CHEMICAL SHIFT DATA (AT 21° IN CH_3CN)

	τ values for ring protons at position	
	3	5
s-Triazole	1.82	1.82[a]
4-Amino-*s*-triazole	1.73	1.73[a]
N-Acetyl-*s*-triazole	1.97	1.05[b]
N,N'-Carbonyldi-*s*-triazole	1.82	0.63[b]
1,3-Diphenyl-*s*-triazole		1.65
1,5-Diphenyl-*s*-triazole	2.08	

[a] One intense peak only observed. [b] Two peaks of equal intensity observed.

Application of this symmetry principle to the *s*-triazole derivatives listed in the table has enabled the assignments shown to be made and establishes that these *N*-acyl-*s*-triazoles are best represented as 1-acetyl-*s*-triazole (I, R = CH_3) and 1,1'-carbonyldi-*s*-triazole (I, R = 1-*s*-triazolyl).

Removal of the carbonyl group of (I, R = 1-*s*-triazolyl) by hydrolysis (addition of a small amount of water to the sample tube) resulted in the disappearance of the low-field peak and an increase in intensity of the peak at τ value 1.82. This corresponded to the formation of *s*-triazole. The low τ value for the C-5 proton in (I, R = 1-*s*-triazolyl) is attributed to a double deshielding effect: (i) that exerted by the carbonyl group and (ii) that exerted by the second aromatic *s*-triazole ring which is able to orientate itself with respect to the C-5 proton so that it is in the position of maximum deshielding.[8]

Experimental

The compounds used in this investigation were prepared by methods described in the literature.[9] The spectra were recorded from a Varian V-4302 Dual Purpose, 60 Mc., NMR spectrometer, equipped with a flux stabilizer and field homogeneity controls. The calibrations were made by the side-band technique[10] and chemical shift values are reported in τ units.[11] Samples were examined as saturated solutions in anhydrous methyl cyanide solvent or at concentrations not exceeding 10%, depending on solubility. 1,3-Diphenyl-*s*-triazole and *s*-triazole were examined in carbon tetrachloride solvent and preliminary studies indicated that there were only minor solvent effects by carbon tetrachloride and methyl cyanide on the τ values.

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[8] Ref. 7, pp. 125–129.

[9] See ref. 4 and ref. 2.

[10] J. T. Arnold and M. G. Packard, *J. Chem. Phys.*, **19**, 1608 (1951).

[11] G. V. D. Tiers, *J. Phys. Chem.*, **62**, 1151 (1958).

Cyclopropyl Sulfones[1]

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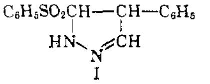
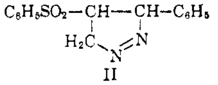
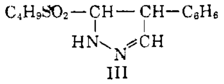
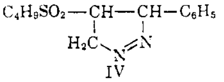
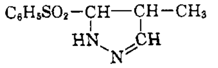
Numerous cases have been cited in which cyclopropanes result when pyrazolines are decomposed thermally in the presence of platinum. Simple pyrazolines often produce olefinic products, while more complex pyrazolines generally give cyclopropanes.[4] The availability[5] of a number of sulfonylpyrazolines has prompted us to investigate this reaction as a possible source of cyclopropyl sulfones.

The sulfonylpyrazolines were decomposed thermally (*ca.* 140°) in the presence of polished platinum, and in an atmosphere of nitrogen. The results are summarized in Table I.

TABLE I

Pyrazoline	Product (yield) thermal decomposition
 I	4-Phenylpyrazole (92%)
 II	3-Phenylpyrazole (90%)
 III	4-Phenylpyrazole (58%)
 IV	3-Phenylpyrazole (63%)
 V	4-Methylpyrazole (64% as the picrate)

It can be seen that the principal product from each reaction was the pyrazole, formed by elimination of alkyl- or arylsulfinic acid.[6] Furthermore, there was no significant difference in behavior of the Δ^1-pyrazolines (II and III) and the isomeric Δ^2-pyrazolines (I and IV). In no case was any cyclopropane noted; in this respect the sulfonyl pyrazolines behave in a manner similar to the nitropyrazolines which lose nitrous acid to give pyrazoles.[7]

Rinehart and Van Auken[8] recently reported that the light-induced decomposition of certain stereoisomeric pyrazolines leads to the formation of cyclopropanes in which the stereochemistry of the

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[1] Supported in part by the Office of Ordnance Research, U.S. Army, Contract No. DA-ORD-31-124-61-G13, and by the Smith Kline and French Research Foundation.

