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Onium Ylide Chemistry. 2. Methylenedialkyloxonium Ylides[1]

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We report evidence for the long sought after methylenedialkyloxonium ylides from methyloxonium ions by two independent routes, proving their intermediate formation through derived product analysis. Reaction of trimethyloxonium salts with sodium hydride results in competing proton abstraction besides methane formation (hydride methylation). Subsequent methylation of the formed methylenedimethyloxonium ylide by excess trimethyloxonium ion is resulting in $C_1 \rightarrow C_2$ conversion and formation of dimethylethyloxonium ion which with sodium hydride gives ethane (and methane) or by β-elimination ethylene. Besides expected fluoride alkylation products, i.e., alkyl fluorides and fluorosilanes, fluoride-induced desilylation of dimethyl((trimethylsilyl)methyl)oxonium tetrafluoroborate also results in the formation of methylenedimethyloxonium ylide giving via subsequent methylation and cleavage methyl ethyl ether and ethyl fluoride.

Introduction

Since Wittig's[2a] pioneering studies on phosphonium ylides, ylides have attracted continued and ever increasing interest.[2b] Stable ylides of sulfur, nitrogen, phosphorus and other heteroatoms have been prepared and used in synthetic chemistry. Generation of these ylides generally is achieved either via α-deprotonation of the corresponding onium salts[2] (eq 1, path a) or electrophilic carbene attack on the corresponding heteroatom compounds[2b,3] (eq 1, path b). More recently, various sulfur,

$$R_nX^+{-}CR'_2H \xrightarrow[a]{-H^+} R_nX^+{-}C^-R'_2 \xleftarrow[b]{:CR'_2} R_nX \qquad (1)$$

$$X = S, N, P, \text{etc.}$$

nitrogen, and phosphorus ylides have also been generated by fluoride ion induced desilylation of the corresponding dialkyl((trimethylsilyl)methyl) onium salts (eq 2).

$$R_nX^+{-}CH_2Si(CH_3)_3 \xrightarrow[-(CH_3)_3SiF]{F^-} R_nX^+{-}CH_2^- \qquad (2)$$

Oxonium ylides have thus far received little attention and have not been firmly established. There are only a few examples of possible formation of oxonium ylides mentioned in the literature.[5] A recent theoretical study[6] indicates that the parent methyleneoxonium ylide $C^-H_2{-}O^+H_2$ is to be considered more as a hydrated carbene than an oxonium ylide, with a calculated lengthening of the C–O bond by 0.4 Å compared to that in methyl alcohol.

We became interested in the possible role of oxonium ylide intermediates during our investigation of the conversion of heterosubstituted methanes into ethylene and lower olefins by bifunctional acid–base catalysis.[7] The decomposition of tetramethylammonium amide giving inter alia ethylene and dimethylethylamine was suggested to proceed through the methylenetrimethylammonium ylide.[8] Similar formation of ethylene from the methylenedimethylsulfonium ylide has been previously observed as a side reaction at more elevated temperatures by both Franzen and Driesen[9a] as well as by Corey and Chaykovsky.[9b] However because they were primarily interested in exploring the chemistry of sulfonium ylides at lower temperatures where they are stable, this side reaction attracted little interest.

Table I. Reaction of $^{13}CH_3O^+(CH_3)_2BF_4^{-}$[a] with NaH

		isotopic distribution, %		
products	yield, %[b]	$^{13}C_0$	$^{13}C_1$	$^{13}C_2$
methane	58.4	60.3	39.7	
MeF	4.6	*c*		
ethylene	2.5	55.0[d]	36.9	8.1
ethane	2.1	*c*		
Me_2O	32.4	41.0	51.3	7.7

[a] $^{13}CH_3$ group 90% labeled. [b] Unlabeled trimethyloxonium ion with BF_4^-, PF_6^-, and $SbCl_6^-$ as counter ion gave similar product distributions. [c] Not determined. [d] Calculated for intermolecular path (Scheme I): 49.0 $^{13}C_0$, 42.0 $^{13}C_1$, 9.0 $^{13}C_2$. Calculated for intramolecular path (Scheme I): 36.6 $^{13}C_0$, 63.4 $^{13}C_1$.

