unaffected by the isolation procedure, and the analysis was calibrated by known mixtures frequently.

Rate constants were calculated from the slope of a plot of bromo ketone–ketone against time, since the reactions were not carried to a large enough extent of completion to consider the variation of ketone concentration with time.

Isotopic Dilution Analysis Kinetics.—A weighed amount (≤ 80 mg) of the tritiated ketone was mixed with the heated solvent and an excess of bromine (five- to tenfold) was added and the vessel placed in the thermostat. At the desired time (1–8 days) the reaction was quenched by cooling and dilution with petroleum ether (bp 30–60°); then a weighed amount (40–50 mg) of the inactive bromo ketone was added. Successive washings with water, 0.05 *M* sodium thiosulfate, water, 10% sodium carbonate, water, and saturated brine gave a colorless solution which was concentrated to about 1–2 ml at not greater than 50° on a rotary evaporator. Further concentration or higher temperatures sometimes led to discoloration. The concentrate was then subjected to chromatography on Florisil, from which the bromo ketone was eluted with petroleum ether and then the unchanged ketone with toluene. The bromo ketone rich fractions were mixed with inactive ketone and rechromatographed, and the ketone fraction was counted; if the activity was low enough the bromo ketone fraction was chromatographed once more before uv and radioassay, but if the activity was significant, the "holdback" separation was repeated.

After the final chromatographic separation the petroleum ether was mostly removed and replaced with toluene, again taking precautions not to overheat or remove all solvent. When the volume reached about 6 ml the uv spectrum was taken and the concentration calculated [λ_{max} 327 nm (ϵ 153) in toluene]. A 5-ml sample of the same solution was transferred to a counting vial, 15 ml of scintillator solution [4 g of 2,5-diphenyloxazole and 0.1 g of 2,2-*p*-phenylenebis(5-phenyloxazole) in 1 l. of toluene] was added and the sample was counted. Efficiency of counting was determined by automatic external standardization, and varied little except when much higher concentrations of bromo ketone were used, when some quenching appeared.

Registry No.—2-Benzoylbutane-2-*d*, 18321-26-1.

Acknowledgment.—We acknowledge gratefully the support for this work by a grant from the Robert A. Welch Foundation and a predoctoral fellowship from the National Institute of General Medical Science (to E. T. W.).

The Mass Spectra of Cyclobutyl and Cyclopropylcarbinyl Methyl Ethers and the Methanolysis of Bicyclobutane[1]

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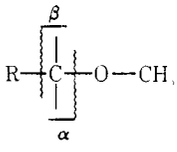
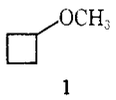
The mass spectral fragmentation patterns of cyclobutyl and cyclopropylcarbinyl methyl ethers were found to be similar and the mechanisms of the fragmentations were evaluated by use of deuterium-labeled material and by means of high-resolution mass spectrometry. In both materials the base peak was *m/e* 58, corresponding to the loss of ethylene. The mechanism of the acid-catalyzed addition of methanol to bicyclobutane was studied using the above mass spectral results. The addition was not concerted but proceeded *via* protonation to yield a bicyclobutonium ion (or equivalent activated complexes) which partially equilibrated before the nucleophilic attack of methanol occurred. When 1,3-butadiene in methanol was irradiated with ultraviolet light, cyclobutyl and cyclopropylcarbinyl methyl ethers were formed in low yield. These ethers were shown to be derived in a dark reaction of methanol with bicyclobutane.

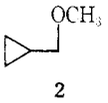
Alkyl ethers undergo two major fragmentation reactions upon electron impact in the mass spectrometer. These are "α" cleavage of the carbon–oxygen bonds leading to carbonium ions and "β" cleavage leading to oxonium ions.[3,4] The oxonium ions of ethers where both groups are larger than methyl undergo further rearrangements[3,4] which are of no concern to the present study. Generally, β cleavage has been found to yield the base peak of methyl ethers.[3]



In the course of a study of the photochemistry of 1,3-butadiene in methanol,[5] it was discovered that the mass spectra of cyclobutyl methyl ether (CBME), **1**, and cyclopropylcarbinyl methyl ether (CPCME), **2**, have one main feature which distinguishes them from the spectra reported for other methyl ethers. The



1



2

base peaks for **1** and **2** are at *m/e* 58, corresponding neither to α cleavage nor to β cleavage, but to the loss of the elements of ethylene. It was considered that these fragmentations involve cleavage of the cyclobutane and cyclopropane rings as shown in eq 1–2. In accord with eq 1 are the mass spectra of several cyclobutane derivatives which were recently reported.[6] In each case it was found that fission of the cyclobutane ring leads to the most abundant ion. Similarly it has been suggested that fission of the cyclopropane ring gives rise to the M − 28 peak in the mass spectrum of benzylcyclopropane.[7] It is of interest, however,

(1) This work was supported in part by PHS Grant No. AM-00709, National Institute for Arthritis and Metabolic Diseases, U. S. Public Health Service.

(2) (a) NASA Predoctoral Trainee, 1964–1967; (b) NSF Postdoctoral Fellow, 1964.