[2] In part from the Ph.D. thesis of H. G. Braxton, Jr., the University of Minnesota.

[3] (a) In part from the Ph.D. thesis of D. R. Theissen, the University of Minnesota, 1961; (b) Sinclair Research Fellow, 1959–61.

[4] *Cf.* K. von Auwers and F. König, *Ann.*, **496**, 252 (1932).

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

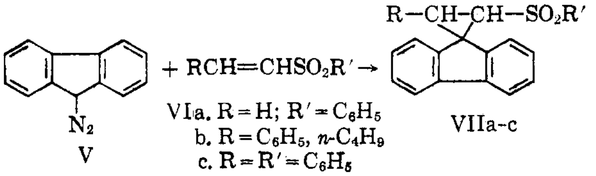
[6] The same pyrazoles result in higher yield when the pyrazolines are treated with methanolic potassium hydroxide; *cf.* ref. 5.

[7] (a) W. E. Parham and J. L. Bleasdale, *J. Am. Chem. Soc.*, **73**, 4664 (1951); (b) In certain cases pyrazolines derived from nitroolefins and diphenyldiazomethane give nitrocyclopropanes when decomposed thermally; *cf.* W. E. Parham, H. G. Braxton, Jr., and C. Serres, Jr., *J. Org. Chem.*, **26**, 1831 (1961).

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

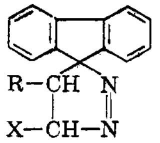
pyrazoline is maintained. In pursuit of this approach to cyclopropyl sulfones, three sulfonylpyrazolines were irradiated at room temperature, using the 125-watt high pressure mercury vapor lamp. These reactions were not as clean as those conducted thermally, but in each case moderate to good yields of substituted pyrazoles resulted. In no case was a cyclopropane detected: (a) 3-phenyl-4-benzenesulfonylpyrazoline (II) gave 3-phenylpyrazole (70% yield); (b) 4-phenyl-5-benzenesulfonylpyrazoline (I) gave 4-phenylpyrazoline (58%). together with an almost equal weight of an unidentified nitrogen containing product (m.p. 138–139°); and (c) 3-phenyl-4-butylsulfonylpyrazoline (IV) gave 3-phenylpyrazole (43%).

Acyclic vinyl sulfones were found to react readily with 9-diazofluorene (V) to give sulfonylspiro (cyclopropane-1,9-fluorenes) (VII):

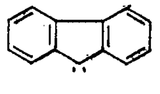


VIa. $R = H; R' = C_6H_5$
b. $R = C_6H_5, n\text{-}C_4H_9$
c. $R = R' = C_6H_5$

(a) phenyl vinyl sulfone (VIa) gave VIIa in 98% yield; (b) *cis*-*n*-butyl β-styryl sulfone (VIb) gave VIIb (70.2%) and bis(biphenylene)ethylene (19%); and (c) phenyl β-styryl sulfone (VIc) gave VIIc (*ca.* 70%), and a red impurity assumed to be bis(biphenylene)ethylene. Mustafa and Harbash[9] have reported that the reaction of 9-diazofluorene with nitroolefins of the type $RCH{=}CHNO_2$ gives 2-alkyl-3-nitrospiro-(cyclopropane-1,9′-fluorenes) directly, and have suggested that these result by loss of nitrogen from the intermediate nitropyrazoline VIII ($X = NO_2$). The pyrazolines VIII have not, however, been isolated. This fact, together with the quantities of bis-(biphenylene)ethylene formed, suggests that these reactions may involve combination of the carbene IX with the olefins.



