# The Reactions of Diazo Compounds. VIII. The Reaction of Diazomethane with α,β-Unsaturated Sulfones[1]

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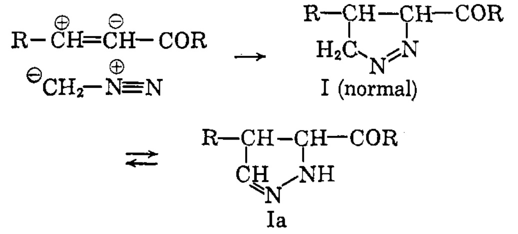
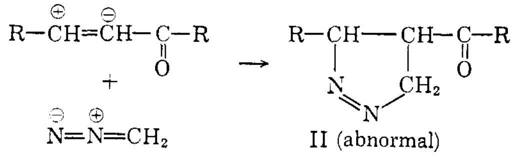
The reaction of seven α,β-unsaturated sulfones with diazomethane has been examined. In four of the seven cases abnormal addition predominated, affording pyrazolines in which the carbon atom of diazomethane had become attached to the alpha carbon atom of the olefin. These cases are the first reported in which diazomethane has added to a conjugated olefin in an "abnormal manner." The structure of the normal pyrazolines show NH absorption in the infrared spectra, and are thus Δ²-pyrazolines, while the abnormal pyrazolines show —N=N— absorption and are Δ¹-pyrazolines. The skeletal structures of the pyrazolines were established by their conversion, in high yield, to pyrazoles.

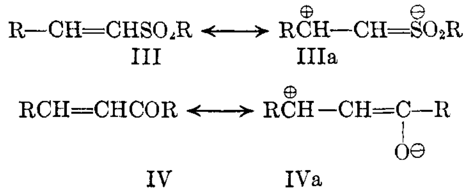
Diazomethane has been added to a large number of conjugated olefins, and the reaction leading to the formation of pyrazolines can be considered to occur as shown below. Such reactions are considered to be concerted, since the stereochemistry of the olefin is generally maintained in the resulting pyrazoline.[5] Of more importance to this study, however, is the orientation of addition that is observed. If fact, two pyrazolines[6] can result (I or II) depending upon whether the carbon atom of diazomethane attaches itself to the beta-carbon or to the alpha-carbon atom of the olefin. The latter reaction would lead to pyrazolines of type II, which are designated in this report as "abnormal." Of the many reactions studied involving diazomethane and conjugated olefins, only normal (type I) pyrazolines have been reported.[7] These results are to be expected if we conclude that the carbon atom of diazomethane is more nucleophilic than either nitrogen atom, for their is little doubt concerning the relative charge density on the olefin carbon atoms of most olefins.


I (normal)

Ia


II (abnormal)

The electronic distribution in α,β-unsaturated sulfones is, however, far less certain than for other conjugate systems. Consideration of resonance in the α,β-unsaturated sulfone (III ↔ IIIa) would lead to the conclusion that the same orientation of addition of diazomethane should be observed as with other conjugated systems, such as the α,β-unsaturated carbonyl (IV ↔ IVa)



$$\underset{\text{III}}{\mathrm{R{-}CH{=}CHSO_2R}} \longleftrightarrow \underset{\text{IIIa}}{\mathrm{R\overset{\oplus}{C}H{-}CH{=}\overset{\ominus}{S}O_2R}}$$

$$\underset{\text{IV}}{\mathrm{RCH{=}CHCOR}} \longleftrightarrow \underset{\text{IVa}}{\mathrm{R\overset{\oplus}{C}H{-}CH{=}C(O^{\ominus}){-}R}}$$

However, it is also apparent that these resonance effects are not comparable in magnitude, since the former involves a less favorable d-orbital interaction of sulfur.[8] It was concluded, therefore, that the sulfonyl group may be less effective in directing the orientation of addition of diazomethane than other electronegative groups which can conjugate with an olefin, and that the orientation of addition of diazomethane to conjugated sulfones could not be anticipated with confidence. This paper reports a study of the reaction of seven α,β-unsaturated sulfones with diazomethane and proof of structure of the resulting pyrazolines.

The α,β-unsaturated sulfones were treated with an excess of diazomethane under comparable conditions. The sulfones studied, and the products isolated are shown in Table I.

It was assumed that the stereochemistry of olefins was maintained in formation of the pyrazolines[5]; however, it was noted that the product assumed to be VIe (m.p. 72–73°) isomerized to VIf upon recrystallization from ethanol. Therefore, the exact stereochemistry of the pyrazolines cannot be considered established with certainty.