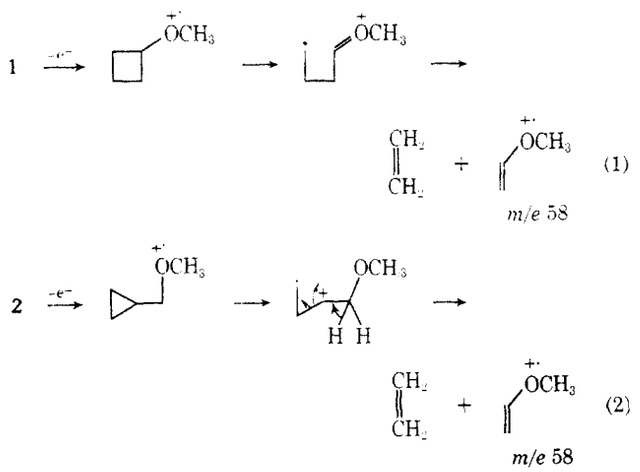
(3) F. W. McLafferty, *Anal. Chem.*, **29**, 1782 (1957).

(4) C. Djerassi and C. Fenselau, *J. Amer. Chem. Soc.*, **87**, 5747 (1965).

(5) J. H. Smith J. Saltiel, and W. G. Dauben, unpublished results.

(6) D. A. Bock and K. Conrow, *J. Org. Chem.*, **31**, 3608 (1966).

(7) N. J. Turro, D. C. Neckers, P. A. Leermakers, D. Seldner, and P. D. 'Angelo, *J. Amer. Chem. Soc.*, **87**, 4097 (1965).



(1)

(2)

that, unlike 2, cyclopropylcarbinyl *sec*-butyl ether shows no M − 28 peak.[8] Mechanisms 1 and 2 have now been investigated using specifically labeled ethers.

Cyclobutyl Methyl Ether.—CBME-1-d_1 was prepared by reducing cyclobutanone with lithium aluminum deuteride followed by reaction of the resulting alcohol with sodium hydride and methyl iodide. The infrared spectrum of the ether showed a peak at 2092 cm^{-1}, corresponding to the C–D stretching frequency. The nmr spectrum showed no detectable α proton on the cyclobutane ring and the integration of the spectrum suggested one deuterium. It was not possible by mass spectrometry to determine directly the per cent deuterium in the ether since both the molecular ion and the M − 15 peaks were very weak and since there was an appreciable M − 1 peak. As can be seen in Figure 1, the *m/e* 58 peak has moved entirely to *m/e* 59, and, assuming that all the deuterium is in the *m/e* 59 ion, it can be estimated that the percentage of deuterium in **3** is 99% 1-*d*. This figure sets the lower limit of the isotopic purity of the sample. Furthermore, the fact that at least 99% of the *m/e* 58 ion from unlabeled CBME occurs as a deuterated moiety in the mass spectrum of the deuterated ether supports the mechanism proposed in eq 1.

In the undeuterated CBME (**1**), the other peaks which are larger than 5% of the base peak are *m/e* 43 and 55. A small peak is found at *m/e* 71 (0.4%). Cleavage of the carbon–oxygen bonds account for the *m/e* 55 and 71 while *m/e* 43 requires a hydrogen migration. Mechanisms leading to these ions are suggested below and the results shown in Figure 1 substantiate the proposals. As expected, ions *m/e* 71, 55, and 43 all increase by 1 mass unit in the deuterated species. Two pathways can be suggested for the formation of *m/e* 43 ion (Scheme I). the ion being either $C_3H_7^+$ or $C_2H_3O^+$; high-resolution mass spectral results obtained with cyclopropylcarbinyl ether (see later) indicate the involvement of only the latter ion.

Cyclopropylcarbinyl Methyl Ether.—CPCME-1-d_2 was prepared by reduction of methyl cyclopropylcarboxylate with lithium aluminum deuteride followed by methylation of the resulting alcohol. The ether possessed a maximum in the infrared spectrum at 2068 cm^{-1}, characteristic of C–D bonds and the nmr

(8) S. Meyerson and J. D. McCollum, *Advan. Anal. Chem. Instr.*, **2**, 213 (1963).

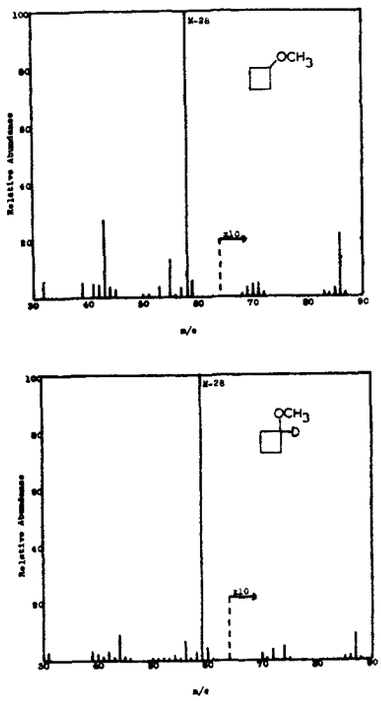
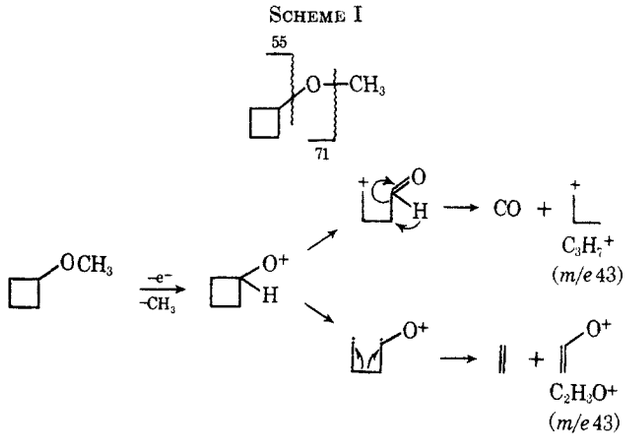


