

Ring Cleavage of Some Pyrazole-4-sulphonyl Chlorides by Chlorine

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3-Methyl-1,5-diphenylpyrazole-4- and 3-methyl-1-(*p*-nitrophenyl)-5-phenylpyrazole-4-sulphonyl chlorides give polychlorophenylazobutanone derivatives upon treatment with chlorine in aqueous acetic acid. This cleavage of the pyrazole ring is preceded by elimination of the sulphonyl group as sulphate ion.

3-METHYL-1,5-DIPHENYLPYRAZOLE-4-SULPHONYL CHLORIDE¹ (1a), prepared by controlled chlorination of the corresponding disulphide (2a) in aqueous acetic acid, is decomposed by further chlorination in the same solvent to give compounds which contain no sulphur. The

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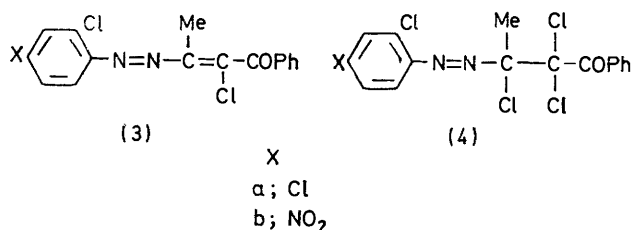
sulphur is eliminated as sulphur dioxide in the first stage of decomposition and immediately oxidized to sulphate ion, and recovered quantitatively as barium sulphate. Two new and highly coloured azo-compounds were isolated as the decomposition products: 2-chloro-3-(2,4-dichlorophenylazo)-1-phenylbut-2-en-1-one (3a) (red

¹ R. J. Alabaster and W. J. Barry, *J. Chem. Soc. (C)*, 1970, 78.

solid) and 2,2,3-trichloro-3-(2,4-dichlorophenylazo)-1-phenylbutan-1-one (4a) (yellow solid). Their formation involves a rupture of the pyrazole ring which is unusual, although a few instances have been reported.² Compounds (3a) and (4a) appear to be new, although



R ¹	R ²
a; Ph	Ph
b; 4-NO ₂ -C ₆ H ₄	Ph
c; Ph	Me
d; Me	Me



X
a; Cl
b; NO ₂



R	X	R ¹	R ²
a; Ph	Cl	a; Me	Ph
b; 2,4-Cl ₂ C ₆ H ₃	Cl	b; Me	Me
c; 2,4-Cl ₂ C ₆ H ₃	H		

Bülow,³ in 1918, isolated an orange substance formed during the chlorination of 3-methyl-1-(2,4-dichlorophenyl)-5-phenylpyrazole, in ethanol, which could have been the butenone (3a). Bülow did not identify this compound, nor study the reaction further. The butenone (3a) was only formed in a significant amount during the preparation of the sulphonyl chloride (1a) when the pale yellow reaction mixture was quenched in ice. The precipitated yellow, semisolid sulphonyl chloride (1a) rapidly developed a deep red colour as some butenone (3a) was formed. A possible explanation involving a pyrazoline intermediate is given later. Prolonged treatment of the sulphonyl chloride (1a) with chlorine afforded the yellow butanone (4a).

T.l.c. showed that the formation of the azo-compounds (3a) and (4a) was very slow under anhydrous conditions, but the addition of water (10–40 mol. equiv.) to the solution in acetic acid caused a rapid build-up of the

butanone (4a). The butenone (3a) was never present in the reaction mixture in more than trace amounts, which suggested that it was being continuously converted into the butanone (4a) by addition of chlorine to the double bond. The butenone (3a) was, in fact, easily converted into the butanone (4a) by chlorination in acetic acid.