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[2] In part from the M.S. thesis of F. D. Blake, the University of Minnesota, 1959.

[3] In part from the Ph.D. thesis of D. R. Theissen, the University of Minnesota, 1961.

[4] Sinclair Research Fellow, 1959–61.

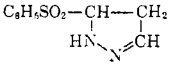
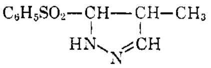
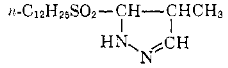
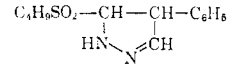
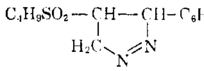
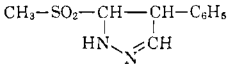
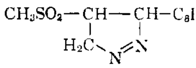
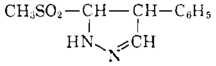
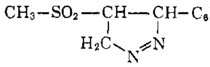
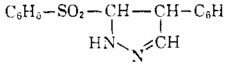
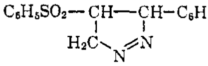
[5] K. L. Rinehart, Jr., and T. V. Van Auken, *J. Am. Chem. Soc.*, **82**, 5251 (1960).

[6] Tautomerization in pyrazolines (*i.e.*, I and Ia) is quite common—such isomers are not under consideration.

[7] Diphenyldiazomethane adds to nitroolefins, and presumably other conjugated olefins, to give type II pyrazolines. *Cf.*, W. E. Parham, H. G. Braxton, and P. R. O'Connor, *J. Am. Chem. Soc.*, **26**, 1805 (1961), and other papers in this series. Both orientations have been observed, although infrequently, with diazoacetic ester. *Cf.*, E. P. Kohler and L. L. Steele, *ibid.*, **41**, 1093 (1919).

[8] *Cf.*, G. Cilento, *Chem. Rev.*, **60**, 147 (1960).

TABLE I

| | Product | |
|---|---|---|
| Sulfone | Normal pyrazoline isolated (yield) | Abnormal pyrazoline isolated (yield) |
| $C_6H_5SO_2CH{=}CH_2$<br>Va | <br>VIa. (87%)<br>m.p. 96-97° | . . . |
| *trans*-$C_6H_5SO_2CH{=}CHCH_3$<br>Vb | <br>VIb. (76%)<br>m.p. 98.5-99.0° | . . . |
| *trans*-$C_{12}H_{25}SO_2CH{=}CHCH_3$<br>Vc | <br>VIc. (86%)<br>m.p. 73-74° | . . . |
| *cis*-*n*-$C_4H_9SO_2CH{=}CHC_6H_5$<br>Vd | <br>VId. (24%)<br>m.p. 57-59° | <br>VIId. (55%)<br>m.p. 71-72° |
| *trans*-$CH_3SO_2CH{=}CHC_6H_5$<br>Ve | <br>VIe, f. (24%)<br>m.p. 72-73°;<br>124-125° | <br>VIIe. (58%)<br>m.p. 82-83° |
| *cis*-$CH_3SO_2CH{=}CHC_6H_5$<br>Vf | <br>VIf. (26%)<br>m.p. 124-125° | <br>VIIf. (60%)<br>m.p. 109-110° |
| *cis*-$C_6H_5SO_2CH{=}CH{-}C_6H_5$<br>Vg | <br>VIg. (19%+)<br>m.p. 110° | <br>VIIg. (56%)<br>m.p. 131° |

It is also of interest to note that each of the normal pyrazolines showed absorption in the infrared spectrum at 3340 cm.$^{-1}$, characteristic for the NH group, and absence of absorption near 1600 cm.$^{-1}$, characteristic of the $-N{=}N-$ group. Each of the abnormal pyrazolines showed absorption near 1600 cm.$^{-1}$, but no absorption near 3340 cm.$^{-1}$. Therefore, the position of the double bonds can be placed with more certainty; the normal pyrazolines are $\Delta^2$-pyrazolines, and the abnormal pyrazolines are $\Delta^1$-pyrazolines.