VIII



IX

Experimental

Thermal Degradation of Pyrazolines.—The general procedure used is illustrated below. The results for other pyrazolines are summarized in Table I.

Thermal Decomposition of 4-Phenyl-5-benzenesulfonylpyrazoline (I).—A mixture of I (2.30 g., 8.04 mmoles) and polished platinum (5.2 g.) was heated slowly to 140° in an atmosphere of nitrogen. Heating was continued until evolution of gases ceased. The cooled solid (tan-orange) was triturated with ether and the resulting yellow powder (1.0 g., m.p. 151–155°) was recrystallized from ethanol. The white solid (m.p. 228–230°, 0.95 g., 81.9% yield) was identified[5] (melting point and mixture melting point) as **4-phenylpyrazole.** Additional 4-phenylpyrazole (0.12 g.) was obtained from the ether wash; the total yield was (1.07 g., 92.3%).

In the case of 3-phenyl-4-benzenesulfonylpyrazole (II) no gas was evolved. The product (m.p. 151–153°) was water soluble and assumed to be a salt of 3-phenylpyrazole and benzenesulfinic acid. The action of aqueous sodium hydroxide on this product generated 3-phenylpyrazole (90% yield).

Irradiation of Pyrazolines. 1. 3-Phenyl-4-benzenesulfonylpyrazolene (II).—A sample of II[5] (0.20 g., 0.7 mmole) was irradiated with a 125-watt ultraviolet lamp at 30–40° for 1 day. The reaction mixture was chromatographed on alumina using petroleum ether (b.p. 30–60°) and mixtures of this ether and benzene as eluent. The solids obtained were combined and recrystallized from benzene–petroleum ether (b.p. 30–60°). The white powder (0.07 g., 70% yield, m.p. 72–73°) was 3-phenylpyrazole (m.p. and mixture m.p.[5] 72–73°).

2. **4-Phenyl-5-benzenesulfonylpyrazoline** (I).—The solid obtained when I[5] (0.98 g., 3.4 mmoles) was treated as described in (1), above, was recrystallized from ethanol. The white solid (0.28 g., 58% yield, m.p. 227–229°) was 4-phenylpyrazole.[5]

The ethanol filtrate was concentrated to a white solid (0.27 g., m.p. 134–136°). This material melted at 138–139° after recrystallization from ethanol, and was not identified. The infrared spectrum was similar to starting material, but showed no absorption at 3340 cm.$^{-1}$ (N—H)[5] and a new band at 1600 cm.$^{-1}$, characteristic of the N=N group.[5]

Anal. Found: C, 59.88; H, 4.62; N, 8.88; S, 10.77. Calcd. for $C_{15}H_{14}O_2S$ (cyclopropane): C, 69.74; H, 5.46; N, 0.00; S, 12.41: for $C_{15}H_{14}N_2O_2S$ (isomeric pyrazoline): C, 62.91; H, 4.93; N, 9.78; S, 11.20.

3. **3-Phenyl-4-butylsulfonylpyrazoline** (IV).—The green oil obtained when IV (0.65 g., 2.44 mmoles) was irradiated was chromatographed on alumina as described in (1), above. 3-Phenylpyrazole (m.p. and mixture[5] m.p. 73°, 0.15 g., 42.9% yield), and a pale green fluorescent liquid were obtained. The infrared spectrum of the oil showed no absorption near 1020 cm.$^{-1}$, characteristic[10] of the cyclopropane structure.

Reactions of 9-Diazofluorene with Vinyl Sulfones. The Synthesis of Cyclopropyl Sulfones. 1. With *cis*-*n*-Butyl β-Styryl Sulfone (VIb).—A solution of VIb[5] (1.30 g., 5.8 mmoles) in anhydrous benzene (15 ml.) was combined with a solution of diazofluorene[11] (1.11 g., 5.8 mmoles, m.p. 98–100°) in anhydrous benzene (10 ml.), and the resulting solution was heated at the reflux temperature for 3 days. The benzene was removed and the red solid was dissolved in ethanol. The solution was cooled and fine red needles of bis(biphenylene)ethylene[12] (0.18 g., 19%, m.p. 195–197°) were separated. The filtrate was concentrated and cooled, and 2-phenyl-3-butylsulfonylspiro(cyclopropane-1,9′-fluorene) (VIIb, 1.58 g., 70.2% yield, white powder, m.p. 161–164°, m.p. 166° from ethanol) was obtained.