Figure 1.—Mass spectrum of cyclobutyl methyl ether.

SCHEME I



spectrum showed that absorption of the α-methylene protons was less than 5% of that for the correspond ing peak in undeuterated material. The calculated isotopic distribution is 96% 2-*d*, 3% 1-*d*, and 1% O-*d*, assuming that all α-methylene protons are in the *m/e* 58 peak which moves to *m/e* 60 in the dideuterio ether (see Figure 2). Such an assumption is reasonable since the *m/e* 58 peak was shown to be $C_3H_6O^+$ by high-resolution mass spectroscopy (see Figure 3). These mass spectrographic values agree well with the nmr results and set the lower limit for the per cent of dideuterated material. The finding that the *m/e* 58 peak moves to 60 (containing all of the deuterium) strongly supports the mechanism proposed in eq 2.

Other peaks of CPCME (**1**) found in greater abundance than 5% of the base peak are *m/e* 43 (24%), 45 (53%), 53 (8%), and 55 (31%). In addition, the M − 1 peak at *m/e* 85 is 2%; the M − 15 peak at *m/e* 71 is 1%. The fragmentation pathways given in Scheme II can be proposed to account for these ions.

The results shown in Figure 2 substantiate these proposals; in the dideuterated species the original

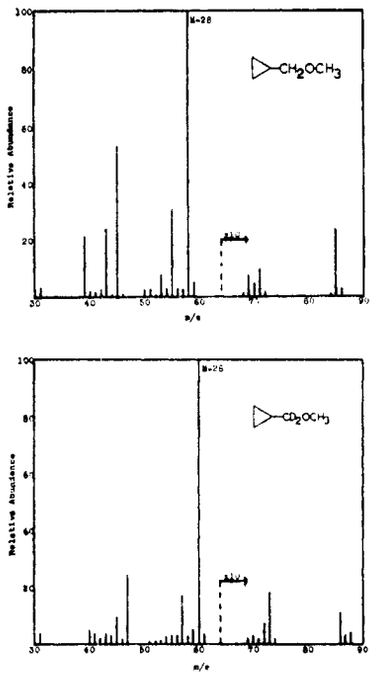


Figure 2.—Mass spectrum of cyclopropylcarbinyl methyl ether.

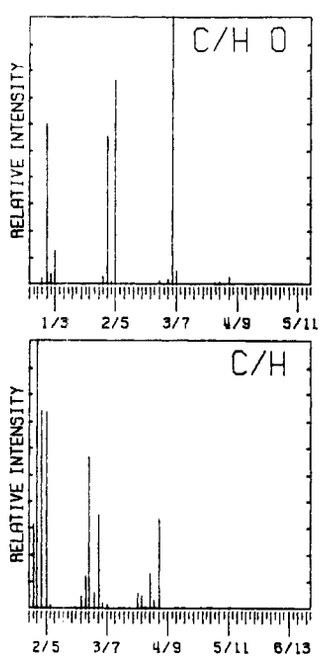


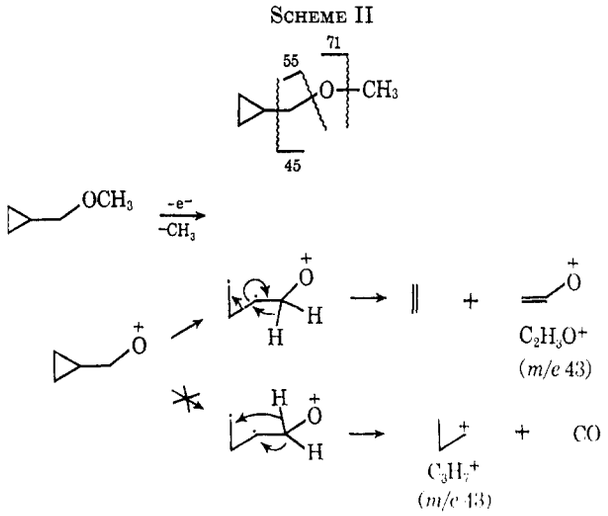
Figure 3.—High-resolution mass spectrum of cyclopropylcarbinyl methyl ether.

major peaks at *m/e* 43, 45, 55, and 71 all increase by two mass units. The high-resolution mass spectrum of CPCME is shown in Figure 3 and it proves that the compositions of the peaks found in the low-resolution spectra are, indeed, those predicted by the mechanism and, in addition, shows that the *m/e* 43 peak is due to $C_2H_3O^+$. The findings of large amounts of $C_2H_3^+$ and $C_2H_4^+$ support the mechanism for the loss of ethylene to give the *m/e* 58 peak. The nature of peak *m/e* 53 is undetermined.

