Tetrahedron Letters No.9, pp. 687-690, 1969. Pergamon Press. Printed in Great Britain.

ORGANIC SYNTHESIS BY ELECTROLYSIS IV
ELECTROLYTIC GENERATION OF SULFONIUM YLIDE

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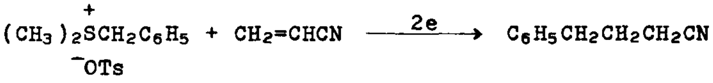
(Received in Japan 20 December 1968; received in UK for publication 16 January 1969)

In the previous study, we have found a novel electrolytic generation of phosphonium ylides from the corresponding phosphonium salts[1].

$$(C_6H_5)_3\overset{+}{P}\text{-}CH_2R \xrightarrow{e} (C_6H_5)_3P{=}CHR$$

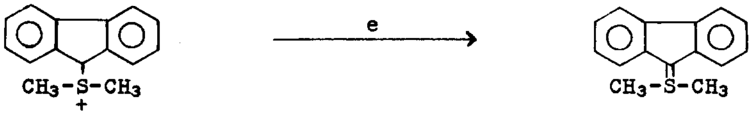
In the present study, we wish to report a novel electrolytic generation of sulfonium ylides. The electrolysis of some sulfonium salts in the presence of acrylonitrile has been studied and the formation of a coupling product has been observed[2].



$$(CH_3)_2\underset{^{-}OTs}{\overset{+}{S}}CH_2C_6H_5 + CH_2{=}CHCN \xrightarrow{2e} C_6H_5CH_2CH_2CH_2CN$$

This coupling reaction was elucidated by an anionic reaction mechanism, in which the anion was formed by the reductive cleavage of the sulfonium salt.

In our preliminary study, the electrolysis of an aqueous solution of dimethyl-9-fluorenylsulfonium bromide or dimethyl-9-(2-nitrofluorenyl)sulfonium bromide with a carbon cathode gave immediately the corresponding sulfonium ylide on the surface of the cathode.



The formation of the stable ylide suggested the possibility of the electrolytic generation of the unstable ylide which may be trapped by an appropriate acceptor such as carbonyl compound or electrophilic olefinic compound.

Thus, in the present study, the electrolysis of trimethylsulfonium iodide in the presence of an acceptor, such as benzaldehyde, cyclohexanone, acetophenone, benzophenone, ethyl fumarate or ethyl maleate was investigated to demonstrate the formation of the sulfonium ylide.

Table I Products and Yields

Carbonyl Compound or Olefinic Compound	Product	Yield (%) [a]
Benzaldehyde	Styrene oxide	28 [b]
Benzaldehyde	Styrene oxide	32
Cyclohexanone	Methylenecyclohexane oxide	10
Acetophenone	α-Methylstyrene oxide	7
Benzophenone	α-Phenylstyrene oxide	40
Ethyl maleate	Diethyl 1,2-Cyclopropane-dicarboxylate	10 (trans) 6 (cis)
Ethyl fumarate	Diethyl 1,2-Cyclopropane-dicarboxylate	6 (trans) 6 (cis)
Benzaldehyde	β-Methylstyrene oxide	10 [b,c]

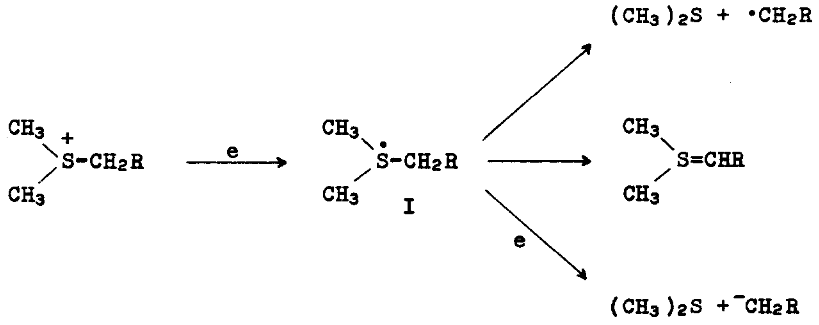
[a] Yields were determined by VPC.

[b] DMSO was not used as solvent.

[c] The sulfonium salt is diphenylethylsulfonium fluoroborate.

The electrolysis was carried out with a carbon electrode at 15-50 V in a cylindrical cell, and a mixture of an acceptor and dimethyl sulfoxide was used as solvent³⁾. An unglazed pottery filter was used as a diaphragm. The yields of the products are shown in the Table I.

The preliminary study suggested that the difference of the reduction potential of the acceptor and the sulfonium salt may not be so large as the reaction mechanism can be established by the polarographic technique. Although the establishment of the reaction mechanism is not the object of this communication, the reaction mechanism may be able to be classified into two types. In one of them, the sulfonium salt behaves as a supporting electrolyte and the acceptor is reduced to an anionic species which may act as a base to eliminate a proton from the sulfonium salt to yield the ylide. In another mechanism, the sulfonium salt itself is electrolytically reduced to the ylide. As was observed in the preliminary study, the formation of the stable sulfonium ylides in the absence of the acceptor might suggest a preference for the latter mechanism. Furthermore, the fact that in the electrolysis of a solution of carboethoxymethyl-dimethylsulfonium bromide and small amount of cyclohexene in dimethylformamide, the formation of ethyl acetate was observed might suggest the generation of a radical intermediate (I) in the electrolytic reduction of sulfonium salts.



The formation of the sulfonium ylide from the radical intermediate (I) may be a competing reaction with the homolytic decomposition or further reduction of I, and the relative rates of these competing reactions may be influenced by the nature of the substituent R.

Acknowledgment. We are extremely grateful to Professor R.Oda of Kyoto University for his kind encouragement.

References

1) Tatsuya Shono and Michiharu Mitani, J. Am. Chem. Soc., 90 2728 (1968)
2) M.M.Baizer, J. Org. Chem., 31 3847 (1966)
3) Owing to the low solubility of the sulfonium salt in acceptors, dimethyl sulfoxide was used as a co-solvent.