It can be concluded from the results summarized in Table I that diazomethane reacts readily with acyclic vinyl sulfones to give good yields of sulfonylpyrazolines.[9] Whether normal or reverse addition of diazomethane to vinyl sulfones of the type $RSO_2CH{=}CHR'$ occurs is dependent upon the nature of R'. Reverse addition has not been observed when R' is alkyl (Va–Vc). When R' is aromatic (VId–VIg) reverse addition is dominant, although both normal and abnormal products result. In the three cases VId–VIf, where better material balances were obtained, the ratio of abnormal to normal pyrazolines was 2.3 ± 0.1, regardless of the nature of R. Furthermore, the stereochemistry of the vinyl sulfone, as judged from olefins Ve and Vf, does not appear to be a significant factor in determining the orientation of addition.

The cases cited above represent the first reported examples in which diazomethane has added abnormally to a conjugated olefin. We believe that resonance in the conjugated sulfone (either the ground state or transition state of the reaction cited), which involves d-orbital interaction of sulfur, is feeble compared to resonance effects by other electronegative groups not involving d-orbital interaction. Thus, the reaction of the former with diazomethane is sensitive to subtle changes in structure not observed in reactions of the latter. Diazomethane can obviously add to $\alpha,\beta$-unsaturated sulfones by two processes, and the fact that small differences in energy of activation of these processes can cause a large difference in relative yield, is reflected in the results observed. It is hoped that studies in progress will be helpful in providing a more detailed explanation for the specific differences noted.

The structures of the pyrazolines were established by their conversion to pyrazoles, by reaction with

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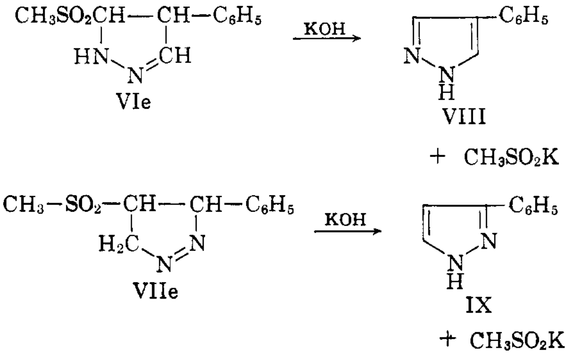
[9] H. J. Backer, N. Dost, and J. Knotnerus, *Rec. trav. chim.*, **68**, 237 (1949) report that cyclic sulfones with single $\alpha,\beta$-unsaturation do not react with diazomethane.

potassium hydroxide in cold methanol. The normal pyrazolines, illustrated by the conversion of VIe to VIII, gave 4-substituted pyrazoles, while the abnormal pyrazolines (such as VIIe) gave 3-substituted pyrazoles (IX). The yields in all cases were 73–83%, and in view of the ease of synthesis of many vinyl sulfones, the method appears to be an attractive one as a source of pyrazoles. This method of structure proof was not useful for VIa, since either the normal or the abnormal pyrazoline would give pyrazole (obtained in 74% yield). The structure of VIa was assigned by analogy, and by the fact that all of the normal pyrazolines obtained showed —NH absorption at 3340 cm.$^{-1}$ (infrared). The assignment of structure VIa, however, cannot be considered as unequivocal.



## Experimental

**Phenyl Vinyl Sulfone** (Va).—β-Chloroethyl phenyl sulfide (b.p. 85–87°/1.7 mm., $n^{20}$D 1.5837; reported,[10] b.p. 117°/12 mm., $n^{20}$D 1.5838, 90% yield from thiophenol and ethylene chlorohydrin) was converted in 84% yield to phenyl vinyl sulfide (b.p. 66–68°/5.9 mm., $n^{25}$D 1.5863; reported,[11] b.p. 84.5°; $n^{25}$D 1.5878) by reaction with potassium hydroxide.[13] Hydrogen peroxide (30%, 125 ml.) was added carefully to a solution of phenyl vinyl sulfide (28.1 g., 0.207 mole) in acetic acid (150 ml.), and the resulting mixture was heated at the reflux temperature for 0.5 hr. and then allowed to stand at room temperature overnight. Water was added, and the white solid was collected and recrystallized from methylene chloride–petroleum ether (b.p. 30–60°). Phenyl vinyl sulfone was obtained as a fine white powder (28.7 g., 83% yield, m.p. 66.5–68°; reported,[11] 50% yield, m.p. 65–68°).

*trans*-**Phenyl Propenyl Sulfone** (Vb).—*trans*-Phenyl propenyl sulfide[13] (60 g., 0.40 mole) in acetic acid (500 ml.) was oxidized with 30% hydrogen peroxide (300 ml.). The mixture was heated at the reflux temperature for 1.5 hr., then diluted with 2.5 l. of water. The solid which separated from the cold mixture was recrystallized from ethanol. *trans*-Phenyl propenyl sulfone (29.0 g., 40%, m.p. 67–68°) showed absorption in the infrared spectrum at 970 cm.$^{-1}$, but not at 695 cm.$^{-1}$,[14] as expected for the *trans*-olefin structure.

