraphenylboronate precipitated the corresponding tetraphenylboronate ylides: **4**, mp 159–159.5°; **5**, mp 119.5–121.5°; and **6**, mp 115–118°. The purified tetraphenylboronate ylides can be kept in dry vials at 4° for several weeks without noticeable decomposition.

The following evidence permits the assignment of structures **4–6** to the fluoroborate ylides. Treatment of compounds **4–6** with aqueous fluoroboric acid regenerates the corresponding bissulfonium salts **1–3** in high yields. The nmr spectra of both the fluoroborates and tetraphenylboronates are consistent with the ylide structures. For example, **6**-$B(C_6H_5)_4^-$ in methylene chloride gave the following spectrum: τ 2.50–3.27[3] (complex multiplet, 20 protons), 7.72 (quartet, 8 protons), 8.65 (singlet, 1 proton), and 8.95 (triplet, 12 protons). The ultraviolet spectra of the fluoroborate ylides have moderately intense absorption maxima near 215 mμ (**6** has $\lambda_{\max}^{\text{MeOH}}$ 215 mμ (ϵ ~10,000)). Potentiometric titration curves for the starting methylenebis(dialkylsulfonium) salts indicate the formation of conjugate bases by loss of only one proton. Finally, satisfactory elemental analyses have been obtained for **4**-$B(C_6H_5)_4^-$ and **6**-$B(C_6H_5)_4^-$.

These ylides are inert to carbonyl compounds in contrast to less stable sulfonium ylides.[4] The tetraphenylboronate ylides can be recrystallized from hot aqueous acetone, and none of these ylides reacted with *p*-nitrobenzaldehyde which reacts readily with the stable dimethylsulfoniumfluorenylide.[5] The ylides also gave no reaction with benzaniline, which reacts with carbonyl-stabilized sulfonium ylides,[6] or with methyl propiolate. The nucleophilic character of these ylides is apparent, however, in their reactions with alkyl and acyl halides. Treatment of bis(methylethylsulfonium)methylide fluoroborate (**5**) with benzoyl chloride resulted in a vigorous reaction. The resulting deep orange oil was hydrolyzed at room temperature in the presence of iodide ion to give phenylglyoxal hydrate among other products. This reaction is formulated as a nucleophilic displacement of chloride ion by the

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[1] C. P. Lillya and P. Miller, *J. Am. Chem. Soc.*, **88**, 1559 (1966).

[2] Other isolable sulfonium ylides have been reported by C. K. Ingold and J. A. Jessop, *J. Chem. Soc.*, 713 (1930); J. Nozaki, K. Kondo, and M. Takaku, *Tetrahedron Letters*, 251 (1965); von A. Hochrainer and F. Wesseley, *ibid.*, 721 (1965); H. Behringer and F. Scheidl, *ibid.*, 1757 (1965).

[3] Tetramethylsilane was employed as an internal standard.

[4] See, for example, E. J. Corey and M. Chaykovsky, *J. Am. Chem. Soc.*, **87**, 1353 (1965).

[5] A. W. Johnson and R. B. LaCount, *ibid.*, **83**, 417 (1961).

[6] A. J. Speziale, C. C. Tung K. W. Ratts, and A. Yao, *ibid.*, **87**, 3460 (1965).