The reaction of methylene, generated by the photolysis of diazomethane, with dialkyl ethers[10] was suggested to involve initial attack on oxygen forming intermediate methylenedialkyloxonium ylides.[5a] However this suggestion was questioned by following labeling studies showing that only direct methylene insertion into C–H bonds took place[10b] although the studies also found methyl alkyl ethers in the reaction products.

In the following paper[11] we report the investigation of the reaction of methylene with various dialkyl ethers (cf. eq 1, path b, X = O) providing evidence for competing oxonium ylide formation with direct C–H insertion in these reactions.

We would like to report now independent evidence for the formation of methylenedialkyloxonium ylides, achieved by deprotonation of trimethyloxonium ion and desilylation of dialkyl((trimethylsilyl)methyl)oxonium ions.

Results and Discussion

Deprotonation of Trimethyloxonium Ion. When trimethyloxonium tetrafluoroborate was reacted with sodium hydride in dimethyl ether as solvent in a stirred autoclave, 1–3% of ethylene (and traces of ethane) and methyl fluoride were formed besides methane, the major

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[1] For part 1, see: Olah, G. A. et al. *J. Am. Chem. Soc.* **1984**, *106*, 2143.

[2] (a) Wittig, G.; Rieber, M. *Liebigs Ann. Chem.* **1949**, *562*, 177. (b) Johnson, A. W. "Ylid Chemistry"; Academic Press: New York, 1966.

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

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[5] (a) Huisgen, G. R. *J. Am. Chem. Soc.* **1955**, *67*, 439. (b) Iwamura, H.; Imahashi, Y. *Tetrahedron Lett.* **1975**, 1401. (c) Wolthuizen, J. P.; Van Hooff, J. H. C. "Proceeding of the 5th International Conferences on Zeolites"; Reed, L. V., Ed.; Heyden: London, 1980; p 649. (e) Olah, G. A. *Pure Appl. Chem.* **1981**, *53*, 201. (f) Kirmse, W.; Loosen, K.; Sluma, H. D. *J. Am. Chem. Soc.* **1981**, *103*, 5935. (g) Mole, T.; Whiteside, J. A. *J. Catal.* **1982**, *75*, 284.

[6] Eades, R. A.; Gassmann, P. G.; Dixon, D. A. *J. Am. Chem. Soc.* **1981**, *103*, 1066.

[7] (a) Olah, G. A. U.S. Patent 4 373 109, 1983. (b) Reference 1.

[8] Musker, W. K. *J. Org. Chem.* **1967**, *32*, 3189.

[9] (a) Franzen, V.; Driesen, H. E. *Chem. Ber.* **1963**, *96*, 1881. (b) Corey, E. J.; Chaykovsky, M. *J. Am. Chem. Soc.* **1965**, *87*, 1353.

[10] (a) Meerwein, H.; Rathjen, H.; Werner, H. *Chem. Ber.* **1942**, *75*, 1610. (b) Franzen, V.; Fikentscher, L. *Liebigs Ann. Chem.* **1958**, *617*, 1. (c) Frey, H. M.; Voisey, M. A. *Trans. Faraday Soc.* **1968**, *64*, 954.

[11] Olah, G. A.; Doggweiler, H.; Felberg, J. D. *J. Org. Chem.*, the following paper in this issue.

