

## NITRONES AND OXAZIRANS

### V.\* PERACID OXIDATION OF 1,3,5-TRIPHENYL-2-PYRAZOLINE

By J. B. BAPAT,† D. ST.C. BLACK,‡§ and R. W. CLARK†

[Manuscript received January 7, 1972]

Pyrazolines have been oxidized to pyrazoles by a variety of oxidizing agents such as bromine,<sup>1</sup> chromic oxide,<sup>1</sup> mercuric oxide,<sup>1</sup> potassium permanganate,<sup>2</sup> lead dioxide,<sup>1,3</sup> lead tetraacetate,<sup>4</sup> potassium ferricyanide,<sup>5</sup> and manganese dioxide.<sup>6</sup> The use of bromine sometimes results in bromination as well as oxidation and the oxidation of side-chains is often a feature of permanganate reactions.

We have found that 1,3,5-triphenyl-2-pyrazoline (1)<sup>7</sup> is smoothly oxidized by peracetic or perbenzoic acid to 1,3,5-triphenylpyrazole (3):<sup>8</sup> the conversion is experimentally easier using perbenzoic acid and the yield of pyrazole is essentially quantitative.

Imines are readily oxidized<sup>9</sup> to oxazirans by peracids and therefore the oxaziran (2) is postulated as an intermediate in the conversion of the pyrazoline (1) into the pyrazole (3). Such an oxaziran (2) would be destabilized by the pair of non-bonded electrons on the nitrogen atom adjacent to the oxaziran ring and undergo rapid

\* Part IV, *Aust. J. Chem.*, 1968, **21**, 2521.

† Department of Chemistry, Caulfield Institute of Technology, East Caulfield, Vic. 3145.

‡ Department of Chemistry, Monash University, Clayton, Vic. 3168.

§ Author to whom correspondence should be addressed.

<sup>1</sup> Auwers, K. von, and Heimke, P., *Liebigs Ann.*, 1927, **458**, 186.

<sup>2</sup> Smith, L. I., and Howard, K. L., *J. Am. chem. Soc.*, 1943, **65**, 159; Häring, M., and Wagner-Jauregg, T., *Helv. chim. Acta*, 1957, **40**, 852.

<sup>3</sup> Birkinshaw, J. H., Oxford, A. E., and Raistrick, H., *Biochem. J.*, 1936, **30**, 394.

<sup>4</sup> Duffin, G. F., and Kendall, J. D., *J. chem. Soc.*, 1954, 408; Gladstone, W. A. F., and Norman, R. O. C., *J. chem. Soc. (C)*, 1966, 1536.

<sup>5</sup> Buchner, E., and Dessauer, H., *Ber. dt. chem. Ges.*, 1893, **26**, 258.

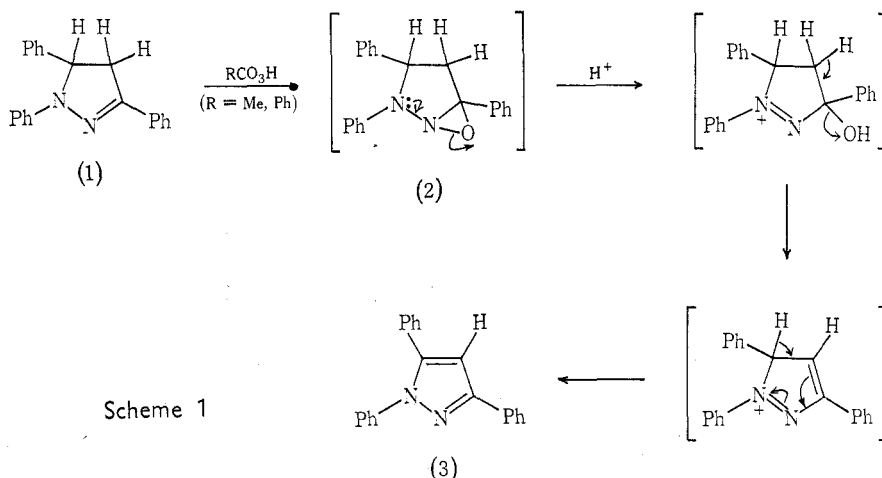
<sup>6</sup> Bhatnagar, I., and George, M. V., *Tetrahedron*, 1968, **24**, 1293.

<sup>7</sup> Rupe, H., and Schneider, F., *Ber. dt. chem. Ges.*, 1895, **28**, 957; Wiley, R. H., Jarboe, C. H., Hayes, F. N., Hansbury, E., Nielsen, J. T., Callahan, P. X., and Sellars, M. C., *J. org. Chem.*, 1958, **23**, 732; Raiford, L. C., and Davis, H. L., *J. Am. chem. Soc.*, 1928, **50**, 156.

