1044. *Extrusion of Sulphur. Part VI.*[1] *Novel Ring-contractions Giving Pyridazines and Pyrazoles.*

By J. D. Loudon and L. B. Young.

2,7-Dihydro-3,6-diphenyl-1,4,5-thiadiazepine (II) yields 3-6-diphenylpyridazine (VI) by halogenation–dehalogenation or by thermal decomposition. When heated in acetic acid its *SS*-dioxide also yields the pyridazine, whereas its *S*-mono-oxide affords 3,5-diphenylpyrazole (X) and hence, in presence of hydrogen peroxide, 2,5-diphenyl-1,3,4-oxadiazole (XII) and 1,2-dibenzoylhydrazine. The *SS*-dioxide is isomerised by sodium ethoxide in ethanol to a sulphinic acid which loses sulphur dioxide when melted and yields 3-methyl-4,5-diphenylpyrazole (XIII).

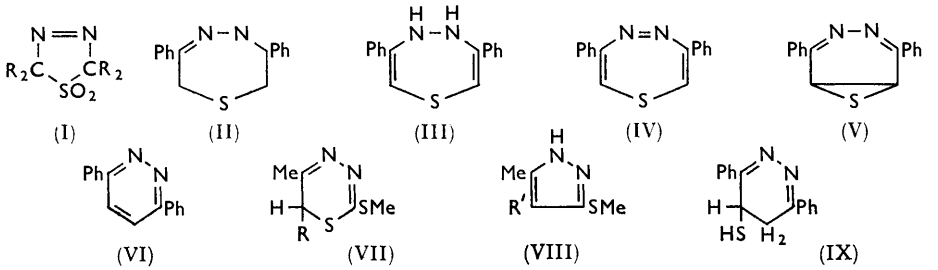
Previous papers in this series have been concerned with the contraction of 7-membered thia-heterocycles, at their lowest state of hydrogenation, to aromatic 6-membered systems by extrusion either of sulphur (from cyclic sulphides) or of oxidised sulphur (from cyclic sulphoxides or sulphones). However, extrusion is not confined to cyclic systems where the immediate product is aromatic. Thus under suitable conditions ethylene sulphides (thiirans) [2] and sulphones [3] yield the corresponding ethylenes; butadiene sulphone (2,5-di-

[1] Part V, *J.*, 1962, 3262.

[2] Staudinger and Siegwart, *Helv. Chim. Acta*, 1920, **3**, 833; Schönberg and Vargha, *Annalen*, 1930, **483**, 176; Culvenor, Davies, and Heath, *J.*, 1949, 278, 282.

[3] Hesse, Reichold, and Majmudar, *Chem. Ber.*, 1957, **90**, 2106.

hydrothiophen dioxide),[4] a cyclic vinylogue of ethylene sulphone, yields butadiene; and in the thiadiaza-series compounds of the probable structure (I) [5] can yield either the ketazine, $R_2C{:}N{\cdot}N{:}CR_2$, or the olefin, $R_2C{:}CR_2$. 2,7-Dihydrothiepin, a higher cyclic vinylogue of ethylene sulphide, is unknown and attempted rational synthesis of one of its derivatives gave a benzene derivative instead.[6] 2,7-Dihydrodibenzo[*c*,*e*]thiepin, however, when heated in xylene with hydrogen-deficient Raney nickel affords some phenanthrene, probably formed *via* dihydrophenanthrene, together with 2,2′-dimethyldiphenyl which is the normal desulphurisation product.[7] 2,7-Dihydro-1,4,5-thiadiazepine is again unknown, but its accessible 3,6-diaryl derivatives [8] have now been examined and found to undergo ring-contraction in several different ways.



