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## References and Notes

- (1) (a) Presented at the 58th Annual C.I.C. Meeting, Toronto, 1975, and in part at the International Conference on Nucleophilic Substitutions, Pocono Manor, Pa., 1975; (b) From the M.S. Thesis of C. D. Malkiewich, submitted in partial fulfillment of the degree requirements, University of Guelph.
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# Gas-Phase Methylene Reactions with Carbonyls.

## 1. Propanal

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**Abstract:** Gas-phase reactions of methylene with propanal in oxygen scavenged systems have been studied over a pressure range of 8 to 100 Torr. The reaction products were butanal, 2-methylpropanal, epoxybutane, and methyl propionate. No chemically activated isomerization or decomposition was observed over the pressure range. Large yields of methyl ethyl ketone were observed but were formed almost entirely from direct reaction of propanal with diazomethane, the methylene precursor. The relative reactivity of singlet methylene with  $C=O:C-H(\alpha):C-H(\beta)$  is 1.0:0.05:0.08; the  $C=O$  reactivity relative to the  $C-H$  bonds in neopentane was 4.8. A direct insertion reaction into the  $C=O$  bond is thought to be a more likely pathway to the epoxide than a biradical intermediate formed by addition of the methylene to the oxygen end of the  $C=O$ . Methyl propionate is attributed to reaction by  $^3CH_2$  with propanal, followed by reactions of the intermediate with oxygen.

## Introduction

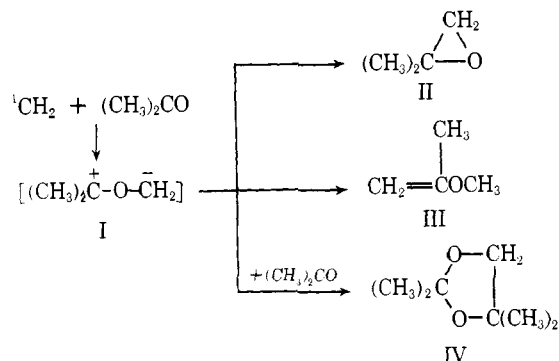
The reactions of methylene ( $CH_2$ ), the simplest carbene, have been of continued interest since Doering's initial work in 1956.<sup>1</sup> Nevertheless, a perusal of the recent reviews<sup>2,3</sup> indicates that there is little qualitative, and virtually no quantitative, information on the gas-phase reactions of methylene with carbonyls.

Back's<sup>4</sup> studies of reactions of methylene produced by photolysis of ketene in unscavenged propanal and ethanal systems is of limited value because of (1) the substantial reaction of methylene with ketene itself, (2) the occurrence of both triplet and singlet state methylene reactions, and (3) the significant photodecomposition of the carbonyl reactants and products at the wavelengths employed. Thus even such basic questions as the relative reactivity of  $C=O$  addition to  $C-H$  insertion and the mechanism of  $C=O$  addition are largely unanswered.

Some studies have been reported on methylene interactions with  $CO_2$ <sup>5</sup> and a great deal of work has been done on the ketene system.<sup>5a,6,7</sup> Although these molecules contain a  $C=O$  bond rather different from the carbonyl compounds, three general observations are relevant. Matrix isolation studies<sup>5b</sup> on  $CO_2$  showed that the intermediate has spectral characteristics most indicative of an  $\alpha$ -lactone structure, although the presence of

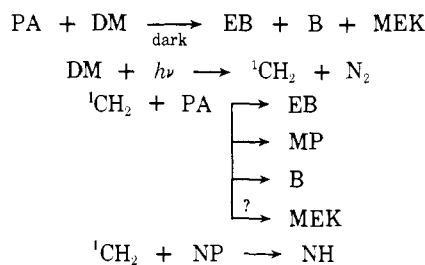
the open chain biradical  $O=\dot{C}-O-\dot{C}H_2$  could not be completely excluded. Both product formation in the gas-phase<sup>6</sup> and matrix studies<sup>7</sup> on ketene support a mechanism involving  $C=C$  addition as the primary adduct rather than interaction with the  $C=O$  end of the molecule. Finally, the rate of  $^1CH_2$  reaction with ketene is probably over a 100 times faster than the  $^3CH_2$  rate.<sup>6d</sup>

