J. Am. Chem. Soc. **1984**, *106*, 2143-2149

Onium Ylide Chemistry. 1. Bifunctional Acid-Base-Catalyzed Conversion of Heterosubstituted Methanes into Ethylene and Derived Hydrocarbons. The Onium Ylide Mechanism of the $C_1 \rightarrow C_2$ Conversion[1]

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Revised Manuscript Received October 24, 1983

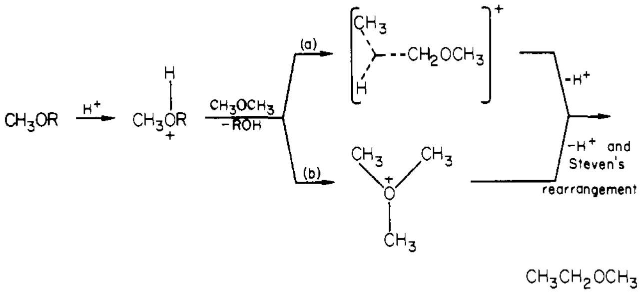
Abstract: The conversion of heterosubstituted methanes, such as methyl alcohol, dimethyl ether, methyl mercaptan, dimethyl sulfide, methylamines, and methyl halides, to ethylene and hydrocarbons derived thereof takes place over bifunctional acidic-basic-supported transition-metal oxide or oxyhalide catalysts, such as tungsten oxide supported on alumina, between 300 and 350 °C. The conversion of methyl alcohol starts with bimolecular dehydration to dimethyl ether followed by acid-catalyzed transmethylation giving trimethyloxonium ion (or related catalyst-bound methyloxonium ion). The trimethyloxonium ion then undergoes base-induced deprotonation forming a catalyst surface-bound methylenedimethyloxonium ylide. Intermolecular methylation of the ylide, indicated by experiments using singly ^{13}C-labeled dimethyl ether, gives methylethyloxonium ion thus providing the crucial first C–C bond. No intramolecular Steven's-type rearrangement takes place, and methyl ethyl ether is not a significant intermediate as also shown in experiments comparing the products formed from reacting $CD_3OCH_2CH_3$ under similar conditions. The ethyloxonium ion readily undergoes β-elimination forming ethylene. Initialy formed ethylene subsequently can undergo further reaction with the ylide giving via cyclopropane propylene or it can undergo more complex alkylation/oligomerization/cracking reactions giving a mixture of alkenes, alkanes and via cyclization–dehydrogenation aromatics. The complexity of these processes was shown by reacting ethylene itself, as well as $^{13}CH_3OH$ and ethylene, under conditions of the condensation reaction. It is also necessary to differentiate initially formed ethylene via direct $C_1 \rightarrow C_2$ conversion from that formed in secondary processes together with higher condensation products. The conversion of methyl mercaptan (dimethyl sulfide), methyl halides, and methylamines to ethylene follows similar onium ylide pathways.

The conversion of methyl alcohol or dimethyl ether into open-chain hydrocarbons of the gasoline range, as well as of cyclic aromatic nature, is of recent substantial significance in the context of the utilization of inexpensive starting materials, which can be produced from a variety of sources, including coal, wood products, natural gas, or other sources of methane gas, including any source of biomass.

A century ago, LeBel and Greene[2] first reported the production of gaseous saturated hydrocarbons (and some hexamethylbenzene) by adding methyl alcohol dropwise to "hot" zinc chloride. Grosse[3] described the formation of hydrocarbons from methyl alcohol over zinc chloride at 400–425 °C and pressures ranging from 1000 to 2500 psi. Kim et al.[4] recently reported that when methyl alcohol was reacted with a large excess of zinc iodide or bromide at 200 °C under 200 psi of nitrogen, a mixture of C_4–C_{13} hydrocarbons containing almost 50% of 2,2,3-trimethylbutane (triptane) was obtained. This unusual selectivity was considered to be the consequence of a carbenoid-type mechanism involving organozinc (Simmons–Smith type) complexed carbene intermediates.

The conversion of dimethyl ether mixed with "a normally gaseous alkane, generally isobutane," over a silica–alumina catalyst at 350–400 °C and 10–800 psi has been reported to give a mixture of normally liquid hydrocarbons, predominantly of the isoparaffinic and aromatic types.[5]

Scheme I



Supported aluminum sulfate has also been used for the conversion of methyl alcohol and dimethyl ether into higher hydrocarbons by contacting them at 250–400 °C.[6] The overall conversion was, however, low.

Pearson[7] described the conversion of methyl alcohol to hydrocarbons at 190 °C using phosphorus pentoxide in equimolar amount as condensing agent. The formation of the first C–C bond was suggested to be due either to invokement of a five-coordinate carbonium ion or to carbene insertion into C–H bonds (vide infra).

The Mobil Oil Co. in recent years disclosed a new efficient catalytic process using the acidic form of an intermediate pore size zeolite catalyst (aluminosilicate molecular sieve[8]) called ZSM-5, which allows the conversion of methyl alcohol into gasoline-range hydrocarbons.[9] The key to the process is stated to be the favorable shape selectivity of the catalyst allowing methyl alcohol conversion to take place in the cavities and channels of the zeolite. Chang and Silvestri[10a] described in detail the Mobil

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(1) A preliminary report of the mechanism was presented at the IUPAC Symposium on Physical Organic Chemistry at Santa Cruz, CA August 1980; see also ref 18.

(2) *Beilstein* **1918**, *1*, 277.

(3) Grosse, A. V.; Snyder, J. C. U.S. Patent 2492984, 1950.

(4) Kim, L.; Wald, M. M.; Brandenberger, S. G. *J. Org. Chem.* **1978**, *43*, 3432.

(5) Gorvin, E.; Gorvin, M. H. U.S. Patent 2456584, 1948.

(6) Hargis, D. C.; Kehoe, L. J. U.S. Patent 4072732, 1978.

(7) Pearson, D. E. *J. Chem. Soc., Chem. Commun.* **1974**, 397.

(8) Weisz, P. B. *CHEMTECH* **1973**, *3*, 498 and references therein.

(9) Meisel, S. L.; McCullough, J. P.; Lechthaler, C. H.; Weisz, P. B. *CHEMTECH* **1976**, *6*, 86 and references therein.

