

of methyl fluoride, about 1% of ethylene and traces of ethane were found in the resulting products. By raising the temperature to 130 °C the amount of ethylene formed increased to about 3% of products.

(b) 1 mmol of the corresponding trimethyloxonium salt and 10 mmol of sodium hydride were thoroughly mixed under argon atmosphere in a flask cooled to -78 °C. The flask was then connected to a cold trap (-78 °C) and closed with a rubber balloon in order to prevent any gaseous products from escaping. The salt mixture was carefully heated with a small flame close to its surface in order to initiate the reaction which when started proceeded rapidly and exothermically. Samples of condensed and gaseous products were analyzed by GC and GC/MS. The balance of the reaction mixture was then passed through a solution of 60 mg of bromine in 1 mL of carbon tetrachloride in order to trap the formed olefins as dibromoalkanes which were analyzed including their isotopic label distribution by GC/MS.

Reaction of Dialkyl(trimethylsilyl)methyloxonium Tetrafluoroborates with Cesium Fluoride. A mixture of 3 mmol of oxonium salt and 30 mmol of cesium fluoride was reacted in the same manner as described under b for the previous reaction. After completed reaction the condensed products (in the cooling trap) and gaseous products were separately analyzed by GC and

GC/MS. Olefins were trapped and analyzed as 1,2-dibromoalkanes.

Analyses. GC analyses of the reaction mixtures were conducted on the following instruments: (a) Varian 3700 with an OV 101 glass capillary column (50 m); (b) Hewlett Packard 5130A with a Poropak Q column (12 ft × 1/8 in.). All percentage numbers are corrected for FID response factors and are given in mol%.

MS data of gas samples were obtained using a Hewlett Packard 5985 A GC/MS system equipped with a Poropak column. For the analysis of 1,2-dibromoethane an OV 101 column (6 ft × 1/8 in.) was used.

Acknowledgment. Support of our work by the National Science Foundation is gratefully acknowledged.

Registry No. (CH₃)₃O⁺BF₄⁻, 420-37-1; Me₃SiCH₂O⁺(CD₃)-CH₂BF₄⁻, 89909-26-2; ¹³CH₃O⁺(CH₃)₂BF₄⁻, 89909-30-8; Me₃SiCH₂OCH₃, 14704-14-4; (CD₃)₃O⁺BF₄⁻, 89909-32-0; dimethyl(trimethylsilyl)methyloxonium tetrafluoroborate, 89909-24-0; tetramethylene(trimethylsilyl)methyloxonium tetrafluoroborate, 89909-28-4; methyl iodide, 74-88-4; ethyl iodide, 75-03-6; (trimethylsilyl)methyl bromide, 18243-41-9; tetrahydrofuran, 109-99-9.

Onium Ylide Chemistry. 3. Evidence for Competing Oxonium Ylide Formation with C-H Insertion in Meerwein's Reaction of Methylene and Methylene-d₂ with Dialkyl Ethers¹

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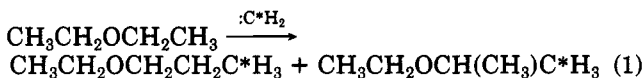
Received December 12, 1983

Meerwein's reaction of singlet methylene, produced by photolysis of diazomethane, with dialkyl ethers has been reinvestigated on the basis of reactions using CD₂N₂. In competition with methylene insertion into the various C-H bonds, about 10% of methyl alkyl ether and small amounts of dimethyl ether formation are also observed. This indicates evidence for competing attack of methylene on oxygen leading to the corresponding intermediate methylenedialkyloxonium ylides which are immediately protonated by methyl alcohol (or water) impurity present in the reaction medium to give the corresponding methylalkyloxonium ions. Dealkylative cleavage of the latter gives the observed methyl alkyl ethers. By the use of deuterium-labeled diazomethane CD₂N₂ it has been shown that ethylene and propylene formed under the reaction conditions are coming predominantly from diazomethane itself and not via intramolecular β-elimination of the oxonium ylides.

Introduction

In 1942 Meerwein and co-workers² described the formation of ethyl *n*-propyl ether and ethyl isopropyl ether upon illuminating an ethereal solution of diazomethane.