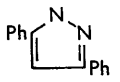
The dihydrothiadiazepine (II) is readily obtained by the action of hydrazine hydrate on diphenacyl sulphide. Attempts to convert it into the thiadiazepine (IV) by dehydrogenation were unsuccessful. Structure (II) as distinct from (III), is consistent with the compound's failure to form an acetyl derivative and with its stability towards oxidation by mercuric oxide. Its infrared spectrum shows no imino-absorption for the solid, but in carbon tetrachloride a peak at 3418 cm.$^{-1}$ may indicate the presence of an imino-form in solution. When treated with *N*-bromosuccinimide in carbon tetrachloride the compound was converted into 3,6-diphenylpyridazine (VI) almost quantitatively. The pyridazine would be the expected product of extrusion of sulphur from the thiadiazepine (IV): moreover, since *N*-bromosuccinimide is known to effect α-bromination of alkyl sulphides [9] and more particularly of phenacyl sulphides,[10] a reasonable course for the reaction is bromination–dehydrobromination leading to the pyridazine *via* an episulphide (V) whose structure is likely [11] to be related intimately to that of the thiadiazepine itself. The same overall change, *viz.*, (II) ⟶ (VI), but with poorer yield, was effected by bromine in acetic acid, or by chlorinating the dihydrothiadiazepine with sulphuryl chloride and heating the resultant dichloro-compound with sodium iodide in acetone. On the other hand, the dihydrothiadiazepine resisted oxidation by chloramine-T or by chloranil.

Although the dihydrothiadiazepine was recoverable after prolonged boiling of its solution in xylene, it was decomposed in boiling ethylene glycol affording, with evolution of hydrogen sulphide, the pyridazine (VI) in high yield. Thermal instability was more pronounced in the corresponding *SS*-dioxide (II; SO_2 for S). This was prepared both by the action of hydrazine hydrate on diphenacyl sulphone and by oxidation of the dihydrothiadiazepine with potassium permanganate. Heated in ethanol or, more rapidly, in

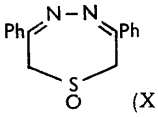
[4] Cf. Houben-Weyl, "Methoden d. Org. Chem.," 4th edn., Vol. IX, p. 237; Staudinger and Ritzenthaler, *Ber.*, 1935, **68**, 455; Backer and Blaas, *Rec. Trav. chim.*, 1942, **61**, 785.
[5] Hesse and Reichold, *Chem. Ber.*, 1957, **90**, 2101.
[6] Loudon and Steel, *J.*, 1954, 1163.
[7] Badger, Cheuychit, and Sasse, *J.*, 1962, 3241.
[8] Fromm and Erhardt, *Ber.*, 1921, **54**, 187.
[9] Horner and Winkelmann, *Angew. Chem.*, 1959, **71**, 349.
[10] Groebel, *Chem. Ber.*, 1959, **92**, 2887; 1960, **93**, 896.
[11] Loudon in "Organic Sulphur Compounds," ed. Kharasch, Pergamon Press, London, 1961, p. 300.

acetic acid it gave the pyridazine almost quantitatively. It is noteworthy that thiadiazines of type (VII) [12] can form pyrazoles either by extrusion of sulphur, (VII; R = Ph or CO_2Et) ⟶ (VIII; R′ = Ph or CO_2Et), or by rearrangement with retention of sulphur, (VII; R = H) ⟶ (VIII; R′ = SH). Accordingly the present thermal decompositions may be regarded as involving rearrangement, *e.g.*, (II) ⟶ (IX), followed by appropriate elimination of hydrogen sulphide or sulphoxylic acid, the latter accounting for the joint evolution of hydrogen sulphide and sulphur dioxide which is observed during decomposition of the sulphone.