Bradley and Ledwith have considered the mechanism of singlet methylene reaction with the carbonyl group in liquid acetone.<sup>8</sup> In addition to direct addition across the  $C=O$  bond they proposed a singlet dipolar intermediate I which can close



to form the epoxide II, undergo a five-center cyclic hydrogen shift to give 2-methoxypropene (III), or add to a second acetone molecule to give 2,2,4,4-tetramethyl-1,3-dioxolane (IV). In the liquid phase the last product is formed in the highest yield. Additions to the nonbonded electrons of the oxygen atoms have also been postulated as intermediates in the insertion into the C-O bonds of ethers and perhaps the O-H bonds of alcohols.<sup>9</sup>

In this paper the results of the reactions of singlet methylene with propanal (PA) in oxygen scavenged systems are reported.<sup>10</sup> Neopentane (NP) was added to the reaction mixture for use as an internal standard<sup>11</sup> since its only reaction product from singlet methylene is neohexane (NH) which is entirely stabilized at the pressure range used.<sup>12</sup> The resulting C<sub>4</sub>H<sub>8</sub>O products formed were butanal (B), 2-methylpropanal (MP), 1,2-epoxybutane (EB), and probably some methyl ethyl ketone (MEK). Except for MP, these products were also produced by direct reaction of propanal with diazomethane (DM),<sup>13</sup> the methylene precursor. This reaction necessitated correction of the yields. Over the pressure range of 10-100 Torr, no significant chemically activated isomerization of these products could be measured. The product spectrum is accounted for by the following reactions:



In addition to the C<sub>4</sub>H<sub>8</sub>O products, methyl propionate (C<sub>4</sub>H<sub>8</sub>O<sub>2</sub>) was found in substantial yields when oxygen was present in the reaction vessel. No analogous product has been reported in methylene-hydrocarbon systems. As will be discussed, this product is attributed to consecutive reaction between triplet methylene, oxygen, and propanal in some as yet undetermined order.

The reaction of methylene with carbonyls yields intermediates which are isoelectronic with those produced by oxygen atom reactions with olefins which have been extensively studied.<sup>14-19</sup> Comparison of the reaction product spectrum from the two radical precursors may give information about the mechanism, spin state, and energetics associated with the methylene-carbonyl systems. For our work the reactions of O(<sup>3</sup>P) and O(<sup>1</sup>D) with 1-butene are particularly relevant.<sup>14,15a</sup>

## Experimental Section

**Materials.** Diazomethane was prepared according to the method described by Frey<sup>20</sup> and stored in a butyl phthalate matrix at liquid nitrogen temperatures. Ketene was generated from the pyrolysis of acetic anhydride.<sup>21</sup> Propanal was obtained from Eastman Kodak and distilled to give a 99% pure material as indicated by gas chromatographic analysis. Neopentane (Phillips, 99% pure) and oxygen (Matheson, bone dry grade 99%) were used directly from the cylinders. Pure samples of the products were obtained commercially except propenyl methyl ether which was prepared by pyrolyzing a sample of 1,2-epoxybutane at 350 °C. As expected from the isomerization of other epoxides,<sup>22</sup> two pyrolysis products formed in small amounts were tentatively identified by mass spectrometry as the *cis* and *trans* isomers.

The experiments were done in a conventional grease and mercury-free glass vacuum line capable of reaching an ultimate vacuum <10<sup>-4</sup> Torr. The reaction vessel was a glass cylinder with a volume of about 350 cm<sup>3</sup>. Pyrex flats were fastened with Torrseal (Varian) to the ends of the cylinder. The light source was a PEK Model 911 system using a 200-W high-pressure mercury arc lamp. A 436-nm

interference filter was employed to select the wavelength of light used to photolyze the reaction mixtures. The filter was obtained from Industrial Optics and had 40% transmission with a half-bandwidth of ±10 nm. Changes in the relative intensity of transmitted light were monitored with a RCA 910 phototube; no attempt was made to monitor the absolute intensity of the light. Irradiations were generally run for 1 h.

A 1/8 in. × 40 ft stainless steel gas chromatography column filled with 10% polypropylene glycol on Anakom C22-A and run at 60 °C was used to separate the components of the reaction mixture. The products were identified by comparison of their retention times with known samples on the aforementioned column and on a silicon oil boiling point column. In addition, the mass spectra of 1,2-epoxybutane, butanal, methyl ethyl ketone, and methyl propionate were taken and compared with spectra of known samples.

The peak areas were determined by electronic integration. The measured sensitivity of the flame ionization detector to the reactants and products relative to propanal equal to 1.00 was neopentane 1.88, neohexane 2.33, 2-methylpropanal 1.49, 1,2-epoxybutane 1.56, butanal 1.41, methyl ethyl ketone 1.43, and methyl propionate 1.15.

