The Preparation and Properties of Some Derivatives of 1-*Phenylpyrazole.*

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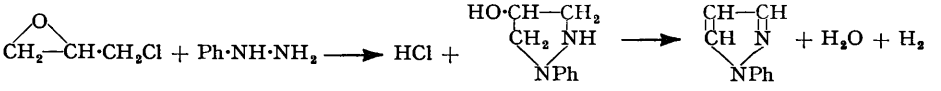
The preparation of 1-phenylpyrazole from epichlorohydrin and phenylhydrazine has been improved, and the method has been extended to include the use of nitrophenylhydrazines. Some 4-substituted derivatives of 1-phenylpyrazole have been prepared, and their properties have been investigated.

1-PHENYLPYRAZOLE is best prepared by a modification of Balbiano's method (*Gazzetta*, 1887, **17**, 177; 1889, **19**, 128); yield was raised from 58 to 72% (cf. Stoermer and Martinsen, *Annalen*, 1907, **352**, 333; Knorr and Laubman; *Ber.*, 1889, **22**, 180; Claisen, *Ber.*, 1903, **36**, 3664; Alvisi, *Gazzetta*, 1892, **22**, 158); 4-hydroxy-1-phenylpyrazolidine is known to be an intermediate (Gerhard, *Ber.*, 1891, **24**, 352), and we have shown that, when heated to 150°, the latter decomposes to give 1-phenylpyrazole:



The corresponding two *p*-tolyl compounds were similarly prepared, but pyrazolidines could not be obtained in the preparation of 1-*o*-tolyl-, 1-*m*-nitrophenyl-, or 1-*p*-nitrophenylpyrazole.

Attempts to prepare 1-*o*-nitrophenyl- and 1-(2 : 4-dinitrophenyl)-pyrazole (Copenhaver, U.S.P. 2,515,160; 2,527,533) failed. Balbiano's original method gave better yields of *o*- and *p*-tolylpyrazole (*Gazzetta*, 1888, **18**, 362, 368) than our modified method, and so was used for 1-*m*-tolylpyrazole.

Chloromethylation of 1-phenylpyrazole, best carried out in boiling ligroin by Blanc's

method (*Bull. Soc. chim.*, 1923, **33**, 313) using zinc chloride and sulphuric acid, gave the 4-chloromethyl derivative. Reaction in aqueous media (Cambron, *Canad. J. Res.*, 1939, **17**, *B*, 10) and working up with propanol (Dvoretzky and Richter, *J. Org. Chem.*, 1950, **15**, 1285), gave 4-chloromethyl-1-phenylpyrazole and 1-phenyl-4-propoxymethylpyrazole, with smaller amounts of di-(1-phenyl-4-pyrazolyl)methane and di-(1-phenyl-4-pyrazolylmethyl) ether. The propoxymethyl compound was also obtained by heating the chloromethyl compound with propanol; this unusual reactivity of the chloromethyl group (cf. 1-benzyl-4-chloromethylpyrazole hydrochloride; Jones, *J. Amer. Chem. Soc.*, 1949, **71**, 3994) is confirmed by hydrolysis of 4-chloromethyl-1-phenylpyrazole with boiling water to the pyrazolylmethyl ether as sole product. This ether is obtained by self-condensation of 4-hydroxymethyl-1-phenylpyrazole (prepared from its acetyl derivative) in the presence of zinc chloride and sulphuric acid or by heating the hydroxymethyl compound with 4-chloromethyl-1-phenylpyrazole, and the last reaction presumably occurs during the hydrolysis by water.

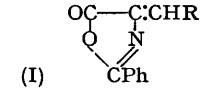
Although obtained in the aqueous chloromethylations, di-(1-phenyl-4-pyrazolyl)-methane was not formed under anhydrous conditions. It was, however, formed by heating 1-phenylpyrazole in water with paraformaldehyde (no hydrochloric acid), 4-chloromethyl-1-phenylpyrazole, or 4-hydroxymethyl-1-phenylpyrazole: 1-phenylpyrazole fails to condense with its 4-chloromethyl derivative in ligroin, where no hydrolysis is possible, so that the hydroxymethyl compound is probably an intermediate in the formation of di-(1-phenyl-4-pyrazolyl)methane (cf. Elderfield, " Heterocyclic Compounds," John Wiley and Sons, Inc., New York, 1950, Vol. I, p. 318; Stephen, Short, and Gladding, *J.*, 1920, **117**, 511).