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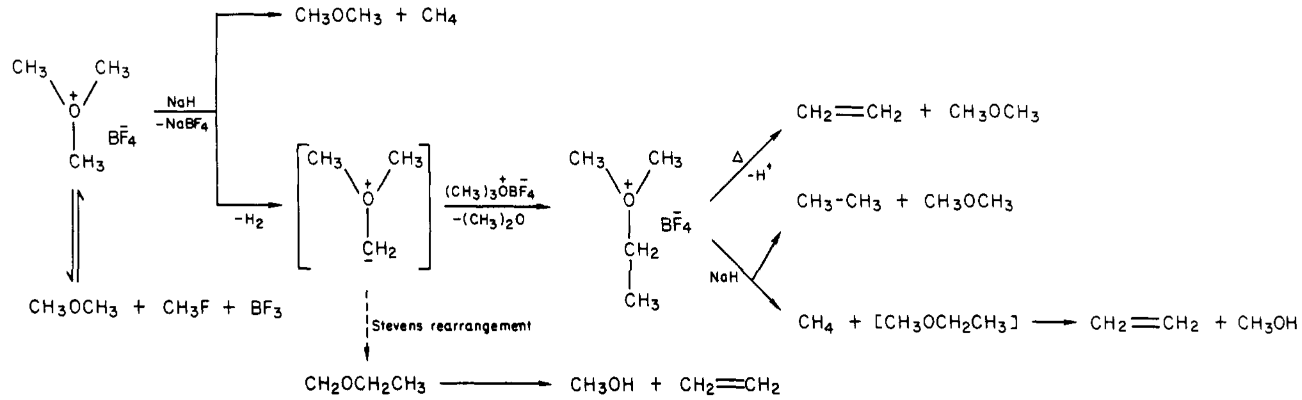
Scheme I



product of hydride methylation. To avoid the possibility that under these conditions Wittig type reaction[12] of the hydride with dimethyl ether itself would give ethylene (although such reactions were reported only with higher homologous branched ethers), we also studied the reaction of dimethyl ether itself with sodium hydride under similar conditions, which gave no ethylene. Subsequently we have carried out the reaction in the absence of ether, i.e., by warming a mixture of trimethyloxonium salts with sodium hydride, thus avoiding any solvent interaction. (Heterogeneous reaction conditions were also used in the previously studied conversion of dimethyl ether over bifunctional acidic–basic catalysts.[1]) Analysis of the gaseous products of the strongly exothermic reaction again showed the formation of ethylene and ethane. We also carried out control experiments in which trimethyloxonium tetrafluoroborate was thermally decomposed either in dimethyl ether or neat, without added sodium hydride. No ethylene was found and products were only methyl fluoride and dimethyl ether (as well as BF_3).

To gain further understanding of the hydride-induced reaction we carried out a similar reaction using singly ^{13}C labeled trimethyloxonium tetrafluoroborate with sodium hydride. Product distribution obtained is shown in Table I. The formation of methane and methyl fluoride are due to methylation of NaH or F^- (from BF_4^-) by the trimethyloxonium ion. For the formation of ethylene and ethane involving $C_1 \rightarrow C_2$ transformation we propose the mechanistic pathway shown in Scheme I.

Proton abstraction from trimethyloxonium ion forms in competition with methylation of hydride, the methylenedimethyloxonium ylide which is methylated by the excess of trimethyloxonium ion to give the dimethylethyloxonium ion. Subsequent β-elimination results in ethylene, whereas alkylation of hydride forms ethane (and methane).

Competing intramolecular Stevens rearrangement of the oxonium ylide, resulting in methyl ethyl ether and subsequent decomposition into methyl alcohol and ethylene, cannot be ruled out completely but seems improbable (see also subsequent discussion of the cleavage of β-trimethylsilylated oxonium ions) as the isotopic distribution of ethylene obtained from $^{13}CH_3O^+(CH_3)_2\ BF_4^-$ much more closely resembles the calculated distribution expected from the intermolecular than the intramolecular path (see Table I, note d). Dilabeled ethylene formation also is in accord with this pathway, although some dilabeled dimethyl ether observed indicates reversible demethylation–methylation leading to some label disproportionation in the oxonium ion.

Table II. Reaction of $(CD_3)_3O^+BF_4^{-\,a}$ with NaH

products	yield, %	d_0	d_1	d_2	d_3	d_4	d_5	d_6
methane	9.1				~84	~16		
MeF	16.8	b						
ethylene	0.3	5.5	16.4	18.3	26.5	33.3		
ethane	0.3	b						
Me_2O	73.5						7.0	93.0

[a] Isotopic purity 99%. [b] Not determined.