*Anal.* Calcd. for $C_9H_{10}O_2S$: C, 59.32; H, 5.53; S, 17.59. Found: C, 59.04, H, 5.54; S, 17.85.

*trans*-*n*-**Dodecyl Propenyl Sulfone** (Vc). *n*-**Dodecyl allyl sulfide** (b.p. 114–120°/0.7 mm., $n^{25}$D 1.4663–1.4677) was prepared in 87% yield from thiophenol and allyl chloride by a procedure similar to that reported by Hurd and Greengard[15] for the preparation of other allyl sulfides. The sulfide showed absorption at 917 cm.$^{-1}$ and 990 cm.$^{-1}$ in the infrared spectrum, characteristic of terminal olefin.[14]

A solution prepared from sodium (87.0 g., 3.8 g.-atoms), anhydrous ethanol (1 l.) and *n*-dodecyl allyl sulfide (75.0 g., 0.310 mole) was heated at the reflux temperature, in an atmosphere of nitrogen, for 16 hr. The mixture was diluted with water (4.2 l.) and extracted with ether. The dried ether extract was distilled to give: (A) recovered *n*-dodecyl allyl sulfide (<16 g., 21%, b.p. 96–116°/0.7 mm., $n^{25}$D 1.4630) and (B) *n*-dodecyl propenyl sulfide (29.5 g., 39%, b.p. 124–125°/0.7 mm., $n^{25}$D 1.4729). The infrared spectrum of *trans*-*n*-**dodecyl propenyl sulfide** showed absorption at 937 cm.$^{-1}$, and no absorption at 917 cm.$^{-1}$ or 990 cm.$^{-1}$. These data indicate that isomerization to the expected *trans* olefin had occurred.[13,16]

Oxidation of *trans*-*n*-dodecyl propenyl sulfide (24.5 g. 0.1 mole) in acetic acid (430 ml.) with hydrogen peroxide (30%, 56 ml.) was carried out as described above. The product was recrystallized from ethanol to give a sulfone (24.4 g., 89% yield) melting at 30–41°. This material was chromatographed on alumina, and eluted with petroleum ether (b.p. 30–60°) and mixtures of benzene–petroleum ether. The small amount of solid (m.p. 34°) eluted with petroleum ether was discarded; the principal product (17.0 g., 72%, m.p. 41–46°), eluted with benzene–petroleum mixtures, melted at 48–48.5° after recrystallization from ethanol.

*Anal.* Calcd. for $C_{15}H_{30}O_{25}$: C, 65.65; H, 11.02; S, 11.68. Found: C, 65.07; H, 10.90; S, 11.70.

The infrared spectrum of *trans*-*n*-**dodecyl propenyl sulfone** showed a peak at 960 cm.$^{-1}$ and none at 695 cm.$^{-1}$, characteristic[14] of the *trans* olefin structure.

*cis*-*n*-**Butyl** β-**Styryl Sulfone** (Vd). *cis*-*n*-**Butyl** β-**styryl sulfide** (49 g., 25% yield, b.p. 89°/0.17 mm., $n^{25}$D 1.5856; was prepared (51% recovery of phenylacetylene) from butyl mercaptan (93 g., 1.03 mole) and phenylacetylene (102 g., 1.0 mole) by a procedure similar to that described[17] for the preparation of *cis*-methyl β-styryl sulfide.

*Anal.* Calcd. for $C_{12}H_{16}S$: C, 74.94; H, 8.39. Found: C, 74.75; H, 8.63.

The infrared spectrum of this sulfide showed absorption at 690 cm.$^{-1}$ and no absorption at 970 cm.$^{-1}$, the spectrum expected for the *cis* olefin.[14,17]

A mixture of acetic acid (150 ml.), *cis*-*n*-butyl β-styryl sulfide (9.6 g., 0.05 mole) and hydrogen peroxide (30%, 25 ml.) was allowed to stand at room temperature for 2 days and then poured into ice water. The solid thus obtained (5.7 g., 51%, m.p. 59–60°) melted at 63° after recrystallization from ethanol.

*Anal.* Calcd. for $C_{12}H_{16}O_2S$: C, 64.25; H, 7.19; S, 14.29. Found: C, 64.05; H, 7.29; S, 14.44.

