

A New Reaction of Methylene: Insertion in the Carbon-Oxygen Bond

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METHYLENE generated by the photolysis of diazomethane in both the gas and liquid phase, and from keten in the gas phase reacts with ethers predominantly by insertion in the carbon-hydrogen bonds to yield homologous ethers. Thus reaction with dimethyl ether produces ethyl methyl ether and with diethyl ether produces a mixture of ethyl n-propyl ether and ethyl isopropyl ether.^{1,2} There are other minor reaction paths involving hydrogen atom-abstraction by the methylene and also an intramolecular elimination of ethylene in some cases.

The formation of ethyl n-propyl ether from methylene and diethyl ether could result from both insertion in a carbon-hydrogen bond and, in addition, by insertion in the carbon-oxygen bond. To eliminate this second possibility Franzen and Fikentscher³ investigated the reaction using ¹⁴CH₂ (from ¹⁴CH₂N₂) and were able to show that insertion in the carbon-oxygen bond did not occur. In another attempt to test this particular point, Doering *et al.*⁴ investigated the photolysis of diazomethane in the presence of tetrahydrofuran (as solvent) and isolated only the 2- and 3-methyltetrahydrofurans as products. No tetrahydropyran (the expected product from a carbon-oxygen insertion reaction) was detected. The authors note that as little as 0.5% would have been easily detectable.

We now report that the photolysis of both diazomethane and keten in the presence of tetrahydrofuran *in the gas phase* does lead to the formation of some tetrahydropyran. In typical experiments with a ratio of tetrahydrofuran to diazomethane of 7:1 with a Pyrex reaction vessel and a medium-pressure mercury arc, the relative yields of 2-methyltetrahydrofuran, 3-methyltetrahydrofuran, and tetrahydropyran were 55%, 34%, and 11% respectively. In similar experiments with keten the relative yields were 50%, 29%, and 21%. Under these conditions it can be seen that the insertion reaction in the carbon-oxygen bond represents a major reaction pathway. We have repeated the experiments of Doering *et al.*⁴ by photolysing diazomethane in tetrahydrofuran in

the liquid phase in a micro-cell at -70°. Under our conditions less than 2% of tetrahydropyran was detected. This represents an upper limit since (a) the amount formed was so small that its accurate measurements presented considerable difficulties and an over- rather than an under-estimate was likely; (b) we cannot rule out the possibility of the presence of another compound of the same retention time as the tetrahydropyran on the gas-chromatography column (secondary analysis was not possible in this case); and (c) with the experimental apparatus used, a small residual gas-phase photolysis probably took place. Our liquid-phase results are certainly consistent with the complete absence of tetrahydropyran as noted previously.

It is tempting to ascribe the insertion of methylene in the carbon-oxygen bond as a reaction of the triplet species since many of the differences between the observations of the reactions of methylene in the two phases can be rationalised on the basis of the occurrence of triplet methylene in gas-phase photolyses and its absence in normal liquid-phase work. However a number of observations rule out this possibility. Gas-phase photolyses in the presence of sufficient oxygen to eliminate products due to radical processes and triplet methylene do not result in a reduction in the yield of tetrahydropyran. Experiments in the gas phase with triplet methylene produced by the mercury-photosensitised decomposition of keten⁵ did not yield tetrahydropyran as a product. In a similar manner, photosensitised experiments in the liquid phase using diazomethane and acetophenone with light of 3130 Å which would be expected to yield only triplet methylene⁶ did not result in the production of tetrahydropyran.

The yield of tetrahydropyran could, however, be affected by gas-phase photolysis in the presence of inert gases (nitrogen, argon, perfluoropropane). The experimental data (which will be published in detail shortly) support the hypothesis that the insertion reaction in the carbon-oxygen bond is due to singlet methylene which has lost some of the excess of energy that it possessed on its genesis.

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