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Table I. Conversion of Heterosubstituted Methanes over Bifunctional Acid-Base Catalysts

reactant	CH_3OH	CH_3OCH_3	CH_3OCH_3	CH_3OCH_3	CH_3SCH_3	CH_3NH_2	$(CH_3)_2NH$	$(CH_3)_3N$	CH_3Cl
catalyst	WO_3 on alumina	WO_3 on alumina	tantalum oxyfluoride on alumina	zirconium oxyfluoride on alumina	WO_3 on alumina	WO_3 on alumina	WO_3 on alumina	WO_3 on alumina	WO_3 on alumina
temp, °C	325	320	250	370	380	360	350	340	327
GHSV[a]	50	50	50	50	50	900	360	360	50
conversion, %	99[c]	70	25	86	32	15	100	100	36
product distribution,[b] mol %	CH_3OH	CH_3OCH_3	CH_3OCH_3	CH_3OCH_3	CH_3SCH_3	CH_3NH_2	$(CH_3)_2NH$	$(CH_3)_3N$	CH_3Cl
CH_4	46.2	39.8	30.1	46.3	63.8	34.5	29.9	25.1	57.3
C_2H_4	29.8	28.6	26.2	20.6	15.4	10.8	31.5	61.7	15.8
C_2H_6	0.8	1.2	3.7	7.5	1.0	8.9	2.0		2.2
C_3H_6	19.3	20.6	19.9	12.9	18.5	13.0	17.2	0.9	9.3
C_3H_8	traces	0.8	1.8	2.4	traces	traces			2.4
C_4H_8	3.9	7.9	15.2	9.4	1.3	28.4	19.2	12.3	12.0
C_5H_{10}	traces	1.1	3.1	0.9		4.3	0.2	traces	1.0

[a] Gaseous hourly space velocity (mL g^{-1} h^{-1}). [b] Excluding higher aromatics, such as hexamethylbenzene and eventual coke formation on catalyst, as discussed in text. [c] Including 30% dimethyl ether.

process, proposing a carbenoid-type mechanism to account for the initial $C_1 \rightarrow C_2$ step (see also ref 10b and 11).

$$CH_3OR \underset{-ROH}{\rightarrow} [:CH_2] \xrightarrow{CH_3OR} CH_3CH_2OR \rightarrow C_2H_4 + HOR$$

$$R = H \text{ or } CH_3$$

Derouane et al.[12] elucidated other aspects of the methyl alcohol conversion by ^{13}C NMR studies, proposing a propagating carbocation mechanism to explain the products obtained.

Subsequently the conversion of methyl alcohol to hydrocarbons was studied over various catalysts by numerous research groups,[13-34] but still the mechanism of the crucial initial C–C bond formation remains unresolved. Bimolecular acid-catalyzed methyl alcohol dehydration giving dimethyl ether is generally believed to be the first step, followed by attack of an incipient methyl cation on dimethyl ether (Scheme I), thus forming either pentacoordinated carbocation intermediates (direct attack on carbon, path a)[7,14-16] or oxonium ions (attack on oxygen, path b).[17-21]

Transformation of oxonium ions via oxonium ylides (Stevens' rearrangement) could produce methyl ethyl ether, thus providing the first C–C bond. The oxonium ion to ylide to olefin pathway was independently first suggested in 1980 by Van den Berg et al.[17] and Olah,[1,18] but up till now no detailed report appeared nor was the nature of the initial C–C bond formation established (intra- or intermolecular).

In many studies[12,13,15,22,23] ethylene is considered to be the primary intermediate leading to higher hydrocarbons, whereas other authors[24-26] question its importance.

The autocatalytic nature of the methyl alcohol conversion over zeolites has also been pointed out.[15,22,27,28]

Similar studies of methyl alcohol conversion to hydrocarbons were carried out over zeolites other than ZSM-5,[29,30] as well as over heteropolyacids such as $H_3PW_{12}O_{40}$[16] and its inorganic[31] and organic[32] salts.

A recent ^{13}C NMR study[34] seems to support Chang and Silvestri's[10a] originally proposed mechanism, by observing surface-bound methoxy groups which are suggested to be converted into carbenes, but the results are also compatible with the onium ion–ylide mechanism (vide infra).

In our studies on utilizing methane (natural gas) directly as a building block for higher hydrocarbons as a viable alternative to the Fischer–Tropsch synthesis, we found highly selective methods to monofunctionalize methane into its substituted derivatives.[35a] We have been consequently interested in the conversion of substituted methanes into higher hydrocarbons. As part of this study, we now report results of our investigation of the conversion of substituted methanes including methyl alcohol and dimethyl ether, dimethyl sulfide, methylamines, and methyl chloride (bromide) over bifunctional acid–base catalysts such as WO_3/Al_2O_3, which lack any oriented structure considered essential in shape-selective zeolite catalysis, into ethylene and lower olefins. In particular we discuss, on the basis of our results, the mechanism for these novel and significant conversions.

Results and Discussion

When a heterosubstituted methane such as methyl alcohol, mercaptan, chloride, or methylamines are passed at 300–350 °C

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(10) (a) Chang, C. D.; Silvestri, A. J. *J. Catal.* **1977**, *47*, 249. (b) Chang, C. D.; Chu, C. T. W. *J. Catal.* **1982**, *74*, 203.

(11) Venuto, P. B.; Landis, P. S. *Adv. Catal.* **1968**, *18*, 259.

(12) Derouane, E. G.; Nagy, J. B.; Dejaifve, P.; van Hooff, J. H.; Spekman, B. P.; Vedrine, J. C.; Naccache, C. *J. Catal.* **1978**, *53*, 40.

(13) Kaeding, W. W,; Butter, S. A. *J. Catal.* **1980**, *61*, 155.

(14) Kagi, D. *J. Catal.* **1981**, *69*, 242.

(15) Ono, Y.; Mori, T. *J. Chem. Soc., Faraday Trans. 1.* **1981**, *77*, 2209.

(16) Baba, T.; Sakai, J.; Watanabe, H.; Ono, Y. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 2555.

(17) (a) Van den Berg, J. P.; Wolthuizen, J. P.; Van Hooff, J. H. C. in "Proceedings of the 5th International Conference on Zeolites"; Reed, L. V., Ed.; Heyden: London, 1980; p 649. (b) Van den Berg, J. P. Ph.D. Thesis, Eindhoven, 1981.

(18) Olah, G. A. *Pure Appl. Chem.* **1981**, *53*, 201 based on lecture given at the IUPAC Conference on Physical Organic Chemistry, Santa Cruz, CA, August 1980.