Huisgen's^{3a} suggestion that this reaction might proceed via the initial attack of methylene on oxygen, followed by rearrangement of the intermediate ylide, was subsequently claimed to be incorrect by Franzen and Fikentscher.^{3b} Using ¹⁴C-labeled methylene they observed only end-labeled ethyl *n*-propyl ether, indicating direct insertion in the C-H bonds (eq 1).

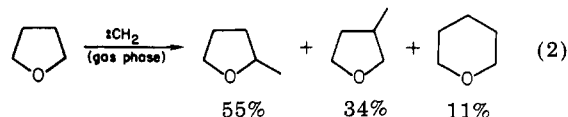


(1) For part 2, see: Olah, G. A.; Doggweiler, H.; Felberg, J. D. *J. Org. Chem.*, the preceding paper in this issue.

(2) Meerwein, H.; Rathjen, H.; Werner, H. *Chem. Ber.* 1942, 75, 1610.

(3) (a) Huisgen, R. *Angew. Chem.* 1955, 67, 439. (b) Franzen, V.; Fikentscher, L. *Liebigs Ann. Chem.* 1958, 617, 1.

Doering and co-workers⁴ studied the reaction of methylene with tetrahydrofuran in an effort to detect tetrahydropyran (the expected product from the oxonium ylide or methylene insertion in the C-O bond). They found only products resulting from methylene insertion into the α- and β-C-H bonds, i.e. 2-methyl- and 3-methyltetrahydrofuran and therefore concluded that oxonium ylide formation is not involved in the reactions of ethers with methylene. In contrast to these liquid phase results, Frey and Voisey⁵ observed tetrahydropyran (~10% of the products) formed in the gas phase photolysis of diazomethane in tetrahydrofuran (eq 2).

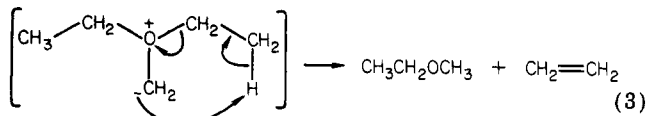


(4) Doering, W. von E.; Knox, L. H.; Jones, M., Jr. *J. Org. Chem.* 1959, 24, 136.

(5) Frey, H. M.; Voisey, M. A. *Chem. Commun.* 1966, 454.

However, similar studies of other ethers^{6,7} showed in all cases that methylene insertion into C-H bonds is the major reaction.

Franzen and Fikentscher^{9b} studying the irradiation of diazomethane in diethyl ether observed that besides direct methylene insertion giving ethyl propyl (*i*-propyl) ether, methyl ethyl ether was also formed. Since ethylene was also obtained in the reaction the formation of these latter products was explained by intramolecular β -elimination from the intermediately formed methyleneoxonium ylide (eq 3). Equation 3 is the equivalent of the ylide mecha-



nism for Hofmann elimination, suggested for nitrogen ylides in 1956 by Wittig.⁸

Unfortunately no attempt was made to confirm the proposed oxonium ylide pathway either by quantitative comparison of the amount of formed methyl ethyl ether and ethylene (which should be produced in equimolar amounts), or by isotopic labeling experiments as ethylene can also be formed directly from diazomethane (vide infra). Nevertheless the formation of methyl ethyl ether indicates attack of methylene on oxygen with intermediate formation of an oxonium ylide intermediate.

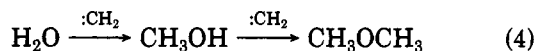
The ability of carbenes to form methylene ylides with heteroatom-containing donors having unshared electron pairs (other than oxygen) such as nitrogen, phosphorous, sulfur, etc. pioneered by Wittig is well-known and has been extensively reviewed.⁹ In contrast, to date little is known about oxonium ylides.

We would like to report a reinvestigation of Meerwein's light irradiated reaction of diazomethane with dialkyl ethers, in which we provide evidence for the competing formation of oxonium ylide intermediates with C-H insertion products.

Results and Discussion

Photolysis of Diazomethane in Dialkyl Ethers.

Gaseous diazomethane¹⁰ or diazomethane-*d*₂¹¹ was condensed into the corresponding dialkyl ether (MeOEt, MeO-*n*-Pr, EtOEt, EtO-*n*-Pr, THF). The solution was then photolyzed using a sunlamp at room temperature in a glass reaction vessel fitted with a low-temperature reflux condenser to prevent escaping of diazomethane and low-boiling products. The amount of diazomethane in relation to ethers was kept low (~10 mol%) in order to minimize secondary reactions of formed products. As diazomethane is generated from aqueous solution, the reaction mixtures inevitably always contained impurities of methyl alcohol and dimethyl ether resulting from the reaction of methylene with water (eq 4).