The dipyrazolylmethane was oxidised by alkaline permanganate to di-(1-phenyl-4-pyrazolyl) ketone; the homologue, di-(1-phenyl-4-pyrazolyl)ethane, was prepared from 4-chloromethyl-1-phenylpyrazole by the Wurtz reaction. The chloromethyl compound was oxidised by alkaline permanganate to 1-phenylpyrazole-4-carboxylic acid, apparently the best route to the acid (cf. Balbiano and Marchetti, *Gazzetta*, 1893, **23**, 484; Claisen, *Annalen*, 1897, **295**, 319; Wislicenus and Bindemann, *Annalen*, 1901, **316**, 36; Dyer and Johnson, *J. Amer. Chem. Soc.*, 1934, **56**, 223; Panizzi, *Gazzetta*, 1946, **76**, 56).

Attempts to prepare 4-cyanomethyl-1-phenylpyrazole from the chloromethyl compound failed.

By the Sommelet reaction (Sommelet, *Compt. rend.*, 1913, **157**, 852; Angyal, Morris, Tetaz, and Wilson, *J.*, 1950, 2144), 4-chloromethyl-1-phenylpyrazole was converted into 4-formyl-1-phenylpyrazole, which was converted into the acid by permanganate, and by the Cannizzaro reaction (Cannizzaro, *Annalen*, 1853, **88**, 129) gave 4-hydroxymethyl-1-phenylpyrazole and 1-phenylpyrazole-4-carboxylic acid; by the Doebner modification of the Knoevenagel condensation (Doebner, *Ber.*, 1900, **33**, 2140) or by the Perkin reaction (Kalnin, *Helv. Chim. Acta*, 1928, **11**, 977) it gave β-(1-phenyl-4-pyrazolyl)acrylic acid.

The Erlenmeyer azlactone condensation with hippuric acid (Kropp and Decker, *Ber.*, 1909, **42**, 1184) gave 2-phenyl-4-(1-phenyl-4-pyrazolylmethylene)oxazol-5-one (I), reduced by red phosphorus and hydriodic acid (Gillespie and Snyder, *Org. Synth.*, 1934, **14**, 80) to α-amino-β-(1-phenyl-4-pyrazolyl)propionic acid (II). The pyrazole-aldehyde condenses with acetone to form 4-(1-phenyl-4-pyrazolyl)but-3-en-2-one (III) and 1 : 5-di-(1-phenyl-4-pyrazolyl)penta-1 : 4-dien-3-one (IV) (Claisen, *Ber.*, 1881, **14**, 2468, 2470), even when excess of acetone is used.

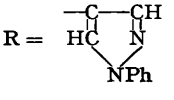


(I)

$HO_2C{\cdot}CH(NH_2){\cdot}CH_2R$ (II)

$CH_3{\cdot}CO{\cdot}CH{:}CHR$ (III)

$R{\cdot}CH{:}CH{\cdot}CO{\cdot}CH{:}CHR$ (IV)

R = 

4-Acetoxymercuri-1-phenylpyrazole was prepared by direct mercuration of the pyrazole (cf. Paolini and Silbermann, *Gazzetta*, 1915, **45**, II, 385), and was orientated by conversion into 4-bromo-1-phenylpyrazole (Balbiano, *Gazzetta*, 1889, **19**, 128). The acetoxymercuri-compound with sodium chloride in aqueous acetic acid (Whitmore and Hanson, *Org. Synth.*, 1925, **4**, 13) gave 4-chloromercuri-1-phenylpyrazole, similarly converted into 4-bromo-1-phenylpyrazole. The chloromercuri-compound was also

prepared directly with mercuric chloride (cf. Gilman and Wright, *J. Amer. Chem. Soc.*, 1933, **55**, 302). Both mercuri-compounds regenerated 1-phenylpyrazole on treatment with dilute hydrochloric acid (cf. Dimroth, *Ber.*, 1899, **32**, 759).