(19) Mole, T.; Whiteside, J. A. *J. Catal.* **1982**, *75*, 284.

(20) Perot, G.; Cormerais, F. X.; Guisnet, M. *J. Chem. Res. Synop.* **1982**, 58.

(21) Perot, G.; Cormerais, F. X.; Guisnet, M. *J. Mol. Catal.* **1982**, *17*, 255.

(22) Chen, N. Y.; Reagan, W. J. *J. Catal.* **1979**, *59*, 123.

(23) Haag, W. O.;Lago, R. M.; Rodewald, P. G. *J. Mol. Catal.* **1982**, *17*, 161.

(24) Ahn, B. J.; Armando, J.; Perot, G.; Guisnet, *Hebd. Seances C. R. Acad. Sci., Ser. C* **1979**, *288*, 245.

(25) Anderson, J. R.; Mole, T.; Christov, V. *J. Catal.* **1980**, *61*, 477.

(26) Dessau, R. M.; LaPierre, R. B. *J. Catal.* **1982**, *78*, 136.

(27) Ono, Y.; Imai, E.; Mori, T. *Z. Phys. Chem. (Wiesbaden)* **1979**, *115*, 99.

(28) Jaeger, N.; Jahn, A.; Schulz-Ekloff, G. *React. Kinet. Catal. Lett.* **1982**, *19*, 79.

(29) Ceckiewicz, S. *React. Kinet. Catal. Lett.* **1981**, *16*, 11.

(30) Ceckiewicz, S. *J. Colloid Interface Sci.* **1982**, *90*, 183.

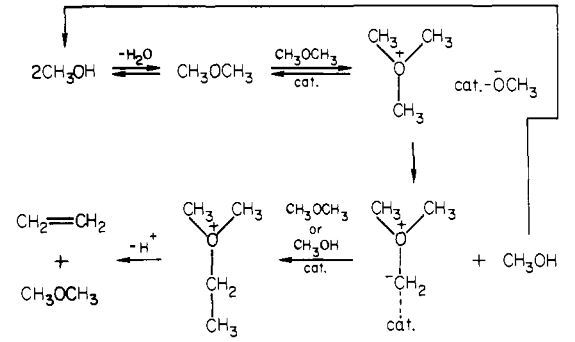
(31) Baba, T.; Sakai, J.; Ono, Y. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 2657.

(32) (a) Kasai, A.; Okuhara, T.; Misono, M.; Yoneda, Y. *Chem. Lett.* **1981**, 449. (b) Hibi, T.; Okuhara, T.; Misono, M.; Yoneda, Y. *Ibid.* **1982**, 1275.

(33) A referee has pointed out a report by R. G. Anthony et al. (*Oil Gas J.* **1978**, *76*, 92; **1977**, *75*, 106) on various catalysts and quoting inter alia the use of a tungsten oxide catalyst.

(34) Kotanigawa, T.; Shimokawa, K.; Yoshida, T. *J. Chem. Soc., Chem. Commun.* **1982**, 1185.

Scheme II



in a stream of dry nitrogen over a bifunctional acidic–basic transition-metal oxide or oxyhalide catalyst, such as tungsten oxide, tantalum oxyfluoride, or zirconium oxyfluoride supported on alumina, ready conversion to predominantly ethylene and propylene takes place.[35b] Products also include, besides significant amounts of methane, some lower saturated hydrocarbons, i.e., ethane, propane, etc. Table I summarizes the results of typical conversions. In the condensation of dimethyl ether over 10% WO_3/Al_2O_3 catalyst, as in the other condensation reactions, there is also formation of some aromatics. Benzene and toluene were observed only in trace amounts but C_8-C_{12} aromatics represent from 2 to 18% of products, building up generally with continued on-stream time. From the used catalyst solid aromatics were isolated by solvent extraction. Hexamethylbenzene was identified as a major component of the extracted aromatics. As coking on the surface eventually deactivates the catalyst, this obviously also involves formation of high molecular weight deposits. We have, however, carried out reactions without significant deactivation up to 8–12 h of on-stream time. Deactivated oxide catalysts are generally readily regenerated by treatment with steam at elevated temperatures and subsequent calcination.

Initial considerations presented by Venuto and Landis[11] as well as Chang and Silvestri[10a] concerning C–C bond generation from methyl alcohol over ZMS-5 catalyst suggested a carbene insertion mechanism facilitated by the specific sized channels and cavities of the zeolite catalyst. However, the monomolecular dehydration of methyl alcohol to methylene or the monomolecular formation of methylene from dimethyl ether is energetically highly unfavorable.

It also seems unlikely that initial C–C bond formation arises via incipient methyl cation attack on carbon forming pentacoordinated carbocation intermediates as postulated by Pearson,[7] Kagi,[14] and Ono[15,16] (see Scheme I, path a). Clearly an incipient methyl cation is not expected to attack a C–H bond in dimethyl ether in preference to the oxygen atom containing nonbonded electron pairs. The demonstration of superacid-catalyzed carbocationic reactions of alkanes[36] cannot be used as an analogy to the methylation of dimethyl ether which gives trimethoxyloxonium ion.

Results of our studies, discussed subsequently, suggest for the $C_1 \rightarrow C_2$ conversion in the condensation of methyl alcohol to ethylene the sequence of steps in Scheme II, which we for simplicity refer to as the onium-ylide mechanism.

Comparable reaction sequences involving onium ion to surface-bound ylide formation, followed by methylation of the ylide to give ethyl onium ion, are suggested for methyl sulfide, methyl chloride, or any of the heterosubstituted methanes shown in Table I. (See subsequent discussion.)

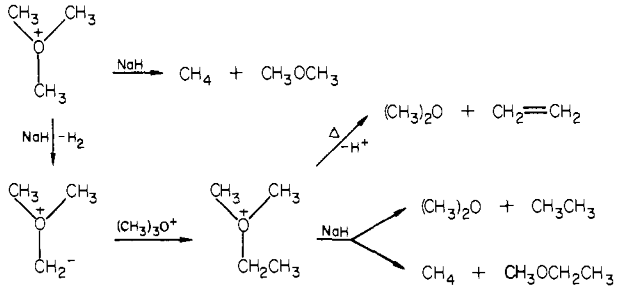
The first step in the conversion of methyl alcohol is the well-known acid-catalyzed bimolecular dehydration to dimethyl ether. Dimethyl ether is always found among the products of the methyl alcohol conversion reactions. It is itself converted over the bifunctional catalysts, but the rates are different. The further conversion of dimethyl ether proceeds via acid-catalyzed transmethylation, utilizing the well-recognized alkylating ability of ethers producing trialkyloxonium ions.