Analogous results were obtained with bis-3-methyl-1-(*p*-nitrophenyl)-5-phenylpyrazol-4-yl disulphide (2b) and 3-methyl-1-(*p*-nitrophenyl)-5-phenylpyrazole-4-sulphonyl chloride (1b), giving the phenylazo-ketones (3b) and (4b). The position of the chlorine atom on the phenyl group in these compounds was deduced from n.m.r. data, and the formation of the tetrachlorobutanone (4b) was accompanied by quantitative formation of sulphate ion. Treatment of 3,5-dimethyl-1-phenylpyrazole-4- and 1,3,5-trimethylpyrazole-4-sulphonyl chloride (1c and d) [prepared in poor yield from the corresponding disulphides (2c and d) and characterised as their anilides (6a and b)] with chlorine caused decomposition to give inseparable mixtures. Indications were obtained that some fission of the pyrazol ring occurred (formation of carbonyl-containing compounds and sulphate ion). The cleavage was slower than that of the sulphonyl chlorides (1a and b): only 60–70% of the sulphur was eliminated as sulphate ion under similar conditions. A compound was also isolated from the chlorination products of the sulphonyl chloride (1d) with the chlorosulphonyl group still intact. Physical data were in accord with 5-chloromethyl-1,3-dimethyl- or 3-chloromethyl-1,5-dimethyl-pyrazole-4-sulphonyl chloride.

The pyrazole-4-sulphonyl chlorides (1a and b) would be expected to display much lower basicity than the sulphonyl chlorides (1c and d), and the higher basicity of the latter might confer a measure of protection against the cleavage reaction. This, however, needs further investigation. The instability of many heterocyclic sulphonyl chlorides in aqueous acetic acid in the presence of chlorine has been reported,^{4–6} and their preparation by chlorination gives good yields in some cases⁷ but in others no sulphonyl chloride is isolated.⁶ This decomposition by chlorine often involves replacement of the chlorosulphonyl group by chlorine and elimination of the sulphur as sulphate ion. Kwart and Body⁶ have shown that sulphonyl chlorides of the type $-N=C-[C=C]_n-SO_2Cl$ decompose in this manner, probably by an S_Ni mechanism. Pyrazole-4-sulphonyl chlorides do not possess this structural feature but a similar decomposition to 4-chloropyrazoles still appears possible. If this were so, the action of chlorine on the resulting chloropyrazoles could then give the butenone and butanone derivatives.

To investigate this idea, 4-chloro-3-methyl-1,5-diphenylpyrazole (5a) was treated with chlorine in aqueous acetic acid; an immediate red colouration was produced

⁴ R. H. Baker, R. M. Dodson, and B. Reigel, *J. Amer. Chem. Soc.*, 1946, **68**, 2636.

⁵ H. Kwart and L. Miller, *J. Amer. Chem. Soc.*, 1958, **80**, 884.

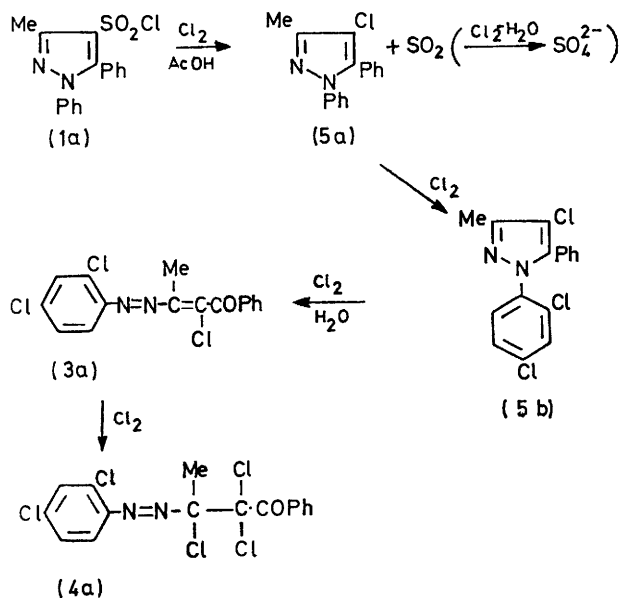
⁶ H. Kwart and R. W. Body, *J. Org. Chem.*, 1965, **30**, 1188.

⁷ R. O. Roblin and J. W. Clapp, *J. Amer. Chem. Soc.*, 1950, **72**, 4890.

² L. C. Behr, R. Fusco, and C. H. Jarboe, 'Heterocyclic Compounds: Pyrazoles, Pyrazolines, Pyrazolidines, Indazoles, and Condensed Rings,' Wiley, New York, 1967, ch. 5.