## Results

The reactions of methylene with propanal produced 1,2-epoxybutane, butanal, 2-methylpropanal, methyl propionate, and methyl ethyl ketone. No product was observed at the retention time of *cis* methyl propenyl ether.<sup>23</sup> A comparison of the total C<sub>4</sub> product yield was made with that obtained in photolysis of oxygen scavenged neopentane mixtures. The C<sub>4</sub> yield was within the experimental error of the total CH<sub>2</sub> produced taking into account the production of about 20% triplet methylene. Some cloudiness was observed in the reaction vessel, and after several runs the vessel's walls were coated with a film. No attempt was made to analyze this film. It did not appear, however, to significantly affect the relative yields of the volatile products formed.

Several experiments were run to show that the system was well behaved. Mixtures of all the reactants except diazomethane were photolyzed; no products were observed. Irradiation of a mixture of the reaction products had no effect on their absolute yields, eliminating the possibility of secondary photolysis of the products. Varying the oxygen from 3 to 30% concentrations did not affect the yields within experimental error except that of methyl propionate which decreased sharply at lower oxygen concentrations (*vide infra*).

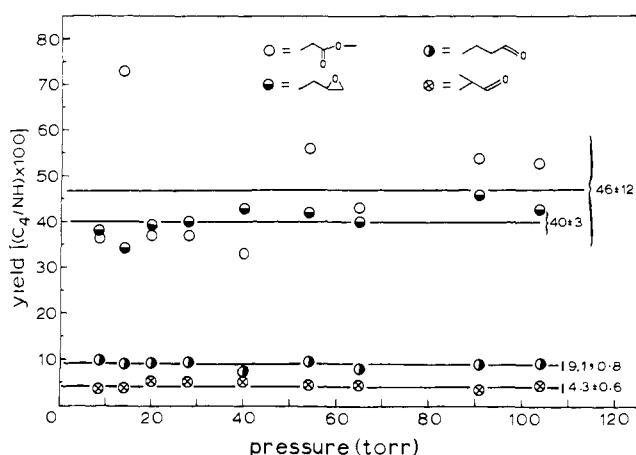
There was some expectation that a significant dark reaction might occur between diazomethane and propanal.<sup>13</sup> In fact, sampling of the reaction mixture before photolysis showed substantial yields of MEK, EB, and B. No neohexane was observed, indicating that no singlet methylene had been generated. The ratio of these three products was 16 ± 3.7:3.4 ± 0.9:1.0 ± 0.2 for MEK:EB:B, respectively, and was independent of the pressure in the reaction vessel over a range 40 to 140 Torr.<sup>24</sup> These products were thought to arise from a dark reaction, but the absolute yield of these products was nearly independent of the time the reactants were in the vessel. The effect is attributed, therefore, to a rapid surface reaction occurring in the gas sampling loop of the gas chromatograph. The problem could, in theory, be eliminated by complete photolysis of the diazomethane in the reaction vessel. In fact, this condition was seldom attained, and corrections for this "loop" effect had to be made.

The results for runs at a number of pressures are listed in Table I. Yields are given relative to the yield of neohexane. They have been corrected for the initial reactant concentration ratio of propanal to neopentane and have been averaged and then corrected for the "loop" reaction as follows: the uncorrected yields observed for MEK were very large relative to the other C-H insertion products and showed a distinct increase at higher pressures not observed for MP and methyl propionate which are the products not formed in the "loop" reaction. Since the statistically expected value for MEK of about one-half that

**Table I.** Yields of C<sub>4</sub> Products in Reactions of Methylene with Propanal<sup>a</sup>

Reactant total pressure, Torr	Number of measurements	Relative yield (×100) <sup>b</sup>			
		EB	B	MP	Methyl propionate
8.5 ± 2 <sup>c</sup>	7	38 ± 13	9.9 ± 4.9	3.5 ± 0.8	36 ± 20
14 ± 1	2	34 ± 4	9.0 ± 1.0	3.8 ± 0.4	73 ± 34
20 ± 1	2	39 ± 2	9.1 ± 1.7	5.2 ± 0.7	37 ± 3
28	1	40	9.1	5.1	37
40 ± 1	2	43 ± 27	7.3 ± 4.9	5.1 ± 3.4	33 ± 2
54 ± 3 <sup>d</sup>	5	42 ± 28	9.4 ± 7.0	4.6	56
65 ± 1 <sup>d</sup>	3	40 ± 12	7.8 ± 2.7	4.4 ± 1.0	43 ± 19
91	1	46	9.1	3.7	54
104 ± 1	4	43 ± 25	9.0 ± 6.1	4.5 ± 1.0	53 ± 4
Av		40 ± 3	9.1 ± 0.8	4.3 ± 0.6	46 ± 12

