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Chemical Evidence for the Existence of pπ-dπ Interaction between the Unsaturated Bond and the Sulfur Atom in Allyl and Vinyl Sulfide Systems[1]

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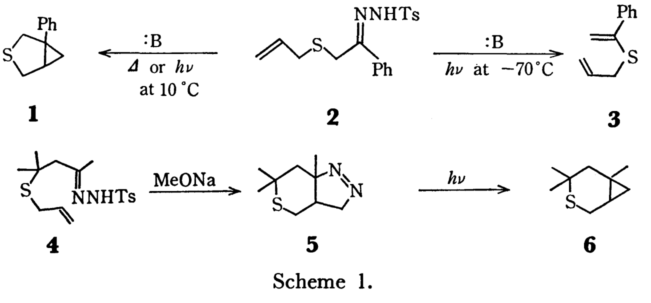
Chemical evidence for the activation of double bonds by the use of 3d orbitals of the sulfur atom was observed in the reaction of allyl benzyl sulfide and phenyl vinyl sulfide with diazomethane. Similar supporting evidence was also obtained in the reaction of acetophenone tosylhydrazone with allyl benzyl sulfide in the presence of sodium methoxide at 150 °C. It was found that there should not be any important role of the oxygen atom of allyl benzyl ether in directing the orientation of the 1,3-dipolarophile.

It is well known that the thermal cycloaddition of diazoalkanes to the simple non-conjugated olefins is a very slow and difficult process.[2,3] Thus, nowadays the thermal or photochemical formation of cyclopropanes from diazoalkanes and non-conjugated olefins is believed to be a carbenic process.[4] Certain diazoalkanes bearing an allylthio-substituent have, however, been found to undergo a ready intramolecular cycloaddition to produce pyrazolines, which were thereafter further transformed into cyclopropanes under the same reaction conditions.[5] 1-Phenyl-3-thiabicyclo[3.1.0]-hexane (**1**) was obtained by the thermal decomposition at 150 °C, or by the photolysis at 10 °C, of α-(allylthio)acetophenone tosylhydrazone (**2**) in the presence of sodium methoxide. The carbenic process could be observed in this α-allylthio system when the photolysis was carried out at −70 °C; this process afforded an entirely different product, **3**.[6] Thus, the formation of **1** may mean that an intramolecular cycloaddition of the diazoalkane moiety to the double bond of the allylthio group and a subsequent elimination of molecular nitrogen really do occur under the present reaction conditions. Conclusive evidence for the intramolecular thermal cycloaddition of the diazoalkane was observed when 4-allylthio-4-methylpentan-2-one tosylhydrazone (**4**) was used as a substrate. Thus, the bicyclic pyrazoline, **5**, was actually isolated in the thermal decomposition of **4** in the presence of sodium methoxide; the pyrazoline, **5**, was then further converted to the 3-thiabicyclo[4.1.0]heptane, **6**, by irradiation.[5] These facts seem to indicate that the intramolecular thermal cycloaddition is a ready process even at 10 °C and that the subsequent elimination of nitrogen is also an effective process under the photolytic conditions. The high efficiency of the intramolecular cycloaddition to the isolated double bond may be partly due to some kind of activating effect of the sulfur atom in the molecule as well as to the *intramolecular* nature of the reaction.



Scheme 1.

In order to clarify the activating effect of the sulfur atom, *intermolecular* cycloadditions of diazoalkanes to allyl sulfide and vinyl sulfide systems were investigated. This paper will deal with the evidence for the existence of pπ–dπ interaction between the sulfur atom and the unsaturated bond.

Results and Discussion

Acetophenone tosylhydrazone was thermally decomposed in the presence of an equivalent of sodium methoxide and two equivalents of allyl benzyl sulfide in diglyme at 150 °C. The products were separated by column chromatography on silica gel to give 1-(benzylthio)methyl-2-methyl-2-phenylcyclopropane (**9**) in a 28% yield (**9a**/**9b**=29/71). The formation of the cyclopropane, **9**, can be accounted for either by the attack of a carbene intermediate on the olefin or by the 1,3-dipolar cycloaddition of phenylmethyldiazomethane to the unsaturated bond, followed by the loss of a nitrogen molecule. The former possibility seems to be less likely, for recent investigations have shown that the reaction of allylic sulfides with carbene or carbenoid species appears to involve mainly a [2.3]sigmatropic rearrangement of the intermediately-formed allyl sulfonium ylides.[7] Moreover, in the above system, the generated carbene is prone to be converted to acetophenone azine or styrene smoothly.[8] Though the reaction mixture was carefully examined, the sulfide, **7**, could not be detected in the product.

