amine. The triplet and the quartet of I were assigned to the coordinated diethyl ether. The 32.0-Mc/sec ^{11}B nmr spectrum in methylene chloride solution showed five unresolved resonances for both I and II, and the spectrum envelope was very similar to that of 3-phenyl-1,2-dicarba-*closo*-dodecaborane(12). The ^{11}B nmr chemical shifts for II are 6.0, 12.0, 15.9, 19.5, and 25.0 ppm relative to $BF_3 \cdot OEt_2$.

Treatment of II with ethanolic potassium hydroxide produced the (3)-1,2-$B_9C_2H_{12}^-$ ion which was isolated as the white tetramethylammonium salt in 79% yield and identified by its infrared spectrum.[4] Our proposed structure for II is shown in Figure 1.

Further work is in progress on the reactions of metal alkyls and carboranes and will be reported at a later time.

Acknowledgment. This research was supported, in part, by the Office of Naval Research. The authors wish to thank Professor G. E. Coates for a gift of dimethylberyllium and the U. S. Air Force for the delivery of this material to Norton AFB, California.

(4) M. F. Hawthorne, D. C. Young, P. M. Garrett, D. A. Owen, S. G. Schwerin, F. N. Tebbe, and P. A. Wegner, *J. Am. Chem. Soc.*, **90**, 862 (1968).

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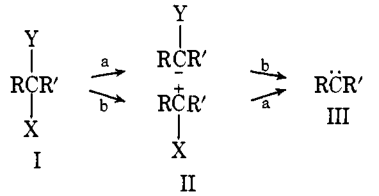
Carbenes from Carbonium Ions. I. Dithiomethoxymethyl Cation and Its Conversion to Tetrathiomethoxyethylene

Sir:

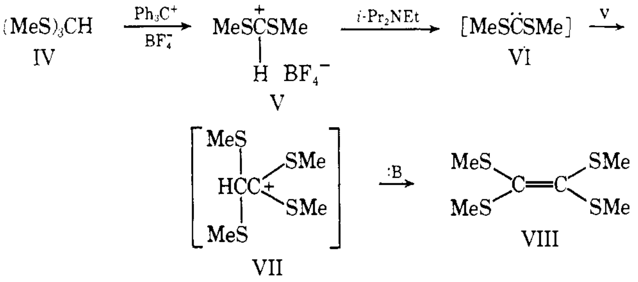
Most methods for the generation of carbenes may be classified as examples of the general reaction 1, though other reactions proceeding by a homolytic or concerted abstraction of X and Y from I are also known.[1] From


(1)
(2)

this generalization one might logically anticipate a final and extensive series of carbene syntheses which could be formalized as representatives of a process (2) in which the nucleophile is removed prior to the elimination of the electrophile, a mechanism in which the two steps of (1) are just reversed in order. However, though isolated reactions which may be interpreted as illustrations of (2) are known,[1] this scheme has not yet received systematic investigation. Historically this may be justified, but in view of the rapidly increasing numbers of "stable" carbonium ions (II), this excuse is no longer tenable.

In this communication we describe preliminary experiments in which systems of the general carbonium ion structure II (with X = H) are deprotonated with base to yield the carbenes III. Two factors must be considered in choosing the base with which to accomplish this transformation: the base must be powerful enough to abstract the proton, and it must not preferentially react with other electrophilic sites on the carbonium ion. With the substrates picked for initial study, dithiomethoxymethyl fluoroborate (V) and dimethoxymethyl fluoroborate (IX), the problem of required base strength was readily resolved in favor of an amine base by extrapolation from research on heterocyclic C–H acidities.[2] Side reactions might, however, seem insurmountable, since it is known that anions react with $(MeO)_2C^+R$ to neutralize the plus charge at C while other nucleophiles (*i.e.*, R_3N) are methylated with concomitant production of methyl esters.[3] Still, since attack at methyl or C^+ in V or IX should be much more sensitive to the steric requirements of the nucleophile than reaction at H, we felt we could promote the desired process by using a base such as diisopropylethylamine which is a good proton abstractor but a very poor base toward larger acids.[4]

Dithiomethoxymethyl fluoroborate (V) is conveniently synthesized by treatment of methyl orthothioformate (IV) with trityl fluoroborate in dichloromethane[5] (V: mp *ca.* 30°; nmr, δ 11.23 (1) and 3.13 (6) in $MeNO_2$ at room temperature; 11.12 (1), 3.00 (3), and 3.25 (3) in FSO_3H at $-50°$[6]). When diisopropylethylamine is added to V in dichloromethane at $-10°$ a rapid reaction ensues, yielding tetrathiomethoxyethylene (VIII; mp 61–62°, lit.[7] mp 59–60°; nmr, δ 2.33 in CCl_4; 77% over-all from IV). The product VIII is best explained as the result of a base-induced deprotonation of V affording dithiomethoxycarbene (VI)[7] which then reacts as a nucleophile toward additional carbonium ion V, finally yielding the alkene *via* the cation VII.[8]



Similar base treatment of dimethoxymethyl fluoroborate (IX; prepared by mixing methyl orthoformate

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(1) J. Hine, "Divalent Carbon," The Ronald Press, New York, N. Y., 1964; W. Kirmse, "Carbene Chemistry," Academic Press, New York, N. Y., 1964.