<sup>a</sup> Reaction mixtures consisted of 1:1:1:10 ratio of oxygen, neopentane, diazomethane, and propanal, respectively. <sup>b</sup> Yields are given relative to the neohexane yield and have been corrected for the direct reaction of diazomethane with propanal. <sup>c</sup> Oxygen concentrations ranged from 3 to 30% with no appreciable effect on the C<sub>4</sub>H<sub>8</sub>O yields. Methyl propionate yield given for 10% oxygen runs (see Table II). <sup>d</sup> Variation of irradiation times from 1 to 3 h showed no significant trends in the yields.



**Figure 1.** Plot of C<sub>4</sub> product yields as a function of pressure from the reaction of methylene with propanal in a 10% oxygen scavenged system. Yields are relative to that of neohexane (NH) formed from the neopentane added as an internal standard. Lines are the average values for each product assuming no pressure dependence in the yield.

of MP was a factor of 10 to 100 less than that actually obtained, it was assumed all the MEK arose from the "loop" reaction. The yields of EB and B were then reduced according to the ratio of these products found for the "loop" reaction. This correction not only greatly reduced the scatter of the EB and B average yields but also removed the apparent pressure trends in their yields.

The insensitivity of the four product yields with pressure is depicted in Figure 1. A least-squares analysis of a kinetic plot of the data, i.e., the reciprocal of the C<sub>4</sub> yield vs. the reciprocal pressure, indicates that the slopes are less than 0.04 Torr and the infinite pressure intercept is within 10% of the average values shown in Table I.

The relative rates of singlet methylene reaction with the different positions in the propanal molecule can be calculated from the average values of the product ratios given in the last line of Table I. Adjusting the average values for the statistical number of C-H bonds at each position in propanal and neopentane, the following per bond rates are obtained relative to insertion into the C-H bond of neopentane:  $k(\text{C}=\text{O}) = 4.8$ ,  $k(\text{C}-\text{H}, \beta) = 0.36$ ,  $k(\text{C}-\text{H}, \alpha) = 0.26$ .

The surprise appearance of methyl propionate as a reaction product instigated several changes in reaction conditions designed to characterize the source of this compound which contains an additional oxygen atom. A series of runs at 8 Torr and varying oxygen concentrations were done with the results

**Table II.** Yield of Methyl Propionate at Different Oxygen Concentrations<sup>a</sup>

O <sub>2</sub> /PA	Rel yield methyl propionate (×100) <sup>b</sup>
0	<1.4
3.5	4.4
7.1	18
8.3	13
10.0	36
58.4	30

<sup>a</sup> All runs at 8.5 ± 0.5 Torr total pressure. <sup>b</sup> See footnote b, Table I.

given in Table II. As with the methyl propionate results in Table I, there is considerable scatter in the data. Nevertheless the very marked oxygen sensitivity is indicated with the methyl propionate yield rising rapidly with increasing oxygen concentration up to 5-6% and leveling off at a relative value of about 30, somewhat lower than the average value at higher pressure (Table I). Photolysis at  $\lambda \approx 360$  nm using ketene as the methylene precursor gave no C<sub>4</sub>H<sub>8</sub>O products or methyl propionate when oxygen was not present and only methyl propionate when 10% oxygen was added. Since ketene photolysis at this wavelength produces greater than 90% triplet methylene,<sup>25</sup> the methyl propionate is attributed to <sup>3</sup>CH<sub>2</sub> reactions. This conclusion is consistent with no decrease in the C<sub>4</sub>H<sub>8</sub>O product yield accompanying the methyl propionate yield changes with increasing O<sub>2</sub> concentration.

## Discussion

**Comparison with Previous Work.** The only previously reported work on methylene reactions with propanal was done by Back<sup>4</sup> who photolyzed ketene at >350 nm in propanal and CO<sub>2</sub> mixtures at 85 and 44 °C over total pressure ranges of 20 to 600 Torr. The principal products observed were C<sub>1</sub> and C<sub>2</sub> molecules; small amounts of C<sub>4</sub> products were observed in yield about 1/100 of the smaller molecules. At 44 °C the ratios of EB:MEK:MP were about 2:1.5:1 with a decreasing total yield at increasing pressures. No butanal was found. The present work using diazomethane shows relatively little similarity to Back's work. Although the low molecular weight products were not determined in our work, over 80% of the available methylene is accounted for in the C<sub>4</sub> products. We observe in addition to the three C<sub>4</sub>H<sub>8</sub>O products found by Back, yields of butanal which are larger than those of 2-methylpropanal.