When dimethyl ether was reacted with tantalum or niobium pentafluoride in an autoclave, trimethyloxonium salts were isolated as byproducts of the condensation reaction.[37] Their formation has known counterparts in the disproportionation of BF_3 or PF_5 complexes of dimethyl ether to the corresponding onium ions.[38]

$$3(CH_3)_2O \xrightarrow{PF_5} 2(CH_3)_3O^+PF_6^- + POF_3$$

Similar oxonium ion formation is facilitated by the electron-deficient acidic sites of heterogeneous bifunctional acid–base catalysts. The subsequent conversion of the initially formed trimethyloxonium ion into ethylene is the key step in the conversion of methyl alcohol or dimethyl ether (as well as other substituted methanes) into higher hydrocarbons. A significant clue as to the nature of this conversion is provided by the fact that the effective catalysts in bringing about the $C_1 \rightarrow C_2$ conversion are all of bifunctional acidic-basic nature. Purely acidic catalysts show no similar activity.[37] Whereas superacidic systems can bring about Friedel–Crafts-type condensations of heterosubstituted methanes, the products formed in these reactions are entirely different from the products of the bifunctional acid–base-catalyzed condensation reactions and generally do not contain lower olefins such as ethylene and propylene, but saturated aliphatics and aromatics.[37] Thus it is indicated that the next step in the reaction sequence involves the basic site. Its preferred role is to cause catalyzed deprotonation of the oxonium ion to form surface-bound methylenedimethyloxonium ylide. In acid-catalyzed methylations with dimethyl ether catalyst-bound methoxide counterion is intermediately formed, which via subsequent proton abstraction gives methyl alcohol. Methyl alcohol of course can reenter the catalytic condensation cycle. However, in experiments using dimethyl ether as starting material methyl alcohol was always found in the reaction products if the reaction was carried out to lower conversion.

As far as the proposed oxonium ylide intermediate is concerned, such ylides are elusive because (a) the starting trialkyloxonium ions are good alkylating agents and tend to alkylate bases instead of undergoing deprotonation and (b) they can not be stabilized by d-orbital participation. In subsequent papers,[39,40] however, we provide via three independent pathways evidence for the formation of methylenedialkyloxonium ylide intermediates. Reaction of trimethyloxonium salts with sodium hydride results as the major reaction in formation of methane (hydride methylation) and dimethyl ether. However, a smaller amount of ethylene, as well as ethane formation, can be explained only by competing proton abstraction forming the methylenedimethyloxonium ylide. Subsequent methylation of the ylide by excess trimethoxyloxonium ion and cleavage of the intermediately formed dimethylethyloxonium ion leads to formation of methane and ethane, besides ethylene and dimethyl ether.



Fluoride-induced desilylation of dimethyl((trimethylsilyl)-methyl)oxonium tetrafluoroborate results, besides the major ex-

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[35] (a) Olah, G. A., patents applied for. (b) Olah, G. A. U.S. Patent 4 373 109, 1983.

[36] Olah, G. A.; Schilling, P.; Staral, J. S.; Halpern, Y.; Olah, J. A. *J. Am. Chem. Soc.* **1975**, *97*, 6807.

[37] Salem, G. Ph.D. Thesis, University of Southern California, Los Angeles, 1980.

[38] Goodrich, R. A.; Treichel, P. M. *J. Am. Chem. Soc.* **1966**, *88*, 3509.

[39] Olah, G. A.; Doggweiler, H.; Felberg, J. D. *J. Org. Chem.*, in press.

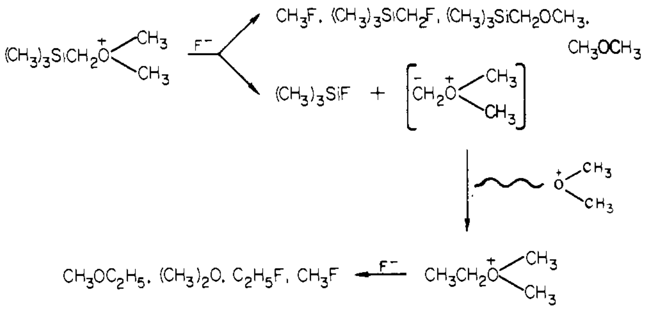
[40] Olah, G. A.; Doggweiler, H.; Felberg, J. D. *J. Org. Chem.*, in press.

Table II. Conversion of $^{13}CH_3OCH_3$ over WO_3/Al_2O_3

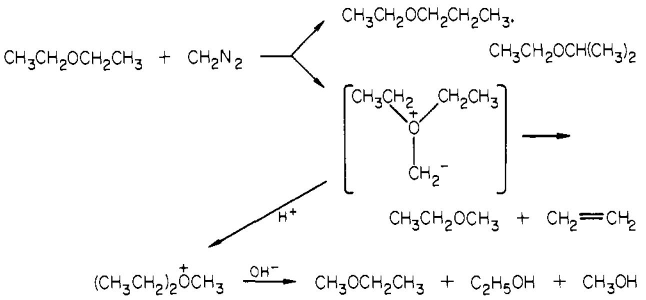
					isotopic distribution[a]			
						distribution, %		
run	temp, °C	amount of catalyst, g	GHSV, h^{-1}	conversion to hydrocarbons, %	material	$^{13}C_0$	$^{13}C_1$	$^{13}C_2$
1	300	12.0	50	70.0	Me_2O (starting material)	8.5	91.5	
					C_2H_4[b]	31.2	48.8	20.0
					Me_2O (recovered)	24.3	61.7	14.0
					calcd random distr in C_2 compds	29.4	49.7	20.9
2	350	0.5	1500	70.0	Me_2O (starting material)	6.7	93.3	
					CH_4	49.2	50.8	
					C_2H_4	29.7	48.3	22.0
					Me_2O (recovered)	26.1	52.7	21.2
					calcd random distr in C_2 compds	28.5	49.8	21.7
3	350	0.12	6000	5.0	Me_2O (starting material)	7.2	92.8	
					CH_4	57.5	42.5	
					C_2H_4[b]	38.8	42.1	19.1
					Me_2O (recovered)	17.4	69.8	12.8
					calcd random distr in C_2 compds	28.8	49.7	21.5