When this work was completed, it was learned that Hofman had published the high-resolution mass spectrum of cyclopropylcarbinol.[9] In this spectrum the

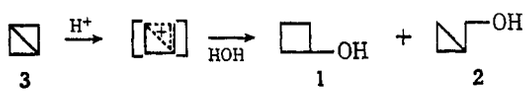
(9) H. J. Hofman, Ph.D. Thesis, University of Amsterdam, 1966.

SCHEME II



base peak was at *m/e* 44, corresponding to the loss of ethylene. His suggested fragmentation mechanism is essentially the same as that discussed above. He also proposed detailed fragmentation pathways leading to the other major peaks, substantiating many of the suggestions by observations of related metastable peaks. His results support the mechanism proposed in this investigation.

The Acid-Catalyzed Addition of Methanol to Bicyclobutane.—Numerous workers have reported that bicyclobutane (BCB, **3**) and its derivatives are unstable in the presence of dilute acid.[10] Considering the simplest case first, Wiberg[10e] found that BCB in deuterium oxide at pH 2.3 yields cyclopropylcarbinol and cyclobutanol.[10e] Moore,[10a] Doering,[10c] and Wiberg[10e] suggested that, since these products resemble those obtained from reactions thought to involve bicyclobutonium ions,[11] the same intermediate might be formed when BCB (or its derivatives) is attacked by a proton. The present study has yielded additional evidence in support of this proposal.



3 **1** **2**

A solution of BCB in neutral methanol was prepared and after an initial decrease of 10% within 13 hr, possibly attributable to oxygen in the sample tube since an equal decrease was observed when benzene was used as the solvent, no decrease in the concentration of BCB was observed after 88 hr at 50°. When a solution of BCB in methanol containing a small amount of dilute perchloric acid was allowed to stand for a short period of time, three ethers were formed: CBME, 44%; CPCME, 51%; and homoallyl methyl ether, 5%. These ethers were isolated by preparative vpc and shown to be identical with authentic samples.

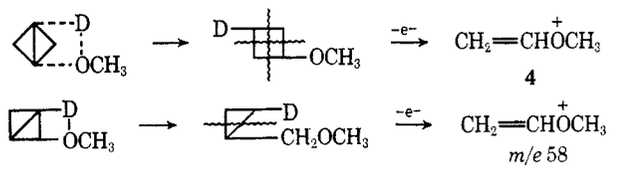
To study the mechanism of the reaction, BCB was allowed to react with methanol-O-*d* in the presence of

(10) (a) W. R. Moore, H. R. Ward, and R. F. Clark, *J. Amer. Chem. Soc.*, **83**, 2019 (1961); (b) W. G. Dauben and W. T. Wipke, *Pure Appl. Chem.*, **9**, 539 (1964); (c) W. von E. Doering and J. F. Coburn, Jr., *Tetrahedron Lett.*, 991 (1965); (d) R. B. Turner, P. Goebel, W. von E. Doering, and J. F. Coburn, Jr., *ibid.*, 997 (1965); (e) K. B. Wiberg, G. M. Lampman, R. P. Ciula, D. S. Connor, P. Schertler, and J. Lavanish, *Tetrahedron*, **21**, 2749 (1965); (f) E. P. Blanchard and A. Cairncross, *J. Amer. Chem. Soc.*, **88**, 487 (1966).

(11) For discussions of this ion, see L. Birladeanu, T. Hanafusa, B. Johnson, and S. Winstein, *ibid.*, **88**, 2316 (1966); P. von R. Schleyer and G. W. VanDine, *ibid.*, **88**, 2321 (1966).

acid; the resulting ethers were analyzed by mass spectrometry. Two samples of BCB in methanol-O-*d* were prepared, one containing 0.075 *M* perchloric acid and the other containing 0.0007 *M* acid. CBME and CPCME were isolated from each sample by preparative vpc of the crude, neutralized reaction mixtures. The mass spectra of each ether from the two sources (see Table I) showed a slightly different deuterium distribution, indicating that the concentration of acid had an effect on the products formed. As discussed earlier, an important fragment from CBME and CPCME is the vinyl ether ion (**4**), *m/e* 58 (Scheme III).