To obtain further proof for ethylene formation from trimethyloxonium ion we also prepared the fully deuterated oxonium salt $(CD_3)_3O^+BF_4^-$, and studied its reaction with NaH (Table II). Indeed, tetradeuterated ethylene was obtained besides lower deuterated ethylenes, which can be explained by hydrogen/deuterium exchange involving protonation of the intermediate ylide by moisture impurity. Some unlabeled ethylene and lower hydrocarbons can result from hydrocarbon impurities resulting from used sodium hydrid dispersion (see below). CD_3H formed as the major alkylation product of the reaction also contained some fully deuterated methane, indicating hydrogen/deuterium exchange processes in the reaction.

Caution must be exercised in the preparation of the trimethyloxonium salt used in the experiments probing the formation of ethylene. Commercial samples of trimethyloxonium salts always contain ethylated oxonium ions as impurities. This may be due to the fact that they are prepared from triethyloxonium ion and dimethyl ether,[13] or the product was washed with diethyl ether, which can undergo trans ethylation giving diethylmethyloxonium ion (proven by high-field NMR spectroscopic study of samples). The ethylated oxonium ions can readily undergo thermal or base-catalyzed β-elimination giving ethylene and thus could confuse the results.

In order to avoid this pitfall we carefully prepared trimethyloxonium ion from high purity dimethyl ether with methyl iodide–silver tetrafluoroborate in dichloromethane–sulfur dioxide solution. As no diethyl ether was used in the preparation or washing of the oxonium salt, it was free of any ethyloxonium ions.

Similarly care must be exercised purifying sodium hydride. Commercial sodium hydride is generally available in hydrocarbon (mineral oil) suspensions. If the sodium hydride is not sufficiently purified by heating in vacuum until all hydrocarbons are desorbed, remaining hydrocarbons can contribute to byproducts. In a control experiment when sodium hydride was heated on its own

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(12) Schollkopf, U. *Angew. Chem.* **1970**, *82*, 795.

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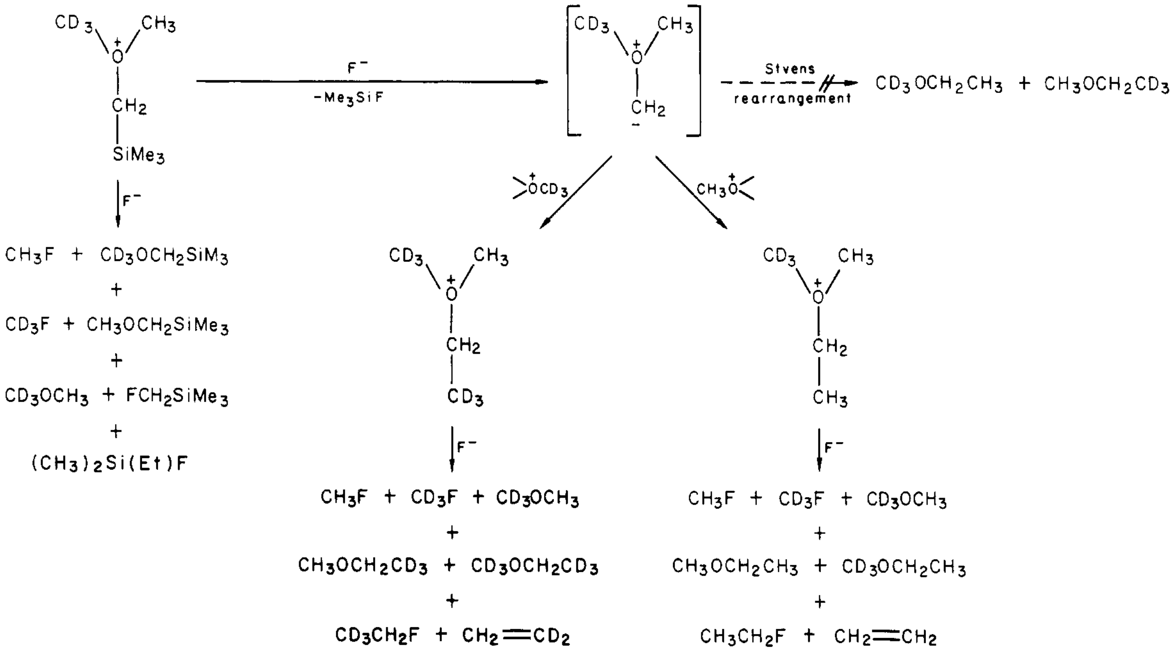
Scheme II