1-Phenyl-4-thiocyanatopyrazole was obtained by the action of thiocyanogen on either of the mercuri-compounds (cf. Söderbäck, *Annalen*, 1919, **419**, 217), but direct thiocyanation of 1-phenylpyrazole (cf. Kaufmann and Liepe, *Ber.*, 1923, **56**, 2514) gave only thiocyanogen polymers. Reduction of the thiocyano-compound with zinc and acetic acid produced an oil with a thiol odour, which with benzyl chloride produced 4-benzylthio-1-phenylpyrazole.

Even under forcing conditions, with methylmagnesium iodide (de Jonge, den Hertog, and Wibaut, *Rec. Trav. chim.*, 1951, **70**, 989), 4-chloromethyl-1-phenylpyrazole gave no Grignard compound. Under similar conditions, however, 4-bromo-1-phenylpyrazole gave a small yield of the Grignard compound, as indicated by its conversion into 1-phenylpyrazole-4-carboxylic acid on treatment with carbon dioxide.

Experimental

Light petroleum was material of b. p. 40—60°, ligroin had b. p. 90—100°.

1-*Phenylpyrazole.*—To epichlorohydrin (40 g.) in 60% ethanol (150 c.c.) contained in a 2-l. flask was added phenylhydrazine (95 g.). The mixture was warmed cautiously on the steam-bath until the vigorous reaction began (external cooling then necessary), then, when the reaction subsided, refluxed for 1 hr. The solvent was then evaporated, and the residue heated at 170° (bath). After about 30 min. the solid mass changed to a dark brown liquid and a vigorous reaction set in, with evolution of water and ammonia. Removal of the bath was necessary at this stage to moderate the reaction; after the reaction had subsided, the bath was replaced and the temperature was raised to 200° for a further 10 min. Water (1·5 l.) was added, and the mixture was extracted 7—8 times with ether. After removal of the ether, vacuum-distillation gave aniline (32 g.), b. p. 30—58°/0·01 mm., and 1-phenylpyrazole (44·9 g., 72%), b. p. 58—62°/0·01 mm. The aniline may also be removed by washing with a large amount of N-hydrochloric acid.

4-*Hydroxy*-1-*phenylpyrazolidine.*—Phenylhydrazine (10 g.) and epichlorohydrin (4·2 g.) were refluxed in dry benzene (40 c.c.) for 4 hr. The liquid was cooled and filtered, and the filtrate evaporated to small bulk. This was washed with N-hydrochloric acid, and the residual benzene was then evaporated. Recrystallisation of the solid residue from benzene (charcoal) gave the pyrazolidine (0·95 g., 12·6%), m. p. 99—101°. Repeated recrystallisation gave very pale yellow needles, m. p. 102—103° (Gerhard, *loc. cit.*, gives m. p. 103—104°). When this was heated at 150° for a few minutes, 1-phenylpyrazole was obtained.

4-*Hydroxy*-1-p-*tolylpyrazolidine.*—A similar procedure gave 4-*hydroxy*-1-p-*tolylpyrazolidine* (7·2%), pale yellow plates, m. p. 107—108° (Found: C, 67·9; H, 7·1. $C_{10}H_{14}ON_2$ requires C, 67·5; H, 7·8%). At 150° this gave 1-*p*-tolylpyrazole, characterised as the 4-*bromo*-derivative, colourless needles (from ethanol), m. p. 90·5—91° (Found: N, 12·1; Br, 33·8. $C_{10}H_9N_2Br$ requires N, 11·8; Br, 33·75%).

