ml.) containing freshly sandpapered aluminum weighing pans (Fisher Scientific Company) cut into half-inch squares (3 g.) and mercuric chloride (0.12 g.) was added 10 g. of the ketone I.[8] The mixture was heated under reflux on a steam bath causing immediate reaction. After 3 hr. the mixture was almost solid with a gray material. An additional portion of absolute ethanol (50 ml.) was added and the mixture was heated under reflux for 5 more hours. The mixture was then poured into ice and dilute hydrochloric acid and the organic material was thoroughly extracted with benzene. Removal of the benzene left a solid which was recrystallized from 95% ethanol as light tan colored needles, 6.0 g. (67%), m.p. 136.5–138°. An analytical sample, recrystallized from the same solvent melted at 136.5–138°.

Anal. Calcd. for $C_{16}H_{14}S_2$: C, 71.06; H, 5.22. Found: C, 70.83; H, 5.33.

1,2,7,8,9,10,11,12-Octahydro[3,4-*b*:6,5-*b'*]dithienophenanthrene-9,10-dicarboxylic Acid Anhydride (III).—When a mixture of II (5.3 g., 0.019 mole) and maleic anhydride (3.0 g., 0.031 mole) in technical xylene (100 ml.) was heated under reflux for 4 hr. and then allowed to cool over a 12-hr. period, a white solid separated, 4.9 g. (69%), m.p. 255–257°. Recrystallization from xylene gave an analytical sample, as white feathery needles, m.p. 259.5–260°. An infrared spectrum of the adduct in Nujol mull showed strong bands at 1780 cm.$^{-1}$ and 1855 cm.$^{-1}$ characteristic of the anhydride grouping.

Anal. Calcd. for $C_{20}H_{16}O_3S_2$: C, 65.19; H, 4.38; S, 17.41; mol. wt. 368. Found: C, 65.15; H, 4.44; S, 17.28; mol. wt. (Rast) 358, 365.

[3,4-*b*:6,5-*b'*]Dithienophenanthrene-9,10-dicarboxylic Acid Anhydride (IV).—Dehydrogenation of the adduct IV was accomplished by heating a mixture of IV (0.5 g., 0.0014 mole) with sulfur (0.18 g., 0.0056 mole) in a nitrogen atmosphere under a pressure of slightly less than 1 atm. in a salt bath at a bath temperature of 300° for 45 min. The crude product was crystallized from acetic anhydride and melted at 296–303°. This material was found to be satisfactory for use in the subsequent step; no percentage yields are reported as purification was not carried out except to prepare an analytical sample by sublimation followed by recrystallization from acetic anhydride affording a sample of an orange colored solid, m.p. 306–307°. The purified sample exhibited a strong green fluorescence in both acetic anhydride and chloroform solutions. The infrared spectrum of IV in Nujol mull absorbed strongly at 1770 cm.$^{-1}$ and 1830 cm.$^{-1}$. The ultraviolet spectrum in 95% ethanol solution showed λ_{max} 264 mμ (log ϵ 4.55), λ_{max} 298 mμ (log ϵ 4.70).

Anal. Calcd. for $C_{20}H_8O_3S_2$: C, 66.65; H, 2.24; S, 17.80. Found: C, 66.79; H, 2.37; S, 17.90.

4,5-Diethylphenanthrene-9,10-dicarboxylic Acid Anhydride (V).—To a solution of 400 ml. of 10% sodium hydroxide solution was added 2.85 g. of unpurified IV from the dehydrogenation of III. The mixture was boiled until a clear solution was obtained. The solution was allowed to cool and Raney nickel alloy (25 g.) was added in 0.5-g. portions over a period of 1 hr. The solution was stirred and maintained at a temperature just below the boiling point for 1 hr. It was then filtered while hot. Acidification of the cooled filtrate with dilute hydrochloric acid followed by extraction with chloroform afforded a dark red oil on removal of the chloroform. Crystallization of the oil from glacial acetic acid gave yellow crystals, 0.80 g. (34%), m.p. 165–172°. An analytical sample was prepared by chromatography of a solution of the yellow anhydride in petroleum ether solution (b.p. 65–67°) over alumina followed by recrystallization from glacial acetic acid and melted at 170–171°. The infrared spectrum of a chloroform-solution of V showed bands at 1770 cm.$^{-1}$ and 1845 cm.$^{-1}$. The ultraviolet spectrum in 95% ethanol showed λ_{max} 263 mμ (log ϵ 4.52), λ_{max} 320 mμ (log ϵ 4.02).

