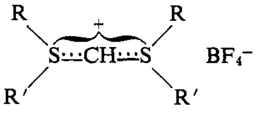
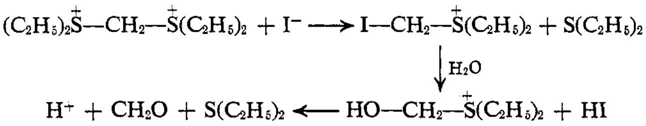
phonium) salts.[6,7] These ylides are discussed in more detail in the following communication.



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**



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

$$\downarrow H_2O$$

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

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.

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(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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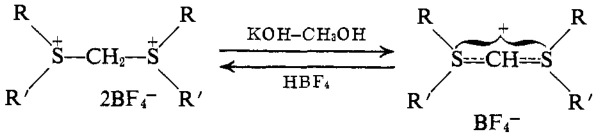
*Received February 9, 1966*

## 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: $\tau$ 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 m$\mu$ (**6** has $\lambda_{max}^{MeOH}$ 215 m$\mu$ ($\epsilon$ ∼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).

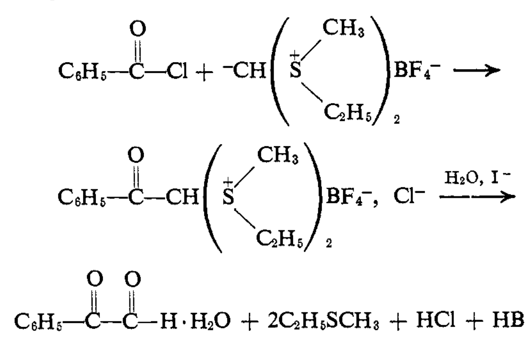
(3) Tetramethylsilane was employed as an internal standard.

(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).

ylide followed by an iodide-catalyzed hydrolysis of the resulting substituted bissulfonium salt.[1]



$$C_6H_5-\overset{\overset{O}{\|}}{C}-Cl + {}^{-}CH\left(\overset{+}{S}\begin{matrix}CH_3\\C_2H_5\end{matrix}\right)_2 BF_4^- \longrightarrow$$

$$C_6H_5-\overset{\overset{O}{\|}}{C}-CH\left(\overset{+}{S}\begin{matrix}CH_3\\C_2H_5\end{matrix}\right)_2 BF_4^-,\ Cl^- \xrightarrow{H_2O,\ I^-}$$

$$C_6H_5-\overset{\overset{O}{\|}}{C}-\overset{\overset{O}{\|}}{C}-H\cdot H_2O + 2C_2H_5SCH_3 + HCl + HBF_4$$

The preparation of bis(dimethylsulfonium)methylide tetraphenylboronate ($4\text{-}B(C_6H_5)_4^-$), a typical case, is described below. Dry methanol (10 ml), 1.35 g of methylenebis(dimethylsulfonium) fluoroborate,[1] and 0.27 g of potassium hydroxide were stirred together for 10 min. The mixture was filtered to remove suspended potassium fluoroborate, and the filtrate was concentrated under reduced pressure. The concentrate was taken up in 10 ml of deionized water and treated with 1.51 g of sodium tetraphenylboronate in 20 ml of deionized water to precipitate $4\text{-}B(C_6H_5)_4^-$. Three crystallizations from hot acetone–deionized water yielded glistening white crystals, mp 159–159.5° (yield 79%). *Anal.* Calcd: C, 76.30; H, 7.29; S, 14.05. Found: C, 76.30; H, 6.86; S, 14.40.

**Acknowledgment.** We wish to thank the research council of the University of Massachusetts for a grant in support of this work.

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*Received February 9, 1966*

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## The Acid-Catalyzed Decomposition of 3-Diazonorcamphor. A Novel Rearrangement

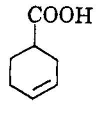
*Sir:*

3-Diazonorcamphor[1] in aqueous tetrahydrofuran at pH 5 has been found to undergo decomposition at room temperature to give 3-cyclohexenecarboxylic acid (I, 17%), *endo*-3-hydroxybicyclo[2.2.1]heptan-2-one (II, 33%), and 2β-hydroxybicyclo[3.1.1]heptan-6-one (III, 29%).

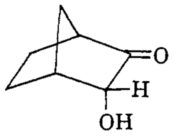
The acid I was identified by spectral comparison with an authentic sample prepared by oxidation of 3-cyclohexenecarboxaldehyde with silver oxide[2] and by comparison of the corresponding amides.[3]

The hydroxy ketone II, mp 143–151°[4] (*Anal.* Found: C, 66.57; H, 8.07), had $\lambda_{max}$ ($CCl_4$) 2.78, 2.88 (br), and 5.70 μ, δ ($CDCl_3$) 1.3–2.2 (6 H), 2.72 (2 H), 3.32 (1 H, absent after treatment with $D_2O$), and 3.93 ppm (1 H, doublet of doublets, $J$ = 5 and 1.5 cps). Reduction with $LiAlH_4$ gave *cis-endo*-2,3-dihydroxybicyclo[2.2.1]heptane (IV), mp 207–208°, identified by spectral comparison with an authentic sample,[5] prepared by reduction of bicyclo[2.2.1]heptane-2,3-dione (V) with $LiAlH_4$. Reduction of V with zinc and acetic acid gave II (56%).