These considerations lead us to speculate that the cyclopropanes (**9a** and **7b**) were formed through the pyrazoline (**8a** or **8b**), and that subsequently the

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[1] A part of this work was reported in preliminary form: K. Kondo and I. Ojima, *Chem. Lett.*, **1972**, 771.

[2] R. Huisgen, R. Grashey, and J. Sauer in "The Chemistry of Alkenes," ed. S. Patai, Interscience, New York (1964), pp. 830—831.

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[4] W. Kirmse, "Carbene Chemistry," Academic Press, New York (1964).

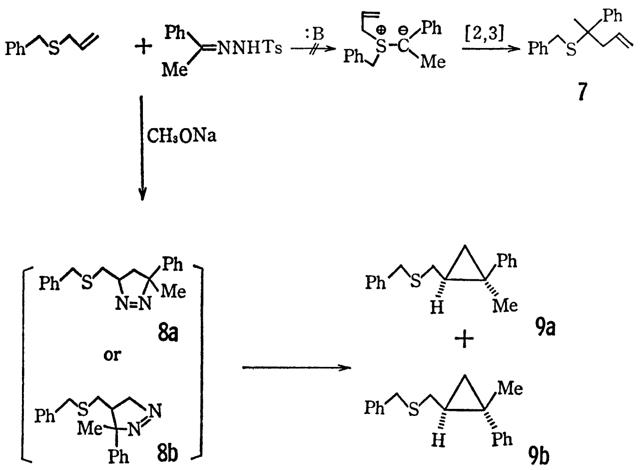
[5] K. Kondo and I. Ojima, *Chem. Commun.*, **1972**, 63.

[6] K. Kondo and I. Ojima, *ibid.*, **1972**, 62.

[7] For example, W. Kirmse, and M. Kapps, *Chem. Ber.*, **101**, 994, 1004 (1968); W. Ando, T. Yagihara, S. Tozune, and T. Migita, *J. Amer. Chem. Soc.*, **91**, 2786 (1969); W. Ando, T. Yagihara, S. Tozune, I. Imai, J. Suzuki, T. Toyama, S. Nakaido, and T. Migita, *J. Org. Chem.*, **37**, 1721 (1972).

[8] C. G. Overberger and J-P. Anselme, *ibid.*, **29**, 1188 (1964).

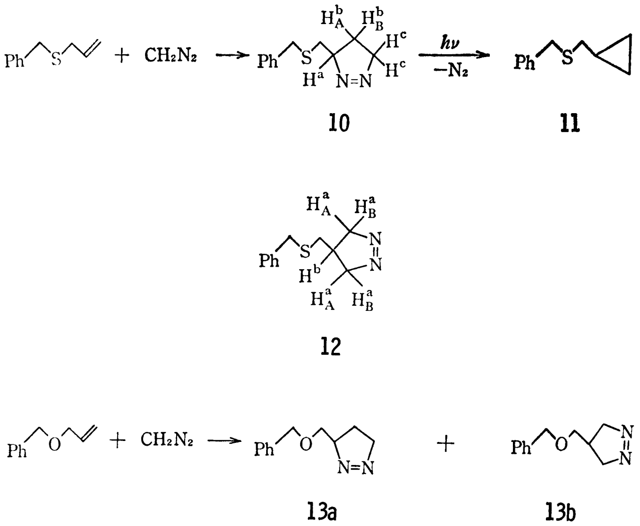
molecular nitrogen was eliminated, as is shown in Scheme 2. The observed ratio of the **9a** and **7b** isomers seems to reflect the relative degree of their thermodynamic stabilities, supporting the intermediacy of the 1,3-diradical produced by the thermal fragmentation of **8** under the present reaction conditions.[5,9]



Scheme 2.

