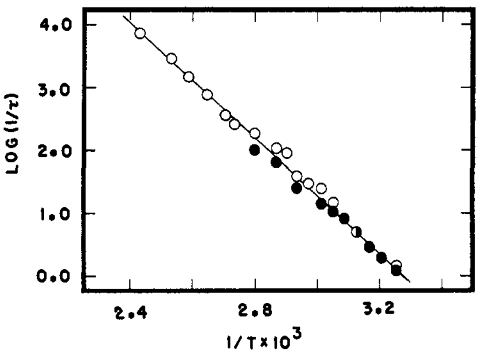

Figure 1. Arrhenius plot of rate data from the isopropyl resonances (open circles) and the bitolyl methyl resonances (filled circles) of **1**. The Arrhenius parameters derived from a least-squares fitting to all the points are $E_a = 20.8 \pm 0.4$ kcal/mole; $\log A = 15.0 \pm 0.3$.

we can obtain excellent agreement between calculated and observed spectra for each group of lines, using an exchange scheme in which pseudo-rotation converts each one of the conformations **1**, **2**, **3**, or **4** with equal probability into the other three. Specifically, the kinetic exchange matrix K[10] used for this problem had elements $K_{ij} = -1$, $i = j$, and $K_{ij} = {}^1/_3$, $i \neq j$, for the four bitolyl methyl peaks, and $K_{ij} = -{}^2/_3$, $i = j$, and $K_{ij} = {}^2/_3$, $i \neq j$, for the isopropyl methyl doublets, and implies that the rate constants k_{12}, k_{13}, and k_{14} describing conversion of **1** to **2**, **3**, and **4**, respectively, are equal.[11] Although spectra calculated on the assumption that $k_{12} = k_{14}$ and $k_{13} = 0$ were in equally close agreement with the spectra observed for the bitolyl methyl protons, spectra calculated assuming either that $k_{12} \geq 2k_{14}$ or that $k_{14} \geq 2k_{12}$ had line shapes which were qualitatively distinguishable from those observed.[12]

An Arrhenius plot of the rate data obtained by comparison of the observed spectra with those calculated using the assumption that $k_{12} = k_{13} = k_{14}$ (Figure 1) indicates that within our experimental error the points obtained from the isopropyl resonances fall along the same line as those from the bitolyl methyl resonances and implies that the interchange of axial and equatorial positions on the bridging bitolyl groups occurs at the same rate as the interconversion of enantiomers. This observation strongly suggests that axial–equatorial interchange and racemization share a common mechanism and is entirely consonant with the Berry mechanism.

Although this result in no sense establishes the correctness of the Berry mechanism, it does argue against certain other mechanistic possibilities. For example, a plausible alternative mechanism, which would involve an intermediate such as **5** in the exchange process, would be expected to result in a rate of interchange of enantiomers approximately twice that of interchange of axial and equatorial bitolyl methyl groups. The data of Figure 1 indicate that the rates of these two processes are in fact equal, and, although the difference between this observed rate equality and the twofold difference in rates predicted to result from the intermediacy of **5** is small, it is probably outside the experimental error in our measurements.

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[11] The symmetry of this exchange matrix makes it unnecessary to assign chemical shifts to the individual bitolyl methyl groups.

[12] The particular limiting exchange scheme in which $k_{12} = 0$ leads to a doublet for the bitolyl methyl protons in the fast-exchange limit, rather than the observed singlet.