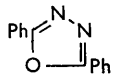
In contrast to these contractions of a 7- to a 6-membered ring two types of contraction leading to the 5-membered pyrazole system were discovered. The first of these occurred when the dihydrothiadiazepine (II) was heated in solution with hydrogen peroxide. This treatment, which is usual for oxidising a sulphide but occasionally results in extrusion of sulphur,[13] here gave rise to a series of deep-seated changes. Under specific conditions the main product, formed in good yield, was 3-5-diphenylpyrazole (X). Since neither the *SS*-dioxide nor the pyridazine (VI) gives rise to this pyrazole, the *S*-mono-oxide (XI) was examined as the likeliest precursor. It could be isolated after brief oxidation of the dihydrothiadiazepine with hydrogen peroxide in hot acetic acid, but by longer treatment or when heated at 100° in the solvent alone it was converted into the pyrazole. This remarkable ring contraction occurs with loss of a fragment, CH_2OS, whose fate was not established. It contrasts with the simple oxidation of the *S*-mono-oxide to the *SS*-dioxide as effected by potassium permanganate and seems to be favoured by a mildly acidic environment since the *S*-mono-oxide is stable in hot ethanol, is only slowly affected by hot aqueous ethanol, and is rapidly resinified by alkali. Unexpectedly also 3,5-diphenylpyrazole was found to be highly susceptible to oxidation by hydrogen peroxide in acetic acid. Among the products 1,2-dibenzoylhydrazine, 2,5-diphenyl-1,3,4-oxadiazole (XII), and benzoic acid were identified, and their rapid formation in this way is the more remarkable in view of the slow and incomplete oxidation of the same pyrazole to benzoic acid by potassium permanganate.



(X)



(XI)

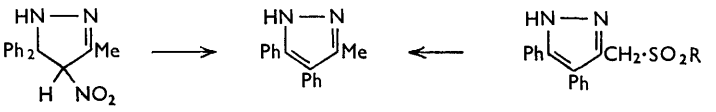


(XII)

Derivatives of the dihydrothiadiazepine (II) were likewise prepared from di-4-bromophenacyl and di-4-methylphenacyl sulphide. They and their *SS*-dioxides provided further examples of the ring-contractions to products of types (VI) and (X) as described for the parent compounds. The resultant pyridazines were already known: the new pyrazoles were identified by analyses, by their infrared spectra (ν *ca.* 970 cm.$^{-1}$, which appeared to be a characteristic of the free imino-compounds),[14] and by the high amide-carbonyl absorption [15] (ν 1735 cm.$^{-1}$) of their *N*-acetyl derivatives. Attempts to obtain more informative results through compounds derived from desyl sulphide, $(Ph{\cdot}CO{\cdot}CHPh)_2S$, failed because the latter reacted with hydrazine to form a mixture of products including deoxybenzoin azine, $(Ph{\cdot}CH_2{\cdot}CPh{:}N{\cdot})_2$, and benzil monohydrazone, $Ph{\cdot}CO{\cdot}CPh{:}N{\cdot}NH_2$. The known conversion [16] of desyl sulphide by alkali into deoxybenzoin and benzilic acid (presumably *via* benzil) provides some analogy for these findings. Desyl sulphone, suspended in a hot ethanolic solution of either hydrazine hydrate or potassium hydroxide, was rapidly hydrolysed to benzyl sulphone.

[12] Beyer, Bulka, and Beckhaus, *Chem. Ber.*, 1959, **92**, 2593.
[13] Bradsher and McDonald, *J. Org. Chem.*, 1962, **27**, 4475.
[14] Hüttel, Wagner, and Jochum, *Annalen*, 1955, **593**, 179; Rondestvedt and Chang, *J. Amer. Chem. Soc.*, 1955, **77**, 6532; Zerbi and Alberti, *Spectrochim. Acta*, 1962, **18**, 407; but cf. Farnum and Yates, *J. Org. Chem.*, 1962, **27**, 2209.
[15] Staab, *Annalen*, 1959, **622**, 31.
[16] Schönberg and Iskander, *J.*, 1942, 90.