The infrared spectrum of the *cis*-*n*-**butyl**-β-**styryl sulfone** showed expected[14,17] absorption at 695 cm.$^{-1}$ (*cis* olefin) but none at 970 cm.$^{-1}$ (*trans* olefin).

*trans*-**Methyl** β-**styryl sulfone** (Ve) (22% yield, m.p. 77–78°; reported,[18] 32% yield, m.p. 78–79°) was prepared from ω-styrenesulfonyl chloride (60% yield, m.p. 86–89°; reported,[19] m.p. 86–89°), by reduction to zinc ω-styrene

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[10] G. M. Bennett and W. A. Berry, *J. Chem. Soc.*, 1679 (1927).

[11] W. E. Parham and R. F. Motter, *J. Am. Chem. Soc.*, **81**, 2146 (1959).

[12] J. von Braun and G. Kirschbaum, *Ber.*, **53**, 1399 (1920).

[13] D. S. Tarbell and M. A. McCall, *J. Am. Chem. Soc.*, **74**, 48 (1952).

[14] L. J. Bellamy, The Infrared Spectra of Complex Molecules," Methuen and Co., Ltd., London, 1956.

[15] C. D. Hurd and H. Greengard, *J. Am. Chem. Soc.*, **52**, 3356 (1930).

[16] D. S. Tarbell and W. E. Lovett, *ibid.*, **78**, 2259 (1956).

[17] W. E. Truce and I. A. Simms, *ibid.*, **78**, 2756 (1956).

[18] W. E. Truce, I. A. Simms, and H. E. Hill, *ibid.*, **75**, 5411 (1953).

[19] F. G. Bordwell, C. M. Suter, J. M. Holbert, and C. S. Rondestvedt, *ibid.*, **68**, 139 (1946).

sulfinate, and subsequent reaction of the derived sodium sulfinate with methyl iodide as described by Truce and coworkers.[17] The infrared spectrum showed absorption at 970 cm.$^{-1}$ and none at 695 cm.$^{-1}$, characteristic of the *trans* olefin structure.[17]

*cis*-**Methyl β-styryl sulfone** (Vf, m.p. 65°, infrared absorption at 695 cm.$^{-1}$) was prepared as previously described[17] by Truce and Simms.

*cis*-**Phenyl β-styryl sulfone** (Vg, m.p. 73–74°) was prepared from methyl phenyl sulfone and benzaldehyde as described by Field,[20] and by oxidation of phenyl β-styryl sulfide[21] with hydrogen peroxide. The second procedure was essentially identical[17] to that described above for *cis*-*n*-butyl β-styryl sulfone.

**Reaction of Diazomethane with Vinyl Sulfones. 1. With Phenyl Vinyl Sulfone (Va).**—A solution of Va (5.6 g., 0.033 mole) in anhydrous ether (100 ml.) was added to an ethereal solution of diazomethane[22] (0.06 mole approx.), freshly prepared from *p*-tolylsulfonylmethylnitrosoamide (21.5 g., 0.10 mole). The solution was refrigerated for 48 hr., and the resulting needles were collected and washed with cold ether. The solid (4.80 g., 68.6%; m.p. 96–97°) was recrystallized from ethanol without change in melting point.

*Anal.* Calcd. for $C_9H_{10}N_2O_2S$: C, 51.41; H, 4.79; N, 13.33; S, 15.25. Found: C, 51.67; H, 4.77; N, 13.19; S, 15.54.

The infrared spectrum of this product showed characteristic N—H absorption[14] at 3340 cm.$^{-1}$ ($\Delta^2$-pyrazoline), and the structure assigned was the 5-benzenesulfonylpyrazoline (VIa).

An additional 1.40 g. of the same product (88.6% total yield) was recovered from the ether mother liquor.

**2. With** ***trans*****-Phenyl Propenyl Sulfone (Vb).**—The reaction of Vb (9.1 g., 0.05 mole) in anhydrous ether (200 ml.) with diazomethane (∼ 0.09 mole) was carried out as described in (1). The cold solution was concentrated without external heating until a few crystals formed, and the solution was placed in the refrigerator for an additional 48 hr. The solid was separated and the mother liquor was concentrated. There was obtained a total of 8.5 g. (75.9%) of **4-methyl-5-benzenesulfonylpyrazoline** (VIb, m.p. 93.5–95°, from ethanol; infrared-spectrum, NH absorption at 3340 cm.$^{-1}$), and a small amount of oil which did not crystallize.