SCHEME III

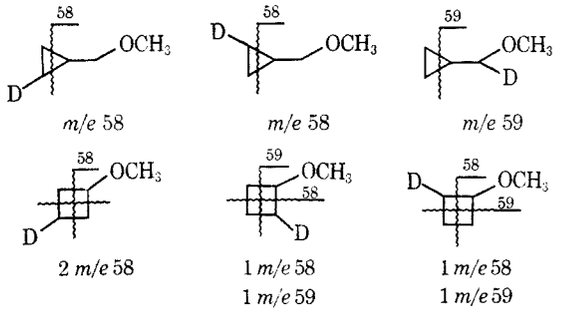


The finding of an *m/e* 59 ion (greater intensity than expected from natural abundance of ^{13}C) requires deuterium from the solvent on the α or β carbon atoms of these two ethers. Concerted addition of methanol-O-*d* to BCB would yield CBME-3-d_1 and CPCME 2-d_1, and the fragmentation of each should show no *m/e* 59 ion in the mass spectra. The finding of a significant *m/e* 59 ion is in agreement with the earlier suggestion that the acid-catalyzed addition of methanol to BCB involves an initial protonation step to give an intermediate carbonium ion which can rearrange before nucleophilic attack of methanol can occur.

TABLE I
DISTRIBUTION OF DEUTERIUM IN ETHERS

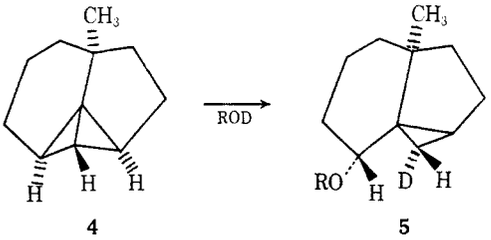
Ethers	Concn of acid, *M*	Relative amounts of $C_3H_6O^+$ and $C_3H_5DO^+$, % *m/e* 58	% *m/e* 59	% of statistical distribution
CBME	0.0007	85	15	46
	0.075	81	19	56
CPCME	0.0007	86	14	42
	0.075	83	17	50

In the carbonium ion formed, if the deuterium is statistically distributed among the methylene carbons prior to reaction with methanol, CPCME should have 33% of the deuterium on the α carbon atom. The



possible locations for the deuterium in these materials are shown above. Since in CPCME there is only one fragmentation pathway to the $C_3H_6O^+$ ion, only one of the three deuterated isomers will yield a *m/e* 59 peak and the ratio of the *m/e* 59:58 peaks should be 1:2. Consideration of the possible locations of the deuterium in CBME and the fragmentation pattern shows again that the *m/e* 59:58 ratio should be 1:2 since there are four ways to obtain the *m/e* 58 peak and only two ways to get the *m/e* 59 peak.[12] The mass spectral values (see Table I) show that the distribution of deuterium is between 42 and 56% of the statistical values. These similar data for deuterium scrambling in both CBME and CPCME may be accommodated by collapse of a protonated BCB to a bicyclobutonium ion (or rapidly equilibrating cyclobutyl and cyclopropylcarbinyl cations) whose short lifetime does not allow complete scrambling; *i.e.*, partial equilibration occurs prior to the irreversible attack of the nucleophile.

The foregoing results are in complete accord with earlier published work which indicated the involvement of similar ionic species.[10e,13] Recently, the concept of "twist" bent bonds was postulated and the concept was applied to the reactions of bicyclobutanes.[14] It was suggested that reaction of a protic solvent with the bicyclobutane derived from 3,5-hexalins[10e,15,16] might proceed by an initial nucleophilic attack by the solvent. In view of the complete parallelism of the reactions of all of the bicyclobutanes studied and a carbonium ion process, there appears to be little basis for considering a nucleophilic process in the reactions of bicyclobutanes containing only alkyl substituents. For example, the protolysis of the bicyclobutane **4** occurs with retention of configuration leading to the carbonium ion by reaction from the *endo* side of the ring, the side which has been suggested to be electron rich.[17] The subsequent addition of the anion occurs from the opposite side, a result anticipated by the involvement of a bicyclobutonium-type cation, to yield the cyclopropylcarbinyl ether **5** resulting from



4 **5**

inversion of C-6. The absence of product derived from cleavage of the center bond of the bicyclobutane cannot be taken as proof that such a bond was not initially broken[18] since the resulting cyclobutyl cation could readily rearrange to the cyclopropylcarbinyl cation. This stepwise addition has been found to occur with all bicyclobutanes containing only alkyl substituents.[13] With 1-cyano-3-methylbicyclo[1.1.0]-

(12) This analysis assumes that there is no deuterium isotope effect in the fragmentation reaction as deuterium is not directly involved in the reaction leading to the loss of ethylene; *cf.* J. K. MacLeod and C. Djerassi, *Tetrahedron Lett.*, 2183 (1966).

(13) W. G. Dauben and C. D. Poulter, *Tetrahedron Lett.*, 3021 (1967).

(14) P. G. Gassman, *Chem. Commun.*, 793 (1967).

(15) W. G. Dauben and F. G. Willey, *Tetrahedron Lett.*, 893 (1962).

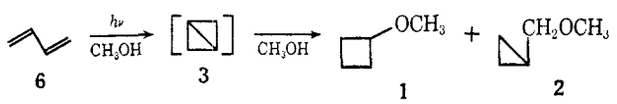
(16) G. Just and V. DiTullio, *Can. J. Chem.*, **42**, 2153 (1964).

(17) M. Pomerantz and E. W. Abrahamson, *J. Amer. Chem. Soc.*, **88**, 3970 (1966).