For the preparation of diazomethane-*d*₂ unlabeled nitrosomethylurea was treated with NaOD in D₂O.¹¹ The resulting dimethyl ether impurity (from reaction with D₂O as well as DHO and H₂O) reflects the isotopic composition

Table I. Deuterium Distribution^a in Percent in Dimethyl Ether^b from the Reaction of Ethers with :CD₂

	starting ether				
	MeOEt	MeO- <i>n</i> -Pr	Et ₂ O	EtO- <i>n</i> -Pr	THF
<i>d</i> ₆	5.3		10.4	15.4	3.5
<i>d</i> ₅	6.7	6.5	18.2	39.8	
<i>d</i> ₄	6.7	14.6	36.4	33.7	24.4
<i>d</i> ₃	12.6	25.2	24.7	6.2	41.1
<i>d</i> ₂	38.5	37.8	8.2	3.5	11.4
<i>d</i> ₁	6.3	6.1		1.4	10.8
<i>d</i> ₀	23.9	9.8	2.1		8.8

^a Calculated from mass spectra (assuming no isotope effect).
^b Detected in the reaction mixture after photolysis. The starting ethers and yields of Me₂O are as follows: MeOEt, 0.0613 mmol; MeO-*n*-Pr, 0.0117 mmol; Et₂O, 0.0059 mmol; EtO-*n*-Pr, 0.0081 mmol; THF, 0.0026 mmol.

Table II. Deuterium Distribution in Percent in Ethylene^a Found in the Reaction of Ethers with :CD₂

	starting ether				
	MeOEt	MeO- <i>n</i> -Pr	Et ₂ O	EtO- <i>n</i> -Pr	THF
<i>d</i> ₄	73.5	76.4	70.1	76.4	64.6
<i>d</i> ₃	18.1	18.7	20.7	17.2	26.0
<i>d</i> ₂	3.3	1.7	2.2	1.7	6.1
<i>d</i> ₁	1.9	1.3	1.2	1.0	1.4
<i>d</i> ₀	3.2	1.9	5.8 ^b	3.7	1.9

^a Trapped as 1,2-dibromoethane. The starting ethers and yields of ethylene are as follows: MeOEt, 0.0092 mmol; MeO-*n*-Pr, 0.008 mmol; Et₂O, 0.0016 mmol; EtO-*n*-Pr, 0.003 mmol; THF, 0.0045 mmol. ^b Only 0.0001 mmol of unlabeled ethylene, compared to 0.0054 mmol of MeOEt, is formed in the reaction (see Table IV, note e).

of used D₂O as well as any moisture impurity in the system. In comparison dimethyl ether formed in the reaction of CD₂N₂ with MeOEt and MeO-*n*-Pr (Table I) shows that it is to a significant degree formed from the reaction of CD₂N₂ with these methyl ethers (see subsequent discussion).

We also carried out an analysis of ethylene, which was formed in all reactions, after trapping it quantitatively as 1,2-dibromoethane. In Table II are given the yields and isotopic distributions of ethylene produced from diazomethane-*d*₂ in various ethers. The high proportions of *d*₄- and *d*₃-labeled ethylene in all reactions clearly indicate that ethylene is predominantly formed directly from diazomethane-*d*₂.¹² β -elimination of ethylene from the methylene oxonium ylides of the ethyl ethers (cf. Eq. 3) in contrast yields unlabeled ethylene but under the reaction conditions its amount is very small (see Table II, note b). An additional byproduct found in all reactions was propylene, which in all probability is formed from the reaction of ethylene with methylene via cyclopropane. In the following discussion ethylene and propylene will therefore not be discussed when they derive from methylene itself. Similarly, dimethyl ether will only be considered in those reactions where it has undoubtedly been formed from the investigated ethers and not from the side reaction of diazomethane with water.

The Reaction of Methyl Ethyl Ether with Methylene. The reaction of methyl ethyl ether with diazo-

(12) The formation of dimers from diazoalkanes is a frequently observed process. Cf.: Wulfman, D. S.; Linstrumelle, G.; Cooper, C. F. In "The Chemistry of Dizonium and Diazo Groups"; Patai, S., Ed.; Wiley: New York, 1978; part 2, p 912.