In order to elucidate the orientational effect of hetero atoms in the allylic systems, the thermal reactions of allyl benzyl sulfide and allyl benzyl ether with diazomethane were examined. 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 then purified by column chromatography on silica gel to give 3-(benzylthio)-methyl-Δ^1-pyrazoline (**10**) in a 79% yield; this substance subsequently afforded a cyclopropane derivative, **11**, on irradiation with a high-pressure mercury lamp. The structure of the pyrazoline **10** was determined by studing its NMR spectrum. The NMR spectrum of the pyrazoline displayed three multiplets, at τ 8.80 (1H), at τ 8.40 (1H), and in the τ 6.18—5.35 (3H) region. The former two can be assigned to the resonance of non-equivalent H^b methylene protons, and the latter, to that of the H^a methine proton and of H^c methylene protons.[10] If the structure of the pyrazoline is 4-benzylthiomethyl-Δ^1-pyrazoline (**12**), H^a protons should appear as a double AB quartet (4H) in the region near τ 6.00, and the H^b proton, as a multiplet (1H) in a higher field (see the Experimental section for the case of **13b**). Thus, the structure of the pyrazoline obtained can be assigned to 3-(benzylthio)methyl-Δ^1-pyrazoline (**10**).

In contrast with the observed specific orientation in the case of the allyl sulfide system, the reaction of allyl benzyl ether with diazomethane under similar conditions afforded a mixture of two Δ^1-pyrazolines, **13a** and **13b** (**13a**/**13b**=67/33), in a 74.5% yield. These pyrazolines could fortunately be separated and purified by column chromatography on silica gel, and their structures were established by means of their NMR spectra. The fact that two different adducts were obtained in the case of allyl benzyl ether implies that



Scheme 3.

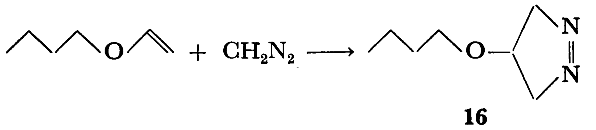
the oxygen atom plays no important role in directing the orientation of the 1,3-dipolarophile.

It has recently been suggested that the through-space $p\pi$–$d\pi$ conjugation between the double bond and the sulfur atom is operative in the reactions of allyl aryl sulfones with diazomethane.[11] The exclusive nucleophilic attack of diazomethane on the terminal carbon found in the present investigation appears to provide chemical evidence for the existence of homoallylic $p\pi$–$d\pi$ conjugation even in the case of a simple allyl sulfide system.

A similar activating effect of the hetero atom on the double bond can also be expected to emerge in the case of vinyl sulfides. Both vinyl ethers and sulfides are known to be electron-rich olefins because of the contributing structures, such as **14A** and **15A**. Thus, these compounds can easily be hydrolyzed under acidic conditions.[12] It is also known, however, that the sulfur atom has the ability to stabilize a carbanion on the α-position using its 3d orbitals.[13]

$$\underset{\textbf{14}}{R\text{-}O\text{-}CH{=}CH_2} \longleftrightarrow \underset{\textbf{14A}}{R\text{-}\overset{+}{O}{=}CH\text{-}\overset{-}{C}H_2}$$

$$\underset{\textbf{15}}{R\text{-}S\text{-}CH{=}CH_2} \longleftrightarrow \underset{\textbf{15A}}{R\text{-}\overset{+}{S}{=}CH\text{-}\overset{-}{C}H_2} \longleftrightarrow \underset{\textbf{15B}}{R\text{-}\overset{-}{S}{=}CH\text{-}\overset{+}{C}H_2}$$



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Scheme 4.

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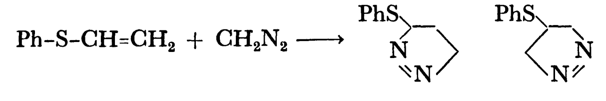
[11] V. N. Mikhailova and A. D. Bulat, *J. Org. Chem. USSR*, **3**, 1597 (1967) (in English); *Chem. Abstr.*, **68**, 12897q

[12] L. Brandsma and J. F. Arens in "The Chemistry of the Ether Linkage" ed. S. Patai, Interscience, New York, p. 568.

[13] 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).