Rapid Rotation about Carbon–Carbon Bonds in Alkyl Diradicals. Mixtures of Singlet and Triplet Methylene

Sir:

Triplet methylene reacts with olefins to form alkyl diradicals, as in the addition to RCH=CHR to form $R\dot{C}H\text{-}CHR\text{-}\dot{C}H_2$; the diradicals undergo various further reactions leading to stable products, including the ring-closure reaction to form the substituted dimethylcyclopropanes (DMC).[1–5] Stereospecificity in the formation of the *cis*- and *trans*-DMC molecules from the corresponding 2-butenes has been widely used as a criterion for identification of the reactions of singlet methylene, assuming complete retention of orientation of the methyl groups.[6] The absence of complete stereospecificity for some methylene reactions, and therefore evidence for the presence of an appreciable fraction of triplet methylene, has been demonstrated in several systems, most prominently the photosensitization reactions of ketene by Hg 6($^3P_1$) in the gas phase,[7] of diazomethane by benzophenone in the liquid phase,[8] and the collisional deactivation of methylene in excess Ar or N_2.[9]

The degree of nonstereospecificity in triplet methylene reactions depends directly upon the relative rate constant, k_1, of the ring-closing reaction in competition with the rate of rotation, k_2, about the C–C bonds in the diradical. If $k_1 \gg k_2$, the triplet reactions would also be completely stereospecific. If $k_1 \ll k_2$, the same distribution of DMC molecules would be anticipated from either 2-butene as the reaction partner. We present here evidence for the latter: rotation *is* much more rapid than ring closure, at least in the gas phase, and the resulting DMC molecules are formed in the same ratio, within the errors of measurement, from triplet methylene reaction with either 2-butene as the precursor.

Our experimental procedure has involved the formation of CHT by photolysis of CHTCO in the presence of (a) 2-butene alone; (b) 2-butene + O_2; and (c) 2-butene + CH_3X (X = I or Br). The O_2 serves as a total scavenger for all triplet products;[10–12] CH_3I pre-

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[1] H. M. Frey, *Progr. Reaction Kinetics*, 2, 131 (1964).

[2] W. Kirmse, "Carbene Chemistry," Academic Press Inc., New York, N. Y., 1964, including chapters by H. M. Frey and P. P. Gaspar and G. S. Hammond.

[3] J. Hine, "Divalent Carbon," The Ronald Press Co., New York, N. Y., 1964.

[4] J. Bell, *Progr. Phys. Org. Chem.*, **2**, 1 (1964).

[5] W. B. DeMore and S. W. Benson, *Advan. Photochem.*, 2, 219 (1964).

[6] R. C. Woodworth and P. S. Skell, *J. Am. Chem. Soc.*, **81**, 3383 (1959); **78**, 4496 (1956).

[7] F. J. Duncan and R. J. Cvetanović, *ibid.*, **84**, 3593 (1962).

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

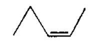
[9] H. M. Frey, *ibid.*, **82**, 5947 (1960).

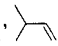
[10] R. W. Carr Jr., and G. B. Kistiakowsky, *J. Phys. Chem.*, **70**, 118 (1966).

[11] C. McKnight and F. S. Rowland, *J. Am. Chem. Soc.*, **88**, 3179 (1966).

[12] C. McKnight, E. K. C. Lee, and F. S. Rowland, *ibid.*, **89**, 469 (1967).

Table I. Products from Methylene Reactions with 2-Butene

Reactants^a		Additive/ 2-butene	Total pressure, mm	Exciting wave-length	Relative yields^b			
2-Butene	Additive							
cis	CH_3I	4	100	3660	1.00	0.36	0.00	0.03
trans	CH_3I	4	100	3660	1.00	0.34	0.03	0.00
cis	O_2	0.02	800	3130	0.02	1.00	0.00	0.77
cis	. . .	. . .	800	3130	0.27	1.00	0.09	0.73
			Estd	Singlet	0.02	0.91	0.00	0.69
				Triplet	0.25	0.09	0.09	0.04
cis	CH_3I	4	500	3130	1.33	1.00	0.00	0.52
cis	CH_3I	10	500	3130	0.92	1.00	0.00	0.55
			Estd	Singlet	0.02	0.69	0.00	0.55
				Triplet	0.90	0.31	0.00	0.00
trans	CH_3I	10	500	3130	1.00	0.12	0.38	0.00
trans	O_2	0.02	1100	3130	1.00	0.00	0.88	0.00
trans	O_2	0.02	300	3660	1.00	0.03	0.78	0.00
trans	. . .	. . .	300	3660	1.00	0.25	0.41	0.03
cis^c	Hg* 6(^{3}P) + CH_2CO		500	2537	1.27	1.00	0.50	0.79
cis^d	CH_2N_2 in 1600-fold excess Ar		>2100	4358	0.96	1.00	0.59	0.61

