

## The Reaction of Methyl Azidoformate with Norbornene. Evidence for the Mechanism of Triazoline Cleavage

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RECENT investigations<sup>1,2</sup> have shown that when azides containing strong electron-withdrawing groups (I; R = CN, PhCO, PhSO<sub>2</sub>, picryl) react with strained olefins, the intermediate triazolines

are unstable and aziridines (V) and imines (VI) are usually isolated directly. Thus while electron-withdrawing groups, R, appear to facilitate the 1,3-dipolar addition of azides to strained olefins<sup>3</sup>

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<sup>1</sup> R. Huisgen, *Angew. Chem. Internat. Edn.*, 1963, **2**, 565.

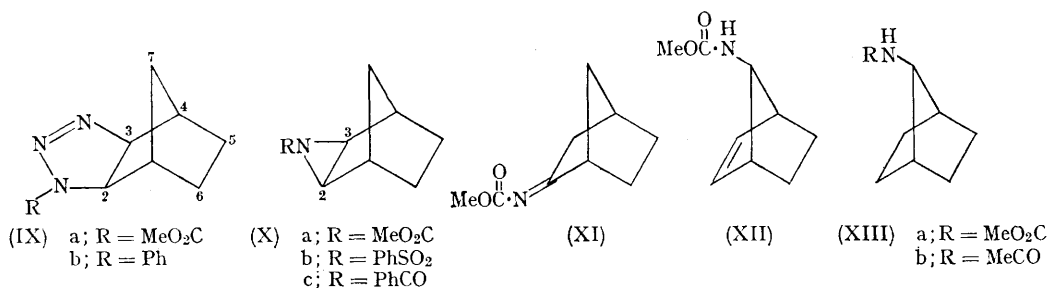
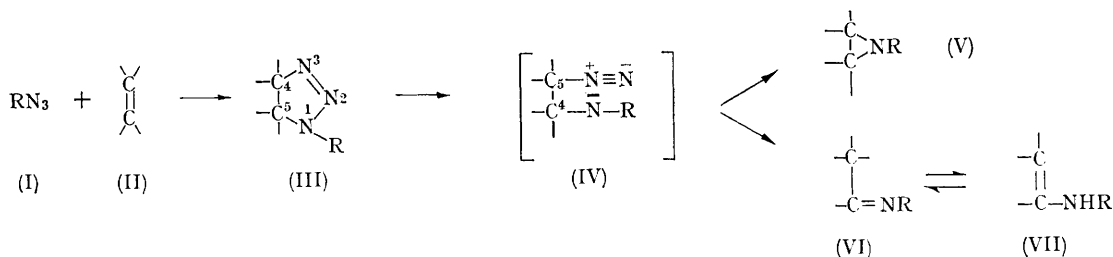
<sup>2</sup> (a) F. D. Marsh and M. E. Hermes, *J. Amer. Chem. Soc.*, 1964, **86**, 4605; (b) A. S. Bailey, J. J. Mercer, and J. E. White, *Chem. Comm.*, 1965, **4**; (c) L. H. Zalkow, A. C. Oehlschlager, G. A. Cabat, and R. L. Hale, *Chem. and Ind.*, 1964, 1556; (d) J. E. Franz, C. Osuch, and M. W. Dietrich, *J. Org. Chem.*, 1964, **29**, 2922; (e) K. D. Berlin and L. A. Wilson, *Chem. Comm.*, 1965, 280; (f) A. C. Oehlschlager and L. H. Zalkow, *J. Org. Chem.*, 1965, in the press.

<sup>3</sup> (a) P. Scheiner, J. H. Schomaker, S. Deming, W. J. Libbey, and G. P. Nowack, *J. Amer. Chem. Soc.*, 1965, **87**, 306; (b) R. Huisgen, *Angew. Chem. Internat. Edn.*, 1963, **2**, 633.

the evidence<sup>1,2,4</sup> suggests that the ability of R to stabilize a negative charge on N-1 of (III) facilitates loss of molecular nitrogen from the incipient triazolines. This phenomenon has been interpreted in terms of intermediates such as (IV)<sup>1,2a,2f,4</sup>

