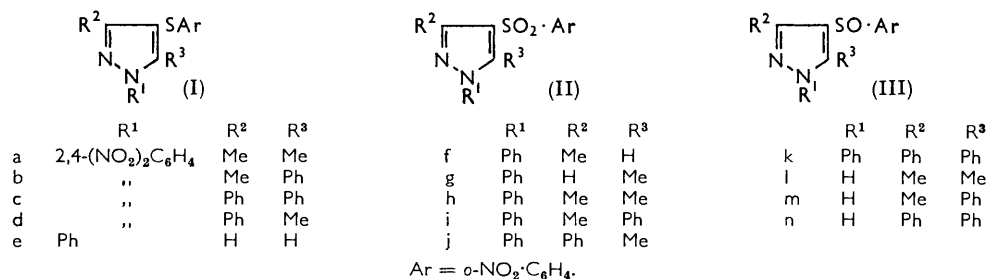


### 941. The Reactions of Some Aryl Pyrazolyl Sulphides.

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1-Phenyl- and 1-(2,4-dinitrophenyl)pyrazolyl sulphides have been prepared by methods used previously, and oxidised to the corresponding sulphoxides and sulphones. When the pyrazole nucleus contains 3- and 5-phenyl groups oxidation gives only the sulphone. Naphthalene, phenanthrene, and anthracene react with *o*-nitrobenzenesulphenyl chloride in the absence of catalysts.

1-(2,4-DINITROPHENYL)PYRAZOLYL SULPHIDES (Ia—d) have been prepared by methods similar to those described previously<sup>1</sup> for other pyrazoles. 2-*o*-Nitrophenylthio-1-phenylbutane-1,3-dione,<sup>2</sup> however, reacted with 2,4-dinitrophenylhydrazine to give only 1-(2,4-dinitrophenyl)-3-methyl-5-phenylpyrazolyl 2-*o*-nitrophenyl sulphide (cf. the reaction of benzoylacetone).<sup>3</sup> The 4-position of 1-(2,4-dinitrophenyl)pyrazoles is less active than in 1-phenylpyrazoles, more forcing conditions being required for direct reaction with *o*-nitrobenzenesulphenyl chloride.



Fission of sulphides (Ia—d) by methanolic sodium methoxide gave the corresponding 1-unsubstituted pyrazolyl sulphides and 2,4-dinitrophenol. This reaction is slower than with 1-(2,4-dinitrophenyl)-4-nitropyrazole,<sup>4</sup> and for this reason produces 2,4-dinitrophenol and not 2,4-dinitroanisole,<sup>4</sup> a view supported by the fact that 2,4-dinitroanisole gives 2,4-dinitrophenol under these conditions.

Oxidation of these sulphides, and other pyrazolyl sulphides previously reported,<sup>1</sup> by hydrogen peroxide (excess) in a mixture of acetic acid and acetic anhydride gave good yields of the sulphones (IIa—n). Sulphoxides (IIIa, b, d—j, l, m) were prepared by the action of the

<sup>1</sup> Cowell and Finar, *J.*, 1962, 4146.

<sup>2</sup> Finar and Montgomery, *J.*, 1961, 367.

<sup>3</sup> Finar and Simmonds, *J.*, 1958, 200.

<sup>4</sup> Finar and Hurlock, *J.*, 1957, 3024.

calculated amount of hydrogen peroxide in cold acetic acid. The sulphoxides were stable for at least a year. Sulphoxides were not obtained from 3,5-diphenylpyrazoles; mixtures of sulphone and sulphide were obtained from 1,3,5-triphenyl- and 1-(2,4-dinitrophenyl)-3,5-diphenyl-pyrazolyl sulphide, and unchanged sulphide from 3,5-diphenylpyrazolyl sulphide.

Since pyrazolyl sulphides could be prepared by direct action of *o*-nitrobenzenesulphenyl chloride on a pyrazole without the use of a catalyst,<sup>1</sup> we applied this technique to some aromatic compounds. Naphthyl and phenanthryl sulphides were prepared by melting the reactants together. These and anthryl sulphides were prepared by heating a solution of the aromatic compound and *o*-nitrobenzenesulphenyl chloride in nitrobenzene. A modification of Kharasch's technique,<sup>5</sup> with anhydrous aluminium chloride as a catalyst, was also used to prepare the same three sulphides to compare yields obtained by the two methods—they were very similar. Attempts to introduce more than one arylthio-group were unsuccessful.