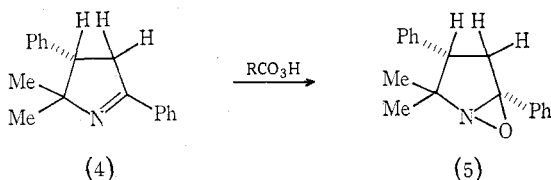
<sup>8</sup> Knorr, L., and Laubmann, H., *Ber. dt. chem. Ges.*, 1888, **21**, 1205; Croxall, W. J., and Van Hook, J. O., *J. Am. chem. Soc.*, 1949, **71**, 2422.

<sup>9</sup> Emmons, W. D., in "Heterocyclic Compounds with Three- and Four-membered Rings." (Ed. A. Weissberger.) Part I, p. 624. (Interscience: New York 1964); Schmitz, E., *Adv. heterocyc. Chem.*, 1963, **2**, 85.

acid-catalysed ring cleavage. Thus, the mechanistic pathway shown in Scheme 1 is proposed. The instability of the oxaziran (2) is in marked contrast to the stability of



the related oxaziran (5), which can be isolated<sup>10</sup> from the peracid oxidation of the pyrroline (4).



### Experimental

Infrared absorption spectra of Nujol mulls were measured using a Perkin-Elmer 257 spectrometer. N.m.r. spectra were measured in deuteriochloroform at 60 MHz using a Varian A56/60 spectrometer. Chemical shifts are reported in p.p.m. relative to tetramethylsilane ( $\delta$  0.00) as an internal standard. Each n.m.r. signal is described in terms of chemical shift, multiplicity, coupling constant, and assignment, in that order, with the use of the following abbreviations: s, singlet; d, doublet; q, quartet; m, multiplet. Mass spectra were measured using a Hitachi Perkin-Elmer RMU6E spectrometer. Melting points are uncorrected.

#### Benzalacetophenone Phenylhydrazone

This compound was prepared<sup>7</sup> from benzalacetophenone and phenylhydrazine with m.p. 119° (lit.<sup>7</sup> 117–120°).  $\nu_{\text{max}}$  3305, 1600, 1545, 1305, 1250, 1135, 1100, 1070, 1025, 965, 885, 850, 780, 760, 715, and 695  $\text{cm}^{-1}$ . N.m.r. spectrum: 6.20, d,  $J$  16 Hz (1H,  $\text{PhCH}=\text{CH}$ ); 6.70–7.73, m, (16H, phenyl protons and  $\text{PhCH}=\text{CH}$ ). Mass spectrum: 298 (84%, M), 221 (36), 206 (27), 194 (20), 193 (18), 191 (12), 189 (11), 178 (15), 165 (14), 128 (15), 115 (40), 106 (20), 105 (39), 104 (22), 103 (37), 102 (16), 92 (18), 91 (61), 77 (100), 65 (35), 51 (30), and 39 (15).

<sup>10</sup> Bapat, J. B., and Black, D. St.C., *Aust. J. Chem.*, 1968, **21**, 2507.

*1,3,5-Triphenyl-2-pyrazoline (1)*

This compound was prepared<sup>7</sup> from the above phenylhydrazone, m.p. 135–136° (lit.<sup>7</sup> 135–136°). N.m.r. spectrum: 2.81–3.09, m (2H, CH<sub>2</sub>); 5.18, q (1H, PhCHN); 6.50–7.80, m (15H, phenyl protons). Mass spectrum: 298 (100%, M), 221 (33), 195 (13), 115 (10), 104 (12), 91 (58), 77 (25), 64 (12), and 51 (10).

*Oxidation of 1,3,5-Triphenyl-2-pyrazoline with Perbenzoic Acid*

A solution of the pyrazoline (1.0 g, 0.003 mol) in chloroform (15 ml) was treated with a solution of perbenzoic acid (0.5 g, 0.003 mol) in chloroform (10 ml) at 0° during 30 min. The stirred solution was then allowed to stand at room temperature for 12 hr. The resulting chloroform solution was washed with water (2 × 15 ml), 2M ammonium hydroxide (2 × 15 ml), and 2M sulphuric acid (2 × 15 ml), then dried and concentrated to yield 1,3,5-triphenylpyrazole, which was recrystallized from ethanol (0.9 g, 90%), m.p. 142° (lit.<sup>8</sup> 137–139°). N.m.r. spectrum: 6.81, s (1H, =CH–); 6.93–8.03, m (15H, phenyl protons). Mass spectrum: 296 (100%, M), 192 (25), 191 (12), 190 (15), 189 (15), 165 (25), 91 (18), 89 (20), 77 (56), 64 (15), 63 (10), and 51 (28).

The pyrazole was identical in all respects with an authentic sample prepared<sup>8</sup> from dibenzoylmethane and phenylhydrazine.

Using a similar procedure, the pyrazoline (1.0 g) was converted by oxidation with peracetic acid into the pyrazole (0.4 g, 40%).