(13) A rough calculation shows that at a conversion of 1.1% of the starting MeOEt (0.5 g = 8.3 mmol) and 37.2% yield of Me₂O originating from the ylide pathway only 0.54 mg (0.034 mmol) of H₂O or the corresponding methyl alcohol are needed to protonate the oxonium ylide.

(6) Frey, H. M.; Voisey, M. A. *Trans. Faraday Soc.* 1968, 64, 954.

(7) Voisey, M. A. *Trans. Faraday Soc.* 1968, 64, 3058.

(8) Wittig, G.; Polster, R. *Liebigs Ann. Chem.* 1956, 599, 13.

(9) Nikolaev, V. A.; Korobitsyna, I. K. *Mendeleev Chem. J. (Engl. Transl.)* 1979, 24 (5), 88.

(10) Dessaux, O.; Durand, M. *Bull. Soc. Chim. Fr.* 1963, 41.

(11) Hecht, S. M.; Kozarich, J. W. *Tetrahedron Lett.* 1972, 1501.

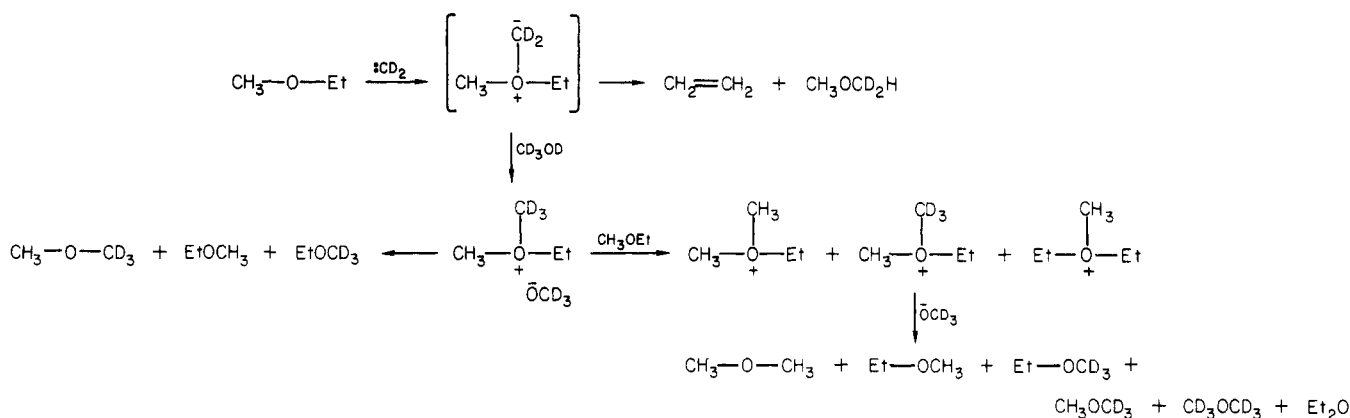
Table III. Reaction of Methyl Alkyl Ethers with Methylene

ether	methylene	conversion, %	C-H insertion products, %			cleavage product Me ₂ O, %
			MeO- <i>i</i> -Pr	Et ₂ O	MeO- <i>n</i> -Pr	
MeOEt	CH ₂ ^a	0.5	33.2	34.0	32.8	<i>b</i>
	CD ₂	1.1	17.9	29.7	15.2 ^c	37.2 ^d

ether	methylene	conversion, %	C-H insertion products, %				cleavage product Me ₂ O, %
			MeO- <i>i</i> -Bu	MeO- <i>s</i> -Bu	EtO- <i>n</i> -Pr	MeO- <i>n</i> -Bu	
MeO- <i>n</i> -Pr	CH ₂ ^a	1.6	19.2	19.6	31.4	29.8	<i>b</i>
	CD ₂	1.0	19.9	20.6	23.0	32.1 ^e	4.4 ^d

^aResults are the average of three separate runs. ^bCould not be determined without isotopic labeling. ^cDeuterium content: 83.6% *d*₂, 16.4% *d*₁. ^dCalculated from the total Me₂O content and corrected to represent the Me₂O formed via an oxonium ylide, using the *d*₂, *d*₁, and *d*₀ values shown in Table I. ^eDeuterium content: 82.9% *d*₂, 17.1% *d*₁.