³ K. Bülow, *Ber.*, 1918, **51**, 413.

[t.l.c. confirmed the presence of the butenone (3a)] and a high yield of the butanone (4a) was obtained on further treatment with chlorine. Chlorination of the phenyl group is probably complete before ring opening occurs, as no unchlorinated phenylazo-compounds were ever isolated from the reactions of the sulphonyl chlorides (1a and b) and no monochlorophenylazo-compound was isolated from the reaction of the sulphonyl chloride (1a). Carefully controlled treatment of 4-chloro-1-(2,4-dichlorophenyl)-3-methyl-5-phenylpyrazole (5b) with chlorine afforded the butenone (3a) in 51% yield, and treatment of the liquors with chlorine gave the butanone



SCHEME 1

(4a) in 30% yield. A suggested route by which the sulphonyl chloride (1a) is converted into the butanone (4a) is shown in Scheme 1. The work of Kwart and Body⁶ indicates that chlorination in hydrochloric acid as solvent might alter the course of the reaction owing to protonation of a nitrogen atom.

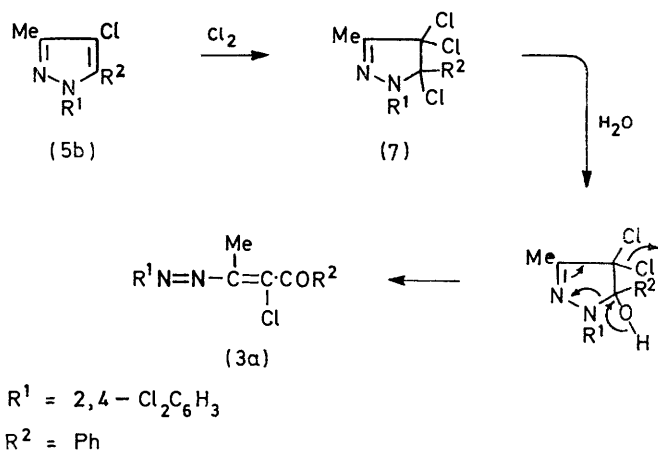
Chlorination of pyrrole derivatives^{8,9} and thiophen¹⁰ gives polychloro-derivatives that can be hydrolysed, respectively, to maleic imides and maleic thioanhydrides. It is possible that a similar chlorination of the trichloropyrazole (5b) could have given 4,4,5-trichloro-1-(2,4-dichlorophenyl)-3-methyl-5-phenylpyrazoline (7). Hydrolysis of this compound *in situ* could have resulted in opening of the pyrazole ring to form the butenone (3a) (Scheme 2). Attempts to prepare the pyrazoline (7) under anhydrous conditions, by chlorination of the 4-chloropyrazole (5b), resulted in no reaction. However, if a sample of the chlorinated reaction solution was allowed to come into contact with water, for instance by 'spotting' on a t.l.c. plate, an immediate red colouration

⁸ G. Muzzari, *Gazzetta*, 1920, **32**, 28.

⁹ H. El Khadem, L. A. Kemler, Z. M. El-Shafei, M. M. A. Abdel Rahman, and S. El Sadany, *J. Heterocyclic Chem.*, 1972, **9**, 1413.

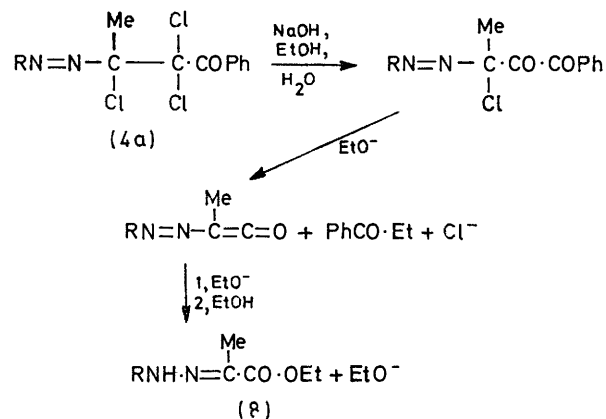
¹⁰ H. D. Scharf and A. Wittig, *Chem. Ber.*, 1973, **106** (5), 1707.

