spectrum of the synthetic product was identical with that of naturally occurring cannabicyclol: all the characteristic "cannabicyclol peaks"[2a] were exhibited, including the significant peaks at *m/e* 314 (M^+), 299 (M − 15), 232, 231 (base peak), 187, and 174.

Further elution with petroleum ether–ether (95:5 and 94:6) gave a reddish oil. This was rechromatographed twice on thick silica gel plates and evaporatively distilled at 150° (0.01 mm) to give a colorless liquid in 20% yield, homogenous by tlc and glc; nmr (CCl_4), δ 0.87 (3 H, t, ω-CH_3), 1.34 (3 H, s, α to OCH_3), 1.55 and 1.64 (6 H, 2 s, olefinic CH_3), 5.06 (1 H, broad t, olefinic H), 5.36 and 6.56 (2 H, AB quartet, J_{AB} = 10 cps, olefinic H), 5.99 (1 H, d, J = 2 cps, aromatic H), 6.16 (1 H, d, J = 2 cps, aromatic H), and 5.55 (1 H, s, OH; D_2O exchangeable; λ_{max}^{EtOH} 280 (ϵ 9700 and 225 mμ (27,500). The mass spectrum showed principal ions at *m/e* 314, 299, 232, 231 (base peak), and 174, in accord with the data presented for an authentic sample.[9] Furthermore, the ir spectrum of the synthetic cannabichromene in CCl_4 solution is virtually superimposable with that of natural cannabichromene (**10**).[2b] Also, as expected, heating **10** with *p*-toluenesulfonic acid in refluxing benzene gave mainly **4** along with **8**.[2d]

The success of these experiments has prompted us to continue an examination of this reaction and its mechanism, which will be the subject of future communications.

Acknowledgment. We are grateful to Arthur D. Little, Inc., for generous support of this work. The authors wish to thank Dr. P. Levins and Miss D. Wilson for recording the mass and nmr spectra, respectively, and Dr. Harry G. Pars for his encouragement of this work.

(9) (a) U. Claussen, F. V. Spulak, and F. Korte, *Tetrahedron*, **22**, 1477 (1966); (b) Y. Gaoni and R. Mechoulam, *Chem. Commun.*, 20 (1966).

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1-Trimethylamino-1-beryl-2,3-dicarba-*closo*-dodecaborane(12). An Analog of the $B_{11}CH_{12}^-$ Ion

Sir:

The continued substitution of a beryllium atom–carbon atom pair for a pair of boron atoms in polyhedralborane ions and carborane species would ultimately produce a series of beryllium–carbon species which are isoelectronic with the corresponding polyhedral $B_nH_n^{2-}$ ion and $B_{n-2}C_2H_n$ carborane (n = even number). Examples would include $Be_6C_6H_{12}^{2-}$, $BBe_5C_6H_{12}^-$, and $Be_5C_7H_{12}^0$ of probable icosahedral geometry which are isoelectronic with $B_{12}H_{12}^{2-}$, $B_{11}CH_{12}^-$, and $B_{10}C_2H_{12}$, respectively. We now wish to report the synthesis of species in which the first step of the Be + C for 2B substitution has been formally accomplished.

The reaction of a benzene solution of (3)-1,2-$B_9C_2H_{13}$[1] with a diethyl ether solution of dimethylberyllium produced 2 moles of CH_4 which was quantitatively determined and identified by its characteristic vpc retention time. Subsequent work-up of the reaction solution in the absence of air and moisture led to the

$$B_9C_2H_{13} + Be(CH_3)_2\cdot(OEt_2)_2 \longrightarrow B_9BeC_2H_{11}\cdot OEt_2 + OEt_2 + 2CH_4$$

isolation of a nonvolatile crystalline solid (I) which could be recrystallized from dry, oxygen-free CH_2Cl_2–pentane solutions. This substance was very sensitive to air and water and melted at 120–121°. Elemental analysis was unsuccessful because of the extreme air sensitivity of the compound. Proton nmr and infrared spectra suggested that I was $B_9BeC_2H_{11}\cdot O(C_2H_5)_2$ in which diethyl ether was coordinated with the beryllium atom, thus formally replacing a hydride ion in the parent $B_9BeC_2H_{12}^-$ ion. The latter ion is isoelectronic with the $B_{11}CH_{12}^-$ ion,[2] as suggested above, and would most likely possess an icosahedral geometry.

