CHEMISTRY LETTERS, pp. 771-774, 1972. Published by the Chemical Society of Japan

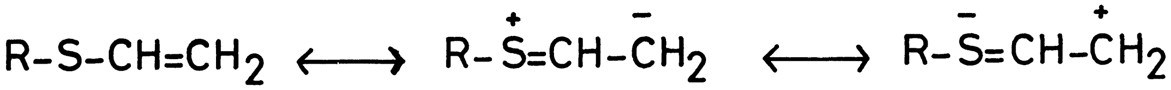
CYCLOADDITIONS OF DIAZOALKANES TO VINYL AND ALLYL SULFIDE SYSTEMS

Kiyosi KONDO and Iwao OJIMA
Sagami Chemical Research Center 3100 Onuma
Sagamihara 229

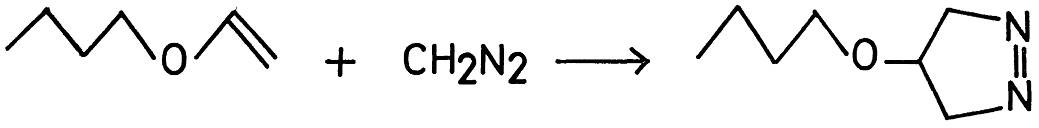
Chemical evidence for the activation of double bonds by the use of 3d orbitals of sulfur atom on cycloadditions was obtained in the reaction of phenyl vinyl sulfide and allyl benzyl sulfide with diazomethane.

Both vinyl ethers and sulfides are known to be electron rich olefins due to contributing structures such as 1A and 2A. It is also known, however, that a sulfur atom has an ability of stabilizing a carbanion on α-position using its 3d orbitals.[1] Thus the contribution of a resonance structure 2B seems to be important in determining the character of the double bond in a vinyl sulfide, but the effect of sulfur atom to withdraw electrons in such a way has not yet been realized in cycloaddition reactions. D'yakonov reported that the reaction of n-butyl vinyl ether with diazomethane produced 4-butoxy-Δ^1-pyrazoline 3.[2] This result is apparently consistent with the importance of the resonance structure 1A. Now, we wish to report evidence for the existence of the activating effect of a sulfur atom to the double bond by pπ-dπ interaction.[3]

$$\underset{1}{\text{R-O-CH=CH}_2} \longleftrightarrow \underset{1A}{\text{R-}\overset{+}{\text{O}}\text{=CH-}\overset{-}{\text{C}}\text{H}_2}$$



$$\underset{2}{\text{R-S-CH=CH}_2} \longleftrightarrow \underset{2A}{\text{R-}\overset{+}{\text{S}}\text{=CH-}\overset{-}{\text{C}}\text{H}_2} \longleftrightarrow \underset{2B}{\text{R-}\overset{-}{\text{S}}\text{=CH-}\overset{+}{\text{C}}\text{H}_2}$$