[a] All samples contain a few millimeters of CHTCO. [b] Other products (=, , , etc.) are not listed. [c] Ref 7. [d] Ref 9.

vents the formation of triplet products involving monoradicals in their formation but does not totally suppress the diradical reactions; both mono- and diradical processes proceed in the presence of CH_3Br, or of 2-butene alone. An extensive series of reactions has been carried out at 3130 and 3660 Å with each 2-butene, over a total pressure range from 15 to 1100 mm. Additional experiments with CH_3Br present were carried out at 2860 Å. The photolysis procedures and radio gas chromatographic analyses were routine,[11,12] while the use of radioactive ketene and the assay of radioactive products has ensured that all products contained CHT from the original CHTCO. The lack of isomerization of small macroscopic amounts of nonradioactive *cis*-DMC during the formation of the usual mixture of radioactive products demonstrated that the DMC molecules are stereochemically stable under the photolytic conditions employed. Singlet methylene, as observed at high pressures in the presence of O_2, forms only the stereospecific DMC and 2-pentene. At lower pressures, geometric isomerization to the opposite DMC is observed; at the lowest pressures, additional formation of both 2-pentenes is found, as the result of structural isomerization of the excited 1,2-DMC molecules.[13] The 2-butenes showed negligible isomerization under all photolytic conditions employed.

The first two lines of data in Table I show that the *trans*-DMC/*cis*-DMC ratio is approximately 2.9 from both 2-butenes at 3660 Å and indicate a diradical for which rotation is much more rapid than ring closure. Simultaneously, very little insertion into C–H bonds to form the corresponding 2-pentene is found, and one can conclude that the reacting CHT must be >95% triplet. The next several lines of Table I contain typical data for a variety of experimental conditions. The data with CH_3Br are completely consistent with these data, with ratios of *trans*-DMC/*cis*-DMC approaching 2.9 at high CH_3Br/2-butene compositions, *e.g.*, at CH_3Br/2-butene = 84, the ratios are 2.0 and 3.4 from *cis*- and *trans*-2-butene, respectively. By assuming that the DMC and 2-pentene products from triplet reaction favor the formation of the *trans* isomer over the *cis* by ratios of 2.9 and 2.2,[14] the pure 2-butene and excess CH_3X experiments can be divided into singlet and triplet components, as shown in Table I for two sets of the experimental data. Summation of the various C_5 hydrocarbon components (including those not listed in Table I) indicates that about one-half of the methylene reacting with 2-butene was singlet in 10-fold excess CH_3I,[15] and about three-fourths was singlet in 2-butene without additives. The ratio of C–H insertion to double-bond addition is somewhat different for the two O_2-scavenged *trans*-2-butene samples irradiated at different wavelengths and apparently depends to some extent on the other parameters of the system.

Inasmuch as the quantum yield is essentially unity at all pressures for 2860-Å irradiations,[16] the observed reactions at this wavelength must be those of free methylene. The low-pressure experiments at 3130 Å (quantum yield = 0.8 at 75 mm)[17] must also largely be the reactions of the free CHT, while the general consistency of all experiments at all pressures and wavelengths suggests that possible complications from reactions with 2-butene of excited ^{1}CHTCO or ^{3}CHTCO are of negligible importance.

The data of Duncan and Cvetanović[7] and of Frey,[9] as shown in the last two lines of Table I, are semiquantitatively similar to our own data at 3130 Å and apparently also correspond to a mixture of reactions of both $^1CH_2$ and $^3CH_2$, with the latter predominating. Our gas-phase results on the relative magnitudes of k_1 and k_2 are not necessarily directly applicable to the liquid-phase experiments involving the photosensitization of benzophenone. However, inasmuch as Hammond, *et al.*, reported appreciable yields of insertion

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(13) D. W. Setser, B. S. Rabinovitch, and J. W. Simons, *J. Chem. Phys.*, **40**, 1751 (1964).