Scheme I

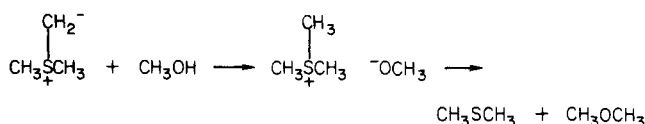


methane yielded the C-H insertion products methyl isopropyl ether, diethyl ether, and methyl *n*-propyl ether in nearly equal amounts, in good agreement with previous observations.^{6,7} (Results are summarized in Table III). Dimethyl ether was also detected in all runs, but as it also can come from the reaction of diazomethane with water, only the use of deuterated diazomethane enabled us to distinguish between dimethyl ether formed directly from diazomethane (see eq 4) and that originating from methyl ethyl ether. The corresponding deuterium distribution of dimethyl ether in Table I shows high amounts of *d*₂ and *d*₀ as well as significant *d*₃. These results can be rationalized by competing attack of methylene-*d*₂ on the oxygen atom of methyl ethyl ether forming oxonium ylide which is then immediately protonated (deuterated) by impurities of deuterated methyl alcohol (or D₂O) as shown in Scheme I.

Methyl transfer from the resulting labeled oxonium ion to excess methyl ethyl ether yields the unlabeled dimethylethoxyxonium ion or CD₃ transfer gives the *d*₃ oxonium ion. They subsequently form dimethyl-*d*₃ ether and unlabeled dimethyl ether, respectively, by alkylation of CH₃O⁻. Similar protonation could also take place with water impurities. Small amounts of ethyl or methyl alcohol possibly produced could not be detected. However, ethyl (methyl) alcohol can also further react with methylene via O-H insertion (a reaction which is 20 times faster than C-H insertion¹⁴) to give methyl ethyl (dimethyl) ether. We have also obtained small amounts of unlabeled ethylene indicative of β-elimination of the ethylmethylenoxonium ylide.

To substantiate the suggested ready protonation of the intermediate methylenedialkylxonium ylide with methyl

alcohol resulting in the formation of methyldialkylxonium ion, we have performed a model reaction by reacting Corey's stable methylenedimethylsulfonium ylide¹⁵ with methyl alcohol. When an equimolar quantity of methyl alcohol was added to the sulfonium ylide and the mixture stirred at 0 °C, dimethyl ether and dimethyl sulfide are formed indicative of the reaction. Labeling experiments exclude direct methylene transfer from the ylide.



The deuterium distribution found in the C-H insertion product methyl *n*-propyl ether (Table III) corresponds to the isotopic purity of diazomethane (83.6% *d*₂, 16.4% *d*₁). Approximately the same ratio of *d*₂:*d*₁ was found in the cleavage product dimethyl ether (85.9:14.1) (see Table I).

The Reaction of Methyl *n*-Propyl Ether with Methylene. The four C-H insertion products were formed (see Table III) in a similar ratio as reported by Frey and Voisey.⁶ The isotopic purity of diazomethane-*d*₂ was determined from methyl *n*-butyl ether to be 82.9% *d*₂, 17.1% *d*₁. As it can be seen from Table I, less dimethyl ether was produced as compared to the reaction of methylene with methyl ethyl ether, however, the high proportions of Me₂O-*d*₂ and Me₂O-*d*₀ are significant. They indicate that part of the dimethyl ether is being formed via an oxonium ylide (cf. Scheme I, considering CH₃O-*n*-Pr instead of CH₃OEt) and its subsequent reaction with methyl alcohol (or water) impurity. In addition to these products, Frey and Voisey⁶ also reported the formation of methyl ethyl ether, whereas in our reaction we could not detect it.

(14) Kerr, J. A.; O'Grady, B. V.; Trotman-Dickenson, A. F. *J. Chem. Soc. A* 1967, 897.

(15) Corey, E. J.; Chaykovsky, M. *J. Am. Chem. Soc.* 1965, 87, 1353.