Anal. Calcd. for $C_{20}H_{16}O_3$: C, 78.93; H, 5.30. Found: C, 78.82; H, 5.35.

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[8] P. Cagniant and P. Cagniant, *Bull. soc. chim. France*, **62** (1953).

Structure of *N*-Acyl-*s*-triazoles[1]

K. T. Potts and T. H. Crawford

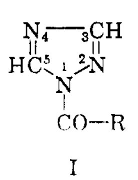
Department of Chemistry, College of Arts and Sciences, University of Louisville, Louisville, Ky.

Received February 12, 1962

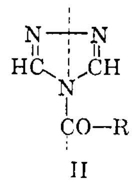
The recent application of *N,N'*-carbonyldi-*s*-triazole to peptide synthesis[2] makes our results that establish the structure of *N*-acyl-*s*-triazoles of considerable theoretical interest.

Acylation of *s*-triazole with an acid anhydride or acyl chloride[3] readily gives the corresponding acyl derivative which is extremely sensitive to moisture, being hydrolyzed to *s*-triazole and the acid (or in the case of carbonyldi-*s*-triazole, carbon dioxide). The lability of this acyl group can be attributed to the aromatic nature of the *s*-triazole nucleus[4] and has precluded the usual chemical methods for determining the position of substitution of the acyl group. Thus, lithium aluminum hydride reduction of *N*-acetyltriazole gave *s*-triazole and acetaldehyde.[5] As alkylation occurs predominantly at position 1 of the nucleus,[3a,6] it is to be expected that acylation would occur at the same position.

Experimental verification of substitution occurring at position 1 has now been found from the NMR spectra of the acyl derivatives and suitable model substances. A 1-substituted *s*-triazole (I) has no plane of symmetry, whereas a 4-substituted *s*-triazole (II) has one as shown. Hence in I the deshielding effect of the carbonyl function[7] of the acyl group would influence only one proton (that at C-5), causing it to shift to lower field, whereas in II it would have an equal effect on both the protons at C-3 and C-5.



I



II

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[1] Part V in this series. Support of this investigation by PHS research grant CY-5973 from the National Cancer Institute, Public Health Service, is gratefully acknowledged.

[2] H. C. Beyerman and W. Maassen van Den Brink, *Rec. trav. chim.*, **80**, 1372 (1961); H. A. Staab, *Annalen*, **609**, 75 (1957).

[3] (a) M. R. Atkinson and J. B. Polya, *J. Chem. Soc.*, 141 (1954); (b) H. A. Staab, *Chem. Ber.*, **89**, 1927 (1956).

[4] K. T. Potts, *Chem. Rev.*, **61**, 87 (1961).

[5] K. T. Potts, unpublished results.

[6] C. Ainsworth and R. G. Jones, *J. Am. Chem. Soc.*, **77**, 621 (1955).

[7] L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press, N. Y., 1959, pp. 121–125.

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]

WILLIAM E. PARHAM, HENRY G. BRAXTON, JR.,[2] AND
DONALD R. THEISSEN[3]

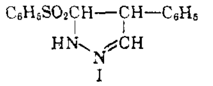
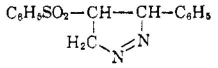
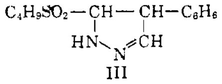
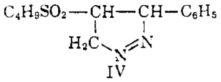
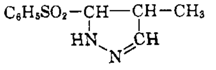
*School of Chemistry of the University of Minnesota,
Minneapolis 14, Minnesota*

Received December 11, 1961

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).