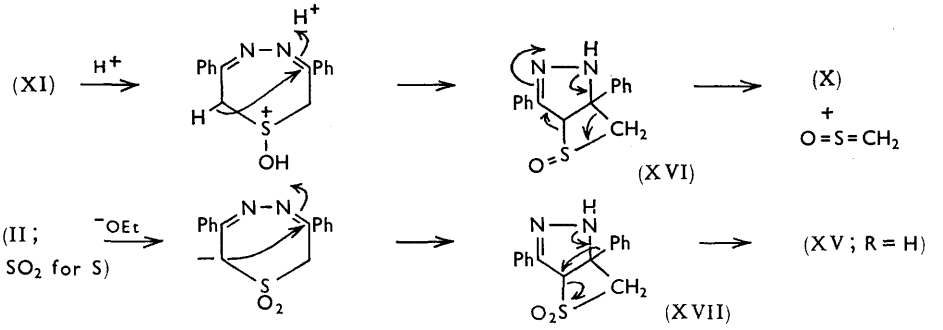
The second type of ring-contraction leading to a pyrazole derivative came to light during attempts to effect a base-catalysed conversion of the *SS*-dioxide (II; SO_2 for S) into the pyridazine (VI) on the lines proposed for the thermal decomposition. Although the pyridazine was isolated from several of these experiments (cf. Experimental) its origin is uncertain, and the principal result of heating a suspension of the dioxide in ethanolic sodium ethoxide was isomerisation to a sulphinic acid of which the properties cannot be reconciled with a structure such as (IX; SO_2H for SH). Thus when melted, or heated with mineral acid in ethanol, the sulphinic acid lost sulphur dioxide and gave a pyrazole derivative (*M*, 234; ν 970 cm.$^{-1}$; *N*-acetyl derivative, ν 1730 cm.$^{-1}$) whose mass spectrum contained a major fragment of mass 165 indicative of two, closely positioned, phenyl substituents. 3-Methyl-4,5-diphenylpyrazole (XIII) has been prepared by Parham and his colleagues [17] through acid- or base-catalysed rearrangement of the pyrazoline (XIV) which is the adduct from diphenyldiazomethane and 1-nitroprop-1-ene. Comparison



(XIV) (XIII) (XV)

with a specimen prepared in this way identified our pyrazole as (XIII). The sulphinic acid from which it was formed is assigned the structure (XV; R = H) thus accounting for the ready elimination of sulphur dioxide and for methylation, under very mild conditions, to a methyl sulphone (XV; R = Me) which is stable alike to heat and mineral acid.

A tentative but coherent interpretation of the pyrazole-forming ring-contractions is suggested in the annexed scheme, wherein similarly constituted pyrazolines, (XVI) and (XVII), are formed by transannular interactions and are converted into pyrazoles by



alternative paths determined by the oxidation level of the sulphur atom. Although analogy for the step (XVI) ⟶ (X) is lacking, the rearrangement of (XVII) to (XV; R = H) is closely akin to that involved in the reaction (XIV) ⟶ (XIII).

Experimental

Wherever possible, products were identified by mixed m. p. with authentic specimens and by comparison of infrared spectra. Petroleum refers to light petroleum, b. p. 60—80°.

2,7-*Dihydro*-3,6-*diphenyl*-1,4,5-*thiadiazepine* (II).—Hydrazine hydrate (3 g.; 100%) was added to a solution of diphenacyl sulphide [18] (10 g.) in hot acetic acid (30 ml.), and the mixture was heated for a few minutes at 95°. The dihydrothiadiazepine [8] separated as colourless

[17] Parham and Hasek, *J. Amer. Chem. Soc.*, 1954, **76**, 799; Parham, Braxton, and O'Connor, *J. Org. Chem.*, 1961, **26**, 1805.

[18] Fromm and Flaschen, *Annalen*, 1912, **394**, 310.

needles, m. p. 174—175° (from acetic acid) (Found: C, 71·75; H, 5·35. Calc. for $C_{16}H_{14}N_2S$: C, 72·15; H, 5·3%). Its 1,1-dioxide,[8] m. p. 196° (from benzene), was prepared (*a*) similarly from diphenacyl sulphone [18] but with minimal heating, and (*b*) by oxidising a solution of the dihydrothiadiazepine (0·5 g.) in acetic acid (30 ml.) with aqueous potassium permanganate (0·5 g. in 10 ml.) at 20° (1 hr.) and then decolorising the mixture with sulphur dioxide (Found: C, 64·3; H, 4·4; N, 9·45. Calc. for $C_{16}H_{14}N_2O_2S$: C, 64·4; H, 4·75; N, 9·4%).