was produced and this colour was shown to be due to the butenone (3a) by developing the plate. This could indicate that the pyrazoline (7), if formed, is only stable



SCHEME 2

in the presence of an excess of chlorine, and removal of this excess allows it to revert to the 4-chloropyrazole (5b). However, the presence of water in the reaction mixture would hydrolyse the pyrazoline (7) to the butenone (3a). The formation of the butanone (3a) during the isolation of the sulphonyl chloride (1a) could therefore be explained by the presence of some of the



SCHEME 3

pyrazoline (7) in the reaction mixture which would undergo hydrolysis to the butenone (3a) on contact with water. In a separate experiment, when the sulphonyl chloride (1a) in aqueous acetic acid was treated with chlorine and then the excess of chlorine was removed and the mixture quenched in ice, no red colour or butenone was formed. If the excess of chlorine was not removed, the same treatment resulted in rapid formation of a red colour, and the butenone (3a) was present in the product.

The reactivity of the butanones (4a and b) has not been fully investigated, but an attempt to dehalogenate the butanone (4a) with zinc dust in ethanol produced 1-(2,4-dichlorophenyl)-3-methyl-5-phenylpyrazole (5c), whereas

with zinc dust in acetic acid the products were the dichlorophenylpyrazole (5c) and the 4-chloropyrazole (5b). Hydrolysis of the butanone (4a) with sodium hydroxide in ethanol gave the 2,4-dichlorophenylhydrazone (8) of ethyl pyruvate, ethyl benzoate, and benzoic acid. A suggested mechanism is shown in Scheme 3. The benzoic acid could have been formed by some hydrolysis of ethyl benzoate or by attack of hydroxide on the α -diketone intermediate. Two geometric isomers of the hydrazone (8) were obtained (*cf.* refs. 11 and 12).

EXPERIMENTAL

Spectroscopic data for compounds indicated with an asterisk are available as Supplementary Publication No. SUP 21627 (13 pp., 1 microfiche). † Analytical data are in the Table.

Compd.	Formula	Analytical data					Analytical data				
		Found (%)					Calc. (%)				
		C	H	Cl	N	S	C	H	Cl	N	S
(1b)	C ₁₆ H ₁₂ ClN ₃ O ₄ S	50.8	3.2	9.2	11.25	8.45	50.9	3.2	9.4	11.2	8.5
(2d)	C ₁₂ H ₁₈ N ₄ S ₂	51.15	6.2		19.5	22.6	51.0	6.4		19.8	22.7
(3a)	C ₁₆ H ₁₁ Cl ₂ N ₃ O	54.8	3.2	29.9	8.0		54.4	3.1	30.1	7.9	
(4a)	C ₁₆ H ₁₁ Cl ₂ N ₃ O	44.45	2.7	41.7	6.75		45.3	2.6	41.8	6.6	
(3b)	C ₁₆ H ₁₁ Cl ₂ N ₃ O ₃	52.65	3.1	19.3	11.8		52.8	3.0	19.5	11.5	
(4b)	C ₁₆ H ₁₁ Cl ₂ N ₃ O ₃	44.2	2.6	32.55	9.6		44.2	2.5	32.6	9.7	
(5b)	C ₁₆ H ₁₁ Cl ₂ N ₃ O ₂	56.15	3.3	31.3	8.15		56.9	3.3	31.5	8.3	
(5c)	C ₁₆ H ₁₂ Cl ₂ N ₃ O ₂	63.45	4.1	23.5	9.2		63.4	4.0	23.4	9.2	
(6a)	C ₁₇ H ₁₇ N ₂ O ₂ S	62.5	5.2		12.8	9.8	62.2	5.2		12.8	9.8
(6b)	C ₁₂ H ₁₅ N ₃ O ₂ S	54.6	5.8		15.95	12.7	54.3	5.7		15.8	12.7
(8) α -form	C ₁₁ H ₁₂ Cl ₂ N ₂ O ₂	48.2	4.4	25.1	10.2		48.0	4.4	25.7	10.2	
(8) β -form	C ₁₁ H ₁₂ Cl ₂ N ₂ O ₂	47.8	4.2	25.4	10.3		48.0	4.4	25.7	10.2	
(A) †	C ₆ H ₈ Cl ₂ N ₂ O ₂ S	29.7	3.25	29.0	11.2	13.2	29.6	3.3	29.2	11.5	13.2

† 3-(or 5)-Chloromethyl-1,5-(or 3)-dimethylpyrazole-4-sulphonyl chloride.