(2) For leading references see: R. A. Olofson and J. M. Landesberg, *J. Am. Chem. Soc.*, **88**, 4263 (1966); R. A. Olofson, J. M. Landesberg, K. N. Houk, and J. S. Michelman, *ibid.*, **88**, 4265 (1966); R. A. Olofson, W. R. Thompson, and J. S. Michelman, *ibid.*, **86**, 1865 (1964); H. Prinzbach, H. Berger, and A. Lüttringhaus, *Angew. Chem. Intern. Ed. Engl.*, **4**, 435 (1965).

(3) S. Kabuss, *ibid.*, **5**, 675 (1966); K. Dimroth and P. Heinrich, *ibid.*, **5**, 676 (1966).

(4) S. Hünig and M. Kiessel, *Chem. Ber.*, **91**, 380 (1958).

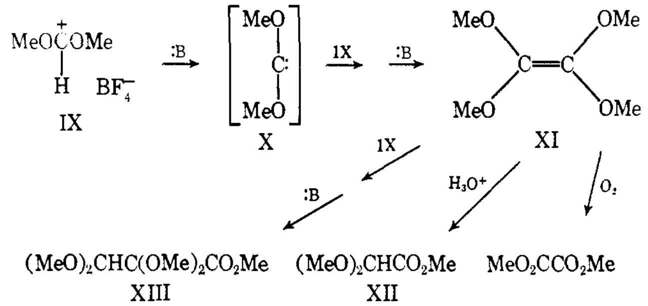
(5) Note that trityl cation exclusively detaches SMe and not hydride from IV. This procedure has been used by others, including W. P. Tucker and G. L. Roof [*Tetrahedron Letters*, 2747 (1967)], in the synthesis of $(MeS)_3C^+BF_4^-$ from $(MeS)_4C$.

(6) The nonequivalence of the two methyls suggests a "sickle" structure also found for dimethoxycarbonium ions [B. G. Ramsey and R. W. Taft, *J. Am. Chem. Soc.*, **88**, 3058 (1966)] and is in accord with predictions for methylallyl anion like systems [R. Hoffmann and R. A. Olofson, *ibid.*, **88**, 943 (1966)].

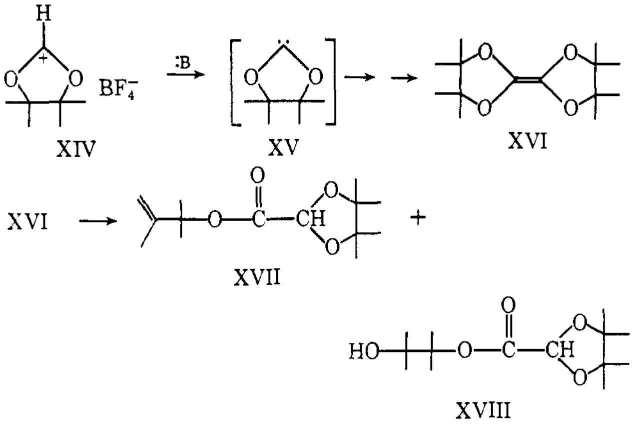
(7) J. Hine, R. P. Bayer, and G. G. Hammer, *ibid.*, **84**, 1751 (1962); D. M. Lemal and E. H. Banitt, *Tetrahedron Letters*, 245 (1964); U. Schöllkopf and E. Wiskott, *Ann.*, **694**, 44 (1966).

(8) The reverse process is known for tetraaminoethylenes → formamidinium salts [D. M. Lemal, R. A. Lovald, and K. I. Kawano, *J. Am. Chem. Soc.*, **86**, 2518 (1964)].