*Anal.* Calcd. for $C_{10}H_{12}N_2O_2S$: C, 53.55; H, 5.40; N, 12.50; S, 14.30. Found: C, 53.65; H, 5.35; N, 12.62; S, 14.55.

**3. With** ***trans-n*****-Dodecyl Propenyl Sulfone (Vc).**—The reaction of Vc (8.5 g., 0.031 mole) with diazomethane was carried out essentially as described in (2), above. The first crop of crystals (5.9 g., 60%, m.p. 64–66°) was recrystallized from ethanol to give a product melting at 73–74°. The solid (3.8 g., m.p. 40–62°) obtained by evaporation of the ether was chromatographed on alumina using petroleum ether and benzene–petroleum ether (b.p. 30–60°) as eluent. Starting material (1.2 g., m.p. 47–48°, 14.1% covery) and additional **4-methyl-5-dodecylsulfonylpyrazoline** (VIc, m.p. 72–73°, 8.4 g. total, 85.7% yield) were obtained.

*Anal.* Calcd. for $C_{16}H_{32}N_2O_2S$: C, 60.71; H, 10.19; N, 8.85; S, 10.13. Found: C, 60.57; H, 10.26; N, 8.69; S, 10.38.

The infrared spectrum showed a characteristic N—H absorption ($\Delta^2$-pyrazoline) band at 3340 cm.$^{-1}$.

**4. With** ***trans*****-Methyl β-Styryl Sulfone (Ve).**—A solution of Ve (1.30 g., 7.14 mmoles) in anhydrous ether (75 ml.) was added to an ethereal solution of diazomethane (∼0.02 mole). The solution was refrigerated for 48 hr., then concentrated without applying external heat to turbidity, and replaced in the refrigerator for 48 hr.

The solid that separated (0.92 g., 57.5% yield, m.p. 82–83°) was recrystallized from ethanol with no change in melting point. The infrared spectrum of the product showed absorption at 1585 cm.$^{-1}$ and no absorption at 3340 cm.$^{-1}$ ($\Delta^1$-pyrazoline).[5] The structure of this product was subsequently confirmed as **3-phenyl-4-methylsulfonylpyrazoline (VIIe)**.

*Anal.* Calcd. for $C_{10}H_{12}N_2O_2S$: C, 53.57; H, 5.36; N, 12.50; S, 14.30. Found: C, 53.46; H, 5.49; N, 12.45; S, 14.28.

The ethereal filtrate was concentrated until a few crystals formed. The solution was refrigerated and the resulting precipitate was filtered and washed with cold ether. The solid (0.38 g., 23.8% yield, m.p. 72–73°) was recrystallized from ethanol to give pure white needles which melted at 124–125°.

*Anal.* Calcd. for $C_{10}H_{12}N_2O_2S$: C, 53.57; H, 5.36; N, 12.50; S, 14.30. Found: C, 53.48; H, 5.43; N, 12.52; S, 14.51.

The infrared spectrum of this compound showed characteristic —NH ($\Delta^2$-pyrazoline) absorption[14] at 3340 cm.$^{-1}$, and the structure was subsequently established as **4-phenyl-5-methylsulfonylpyrazoline (VIf)**. This material was identical (melting point and mixed melting point) to that described below, obtained from *cis*-methyl β-styryl sulfone. *cis-trans* isomerization of the pyrazoline is assumed, therefore, to account for the unexpected change in melting point noted during recrystallization.

**5. With** ***cis*****-Methyl β-Styryl Sulfone (Vf).**—The reaction of Vf (5.6 g., 0.031 mole) with diazomethane was carried out as described above. The solid (4.50 g., 65.2% yield, m.p. 108–112°) which separated from the ether solution was recrystallized from ethanol to give white plates (4.15 g., 60%, m.p. 109–110°). The infrared spectrum of this product showed no NH absorption at 3340 cm.$^{-1}$, but did show absorption at 1600 cm.$^{-1}$ (N=N, $\Delta^1$-pyrazoline).[5] These data were consistent with the structure **3-phenyl-4-methylsulfonylpyrazoline (VIIf)**, subsequently established.

*Anal.* Calcd. for $C_{10}H_{12}N_2O_2S$: C, 53.57; H, 5.36; N, 12.50; S, 14.30. Found: C, 53.38; H, 5.54; N, 12.43; S, 14.43.