(18) K. B. Wiberg, *Tetrahedron*, **24**, 1083 (1968).

butane, however, electronic effects of the substituents greatly affect the reaction of the ring system and an *endo-cis* addition occurs.[10f,19] Elucidation of the mechanistic details of the reactions of this latter type of bicyclobutane awaits further study.

The Irradiation of 1,3-Butadiene in Methanol.—When a solution of 1,3-butadiene (**6**) in methanol contained in a flask which had not been base washed before use was irradiated through quartz with a 450-W Hanovia mercury lamp, about equal amounts of CBME (**1**) and CPCME (**2**) were isolated in a total yield of about 3%. Repetition of this reaction in methanol-O-*d* as the solvent gave ethers with the same deuterium distribution as the ethers obtained by the acid-catalyzed addition of the deuterated solvent to BCB (**3**).



When the irradiation of 1,3-butadiene was conducted in quartz tubes which had been washed with concentrated ammonium hydroxide and dried for 12 hr at 110°, no ethers were formed. The vpc trace of the total reaction mixture showed a peak corresponding in retention time to BCB (**3**). Upon addition of perchloric acid to make the solution 0.1 *M* in acid, the BCB peak immediately disappeared and peaks corresponding in retention time to the ethers appeared.

These studies show that in the direct irradiation of 1,3-butadiene in methanol there is no light-induced addition of solvent. This result is similar to that found[20,21] for other unconstrained 1,3-dienes and shows that the light-induced addition of a protic solvent to a 1,3-diene occurs only when the diene is constrained from adopting a nonplanar excited state.

Experimental Section

Physical Measurements.—Infrared spectra were taken in carbon tetrachloride, unless otherwise noted, using a Perkin-Elmer Model 137 Infracord. Nuclear magnetic resonance spectra were determined using a Varian Model A-60 spectrometer with samples in carbon tetrachloride containing tetramethylsilane as internal standard, unless otherwise specified. Combustion analyses were carried out by the Microanalytical Laboratory, College of Chemistry, University of California at Berkeley. Mass spectra were obtained on a CEC Model 21-103C spectrometer which was equipped with an ion multiplier and run at 70 eV. The high-resolution mass spectrum was determined on a Model CEC 110 mass spectrometer.

Cyclobutyl Methyl Ether (1).—A slurry of 297 mg (7.9 mmol) of lithium aluminum hydride in 7 ml of dry ether was cooled to 0°. A solution containing 562 mg (7.9 mmol) of cyclobutanone in 1.3 ml of dry ether was added dropwise to the cooled slurry. The reaction flask was protected from moisture with a drying tube and stirred at 0° for 0.5 hr. The aluminum salts were precipitated with saturated aqueous ammonium chloride solution. The ether was decanted from the salts, which were washed three times with ether. The combined ether layers were filtered through sodium sulfate and concentrated under a stream of nitrogen to about 2 ml.

A 1.7-g (38 mmol) sample of 53% sodium hydride suspended in mineral oil was washed twice with dry ether, suspended in 10 ml of ether, and cooled to 0°. The above ethereal solution of cyclobutanol was added dropwise to the cooled suspension. The mixture was allowed to come to room temperature and stirred for 4 hr. Methyl iodide (0.98 ml, 16 mmol) was added; the flask was stoppered and stirred for 4 days. Vpc of the crude reaction mixture showed that all of the cyclobutanol had reacted and only cyclobutyl methyl ether (CBME) had formed.

To decompose the unreacted methyl iodide, 3.8 ml (16 mmol) of tri-*n*-butylamine was added, and stirring continued for another 2 days. Vpc showed that no methyl iodide remained after this treatment.

The ethereal solution was filtered and the CBME collected by preparative vpc: $\nu_{max}^{CHCl_3}$ 1351, 1236, 1125, 1027; nmr τ 6.3 (1 H, complex multiplet, α H), 6.90 (3 H, singlet, methoxy H), 7.6–8.8 (6 H, complex multiplet, methylene H).

Cyclobutyl-1-d_1 methyl ether was prepared in an identical manner starting with 630 mg (15 mmol) of lithium aluminum deuteride and 2.13 g (30.5 mmol) of cyclobutanone. The product was isolated by preparative vpc: ν_{max} 2092, 1255, 1176, 1055, 929 cm^{-1}; nmr (external TMS) τ 6.98 (3 H, singlet, methoxy H), 7.7–8.8 (6 H, broad multiplet, methylene H).

Cyclopropylcarbinyl Methyl Ether (2).—Following the exact procedure described above, 7.0 g (81.3 mmol) of cyclopropanecarboxylic acid was reduced with 2.8 g of lithium aluminum hydride. After the methylation the solvent was distilled through a spinning-band column. All higher boiling material was collected in one fraction and the CPCME purified by preparative vpc: ν_{max} 3090, 1109, 1018, 978, 897 cm^{-1}; nmr (external TMS) τ 6.76 (3 H, singlet, methoxy H), 6.85 (2 H, doublet, J = 6.1 cps, α H), 8.8–9.2 (1 H, multiplet, cyclopropylmethyne H), 9.2–10.0 (4 H, multiplet, cyclopropylmethylene H).