2-Chloro-3-(2,4-dichlorophenylazo)-1-phenylbut-2-en-1-one (3a).—(a) *From the sulphonyl chloride (1a).*¹ In the preparation of the sulphonyl chloride (1a),¹ when the pale yellow reaction mixture was poured onto ice, a crude yellow product was deposited that rapidly developed a red colour. A bright red solid, m.p. 113.5—115° (0.5 g) was obtained from the crystallisation liquors of the sulphonyl chloride (1a), and was identified as the *phenylazo-butenone* (3a); 41% of the original sulphur content of the disulphide (2a) was present as sulphate ion in the aqueous liquor.

Effect of removing the excess of chlorine from the crude mixture. A solution of the sulphonyl chloride (1a) (1 g) in acetic acid (20 ml) and water (2 ml) was treated with a slow stream of chlorine for 10 min, and the yellow solution was divided. Half was poured onto ice-water; a red colour rapidly developed and t.l.c. demonstrated the presence of the butenone (3a). Chlorine was removed from the second half under vacuum; no red colour developed when this solution was poured onto ice, and t.l.c. showed that virtually no butenone (3a) was present. In each case the major component present was the sulphonyl chloride (1a).

(b) *By chlorination of 4-chloro-1-(2,4-dichlorophenyl)-3-methyl-5-phenylpyrazole (5b).* 1-(2,4-Dichlorophenyl)-3-methyl-5-phenylpyrazole³ (5c) was treated with 1 mol. equiv. of chlorine in dry carbon tetrachloride to give the 4-chloropyrazole (5b) as an oil, τ (CCl₄) 7.7 (3 H, s, Me) and 2.7—2.9 (8 H, m, aryl). This oil (5b) (10.8 g) was dissolved

in acetic acid (30 ml) and water was added to turbidity. Chlorine was then passed over the surface of the stirred solution, causing formation of a deep red colour and crystallisation of a red solid. The mixture was filtered and the mother liquor treated again with chlorine, producing another crop of solid. The process was repeated until no more red solid crystallised out. The combined solids were crystallised from petroleum at -80 °C to give the phenylazobutenone (3a) (5.8 g, 51%), identical with the compound obtained in (a). Further treatment of the acetic acid liquors with chlorine produced the phenylazobutanone (4a) as a yellow solid (4.1 g, 30%).

2,2,3-Trichloro-3-(2,4-dichlorophenylazo)-1-phenylbutanone (4a).—(a) *From the butenone (3a).* A solution of the butenone (3a) in aqueous 10% acetic acid was saturated with chlorine and left for 24 h. T.l.c. (silica gel; chloroform-light petroleum, 4 : 1) showed that total conversion into the butanone (4a) had occurred.

(b) *From the sulphonyl chloride (1a).* Chlorine was bubbled, for 2 h, through a stirred solution of the sulphonyl chloride (1a) (2.2 g) in acetic acid (50 ml) and water (4 ml). The solid that crystallised out was recrystallised from ethanol-water to give the yellow *butanone** (4a) (0.6 g), m.p. 88—89°. The original acetic acid liquors afforded a further 0.7 g (after purification) of the same material when poured into ice-water, and these aqueous liquors yielded barium sulphate [1.6 g; 100% of original sulphur content of the sulphonyl chloride (1a)] when treated with barium chloride.

(c) *From 4-chloro-3-methyl-1,5-diphenylpyrazole (5a).* Chlorine was bubbled into a stirred solution of the 4-chloropyrazole¹³ (5a) (30 g) in acetic acid (300 ml) and water (9 ml). A red colour was immediately formed, and after 1½ h water was added to the resultant yellow solution and the yellow solid that crystallised out was collected and recrystallised from aqueous ethanol to give the butanone (4a) (37.6 g, 78.5%).