From the ethanol mother liquor, and the original ether filtrate, a second solid was obtained. This material (1.81 g., 26.2% yield, m.p. 124–126° from ethanol) was identical with **4-phenyl-5-methylsulfonylpyrazoline (VIf)** obtained from *trans*-methyl β-styryl sulfone (4, above).

**6. With** ***trans-n*****-Butyl β-Styryl Sulfone (Vd).**—The reaction of Vd (7.5 g., 0.033 mole) in ether (100 ml.), with diazomethane was carried out as described in (5), above. From the refrigerated solution, obtained by concentrating the ether solution to about one-half its volume, there was obtained a white solid (4.9 g., 55.1% yield) melting at 71–72°. This material could not be recrystallized without decomposition; therefore elementary analysis not obtained. The infrared spectrum of this product showed absorption at 1600 cm.$^{-1}$, and no absorption at 3340 cm.$^{-1}$, data consistent with the $\Delta^1$-pyrazoline structure (N=N).[14] The structure of this material was subsequently established as **3-phenyl-4-butylsulfonyl pyrazoline (VIId)**.

The ethereal solution was concentrated almost to dryness, and the solid, thus obtained, was washed with cold ether. The pale yellow solid (2.1 g., 23.6% yield, m.p. 57–59°) could not be recrystallized without decomposition. The infrared spectrum showed characteristic NH absorption ($\Delta^2$-pyrazoline) at 3340 cm.$^{-1}$. The structure was subsequently established as **4-phenyl-5-butylsulfonylpyrazoline (VId)**.

**7. With** ***cis*****-Phenyl β-Styryl Sulfone.**—The reaction of Vg (8.00 g., 0.033 mole) in anhydrous ether (125 ml.) with ethereal diazomethane (0.6 mole, from 21.5 g., 0.1

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[20] L. Field, *ibid.*, **74**, 3919 (1952).

[21] H. R. Davis, Ph.D. thesis, p. 42, University of Minnesota (1949).

[22] T. J. DeBoer and H. J. Backer, *Org. Syn.*, **36**, 16 (1956).

mole of *p*-tolylsulfonylmethylnitrosoamide) was carried out as described above for other olefins.

The white needles (5.27 g., 56.3% yield, m.p. 129–131°) that separated from the cold ether were recrystallized from acetone–water to give **3-phenyl-4-benzenesulfonylpyrazoline** (VIIg m.p. 131–132°).

*Anal.* Calcd. for $C_{15}H_{14}N_2O_2S$: C, 62.91; H, 4.93; N, 9.78; S, 11.20. Found: C, 62.99; H, 5.06; N, 9.47; S, 11.21.

The ethereal solution was concentrated (no heat) until considerable crystallization was evident, and the solution was placed in the refrigerator. The solid (1.85 g., 19.6%, m.p. 107–110°) obtained was recrystallized from methanol–water to give **4-phenyl-3-benzenesulfonylpyrazoline** (VIg, m.p. 110–111° from methanol).

*Anal.* Calcd. for $C_{15}H_{14}N_2O_2S$: C, 62.91; H, 4.93; N, 9.78; S, 11.20. Found: C, 63.17; H, 4.81; N, 9.65; S, 11.39.

The ether mother liquors contained a solid (~ 1.14 g.) and an oil (0.7 g.) which were not resolved into pure components but contained some VIg.

**Proofs of Structure of Pyrazolines.**—The procedure used for conversion of the sulfonylpyrazolines to pyrazoles, in each case, was essentially identical.

1. **5-Benzenesulfonylpyrazoline (VIa).**—Pyrazoline VIa (2.1 g., 0.01 mole) was dissolved in a solution of potassium hydroxide (1.5 g., 0.27 mole) in methanol (20 ml.). The solution was allowed to stand in the cold (~0–15°) overnight, and was then diluted with salt water. The oil which separated crystallized (0.5 g., 73.5%, m.p. 66–67°, 66.5–67° from petroleum ether (b.p. 90–100°).

*Anal.* Calcd. for $C_3H_4N_2$: C, 52.92; H, 5.92. Found: C, 52.67; H, 6.03.

The picrate melted at 158–160° (from methanol). These data are in agreement with the assigned structure **pyrazole** (reported,[23] m.p. 69.5–70°; picrate, m.p. 158–160°).

