Matrix Photolysis of Diazoacetaldehyde

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Summary The photolysis of diazoacetaldehyde in argon and ethylene matrices leads to keten; photolysis of the corresponding ester in solid argon or nitrogen gives ethoxyketen, a product which is substantially reduced when the photolysis is carried out in hydrocarbon matrices.

Although many studies of the photochemistry of diazoketones and esters have been reported,[1,2] no study of the photoreactions of even simple diazoaldehydes has appeared despite reports describing their synthesis.[3,4]

Photolysis of diazoacetaldehyde[3] (**1**) in solid argon (matrix/reagent, M/R = 117—700) at 8 K with light filtered through Pyrex gave keten (**2**) essentially quantitatively, identified by comparison with published spectra of the matrix-isolated species.[5] In a typical experiment, a 19 mm sample (M/R *ca.* 117) was irradiated for 45 min to effect complete conversion of (**1**) into (**2**).† Under these conditions, oxiren[6] (**3**), if formed from (**1**), is not stabilized by the matrix environment, for no new bands other than those of keten were detected even with thick matrices and low matrix/reagent ratios. Furthermore, irradiation of (**1**) in ethylene (M/R *ca.* 825, 42·5 mm), also resulted in the formation of keten, with no other detectable changes in the i.r. spectrum.

Photolysis of ethyl diazoacetate[7] (**4**) in argon and nitrogen (M/R = 500—1000) with light filtered through nickel sulphate gives rise to a typically intense keten absorption at 2120 cm^{-1}, and the complete decomposition of a 34 mm sample can be accomplished in 30 min.‡ However, in

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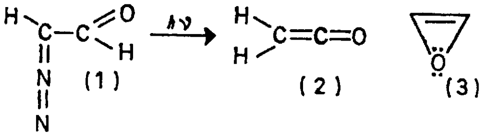
† No other carbonyl species was formed, based on inspection of the region between 1670—1850 cm^{-1} under conditions in which absorption of 2—3% of the keten carbonyl intensity could have been detected.

‡ A band at 1850 cm^{-1} in the photolysate of (**4**) is tentatively attributed to β-butyrolactone and is under study.

contrast to the results with (**1**), ethoxyketen formation[7] can be substantially reduced using reactive matrices such as methane, ethane, and ethylene. For example, a 19 min irradiation of a 36 mm sample of (**4**) in methane (M/R *ca.* 268) produced a new carbonyl band at 1730 cm^{-1} which was *ca.* 65% of the intensity of the co-product band at 2120 cm^{-1}. The i.r. spectrum of the photolysate contained the bands due to ethyl propionate, the product of C–H insertion. In ethylene (M/R = 750), the intensity of the new carbonyl band produced after a 30 min irradiation is at least twice as great as the band at 2120 cm^{-1}.

These observations are noteworthy in that the hydrogen shift, which leads to keten is faster than the reaction of ethylene with any intermediate species or excited state generated from (**1**). This result suggests that (**1**) should have only limited synthetic value as a carbene precursor, using direct irradiation, and falls into the same category as diazoketones, whose photochemistry is dominated by intramolecular rearrangement.[1,2] On the other hand, the formation from (**4**) of ethoxycarbonylcarbene, a species which must clearly possess a finite activation energy to migration of the ethoxy-group and is capturable by hydrocarbon hosts, holds forth the intriguing possibility that vibrational energy transfer may be efficient enough to give rise to a stabilized unreactive form of this carbene in an appropriate matrix near absolute zero.



(1) (2) (3)

The gift of a sample of (**1**) from Mr. C. T. Stier is acknowledged, as are grants from the Research Foundation of S.U.N.Y. and the Petroleum Research Fund of the American Chemical Society.

(*Received*, 27*th June* 1973; *Com.* 924.)

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