(14) ΔG_{298}(*cis*-2-pentene $\rightleftarrows$ *trans*-2-pentene) = −460 cal/mole; K_{298}(*cis* $\rightleftarrows$ *trans*) = 2.2. The ratio of 2.9 for *trans*-DMC/*cis*-DMC also corresponds closely to the thermodynamic equilibrium ratio at the temperature of the experiment.

(15) Determination of the fraction singlet actually present in the system requires the additional assay of all products of both singlet and triplet reaction with CH_3X.

(16) A. N. Strachan and W. A. Noyes, Jr., *J. Am. Chem. Soc.*, **76**, 3258 (1954).

(17) G. A. Taylor and G. B. Porter, *J. Chem. Phys.*, **36**, 1353 (1962).

products in similar experiments with cyclohexene, which they attributed to "insufficient filtering of radiation,"[8] it seems quite likely that the reacting methylene in those experiments also contained a singlet component.[18]

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[18] See also L. M. Stephenson, D. G. Whitten, G. F. Vesley, and G. S. Hammond, *J. Am. Chem. Soc.*, **88**, 3665 (1966). Some substrates react with singlet benzophenone before it can cross over to the triplet state.

[19] Applied Research Laboratory, Ford Motor Co., Dearborn, Mich.

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The Reaction of Functionally Substituted Ylides with Organoboranes

Sir:

We have already reported that dimethyloxosulfonium methylide (I, M = $(CH_3)_2SO$) reacts with organoboranes to afford the corresponding homologated boranes (*e.g.*, IIIa).[1] Since our initial report this reaction has been extended to include several diverse classes of ylides. Thus, both trimethylammonium methylide (I, M = $(CH_3)_3N$)[2] and triphenylphosphonium methylide (I, M = $(C_6H_5)_3P$)[3] have been shown to react with organoboranes in a manner analogous to I.

$$\underset{\text{I}}{\overset{+}{M}\overset{-}{C}H_2} + R_3B \longrightarrow \underset{\text{II}}{[\overset{+}{M}CH_2\overset{-}{B}R_3]} \longrightarrow \underset{\substack{\text{IIIa, } n\,=\,1\\ \text{b, } n\,=\,2}}{R_2B(CH_2)_nR} + M$$

Moreover, we have shown[4] that use of dimethylsulfonium methylide (I, M = $(CH_3)_2S$) yields principally monohomologated boranes, thus avoiding the problem of higher homologation (*i.e.*, formation of IIIb) apparent in the reactions of the oxosulfonium ylide with boranes. Recently it has been demonstrated[5] that the homologation of organoboranes can be accomplished through the use of carbon monoxide in the presence of borohydride.

The results of the ylide–organoborane reactions discussed above suggest that boron-bound organic groupings might be functionalized through the selection of an appropriately substituted ylide provided that such ylides would be sufficiently reactive to attack boron and form the requisite betaine intermediates. Such a process, in concert with hydroboration, would provide a facile means of functionalizing olefins.

We wish to report that several functionally substituted ylides do indeed react with organoboranes in a manner analogous to the more reactive methylene ylides. For example, ethyl (dimethylsulfuranylidene)-acetate[6] reacts with a variety of organoboranes (*cf.* Table I) to afford the corresponding functionally homologated derivatives. These homologated boranes

$$R_3B + \underset{\text{IV}}{(CH_3)_2\overset{+}{S}\overset{-}{C}HCO_2C_2H_5} \longrightarrow \underset{\text{V}}{[R_2BCHRCO_2C_2H_5]} + (CH_3)_2S$$