2. **4-Methyl-5-benzenesulfonylpyrazoline (VIb).**—The combined dried ether extract, obtained after treating VIb (4.5 g., 0.02 mole) as described above, was concentrated to a colorless oil (1.22 g., 75.3%). The material was identified as **4-methylpyrazole** by its conversion into: the picrate, m.p. 140–142°, from methanol; the silver double salt, m.p. 139–142°; and pyrazole-4-carboxylic acid, m.p. 275–280° from water. Basic permanganate was used for the oxidation to the acid. The reported[24] constants for 4-methylpyrazole are: picrate, m.p. 142°; silver double salt, m.p. 142°; pyrazole-4-carboxylic acid, m.p. 275°. The data reported[25] for the isomeric 3-methylpyrazole are: picrate, m.p. 142°; silver double salt, m.p. 121°; pyrazole-3-carboxylic acid, m.p. 212°.

3. **4-Methyl-5-dodecylsulfonylpyrazoline (VIc).**—The colorless liquid obtained from VIc (1.58 g., 5.0 mmoles) possessed an infrared spectrum identical to that of 4-methylpyrazole, obtained in (2) above. The picrate of this material (m.p. 141–142°) caused no depression in melting point when admixed with the picrate described in (2), above.

4. **3-Phenyl-4-butylsulfonylpyrazoline (VIId).**—The solid obtained when VIId (1.33 g., 5.0 mmoles) was treated with methanolic potassium hydroxide was recrystallized from petroleum ether (b.p. 90–100°) to give **3-pyenylpyrazole** (0.6 g., 83.3%, m.p. 73°, mixture m.p. with an authentic sample,[26] m.p. 72–73°, was 72–73°).

5. **4-Phenyl-5-butylsulfonylpyrazoline (VId).**—Pyrazoline VId (1.33 g., 5.0 mmoles) was converted, as described above, into 4-phenylpyrazole (0.55 g., 76.4% yield, m.p. 221–230°, m.p. 228–230 from methanol; mixture m.p. with authentic,[27] m.p. 231°, was 230–231°).

6. **Other Pyrazolines.**—By the procedures described above: **3-phenyl-4-methylsulfonylpyrazoline** (VIIe) gave 3-phenylpyrazole (80% yield), **4-phenyl-5-methylsulfonylpyrazoline** (VIe,f) gave 4-phenylpyrazole (78% yield), **3-phenyl-4-methylsulfonylpyrazoline (VIIf)** gave 3-phenylpyrazole (82% yield), **4-phenyl-5-benzenesulfonylpyrazoline** (VIg) gave 4-phenylpyrazole (95% yield), **3-phenyl-4-benzenesulfonylpyrazoline** (VIIg) gave 3-phenylpyrazole (75% yield).

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[23] D. L. Balbiano, *Gazz. chim. ital.*, **20**, 459 (1890).

[24] H. von Pechman and E. Burkard, *Ber.*, **33**, 3593 (1900); E. Büchner and M. Fritsch, *Ann.*, **273**, 253 (1813).

[25] R. von Rothenberg, *J. prakt. Chem.* [2], **52**, 46, 49 (1895); L. Knorr, *Ann.*, **279**, 227, 231 (1894).

[26] L. Knorr, *Ber.*, **28**, 696 (1895).

[27] H. Rupe and A. Huber, *Helv. Chim. Acta*, **10**, 848 (1927).

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# Reaction of 1,5-Diazacycloöctane with Aldehydes

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1,5-Diazacycloöctane undergoes an intramolecular condensation reaction with aldehydes to form exclusively 9-substituted 1,5-diazabicyclo[3.3.1]nonanes, hitherto unknown. This is in contrast to the reaction of piperazine and aldehydes which proceeds intermolecularly to form polymers.

It has been shown that piperazine reacts with aliphatic and aromatic aldehydes to form polymeric condensation products. Herz[2] reported that when an excess of benzaldehyde was mixed with piperazine at room temperature or in a sealed tube at 60°, a white solid was obtained which appeared to decompose on standing in a desiccator. Herz assigned no structure for this product. However, formaldehyde was reported to react with piperazine to form a polymeric solid with an empirical formula of $C_4H_{10}N_2 . 2H_2O$.

Forsee and Pollard[3] made a more thorough study of these condensation reactions. In all cases, except in the reaction of butyraldehyde and acetaldehyde, they were able to assign the polymethylene piperazine structure (I) for these polymeric condensation products.

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[2] Herz, W., *Ber.*, **30**, 1584 (1897).

[3] W. F. Forsee, Jr., and C. B. Pollard, *J. Am. Chem. Soc.*, **57**, 2363 (1935).