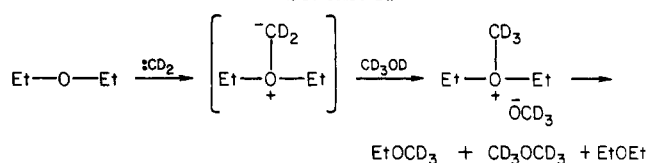
Table IV. Reaction of Ethyl Alkyl Ethers with Methylene

ether	methylene	conversion, %	C-H insertion products (isotopic distributions), %		cleavage product (isotopic distributions), %
			EtO- <i>i</i> -Pr	EtO- <i>n</i> -Pr	MeOEt ^a
Et ₂ O	CH ₂ ^b	4.4	42.2	46.1	11.7
	CD ₂ ^c	1.1	43.1 (85.3 d ₂ , 14.7 d ₁)	43.5 (86.3 d ₂ , 13.7 d ₁)	13.4 (59.0 d ₃ , 36.4 d ₂ , 4.6 d ₁)
	CD ₂ ^d	0.6	41.7 (83.2 d ₂ , 16.8 d ₁)	45.0 (83.2 d ₂ , 16.8 d ₁)	13.3 ^e (7.3 d ₃ , 77.4 d ₂ , 15.3 d ₁)
	CD ₂ ^f	1.0	41.3 (80.9 d ₂ , 19.1 d ₁)	46.4 (84.9 d ₂ , 15.1 d ₁)	12.3 (33.4 d ₃ , 58.6 d ₂ , 8.0 d ₁)

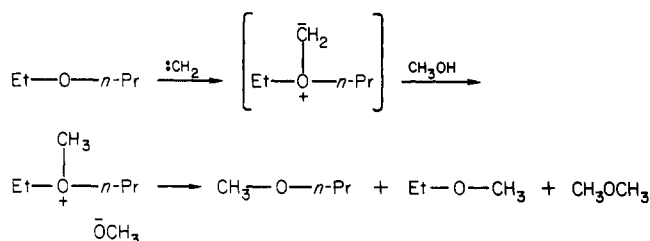
ether	methylene	conversion, %	C-H insertion product (isotopic distribution), ^g	cleavage products (isotopic distributions), %	
			%	MeOEt ^a	MeO- <i>n</i> -Pr ^a
EtO- <i>n</i> -Pr	CH ₂ ^b	6.0	93.2	2.4	4.4
	CD ₂	2.7	92.5 (88.0 d ₂ , 12.0 d ₁)	3.3 (37.4 d ₃ , 55.5 d ₂ , 7.1 d ₁)	4.2 (32.3 d ₃ , 60.9 d ₂ , 6.8 d ₁)

^a Label exclusively in methyl group. ^b Results are the average of three separate runs. ^c Diazomethane contained impurities of D₂O. ^d Diazomethane was twice distilled. ^e 0.0054 mmol (based on 0.5 g (6.8 mmol) of starting Et₂O). ^f Et₂O contained 0.7% added D₂O. ^g 5 C-H insertion products were detected; *n*-ProO-*n*-Pr was analyzed by MS.

Scheme II



Scheme III



The Reaction of Diethyl Ether with Methylene. The reactions of diethyl ether with unlabeled and labeled diazomethane (see Table IV) yielded the C-H insertion products ethyl isopropyl ether and ethyl *n*-propyl ether as well as the cleavage product methyl ethyl ether in a ratio independent of the conversion of the starting material (0.6–4.4%). In addition we also observed dimethyl ether. Mass spectroscopical examination of methyl ethyl ether, obtained from the reaction of deuterated diazomethane with diethyl ether, showed deuterium exclusively in the methyl group, thus giving direct proof for attack of methylene on oxygen. The high yield of MeOEt-*d*₃ is striking, but can be explained by deuteration of the intermediate oxonium ylide by CD₃OD present in the system and transethylation of the [−]OCD₃ counter ion (Scheme II). This path is also indicated by observation of dimethyl-*d*₆ ether in the reaction products. In the presence of a large excess of diethyl ether in the system the very low concentration of methyl ethyl ether could not account for itself reacting with diazomethane to give observed dimethyl ether. The isotopic distribution of methyl ethyl ether and dimethyl ether reflects related reactions with the impurity CH₂ (and CHD) as well as mixed labeled methyl alcohol (or water).