The differences in the two sets of results can be attributed to the very different reaction conditions of the two experiments. The ratios of propanal to ketene ranged from 1:1–10:1 in Back's study, leading to significant reaction of the methylene with ketene itself. At the wavelength she utilized, most of the methylene is produced in the triplet state.<sup>24</sup> The low  $C_4$  yields in her system concur with our experiments in which virtually no  $C_4$  products were observed when photolyzing ketene in the absence of oxygen.

**Isomerization of Chemically Activated Products.** As seen in Figure 1, there is no indication of a pressure dependence in the product yields over the pressure range from 10–100 Torr. The energy of the chemically activated 1,2-epoxybutane is calculated<sup>26</sup> to be about 95 kcal/mol using Simon's value for the energy of the methylene produced by photolysis of diazomethane at 436 nm<sup>27</sup> and a value of  $\Delta H^\circ_{f,298} = -27.1$  kcal/mol for epoxybutane estimated by group additivity.<sup>28</sup> The Arrhenius parameters for the isomerization of 1,2-epoxybutane have not been reported, but from the studies on other epoxide systems<sup>22,29</sup> and thermochemical estimates,<sup>28a</sup> the values are probably in the range  $\log A = 14 \pm 1$  and  $E_a = 58 \pm 2$  kcal/mol. Using the average values in an RRK calculation with  $s = 16.5$ , an isomerization rate on the order of  $1 \times 10^{+7} \text{ s}^{-1}$  is obtained.<sup>30</sup> Since this rate is a factor of 10 less than the collisional stabilization frequency at 10 Torr, the decomposition to stabilization percentage would change only from 90 to 99% over our pressure range. The scatter in the present data is too large to quantitatively evaluate this change.

The excitation energy of the chemically activated 1,2-epoxybutane is 17 kcal/mol less than for 1,1-dimethylcyclopropane produced from methylene addition to isobutene<sup>11</sup> and 20 kcal/mol less than for *cis*-1,2-dimethylcyclopropane produced from *cis*-2-butene.<sup>27a</sup> These two cyclopropane derivatives had experimental structural isomerization rates of  $13 \times 10^7 \text{ s}^{-1}$  and  $7 \times 10^7 \text{ s}^{-1}$ , respectively. The vinylcyclopropane system produced from methylene addition to butadiene is chemically activated to 110 kcal/mol.<sup>26b</sup> This molecule has the same number of degrees of freedom as 1,2-epoxybutane, and the Arrhenius factors for isomerization to the pentadiene isomers are similar to those estimated for the epoxide.<sup>26b</sup> RRKM calculations for vinylcyclopropane with an excitation energy of 95 kcal/mol predict an isomerization rate constant in the range  $1\text{--}3 \times 10^7 \text{ s}^{-1}$  in agreement with that estimated from the RRK calculation of 1,2-epoxybutane.

The reaction of  $O(^3P)$  with 1-butene leads to 1,2-epoxybutane formation with an internal energy of 87 kcal/mol if it assumed the oxygen atom does not possess excess translational energy. Sato and Cvetanović<sup>14c</sup> observed no decrease in the 1,2-epoxide yield between pressures of 10 to 80 Torr in agreement with the results observed in our experiments.

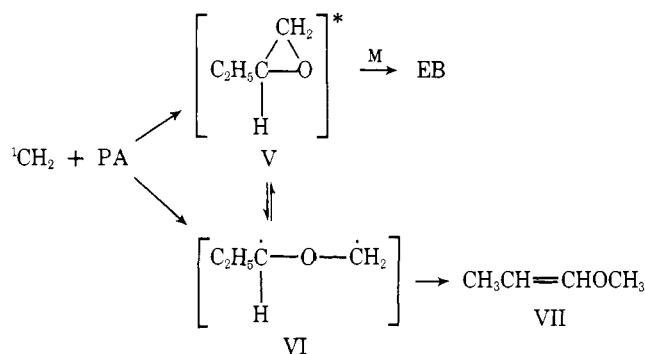
**Selectivity of Methylene Reactions with Propanal.** The sum of the average  $C_4H_8O$  product yields of 0.53 indicates that the overall reactivity of  $^1CH_2$  with propanal is about half that of neopentane on a per molecule basis. The comparison here is between twelve C–H bonds of neopentane vs. six C–H bonds and a C=O bond. The methyl propionate yield is about equal to the  $C_4H_8O$  isomers and, therefore, accounts for about 25% of the total ( $^1CH_2 + ^3CH_2$ ) methylene produced which is in reasonable agreement for the amount of  $^3CH_2$  produced in diazomethane photolysis.<sup>31,32</sup>