[a] C_3, C_4, and C_5 were also analyzed and showed randomization of label. [b] Calculated distribution resulting from intramolecular rearrangement (based on partial scrambling in recovered Me_2O): run 1, 28.2:53.8:18.0; run 3, 24.2:56.6:19.2.

pected fluoride alkylation products, i.e., methyl fluoride and trimethyl(fluoromethyl)silane and the corresponding ethers, in the formation of trimethylfluorosilane, methyl ethyl ether, and ethyl fluoride, indicating intermediate formation of methylenedimethyloxonium ylide, which via subsequent methylation and cleavage gives the observed ethyl product (i.e., those of $C_1 \rightarrow C_2$ conversion)



Meerwein's reaction of singlet methylene, produced by photolysis of diazomethane, with dialkyl ethers has also been reinvestigated. In competition with methylene insertion into the various C–H bonds, on the basis of reactions using CD_2N_2, evidence for competing attack of methylene on oxygen leading to intermediate oxonium ylides was obtained. The formed unstable methyleneoxonium ylides are immediately cleaved or protonated in the reaction medium (if traces of water are present) to give the corresponding trialkyloxonium ions, which then undergo cleavage forming methyl alkyl ethers.



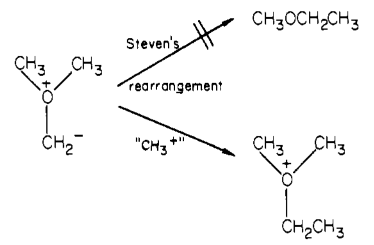
Whereas these studies were carried out in condensed state, we suggest that similar formation of the methylenedimethyloxonium ylide is feasible in the heterogeneous reactions on the catalyst surfaces, even more so because complexation of the methylene ylide with the catalyst could facilitate the reaction.

Table III. Conversion of $CD_3OCH_2CH_3$ over WO_3/Al_2O_3[a]

		isotopic distribution, %				
product	yield, %	d_0	d_1	d_2	d_3	d_4
methane[b]	11.1					
ethylene	86.4	83.5	13.7	2.8		
propylene	2.5	31.2	35.5	21.5	9.5	2.3
butylene[c]	traces	20.3	31.4	28.6	15.3	4.4

[a] At 350 °C, 0.5 g cat., GHSV = 360. [b] Contains d_4, d_3, and d_2 (quantitatively not determined). [c] One of four isomers analyzed.

Concerning the further conversion of the methylenedimethyloxonium ylide two possibilities exist. It could either undergo intramolecular Steven's-type rearrangement to methyl ethyl ether or undergo intermolecular methylation (by excess of dimethyl ether) to give dimethylethyloxonium ion.



Evidence that intermolecular alkylation of the oxonium ylide takes place and that no intramolecular Steven's-type rearrangement is involved was obtained when singly ^{13}C-labeled dimethyl ether was reacted over WO_3/Al_2O_3 catalyst and the label content in the products was determined. The results are summarized in Table II. In runs 1 and 3 the ^{13}C label content in the ethylene formed is much closer to that expected from the intermolecular alkylation process than expected from the intramolecular rearrangement. The $C_1 \rightarrow C_2$ conversion thus proceeds via intermolecular alkylation of the ylide. Deviations are due to the fact that some of the ethylene formed is not coming from the initial conversion, but from secondary processes (vide infra). Dimethyl ether recovered unreacted after passing over the catalyst (runs 1 and 3) shows partial ^{13}C label randomization. This indicates that dimethyl ether and trimethyloxonium ion are exchanging under the reaction conditions. When the conversion to ethylene and higher hydrocarbon is very low (run 3) more complete randomization takes place.

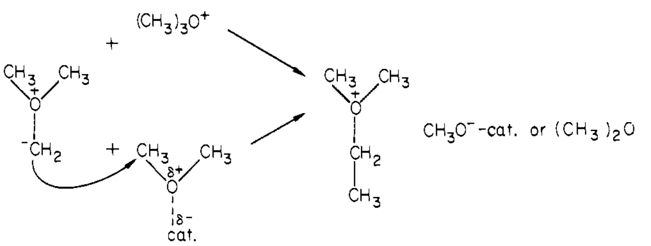
The methylating agent involved in the alkylation of the ylide intermediate can be the trimethyloxonium ion or the excess di-

Table IV. Reactions of $^{13}CH_3OH^a/C_2H_4$ Mixtures[b] over WO_3/Al_2O_3

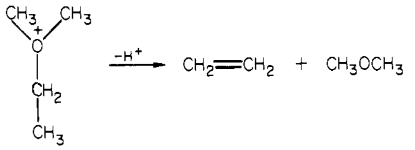
run	temp, °C	amount of catalyst, g	GHSV, h^{-1}	molar ratio of $^{13}CH_3OH:C_2H_4$	products[c]	isotopic distribution					
						distribution, %					
						$^{13}C_0$	$^{13}C_1$	$^{13}C_2$	$^{13}C_3$	$^{13}C_4$	$^{13}C_5$
1	350	0.5	360	10:1	Me_2O		25.0	75.0			
					CH_4	18.6	81.4				
					C_3H_6	5.3	15.4	35.3	44.0		
					C_4H_8[d]	2.4	5.1	17.9	38.6	36.0	
					C_5H_{10}	3.2	0.8	4.7	23.0	39.2	29.1
2	350	0.5	360	1:1	Me_2O		31.6	68.4			
					CH_4	19.8	80.2				
					C_3H_6	23.9	22.8	24.9	28.5		
					C_4H_8[d]	11.2	13.3	19.3	29.4	26.8	
					C_5H_{10}			12.4	26.1	35.0	26.5

[a] ^{13}C content, 90%. [b] Reactants mixed before introduction into reactor. [c] Ethylene not included. [d] One of four isomers analyzed.

methyl ether activated by complexation to the acidic catalyst sites (thus also of methyloxonium ion nature).



The formed dimethylethyloxonium ion subsequently readily undergoes β-elimination to yield ethylene and dimethyl ether, the latter then reentering the condensation reaction.