$$R_2BCHRCO_2C_2H_5 \xrightarrow{[O]} RCH_2CO_2C_2H_5 + 2ROH$$

are then cleaved to the corresponding saturated esters, rather than the α-hydroxy esters, under the usual conditions of organoborane oxidation[7] (*i.e.*, alkaline hydrogen peroxide treatment). This latter process is similar to the alkali-induced dealkylation of the monoalkylboranes derived from *cis*- and *trans*-α,α'-dimethylstilbenes and supports the contention that this fission depends on the ability of the boron-bound organic group to sustain a negative charge.[8] This mode of boron–carbon bond fission may be referred to as hydrolytic cleavage. In the case of V, the cleavage of the functionalized substituent can be brought about by alkali in the absence of peroxide.

Table I. Functionalization of Olefins by Hydroboration Followed by Reaction with IV

Alkene[a]	Product[b]	Yield,[c] %
1-Hexene	Ethyl *n*-octanoate	49
1-Heptene	Ethyl *n*-nonanoate	52
1-Octene	Ethyl *n*-decanoate	48
2-Methyl-1-pentene	Ethyl 4-methylheptanoate	40
Cyclopentene	Ethyl (cyclopentyl)acetate	35
Norbornene	Ethyl (*exo*-2-norbornyl)acetate	31
Phenyl[d]	Ethyl phenylacetate	45

[a] The hydroboration was carried out so as to ensure the formation of trialkylborane. See ref 7. [b] The products were characterized by direct comparison or by comparison of their physical and chemical properties with those reported in the literature. [c] The yields are based on R_3B using a 4:1 molar ratio of ylide to organoborane. [d] Triphenylborane, purchased from the Aldrich Chemical Co., Milwaukee, Wis.

When a 1:1 molar ratio of IV to organoborane is used in the reaction, the yields of functionalized ester, obtained after oxidation of the resultant borane, are excellent. Thus 87% of the theoretical amount[9] of ethyl *n*-nonanoate is obtained from an equimolar mixture of tri-*n*-heptylborane and IV. Similarly 80% of the theoretical quantity of ethyl phenylacetate may be obtained from equimolar amounts of triphenylborane and IV. The efficiency of the process drops markedly after the functionalization of one of the boron-bound groups. The over-all yields of product ester, based on R_3B, are in the range 31–52% if an excess of ylide (*i.e.*, 4:1 molar ratio) is used;[10] however, the unhomologated alcohols, the major by-products in the reaction, are readily separable from the product esters, thus affording the reaction definite synthetic utility. Examination of Table I indicates that less hindered trialkylboranes produce the highest yields of functionalized product.

The general procedure used is illustrated by the reaction between tri-*n*-heptylborane and IV. Tri-*n*-

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[1] J. J. Tufariello and L. T. C. Lee, *J. Am. Chem. Soc.*, **88**, 4757 (1966).

[2] W. K. Musker and R. R. Stevens, *Tetrahedron Letters*, 995 (1967).

[3] R. Koster and B. Rickborn, *J. Am. Chem. Soc.*, **89**, 2782 (1967).

[4] J. J. Tufariello, P. Wojtkowski, and L. T. C. Lee, *Chem. Commun.*, 505 (1967).

[5] M. W. Rathke and H. C. Brown, *J. Am. Chem. Soc*, **89**, 2740 (1967).

[6] K. W. Ratts and A. N. Yao, *J. Org. Chem.*, **31**, 1185 (1966).

[7] G. Zweifel and H. C. Brown, *Org. Reactions*, **13**, 1 (1963).

[8] A. J. Weinheimer and W. E. Marisco, *J. Org. Chem.*, 27, 1926 (1962).

[9] Since the maximum yield of ester to be expected from the reaction of equimolar quantities of organoborane and ylide is 33% based on R_3B, a 29% over-all yield of ester would correspond to 87% of the theoretical amount.

[10] Attempts to functionalize all three boron-bound groups by further increasing the ylide:organoborane ratio were unprofitable, since it was observed that substantial quantities of by-products derived from the ylide were formed in such experiments.