230. *Fission of Di-(3-methyl-1 : 5-diphenyl-4-pyrazolyl) Disulphide by Chlorine.*

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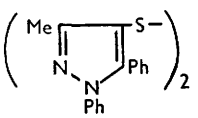
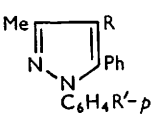
Treatment of di-(3-methyl-1 : 5-diphenyl-4-pyrazolyl) disulphide (I) with chlorine in anhydrous conditions results in desulphurisation, accompanied by nuclear chlorination. Chlorination in aqueous medium gives the thiolsulphonate (III).

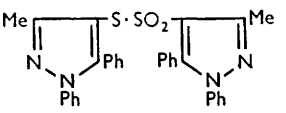
The following investigation was undertaken, because preliminary experiments on the chlorination of di-(3-methyl-1 : 5-diphenyl-4-pyrazolyl) disulphide [1] (I) indicated some unusual features. The primary product from the action of one mol. of chlorine in carbon tetrachloride on the disulphide (I) was a viscous oil which reacted vigorously with water and with bases such as ammonia and aniline. Since the original disulphide was recovered from all these reactions, the oil could not be identified as the sulphenyl chloride [2] (II; R = SCl, R′ = H).



(I)



(II)



(III)

However, addition of further chlorine to the primary product resulted in desulphurisation, and the formation of 4-chloro-3-methyl-1 : 5-diphenylpyrazole (II; R = Cl, R′ = H), and 4-chloro-1-*p*-chlorophenyl-3-methyl-5-phenylpyrazole (II; R = R′ = Cl). This type of bilateral fission between sulphur atoms and aromatic carbon in a disulphide appears to be new, although nuclear chlorination accompanying the fission of a C–S bond is known to occur with certain sulphides.[3,4,5]

By using a standard solution of chlorine, the extent of nuclear chlorination could be controlled to give either of the two chloropyrazoles as the main product. The monochloro-compound was also synthesised from 2-chloro-1-phenylbutane-1 : 3-dione [6] and phenylhydrazine, as well as by treatment of 3-methyl-1 : 5-diphenylpyrazole (II; R = R′ = H) with the calculated amount of chlorine solution. Attempts to prepare the

[1] Barry, Finar, and Simmonds, *J.*, 1956, 4974.
[2] Kharasch, Potempa, and Wehrmeister, *Chem. Rev.*, 1946, **39**, 278 *et seq.*
[3] Douglass, Brower, and Martin, *J. Amer. Chem. Soc.*, 1952, **74**, 5770.
[4] Baker, Dodson, and Riegel, *ibid.*, 1946, **68**, 2638.
[5] Kwart and Miller, *ibid.*, 1956, **78**, 5008.
[6] Morgan, Drew, and Barker, *J.*, 1922, 2456.

dichloro-compound (II; R = R′ = Cl) by cold chlorination of 3-methyl- or 4-chloro-3-methyl-1 : 5-diphenylpyrazole failed, perhaps owing to the absence of an effective catalyst for nuclear chlorination such as may be formed during the decomposition of the disulphide (I). Chlorination of certain disulphides gives rise to unstable compounds which might act in this way (*e.g.*, phenylsulphur trichloride from diphenyl disulphide [4]). The required dichloro-compound (II; R = R′ = Cl) was readily synthesised, however, by condensing benzoylacetone with *p*-chlorophenylhydrazine to give 1-*p*-chlorophenyl-3-methyl-1 : 5-diphenylpyrazole (II; R = H, R′ = Cl), and then chlorinating the pyrazole nucleus. The fact that the pyrazole from 2-chloro-1-phenylbutane-1 : 3-dione and *p*-nitrophenylhydrazine gives the same dichloro-compound (II; R = R′ = Cl) when the nitro-group is replaced by chlorine shows it to be 4-chloro-3-methyl-1-*p*-nitrophenyl-5-phenylpyrazole (II; R = Cl, R′ = NO_2) so that the alternative structure given in the literature may now be disregarded.[6,7] It is clear from the structural relation between the pyrazoles from 2-chloro-1-phenylbutane-1 : 3-dione and 3-methyl-1 : 5-diphenylpyrazole that the chlorine substituent, in common with others in the methylene group of benzoylacetone, does not alter the normal mode of ring closure with phenyl- and *p*-nitrophenyl-hydrazine.[8]

