Reaction of IV with anhydrous hydrogen chloride gave the chloride salt of II as a white solid. Upon metathesis, the hexafluorophosphate salt was recovered in 40% yield.

Diborane reacts rapidly with IV at low temperature, to give the adduct VI. The adduct is a white, hard

$$\underset{\text{IV}}{2(CH_3)_3NBH_2CH_2\ddot{N}(CH_3)_2} + B_2H_6 \longrightarrow$$

$$\underset{\text{VI}}{2(CH_3)_3NBH_2CH_2N(CH_3)_2BH_3}$$

crystalline solid which sublimes unchanged at 100° under high vacuum. Hydrolysis of VI confirmed its composition, giving a hydrolytic hydrogen value of 0.0343 mmole/mg, in good agreement with that calculated for hydrolysis of five BH bonds/formula weight of VI, 0.0347 mmole/mg.

The borane cation II and the cation of III are members of two related new classes of cationic boranes. They are stable in aqueous acid or base and do not reduce aqueous silver ion. A contributing factor in the aqueous stability of II is the strong basicity of its conjugate base IV. The enhancement of base strength by boron hydride substitution is well established. Both $H_2B(NH_3)_2^+$ and $B_{10}H_8(NH_3)_2$, for example, are known to be weak acids of very strong conjugate bases.[7,8]

Acknowledgment. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research. This work was also supported in part by a grant from the research fund of the University of South Dakota.

(7) D. R. Schultz and R. W. Parry, *J. Am. Chem. Soc.*, **80**, 4 (1958).
(8) W. H. Knoth, *ibid.*, **88**, 935 (1966).

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May 27, 1966

Insertion by Triplet Methylene Radicals in Alkane Systems[1]

Sir:

It is commonly believed,[2] based on earlier reports,[3,4] that triplet methylene radicals do not insert into C–H bonds. This letter reports contrary evidence and some quantitative measurements.

Since the finding that photolysis of ketene[5] and of diazomethane[6] both yield triplet methylene besides the singlet radical, we have been interested in the ramifications of this complication for the interpretation of the chemistry of these systems. It is now established[7] that $^3CH_2$ abstracts hydrogen from C–H bonds, and Whitten and Rabinovitch[7a] proposed that at least part of the pentene products[2c] from reaction of $^3CH_2$ with butene-2 have their origin in initial H abstraction. In an effort to clarify these matters, we have investigated the reaction of $^3CH_2$ with propane, *n*-butane, and isobutane, and with alkane–ethylene mixtures.

Triplet methylene was produced[3] by photolysis (4358 A and 25°) of ~1:10 diazomethane–substrate gaseous mixtures that contained at least 800-fold excess of N_2 (~1.6 atm). In some experiments, admixture of from 5 to 20% ethylene was made. Increase in the proportion of N_2 (up to 2500:1) had little effect on product composition, so that $[^3CH_2/(^3CH_2 + {}^1CH_2)] \sim 1$.[8]

Analysis was made by gas chromatography, with calibration of virtually every product of interest with authentic samples. The side products in triplet systems are much more complex than those formed in largely singlet systems and makes the requisite analyses more exacting. Each substrate has only two distinguishable H sites which simplified the possible products. Background calibrations were made from blank experiments with no substrate and with substrate–oxygen mixtures.

The principal reactions of interest are

$$RH + {}^3CH_2 \longrightarrow CH_3 + R \text{ (primary H)} \qquad (1a)$$

$$\longrightarrow CH_3 + R' \text{ (secondary or tertiary H)} \qquad (1b)$$

$$2R \longrightarrow R_2 \qquad (2)$$

$$2R' \longrightarrow R_2' \qquad (3)$$

$$R + R' \longrightarrow RR' \qquad (4)$$

$$2CH_3 \longrightarrow C_2H_6 \qquad (5)$$

$$CH_3 + R \longrightarrow RCH_3 \qquad (6)$$

$$CH_3 + R' \longrightarrow R'CH_3 \qquad (7)$$

plus disproportionation reactions and cyclopropane formation with ethylene. Ethyl radicals also arise in these systems.[7a] They offer both complication and assistance from the occurrence of the reactions

$$2C_2H_5 \longrightarrow n\text{-}C_4H_{10} \qquad (8a)$$

$$\longrightarrow C_2H_6 + C_2H_4 \qquad (8b)$$

$$CH_3 + C_2H_5 \longrightarrow C_3H_8 \qquad (9)$$

$$C_2H_5 + R \longrightarrow RC_2H_5 \qquad (10)$$

$$C_2H_5 + R' \longrightarrow R'C_2H_5 \qquad (11)$$

plus further disproportionation reactions.

