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A NEW METHOD FOR GENERATION OF ETHOXYCARBONYLNITRENE. A BASE-INDUCED DECOMPOSITION OF N-(p-TOLUENESULFONYLOXY)URETHANE IN A CATIONIC MICELLE

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A base-induced decomposition of N-(p-toluenesulfonyloxy)urethane in an emulsifying system leading to ethoxycarbonylnitrene which was trapped by benzene, toluene, and cyclohexane yielding its addition and insertion products is described.

Although it is conceivable by analogy with the common means of forming carbenes that the base-induced α eliminations would give nitrenes as reactive intermediates, they have so far been restricted only to an α elimination of p-nitrobenzenesulfonate from the anion of N-(p-nitrobenzenesulfonyloxy)urethane leading to free ethoxycarbonylnitrene.1) Other similar reactions appear doubtful if nitrenes are involved as discrete intermediates, even if the final products would have also been expected from the characteristic reaction of the nitrenes.2)

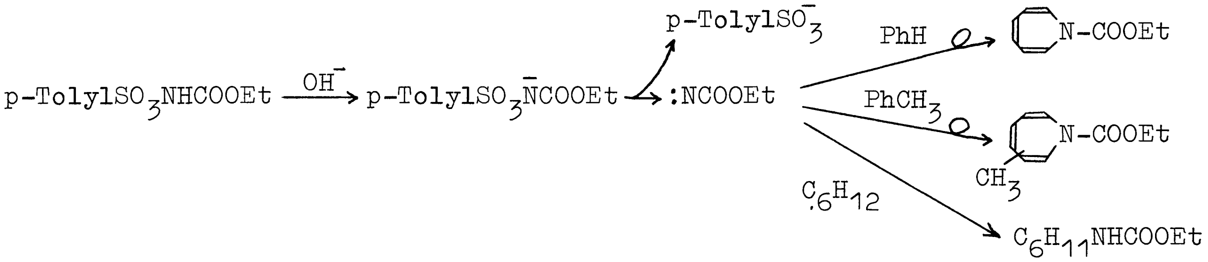
We now wish to report some preliminary results, providing an evidence for the generation of free ethoxycarbonylnitrene, of treating N-(p-toluenesulfonyloxy)urethane (I), a compound that does not generate the nitrene intermediate in homogeneous organic solutions containing triethylamine, with an aqueous alkali in emulsifying systems using cetyltrimethylammonium bromide (II) as a cationic surfactant.3)

N-Ethoxycarbonylazepine was produced in a 13% yield by the caustic soda-induced decomposition of I in an emulsified mixture of benzene and water containing II. In cationic micelles formed from toluene instead of benzene, three isomeric methyl-N-ethoxycarbonylazepines, i.e.2-, 3-, and 4-methyl-N-ethoxycarbonylazepines, were produced in an 18% total yield, in an isomer ratio of 1.0: 1.3: 1.1, on treatment of I with aqueous sodium hydroxide.4)

Furthermore, ethoxycarbonylnitrene which might be generated from the precursor I in the emulsifying system was found to be capable of inserting into a C-H bond of cyclohexane yielding N-cyclohexylurethane (12% yield) when the aromatic substrates were replaced by a mixture of cyclohexane and dichloromethane. Thus, the formation of free ethoxycarbonylnitrene in our emulsifying system is strongly suggested by the above results that the relative ratio of three isomeric methyl-N-ethoxycarbonylazepines was comparable to that in the thermolysis of the azido compound4) and the insertion product into the C-H bond of cyclohexane was obtained. None of those products, however, which could be thought to arise from the distinctive reaction of ethoxycarbonylnitrene, were obtained in the absence of cationic micellar agent II.

In addition to the above findings, any other products, such as urethane, hydroxyurethane, and diethyl hydrazodiformate, have not yet been found in each case even though the nitrene precursor used had been completely decomposed into sodium p-toluenesulfonate on treating with the base.

We now postulate a mechanism in which the anion of I is initially formed by an action of hydroxide anion concentrated at the stern layer of cationic micelles, followed by elimination of p-toluenesulfonate anion, and the resulting anion diffuses into aqueous phase leaving the nitrene so formed in organic phase.



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3) The generation of carbene in emulsifying system has been already reported, G.C.Joshi, N.Singh, and L.M.Pande, Tetrahedron Lett., 1461 (1972); M.Makosza and M.Wawrzyniewicz, ibid, 4659 (1969); I.Tabushi, Z.Yoshida, and N.Takahashi, J.Amer.Chem.Soc., 93, 1820 (1971).

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