Effect of Chlorine on the Sulphonyl Chloride (1a) in Acetic Acid containing Various Amounts of Water.—A solution of the sulphonyl chloride (1a) (3 g, 0.009 mol) in acetic acid was divided into three equal portions. One had no water added [expt. (a)], to the second was added 0.03 mol. [expt. (b)], and to the third was added 0.12 mol of water [expt. (c)].

¹¹ B. Heath-Brown and P. G. Philpott, *J. Chem. Soc.*, 1965, 7185.

¹² H. Henecka, H. Timmler, R. Lorenz, and W. Geiger, *Chem. Ber.* 1957, 90, 1060.

¹³ W. J. Barry, *J. Chem. Soc.*, 1958, 1171.

† For details of Supplementary Publications see Notice to Authors No. 7, *J.C.S. Perkin I*, 1975, Index issue.

(c)]. Each solution was then treated over 2 h with chlorine (10 mol) (in carbon tetrachloride) and the formation of the butenone (3a) and the butanone (4a) was monitored by t.l.c. (silica gel; benzene–light petroleum, 4:1). In expt. (a) only trace amounts of the butenone (3a) and butanone (4a) were formed; 65% of the sulphonyl chloride (1a) was recovered. In expt. (b) only a trace of the butenone (3a) was present; slightly more butanone (4a) was formed than in expt. (a), and 55% of the sulphonyl chloride (1a) was recovered. In expt. (c), little sulphonyl chloride (1a) remained after 2 h; only a trace of the butenone (3a) was present and the main product was the butanone (4a) (47% yield after 2 h).

3-Methyl-1-(4-nitrophenyl)-5-phenylpyrazole-4-sulphonyl Chloride (1b).—The sulphonyl chloride (1b) was prepared in 80.5% yield from the disulphide¹ (2b) as described for the sulphonyl chloride (1a) (t.l.c. indicated when reaction was complete). Compound (1b) was obtained as a white solid, m.p. 163–164° (from benzene–cyclohexane), τ (CCl₄) 7.36 (3 H, s, Me), 7.36 (2 H, d, *J* 9 Hz, aryl), and 2.6 (7 H, m, aryl).

2-Chloro-3-(2-chloro-4-nitrophenylazo)-1-phenylbut-2-en-1-one (3b).—The red mother liquors from the previous experiment were concentrated and the residue was chromatographed (silica; carbon tetrachloride–chloroform, 3:1) to give the butenone* (3b) as a dark red solid, m.p. 151–152.5° (from cyclohexane).

2,2,3-Trichloro-3-(2-chloro-4-nitrophenylazo)-1-phenylbutanone (4b).—A suspension of the finely ground sulphonyl chloride (1b) (2.0 g) in acetic acid (30 ml) and water (4.0 ml) was stirred and treated with chlorine. Dissolution was complete after $\frac{1}{2}$ h and the reaction was monitored by t.l.c. (over-chlorination gives a complex mixture). After 2 h water was carefully added until a yellow solid began to crystallise. The solid* was collected (0.3 g) and crystallised from cyclohexane; m.p. 113.5–114.5°. Treatment of the aqueous mother liquors with barium chloride gave barium sulphate (1.33 g) (equivalent to 100% of the sulphur content of the sulphonyl chloride). The butanone (4b) could also be obtained by treating a solution of the butenone (3a) in aqueous acetic acid with chlorine.

3,5-Dimethyl-1-phenylpyrazole-4-sulphonyl Chloride (1c) and its Anilide (6a).—Bis-(3,5-dimethyl-1-phenylpyrazol-4-yl) disulphide¹⁴ (2c) was treated with chlorine, as described for compound (1b), to give the crude sulphonyl chloride (1c) as a red oil, ν_{\max} (film) 1 740w, 1 370, 1 360, and 1 180 cm⁻¹. The oil (3 g) was treated with aniline (1 ml) in pyridine (5 ml), left for 1 h, and then poured into water. The resulting oil was extracted into benzene and the extract washed (dilute hydrochloric acid then water), dried (Na₂SO₄), and evaporated. The oil produced was purified by column chromatography (silica gel; carbon tetrachloride–chloroform, 9:1) and crystallised from benzene–light petroleum to give the anilide (6a), as a white solid (0.3 g), m.p. 125–126°, τ (CDCl₃) 7.75 (3 H, s), 7.6 (3 H, s), 3.2 (1 H, absent with D₂O), and 2.5–3.0 (10 H, m), ν_{\max} (Nujol) 3 200, 1 325, and 1 170 cm⁻¹.