1-*Nitrophenylpyrazoles.*—Equimol. quantities of *p*- or *m*-nitrophenylhydrazine and epichlorohydrin were refluxed in absolute ethanol for about 12 hr. After evaporation of the alcohol, the residue was heated in a bath, the temperature of which was raised from 120° to 170° during 1 hr. for the *m*-isomer, but to 140° for the *p*-isomer. The bath was removed when necessary to control the reaction. The residue was cooled and extracted several times with hot ethyl acetate, and the combined extracts were washed with 7N-hydrochloric acid. The extracts were evaporated, and the residue was heated on the water-bath to remove nitrobenzene. The residual solid was then crystallised, to give 1-m-*nitrophenylpyrazole* (20%), pale yellow rhombs (from benzene–light petroleum and charcoal), m. p. 94·5—95° (Found: C, 57·3; H, 3·7; N, 21·9. $C_9H_7O_2N_3$ requires C, 57·2; H, 3·7; N, 22·2%), or 1-*p*-nitrophenylpyrazole (42%), pale yellow rhombs (from ethyl acetate), m. p. 169·5—170° (D'Alcontres, *Gazzetta*, 1950, **80**, 441, gives m. p. 168·5—169°) (Found: C, 57·1; H, 3·8; N, 22·0%).

4-*Chloromethyl*-1-*phenylpyrazole.*—A mixture of 1-phenylpyrazole (21·6 g.), paraformaldehyde (7·5 g.), pulverised anhydrous zinc chloride (2·0 g.), and concentrated sulphuric acid (2 drops) was mechanically stirred in refluxing ligroin (250 c.c.), and a stream of dry hydrogen chloride was passed in for 90 min. The ligroin was decanted, and the residue refluxed with 10 × 30 c.c. portions of benzene; the benzene extracts were added to the ligroin, and the whole was washed

with aqueous sodium hydrogen carbonate. Distillation under reduced pressure gave 1-phenylpyrazole (0·8 g.), b. p. 60—107°/0·03 mm., and 4-chloromethyl-1-phenylpyrazole (16·5 g.; 57%), b. p. 108—110°/0·03 mm., white plates (from benzene–light petroleum), m. p. 68—69° (Found: C, 61·6; H, 4·4; N, 14·9; Cl, 18·7. $C_{10}H_9N_2Cl$ requires C, 62·3; H, 4·7; N, 14·55; Cl, 18·45%). The compound gradually decomposes in a stoppered bottle. When refluxed with alkaline permanganate the chloromethyl compound (0·4 g.) gave 1-phenylpyrazole-4-carboxylic acid (0·37 g., 95%), colourless needles (from water), m. p. 221—223°; its methyl ester formed colourless needles (from methanol), m. p. 127—128·5°.

4-*Hydroxymethyl*-1-*phenylpyrazole*.—The chloromethyl compound (2·0 g.) and silver acetate (1·74 g.) were refluxed in glacial acetic acid (275 c.c.) until the precipitate coagulated. 4-*Acetoxymethyl*-1-*phenylpyrazole* (2·0 g., 89%) was obtained; recrystallisation gave colourless plates (from light petroleum), m. p. 41·5—42° (Found: N, 12·6. $C_{12}H_{12}O_2N_2$ requires N, 13·0%). Hydrolysis with aqueous potassium carbonate gave the 4-*hydroxymethyl* compound (1·2 g., 74%), colourless needles (from benzene–light petroleum), m. p. 60·5—61° (Found: C, 68·5; H, 5·85; N, 15·5. $C_{10}H_{10}ON_2$ requires C, 68·9; H, 5·75; N, 16·1%). The p-*nitrobenzoyl* derivative crystallised in colourless needles (from ethanol), m. p. 153—154° (Found: N, 12·5. $C_{17}H_{13}O_4N_3$ requires N, 13·0%).

Di-(1-*phenyl*-4-*pyrazolylmethyl*) *Ether*.—Equimol. quantities of the 4-hydroxymethyl and the 4-chloromethyl compound were heated on the steam-bath for 5 min., the oil solidifying. The *ether* (43%) was obtained as colourless plates (from benzene), m. p. 168—168·5° (Found: C, 72·6; H, 5·85; N, 17·1. $C_{20}H_{18}ON_4$ requires C, 72·7; H, 5·45; N, 17·0%). It was also prepared by heating for 1 hr. the 4-hydroxymethyl compound in ligroin in the presence of zinc chloride and sulphuric acid; the ether (31%) crystallised on cooling.