3,6-*Diphenylpyridazine* (VI).—(*a*) A solution of the dihydrothiadiazepine (II) and *N*-bromosuccinimide (1 mol.) in carbon tetrachloride was refluxed over a lamp-heater (250 w) for 1 hr. The resultant solid was collected and washed with water, affording the pyridazine,[19] m. p. 222° (from ethanol; yield, 83%).

(*b*) Solutions of the compound (II) (4 g.) and sulphuryl chloride (2·5 g.) in methylene dichloride (40 and 15 ml., respectively) were gradually mixed, then heated under reflux for 1 hr. and concentrated. The resultant (2,2- or 2,7-)*dichloro-derivative* was dimorphous (infrared spectra identical), m. p. 158° or 179° (decomp.) (from ethyl acetate) (Found: C, 57·4; H, 4·1; N, 8·4. $C_{16}H_{12}Cl_2N_2S$ requires C, 57·3; H, 3·6; N, 8·35%), and when heated under reflux for 24 hr. with sodium iodide in acetone gave the pyridazine (65%).

(*c*) Solutions of compound (II) and bromine (1 mol.) in acetic acid were gradually mixed (2 hr.) and the resultant suspension was then heated under reflux for 4 hr. before being added to water. The pyridazine (40%) was recovered in ether.

(*d*) Hydrogen sulphide was evolved from a boiling solution of compound (II) in ethylene glycol and, after 4 hr., the pyridazine was recovered in 80% yield.

(*e*) The pyridazine was formed by refluxing a solution of the *SS*-dioxide (II; SO_2 for S) in ethanol for 8 hr. (yield, 80%) or in acetic acid for 1 hr. (yield, 90%).

2,7-*Dihydro*-3,6-*diphenyl*-1,4,5-*thiadiazepine* 1-*oxide*, m. p. 181° (decomp.) (from ethanol), was obtained by oxidising the dihydrothiadiazepine with hydrogen peroxide in cold acetic acid, or, more conveniently, by adding 30% hydrogen peroxide (1 ml.) to a solution of the dihydrothiadiazepine (0·1 g.) in acetic acid (2·5 ml.) at 100°, heating the whole until the suspension became clear, and quenching the reaction by cooling and adding water (Found: C, 68·05; H, 4·8. $C_{16}H_{14}N_2OS$ requires C, 68·05; H, 5·0%). It was oxidised to the 1,1-dioxide by potassium permanganate in cold aqueous acetic acid.

3,5-*Diphenylpyrazole* [20] (X), m. p. 199° (from benzene) (additionally characterised by its picrate,[21] m. p. 160°, and 1-acetyl derivative,[22] m. p. 85°) separated on concentrating, or diluting with water, the reaction solutions which were formed with evolution of hydrogen sulphide when (*a*) the dihydrothiadiazepine (II) was heated under reflux with hydrogen peroxide in ethanol for 1 hr., or (*b*) the *S*-mono-oxide was heated in acetic acid at 100° for 10 min.

2,5-*Diphenyl*-1,3,4-*oxadiazole* (XII).—When a solution of either the dihydrothiadiazepine or 3,5-diphenylpyrazole in acetic acid was heated with hydrogen peroxide at 100° for 1½ hr., subsequent addition of water produced only slight turbidity and ultimately a small amount of solid. This was shown to be the oxadiazole,[23] m. p. and mixed m. p. 138° (from ethanol). The reaction mother-liquor was partially neutralised with solid sodium carbonate and extracted with chloroform. The extract was washed with aqueous sodium carbonate (which removed some benzoic acid), dried, and evaporated, affording 1,2-dibenzoylhydrazine,[24] m. p. 238—241° (from chloroform).