Chlorinolysis of 3,5-Dimethyl-1-phenylpyrazole-4-sulphonyl Chloride (1c).—A solution of the sulphonyl chloride (1c) in aqueous acetic acid was prepared as in the previous experiment and treatment with chlorine was continued for a further 2 h. The solution was poured onto ice, the product was extracted into benzene, and the extract was washed (water), dried (Na₂SO₄), and evaporated *in vacuo* to give an oil which t.l.c. showed to be a complex mixture, ν_{\max} (film)

1 740 cm⁻¹. The aqueous liquors yielded barium sulphate (3.2 g) [equivalent to 68% of the original sulphur content of the disulphide (2c)] when treated with barium chloride.

Bis-(1,3,5-trimethylpyrazol-4-yl) Disulphide (2d).—3,3'-Dithiobispentane-2,4-dione¹⁴ (40 g) was added slowly to a stirred solution of methylhydrazine (14 g) in ethanol, with the temperature kept at 35 °C. The solution was warmed to reflux temperature (1 h), the solvent was removed *in vacuo*, and the residue was crystallised twice from light petroleum to give the disulphide* (2d) as a pale yellow solid (28.3 g, 65.8%), m.p. 99–100°.

1,3,5-Trimethylpyrazole-4-sulphonyl Chloride (1d) and its Anilide (6b).—The sulphonyl chloride (1d) was prepared as an oil as for the sulphonyl chloride (1c); ν_{\max} (film) 1 730w, 1 710w, 1 375, 1 360, 1 215, and 1 160 cm⁻¹. The anilide* (6b) was a white solid, m.p. 146.5–147.5° (from propan-2-ol).

Chlorinolysis of 1,3,5-Trimethylpyrazole-4-sulphonyl Chloride (1d).—The sulphonyl chloride (1d) was prepared in acetic acid solution as described above from the disulphide (2d) (5g), and treatment with chlorine was continued for a further 2 h. Work-up gave an oil, ν_{\max} (film) 1 740 cm⁻¹, which contained five major components (t.l.c.). Column chromatography (silica gel; chloroform–benzene, 5:1) yielded three impure components, each of which had a high chlorine content and ν_{\max} 1 740 cm⁻¹. A fourth component was isolated in pure form (100 mg), m.p. 78.5–79.5° (from light petroleum); its physical data [ν_{\max} (Nujol) 1 355 and 1 175 cm⁻¹, τ (CCl₄) 7.55 (3 H, s), 6.1 (3 H, s), and 5.2 (2 H, s)] were in accord with 3-(or 5-)chloromethyl-1,5-(or 3-)dimethylpyrazole-4-sulphonyl chloride. The aqueous acetic acid liquors gave barium sulphate (5.3 g) [equivalent to 64% of the original sulphur content of the disulphide (2d)] when treated with barium chloride.

Attempted Synthesis of 4,4,5-Trichloro-1-(2,4-dichlorophenyl)-3-methyl-5-phenyl- Δ^2 -pyrazoline (7).—Chlorine (0.015 mol) in carbon tetrachloride (12 ml) was added over 15 min to a stirred solution of the trichloropyrazole (6b) (0.015 mol) in carbon tetrachloride (20 ml). After 16 h t.l.c. (silica gel; carbon tetrachloride–chloroform, 1:1) showed essentially unchanged trichloropyrazole (5b). However on 'spotting' the solution on the plate a red colour developed and a small amount of the butenone (3a) was shown to be present by development. More chlorine (2 mol) was added but t.l.c. showed no change, and the isolated product was essentially unchanged trichloropyrazole (5b).