We have also studied the intra- vs. intermolecular nature of the transformation of the ylide intermediate through the use of labeled methyl ethyl ether, $CD_3OCH_2CH_3$. These results are shown in Table III. As discussed previously methyl ethyl ether was frequently postulated as the key intermediate in the $C_1 \rightarrow C_2$ conversion of dimethyl ether via methylene insertion. We have found, however, substantially different product compositions when methyl ethyl ether was reacted over the catalyst as compared to methyl alcohol or dimethyl ether (see Table I), thereby suggesting that methyl ethyl ether is not to any significant degree an intermediate formed on the path of the reaction. This is in agreement with our conclusion that the oxonium ylide does not rearrange through a Steven's-type process yielding methyl ethyl ether but is intermolecularly alkylated by catalyst-bound dimethyl ether resulting in the intermediate formation of dimethylethyloxonium ion.

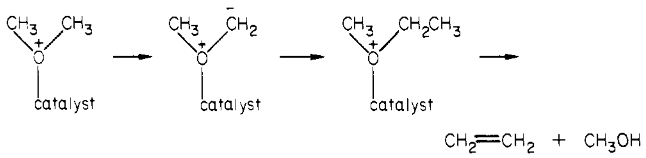
Catalytic cleavage of $CD_3OCH_2CH_3$ gives >80% of unlabeled ethylene.

$$CD_3OCH_2CH_3 \rightarrow CD_3OH + CH_2{=}CH_2$$

Labeled ethylene contains 83% d_1 and 17% d_2, indicating that part of ethylene observed is formed by complex oligomerization–cleavage reactions of the initially formed ethylene as well as its alkylation by CD_3OH formed in the reaction. The smaller amount of propylene formed in the reaction (2.5%) is 31% free of deuterium (thus coming from the initial unlabeled ethylene by oligomerization–cleavage reaction), as is 20% of butylenes formed in trace amounts. Extensive deuterium scrambling in these products (d_1 to d_4) again indicates the complexity of their formation.

Additional evidence concerning the further conversion of ethylene to higher hydrocarbons (propylene, butylenes, etc.) was obtained from the reaction of various ratios of ^{13}C-labeled methyl alcohol with ethylene over the WO_3/Al_2O_3 catalyst (see Table IV). Singly labeled propylene is expected from the methylation or methylenation (via cyclopropane) of ethylene. ^{13}C-labeled methyl alcohol itself also undergoes conversion thereby producing triply and doubly labeled propylene (due to less than 100% isotopic purity in the starting material). Observed unlabeled and scrambled C_2–C_5 olefins can, however, only be formed by ethylene oligomerization–cleavage processes. Indeed when ethylene itself was passed over the 10% WO_3/Al_2O_3 catalyst at 327 °C partial conversion was observed with formation of ethane, propane, propylene, butylenes, etc. as well as some aromatics and polymers. This indicates the complexity of the formation of products from initially formed ethylene either by self condensation or by reacting with excess methyl alcohol (dimethyl ether). It is thus necessary to differentiate initial formation of ethylene directly from methyl alcohol (or other C_1 precursors) from that formed in complex secondary processes involving alkylation–oligomerization–cleavage reactions.

It also should be pointed out that instead of the trimethyloxonium ion itself surface-bound dimethyl ether catalyst donor–acceptor complexes acting as oxonium ion type zwitterions can give similar results.



Methane formed as the major byproduct of the reactions is considered to be due to the thermal radical decomposition of dimethyl ether[41] including the cleavage.

$$CH_3OCH_3 \rightarrow CH_4 + CH_2O$$

We have not attempted in this study to establish carbon and hydrogen balances. Carbon loss is evident from CO observed as byproduct in some reactions, eventual coking of catalysts, and some higher aromatics formation. Hydrogen loss is indicated by methane formation and obvious occurrence of radical decomposition reactions. Methane, however, can be recycled via its selective monofunctionalization[35a] and thus represents no loss.

Formaldehyde was not identified in the products as it readily undergoes, as shown in control experiments, Cannizzaro-type disproportionation giving methyl alcohol (which enters the ethylene forming reaction) and formic acid (which decomposes to water and CO, see also ref 42).

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[41] Benson, S. W.; Jain, D. V. S. *J. Chem. Phys.* **1959**, *31*, 1008.

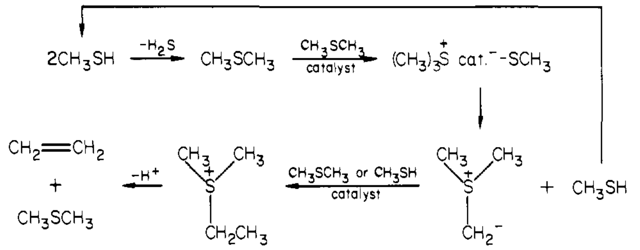
[42] Benziger, J. B.; Ko, E. I.; Madix, R. J. *J. Catal.* **1980**, *64*, 132.

The conversion of other heterosubstituted methanes over the bifunctional acid–base catalysts to ethylene (and subsequently to other derived products) proceeds similarly through the previously discussed onium–ylide mechanism.

The conversion of methyl mercaptan or dimethyl sulfide to ethylene closely resembles that of methyl alcohol/dimethyl ether. Methane (as well as some CS_2 and H_2) formed as byproducts is due to competing radical decomposition of dimethyl sulfide.

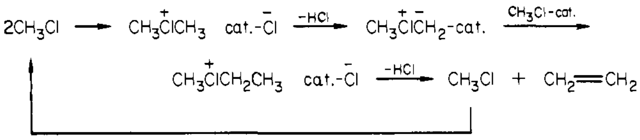
It has been observed previously by Franzen and Corey, respectively,[43] that when treating trimethylsulfonium ion, $(CH_3)_3S^+$, with suitable bases methylenedimethylsulfonium ylide is formed, which at room or more elevated temperature immediately decomposes to give ethylene. As the interest at the time was in the preparation and chemistry of the methylenedimethylsulfonium ylide, this observation arose little interest and was not followed up.

Our studies using mono-^{13}C-labeled trimethylsulfonium ion, $^{13}CH_3S^+(CH_3)_2$ (with 90% ^{13}C label), and sodium hydride indicated intermolecular methylation of the intermediate ylide to dimethylethylsulfonium ion and its subsequent ethylene forming elimination. Ethylene obtained contained 42% mono- and 10% di-^{13}C label, besides 48% unlabeled ethylene. (There was also some scrambling observed in the dimethyl sulfide, indicative of its transmethylation.) Dilabeled ethylene is thus formed by transmethylation of the ylide, but not by intramolecular Steven's-rearrangement (which, if at all, takes place to only a very limited degree). The overall mechanism of the conversion of methyl mercaptan to ethylene thus can be depicted as



Again catalyst complexes of methyl mercaptan or dimethyl sulfide can be also involved instead of the trimethylsulfonium ion itself in the reaction.