The isotopic composition of diazomethane-*d*₂, determined from the C-H insertion products, was similar in all runs. When diazomethane was twice redistilled prior to its reaction with ether, it substantially reduced the ratio of CD₃OD:CH₃OH or (D₂O:H₂O) present as impurity and therefore the formation of MeOEt-*d*₃. To further confirm the effect of traces of water and/or methyl alcohol a small amount of D₂O was added to the starting diethyl ether in one experiment. The yield of MeOEt-*d*₃ was high, due to the deuteration of the intermediate oxonium ylide by the added D₂O.

The Reaction of Ethyl *n*-Propyl Ether with Methylene. In this reaction five C-H insertion products were formed (Table IV). The reaction also yielded three cleavage products, namely methyl ethyl ether, methyl *n*-propyl ether, and dimethyl ether resulting from protonation of the intermediate oxonium ylide and subsequent cleavage of the formed methylethyl-*n*-propyloxonium ion (Scheme III). The experiment with labeled diazomethane

Table V. Quenching of Methylethyl-*n*-propyloxonium Tetrafluoroborate in EtO-*n*-Pr^a with Potassium Hydroxide^b

Me ₂ O, ^c %	MeOEt, %	MeO- <i>n</i> -Pr, %	Et ₂ O, ^c %
35.6	24.8	35.2	4.4
21.3	28.2	47.1	3.4

^a Large excess of solvent. ^b The alcohols formed were not analyzed. ^c Transalkylation products.

Table VI. Reaction of THF with Methylene

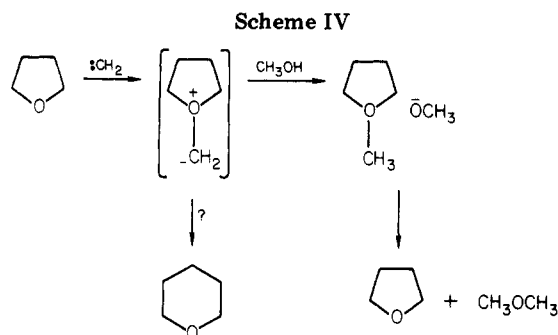
methylene	conversion, %	C-H insertion products, %		
		2-Me-THF	3-Me-THF	THP, %
CH ₂	1.0	51.4	48.2	0.4 ^a
CD ₂	0.9	49.9	50.1 ^b	

^a In two other runs with CH₂ no traces of THP could be detected. ^b Deuterium content = 90.0% *d*₂, 10.0% *d*₁.

shows good agreement in the deuterium distribution between the insertion products and the cleavage products to give observed dimethyl ether.

The deuterium content of the cleavage products again indicates that the impurity methyl alcohol (or water) in the system affects protonation of the oxonium ylide followed by subsequent transalkylation of methoxide (hydroxide), similarly as discussed in the previous reactions of ethers with diazomethane-*d*₂. As a control experiment, methylethyl-*n*-propyloxonium tetrafluoroborate was independently prepared and cleaved with potassium hydroxide (Table V). The products detected were methyl ethyl ether and methyl *n*-propyl ether (in a similar ratio as in the photolysis reaction (cf. Table IV)) as well as dimethyl ether and diethyl ether (resulting from transalkylations).

The Reaction of Tetrahydrofuran with Methylene. Besides the two C-H insertion products, 2-methyl- and 3-methyltetrahydrofuran (found in equal quantities, see Table VI), only the "unusual impurities" ethylene, propylene, and dimethyl ether were detected. In one exper-



iment a very small amount of tetrahydropropyran was found, probably resulting from reaction in the gas phase⁵ above the reaction mixture although limited competing attack of methylene on oxygen in the liquid phase itself cannot be ruled out. The intermediate oxonium ylide is, however, preferentially immediately protonated, giving oxonium tetramethylenemethyloxonium ion, which then gives tetrahydrofuran and dimethyl ether via transmethylation of the methoxide counter ion (Scheme IV).

The isotopic composition of dimethyl ether formed in the reaction products using CD_2H_2 indicates that it comes, at least in part, through reaction of the intermediate oxonium ylide.

Conclusions

The present study shows that the reactive singlet methylene in the liquid phase can attack all available nucleophilic sites of dialkyl ethers, including the non-bonded electron pairs of oxygen. In competition with direct insertion into C-H bonds (major reaction) there is competing attack on oxygen (minor reaction). Such an attack on oxygen forms highly reactive oxonium ylide intermediates.