## EXPERIMENTAL

(1) *Reaction of Arylthio-diketones with 2,4-Dinitrophenylhydrazine.*—3-*o*-Nitrophenylthio-pentane-2,4-dione<sup>2</sup> (2.5 g., 0.01 mole) in hot 95% ethanol (20 c.c.) was added to 2,4-dinitrophenylhydrazine (2.0 g., 0.01 mole) in hot 95% ethanol (50 c.c.) and concentrated sulphuric acid (4 c.c.). The mixture was heated on a steam-bath for 2 hr., and then, on cooling, the yellow precipitate was collected, washed with water, and dried (3.6 g., 87%). Recrystallisation from aqueous ethanol gave yellow needles of 1-(2,4-dinitrophenyl)-3,5-dimethylpyrazol-4-yl *o*-nitrophenyl sulphide (Ia), m. p. 160—162°. Sulphides (Ib and c) were prepared similarly (see Table 1).

(2) *Reaction of o-Nitrobenzenesulphenyl Chloride with 1-(2,4-Dinitrophenyl)pyrazoles.*—(a) A mixture of 1-(2,4-dinitrophenyl)-3,5-dimethylpyrazole<sup>6</sup> (2.6 g., 0.01 mole) and *o*-nitrobenzenesulphenyl chloride (1.9 g., 0.01 mole) was heated at 120° for 3 hr. (evolution of hydrogen chloride had then ceased). The dark brown solid was recrystallised twice from chloroform-light petroleum, to give yellow needles of sulphide (Ia) (60.5%), m. p. 160—162°. Sulphides (Ib—d) were prepared similarly (see Table 1).

TABLE I.  
Arylthiopyrazoles (I).

Compound	Method	M. p.	Yield (%)	Found (%)				Formula	Required (%)			
				C	H	N	S		C	H	N	S
Ia	1	160—162°	87	49.2	3.4	16.5	6.4	C <sub>17</sub> H <sub>13</sub> N <sub>5</sub> O <sub>6</sub> S	49.1	3.2	16.9	7.7
Ib	1	201—202	86	55.5	3.0	14.4	7.0	C <sub>20</sub> H <sub>15</sub> N <sub>5</sub> O <sub>6</sub> S	55.3	3.2	14.7	6.7
Ic	1	208—209	89	59.9	3.4	12.7	6.1	C <sub>27</sub> H <sub>17</sub> N <sub>5</sub> O <sub>6</sub> S	60.1	3.2	13.0	5.9
Id	2a	145—146	64	55.4	3.2	14.4	6.6	C <sub>22</sub> H <sub>15</sub> N <sub>5</sub> O <sub>6</sub> S	55.3	3.2	14.7	6.7

Yields by methods 2a and 2b, respectively, were: Ia, 60.5, 63; Ib, 64, 65; Ic, 59, 62; Id, 64, 63%.

(b) 1-(2,4-Dinitrophenyl)-3,5-dimethylpyrazole (2.6 g., 0.01 mole) and *o*-nitrobenzenesulphenyl chloride (1.9 g., 0.01 mole) were heated in nitrobenzene (10 c.c.) at 120° for 4 hr. (evolution of hydrogen chloride had then ceased). The mixture was run through an alumina column and the yellow band eluted with benzene. The benzene solution was evaporated and the residue recrystallised twice from aqueous acetic acid, to give yellow needles of sulphide (Ia) (2.5 g., 63%), m. p. 160—162°. Sulphides (Ib—d) were prepared similarly (see Table 1).

(3) *Action of Methanolic Sodium Methoxide on 1-(2,4-Dinitrophenyl)pyrazol-4-yl Sulphides.*—To 1-(2,4-dinitrophenyl)-3,5-dimethylpyrazol-4-yl *o*-nitrophenyl sulphide (2.1 g., 0.005 mole) in methanol (50 c.c.), 0.6*N* methanolic sodium methoxide (40 c.c.) was added, and the mixture was refluxed for 1 hr. and then evaporated to dryness. The residue was triturated with hot water and the insoluble material was recrystallised from aqueous ethanol, to give yellow needles of 3,5-dimethylpyrazol-4-yl *o*-nitrophenyl sulphide (1.1 g., 88%), m. p. 170—171°. The aqueous

<sup>5</sup> Kharasch and Swidler, *J. Org. Chem.*, 1954, **19**, 1704.