Treatment of the disulphide (I) with chlorine in aqueous acetic acid did not give the expected 4-chlorosulphonyl-3-methyl-1 : 5-diphenylpyrazole [9] (II; R = SO_2Cl, R′ = H) but, instead, 3-methyl-1 : 5-diphenyl-4-pyrazolyl 3-methyl-1 : 5-diphenylpyrazole-4-thiolsulphonate (III). This thiolsulphonate was also obtained by controlled oxidation of the disulphide (I) with hydrogen peroxide in acetic acid.[10] Reduction of the thiolsulphonate with zinc in acid solution gave the corresponding thiol (II; R = SH, R′ = H), characterised by conversion into the disulphide (I) with ferric chloride. The thiolsulphonate structure of (III) was confirmed by the presence of characteristic infrared bands [11] at 1333 and 1140 cm.$^{-1}$.

Experimental

4-Chloro-3-methyl-1 : 5-diphenylpyrazole.—(a) *From di-(3-methyl-1 : 5-diphenyl-4-pyrazolyl) disulphide.* The disulphide (5·3 g., 0·01 mol.), suspended in dry carbon tetrachloride (60 c.c.) containing chlorine (2·13 g., 0·03 mol.), gave, after storage for 40 min. at 20° and evaporation of the solvent under reduced pressure, a yellow oil (5·5 g.). The solvent, collected at −80° had the odour and reactions characteristic of sulphur dichloride. The residual oil gave crystals of *4-chloro-3-methyl-1 : 5-diphenylpyrazole* (3 g., 56%), m. p. 50° (from methanol), rising to 67—69° on storage, the two forms giving identical infrared spectra in CCl_4 (Found: C, 71·8; H, 4·5; N, 10·7; Cl, 12·9. $C_{16}H_{13}N_2Cl$ requires C, 71·5; H, 4·8; N, 10·4; Cl, 13·2%). Some of the disulphide (0·65 g.), m. p. and mixed m. p. 202°, was recovered.

(b) *From 3-methyl-1 : 5-diphenylpyrazole.* 3-Methyl-1 : 5-diphenylpyrazole (8 g., 0·034 mol.), treated with chlorine in dry carbon tetrachloride (2·4 g., 0·034 mol.) at 20°, gave a precipitate of the hydrochloride of the monochloro-derivative. On removal of the solvent at 100° under reduced pressure, the original precipitate redissolved and a yellowish oil remained. After several days in methanol solution (75 c.c.), this residue gave colourless crystals (8 g., 87%), m. p. 67—68° alone or mixed with 4-chloro-3-methyl-1 : 5-diphenylpyrazole prepared as in (a).

(c) *From 2-chloro-1-phenylbutane-1 : 3-dione.* The diketone (1·96 g., 0·01 mol.) was slowly mixed with phenylhydrazine (1·1 g., 0·01 mol.) in ethanol (cooling). After 3 hr. at 100° and cooling to −80°, crystals of 4-chloro-3-methyl-1 : 5-diphenylpyrazole (1 g., 37%) separated from the dark oily mixture. These had m. p. 50° (from methanol), rising to 67—69°, alone or mixed with the previous preparations.

4-Chloro-1-p-chlorophenyl-3-methyl-5-phenylpyrazole.—(a) *From the disulphide.* A solution of the disulphide (5·3 g., 0·01 mol.) in dry carbon tetrachloride (100 c.c.) containing chlorine

[7] Macbeth, *J.*, 1923, 1128.
[8] Elderfield, "Heterocyclic Compounds," J. Wiley, New York, Vol. V, p. 49.
[9] Fromm, *Z. angew. Chem.*, 1911, **24**, 1125.
[10] Hinsberg, *Ber.*, 1908, **41**, 2836; 1909, **42**, 1278.
[11] Cf. Cymerman and Willis, *J.*, 1951, 1332.