methane, ethane, ethylene and some C_3–C_5 hydrocarbons were observed by GLC. Use of well purified NaH minimizes this difficulty.

Clearly a major difficulty in generating oxonium ylides is the strong alkylating ability of precursor oxonium ions toward bases, which is generally not encountered with P, N, S, etc., ylides.

Desilylation of Dialkyl((trimethylsilyl)methyl)oxonium Ions. While desilylation reactions[4] of ((trimethylsilyl)methyl)sulfonium, -ammonium, and -phosphonium ions with CsF to the corresponding ylides (cf. eq 2) can be carried out in polar organic solvents such as acetonitrile, diglyme, DMF, or Me_2SO, alkyloxonium salts readily alkylate these solvents, even at room temperature. Thus desilylation reactions of ((trimethylsilyl)methyl)alkyloxonium ions can not be studied in these solvents.

When dimethyl((trimethylsilyl)methyl)oxonium tetralfluoroborate (4) was reacted with CsF in SO_2 (a relatively low nucleophilic solvent for cations) in a sealed tube at room temperature, only slow alkylation of fluoride by the oxonium ion occurred. There was no indication for competing fluoride attack on silicon forming fluorotrimethylsilane.

To increase the reaction temperature and avoid any solvent interaction a well-mixed mixture of dimethyl((trimethylsilyl)methyl)oxonium tetrafluoroborate and CsF was carefully heated. The reaction products were condensed in cold traps and analyzed by GC–MS. They contained fluorotrimethylsilane, ethyl fluoride, and methyl ethyl ether, besides the expected fluoride alkylation product[14] (as well as $NaBF_4$). Similar experiments were also carried out with a deuterated oxonium ion. Table III shows the product distribution obtained from the reaction of $Me_3SiCH_2O^+(CD_3)CH_3BF_4^-$ with CsF.

In order to explain the formation of ethyl fluoride and methyl ethyl ether we propose the mechanism presented in Scheme II, which is closely related to the previously discussed mechanism of the reaction of trimethyloxonium ion with sodium hydride (cf. Scheme I). Whereas the major reaction pathway involves S_N2 type displacement of the oxonium ion on carbons (i.e.,alkylation of fluoride), in competition there is also displacement by fluoride on silicon.

Table III. Reaction of $Me_3SiCH_2O^+(CD_3)CH_3BF_4^{-\,a}$ with CsF

products	yield, %[b]	isotopic distribution,[c] %
methane	0.1[d]	*e*
MeF	12.1[d]	60.6 CD_3F 39.4 CH_3F
ethylene	1.0[d]	*e*
EtF	0.5	48.4 CD_3CH_2F 51.6 CH_3CH_2F
Me_2O	55.9	16.8 CD_3OCD_3 69.2 CD_3OCH_3 14.0 CH_3OCH_3
MeOEt	1.6	29.0 $CD_3CH_2OCD_3$[f] 27.0 $CD_3CH_2OCH_3$ 22.7 $CH_3CH_2OCD_3$ 21.3 $CH_3CH_2OCH_3$
Me_3SiF	3.4	no D
$Me_2Si(Et)F$	4.1	no D
Me_3SiCH_2F	9.2	no D
Me_3SiCH_2OMe	12.1	*g*

[a] CD_3 group 99% labeled. [b] Three experiments with the unlabeled oxonium salt showed similar product distributions. [c] Similar isotopic distributions were obtained in two other runs. [d] Values obtained from analysis of gas phase and converted under the assumption mol % MeF = mol % Me_3SiCH_2OMe. [e] Not determined. [f] Calculated distribution for Stevens rearrangement: 16.8:34.6:34.6:14.0. [g] MS data did not allow differentiation between $Me_3SiCH_2OCD_3$ and $Me_3SiCH_2OCH_3$.