Anal. Calcd. for $C_{25}H_{24}O_2S$: C, 77.28; H, 6.23; S, 8.25. Found: C, 77.01; H, 6.43; S, 8.09.

The infrared spectrum of II showed characteristic[10] cyclopropane absorption at 1020 cm.$^{-1}$.

2. **With Phenyl Vinyl Sulfone (VIa).**—A sample of VIa (2.52 g., 0.015 mole) was treated with diazofluorene (2.88 g., 0.015 mole) in anhydrous benzene (65 ml.) as described

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[9] A. Mustafa and A. Harbash, *J. Am. Chem. Soc.*, **76**, 1383 (1954).

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

[11] A. Schonberg, W. Avad, and N. Latib, *J. Chem. Soc.*, 1368 (1951).

[12] Authentic sample supplied by C. F. Koelsch, the University of Minnesota.

above. The solid product obtained directly from the benzene solution (pale yellow, 4.90 g., 98% yield, m.p. 139–140°) was recrystallized from benzene to give 2-benzenesulfonylspiro(cyclopropane-1,9′-fluorene) (VIIa) as a white powder (m.p. 140–141°).

Anal. Calcd. for $C_{21}H_{16}O_2S$: C, 75.88; H, 4.85; S, 9.65. Found: C, 75.70; H, 4.99; S, 9.56.

The infrared spectrum showed absorption at 1025 cm.$^{-1}$, characteristic of the cyclopropane structure.

3. **With Phenyl β-Styryl Sulfone (VIc).**—A solution of VIc (2.24 g., 0.01 mole) and diazofluorene (1.80 g., 0.0094 mole) in benzene (50 ml.) was heated at the reflux temperature for 3 days. The benzene solution was allowed to stand for 7 days at 32° and the resulting red solid (2.72 g., 72%, m.p. 190–220°) was washed with ether and recrystallized from benzene. 2-Phenyl-3-benzenesulfonylspiro-(cyclopropane-1,9-fluorene) (VIIc) was obtained as a white solid, m.p. 238–240°. The benzene solution contained additional VIIc, but this was not processed.

Anal. Calcd. for $C_{27}H_{20}O_2S$: C, 80.97; H, 5.03; S, 7.85. Found: C, 81.23; H, 5.24; S, 7.70.

Dimerization of 3-Carboxybenzoquinone-1,2

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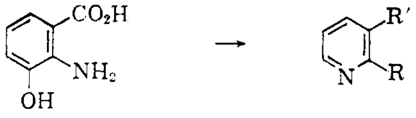
Received February 5, 1962

During the course of a program designed to study the chemistry of the intermediates in the enzymatic transformation of 3-hydroxyanthranilic acid (I) into quinolinic (II. R = R′ = CO_2H), nicotinic (II. R = H, R′ = CO_2H), and picolinic acids (II. R = CO_2H, R′ = H),[1] the possibility of 3-carboxybenzoquinone-1,2 or a dimer being an intermediate was investigated. While neither 3-carboxybenzoquinone-1,2 nor a dimer have been previously reported, some have postulated them as products in the above degradations.[2]



I II

We now wish to report the successful oxidation of 2,3-dihydroxybenzoic acid leading to 3-carboxybenzoquinone-1,2 and the isolation of a dimer of the quinone.

Treatment of 2,3-dihydroxybenzoic acid with silver oxide in anhydrous methanol containing a trace of 98% formic acid afforded 3-carboxybenzoquinone-1,2, which dimerized to III upon refluxing in anhydrous ether for forty-eight hours.