The relative proportions of R and R′ deduced either from the products of reactions 10 and 11, or from reactions 2, 3, and 4, were in general agreement. For propane, the relative rate of secondary/primary H abstraction by $^3CH_2$ is 11 per bond. A value of 9 was given previously[7a] for propane systems in which $^3CH_2$ was only a minor fraction of the methylene. Since the ratio of secondary/primary H abstraction by CH_3 is

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(1) This work was supported by the Office of Naval Research.

(2) For example, see (a) W. Lwowski and F. P. Woerner, *J. Am. Chem. Soc.*, **87**, 5491 (1965); (b) H. M. Frey, *Chem. Commun.*, 260 (1965); (c) J. A. Bell, *Progr. Phys. Org. Chem.*, **2**, 1 (1964); (d) F. J. Duncan and R. J. Cvetanović, *J. Am. Chem. Soc.*, **84**, 3593 (1962).

(3) H. M. Frey, *ibid.*, **82**, 5947 (1960).

(4) K. R. Kopecky, G. S. Hammond, and P. A. Leermakers, *ibid.*, **83**, 2397 (1961); **84**, 1015 (1962).

(5) J. W. Simons and B. S. Rabinovitch, *J. Phys. Chem.*, **68**, 1322 (1964). See also S. Ho, I. Unger, and W. A. Noyes, Jr., *J. Am. Chem. Soc.*, **87**, 2297 (1965); K. W. Watkins, B. S. Rabinovitch, and D. F. Ring, *ibid.*, **87**, 4960 (1965); and ref 7b.

(6) F. H. Dorer and B. S. Rabinovitch, *J. Phys. Chem.*, **69**, 1952, 1964 (1965). Our results were communicated orally to Dr. H. M. Frey in Sept 1964, and were confirmed by him in later work.[2b]

(7) (a) G. Z. Whitten and B. S. Rabinovitch, *J. Phys. Chem.*, **69**, 4348 (1965); (b) R. W. Carr and G. B. Kistiakowsky, *ibid.*, **70**, 119 (1966); (c) H. M. Frey, private communication. It may be noted that D. B. Richardson, M. C. Simmons, and I. Dvoretzky [*J. Am. Chem. Soc.*, **82**, 5001 (1960); **83**, 1934 (1961)] earlier speculated that $^3CH_2$ abstracts H atoms, but on the basis of mechanistic surmises and alleged evidence that have been shown [D. W. Setser and B. S. Rabinovitch, *Can. J. Chem.*, **40**, 1425 (1962)] to be incorrect.

(8) Comparison of results of Watkins, *et al.*,[5] by the present technique for *cis*-butene-2 substrate, with data from earlier work[2d] on triplet radicals in $Hg(^3P_1)$-photosensitized ketene–butene mixtures, shows that the proportion of $^3CH_2$ in N_2 systems is at least as high as in $Hg(^3P_1)$ systems.

$\sim$7 per bond,[9] the ratios given above are merely lower limits to the relative rates *if* H abstraction by alkyl also occurred; however, it has been estimated previously[7b] for the propane system that abstraction by CH_3 is unimportant even at much higher substrate concentrations. The rates relative to $C{=}C$ addition (ethylene) for the three substrates are: primary/secondary/tertiary/$C{=}C$ = 1:11:–:70 (propane) and 1:14:–:120 (butane); and for isobutane the ratios are 1:–:122:125. The average ratios are 1:12.5:122:125. The values were calculated with use of disproportionation and recombination rates[10] employed previously.[7a] A drastic change (to unity) in the assumed relative rates of all radical combinations is largely self-cancelling in its effect and does not alter the approximate magnitude of the abstraction ratios deduced.

The relative amounts of the two products, RCH_3 and $R'CH_3$, from reactions 6 and 7 would be expected to connote similar abstraction ratios. Instead, the amounts bear no correspondence to the numbers above. The ratios, $RCH_3/R'CH_3$, per bond are 1:3 (propane), 1:4 (*n*-butane), and 1:15 (isobutane). Also, the total amount of these products greatly exceeded the possible contribution from reactions 6 and 7, upper limits to whose magnitudes were calculated on the basis that ethane (less reaction 8b) arose from methyl recombination (reaction 5), and that propane arose from methyl reactions 5 and 9; *e.g.*, for RCH_3 products the calculated amounts are 0.11 (propane), 0.09 (*n*-butane), and 0.08 (isobutane), respectively, of the observed quantities. Nor are the amounts and ratios of the two products explicable in terms of a $^{1}CH_2$ component. Although there exists an incompletely understood concomitant process that could conceivably explain *some* of the higher products by successive chain-lengthening steps, this too is inadequate to explain the RCH_3 and $R'CH_3$ products. A simple explanation is that these products arise by insertion and spin inversion

$$RH + {}^{3}CH_2 \rightarrow RCH_3 \text{ and } R'CH_3 \qquad (12a,b)$$

Quite apart from whether this proposition is indeed proven, the fact remains that the older data[3,4] seem inadequate to disprove the occurrence of insertion[11] while the present results, at the least, simulate such a process.