Initial fluoride-induced desilylation generates the methylenedimethyloxonium ylide, which is about equally transmethylated by CD_3 and CH_3 to give the related dimethylethyloxonium ions. Cleavage of these with F^- accounts for the formation of four differently labeled methyl ethyl ethers as well as two differently labeled ethyl fluorides.

Although partial methyl group scrambling in the oxonium ion may have occurred prior to ylide formation (as indicated by the isotopic distribution in Me_2O), intramolecular Stevens rearrangement of ylide to MeOEt can be ruled out. Such a process would clearly provide a different isotopic distribution in MeOEt than that experimentally

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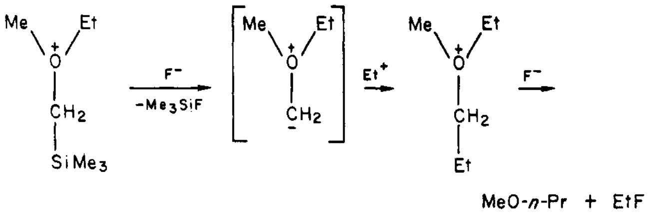
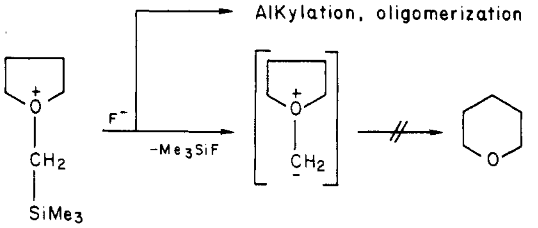
[14] $Me_2Si(Et)F$ is a decomposition product of Me_3SiCH_3F (cf. Voronkov, M. G. et al. *Dokl. Akad. Nauk SSSR, Bull. Div. Chem. Sci.* 1975, 1932).

Scheme III



Scheme IV



observed (cf. Table III, Note f). In addition the formation of ethyl fluoride can only be explained by intermediate formation of the ethylated oxonium ions. In a control experiment we also carried out the thermal decomposition of the silylated oxonium salt without added CsF. This reaction yielded no methyl ethyl ether or ethyl fluoride in sharp contrast to the experiment in which CsF was added.

We also prepared and studied the reaction of methylethyl((trimethylsilyl)methyl)oxonium tetrafluoroborate with CsF. The reaction products contained ethylene (3.9%), Me_2O (2.9%), Et_2O (1.2%), and MeO-*n*-Pr (0.02%) besides Me_3SiF and the usual alkylation products. Whereas ethylene and Me_2O and Et_2O can be formed by either an ylide mechanism or β-elimination and transalkylation, respectively, the formation of MeO-*n*-Pr must be due to ethylation of the intermediate ylide and subsequent cleavage of the oxonium ion (Scheme III).

In a further effort to observe an intramolecular Stevens rearrangement of an oxonium ylide, we investigated the desilylation reaction of the tetramethylene(trimethylsilyl)methyl)oxonium tetrafluoroborate with CsF. If the methylene ylide were generated it would be very favorable for such intramolecular rearrangement (Scheme IV).

We were unable to detect any tetrahydropyran, the expected rearrangement product from the methyleneoxonium ylide in the reaction mixture. The reaction products were Me_3SiF, Me_3SiCH_2F, $Me_2Si(Et)F$, and THF, together with some unidentified higher boiling products, resulting from alkylation and oligomerization reactions.

Although in the gas-phase reaction of methylene with THF[15] tetrahydropyran was found as one of the reaction products indicating intermediacy of the oxonium ylide and its intramolecular rearrangement (or direct insertion of methylene into the C–O bond) the condensed-state reaction conditions do not favor such a path (see also ref 11).