2,7-*Dihydro*-3,6-*di*-p-*bromophenyl*-1,4,5-*thiadiazepine*, m. p. 202° (from benzene–petroleum), was obtained from di-4-bromophenacyl sulphide [25] as described for compound (II) (Found: C, 45·7; H, 2·9; N, 6·8. $C_{16}H_{12}Br_2N_2S$ requires C, 45·3; H, 2·8; N, 6·6%) and afforded the 1,1-*dioxide*, m. p. 225° (from chloroform), when oxidised by potassium permanganate in acetic acid (Found: C, 42·1; H, 2·8; N, 5·9. $C_{16}H_{12}Br_2N_2O_2S$ requires C, 42·1; H, 2·6; N, 6·1%).

This thiadiazepine (*a*) in refluxing ethylene glycol or (*b*) when treated with *N*-bromosuccinimide in carbon tetrachloride gave 3,6-di-*p*-bromophenylpyridazine,[26] m. p. 288° (from ethanol), which was also formed when a solution of the dioxide in acetic acid was heated under

[19] Paal and Schulze, *Ber.*, 1900, **33**, 3798.
[20] Freudenberg and Stoll, *Annalen*, 1924, **440**, 45.
[21] von Auwers and Bergmann, *Annalen*, 1929, **472**, 308.
[22] Widman, *Ber.*, 1916, **49**, 483.
[23] Stollé, *J. prakt. Chem.*, 1904, **69**, 157.
[24] Hatt, *Org. Synth.*, Coll. Vol. II, p. 208.
[25] Chrzaszczewska and Chwalinski, *Chem. Abs.*, 1929, **23**, 1629.
[26] Campbell and Khanna, *J.*, 1949, S33.

reflux, or when di-4-bromophenacyl sulphone [27] was treated with hydrazine hydrate in warm acetic acid.

3,5-*Di*-p-*bromophenylpyrazole*, 262° (from benzene), was obtained when the preceding dihydrothiadiazepine was oxidised with hydrogen peroxide in ethanol (Found: C, 47·7; H, 2·4; N, 7·2. $C_{15}H_{10}Br_2N_2$ requires C, 47·65; H, 2·6; N, 7·4%). Its 1-*acetyl derivative* had m. p. 176° (from petroleum) (Found: C, 48·6; H, 2·9; N, 6·9. $C_{17}H_{12}Br_2N_2O$ requires C, 48·6; H, 2·9; N, 6·7%).

Di-4-*methylphenacyl sulphone*, m. p. 148° (from ethanol), was prepared from the sulphide [25] by oxidation with potassium permanganate in acetic acid (Found: C, 65·3; H, 5·35. $C_{18}H_{18}O_4S$ requires C, 65·45; H, 5·5%).

2,7-*Dihydro*-3,6-*di*-p-*tolyl*-1,4,5-*thiadiazepine*, m. p. 215° (from ethyl acetate), was obtained from di-4-methylphenacyl sulphide and hydrazine hydrate (Found: C, 73·2; H, 5·9; N, 9·6. $C_{18}H_{18}N_2S$ requires C, 73·45; H, 6·1; N, 9·5%). When oxidised by potassium permanganate in acetic acid it gave the 1,1-*dioxide*, m. p. 208° (from chloroform), also obtained from di-4-methylphenacyl sulphone and hydrazine hydrate (Found: C, 66·1; H, 6·0; N, 8·5. $C_{18}H_{18}N_2O_2S$ requires C, 66·2; H, 5·6; N, 8·6%).

This thiadiazepine (*a*) when treated with *N*-bromosuccinimide in carbon tetrachloride or (*b*) in refluxing ethylene glycol gave 3,6-di-*p*-tolylpyridazine,[26] m. p. 236° (from ethanol), which was also obtained by heating a solution of the 1,1-dioxide in acetic acid.

3,5-*Di*-p-*tolylpyrazole*, m. p. 237° (from benzene), was obtained when the preceding dihydrothiadiazepine was oxidised by hydrogen peroxide in ethanol (Found: C, 82·1; H, 6·3; N, 11·4. $C_{17}H_{16}N_2$ requires C, 82·2; H, 6·5; N, 11·3%). Its *N*-acetyl derivative underwent hydrolysis during attempted crystallisation.