On the basis of reactions 12 the following ratios may be calculated. Relative insertion rates are, for secondary/primary CH, 2.2 per bond (propane) and 3.5 per bond (butane); and for tertiary/primary CH, 10.9 per bond (isobutane). These numbers are averages for five to eight experiments. Some relative rates of abstraction/insertion are for primary CH: 0.38 (propane), 0.31 (*n*-butane), and 0.30 (isobutane), or an average of 0.33; secondary CH: 1.9 (propane) and 1.3 (*n*-butane), or an average of 1.5; tertiary CH: 3.0 (isobutane). These last three ratios (but not others above) decrease with decreasing proportion of diazomethane, and approach limiting values about twice these, for mixture dilutions of 1:80.

Since $^{1}CH_2$ has recently been said to abstract hydrogen from C–H bonds in certain cases,[12] the qualitative (but not quantitative) parallelism of this roster of reactions of $^{3}CH_2$ and $^{1}CH_2$ with CH and $C{=}C$ bonds may now be complete.

In view of the lesser magnitude of *D*(allyl H) relative to *D*(tertiary C–H), it continues plausible that a source of pentene products in butene systems is H abstraction by $^{3}CH_2$ followed by radical combination; some insertion could also occur.

Complete details and exposition of the rather complex product calculations will be submitted later.

Acknowledgment. We thank Mr. John Campbell for his assistance.

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[9] J. A. Kerr and A. F. Trotman-Dickenson, *Progr. Reaction Kinetics*, 1, 105 (1961).

[10] Based on k_d/k_r = 2.2 for *t*-Bu; a higher value[9] would raise this ratio. For the reasons that follow from the results cited in the next paragraph, and because of the complexity of triplet methylene systems, it is highly desirable that the R_2, R_2', RR′, and the RC_2H_5 and $R'C_2H_5$ products always be analyzed as diagnostics of abstraction amounts.

[11] For example, ref 4 reports no, or negligible, C_5 olefin products in the photosensitized decomposition of CH_2N_2 with butene-2. By contrast, we find such products of $^{3}CH_2$ to be of importance; *cf.* ref 2d.

[12] D. W. Setser, private communication.

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Received June 9, 1966

Anisotropic Electron Transport in Compounds Containing Polymeric Metal–Metal Bonds[1]

Sir:

A wide variety of complexes which contain metal–metal bonds have been synthesized since the recent realization that metal derivatives may be catenated.[2] We have become interested in the properties of the metal–metal bond because of our belief that compounds which possess a polymeric metal skeleton will exhibit many of the properties of the free metal. If this supposition is valid, one can anticipate that the *one-dimensional* polymeric arrangement of metal atoms in these compounds will result in unique solid-state properties, including *anisotropic* conductivity and photoconductivity.

Few physical measurements have been carried out on compounds which possess more than one metal–metal bond. The esr spectrum of the radical anion of dodecamethylcyclohexasilane indicates that the unpaired electron is delocalized over all six silicon atoms.[3] Likewise the catenation of silicon,[4] germanium,[5] tin,[6] and lead[6] is associated with the appearance of electronic transitions in the ultraviolet and visible regions. These observations provide the only definitive experimental evidence for the hypothesis that adjacent d and p orbitals in chains of metals will overlap to form delocalized band-type orbitals either in the ground or excited states.[7,8a] Seeking model compounds to test the con-

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[1] (a) This work was supported by the Air Force Avionics Laboratory, Research and Technology Division, Air Force Systems Command, U. S. Air Force, under Contract No. AF 33(615)-3334; (b) this work was supported partially by the Advanced Research Projects Agency, under Contract SD-100.

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[3] G. R. Husk and R. West, *J. Am. Chem. Soc.*, 87, 1993 (1965).

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[6] W. Drenth, M. J. Janssen, G. J. M. Van Der Kerk, and J. A. Vliegenthart, *J. Organometal. Chem.*, 2, 265 (1964).

[7] R. E. Rundle, *J. Phys. Chem.*, 61, 45 (1957); J. R. Miller, *J. Chem. Soc.*, 4452 (1961).

[8] (a) J. R. Miller, *ibid.*, 713 (1965); in the latter paper the author