Since the collision diameters of neopentane and propanal probably do not differ by more than 10%, the observed bond yields of products from the aldehyde give relative rates of reaction vs. the insertion into the C–H bond of neopentane. These rates for the C–H ( $\alpha$ ) and C–H ( $\beta$ ) positions of propanal are 0.25 and 0.36, respectively. This factor of 3–4 poorer reactivity may be attributed to the extended electron-withdrawing inductive effect of the carbonyl on the C–H positions. A similar but more pronounced effect has been observed for methylene

insertion into the secondary C–H bonds of 4,4,4-trifluoro-1-butene.<sup>33</sup> This hypothesis would also be consistent with the slight preference of  $\beta$  over  $\alpha$  insertion of 1.4:1. The comparable ratios for singlet methylene C–H insertion ratios in other systems is as follows: primary to secondary in alkanes,<sup>2</sup> 0.8:1, allylic to primary in open chain<sup>2</sup> and cyclic<sup>34</sup> olefins, 1:1;  $\beta$  to  $\alpha$  in alkyl ethers,<sup>2</sup>  $\approx 0.7:1$ .

The reactivity of the C=O bond to form epoxybutane is about 18 times that of C–H insertion into the  $\alpha$  position of propanal and about 13 times that of the  $\beta$  position. The latter value is comparable with the O–H to primary C–H insertion ratio observed in 2-propanol.<sup>35</sup> Bradley and Ledwith have reported a C=O vs. C–H ratio of 15 for reactions of  $^1CH_2$  with liquid acetone.<sup>8</sup> The relative reactivity of the C=O bond in propanal compared with the C–H bond in neopentane is 4.8, about a factor of 2 lower than the ratio of C=C to C–H reactivity for singlet methylene in olefins.<sup>2</sup> The reasons for this reduced reactivity of the C=O bond vs. the C=C  $\pi$  bond is not readily apparent. We are presently studying other carbonyl systems to see if this effect is general.

**Mechanism of Reactions of  $^1CH_2$  with the C=O Bond.** In the propanal case, the two possible intermediates are the excited epoxide (V) formed by direct addition to the C=O bond and the open chain biradical structure (VI). At the excitation energy involved in these reactions V and VI may interconvert. As in other gas-phase studies there are several reasons for favoring the cyclic intermediate V as that leading to EB. First, there is no pressure dependence in the product spectrum which indicates that once EB is formed it does not isomerize to other  $C_4H_8O$  isomers. Thermal isomerization of epoxide molecules analogous to EB leads to carbonyls, alcohols, and unsaturated ethers.<sup>22,29</sup> The expected propenyl methyl ether (VII) in this system formed through intermediate VI has not been observed. The Arrhenius parameters for isobutanal formation from the pyrolysis of isobutylene oxide have been attributed to the ring opening step which is rate determining.<sup>22a</sup> The similarity of the parameters to those for isopropenyl methyl ether formation imply that ring opening is also rate determining for that isomerization. If intermediate VI were formed in our system, a substantial yield of VII would be expected. Finally, the EB



yield shows no sensitivity to changes in oxygen concentration expected if VI were scavengable, and no high boiling products were found which could be attributed to dioxolane formation by VI reacting with propanal.

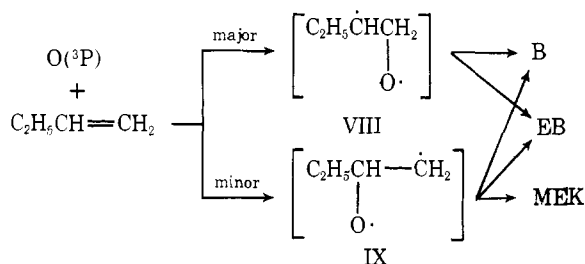
**Formation of Methyl Propionate.** The formation of methyl propionate is unusual since analogous products have not been reported in methylene reactions with hydrocarbons in oxygen scavenged systems. Methyl propionate is not formed in photolysis of a mixture of oxygen and propanal even when diazomethane was added after the photolysis. Nor was it produced in the "loop" reaction between diazomethane and propanal. These experiments eliminate the possibility of propionate formation via reaction of diazomethane with a photochemically or thermally generated intermediate such as propionic acid. Since methyl propionate was the only product formed in the

ketene photolysis at  $\approx 360$  nm where the absence of significant singlet methylene was shown by the zero yield of neohexane from neopentane, methyl propionate formation is attributed to a triplet methylene reaction.