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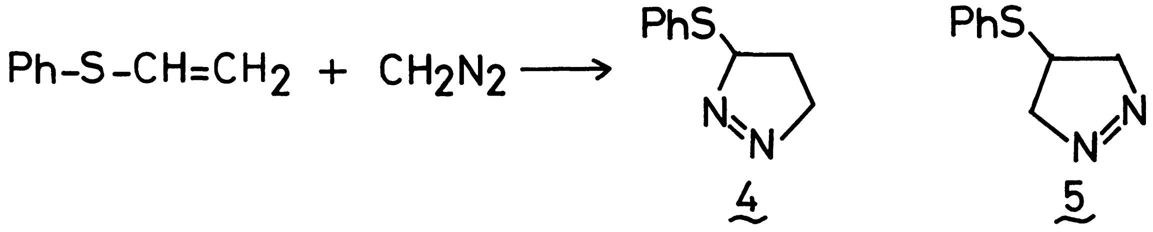
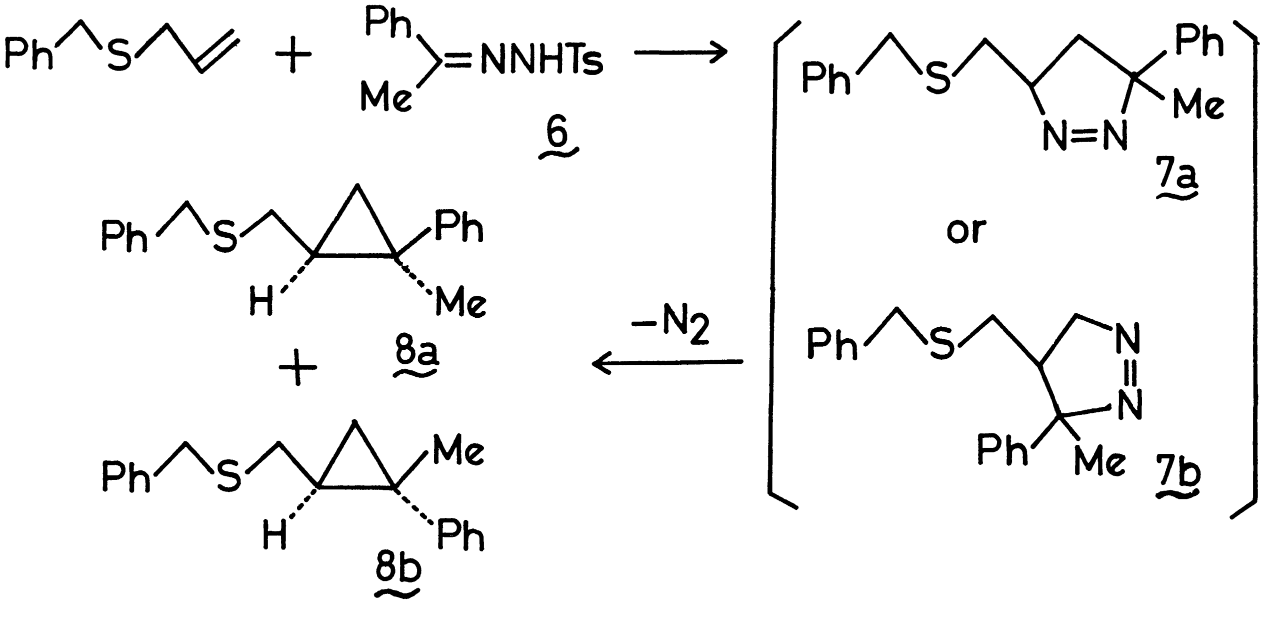
Phenyl vinyl sulfide was allowed to react with excess diazomethane in ether at room temperature in a sealed tube for a week to give 3-phenylthio-Δ^1-pyrazoline(4) in 35% yield and the formation of 4-phenylthio-Δ^1-pyrazoline(5) could not be observed.[4) This finding is to be expected in view of the predominant contribution of the canonical structure 2B in preference to 2A to the resonance hybrid of the reactant sulfide and well corresponds to the case of vinyl sulfones.[5)