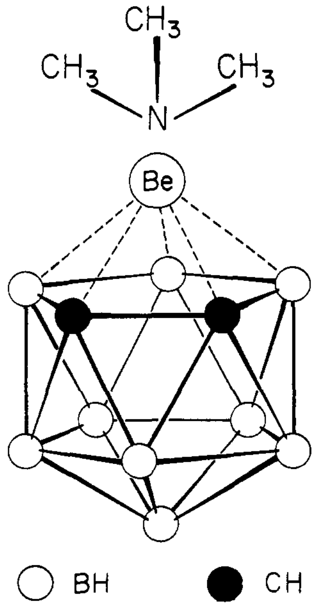

Figure 1. Proposed schematic structure of $B_9BeC_2H_{11}N(CH_3)_3$.

When anhydrous trimethylamine was passed through a solution of I in dry CH_2Cl_2, white crystals (II) precipitated which could be recrystallized from CH_2Cl_2–pentane solutions. The melting point of II was 221–223° dec, and II was much less reactive with moist air than I. *Anal.* Calcd for $B_9BeC_2H_{11}\cdot N(CH_3)_3$: B, 48.54; C, 29.93; H, 10.05; Be, 4.50; N, 6.98. Found: B, 47.45; C, 28.46; H, 9.67; Be, 3.79; N, 7.19. The parent peak in the mass spectrum[3] of II appeared at *m/e* 202 and corresponds to the $(^{11}B_9{}^9Be^{12}C_5{}^1H_{20}{}^{14}N)^+$ ion. The ^1H nmr spectrum of II in methylene chloride showed a broad singlet at δ −2.55 (relative intensity 2) and a sharp singlet at δ −2.90 (relative intensity 9) relative to tetramethylsilane. The ^1H nmr spectrum of I in methylene chloride showed the broad singlet at δ −2.75 (relative intensity 2) together with a triplet at δ −1.80 (relative intensity 6) and a quartet at δ −4.62 (relative intensity 4). The signals at δ −2.55 and −2.75 were assigned to the hydrogen atoms bonded to the carborane carbon atoms, whereas the singlet at δ −2.90 was assigned to the coordinated trimethyl-

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(1) R. A. Wiesboeck and M. F. Hawthorne, *J. Am. Chem. Soc.*, **86**, 1642 (1964).

(2) (a) D. E. Hyatt, F. R. Scholer, L. J. Todd, and J. L. Warner, *Inorg. Chem.*, **6**, 2229 (1967); (b) W. H. Knoth, *J. Am. Chem. Soc.*, **89**, 1274 (1967).

(3) We are indebted to Professor H. D. Kaesz for the determination of the mass spectrum of II.

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.

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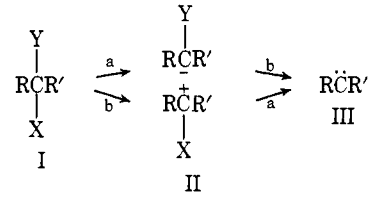
Carbenes from Carbonium Ions. I. Dithiomethoxymethyl Cation and Its Conversion to Tetrathiomethoxyethylene

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



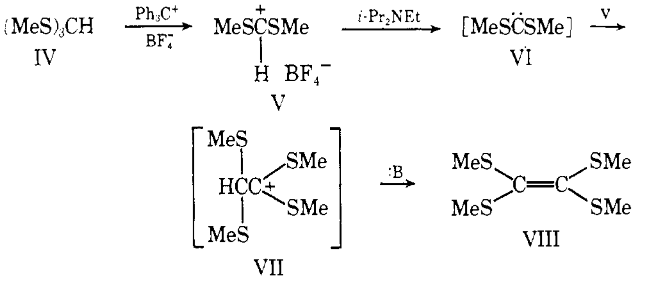
(1)

(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).

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[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)].