Di-(1-*phenyl*-4-*pyrazolyl*)*ethane*.—4-Chloromethyl-1-phenylpyrazole (1·92 g.) was refluxed for 5 hr. in dry ether (30 c.c.) with sodium (0·46 g.). *Di*-(1-*phenyl*-4-*pyrazolyl*)*ethane* (0·2 g., 12·7%) crystallised in colourless needles (from benzene–ligroin), m. p. 120·5—121·5° (Found: C, 76·4; H, 5·65; N, 17·4. $C_{20}H_{18}N_4$ requires C, 76·4; H, 5·7; N, 17·8%).

1-*Phenyl*-4-*propoxymethylpyrazole*.—The chloromethyl compound (0·5 g.) was refluxed for 2 hr. in *n*-propanol (10 c.c.), giving the *propoxymethyl* derivative (0·45 g., 80%), m. p. 36—37°, b. p. 96°/0·05 mm. (Found: C, 72·4; H, 7·5; N, 12·7. $C_{13}H_{16}ON_2$ requires C, 72·2; H, 7·4; N, 12·95%).

Di-(1-*phenyl*-4-*pyrazolyl*)*methane*.—A mixture of 1-phenylpyrazole (8·64 g.), paraformaldehyde (2·4 g.), water (25 c.c.), phosphoric acid (*d* 1·75; 12 c.c.), and glacial acetic acid (20 c.c.) was heated on the water-bath for 12 hr., cooled, and diluted with water (1·2 l.). The solid (2·05 g.) was filtered off; the filtrate on evaporation under reduced pressure to half its bulk gave a further 1·25 g. of the solid. The combined product was washed with sodium carbonate solution and dried; on crystallisation from ligroin (charcoal), 1·8 g. of white crystals, m. p. 85—95°, were obtained. This product was distilled under reduced pressure, to give 1·3 g. of a product melting above 100°, b. p. 300—305°/10 mm. On crystallisation, first from ligroin (charcoal), and then from methanol (charcoal), *di*-(1-*phenyl*-4-*pyrazolyl*)*methane* was obtained as white needles (0·9 g., 10%), m. p. 113—114°. Repeated crystallisation gave colourless needles, m. p. 115—116° (Found: C, 75·75; H, 5·17; N, 19·1. $C_{19}H_{16}N_4$ requires C, 76·0; H, 5·33; N, 18·7%).

Di-(1-*phenyl*-4-*pyrazolyl*) *Ketone*.—The methane derivative (1·1 g.) was refluxed with alkaline permanganate for 3 hr., thereby giving the *ketone* (0·52 g., 45%), colourless needles (from benzene), m. p. 221° (Found: C, 72·1; H, 4·6; N, 18·1. $C_{19}H_{14}ON_4$ requires C, 72·6; H, 4·45; N, 17·8%). The *oxime* crystallised in white rosettes (from alcohol), m. p. 149·5—150° (Found: C, 69·0; H, 4·8; N, 21·2. $C_{19}H_{15}ON_5$ requires C, 69·3; H, 4·55; N, 21·3%).

4-*Formyl*-1-*phenylpyrazole*.—The general method of Angyal *et al.* (*loc. cit.*) was followed, using 4-chloromethyl-1-phenylpyrazole (8·8 g.). The *aldehyde* (5·65 g., 76·5%) was obtained as colourless needles (from aqueous ethanol), m. p. 85° (Found: C, 69·3; H, 4·5; N, 16·7. $C_{10}H_8ON_2$ requires C, 69·8; H, 4·65; N, 16·3%). The *oxime* formed needles (from aqueous ethanol), m. p. 167—167·5° (Found: N, 22·5. $C_{10}H_9ON_3$ requires N, 22·7%), and the *anil* colourless prisms (from ligroin), m. p. 120·5—121° (Found: N, 16·6. $C_{16}H_{13}N_3$ requires N, 17·0%). Oxidation of the aldehyde with alkaline permanganate gave 1-phenylpyrazole-4-carboxylic acid (73%), m. p. 221—222°.