The condensation of methyl chloride to ethylene is also considered to proceed via a related intermediate ylide mechanism.



Acid-catalyzed formation of dimethylhalonium ions from methyl halides was well demonstrated in our previous work as was methylenemethylhalonium ylide formation via deprotonation of dimethylhalonium ions.[44]

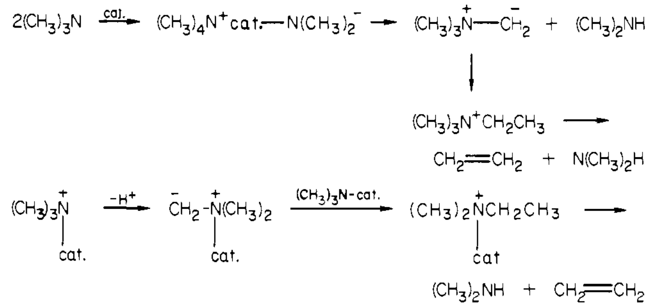
$$2CH_3X \xrightarrow{SbF_5} CH_3X^+CH_3\ SbF_5X^-$$

$$X = Cl, Br, I$$

$$CH_3X^+CH_3 \xrightarrow{-H^+} CH_3X^+CH_2^-$$

An analogous reaction path over the bifunctional acidic–basic catalyst surface could be further facilitated by transition-metal (such as W) complexation of the developing ylide providing external stabilization. Subsequent methylation of the methylene ylide gives the crucial $C_1 \rightarrow C_2$ conversion step followed by ethylene elimination.

The condensation of methylamines to ethylene again is considered to involve an onium–ylide mechanism either by transmethylation leading to the tetramethylammonium ion or via initial complexation with an acidic site of the catalyst providing a zwitterionic methylammonium ion, which then is deprotonated by the basic sites to form a catalyst-complexed ylide. The ylide subsequently via Steven's rearrangement eliminates and forms ethylene and dimethylamine, which reenters to condensation. Alternatively transmethylation of the methylene ylide to ethylammonium ion and subsequent ethylene elimination also can be considered. No labeling studies were performed on this system, but the formation of ethylene from tetramethylammonium ion via intermediate ylide formation is well-known.[45]



Dimethylamine gives results similar to trimethylamine, whereas methylamine gives less ethylene and more butylenes. The transmethylating ability of methylamine may be greatly decreased in comparison to di- and trimethylamine, resulting in the ylide acting as a methylene source converting ethylene into its higher homologues.

Conclusions

Bifunctional acid–base catalysts such as tungsten oxide supported on alumina effectively convert heterosubstituted methanes into ethylene and lower olefins, as well as give some alkanes. The mechanism of the conversion of methyl alcohol/dimethyl ether was studied in particular detail in respect to the fundamental initial C–C bond formation ($C_1 \rightarrow C_2$ conversion). The results of various labeling experiments strongly indicate initial trimethyloxonium ion formation, followed by proton abstraction to give methylenedimethyloxonium ylide. Subsequent methylation of the surface-bound ylide by excess dimethyl ether results in the crucial $C_2 \rightarrow C_2$ conversion step. Cleavage of the intermediately formed dimethylethyloxonium ion then gives ethylene and dimethyl ether, the latter reentering the condensation reaction. Ethylene is the primary product of the reaction, which subsequently can further react via methylation (methylenation) and/or more complex oligomerization/cleavage reactions. Propylene and butylenes, as well as alkanes of the gasoline range and through cyclization–dehydrogenation reaction aromatic hydrocarbons, are formed. The conversions of methyl mercaptan (dimethyl sulfide), methyl chloride (bromide), and methylamines to ethylene follow a similar reaction path.

Whereas our studies centered on bifunctional acidic–basic catalyst systems which posses no shape selectivity of zeolites, it can be argued that the crucial initial $C_1 \rightarrow C_2$ conversion step with the latter too involves a similar reaction pathway and that the channels and cavities of the zeolites only regulate subsequent product formation from ethylene by limiting the size of secondary products, as well as diminishing soot formation.

Experimental Section

Catalysts. Tungsten oxide (10%) on alumina catalyst was prepared by impregnating Al_2O_3 (~200 m^2/g) with an aqueous solution of ammonium tungstate. After evaporation of water, the catalyst was dried in air at 105–115 °C and calcined at 480–550 °C for 5 h.

Commercial pelleted tungsten oxide on alumina (10% WO_3/Al_2O_3) with a surface area of 145 m^2/g obtained from Strem Chemical was also used with comparable results.

Tantalum oxyfluoride (10%) on alumina was prepared by slowly dissolving tantalum pentafluoride into cold methyl alcohol (−78 to −10

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

(44) Olah, G. A. "Halonium Ions"; Wiley-Interscience: New York, 1975 and references therein.

(45) Zugravescu, I. P.; Petrovanu, M. "N-Ylide Chemistry"; McGraw Hill: New York, 1976; and references therein.

°C) with evolution of some hydrogen fluoride. The support was then treated with the solution as before and heated to 250–300 °C to obtain 10% tantalum oxyfluoride deposited on the alumina.

Zirconium oxyfluoride (10%) on alumina was prepared as above by treating alumina with zirconium tetrafluoride dissolved in methyl alcohol.

Reagents. Dimethyl ether (99.8%), methyl chloride (99.5%), and ethylene (99.9%) were purchased from Matheson. Dimethyl sulfide (98%) and trimethylamine (99%) were purchased from Aldrich. Dimethylamine was prepared from dimethylamine hydrochloride (Aldrich) with sodium hydroxide. Methylamine (40% in water) was purchased from MCB. $^{13}CH_3OCH_3$ was prepared from $^{13}CH_3I$ (90%, KOR Isotopes) and sodium methoxide by using the Williamson ether synthesis. $CD_3OCH_2CH_3$ was prepared from CD_3I (99%, KOR Isotopes) and sodium ethoxide. $^{13}CH_3OH$ (90%) was purchased from KOR Isotopes.