In hydrocarbon systems,  $^3\text{CH}_2$  is quantitatively scavenged by small amounts of  $\text{O}_2$  yielding  $\text{CO}_2$  and  $\text{CO}$ .<sup>36</sup> In our system we were unable to detect these permanent gases with the FID; however, the yield of methyl propionate is large enough to account for essentially all of the  $^3\text{CH}_2$  formed.<sup>31,32</sup> This apparently complete scavenging of the  $^3\text{CH}_2$  suggests two possible mechanisms. The methyl propionate is formed either by oxygen scavenging of a triplet  $\text{C}_4\text{H}_8\text{O}$  intermediate or by propanal scavenging the intermediate formed in the reaction of triplet methylene with oxygen. This latter possibility requires that the intermediate is sufficiently long-lived to react with propanal before it decomposes to  $\text{CO}$  and  $\text{CO}_2$ , an unlikely situation in light of the hydrocarbon studies. We tend to favor, therefore, oxygen scavenging of the triplet intermediate formed in the reaction with propanal although the mechanism leading to the resulting ester is unknown.

Because the concentration of propanal is ten times greater than oxygen, the rate of  $^3\text{CH}_2$  reaction with propanal need be only one-ten times faster than with  $\text{O}_2$  to effectively compete for the  $^3\text{CH}_2$ . A rate of this magnitude has been reported for  $^3\text{CH}_2$  reactions with acetylene and with  $\text{NO}$ .<sup>6d</sup> Thus, in contrast to the slightly reduced reactivity of propanal with  $^1\text{CH}_2$  relative to the hydrocarbon systems, the carbonyl group appears more reactive toward  $^3\text{CH}_2$  than is the  $\text{C}=\text{C}$  bond. This reaction preference is the opposite of that suggested for  $^1\text{CH}_2$  reactions. These conclusions, however, remain tentative until the mechanism of methyl propionate formation is better understood.

**Comparison with Reactions of Oxygen Atoms.** The reactions of  $\text{O}(^3\text{P})$  atoms with 1-butene<sup>14</sup> typify the general pattern of reactions with olefins. Addition to the least-substituted carbon atom predominates to give a biradical intermediate which may then undergo ring closure to give an epoxide or an intramolecular hydrogen or alkyl shift to form a carbonyl. Some fragmentation products were observed; there is no C-H insertion. The triplet biradicals VIII and IX from the oxygen



reactions with 1-butene are not the same as VI from our system and would be expected to lead to different products. The B/EB and MEK/EB ratios obtained of 1 and 0.1, respectively, in the oxygen atom study support our reasoning that biradicals isomeric with the epoxide have a significant tendency to lead to open chain carbonyls.

The work with  $\text{O}(^1\text{D})$  atoms is more germane to the singlet methylene studies, but unfortunately much less has been done with olefin systems. It has been reacted with straight and cyclic paraffins to give chemically activated alcohols by insertion into the C-H bonds.<sup>37</sup> The insertion is largely indiscriminate and accounts for 65% of the reaction. The remaining pathways are hydrogen abstraction (20–30%) and molecular elimination to give carbonyls. The excited alcohols generally fragment into radical species.

It is presumed that  $\text{O}(^1\text{D})$  atoms react with olefins by addition to  $\text{C}=\text{C}$  bonds. In the gas-phase studies with 1-butene, however, the major products attributed to the reaction were

fragmentation products.<sup>14a</sup> The higher excitation energy [45 kcal/mol above  $\text{O}(^3\text{P})$ ] precluded stabilization of any appreciable amount of addition products even at pressures of 1 atm, and the mode of reaction remains in doubt. Studies in liquid nitrogen solutions with  $\text{O}(^1\text{D})$  such as are being done with  $\text{O}(^3\text{P})$  atoms<sup>15a</sup> would be very helpful. For the present, little comparison can be made with singlet methylene work, which remains the only way of directly forming epoxide intermediates in an energy range suitable for chemical activation studies.

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## Metathetical Transposition of Bis-*tert*-alkyl Ketones.

