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AZO AND HYDRAZO COMPOUNDS. II.(1)

THE PHOTOLYSIS OF ETHYL AZIDOFORMATE

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The reactions of acyl-substituted nitrenes (2) have been shown to be dependent on the nature of the substituent, (3,5,6) and on the solvent (5,6). In those cases (e.g. N_3CO_2Et) in which the Curtius reaction is not observed the nitrene adds readily to C=C systems (3c,5,6) but if the rearrangement to isocyanate can take place then the solvent may determine the course of the reaction. Thus irradiation of benzoyl azide in benzene led only to phenyl isocyanate (5a) but in dimethyl sulfoxide the nitrene could be intercepted by reaction with the medium (5b). In contrast, however, the nitrene derived from ethyl azidoformate did react with benzene, forming an azepine (6).

The work described in this paper arose from an interest in I. Suspecting that a synthesis by the addition of carbethoxynitrene to ethyl azodiformate (II) (7) might be subject to

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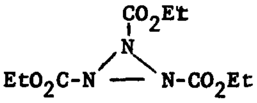
*On sabbatical leave, Harvard University, 1962-63.

alternatives, we first examined the stability of II and also of the pure azide to UV radiation. Rodgman and Wright (9) reported that dimethyl azodiformate is stable to light of wavelength 405 mµ, but these azo esters show additional UV



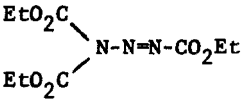
I

$EtO_2C\text{-}N{=}N\text{-}CO_2Et$

II

$N(CO_2Et)_3$

III



$(EtO_2C)_2N\text{-}N{=}N\text{-}CO_2Et$

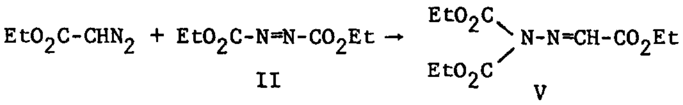
IV

absorption near 220 mµ (e.g. II shows $\lambda_{max,\ EtOH} = 221$ mµ, $\epsilon = 12{,}300$) as well as at 405 mµ ($\epsilon = 24$), so it was necessary to investigate the effect of shorter wavelength radiation on II. Using a 100-watt mercury lamp (Hanovia lamp type SH, medium pressure) we found evidence of a very slow decomposition, ethylene and carbon dioxide being detected (10). This reaction was very much slower than a second photolysis described below.

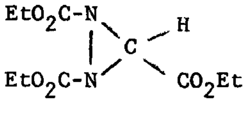
Irradiation of pure ethyl azidoformate (ref. 11, yield 85%) in a manner similar to that for II (external water cooling) rapidly led to gas evolution and an orange color in the solution. Vapor-phase chromatography showed that two products were formed, and the orange one was identified as II. A preparative run gave II and III (12,13).

Since in separate experiments no reaction occurred merely on mixing the azido ester with II and allowing to stand at room temperature (starting materials were recovered quantitatively), and since II itself seemed to be relatively stable to UV radiation, it is reasonable to conclude that III is formed by the attack of the nitrene on II, which in turn arises from reaction of nitrene with the starting material.*

Fahr (14) has shown that the following reaction gave V, not VI (as had been reported earlier (15)). The reaction proceeds at room temperature, and does not require UV radiation.

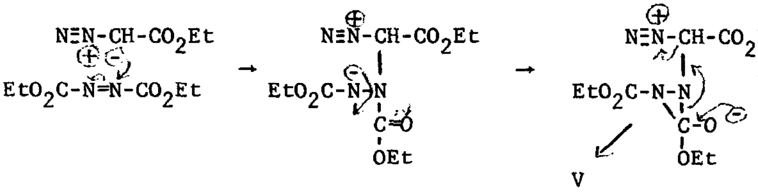


II V



VI

The mechanism shown below accounts for such a transformation.



In our case the analogous product would be IV, which is unknown, but its decomposition (or photolysis) to nitrogen and III would be very probable. Nevertheless, since reaction of azide and II appears to depend on the formation of nitrene, a more likely scheme would appear to be as follows:**

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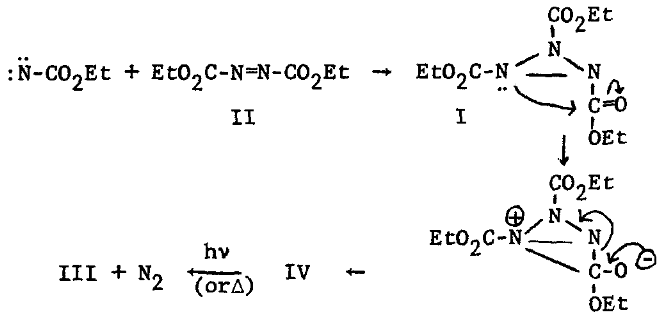
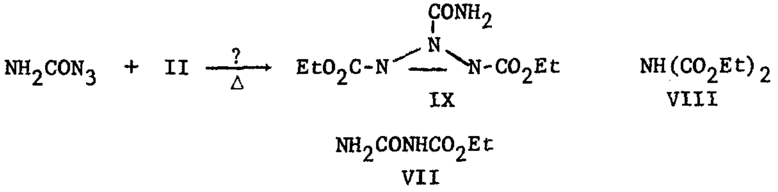
*Infra red spectra of aliquots taken after reaction had begun were completely superposable on those of mixtures of ethylazidoformate and II. This suggests that any cyclic intermediate which retains all the original nitrogen atoms would have to be present in very small concentration.