General Procedure for Heterogeneous Catalytic Conversion of Heterosubstituted Methanes into Ethylene and Lower Olefins. All reactions were carried out at atmospheric pressure in a fixed-bed, continuous-flow, electrically heated 550 × 10 nm Pyrex glass tube reactor, similar to that described in our previous work.[46] Generally 10 g of supported catalyst, previously calcinated, was placed in a stream of dry nitrogen into the reactor, and reactants were introduced in a constant N_2 stream with a gaseous space velocity (volume of gas passed over volume of catalyst per hour) of between 50 and 1000 under conditions shown in Table I. Samples were taken at the outlet of the reactor and analyzed by GC and GC/MS. For isotopic label determination products were passed through a solution of bromine in carbon tetrachloride in order to trap formed olefins as dibromoalkanes and were analyzed as such by GC/MS.

Analyses. GC analyses of the reaction mixtures were conducted on the following instruments: (a) Hewlett Packard 5130 A with a Poropak Q column (12 ft $^1/_8$ in.); (b) Varian 3700 with an OV 101 glass capillary column (50 m). All percentage numbers are corrected for FID response factors and are given in mol %.

MS analyses were carried out on a Hewlett Packard 5985 A GC/MS spectrograph equipped with a Poropak column. For the MS analysis of 1,2-dibromoalkanes an OV 101 column (6 ft $^1/_8$ in.) was used.

Acknowledgment. Our work was supported by the Hydrocarbon Research Institute of the University of Southern California and concerning mechanistic studies by the National Science Foundation. H. D. gives thanks for financial support by the Zentenarfonds of the Swiss Federal Institute of Technology, Zurich.

Registry No. CH_3OH, 67-56-1; CH_3OCH_3, 115-10-6; CH_3SCH_3, 75-18-3; CH_3NH_2, 74-89-5; $(CH_3)_2NH$, 124-40-3; $(CH_3)_3N$, 75-50-3; CH_3Cl, 74-87-3; $^{13}CH_3OCH_3$, 88842-43-7; $CD_3OCH_2CH_3$, 16995-14-5; $^{13}CH_3OH$, 14742-26-8; CH_3SH, 74-93-1; WO_3, 1314-35-8; C_2H_4, 74-85-1; CH_4, 74-82-8; propylene, 115-07-1; butylene, 25167-67-3; tantalum oxyfluoride, 20263-47-2; zirconium oxyfluoride, 14984-80-6; pentylene, 25377-72-4.

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(46) Olah, G. A.; Kaspi, J. *Nouv. J. Chim.* **1978**, *2*, 585.

The Michael Reaction of Silyl Enol Ethers or Ketene Silyl Acetals with Conjugated Nitro Olefins Activated by the Lewis Acid: New Synthesis of 1,4-Diketones and γ-Keto Esters

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Abstract: New one-pot procedures for the synthesis of 1,4-diketones and γ-keto esters utilizing conjugated nitro olefins are described. Reaction of silyl enol ethers with aliphatic nitro olefins in the presence of a Lewis acid affords 1,4-diketones in good yields, while similar reaction of ketene silyl acetals, derived from various esters, with nitro olefins produces a variety of γ-keto esters, after hydrolytic treatment. Regiospecific addition of carbonyl compounds to nitro olefins was observed in both reactions. 1,4-Diketones obtained could be converted into the corresponding cyclopentenones in high yields.

The Michael addition of carbonyl compounds to conjugated nitro olefins is one of the efficient carbon–carbon bond-forming reactions involving nitro compounds,[1] as well as nitro-free structures.[1c,2] The synthetic potential of nitro olefins also lies in the remarkable versatility of nitro groups in the interconversions of organic functional groups,[1c] among which the transformation of nitro aliphatics into carbonyl compounds, the Nef reaction,[3] is the most important from the synthetic viewpoint. Thus nitro groups are synthetically equivalent to carbonyl groups[4] and they provide *an umpolung of reactivity*[1c] of carbonyl derivatives (Figure 1), hence the Michael addition of this type should promise a new entry to 1,4-dicarbonyl compounds.[5,6]

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(1) (a) Müller, E., Ed. "Methoden der Organischen Chemie", Houben-Weyl; G. Thieme Verlag: Stuttgart, 1971; Vol. 10/1, pp 372–397. (b) Corey, E. J.; Estreicher, H. *J. Am. Chem. Soc.* **1978**, *100*, 6294. (c) Seebach, D.; Colvin, E. W.; Weller, T. *Chimia* **1979**, *33*, 1. (d) Ono, N.; Miyake, H.; Kaji, A. *J. Chem. Soc., Chem. Commun.* **1982**, 33.

(2) (a) Ono, N.; Kaji, A. *Yūki Gosei Kagaku Kyokai Shi* **1980**, *38*, 117. (b) Yoshikoshi, A. *Ibid.* **1982**, *40*, 427.

(3) Nef, J. U. *Justus Liebigs Ann. Chem.* **1894**, *280*, 264.

(4) Norland, W. E. *Chem. Rev.* **1955**, *55*, 137. Shechter, H.; Williams, F. T., Jr. *J. Org. Chem.* **1962**, *27*, 3699. Pagano, A. H.; Sechter, H. *Ibid.* **1970**, *35*, 295. McMurry, J. E.; Melton J. *J. Am. Chem. Soc.* **1971**, *93*, 5309; *J. Org. Chem.*, **1973**, *38*, 4367. McMurry, J. E. *Acc. Chem. Res.* **1974**, *7*, 281. Kornblum, N.; Wade, P. A. *J. Org. Chem.* **1973**, *38*, 1418. Alvarez, F. S.; Wren, D. *Tetrahedron Lett.* **1973**, 569. Mc Murry, J. E.; Melton, J.; Padget, H. *J. Org. Chem.* **1974**, *39*, 259. Kirchoff, R. *Tetrahedron Lett.* **1976**, 2553. Akita, Y.; Inaba, M.; Uchida, H.; Ohta, A. *Synthesis* **1977**, 792. Keinan, E.; Mazur, Y. *J. Am. Chem. Soc.* **1977**, *99*, 3861. Bartlett, P. A.; Green, F. R.; Webbm T. R. *Tetrahedron Lett.* **1977**, 331. Hogg, J. L.; Goodwin, T. E.; Nave, D. W. *Org. Prep. Proced. Int.* **1978**, *10*, 9. Williams, J. R.; Unger, L. R.; Moore, R. H. *J. Org. Chem.* **1978**, *43*, 1271. Dubs, P. Schenk, H.-P. *Helv. Chim. Acta* **1978**, *61*, 984.

0002-7863/84/1506-2149$01.50/0