Thus, the contribution of another resonance structure, **15B**, also seems to be important in determining the character of the double bond in a vinyl sulfide, but no such effect of the sulfur atom in withdrawing electrons in such a way has been observed in cycloaddition reactions. D'yakonov has reported that the reaction of *n*-butyl vinyl ether with diazomethane produced 4-butoxy-Δ^1-pyrazoline (**16**).[14] This result is apparently consistent with the importance of the **14A** resonance structure.

Phenyl vinyl sulfide was allowed to react with an excess of diazomethane in ether at room temperature in a sealed tube for a week to give 3-phenylthio-Δ^1-pyrazoline (**17**) in a 40.4% yield; no formation of 4-phenylthio-Δ^1-pyrazoline (**18**) could be observed. This finding is to be expected in view of the predominant contribution of the canonical structure, **15B**, in preference to that of **15A**, to the resonance hybrid of the sulfide, and it well corresponds to the case of vinyl sulfones.[15]



Scheme 5.

It is sufficient to note at this point that both nucleophilic and electrophilic attacks on allyl and vinyl 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 the 3d orbitals of a sulfur atom.

Experimental

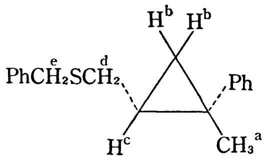
Measurements. The melting points and boiling points are uncorrected. The infrared spectra were recorded on a Hitachi-Perkin-Elmer Model 337 Infracord or a Hitachi EPI-G3 spectrophotometer, using samples as neat liquids or KBr disks or Nujol mulls. The nuclear magnetic resonance spectra were obtained by the use of a Varian HA-100 or Hitachi R20-B spectrometer, using TMS as the internal standard. The mass spectra were measured by means of a Hitachi RMU-6E spectrometer at 70 eV. Photolyses were carried out using a 450-W high-pressure mercury lamp (Ushio Electric Inc.).

Materials. The allyl benzyl sulfide,[16] and allyl benzyl ether[17] were prepared according to the reported method. The phenyl vinyl sulfide[18] was prepared from β-chloroethyl phenyl sulfide[19] by treatment with potassium hydroxide in ethanol. The acetophenone tosylhydrazone was prepared by the condensation of acetophenone and tosylhydrazide; mp 148—150 °C (lit,[20] 147.5—150 °C).

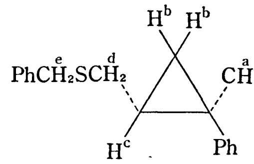
Thermal Decomposition of Acetophenone Tosylhydrazone in Allyl Benzyl Sulfide in the Presence of Sodium Methoxide. In 50 ml of diglyme, 1.64 g (10.0 mmol) of allyl benzyl suifide and 1.44 g (5.0 mmol) of acetophenone tosylhydrazone and 300 mg of sodium methoxide were dissolved. The mixture was heated in an oil bath at 150 °C for 1 hr. After the precipitated sodium *p*-toluenesulfinate had then been filtered off, the filtrate was distilled under reduced pressure to remove the solvent. The residue was submitted to column chromatography on silica, using *n*-hexane as the eluent; 1-(benzylthio)methyl-2-methyl-2-phenylcyclopropane (**9**) (375 mg, 28% yield) was thus obtained. The isomer ratio of the cyclopropane, **9**, was determined to be *cis*(**9a**)/*trans* (**9b**)=29/71 by glpc analysis, using 20% SE-30 on chromosorb W at 200 °C.

9: NMR(CCl_4): **9a**: τ 9.30—8.60 (m, H^b+H^c), 8.73 (s, H^a), 8.06 (octet, H^d, J_{dd}=12 Hz, J_{cd}=6 and 8 Hz), 6.51 (s, H^e, and 3.00—2.65 (m, Ph).

9b: τ 9.05—8.60 (m, H^b+H^c), 8.72 (s, H^a), 7.52 (octet, H^d, J_{dd}=13 Hz, J_{cd}=6 and 7 Hz), 6.36 (s, H^e), 2.95—2.65 (m, Ph).



9a



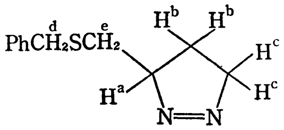
9b

Mass (*m/e*): 268 (M^+, 13.8), 227 (48.8), 177 (13.8), 145 (100), 131 (26.2), 91 (91.3), and 77 (20.0).