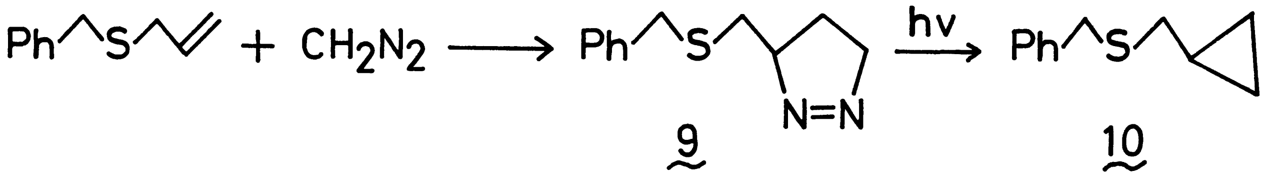


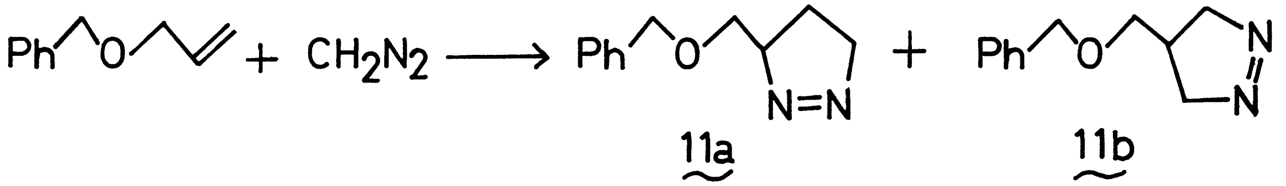
A similar activating influence of the hetero atom on double bonds was also found to emerge in the case of allyl sulfides. Acetophenone tosylhydrazone(6) was thermally decomposed in the presence of an equivalent of sodium methoxide and two equivalents of allyl benzyl sulfide in diglyme at 150°C. Products were separated by column chromatography on silica gel to give 1-benzylthiomethyl-2-methyl-2-phenylcyclopropane(8) in 28% yield (8a/8b = 29/71). The formation of the cyclopropane can be accounted for either by the attack of a carbene intermediate on the olefin or the 1,3-dipolar cycloaddition of diazomethane to the substrate followed by the loss of a nitrogen molecule. The former possibility is less likely since recent investigations have shown that the reactions of allyl sulfides with carbene species appear to involve mainly a [2,3] sigmatropic rearrangement of the intermediary formed allyl sulfonium ylides.[6) Moreover, in the above system, the generated carbene is prone to be converted to acetophenone azine or styrene smoothly.[7) These considerations lead us to a



conclusion that the cyclopropanes(8a and 8b) were formed through the pyrazoline(7a or 7b) with the subsequent elimination of nitrogen. The observed isomer ratio(8a/8b) seems to reflect the relative degree of their thermodynamical stabilities, supporting the intermediacy of the 1,3-diradical produced from 7.

In order to elucidate the orientational effect of hetero atoms in the allylic systems, the reactions of allyl benzyl sulfide and allyl benzyl ether with diazomethane were performed. Thus, allyl benzyl sulfide was allowed to react with diazomethane in ether at room temperature for a week in a sealed tube. The reaction mixture was chromatographed on silica gel to give 3-benzylthiomethyl-Δ^1-pyrazoline(9) in 79 % yield, which afforded a cyclopropane derivative 10 on irradiation. The structure of the pyrazoline was easily determined by its nmr spectrum. In contrast with the observed specific orientation in the case of the allyl sulfide, the reaction of allyl benzyl ether with diazomethane under the similar conditions afforded a mixture of Δ^1-pyrazolines 11a and 11b (11a/11b = 67/33), in 74.5 % yield. These pyrazolines were separated and purified by column chromatography on silica gel and their structures were established by means of their nmr spectral patterns. The fact that the two different adducts were obtained in the case of allyl benzyl ether implies that there should not be any important role of the oxygen atom in directing the orientation of the 1,3-dipolarophile. It has recently been suggested that the through-space $d\pi$-$p\pi$ conjugation between a double bond and a sulfur atom is operative in the reactions of allyl aryl sulfones$^{8)}$ with diazomethane. The exclusive nucleophilic attack of diazomethane on the terminal carbon found in the present investigation appears to provide evidence for the existence of homoallylic $d\pi$-$p\pi$ conjugation even in the case of a simple allyl sulfide system.





It is adequate to note at this point that both nucleophilic and electrophilic attacks on vinyl and allyl sulfides tend to occur at the terminal carbon. Such a versatile character of the olefinic sulfides seems to be associated with the large polarizability of the molecule due to the participation of 3d orbitals of a sulfur atom.

Acknowledgment: This work was supported in part by Kawakami Memorial Foundation.

1) For example, R. B. Woodward and R. H. Eastman, J. Amer. Chem. Soc., 68, 2229 (1946); W. J. Brehm and T. Levenson, ibid., 76, 5389 (1954); D. S. Tarbell and W. E. Lovett, ibid., 78, 2259 (1956); W. E. Parham and R. F. Motter, ibid., 81, 2146 (1959).
2) I. A. D'yakonov, Zh. Obshch. Khim., 17, 67 (1947); Chem. Abstr., 42, 902 (1948).
3) The nmr, ir, and mass spectra and elemental analyses of all new compounds were consistent with the assigned structures.
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(Received July 10, 1972)