Cannizzaro Reaction with the Aldehyde.—The aldehyde (1·7 g.) was kept at room temperature for 65 hr. in a solution of potassium hydroxide (6 g.) in water (6 c.c.). The product was extracted with ether, and by exhaustive extraction of the ethereal solution with sodium hydrogen sulphite solution the bisulphite compound of the unchanged aldehyde (0·54 g.) was

precipitated, and was filtered off. The ether filtrate gave 4-hydroxymethyl-1-phenylpyrazole (0·35 g.), m. p. 59—60°. The alkaline portion, on acidification, gave 1-phenylpyrazole-4-carboxylic acid (0·6 g.), m. p. 217—219°.

β-(1-*Phenyl*-4-*pyrazolyl*)*acrylic Acid.*—The aldehyde (0·85 g.) was heated at 85° for 1 hr. with malonic acid (1·04 g.) in pyridine (4 c.c.) and piperidine (0·01 c.c.) (all dry) and then the solution was refluxed for 2 hr. The crude *acrylic acid* was obtained by acidification with dilute hydrochloric acid; it gave colourless needles (0·77 g., 73%), m. p. 185—186°, from aqueous acetic acid. Repeated crystallisation raised the m. p. to 186—187° (Found: C, 67·1; H, 4·7; N, 12·6. $C_{12}H_{10}O_2N_2$ requires C, 67·3; H, 4·7; N, 13·1%). The acid was also obtained by heating the aldehyde (0·85 g.) with fused potassium acetate (0·77 g.) in acetic anhydride (0·71 c.c.) at 160° for 1 hr., and then at 175—180° for 3 hr. The acrylic acid (0·36 g., 34%), m. p. 185—186°, was obtained by extracting the product with aqueous sodium carbonate, acidifying, and crystallising the precipitate from aqueous acetic acid.

2-*Phenyl*-4-(1-*phenyl*-4-*pyrazolylmethylene*)*oxazol*-5-*one* (I).—The aldehyde (0·43 g.), hippuric acid (0·45 g.), and fused sodium acetate (0·41 g.) were refluxed in acetic anhydride (1·4 c.c.) for 1 min., and then heated on the steam-bath for 30 min. The mixture was kept overnight with excess of cold water, and the crude *oxazolone* was filtered off. Recrystallisation (from benzene–light petroleum) gave fine, yellow needles (1·1 g., 71%), m. p. 182·5—183° (Found: C, 72·9; H, 4·3; N, 13·0. $C_{19}H_{13}O_2N_3$ requires C, 72·4; H, 4·1; N, 13·3%).

α-*Amino*-β-(1-*phenyl*-4-*pyrazolyl*)*propionic Acid* (II).—The oxazolone was reduced with red phosphorus and hydriodic acid, according to the method of Gillespie and Snyder (*loc. cit.*). The precipitated *amino-acid* (0·28 g., 61%) had m. p. 241—242° (decomp.); crystallisation gave colourless leaflets (from water), m. p. 242—243° (decomp.) (Found: C, 62·7; H, 6·1; N, 17·8. $C_{12}H_{13}O_2N_3$ requires C, 62·3; H, 5·6; N, 18·2%).

Condensation of the Aldehyde with Acetone.—The aldehyde (1·72 g.) was dissolved in warm acetone (4·0 c.c.); 12% aqueous sodium hydroxide (0·5 c.c.) was added, and the liquid was warmed to 45°, then kept at room temperature for 24 hr. Ethanol was added, and the solid was filtered off and washed several times with ethanol, and then with water; recrystallisation from chloroform–ethyl acetate gave 1 : 5-*di*-(1-*phenyl*-4-*pyrazolyl*)*buta*-1 : 4-*dien*-3-*one* (IV), pale yellow needles, m. p. 240° (0·36 g., 10%) (Found: C, 74·7; H, 4·9; N, 15·4. $C_{23}H_{18}ON_4$ requires C, 75·4; H, 4·9; N, 15·3%). The original filtrate and washings were further diluted with water, and the precipitate filtered off. The solid was extracted with hot ligroin, and, on cooling, the extract deposited yellow crystals, m. p. 81—82° (0·54 g.). After two more crystallisations from ligroin, 4-(1-*phenyl*-4-*pyrazolyl*)*but*-3-*en*-2-*one* (III) was obtained as pale yellow needles, m. p. 92—93° (0·25 g., 12%). By two further crystallisations the m. p. was raised to 95° (Found: C, 73·6; H, 5·9; N, 13·2. $C_{13}H_{12}ON_2$ requires C, 73·6; H, 5·65; N, 13·2%).