The reaction of ethyl azidoformate with norbornene (VIII) has recently been reported<sup>6</sup> to yield a triazolone adduct but little definitive evidence

a process known<sup>5</sup> to lead exclusively to aziridine products. The imide (XI) was characterized by the absence of N-H absorption in its infrared spectrum and by its facile hydrolysis to norbornanone in nearly quantitative yield. The structure of (XII) was indicated by the presence of two equivalent vinylic protons ( $\delta$ 5.94) and one proton exchangeable with deuterium oxide



was offered for its existence. We have found that the reaction of methyl azidoformate with (VIII) proceeds *via* a 1,3-dipolar cycloaddition [ $\Delta S^\ddagger = -31$  e.u. compared with  $\Delta S^\ddagger = -29$  e.u. for the reaction of phenyl azide with (VIII) which yields (IXb)]<sup>8</sup> to yield an unstable adduct whose n.m.r. spectrum shows the characteristics required of structure (IXa).

Thermal decomposition of (IXa) in toluene resulted in the loss of the theoretical amount of nitrogen and the formation of the aziridine (Xa) (40%), the imide (XI) (55%), and *syn*-norborn-2-ene 7-methylcarbamate (XII) (5%). Periodic n.m.r. analysis showed that the ratio of products remained constant over a period of thirty hours of heating and (Xa) was stable for at least three days under the reaction conditions.

Evidence for the structure of (Xa) was provided by its n.m.r. spectrum and from the fact that it was produced upon ultraviolet photolysis of (IXa),

(N-H,  $\delta$ 5.06) in its n.m.r. spectrum and by N-H absorption at 3300  $\text{cm}^{-1}$  in its infrared spectrum. Hydrogenation of (XII) gave (XIIIa) (m.p. 79–80.5°) which on alkaline hydrolysis gave an amine whose acetate was identical with 7-acetamidonorbornane (XIIIb) and different from 2-*exo*- and 2-*endo*-acetamidonorbornane by gas chromatography.<sup>6</sup>

The formation of the diazonium-betaine intermediate (IV) (R = MeO<sub>2</sub>C) in the decomposition of (IXa) is supported by (a) the fact that the rate of nitrogen evolution increases threefold when triglyme and 20-fold when dimethyl sulphoxide are substituted for 1,1-diphenylethane as solvents and (b) the formation of (XII) by Wagner-Meerwein rearrangement. The large amount of (XI) formed is likewise evidence for an intermediate of type (IV). Although the shift of the C-4 hydrogen of (IV) (R = MeO<sub>2</sub>C) to C-5 is conceptually the simplest mechanism for the formation of (XI),

<sup>4</sup> R. Fusco, G. Bianchetti, and D. Pocar, *Gazzetta*, 1961, **91**, 849, 993; 1962, **92**, 1040.

<sup>5</sup> P. Schneider, *J. Org. Chem.*, 1965, **30**, 7, and references cited therein.

<sup>6</sup> L. H. Zalkow and A. C. Oehlschlager, *J. Org. Chem.*, 1963, **28**, 3303.

this type of rearrangement has been shown to be a slow<sup>7</sup> and an extremely unlikely<sup>8</sup> process compared to Wagner–Meerwein rearrangement in the norbornyl system. An attractive alternative is proton transfer from C-4 to the nitrogen anion of

(IV) to give an enamine type structure (VII). Alder and Stein<sup>9</sup> have demonstrated the existence of enamine–ketimine (VI  $\rightleftharpoons$  VII) equilibria in similar systems.

(Received, October 13th, 1965; Com. 650.)

<sup>7</sup> M. Saunders, P. von R. Schleyer, and G. A. Olah, *J. Amer. Chem. Soc.*, 1964, **86**, 5680.

<sup>8</sup> (a) C. J. Collins, Z. K. Cheema, R. G. Werth, and B. M. Benjamin, *J. Amer. Chem. Soc.*, 1964, **86**, 4913; (b) J. A. Berson, J. H. Hammons, A. W. McRowe, R. C. Bergman, A. Remanick, and D. Houston, *ibid.*, 1965, **87**, 3248.

<sup>9</sup> K. Alder and G. Stein, *Annalen*, 1965, **501**, 1.