Found: C, 80.32; H, 7.28; S, 12.03%. Calcd for $C_{18}H_{20}S$: C, 80.54; H, 7.51; S, 11.95%.

Reaction of Allyl Bnezyl Sulfide with Diazomethane. A mixture of 1.64 g (10 mmol) of allyl benzyl suifide and an excess of diazomethane in 50 ml of ether, which had been prepared from 10 g of *N*-nitroso-*N*-methylurea and aqueous sodium hydroxide, was sealed in a glass tube and stirred for a week at 15 °C. After the solvent and excess diazomethane had then been evaporated, the residue was submitted to column chromatography on silica. The unreacted allyl benzyl sulfide was eluted by the use of *n*-hexane–benzene, and the 3-(benzylthio)methyl-Δ^1-pyrazoline (**10**) was eluted by the use of chloroform (1.62 g, 78.7%).

10: NMR (CCl_4): τ 9.05—8.64 (m, $H_A{}^b$), 8.58—8.18 (m, $H_B{}^b$), 7.25 (octet, H^e, J_{ee}=14 Hz, J_{ea}=5 and 7 Hz), 6.37 (s, H^d), 6.18—5.35 (m, H^a+H^c), and 3.00—2.65 (m, Ph).



Mass (*m/e*): 206 (M^+, 4.1), 178 (M^+-N_2, 3.5), 137 (3.5), 122 (13.5), 91 (100), 83 (51.4), and 69 (16.2).

Found: C, 64.09; H, 6.67; S, 15.58%. Calcd for $C_{11}H_{14}N_2S$: C, 64.04; H, 6.84; S, 15.54%.

Reaction of Allyl Benzyl Ether with Diazomethane. A mixture of 1.58 g (10.7 mmol) of allyl benzyl ether and an excess of diazomethane in 50 ml of ether, which had been prepared from 10 g of *N*-nitroso-*N*-methylurea and aqueous sodium hydroxide in ether, was stirred at 15 °C for a week

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[14] I. A. D'yakonov, *Zh. Obshch. Khim.*, **17**, 67, (1947): *Chem. Abstr.*, **42**, 902 (1948).

[15] W. E. Parham, F. D. Blake, and D. R. Theissen, *J. Org. Chem.*, **27**, 2415 (1962).

[16] H. J. Backer and G. J. de Jong, *Rec. Trav. Chim. Pays-Bas*, **67**, 889 (1948).

[17] R. H. Baker, K. H. Cornell, and M. J. Cron, *J. Amer. Chem. Soc.*, **70**, 1490 (1948).

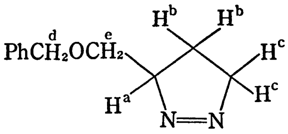
[18] F. Montanari, *Boll. Sci. Fac. Chim. Ind. Bologna*, **14**, 55 (1956): *Chem. Abstr.*, 51, 5723b.

[19] G. M. Bennett and W. A. Berry, *J. Chem. Soc.*, **1927**, 1666.

[20] D. Farnum, *J. Org. Chem.*, **28**, 870 (1963).

in a sealed glass tube. The excess diazomethane and ether were then removed, and the residual reaction mixture was chromatographed on silica. From the *n*-hexane–benzene eluates, unreacted allyl benzyl ether was recovered, and 3-benzylthiomethyl-Δ^1-pyrazoline (**13a**) and 4-(benzylthio)-methyl-Δ^1-pyrazoline (**13b**) were eluted in this order by the use of benzene-chloroform (1.51 g, 74.5%). The ratio of the pyrazoline, **13a**/**13b**, was determined to be 67/33 on the basis of the following NMR spectra.

13a: NMR (CCl_4): τ 8.80—8.30 (m, H^b), 6.24 (octet, H^e, $J_{ea}=4$ Hz, $J_{ee}=10$ Hz), 5.95—5.40 (m, H^a+H^c), 5.61 (s, H^d), and 2.84 (s, Ph).

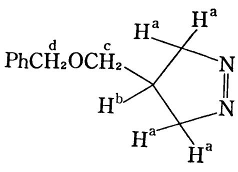


IR (neat): 1550 cm^{-1} ($\nu_{N=N}$). There is no absorption in the 3100—3500 cm^{-1} region because of the isomerization of **13a** to Δ^2-pyrazoline.