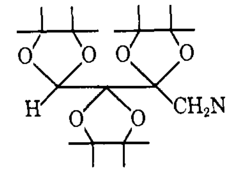
and $BF_3 \cdot Et_2O$[6,9]) affords the esters XII[10] and XIII[11] (bp 93° (5 mm)) almost certainly *via* dimethoxycarbene (X)[10] and the very unstable (to acid and trace water) tetramethoxyethylene (XI).[10,12] As expected, dimethyl oxalate is also obtained when the reaction is run under O_2.[10]



When the carbonium ion XIV[9] is used as the reaction substrate, the products are the alkenes XVI (nmr, δ 1.22) and XVII (nmr, δ 5.05 (1), 4.95 (1), 4.74 (1), 1.78 (3), 1.53 (6), 1.20 (12) in CCl_4) and the alcohol XVIII (mp 88–91°; nmr, δ 5.00 (1) and 1.47, 1.35, 1.30, 1.25, 1.16 (total 24) in CCl_4). This experiment was intended as a test for a synthetic method for converting *vic*-glycols to alkenes, but it would seem that under our experimental conditions (unlike those of Corey[13]) the carbene XV does not spontaneously decompose to CO_2 and tetramethylethylene but instead survives to be trapped by XIV.



It might finally be noted that the above reactions are best carried out in chlorinated hydrocarbons or in sulfolane. Nitromethane as solvent may change the reaction course; *e.g.*, XIV plus diisopropylethylamine in nitromethane yields a compound which we believe has structure XIX (mp 153.5–155°; nmr, δ 4.96 (1), 4.70 (2), and 1.32, 1.20 (36) in CCl_4). XIX could be formed by a reversible reaction of XVI with XIV followed by attack of *aci*-nitromethane on the resulting carbonium ion.



XIX

In future papers we hope to describe: (1) inverse addition experiments in which the carbonium ion is added to the base in the presence of competing carbene trapping agents, (2) extensions to the deprotonation of other carbonium ions with stronger hindered bases, and (3) new synthetic methods involving the extrusion of other electrophilic X moieties from the general cation structure II.

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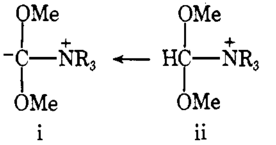
[9] H. Meerwein, K. Bodenbenner, P. Borner, F. Kunert, and K. Wunderlich, *Ann.*, **632**, 38 (1960).

[10] D. M. Lemal, E. P. Gosselink, and S. D. McGregor, *J. Am. Chem. Soc.*, **88**, 582 (1966), and related papers; R. W. Hoffmann and H. Häuser, *Tetrahedron Letters*, 197, 1368 (1964).

[11] Satisfactory analytical data have been obtained for all new compounds.

[12] The intervention of an ylide intermediate (i) is most unlikely considering the amine used[4] and the fact that ii (very unstable solution made by alkylation of amide acetal) gives other products in controls.



i ii

[13] E. J. Corey and R. A. E. Winter, *J. Am. Chem. Soc.*, **85**, 2677 (1963). They generated the carbene XV or its equivalent by reaction of a thionocarbonate with $(RO)_3P$ at 120–160°. Unfortunately XIV decomposes thermally to pinacolone so the fate of XV when obtained from XIV at high temperature could not be determined.

Crystal and Molecular Structure of [16]Annulene[1]

Sir:

[16]Annulene (I) has been the subject of much recent experimental[2,3] and theoretical interest.[4,5] Several conformations have been proposed for [16]annulene,[2–4] and the low-temperature (−110°) nmr spectrum indicates that there are four "inner" protons and twelve "outer" protons.[3] At higher temperatures the protons are magnetically indistinguishable, possibly due to conformational isomerism arising from rotation about carbon–carbon bonds or valence tautomerism of the π bonds.[3,6] The results of an X-ray single-crystal structure analysis of [16]annulene, carried out at 4°, are now reported.

The deep purple crystals (mp 85–89°) belong to the monoclinic system with $a = 8.79 \pm 0.02$, $b = 8.13 \pm 0.02$, $c = 18.60 \pm 0.04$ Å, and $\beta = 109° 10' \pm 10'$ at 4°. There are four molecules of $C_{16}H_{16}$ (mol wt 208.3) in the unit cell ($\rho_{\text{meas}} = 1.08$ g cm^{-3}, $\rho_{\text{calcd}} = 1.11$ g cm^{-3}). The space group is $P2_1/c$. A total of 1205 independent structure amplitudes was obtained by visual estimation of equiinclination Weissenberg films taken at 4° (Cu Kα radiation). The structure

[1] Work supported by U. S. Public Health Service Grant GM 12470-04.

[2] F. Sondheimer and Y. Gaoni, *J. Am. Chem. Soc.*, **83**, 4863 (1961); I. C. Calder, Y. Gaoni, and F. Sondheimer, *ibid.*, **90**, 4946 (1968).

[3] G. Schröder and J. F. M. Oth, *Tetrahedron Letters*, 4083 (1966).

[4] M. J. S. Dewar and G. J. Gleicher, *J. Am. Chem. Soc.*, **87**, 685 (1965).

[5] H. C. Longuet-Higgins, Special Publication No. 21, The Chemical Society, London, 1967, p 109.

[6] I. C. Calder and P. J. Garratt, *J. Chem. Soc.*, *B*, 660 (1967).