### 1. A Model for a Study of Group Migration<sup>1</sup>

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**Abstract:** Partial rate constants  $k_p^{Rm}$  for the migration of alkyl groups are conventionally determined on the basis of approximations and hypotheses such that the set of values obtained is not necessarily consistent. The metathetical transposition of bis-*tert*-alkyl ketones constitutes a model reaction for which such assumptions are reduced to a minimum. A mechanistic study of this reaction shows a sequence of steps in common with two other reactions: the pinacol rearrangement of tetrasubstituted glycols and the fragmentation of the rearranged ketones. Kinetic and tracer studies (<sup>2</sup>H and <sup>13</sup>C) on these three reactions, under strictly identical conditions of acidity which control the preequilibrium (ketone  $\rightleftharpoons$  protonated ketone), bring out the usefulness of this model reaction for studying the influence of structural parameters controlling the migration of the group Rm; these structural parameters are in fact the environments  $\mathcal{E}_{C_o}$  and  $\mathcal{E}_{C_t}$  of the origin and terminal carbons defined by the migration. The constants  $k_p^{Rm}$  for Me and Et corresponding to particular environments  $\mathcal{E}_{C_o}$  and  $\mathcal{E}_{C_t}$  have been determined:  $k_p^{Me}(\mathcal{E}_{C_o}:Me,Me/\mathcal{E}_{C_t}:t-Bu) = 775 \times 10^{-8}$  and  $k_p^{Et}(\mathcal{E}_{C_o}:Et,Et/\mathcal{E}_{C_t}:Et_3C) = 8 \times 10^{-8} s^{-1}$

Certain group properties, generally known as substituent effects, can, on the basis of a defining reaction, be assigned values which are widely applicable for the correlations of physicochemical data. For aliphatic groups the best known are the polar ( $\sigma^*$ ) and steric ( $E_s$ ) parameters.

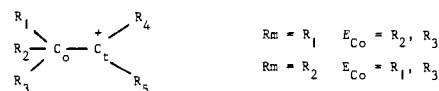
A group property of a rather different type is involved when considering the 1,2-alkyl shifts occurring in carbonium-ion rearrangements. It has not yet been possible to define for the alkyl groups a scale of migratory aptitudes<sup>2</sup> which would express the relative rates of migration of different groups. Thus ethyl vs. methyl migration aptitude varies from 35<sup>3</sup> to 17<sup>4</sup> in pinacol rearrangements and to 1 in the Wagner–Meerwein rearrangement.<sup>5</sup>

These results are probably partly due to the fact that the reactions which have been most often used to study the migration of alkyl groups (the Wagner–Meerwein rearrangement, the pinacol rearrangement, and ketone rearrangements in an acid medium<sup>6</sup>) are frequently unsuitable either because of a concerted mechanism leading to an overall phenomenon, not specifically a migration, or because of the impossibility of measuring the preequilibrium of carbonium or hydroxycarbonium ions which precede migration. For certain reactions, even the nature of the migratory group is uncertain.<sup>7</sup>

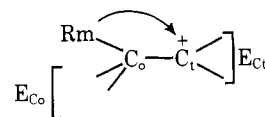
A suitable model system which allows the separation from overall kinetic data of data relating specifically to the migration step is not easy to find.

These problems have been the subject of numerous studies differing in both approach and method. In the experimental approach, the relative group migratory aptitudes are estimated from the product distribution. The results, however, cannot be extrapolated from one structure to another, since, in such intrastructural comparisons, any change in the nature of the migrating group Rm entails some modification of the environment  $\mathcal{E}_{C_o}$  of the origin carbon C<sub>o</sub> (Scheme I). Furthermore, the migratory aptitude of a migrating group Rm depends on not one but two environments associated with two reaction

Scheme I

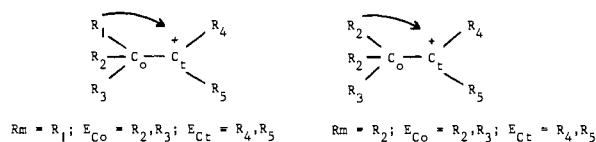


sites: the environment  $\mathcal{E}_{C_o}$  of the origin carbon C<sub>o</sub> and  $\mathcal{E}_{C_t}$  of the terminal carbon C<sub>t</sub>. Consequently, it is necessary to calculate the partial rate constants of migration ( $k_p^{Rm}$ ) for con-



stant environments using interstructural comparisons. In these studies the Rm group must migrate in comparable environments (Scheme II). Collins et al.<sup>8</sup> have shown the usefulness

Scheme II



of this approach in studying the competition between aryl groups, but as already seen the results for alkyl groups are not conclusive.<sup>3–5</sup>

Theoretical approaches to the problem of molecular rearrangements have also been presented. Balaban et al.<sup>9</sup> have proposed a formal estimation of all rearrangement pathways using a method based on graph theory. Schleyer and his co-workers, considering the same kind of analysis, have determined preferred rearrangement pathways of acyclic compounds with blocked conformations<sup>10</sup> by calculating the