

THE PHOTODECOMPOSITION OF ETHYL AZIDIFORMATE

Walter Lwowski and Thomas W. Mattingly

Department of Chemistry, Yale University, New Haven, Connecticut

(Received 28 February 1962)

EVIDENCE has been presented for the occurrence of a short-lived, electron-deficient and electroneutral nitrogen intermediate in the decomposition of various organic azides.<sup>1-5</sup> This nitrogen analog of carbene will here be called "nitrene".\*

Many of the reaction reported are intramolecular<sup>3,4</sup> and involve the decomposition of aryl azides. Acyl azides undergo Curtius rearrangement when decomposed, and it is not clear whether a nitrene is involved in the rearrangement.<sup>6</sup> A case of cyclization of a decomposing acyl azide to an amide, involving bond formation to a methyl carbon under sterically very favourable circumstances has been reported.<sup>5</sup>

---

\* The terms nitrene, imine, and azene are being used in the literature for the species R-N:. All these terms have been used earlier for other, different species. "Nitrene" seems to us to be the best choice, since it stresses the analogy to the iso-electronic carbene, and was used previously to designate compounds containing pentacovalent nitrogen, not likely to be ever found. [Cf. C.H. Hassal and A.E. Lippman, J. Chem. Soc. 1059 (1953)].

<sup>1</sup> T. Curtius, Z. Angew. Chem. 26, III, 134 (1913); 27, III (1914); and many papers in J. Prakt. Chem. 125 (1930).

<sup>2</sup> J.F. Heacock and M.T. Edmison, J. Amer. Chem. Soc. 82, 3460 (1960) and earlier papers cited therein.

<sup>3</sup> P.A.S. Smith et al., Abstracts of papers presented at the American Chemical Society Meeting, St. Louis, 1961, pp. 43-50; J. Org. Chem. 23, 524 (1958) and earlier papers cited therein.

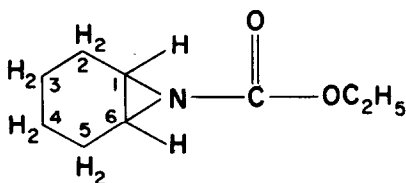
<sup>4</sup> G. Smolinsky, J. Amer. Chem. Soc. 82, 4717 (1960); 83, 2489, 4483 (1961); J. Org. Chem. 26, 4108 (1961).

<sup>5</sup> J. Apsimon and O.E. Edwards, Proc. Chem. Soc. 461 (1961).

<sup>6</sup> Cf. K.R. Brower, J. Amer. Chem. Soc. 83, 4370 (1961).

Since azidoformates do not undergo Curtius rearrangement, we investigated the photodecomposition of ethyl azidoformate<sup>7</sup> in the presence of cyclohexene and cyclohexane. Irradiation was done with a low pressure mercury lamp, such as "Original Hanau PL 368", having maximum emission at 254 m $\mu$ . A cyclohexene solution of ethyl azidoformate produced a better than 50 per cent yield of the adduct I, 7-carboethoxy-7 azabicyclo(4.1.0)heptane. (Found: C, 64.03; H, 8.91; N, 8.22. Calc. for C<sub>9</sub>H<sub>15</sub>N<sub>2</sub>O<sub>2</sub>: C, 63.88; H, 8.94; N, 8.28%.)

Infrared spectrum: no N-H band, no C-H above 3000 cm<sup>-1</sup> (no C=C unsaturation), CO band at 1720 cm<sup>-1</sup>. NMR spectrum: ring CH<sub>2</sub> groups 3 and 4 + CH<sub>3</sub> of ethyl group: multiplet 8.6 to 8.9 $\tau$ . Ring CH<sub>2</sub> groups 2 and 5: 8.2 $\tau$ ; ring C-H at C-1 and 6: 7.5 $\tau$ ; CH<sub>2</sub> of ethyl group: quartet at 6.0 $\tau$ .



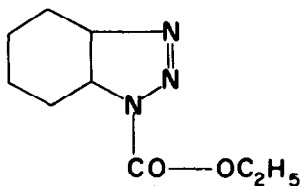
I

Compound I was also synthesized from cyclohexene imine<sup>8</sup> and ethyl chloroformate. The synthetic compound and I had identical IR and NMR spectra and the same retention time in gas chromatography.

To exclude a triazoline intermediate II, we followed the evolution of nitrogen during irradiation at room temperature and compared it with the disappearance of the azide (by I.R. spectrometry). Nitrogen evolution and azide disappearance were simultaneous. Within experimental error, all nitrogen corresponding to the amount of azide decomposed was evolved at

<sup>7</sup> M.O. Forster and H.E. Fierz, J. Chem. Soc. 93, 81 (1908).

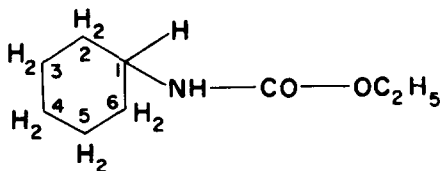
<sup>8</sup> O.E. Paris and P.E. Fanta, J. Amer. Chem. Soc. 74, 3009 (1952).



## II

once, with no storage nitrogen in an intermediate. When the lamp was switched off, nitrogen evolution ceased.

More conclusive evidence for the intervention of a nitrene comes from the decomposition of ethyl azidoformate in cyclohexane. Under the same conditions employed in the cyclohexene experiments, in cyclohexane a yield of about 50 per cent of the N-cyclohexyl-urethane III<sup>9</sup> was obtained.



## III

(Found: C, 63.40; H, 10.00; N, 8.18. Calc. for  $C_9H_{17}NO_2$ : C, 63.13; H, 10.02; N, 8.20%). M.p.:  $56.6^\circ-57.2^\circ$ ; I.R. spectrum: N-H  $3455\text{ cm}^{-1}$ , no C-H above  $3000\text{ cm}^{-1}$ , CO band  $1726\text{ cm}^{-1}$ . NMR spectrum:  $CH_2$  and  $CH_3$ : 8.6-8.8 $\tau$ . C-H on C-1: 8.2 $\tau$ ,  $CH_2$  in ethyl group: quartet 5.9 $\tau$ . The compound was also prepared from cyclohexylamine and ethyl chloroformate. I.R. and NMR spectra were identical, the mixed melting point underpressed at  $56.8^\circ-57.5^\circ$ .

Both the reactions of decomposing ethyl azidoformate with cyclohexene and cyclohexane can be explained by assuming a nitrene intermediate  $EtO-CO-N:$  (with the six electrons on nitrogen paired, singlet state) or

<sup>9</sup> A. Skita and H. Rolfes, Ber. Dtsch. Chem. Ges. **53**, 1242 (1920).

$\text{EtO-CO-N}\cdot$  (with unpaired electrons, a diradical in the triplet state). The singlet species might add to the double bond and insert into the C-H bond, respectively. The triplet nitrene could add to the double bond - conceivably in two steps - and could abstract a hydrogen from cyclohexane, to form the radical  $\text{EtO-CO-NH}\cdot$ , which then combines with the cyclohexyl radical formed in the abstraction step, to give the observed urethane III.

We are indebted to the National Institute of Health for a grant (RG 8762) in support of this research.