Conclusions

It was shown that the intermediate formation of highly reactive methylene dialkyloxonium ylides can be achieved from trimethyloxonium salts via deprotonation by sodium hydride or desilylation of dimethyl((trimethylsilyl)methyl)oxonium ion by fluoride ion in competition with the major alkylation reactions of the precursor oxonium ions. Intermediate methyleneoxonium ylides under the reaction conditions undergo ready alkylation by excess oxonium ion to form their higher homologous oxonium ions with new C–C bond formation rather than undergo intramolecular Stevens type rearrangement.

Experimental Section

Materials and Equipment. $^{13}CH_3I$ (90%) was purchased from KOR Isotopes. CD_3I (99%) and CD_3OD (99.5%) were obtained from Aldrich. CD_3OCD_3 were prepared by passing CD_3OD over Nafion-H catalyst at 180 °C in a reactor described previously.[7b] Methyl (trimethylsilyl)methyl ether was prepared as reported.[15] (Trimethylsilyl)methyl bromide was obtained from Petrarch. Dichloromethane was distilled over P_2O_5. Silver tetrafluoroborate (Aldrich) was used without further purification. Sodium hydride (Alfa, 61% mineral oil dispersion after separation) was washed three times with pentane and subsequently solvent was removed by repeated heating in vacuum. Cesium fluoride (Alfa, 99%) was dried under vacuum at 150 °C for 20 h prior to use. All reactions were carried out in argon atmosphere.

^1H NMR spectra were recorded on a Varian A-56/60 spectrometer in SO_2 solution at −60 °C (δ, external Me_4Si). ^{13}C and ^{29}Si NMR spectra were recorded on a Varian FT-80 spectrometer. GC and GC/MS analyses were conducted as described previously.[7b] All percentage numbers are given in mol%.

Trimethyloxonium Tetrafluoroborate. $(CH_3)_3O^+BF_4^-$, $^{13}CH_3O^+(CH_3)_2BF_4^-$, and $(CD_3)_3O^+BF_4^-$ were prepared by reacting dimethyl ether (or CD_3OCD_3) with methyl iodide ($^{13}CH_3I$ or CD_3I) and silver tetrafluoroborate in dichloromethane.[17] After the solvent was filtered off the oxonium salt was extracted with SO_2. Removal of SO_2 under vacuum gave the trimethyloxonium salt in high purity. Washing of the salt with ether must be avoided as it results in transalkylation.

Dimethyl((trimethylsilyl)methyl)oxonium Tetrafluoroborate. 1.80 g (12.7 mmol) of methyl iodide (or methyl-d_3 iodide for the preparation of the d_3 ion) was added to a cooled mixture of 2.34 g (12.0 mmol) of silver tetrafluoroborate, 1.50 g (12.7 mmol) of methyl (trimethylsilyl)methyl ether, and 15 mL of dichloromethane. The mixture was stirred for 2 at room temperature under exclusion of moisture and light. The precipitated silver iodide was filtered off and the solvent removed under vacuum to give 2.0 g (76%) of the oxonium salt in white crystals (mp ~25 °C): ^1H NMR 0.07 (s, 9 H, $SiCH_3$), 4.18 (s, 6 H, O^+CH_3), 4.45 (s, 2 H, O^+CH_2); ^{13}C NMR -4.4 ($SiCH_3$), 79.2 (OCH_3), 91.6 (O^+CH_2); ^{29}Si NMR 0.5.

Methylethyl((trimethylsilyl)methyl)oxonium Tetrafluoroborate. A mixture of 1.72 g (11.0 mmol) of ethyl iodide, 2.11 g of (10.8 mmol) silver tetrafluoroborate, 1.30 g (11.0 mmol) of methyl (trimethylsilyl)methyl ether, and 15 mL of dichloromethane was stirred for 2 h under exclusion of light and moisture and worked up as described previously. 1.97 g (78%) of methylethyl((trimethylsilyl)methyl)oxonium tetrafluoroborate was obtained as white crystals which liquified above 0 °C: ^1H NMR 0.08 (s, 9 H, $SiCH_3$), 1.44 (t, J = 7 Hz, 3 H, CCH_3), 4.09 (s, 3 H, O^+CH_3), 4.36 (s, 2 H, O^+CH_2Si), 4.53 (q, J = 7 Hz, 2 H, O^+CH_2C); ^{13}C NMR -3.3 ($SiCH_3$), 11.4 ($O^+CH_2CH_3$), 75.2 (O^+CH_3), 87.5 (O^+CH_2Si), 92.7 ($O^+CH_2CH_3$).

