Methanol into Hydrocarbon Conversion. A Mechanistic Study: an Oxygen Ylide Intermediate

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Methyl ethyl ether is formed by treating trimethyloxonium hexachloroantimonate with the strongly hindered base, 2,2,6,6-tetramethylpiperidyl-lithium; this reaction is attributed to the formation of an oxygen ylide followed by a Stevens-type rearrangement or intermolecular methylation.

Since the discovery in the early seventies by workers at Mobil[1] that methanol could be converted into gasoline over ZSM-5 zeolite, numerous attempts have been made to clarify the mechanism of this reaction.

While it is generally agreed that the reaction path can be divided into three key steps: ether formation, initial C–C bond formation, and aromatization, until now the mechanism of the second key step has been unresolved. A variety of hypotheses have been suggested and recently reviewed by Chang.[2] The hypothesis involving an oxonium ylide intermediate, independently suggested by Van den Berg *et al.*[3a] and G. A. Olah,[3b] has recently received more experimental attention.[4,5] In this paper we describe our attempts to prepare methyl ethyl ether, directly, *via* the trimethyloxonium ylide.

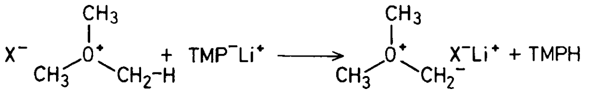
Trimethyloxonium hexachloroantimonate, $Me_3O^+SbCl_6^-$ has been prepared from epichlorohydrin according to the method of Meerwein.[6] However, the salt was washed only with CCl_4, dried, and stored under vacuum.

The oxonium salt (600 mg, 1.5 × 10^{-3} mol) was introduced under vacuum to a vessel containing 2,2,6,6-tetramethylpiperidyl-lithium (TMPLi) (1.5 × 10^{-3} mol) dissolved in excess of 2,2,6,6-tetramethylpiperidine (TMPH) (1 ml).

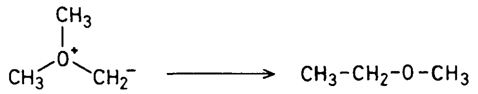
The heterogeneous mixture was shaken for 30 min at room

Table 1. Composition of the head space gases.

						mol %				
Experiment		CH_4	C_2H_4	C_2H_6	C_3H_8	MeCl	MeOMe	C_4H_{10}	EtOMe	EtOEt
1(a)	30 min at room temperature	0.5	0.5	0.5	0.5	15.0	70.0	1.0	0.6	11.0
1(b)	30 min at 70 °C	2.0	2.0	2.0	5.0	15.0	32.0	3.0	25.0	12.0
2	Oxonium salt + TMPH 30 min at 70 °C	—	—	—	—	22.0	70.0	—	—	8.0
3	Oxonium salt + EtOEt 30 mn at 70 °C	—	—	—	—	5.0	10.0	—	—	85.0
4	Oxonium salt + 2,6-di-t-butylpyridine 30 min at 70 °C	—	—	—	—	53.0	47.0	—	—	—



(1)



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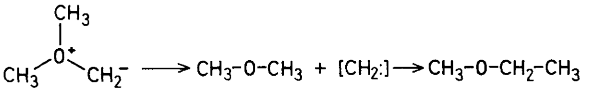

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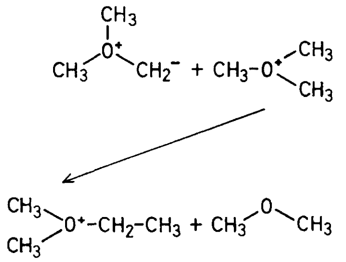
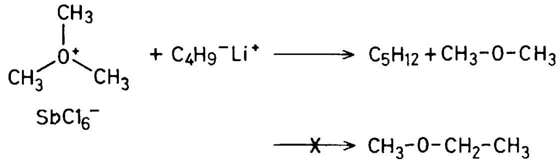


(4)

temperature and then for 30 min at 70 °C. The head space gases were analysed after the first and the second period. The compositions of the gases are given in Table 1.

The presence among the products of methyl ethyl ether and C_2—C_4 hydrocarbons suggests the intermediacy of a trimethyloxonium ion in the methanol conversion process. The strongly hindered base can abstract a proton from the oxonium salt [equation (1)]. This oxygen ylide can then react in one of the following ways which all yield methyl ethyl ether. A Stevens type intramolecular rearrangement, which is a novel reaction for an oxygen ylide but is well known for ammonium ylides [equation (2)]. The mechanism could also involve a carbene [equation (3)]. Finally, the methyl transfer could occur in an intermolecular fashion [equation (4)].

The intermolecular nature of the ylide rearrangement is supported by recent work of Olah and his group[4] using singly ^{13}C-labelled dimethyl ether as the starting material on a bifunctional acid–base catalyst. The intermolecular origin of ethylene obtained from ^{13}C-labelled dimethyl ether over ZSM-5 and silica–alumina catalysts has been shown by Guisnet and his group.[7]



(5)

The other products can be easily explained. MeCl and MeOMe originate from partial decomposition of the oxonium salt. The hydrocarbons are generally supposed to be formed *via* carbene oligomerisation.[8] However, olefins can also be obtained *via* an ylide intermediate.[3a] Traces of diethyl ether (present as an impurity in TMPH, which could not be further purified) are also found in the head space gases. We have shown, however, that under our experimental conditions direct methylation of this ether by the oxonium ion does not occur (Experiment 3, Table 1).

In a separate experiment we treated trimethyloxonium hexachloroantimonate with s-butyl-lithium in hexane. No methyl ethyl ether was detected but direct methylation occurred as shown by the formation of isopentane [equation (5)].

This again shows the necessity of a strongly hindered base to initiate ylide formation. One question which remains, however, is the nature of the basic site on the zeolite catalyst.

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