**Prof. W. Lwowski has kindly informed us that apparently nitrene formed by alpha elimination (see adjoining publication) does not attack II; nor does any II result from attack on azide. Apparently only excited azide (or nitrene) undergoes these reactions. We cordially thank Prof. Lwowski for the opportunity to discuss results before publication.



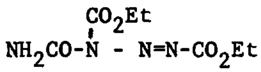
Intermediary formation of I is consistent with the very great electrophilic character of II (e.g. in its ready dehydrogenation of hydroquinones (16) and in its reactions with aldehydes (17) and amines (18)).

Synthesis of a compound belonging to the triazacyclopropane system was attempted by Curtius and Sieber in 1930 (19), using a method similar in approach to that described here:



The products isolated were ethyl allophanate (VII), diethyl-iminodicarboxylate (VIII) and a compound, m.p. 173° (which was probably a mixture). These products may be formed as a result of attack by the nitrene on II to give the intermediate compound IX (analogous to I) which could lose cyanic acid and yield an imino compound, the latter rearranging to VIII in a manner similar to that postulated above for the formation of III.

Collapse of IX could yield X (a or b), possible sources of ethyl allophanate,



$$NH_2CO\text{-}\overset{CO_2Et}{N}\text{ - }N{=}N\text{-}CO_2Et$$

Xa

$NH_2CON{=}N\text{-}N(CO_2Et)_2$

Xb

but the latter may also have arisen from reaction of cyanic acid with ethanol formed from the decomposition of II.

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2. We follow the nomenclature of ref. 3 in the choice of the name azene, imine, or nitrene. Compare also footnote 1, ref. 4.

3. a) W. Lwowski and T.W. Mattingly, *Tetrahedron Letters*, 277 (1962).

   b) R.S. Berry, D. Cornell, and W. Lwowski, *J. Amer. Chem. Soc*. **85**, 1199 (1963).

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4. G. Smolinsky, E. Wasserman, and W.A. Yager, *ibid*., **84**, 3220 (1962).

5. a) L. Horner, E. Spietschka, and A. Gross, *Annalen* **573**, 27 (1951); the solvent, not specified in the article, was dry benzene (Prof. L. Horner, personal communication). In view of Hafner's work (6) this reaction bears re-investigation.

   b) L. Horner and A. Christmann, *Chem. Ber*. **96**, 388 (1963).

6. K. Hafner and C. König, *Angew. Chem. Intl. Ed*. **2**, 96 (1963). The azepine readily rearranged to phenyl urethane.

7. Prepared by Rabjohn's method (8). The dark residue remaining after distillation of the azo ester is largely a mixture of hexachlorocyclohexanes (unpublished work by R.G. Johanson, Reed College).

8. *Org. Syntheses*, *Coll. Vol. III*, 375.

9. a) A. Rodgman and G.F Wright, *J. Org. Chem.* **18**, 479 (1953).

   b) "Irradiation rich in the spectral region in which dimethyl azodicarboxylate displays an absorption peak (405 mμ) fails to change the extinction at this peak or to alter the region of maximum transparency (330 mμ)." No experimental details were given.

10. Only 61 cc. of gas was produced during 247 hrs. irradiation in quartz, using 10.0 g. ester. The products were identified by infrared spectra.

11. M.O. Forster and H.E. Fierz, *J. Chem. Soc.* **93**, 81 (1908). These workers gave sketchy details, reported no yield, and quoted an incorrect b.p. (25°/2mm.). The b.p. of this ester is $\leqslant$ 25°/18 mm. (danger of explosion at 760 mm.).

12. During 188 hrs 25.0 g. of azide gave approximately 40% (2200 ml.) of the theoretical volume of gas, assuming it all to be nitrogen (the reaction slows down with time because of absorption of light by II). Much azide (55%) was recovered unchanged, leaving a residue (6.2 g.) from which 3.4 g. II and 1.4 g. III were obtained, the remainder being an undistillable oil which formed a dark red resin on cooling.

13. *Org. Syntheses*, *Coll. Vol. III*, 415. This compound shows C=O absorption at 1825 (ms), 1780 (vs), and 1740 (ms) cm^{-1} (CCl_4).

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19. Th. Curtius and W. Sieber, *J. prakt. Chem.* 2 , **125**, 444 (1930).