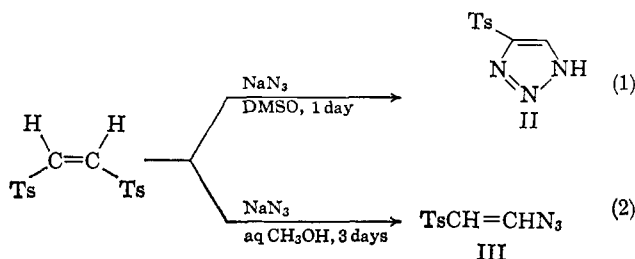


## The Isomerization of a Vinyl Azide to a Triazole

Sir:

The conversion of a vinyl azide to a triazole was first attempted in 1910;<sup>1</sup> in 1962 further unsuccessful attempts to carry out this isomerization were made,<sup>2</sup> and a recent text calls attention to the fact that this is still an unknown reaction.<sup>3</sup>

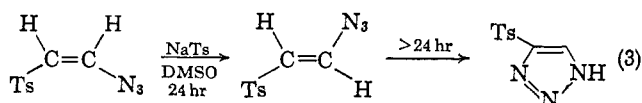
In our studies on addition-elimination reactions of 1,2-di-*p*-toluenesulfonyl ethene (I), we have observed that the reaction of I with sodium azide in dimethyl sulfoxide proceeded to give 4(5)-*p*-toluenesulfonyl-triazole (II) in 45% yield, and not  $\beta$ -azidovinyl *p*-tolyl sulfone (III) as expected.



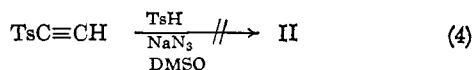
Since I reacted with sodium azide in aqueous methanol to yield a mixture of the *cis* and *trans* isomers of III, we were led to investigate the possible intermediacy of III in the formation of II.

When reaction 1 was shortened to 5 min, a small amount of III was isolated. When reaction 1 was observed from its initiation by use of nmr, the formation and disappearance of III could be followed. When the *trans* isomer of III was isolated, it did not isomerize in dimethyl sulfoxide unless a base, such as sodium azide, sodium *p*-toluenesulfinate, or potassium *t*-butoxide, was present. Sodium *p*-toluenesulfinate in DMSO was the most effective in carrying out the isomerization since with both sodium azide and potassium *t*-butoxide nitrogen loss from the vinyl azide occurred.

When the *cis* isomer of III was allowed to stand in DMSO with sodium *p*-toluenesulfinate for 1 day it was partially converted to the *trans* isomer. If allowed to stand longer, the triazole could be detected by nmr.



The possibility that triazole formation is occurring through elimination of *p*-toluenesulfonic acid to yield *p*-toluenesulfonylacetylene (IV) followed by cycloaddition of hydrazoic acid to IV (4) is very unlikely since the addition of sodium azide and *p*-toluenesulfonic acid to a cold solution of IV in DMSO results in decomposition with gas evolution.



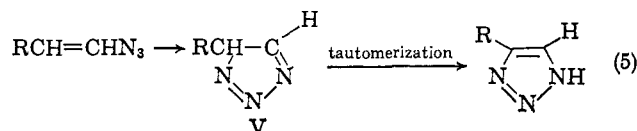
IV

In contrast with the previous observations that many vinyl azides do not cyclize to triazoles is the observation of the very facile cyclization of imidoyl azides to

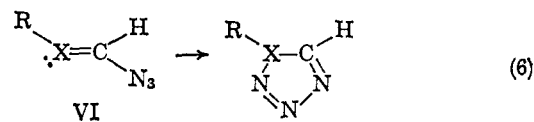
- (1) M. S. Forster and S. H. Newman, *J. Chem. Soc.*, 97, 2570 (1910).
- (2) A. N. Nesmeyanov and M. I. Rybinskaya, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 5, 816 (1962).
- (3) P. A. S. Smith, "Open Chain Nitrogen Compounds," Vol. 2, W. A. Benjamin Inc., New York, N. Y., 1966, p 243.

tetrazoles<sup>4</sup> and of thioacyl azides to thiatriazoles.<sup>5</sup> It has been postulated<sup>3</sup> that electronic structure VI is necessary for cyclization.

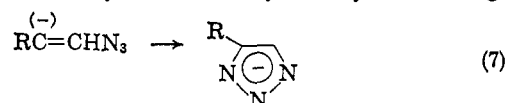
The cyclization of a vinyl azide would involve the intermediate triazolenine, V, which would have to tautomerize in order to gain aromatic stabilization.



However, when a heteroatom such as nitrogen or sulfur is  $\beta$  to the azido group, cyclization to an aromatic species is possible. It can be seen that a carbanion



would also possess the electronic requirement for cyclization. Nesmeyanov and Rybinskaya have sug-



gested that such a carbanion is formed in the reaction of phenyl ethynyl ketone with sodium azide in dimethylformamide to produce 4-benzoyl-1,2,3-triazole.<sup>6</sup>

The acidity of vinyl protons  $\alpha$  to sulfonyl groups has been demonstrated<sup>7</sup> recently, and the conversion of III to II is consistent with the formation of a carbanion which then cyclizes.

The triazole II was acidic and, after recrystallization from water, melted at 158°; the nmr spectrum in deuteriochloroform showed signals at  $\delta$  2.40 (3 H, singlet), 7.66 (4 H,  $A_2B_2$  quartet), and 8.48 (1 H, singlet). *Anal.* Calcd for  $C_9H_9N_3O_2S$ : C, 48.42; H, 4.06; N, 18.82. Found: C, 48.44; H, 3.95; N, 18.87. The structure of II was supported by an independent synthesis using *p*-toluenesulfonylacetylene and trimethylsilyl azide patterned after the method of Birkofer and Wegner.<sup>8</sup>

(4) E. Lieber, E. Oftedahl, and C. N. R. Rao, *J. Org. Chem.*, 28, 194 (1963).

(5) P. A. S. Smith, *J. Am. Chem. Soc.*, 76, 436 (1954).

(6) A. N. Nesmeyanov and M. I. Rybinskaya, *Dokl. Akad. Nauk SSSR*, 166, 1362 (1966).

(7) C. D. Broaddus, *J. Am. Chem. Soc.*, 88, 3863 (1966).

(8) L. Birkofer and P. Wegner, *Chem. Ber.*, 99, 2512 (1966).

(9) National Institutes of Health Predoctoral Fellow, 1966-1967.

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## Photofragmentation of Epoxides. IV. Precursors for Phenylcyanocarbene<sup>1a</sup>

Sir:

Recently we have described photofragmentation reactions of simple aryl- and alkylaryl-substituted

- (1) (a) Presented in part at the Fourth Caribbean Symposium held in Kingston, Jamaica, Jan 2, 1967; (b) H. Kristinsson and G. W. Griffin, *Angew. Chem.*, 77, 859 (1965); *Angew. Chem. Intern. Ed. Engl.*, 4, 868 (1965); (c) H. Kristinsson and G. W. Griffin, *J. Am. Chem. Soc.*, 88, 3259 (1966); (d) H. Kristinsson, *Tetrahedron Letters*, 2343 (1966); (e) P. Petrellis and G. W. Griffin, unpublished results; (f) A. M. Trozzolo, W. A. Yager, G. W. Griffin, H. Kristinsson, and I. Sarkar, *J. Am. Chem. Soc.*, in press.