Cyclopropylcarbinyl-1-d_2 methyl ether was prepared in an identical manner using 1.5 g of lithium aluminum deuteride and 7 g of methyl cyclopropylcarboxylate. The product was isolated by preparative vpc: ν_{max} 3088, 2155, 2068, 1181, 1121, 1022, 937, 901 cm^{-1}; nmr (external TMS) τ 6.76 (3 H, singlet), 8.8–9.2 (1 H, multiplet), 9.2–10.0 (4 H, multiplet).

Rate of Decomposition of Bicyclobutane in Methanol.—In a Pyrex nmr tube which had never contained acidic material but had not been rigorously base washed was sealed a solution of 100 μl (1.3 mmol) of BCB[10e] and 75 μl (1.7 mmol) of benzene in 0.50 ml of methanol (solution A). In a similar tube was sealed a solution of 100 μl (1.88 mmol) of toluene and 100 μl (1.3 mmol) of BCB in 0.50 ml of benzene (solution B). The sealed tubes were placed in an oil bath which was heated to 49.99 ± 0.01°. The reaction was followed by nmr spectroscopy. The concentration of BCB was determined in reference to the internal aromatic hydrocarbon standards. The concentration was checked at 0, 12.9, 39.1, and 87.7 hr. The concentrations of BCB in mmoles per milliliter were as follows: solution A, 1.69 ± 0.03, 1.54 ± 0.04, 1.52 ± 0.05, 1.53 ± 0.05; solution B, 2.56 ± 0.10, 2.36 ± 0.06, 2.35 ± 0.06, 2.38 ± 0.10.

Acid-Catalyzed Decomposition of Bicyclobutane in Methanol.—A solution containing 0.9 ml (12 mmol) of bicyclobutane[10e] in 3 ml of methanol was cooled to 0° in a graduated test tube. A 0.05-ml aliquot of 0.2 *N* perchloric acid in methanol was added. The reaction was immediate and violent. Vpc showed that this solution contained 5% homoallyl methyl ether, 44% CBME, and 51% CPCME. After neutalization with a few milligrams of solid potassium bicarbonate, the three components were isolated from the crude reaction mixture by preparative vpc.

Acid-Catalyzed Decomposition of Bicyclobutane in Methanol-O-*d*.—Into two 5-ml pear-shaped flasks was weighed the following: flask A, 16.3 mg (0.12 mmol) of 70% perchloric acid; flask B, 0.1 mg (0.007 mmol) of 70% perchloric acid. A solution of 0.80 ml (10 mmol) of bicyclobutane[10e] in 3 ml of methanol-O-*d* (>97% D) was prepared. A 1.5-ml aliquot of this solution was added to flask A to give a solution containing 3 *M* BCB and 0.075 *M* acid. A 1.0-ml aliquot was added to flask B to give a solution containing 3 *M* BCB and 0.0007 *M* acid. The flasks were stoppered and placed in the refrigerator for 3 days. The solutions were each subjected to preparative vpc and the deuterated ethers, CPCME and CBME, collected as before, The mass spectra of these ethers were obtained and reported in Figures 1 and 2.

Irradiation of 1,3-Butadiene in Methanol.—A 40-ml aliquot of a 0.56 *M* solution of 1,3-butadiene in methanol (concentration determined by uv spectroscopy) was diluted to 750 ml with methanol. This solution was irradiated for 24 hr through quartz in the usual manner. The glassware was not base washed before use. An additional 10 ml of the 0.56 *M* butadiene solution was

(19) E. P. Blanchard and A. Cairncross, private communication.
(20) W. G. Dauben and W. A. Spitzer, *J. Amer. Chem. Soc.*, **90**, 802 (1968).
(21) W. G. Dauben and C. D. Poulter unpublished observation.

added and the irradiation continued for 20 hr. The vpc trace (using an internal standard) showed a 3% yield of ethers which were composed of CBME and CPCME in a ratio of 47:53 and a trace of homoallyl methyl ether. These yields represent minimum values due to the loss of butadiene during the irradiation under the conditions employed.

The crude irradiation mixture was distilled through a 24-in. spinning-band column and the first 100 ml of distillate collected. The distillate was diluted with an equal volume of water and extracted with two 15-ml portions of pure pentane. The pentane solution was dried and the pentane distilled through a 24-in spinning-band column. The residue was purified by preparative vpc and the CBME and CPCME possessed nmr and mass spectra identical with those of authentic samples.

When the reaction was run in methanol-O-*d*, the ethers obtained possessed mass spectra identical with those reported above for the deuterated species derived from BCB.