Mass (*m*/*e*): 190 (M$^+$ 1.2), 107 (7.2), 91 (100), 77 (4.8), and 69 (7.2).

Found: C, 69.28; H, 7.60%. Calcd for $C_{11}H_{14}N_2O$: C, 69.45; H, 7.42%.

13b: NMR (CCl_4): τ 7.83 (septet, H^b, $J_{ab}=J_{bc}=6$ Hz), 6.96 (d, H^c, $J_{bc}=6$ Hz), 5.84 (d, H^a, $J_{ab}=6$ Hz), 5.68 (s, H^d), and 2.84 (s, Ph).

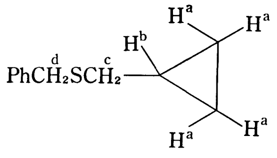


IR (neat): 1550 cm^{-1} ($\nu_{N=N}$). There is no absorption in the 3100—3500 cm^{-1} region, because of the isomerization of **13a** to Δ^2-pyrazoline.

Mass (*m*/*e*): 190 (M$^+$, 2.5), 108 (11.9), 107 (13.5), 91 (100), 77 (8.5), and 69 (17.0). Found: C, 69.24; H, 7.35%. Calcd for $C_{11}H_{14}N_2O$: C, 69.45; H, 7.42%.

Photolysis of 3-(Benzylthio)methyl-Δ^1-pyrazoline (**10**). The pyrazoline **10** (412 mg, 2.0 mmol) was dissolved in 20 ml of monoglyme in a quartz photolysis vessel, after which the solution was irradiated for 3 hr. During irradiation, the vessel was cooled with an air stream and the reaction temperature was maintained at room temperature. After the solvent had been evaporated, the reaction mixture was submitted to column chromatography on silica. Benzylthiomethylcyclopropane (**11**) was obtained from a *n*-hexane-benzene eluate (92.5 mg, 26%).

11: NMR (CCl_4): τ 9.65—9.35 (m, $H_A{}^a$), 9.35—8.95 (m, $H_B{}^a$), 8.85—8.60 (m, H^b), 7.76 (d, H^c, $J_{bc}=7$ Hz), 6.39 (s, H^d), and 2.96—2.65 (m, Ph).

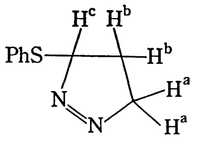


Mass (*m*/*e*): 178 (M$^+$, 22.2), 137 (11.1), 122 (31.9), 91 (100), and 87 (18.1).

Found: C, 73.94; H, 7.80; S, 18.94%. Calcd for $C_{11}H_{14}S$: C, 74.10; H, 7.91; S, 17.98%.

Reaction of Phenyl Vinyl Sulfide with Diazomethane. A mixture of 1.36 g (10 mmol) of phenyl vinyl sulfide and an excess of diazomethane in 50 ml of ether, which had been prepared from 10 g of *N*-nitroso-*N*-methylurea and aqueous sodium hydroxide in ether, was stirred at 15 °C for a week in a sealed glass tube. A small amount of a polymerization product of phenyl vinyl sulfide was precipitated in the solution during that time. After the polymer had been filtered off and the excess diazomethane and ether had been evaporated, the residue was chromatographed on silica. From a chloroform eluate, 720 mg (40.4%) of 3-(phenylthio)-Δ^1-pyrazoline (**17**), bp 84 °C/0.55 mmHg, were obtained.

17: NMR (CCl_4): τ 8.80—8.35 (m, $H_A{}^b$), 8.25—7.80 (m, $H_B{}^b$), 6.25—5.55 (m, H^a), 4.60—4.35 (m, H^c), and 2.85—2.40 (m, Ph). IR (neat): 1540 cm^{-1} ($\nu_{N=N}$). Mass (*m*/*e*): 178 (M$^+$, 4.2), 150 (6.3), 110 (100), 109 (31), 77 (14.1), 68 (33.8), 41 (19.7), and 39 (15.5). Found: C, 60.93; H, 5.40; S, 18.29%. Calcd for $C_9H_{10}N_2S$: C, 60.64; H, 5.65; S, 17.99%.



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