Our studies with methylene- d_2 indicate that the predominant behavior of oxonium ylides formed under the reaction conditions studied is to undergo very fast protonation (deuteration) with methyl alcohol (or water) present as an impurity from the used diazomethane to form trialkyloxonium ions, rather than to undergo intramolecular Stevens type rearrangement.¹⁶ Dealkylations and transmethylation accompanying the reactions are also in accord with intermediate oxonium ion formation. The unstable oxonium ylides have not drawn much attention until recently and have never been characterized because

(16) A referee raised the possibility that diazomethane is protonated upon irradiation and the resulting methyl diazonium ion methylates ethers. In this case results could be explained by a purely carbocationic mechanism. We feel, however, that protonated diazomethane would immediately form methyl alcohol by collapse of the ion pair $\text{CH}_3\text{N}_2^+\text{OH}^-$. It is thus highly improbable that an incipient methyl cation able to methylate ether could be formed under the reaction conditions.

of their instability (they lack the d orbital stabilization of other ylides). They play, as shown in our previous work, a key role in the bifunctional acid-base catalyzed conversion of methyl alcohol into ethylene.

Experimental Section

Materials. Ethers not available commercially were prepared using the Williamson synthesis. All ethers were purified by distillation. To remove alcohol prior to their use ethers were passed through aluminum oxide. Gaseous diazomethane was prepared by treating *N*-nitrosomethylurea with 80% potassium hydroxide solution under exclusion of light at 0 °C.¹⁰ The diazomethane was then passed through potassium hydroxide pellets under an argon stream and transferred into the cooled ether (-78 °C). Diazomethane- d_2 was prepared by the reaction of sodium deuterioxide with *N*-nitrosomethylurea in dimethoxyethane/ D_2O^{11} and transferred directly into the corresponding ether.

Photolysis Reactions. A solution of diazomethane or deuterated diazomethane (prepared from 0.3 g *N*-nitrosomethylurea) in the corresponding ether (0.5 g) in a reaction tube equipped with a reflux condenser (cooled to -78 °C) was irradiated with a 275-W Sylvania sunlamp at room temperature. The apparatus was covered with aluminum foil to ensure that only the liquid phase was exposed to light. After the run was complete (indicated by the disappearance of the yellow color, usually 30–60 min), the reaction mixture was cooled to -78 °C in order to condense the low-boiling products and then analyzed by GC and GC/MS. For determination of deuterium formed ethylene was carried under argon into a solution of bromine (60 mg) in carbon tetrachloride (1.0 g) and then analyzed as 1,2-dibromoethane by GC and combined GC/MS.

Quenching of Methylene-*n*-propyloxonium Tetrafluoroborate with Potassium Hydroxide. A solution of methylethyl-*n*-propyloxonium tetrafluoroborate in ethyl *n*-propyl ether was prepared by stirring a mixture of 2.2 g (25 mmol) of ethyl *n*-propyl ether, 120 mg (0.6 mmol) of silver tetrafluoroborate (Aldrich), and 70 mg (0.5 mmol) of methyl iodide for 15 min at room temperature. 30 mg (0.5 mmol) of potassium hydroxide was then added and the mixture was stirred for another 30 min. To prevent evaporation of the low-boiling products the reflux condenser was closed with a rubber balloon. After cooling to -78 °C the reaction mixture was analyzed by GC.

Analyses. GC analyses of the reaction mixtures were conducted on the following instruments: (a) Varian 3700 with an OV 101 glass capillary column (50 m); (b) Hewlett Packard 5130A with a Poropak Q column (12 ft \times 1/8 in.). All percentage numbers are corrected for FID response factors and are given in mol%.

MS data of gas samples were obtained using a Hewlett Packard 5985 A GC/MS system equipped with a Poropak column. For the analysis of 1,2-dibromoethane an OV 101 column (6 ft \times 1/8 in.) was used.

Acknowledgment. Support of our work by the National Science Foundation is gratefully acknowledged.

Registry No. THF, 109-99-9; CH_2 , 2465-56-7; CD_2N_2 , 14621-84-2; MeOEt, 540-67-0; MeO-*n*-Pr, 557-17-5; Et_2O , 60-29-7; EtO-*n*-Pr, 628-32-0; CD_2 , 14863-68-4; diazomethane, 334-88-3; methylethyl-*n*-propyloxonium tetrafluoroborate, 89909-38-6.