<sup>6</sup> Borsche and Ried, *Ber.*, 1943, **76**, 1011.

filtrate was acidified with concentrated hydrochloric acid and extracted with ether ( $4 \times 25$  c.c.). The extract was evaporated and the residue recrystallised from chloroform–light petroleum, to give 2,4-dinitrophenol (0.8 g., 87%), m. p.  $113^\circ$ . Sulphides (Ib–d) behaved similarly (see Table 2).

TABLE 2.

Action of sodium methoxide on the sulphides (I).			
Starting sulphide	Product	Yield (%)	2,4-(NO <sub>2</sub> ) <sub>2</sub> C <sub>6</sub> H <sub>4</sub> ·OH
Ia	3,5-Me <sub>2</sub> -4-ArS-pyrazole	88	87
Ib	3-Me-5-Ph-4-ArS-pyrazole	87	89
Ic	3,5-Ph <sub>2</sub> -4-ArS-pyrazole	89	88
Id	3-Me-5-Ph-4-ArS-pyrazole	86	87

(4) *Oxidation of Aryl Pyrazolyl Sulphides to Sulphones*.—To 3,5-dimethyl-1-phenylpyrazol-4-yl *o*-nitrophenyl sulphide (3.25 g., 0.01 mole) in glacial acetic acid (10 c.c.) and acetic anhydride (5 c.c.), 30% hydrogen peroxide (3 c.c.) was added. The mixture was warmed on a steam-bath, whereupon an exothermic reaction commenced and continued for 2 min. After 1 hour's heating on the steam-bath the yellow solution had become colourless. Water was added to the hot solution and, on cooling, the pale yellow crystals were collected, washed with water, and dried (3.35 g., 94%). Two recrystallisations from aqueous acetic acid (charcoal) gave colourless needles of 3,5-dimethyl-1-phenylpyrazol-4-yl *o*-nitrophenyl sulphone (IIh) (3.05 g., 86%), m. p.  $143.5\text{--}144.5^\circ$ . Sulphones (IIa–n) were all prepared in this way (see Table 3).

(5) *Oxidation of Sulphides to Sulphoxides*.—To 1,5-diphenyl-3-methylpyrazol-4-yl *o*-nitrophenyl sulphide (2.9 g., 0.01 mole) in cold acetic acid (250 c.c.), 30% hydrogen peroxide (1.2 c.c., 0.01 mole) was added and the mixture was left for 7 days. Water was then added and the yellow precipitate was washed with water and dried (3.65 g., 91%). Recrystallisation from chloroform–light petroleum gave yellow 1,5-diphenyl-3-methylpyrazol-4-yl *o*-nitrophenyl sulphoxide (IIIi) (3.1 g., 77%), m. p.  $183\text{--}184^\circ$ . The sulphoxides listed in Table 4 were all prepared in this way.

Under the same conditions, 1,3,5-triphenylpyrazol-4-yl *o*-nitrophenyl sulphide (4.5 g., 0.01 mole) gave a mixture which was separated with boiling acetone to give sulphone (IIk) (2.2 g.) as the acetone-insoluble component and the starting sulphide (2.0 g.) as the acetone-soluble component.

1-(2,4-Dinitrophenyl)-3,5-diphenylpyrazol-4-yl *o*-nitrophenyl sulphide (5.4 g.), treated in the same way, gave sulphone (IIc) (2.6 g.) and recovered sulphide (2.4 g.).

3,5-Diphenylpyrazol-4-yl *o*-nitrophenyl sulphide, treated similarly, remained unchanged.

(6) *Oxidation of Sulphoxides to Sulphones*.—The sulphoxides of Table 4 were oxidised to the sulphones by the method described above for sulphides (see Table 3).

TABLE 3.