An assignment of III as a Diels-Alder adduct formed by the addition of one molecule of quinone to another based upon infrared absorption from a Nujol mull at 2.84, 5.69, 5.75, 5.80, 5.93, and 6.12 μ is supported by ultraviolet absorption in chloroform λ_{max} 213 mμ (log ε 3.97); 255 mμ (log ε 3.87). Infrared absorption at 2.84 μ could represent the OH absorption of carboxyls while the four peaks, 5.69, 5.75, 5.80, and 5.93 μ are characteristic of carbonyls; the first three corresponding to unconjugated and the last to conjugated carbonyl groups.[3] In addition, the peak at 6.12 μ corresponds to the double bond of the system —COCH=CH— and the ultraviolet spectrum agrees, with a maximum at 255 mμ,[4] a wave length too low for a benzenoid system while the absorption at 213 mμ compares favorably with that for α,β-unsaturated acids.[5]

Heating an ethanolic (10% hydrochloric acid) solution of the dimer causes rapid conversion to a more stable phenolic material, IV (R = H), which gives an intense ferric chloride reaction indicating a phenol nucleus. The infrared spectrum shows new peaks at 2.81 (hydroxyl), 5.57 (γ-lactone), 6.23 and 6.67 μ (benzene ring) and there is a shift in the ultraviolet absorption, $\lambda_{max}^{C_2H_5OH}$ 270 mμ (log ε 4.01).[6]

Treatment of IV (R = H) with acetic anhydride and pyridine gives a monoacetate, IV (R = Ac), and with o-phenylenediamine a phenazine. Refluxing IV (R = H) with 10% sodium hydroxide in methanol results in V (R = H), which when refluxed with acetic anhydride and pyridine gives a diacetate, V (R = Ac). The diacetate has a strong infrared absorption at 8.04 μ (—O·CO—), 6.03 μ (—CH:CH—), and 5.80 μ (—CO·CO—).

Pyrolysis at 200–210° causes III to undergo a smooth reverse Diels-Alder reaction with reduction to two molecules of 2,3-dihydroxybenzoic acid. Under similar conditions V (R = H) is converted to VI. Oxidation of VI with silver oxide in anhydrous methanol gave a good yield of 3,8-dicarboxynaphthoquinone-1,2 (VII). With o-phenylenediamine in acetic acid VII gave a yellow phenazine. the absorption spectrum of which was similar to those reported for benzo[*a*]phenazines.[7]

In accordance with the stereochemical factors

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[1] A. H. Mehler, *Proc. Intern. Congr. Biochem. 4th, Vienna*, **13**, 164 (1958).

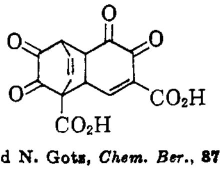
[2] A. Miyake, A. H. Bokman, and B. S. Schweigert, *J. Biol. Chem.*, **211**, 391 (1954).

[3] These peaks are practically identical to those found in substituted and unsubstituted o-benzoquinone dimers [*cf.*, J. Harley-Mason and A. H. Laird, *J. Chem. Soc.*, 1718 (1958) and E. Adler, R. Magnusson, B. Berggren, and H. Thomelius, *Acta Chem. Scand.*, **14**, 515 (1960)].

[4] This value agrees favorably with a value of 252 (log ε 3.95) for the anologous dimer of 4,5-dimethyl-o-quinone [*cf.*, L. Horner and K. Sturm, *Ann.*, **597**, 1 (1955)] and a value 254 mμ (log ε 3.87) for the dimer of o-benzoquinone [*cf.*, A. A. Patchett and B. Witkop, *J. Org. Chem.*, **22**, 1477 (1957)].

[5] H. E. Ungnade and I. Ortega, *J. Am. Chem. Soc.*, **73**, 1564 (1951).

[6] The presence of the lactone in IV allows elimination of the other possible structure for III, *i.e.*,



[7] H. J. Teuber and N. Gotz, *Chem. Ber.*, **87**, 1236 (1954).