4-*Acetoxymercuri*-1-*phenylpyrazole.*—1-Phenylpyrazole (8·64 g.) and mercuric acetate (19·1 g.) were heated at 90° for 15 min. in acetic acid (75 c.c.); water (30 c.c.) was then added, and the solution was left to crystallise, giving the *acetoxymercuri*-compound (17·5 g., 72·5%), colourless needles, m. p. 191° (Found: Hg, 50·05. $C_{11}H_{10}O_2N_2Hg$ requires Hg, 49·85%). A suspension of the mercuri-compound in chloroform, on treatment with bromine in chloroform, gave 4-bromo-1-phenylpyrazole, m. p. 80—81°. When distilled with dilute hydrochloric acid, the acetoxymercuri-compound gave 1-phenylpyrazole (80%).

4-*Chloromercuri*-1-*phenylpyrazole.*—A solution of sodium chloride (0·33 g.) in 50% aqueous acetic acid (20 c.c.) was added to a solution of the acetoxymercuri-compound (2·2 g.) in the same solvent (70 c.c.) at 90°. The precipitated *chloromercuri*-compound (1·55 g., 75%) crystallised from xylene in colourless needles, m. p. 226° (Found: Cl, 8·9; Hg, 52·5. $C_9H_7N_2ClHg$ requires Cl, 9·4; Hg, 52·9%). 4-Bromo-1-phenylpyrazole, m. p. 80—81°, was obtained by treatment of a suspension of the mercury compound in acetic acid with bromine at room temperature. The chloromercuri-compound gave 1-phenylpyrazole (69%) on distillation with dilute hydrochloric acid.

1-*Phenyl*-4-*thiocyanatopyrazole.*—Bromine (1·6 g.) was added to a suspension of lead thiocyanate (3·3 g.) in dry ether (20 c.c.); the resulting thiocyanogen solution was filtered into a suspension of the 4-acetoxymercuri-compound in dry ether (30 c.c.). The mixture was set aside for 3 hr.; the solid was then filtered off and washed with ether. The combined filtrates were evaporated under reduced pressure at room temperature, and the residue kept for a few days. The yellow crystals were extracted with ether, and the residue was discarded; after concentration, the ethereal solution crystallised, giving 1-*phenyl*-4-*thiocyanatopyrazole* (0·35 g., 18%), m. p. 60—62°. After several crystallisations from ether, white prisms, m. p. 62°, were

obtained (Found : C, 59·1; H, 3·35; N, 21·4; S, 16·4. $C_{10}H_7N_3S$ requires C, 59·7; H, 3·48; N, 20·9; S, 15·9%).

4-Benzylthio-1-phenylpyrazole.—A solution of thiocyanogen in acetic acid was added to a suspension of 4-chloromercuri-1-phenylpyrazole in acetic acid, then set aside for 24 hr. before filtration. The filtrate was boiled with zinc dust for 2·5 hr., filtered, diluted with water, and extracted with ether. Evaporation gave a mixture of oil and crystals; the oil was dissolved in aqueous ethanol, and treated with sodium carbonate and sodium dithionite at 90°. Benzyl chloride was added, and the solution was cooled; the *4-benzylthio-1-phenylpyrazole* was filtered off and recrystallised from ethanol, giving colourless leaflets, m. p. 84·5—85° (Found : N, 9·9; S, 11·3. $C_{16}H_{14}N_2S$ requires N, 10·5; S, 12·0%).

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