Aryl pyrazolyl sulphones.											
	M. p.	Yield * (%)	Found (%)				Formula	Required (%)			
			C	H	N	S		C	H	N	S
IIa	168–170°	91, 90	45.4	2.8	15.7	6.9	C <sub>17</sub> H <sub>13</sub> N <sub>5</sub> O <sub>8</sub> S	45.6	2.9	15.7	7.2
IIb	207–209	89, 87	51.5	3.0	13.6	6.4	C <sub>22</sub> H <sub>15</sub> N <sub>5</sub> O <sub>8</sub> S	51.8	3.0	13.8	6.3
IIc	206–208	88, —	56.5	2.9	11.9	5.7	C <sub>27</sub> H <sub>17</sub> N <sub>5</sub> O <sub>8</sub> S	56.7	3.0	12.3	5.6
IId	165–167	88, 86	51.6	2.9	13.5	6.3	C <sub>23</sub> H <sub>15</sub> N <sub>5</sub> O <sub>8</sub> S	51.8	3.0	13.8	6.3
IIe	154–156	78, 77	54.5	3.4	12.8	9.8	C <sub>15</sub> H <sub>11</sub> N <sub>3</sub> O <sub>4</sub> S	54.7	3.4	12.8	9.7
IIf	140–141	89, 85	55.7	3.8	12.1	9.4	C <sub>16</sub> H <sub>13</sub> N <sub>3</sub> O <sub>4</sub> S	55.9	3.8	12.25	9.3
IIg	136–137	82, 83	55.6	3.7	12.0	9.3					
IIh	143.5–144.5	86, 87	56.8	4.4	11.6	8.8	C <sub>17</sub> H <sub>15</sub> N <sub>3</sub> O <sub>4</sub> S	57.1	4.2	11.8	9.0
IIi	187.5–189	84, 83	62.8	4.3	9.8	7.8	C <sub>22</sub> H <sub>17</sub> N <sub>3</sub> O <sub>4</sub> S	63.0	4.1	10.0	7.7
IIj	168.5–169.5	83, 80	63.1	4.2	9.9	7.7					
IIk	215–216	80, —	67.1	4.0	8.5	6.8	C <sub>27</sub> H <sub>19</sub> N <sub>3</sub> O <sub>4</sub> S	67.3	4.0	8.7	6.7
III	139–141	73, 74	46.7	3.8	14.7	11.2	C <sub>11</sub> H <sub>11</sub> N <sub>3</sub> O <sub>4</sub> S	46.95	3.9	14.95	11.4
IIIm	206–207	74, 72	55.7	3.8	12.0	9.4	C <sub>16</sub> H <sub>13</sub> N <sub>3</sub> O <sub>4</sub> S	55.9	3.8	12.25	9.4
IIIn	195–197	71, —	62.0	3.6	10.4	7.8	C <sub>21</sub> H <sub>15</sub> N <sub>3</sub> O <sub>4</sub> S	62.2	3.7	10.4	7.9

\* By methods 4 and 6, respectively.

TABLE 4.

		Aryl pyrazolyl sulphoxides.											
		Yield (%)	Found (%)				Formula	Required (%)					
M. p.			C	H	N	S		C	H	N	S		
IIIa	249—251°	87	47.4	3.2	16.2	7.3	C <sub>17</sub> H <sub>13</sub> N <sub>5</sub> O <sub>7</sub> S	47.3	3.0	16.25	7.4		
IIIb	211—213	85	53.5	3.3	14.2	6.3	C <sub>22</sub> H <sub>16</sub> N <sub>5</sub> O <sub>7</sub> S	53.5	3.1	14.2	6.5		
IIIc	194—196	83	53.3	3.1	14.2	6.5	"	"	"	"	"		
IIIe	148—149	73	57.5	3.2	13.6	10.1	C <sub>15</sub> H <sub>11</sub> N <sub>3</sub> O <sub>3</sub> S	57.5	3.5	13.4	10.2		
IIIf	121—122	69	59.0	4.2	12.7	9.7	C <sub>16</sub> H <sub>13</sub> N <sub>3</sub> O <sub>3</sub> S	58.7	4.0	12.8	9.8		
IIIg	123—124	67	59.0	4.0	12.7	9.9	"	"	"	"	"		
IIIh	153—154	68	59.6	4.2	11.9	9.2	C <sub>17</sub> H <sub>15</sub> N <sub>3</sub> O <sub>3</sub> S	59.8	4.4	12.3	9.4		
IIIi	183—184	77	65.4	5.5	10.3	8.0	C <sub>22</sub> H <sub>17</sub> N <sub>3</sub> O <sub>3</sub> S	65.5	5.5	10.4	7.95		
IIIj	154—156	74	65.2	5.3	10.5	7.9	"	"	"	"	"		
IIIk	164—166	71	49.8	3.9	15.8	12.0	C <sub>11</sub> H <sub>11</sub> N <sub>3</sub> O <sub>3</sub> S	49.8	4.2	15.85	12.1		
IIIm	211.5—213	79	58.7	4.2	12.7	9.8	C <sub>16</sub> H <sub>13</sub> N <sub>3</sub> O <sub>3</sub> S	58.7	4.0	12.8	9.8		

Reaction of *o*-Nitrobenzenesulphenyl Chloride with Aromatic Compounds.—(a) Naphthalene (1.3 g., 0.01 mole) and *o*-nitrobenzenesulphenyl chloride (1.9 g., 0.01 mole) were heated at 120° for 4 hr. The violet solid was recrystallised twice from ethanol (charcoal), to give pale orange needles of 1-naphthyl *o*-nitrophenyl sulphide (1.85 g., 66%), m. p. 148—149°. A mixture of phenanthrene and *o*-nitrobenzenesulphenyl chloride similarly gave yellow needles of 9-phenanthryl *o*-nitrophenyl sulphide (see Table 5).