(3·55 g., 0·05 mol.), gave, after 24 hr. at room temperature, colourless crystals (0·75 g.) of 4-chloro-3-methyl-1 : 5-diphenylpyrazole, m. p. 67° (from methanol) alone or mixed with previous specimens, and *4-chloro*-1-p-*chlorophenyl*-3-*methyl*-5-*phenylpyrazole* (2·2 g.), m. p. 112° (from methanol) (Found: C, 63·7; H, 3·8; N, 9·7; Cl, 22·9. $C_{16}H_{12}N_2Cl_2$ requires C, 63·4; H, 3·96; N, 9·2; Cl, 23·3%).

(b) *From benzoylacetone and* p-*chlorophenylhydrazine.* Equimolecular proportions of benzoylacetone and *p*-chlorophenylhydrazine (prepared by Hunsberger's method [12] for substituted arylhydrazines), when boiled in ethanol for 2 hr., gave 1-p-*chlorophenyl*-3-*methyl*-5-*phenylpyrazole*, m. p. 105° (from ethanol) (Found: Cl, 13·2. $C_{16}H_{13}N_2Cl$ requires Cl, 13·2%). Chlorination of this compound in carbon tetrachloride gave 4-chloro-1-*p*-chlorophenyl-3-methyl-5-phenylpyrazole, m. p. 111° (from methanol) undepressed on admixture with a specimen prepared from the disulphide.

(c) *From 4-chloro-3-methyl-1-p-nitrophenyl-5-phenylpyrazole.* The above compound (1 g.) was heated in ethanol (25 c.c.) with palladised charcoal (0·15 g.) and hydrazine hydrate (2 c.c.). 1-p-*Aminophenyl*-3-*methyl*-5-*phenylpyrazole* crystallised on cooling and had m. p. 181—182° (from ethanol) (Found: C, 67·7; H, 4·9; Cl, 12·6; N, 15·0. $C_{16}H_{14}N_3Cl$ requires C, 67·7; H, 4·9; Cl, 12·5; N, 14·8%). The amine (3 g.) was diazotised at 40°, and the solution run immediately into boiling concentrated hydrochloric acid (25 c.c.) containing cuprous chloride (3 g.). After 0·5 hr. at 100°, a brown oil remained; this product, crystallised from methanol, had m. p. 111—112° alone or mixed with previous specimens of 4-chloro-1-*p*-chlorophenyl-3-methyl-5-phenylpyrazole.

3-*Methyl*-1 : 5-*diphenyl*-4-*pyrazolyl* 3-*Methyl*-1 : 5-*diphenylpyrazole*-4-*thiolsulphonate.*—(*a*) Di-(3-methyl-1 : 5-diphenyl-4-pyrazolyl) disulphide (8 g.) in aqueous acetic acid (containing 20% water by vol.) was treated with a rapid current of chlorine at 0° for 0·5 hr. After a further 0·5 hr. with occasional shaking, the solution was clear. The white solid (5 g., 59%) obtained by addition of ice-water, melted, after several recrystallisations from acetic acid, at 212° (Found: N, 9·65; S, 11·2. $C_{32}H_{26}O_2N_4S_2$ requires N, 9·9; S, 11·4%).

(*b*) The disulphide (2·65 g., 0·005 mol.) in acetic acid (20 c.c.) containing 30% hydrogen peroxide (1 c.c.) was warmed at 100° for 0·5 hr., then left at room temperature with occasional shaking, for 5 days. The white solid (2 g., 70%) was filtered off and, after recrystallisation from acetic acid, melted at 211—212° alone or mixed with the product from method (*a*).

Reduction of the Thiolsulphonate (III).—The thiolsulphonate (3 g.) in hot glacial acetic acid (30 c.c.) containing zinc dust (20 g.) was treated with concentrated hydrochloric acid (50 c.c.), in small amounts during 1 hr. After neutralisation with ammonia (*d* 0·880), the precipitated solid was dissolved in hot glacial acetic acid (50 c.c.), and oxidation to the disulphide completed by addition of anhydrous ferric chloride (1 g.) and further heating for 5 min. at 100°. The crystalline precipitate (2·1 g.) from the cooled solution (2·1 g.) melted at 202—204° alone or mixed with di-(3-methyl-1 : 5-diphenyl-4-pyrazolyl) disulphide.

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[12] Hunsberger, Shaw, Fugger, Ketcham, and Lednicer, *J. Org. Chem.*, 1956, **21**, 394.