Irradiation of 1,3-Butadiene in Methanol in the Absence of Acid.—A 0.10 *M* solution of butadiene in methanol which had been freshly distilled from magnesium was prepared in base-washed glassware. The sample also contained 1,2-*trans*-dimethylcyclohexane (3.4×10^{-4} *M*), which is used as an internal standard. Aliquots (3 ml) of this solution were placed in rigorously base washed quartz tubes,[22] degassed, and sealed. The irradiation was performed in the merry-go-round apparatus using no filter. After 4.5 hr a sample was withdrawn. The concentration of butadiene, measured by uv spectroscopy, was 0.084 *M*. The vpc trace showed a new peak corresponding in retention time to bicyclobutane; no ethers were observed. A 3-μl sample of 70% aqueous perchloric acid was added to the solution, which was allowed to stand a few minutes and analyzed again. There was no peak corresponding to BCB and two new peaks, shown by coinjection with authentic materials to be CBME and CPCME, were found.

Registry No.—**1**, 18593-33-4; **1** (1-d_1), 18593-34-5; **2**, 1003-13-0; **2** (1-d_2), 18593-36-7; **3**, 157-33-5.

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(22) G. S. Hammond, J. Saltiel, A. A. Lamola, N. J. Turro, J. S. Bradshaw, D. O. Cowan, R. C. Counsell, V. Vogt, and C. Dalton, *J. Amer. Chem. Soc.*, **86**, 3197 (1964).

Free-Radical Reactions of 3,3-Dimethylbutene, 3-Methyl-3-phenylbutene, and *t*-Pentylbenzene Induced by Di-*t*-butyl Peroxide[1]

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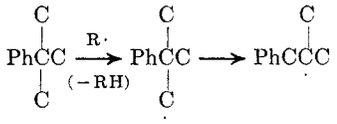
The effect of di-*t*-butyl peroxide (DTBP) at 150° upon skeletal isomerization of some model hydrocarbons was investigated. The hydrocarbons used for this study were 3,3-dimethylbutene, 3-methyl-3-phenylbutene, and *t*-pentylbenzene. The 1,2-vinyl migration in the olefins was not observed. The methyl radical, produced from the decomposition of the DTBP, added to the olefinic double bonds. 3,3-Dimethylbutene formed 2,2-dimethylpentane and the corresponding olefins, and 2,2,3-trimethylpentane. The addition of the methyl radical to 3-methyl-3-phenylbutene was accompanied by phenyl migration leading to the ultimate formation of 2-methyl-3-phenylpentane and of the corresponding olefins. *t*-Pentylbenzene underwent skeletal isomerization in the presence of DTBP at 150° with the production of 2-methyl-3-phenylbutane, 2-benzylbutane, and 2-methyl-2-phenylpentane. The methyl radical was also noted to add to the aromatic ring to form *p*-*t*-pentyltoluene.

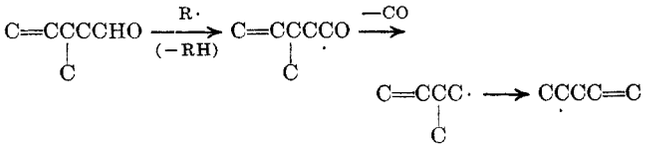
Recent studies in this laboratory have demonstrated that free-radical intermediates are involved in the aromatization of alkanes[2] and cyclanes[3] and in the dehydrogenation of alkylbenzenes[4] over "nonacidic" chromia–alumina catalyst. These free radicals were responsible for the skeletal isomerization accompanying the dehydrogenation reaction either through a phenyl and/or vinyl migration. This was demonstrated in the case of 2-phenylbutane-2-^{14}C, which rearranged to a mixture of 1-phenylbutenes-1-^{14}C and 1-phenylbutenes-2-^{14}C.[4c]

In order to obtain a better understanding of free-radical participation in the catalytic dehydrogenation reactions, it was decided to investigate the behavior of free-radical-induced reactions of hydrocarbons formed under mild conditions by the decomposition of di-*t*-butyl peroxide (DTBP).

It has been shown previously by one of us that *t*-butylbenzene refluxed in the presence of DTBP undergoes isomerization to isobutylbenzene.[5]



More recently, 1,2-vinyl migration had been observed to occur during the decarbonylation of 3-methyl-4-pentenal and *trans*-3-methyl-4-hexenal.[6]



(1) This research was supported by the Atomic Energy Commission Contract AT-(11-1)-1096, COO-1096-19.

(2) H. Pines and C. T. Goetschel, *J. Org. Chem.*, **30**, 3530 (1965).

(3) (a) H. Pines, W. R. Fry, N. C. Sih, and C. T. Goetschel, *ibid.*, **31**, 4094 (1966); (b) W. F. Fry and H. Pines, *ibid.*, **33**, 602 (1968).

(4) (a) H. Pines and C. T. Goetschel, *J. Amer. Chem. Soc.*, **87**, 4207 (1965); (b) H. Pines and C. T. Goetschel, *J. Catal.*, **6**, 371 (1966); (c) H. Pines and C. T. Goetschel, *ibid.*, **6**, 380 (1966); (d) H. Pines and M. Abramovici, *J. Org. Chem.*, **34**, 70 (1969).

(5) H. Pines and C. N. Pillai, *J. Amer. Chem. Soc.*, **82**, 2921 (1960).

(6) L. K. Montgomery, J. Matt, and J. R. Webster, Abstracts, 147th National Meeting of the American Chemical Society, Philadelphia, Pa., April 1964, p 29N.