The m. p. of anthracene is too high for use of this method to prepare the sulphide.

(b) Naphthalene (1.3 g., 0.01 mole) and *o*-nitrobenzenesulphenyl chloride (1.9 g., 0.01 mole) were heated together in nitrobenzene (10 c.c.) at 120° for 6 hr. The dark green solution was passed through an alumina column and the orange band eluted with benzene. The benzene solution was evaporated and the residue recrystallised twice from ethanol, to give pale orange needles of 1-naphthyl *o*-nitrophenyl sulphide (1.8 g., 64%), m. p. 148—149°.

The anthryl and phenanthryl sulphide were prepared similarly (see Table 5).

TABLE 5.

		Aromatic sulphides.											
		Yield (%) and method	Found (%)				Formula	Required (%)					
Sulphide	M. p.		C	H	N	S		C	H	N	S		
1-Naphthyl ...	148—149°	66 (a)	68.3	4.2	5.0	11.1	C <sub>16</sub> H <sub>11</sub> NO <sub>2</sub> S	68.5	3.95	5.0	11.4		
	Other yields:	64 (b), 71 (c), 64 (d)											
9-Anthryl .....	225—227	65 (b)	72.2	4.2	4.4	10.1	C <sub>20</sub> H <sub>13</sub> NO <sub>2</sub> S	72.5	4.0	4.2	9.7		
	Other yields:	69 (c), 66 (d)											
9-Phenanthryl	189—191	69 (a)	72.4	3.8	3.9	9.8	"	"	"	"	"		
	Other yields:	67 (b), 68 (d)											

(c) Naphthalene (1.3 g., 0.01 mole) and *o*-nitrobenzenesulphenyl chloride (1.9 g., 0.01 mole) were dissolved in ethylene chloride (20 c.c.) and the solution cooled to -10° (acetone-solid carbon dioxide). Anhydrous aluminium chloride (4.0 g., 0.03 mole) was added to the stirred solution, the temperature being kept below 0°. After 10 min. absolute ethanol (25 c.c.) was added portionwise in such a manner that the temperature did not rise above 10°. The inorganic material was extracted with 6*N*-hydrochloric acid (3 × 25 c.c.), and the organic layer evaporated in a stream of air. The violet residue was recrystallised twice from ethanol (charcoal), to give pale orange needles of 1-naphthyl *o*-nitrophenyl sulphide (2.0 g., 71%), m. p. 148—149°.

The phenanthryl sulphide was prepared similarly, and the anthryl sulphide was prepared in nitrobenzene solution.

(d) Naphthalene (1.3 g., 0.01 mole) and *o*-nitrobenzenesulphenyl chloride (3.8 g., 0.02 mole) were heated in nitrobenzene (10 c.c.) at 120° for 6 hr. The dark green solution was passed through an alumina column, and the orange band eluted with benzene. The benzene solution was evaporated to dryness, and the residue shaken in ether with 2*N*-sodium carbonate solution. The yellow precipitate of 2,2'-dinitrodiphenyl disulphide was washed with water and dried

(0.95 g.; m. p. 194—196°). Under these conditions *o*-nitrobenzenesulphenyl chloride gave 2,2'-dinitrodiphenyl disulphide in 68% yield. The ethereal layer was evaporated and the residue recrystallised twice from ethanol (charcoal), to give pale orange needles of 1-naphthyl *o*-nitrophenyl sulphide (1.8 g., 64%), m. p. 148—149°. Anthracene and phenanthrene behaved similarly (see Table 5).

The orientation of these compounds has been assumed from the analogous reactions with 2,4-dinitrobenzenesulphenyl chloride in the presence of aluminium chloride.<sup>7</sup>

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[Received, April 2nd, 1963.]

<sup>7</sup> Buess and Kharasch, *J. Amer. Chem. Soc.*, 1950, **72**, 3529.

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