Reactions of Desyl Sulphide and Sulphone.—Hydrogen sulphide was evolved when a solution of desyl sulphide [16] and hydrazine hydrate in ethanol was heated under reflux for 1½ hr. The cooled solution, neutralised with dilute acetic acid, afforded a solid which on fractional crystallisation gave (*a*) deoxybenzoin azine,[28] m. p. 164° (from benzene), and (*b*) benzyl monohydrazone,[29] m. p. 153° (from benzene–petroleum).

Desyl sulphone, m. p. 228° (from chloroform–petroleum), was prepared from the sulphide and hydrogen peroxide in acetic acid at 100° (Found: C, 73·6; H, 5·0. $C_{28}H_{22}O_4S$ requires C, 74·0; H, 4·9%). Suspended in boiling ethanol it reacted with hydrazine hydrate or with 4N-potassium hydroxide, forming dibenzyl sulphone,[30] m. p. 151° (from ethanol), which separated upon concentration of the resultant solution.

Action of Sodium Ethoxide on 2,7-*Dihydro*-3,6-*diphenyl*-1,4,5-*thiadiazepine* 1,1-*Dioxide.*—(*a*) A suspension of the powdered dioxide (0·4 g.) in a cold ethanolic solution (13·6 ml.) of sodium ethoxide (from 0·57 g. of sodium in 250 ml. of ethanol) was shaken for 15 hr. and the resultant solution was diluted with water and acidified. The crude precipitated acid had m. p. 106—112° (with effervescence), but crystallisation from ethanol gave 3,6-diphenylpyridazine as the only product identified.

(*b*) The dioxide (1 g.) rapidly dissolved when heated with the sodium ethoxide solution (34 ml.) and, after 1½ hr. under reflux, water (25 ml.) was added, the ethanol was removed, and the clear aqueous solution was cooled and acidified. The colourless precipitate (0·9 g.) afforded 4,5-*diphenylpyrazol*-3-*ylmethanesulphinic acid*, m. p. 165—167° with effervescence (from ethanol) (Found: C, 64·6; H, 4·8; N, 9·25. $C_{16}H_{14}N_2O_2S$ requires C, 64·4; H, 4·75; N, 9·4%). The corresponding *methyl sulphone* was formed when a solution of the sulphinic acid (0·3 g.) in N-sodium hydroxide (3 ml.) was treated with a little ethanol and then shaken for 15 min. with an excess of methyl iodide. Removal of the volatile compounds gave the sulphone as colourless needles (from ethanol) which at first had m. p. 144—146°, becoming after storage or recrystallisation m. p. 156°, ν 1306 and 1130 cm.$^{-1}$ (KCl disc) (Found: C, 65·6; H, 5·2; N, 9·0. $C_{17}H_{16}N_2O_2S$ requires C, 63·35; H, 5·15; N, 9·0%).

3-Methyl-4,5-diphenylpyrazole (XIII), m. p. 181—182° (from ethanol), was prepared as described by Parham and Hasek and was further characterised as its N-*acetyl derivative*, m. p. 78° (from petroleum) (Found: C, 78·1; H, 5·9; N, 10·0. $C_{18}H_{16}N_2O$ requires C, 78·2; H, 5·8; N, 10·1%). The same pyrazole was obtained from the foregoing sulphinic acid (*a*) by melting

[27] Baliah and Rangarajan, *J. Org. Chem.*, 1961, **26**, 970.
[28] Robinson and Robinson, *J.*, 1918, **113**, 644.
[29] Ritter and Wiedeman, *J. Amer. Chem. Soc.*, 1929, **51**, 3584.
[30] Smythe, *J.*, 1912, **101**, 2079.

it and recovering from the melt after effervescence had ceased, (*b*) by heating it (1·25 g.) in boiling ethylene glycol (20 ml.) for 30 min. (yield, 0·95 g.), and (*c*) by heating it for 3 hr. in ethanol with concentrated hydrochloric acid or for 30 min. in boiling acetic acid.

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