Tetramethylene((trimethylsilyl)methyl)oxonium Tetrafluoroborate. A mixture of 2.67 g (13.7 mmol) of silver tetrafluoroborate, 2.30 g (13.7 mmol) of (trimethylsilyl)methyl bromide, 1.0 g (13.9 mmol) of tetrahydrofuran, and 10 mL of dichloromethane was stirred for three days under exclusion of light and moisture and worked up as described previously [yield, 2.5 g (74%)]: ^1H NMR 0.16 (s, 9 H, $SiCH_3$), 2.24 (m, 4 H, CCH_2CH_2C), 4.40 (s, 2 H, O^+CH_2Si), 4.55 (m, 4 H, O^+CH_2C); ^{13}C NMR 4.3 ($SiCH_3$), 23.8 ($CH_2CH_2Ch_2Ch_2$), 84.3 (O^+CH_2Si), 86.0 (O^+Ch_2C); ^{29}Si NMR 1.0.

Reaction of Trimethyloxonium Salts with Sodium Hydride. (a) A suspension of 25 mmol of carefully purified sodium hydride in 20 mL of dimethyl ether was reacted with 7 mmol of trimethyloxonium tetrafluoroborate in a Teflon-lined magnetically stirred 125-mL autoclave at room temperature for 8 h. Products were analyzed by GC and GC/MS. Besides methane and traces

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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 thouroughly 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)methyl)oxonium 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 Hawlett 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. $(CH_3)_3O^+BF_4^-$, 420-37-1; $Me_3SiCH_2O^+(CD_3)CH_3BF_4^-$, 89909-26-2; $^{13}CH_3O^+(CH_3)_2BF_4^-$, 89909-30-8; $Me_3SiCH_2OCH_3$, 14704-14-4; $(CD_3)_3O^+BF_4^-$, 89909-32-0; dimethyl((trimethylsilyl)methyl)oxonium tetrafluoroborate, 89909-24-0; tetramethylene((trimethylsilyl)methyl)oxonium 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-d_2 with Dialkyl Ethers[1]

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Meerwein's reaction of singlet methylene, produced by photolysis of diazomethane, with dialkyl ethers has been reinvestigated on the basis of reactions using CD_2N_2. 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 methyldialkyloxonium ions. Dealkylative cleavage of the latter gives the observed methyl alkyl ethers. By the use of deuterium-labeled diazomethane CD_2N_2 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.

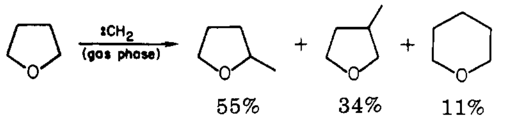
Introduction

In 1942 Meerwein and co-workers[2] described the formation of ethyl *n*-propyl ether and ethyl isopropyl ether upon illuminating an etheral 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 ^{14}C-labeled methylene they observed only end-labeled ethyl *n*-propyl ether, indicating direct insertion in the C–H bonds (eq 1).

$$\mathrm{CH_3CH_2OCH_2CH_3} \xrightarrow{:\mathrm{C^*H_2}} \mathrm{CH_3CH_2OCH_2CH_2C^*H_3} + \mathrm{CH_3CH_2OCH(CH_3)C^*H_3} \quad (1)$$

Doering and co-workers[4] 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 Voisey[5] observed tetrahydropyran (~10% of the products) formed in the gas phase photolysis of diazomethane in tetrahydrofuran (eq 2).



(2)

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[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.

[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.

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