1-(2,4-Dichlorophenyl)-3-methyl-5-phenylpyrazole (5c).—The butanone (4a), zinc dust (2.0 g), and ethanol (30 ml) were stirred at reflux temperature (1 h). The zinc was removed and the yellow filtrate concentrated *in vacuo*, diluted with water, and extracted into chloroform. The product from the chloroform was obtained as a white solid, m.p. 96–98° (from benzene–light petroleum), identical with the dichloropyrazole (5c), m.p. 97–98° (lit.,³ 95°), produced by direct synthesis from benzoylacetone and 2,4-dichlorophenylhydrazine.¹⁵

4-Chloro-1-(2,4-dichlorophenyl)-3-methyl-5-phenylpyrazole (5b) and the Dichloropyrazole (5c).—The butanone (4a) (2.1 g) was dissolved in the minimum of acetic acid at 25 °C and water was added to turbidity followed by zinc dust (2.0 g). The mixture was stirred and heated on a steam-bath until the initially formed red colour ceased to fade. More zinc (1.0 g) was added and the reaction continued until

¹⁴ G. Magnani, *Gazzetta*, 1893, **23**, 415.

¹⁵ F. D. Chataway and C. Pearce, *J. Chem. Soc.*, 1915, **107**, 32.

a pale yellow liquid had been formed. The filtered mixture was evaporated *in vacuo*, the residue dissolved in ether, and this solution washed (with dilute aqueous sodium hydrogen carbonate followed by water), dried (Na_2SO_4), and evaporated to leave an oil. Column chromatography (silica gel; benzene–light petroleum) gave the trichloropyrazole (5b) (0.4 g) and the dichloropyrazole (5c) (0.15 g), as shown by comparing their physical data with those of previously prepared samples.

Ethyl Pyruvate 2,4-Dichlorophenylhydrazone (8).—(a) *From the butanone* (4a). Treatment of the butanone (4a) (5 g) in warm ethanol (90 ml) with sodium hydroxide (2.5 g) in water (25 ml) resulted in a red solution, which was set aside for 16 h (ambient temperature). The then colourless solution was filtered (to remove sodium chloride) and evaporated *in vacuo*, and the residue was triturated with ether and water. The aqueous phase was acidified (HCl) to give a solid (0.8 g), m.p. 120–121°, identified as benzoic acid by comparison with authentic material (mixed m.p. and i.r.). The dried ethereal solution was evaporated and the residual oil crystallised from light petroleum to give a white solid (8)* (1.1 g), m.p. 118–120°. This α -form could be converted, by warming in ethanol solution with a little sulphuric acid, into the β -form, m.p. 117–119°.

The residue from the mother liquor was shown to contain

ethyl benzoate by g.l.c. (6 ft Carbowax 20M column at 150 °C; N_2 at 33 ml min⁻¹; flame ionisation detector).

(b) *By direct synthesis from ethyl pyruvate*. 2,4-Dichlorophenylhydrazine (1.8 g) and ethyl pyruvate (1.2 g) in ethanol (20 ml) afforded the α -form of the hydrazone (1.1 g), m.p. 118.5–120° (from ethanol), i.r. spectrum identical with that of the previously prepared α -form, m.p. undepressed when mixed with the previously prepared α -form but mixed m.p. with β -form <110°. The β -form was shown by t.l.c. to be present in the liquors.

(c) *From pyruvic acid 2,4-dichlorophenylhydrazone*. The pyruvic acid 2,4-dichlorophenylhydrazone¹⁶ could be esterified with ethanol in the presence of sulphuric acid or hydrogen chloride to give the β -form* of the hydrazone (8), m.p. 119–120° (lit.,¹⁶ 122.5°; lit.,¹¹ 119–120°), m.p. <110° on admixture with the previously produced α -form [part (a)] but undepressed when mixed with the previously prepared β -form. The α - and β -forms were indistinguishable by g.l.c. (3 ft Tenax at 265 °C or 12 ft OV101, 20%, at 265 °C; both N_2 at 30 ml min⁻¹).

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¹⁶ G. Pappalardo and T. Vitali, *Gazzetta*, 1958, **88**, 1147.