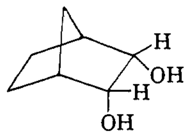
The hydroxy ketone III, mp 113.5–115.5° (*Anal.* Found: C, 66.03; H, 8.11), $\lambda_{max}$ ($CCl_4$) 2.76, 2.90 (br), and 5.62 μ, δ ($CDCl_3$) 1.3–2.5 (6 H), 2.80 (1 H, absent after treatment with $D_2O$), 3.15 (2 H), and 4.55 ppm (1 H, triplet of doublets, $J$ = 6 and 3 cps), formed a 2,4-dinitrophenylhydrazone, mp 170.5–171° (*Anal.* Found: C, 50.88; H, 4.94; N, 18.46), and an ethylene dithioketal (VI), mp 83–84° (*Anal.* Found: C, 53.44; H, 6.84; S, 31.90), $\lambda_{max}$ ($CCl_4$) 2.82 μ, δ ($CDCl_3$) 1.13 (1 H, doublet, $J$ = 9 cps), 1.5–2.9 (7 H), 2.94 (1 H, absent after treatment with $D_2O$), 3.23 (4 H), and 4.15 (1 H) ppm. Attempted vpc of III on a Carbowax 20M column at 175° gave a product, $\lambda_{max}$ ($CCl_4$) 5.61 and 5.78 μ, δ ($CDCl_3$) 1.4–3.5 (9 H) and 9.70 ppm (1 H, triplet, $J$ = 1 cps), considered to be the keto aldehyde VII. Oxidation of III with dichromate and acid gave 4-oxocyclohexanecarboxylic acid, mp 68–69.5°, identified by comparison with an authentic sample[6] and comparison of the corresponding semicarbazones.[7] The gross structure of III follows from these data; its stereochemistry is assigned on the following basis. The position of the signal due to the hydroxyl proton in the nmr spectrum of VI is concentration independent and no nonbonded hydroxyl stretching band appears in the infrared spectrum of this compound. These observations demonstrate the presence of a strong intramolecular hydrogen bond in the dithioketal, which is only possible if the hydroxyl group is β as in III and VI.[8,9]



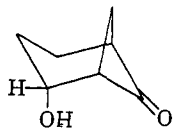
I



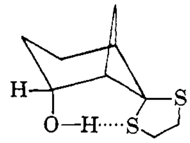
II



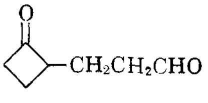
IV



III



VI



VII

The formation of II and III can be interpreted in terms of *exo* protonation of 3-diazonorcamphor to give the diazonium ion VIII, loss of nitrogen to give IX, and *endo* attack by water at C-3 or C-4, respectively; the acid I may arise *via* fission of the C-2–C-3 bond in IX or its hydrated form. Alternatively, formation of II from VIII may involve displacement of nitrogen by *exo* attack of water and epimerization of the resulting *exo*-hydroxy ketone to II;[10] attack of water concerted

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[1] K. B. Wiberg, B. R. Lowry, and T. H. Colby, *J. Am. Chem. Soc.*, **83**, 3998 (1961).

[2] We thank Mr. L. Kilmurry for this sample.

[3] H. K. Hall, Jr., *J. Am. Chem. Soc.*, **82**, 1209 (1960).

[4] The broad melting range for this α-ketol may result from partial conversion to a dimer; *cf.* W. H. Urry, D. J. Trecker, and D. A. Winey, *Tetrahedron Letters*, 609 (1962).

[5] K. Alder, H. Wirtz, and H. Koppelberg, *Ann.*, **601**, 138 (1956).

[6] W. H. Perkin, Jr., *J. Chem. Soc.*, 416 (1904).

[7] D. E. Applequist and J. P. Klieman, *J. Org. Chem.*, **26**, 2178 (1961).

[8] The designation of III as the β isomer is based on arbitrary convention: *cf.* J. Meinwald and P. G. Gassman, *J. Am. Chem. Soc.*, **82**, 2857, 5445 (1960); G. Fodor and K. Nádor, *J. Chem. Soc.*, 721 (1953).

[9] The conformation of III is tentatively assigned on the basis of the nmr data.

[10] This possibility must be entertained since it is unknown whether the formation of the *endo* product results from kinetic or thermodynamic control.