

Methanolysis of Diazoalkynes

By WOLFGANG KIRMSE* and JOACHIM HEESE

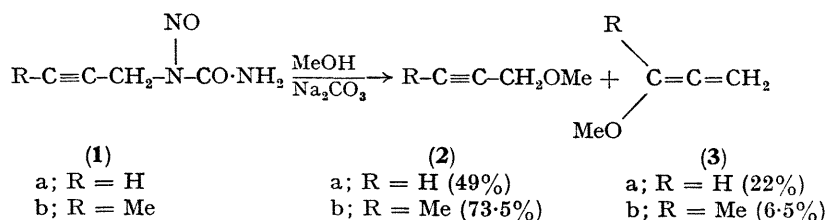
(Abteilung für Chemie der Ruhr-Universität, 463 Bochum, Germany)

Summary The alkaline cleavage of *N*-nitroso-*N*-prop-2-ynylamides (**1**) and (**9**) in methanol and the photolysis of alkynone tosylhydrazones (**4**) and (**10**) in methanol-sodium methoxide afforded both allenyl and prop-2-ynyl methyl ethers; the site of protonation of diazopropynes and the reactivity of prop-2-ynyldiazonium ions have been investigated.

THE contribution of allenic structures to the resonance hybrid of prop-2-ynylic cations has been inferred from their n.m.r. spectra in "super acids".^{1,2} However, allene derivatives have rarely been observed among the products of the solvolysis of prop-2-ynyl halides and tosylates.³ We report the formation of allenyl methyl ethers by alkaline cleavage of *N*-nitroso-*N*-prop-2-ynyl-amides (**1**) in methanol.

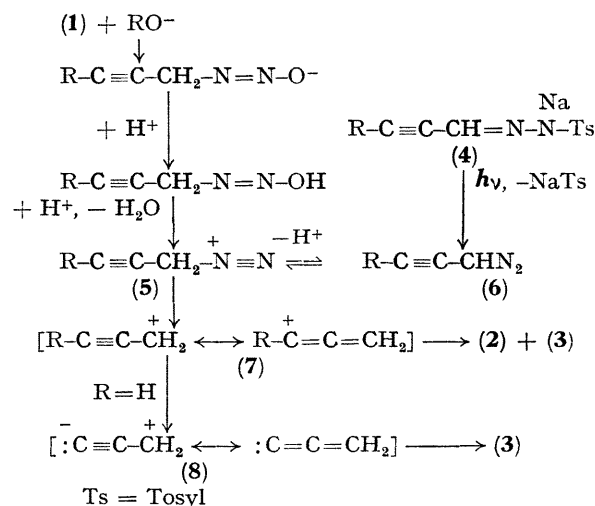
When R=H, compound (**7**) or a precursor may be deprotonated further, to the zwitterion-carbene (**8**).^{6,7} Compound (**3a**) may originate from (**8**), but no such reaction path exists for (**3b**), which can only be formed by solvent attack on the ambient cation (**7**), or by S_N2' displacement on the diazonium ion (**5**). The higher yield of allenyl ether from (**1a**) compared to that from (**1b**) indicates the participation of (**8**). Tracer studies of the reaction are in progress.

The photolysis of tosylhydrazones (**4**) in MeOH-MeONa produces diazoalkynes (**6**) directly which are then protonated to give the diazonium ions (**5**). The product distributions obtained by this alternative mode of "alkaline deamination" agreed with those derived from (**1**). However different product ratios resulted from the analogous reactions of the 1-methylprop-2-ynyl derivatives (**9**) and (**10**).

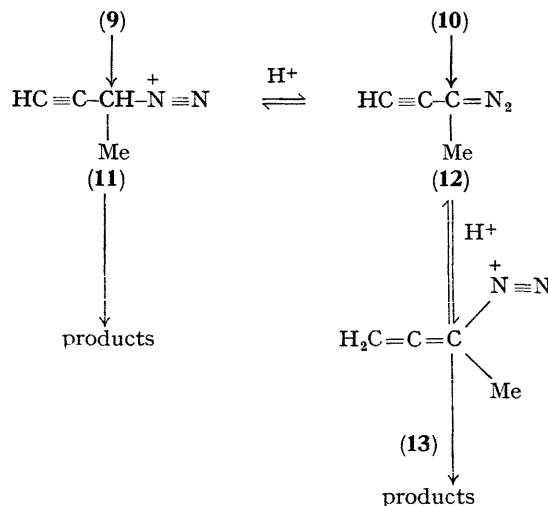


The reaction is thought to occur by "alkaline deamination":^{4,5} deacylation affords the diazotate which is protonated to produce the diazohydroxide and the diazonium ion (**5**). Under weakly alkaline conditions only a small fraction of the diazonium ion (**5**) is deprotonated into the

Products derived from diazonium ion (**11**) predominate in the alkaline cleavage of (**9**) but the major products obtained from (**10**) apparently originate from diazonium ion (**13**). It



SCHEME 1



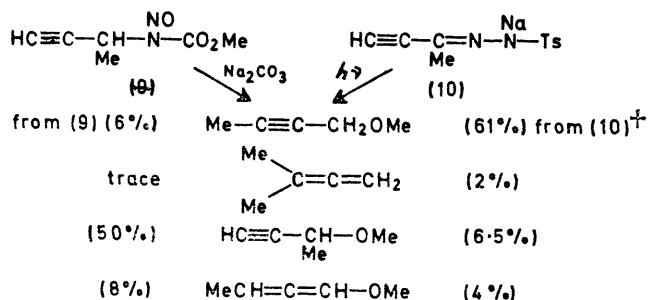
SCHEME 2

diazoalkyne (**6**); the rest loses nitrogen and gives cationic species (**7**).

should be noted that the photolysis of (**10**) leads to 3-diazobutynes (**12**) which plays only a minor role in the

† 3-Methyl-1-tosylpyrazole is a major product from (**10**) (dark reaction). The yields refer to the fraction of (**10**) which is not converted into the pyrazole.

cleavage of (9). Compound (12) is obviously more easily



protonated at C-1 than at C-3. The product distribution obtained from (9) should therefore approach that from (10) in strongly alkaline solution, when most of the diazonium ions (11) are deprotonated. Experimental verification of this was difficult because (9) reacted with sodium methoxide in methanol to give methyl isobutyrate and not the ethers mentioned above.

Compound (1a) produced methyl propionate whereas (1b) did not yield an ester even under strongly alkaline conditions. The mechanism of ester formation will be discussed later.

(Received, December 18th, 1970; Com. 2182.)

¹ C. U. Pittman, jun., and G. A. Olah, *J. Amer. Chem. Soc.*, 1965, **87**, 5632.

² H. G. Richey, jun., J. C. Philips, and L. E. Rennick, *J. Amer. Chem. Soc.*, 1965, **87**, 1381, 4017.

³ R. S. Maccomber, *Tetrahedron Letters*, 1970, 4639, and references cited therein.

⁴ R. A. Moss and S. M. Lane, *J. Amer. Chem. Soc.*, 1967, **89**, 5655.

⁵ W. Kirmse and G. Wächtershäuser, *Annalen*, 1967, **707**, 44.

⁶ H. D. Hartzler, *J. Amer. Chem. Soc.*, 1959, **81**, 2024; *ibid.*, 1961, **83**, 4990.

⁷ V. J. Shiner, jun., and J. W. Wilson, *J. Amer. Chem. Soc.*, 1962, **84**, 2402.