513. *Pyrazolidines. Part II.* Acyl Derivatives of 3-Imino-5-oxo-1,2-diphenylpyrazolidines.*

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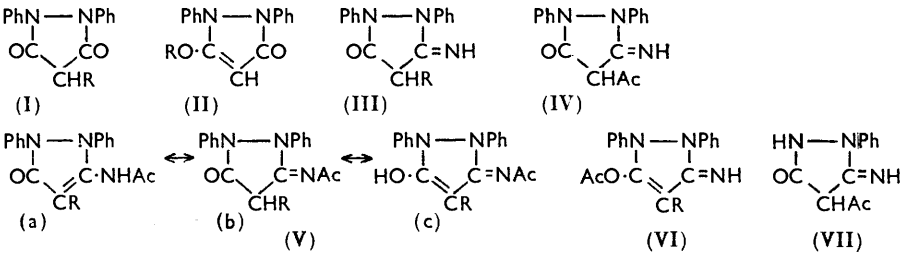
Conversion of 3-imino-5-oxo-1,2-diphenylpyrazolidine into its *N*-acetyl and 4-acetyl derivatives is described. 3-Imino-4-methyl-5-oxo-1,2-diphenylpyrazolidine on acetylation affords an *N*-acetyl derivative and 3-acetamido-5-acetoxy-4-methyl-1,2-diphenylpyrazoline. The *N*-monoacetyl compounds are acidic and can be *N*-methylated, providing a route to 3-methylimino-5-oxo-1,2-diphenylpyrazolidines. Cyclisation of 4-cyanoacetyl-3-imino-5-oxo-1,2-diphenylpyrazolidine into a substituted pyrazolidinopyridine is described.

Acetylation of 3,5-dioxo-1,2-diphenylpyrazolidine (I; R = H) by acetic anhydride–pyridine or by more prolonged treatment with acetic anhydride alone gives the alkali-soluble 4-acetyl-3,5-dioxo-1,2-diphenylpyrazolidine (I; R = Ac) rather than the *O*-acetyl derivative (II; R = Ac).[1] In contrast, treatment of compound (I; R = H) with

* Part I, *J.*, 1960, 1989.

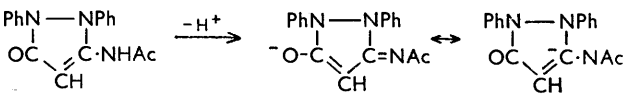
[1] B.P. 778,128.

diazomethane gave 3-oxo-5-methoxy-1,2-diphenylpyrazoline (II; R = Me). 3-Imino-5-oxo-1,2-diphenylpyrazolidine (III; R = H) [2] on acetylation could possibly give three monoacetates, the 4-acetyl derivative (IV), the *N*-acetyl derivative (V; R = H) and the *O*-acetyl derivative (VI; R = H). Heating 3-imino-5-oxo-1,2-diphenylpyrazolidine



(III; R = H) with acetic anhydride gave two monoacetates which were conveniently separated by the solubility of one of them in alkali. The neutral monoacetate, which may also be prepared exclusively by treatment with acetyl chloride in pyridine at 0°, was unaffected by hot aqueous-ethanolic sodium carbonate or sodium hydroxide, whereas sodium carbonate hydrolysed the other to 3-imino-5-oxo-1,2-diphenylpyrazolidine (III; R = H). The stability of the neutral monoacetate towards hydrolysis is characteristic of *C*-acetyl compounds, *e.g.*, (VII) [3]; we have also found that the acetate (I; R = Ac) is stable to alkaline hydrolysis. Since the ferric reaction of the neutral monoacetate eliminates an *O*-acetyl structure we believe that it is 4-acetyl-3-imino-5-oxo-1,2-diphenylpyrazolidine (IV). The longer-wavelength maxima in the ultraviolet spectra of the latter and (I; R = Ac) † are similar, being respectively 265 and 264 mμ in ethanol and, in each case, 264 mμ in aqueous-ethanolic alkali. 4-Acetyl-3-imino-5-oxo-1,2-diphenylpyrazolidine (IV) has also been prepared from 3-imino-5-oxo-1,2-diphenylpyrazolidine (III; R = H) by another route; cyanoacetylation of the latter compound gave 4-cyanoacetyl-3-imino-5-oxo-1,2-diphenylpyrazolidine (III; R = $CO{\cdot}CH_2{\cdot}CN$) which in hot acid gave (IV). 4-Cyanoacetyl-3-imino-5-oxo-1,2-diphenylpyrazolidine, which is alkali-soluble, was also formed as a by-product in the reaction between cyanoacetyl chloride and hydrazobenzene.

The alkali-soluble monoacetate of (III; R = H) was next examined. Its ready hydrolysis suggested the presence of an *O*- or *N*-acetyl group but the red ferric chloride colour favoured the latter structure (V; R = H). The alkali-solubility we attribute to the vinylogous imide feature which allows the formation of the ion as indicated. Support for this process comes from the bathochromic shift in the longer-wavelength ultraviolet maximum from 260 mμ in neutral to 280 mμ in alkaline solution, indicating an increase in conjugation. Prolonged treatment of 3-acetamido-5-oxo-1,2-diphenylpyrazoline (V;

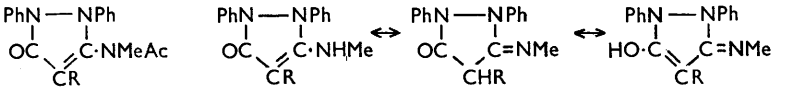


R = H) with diazomethane gave an alkali-insoluble methyl derivative which we formulate as (VIII; R = H) formed from tautomer (Va; R = H); hydrolysis of this compound (VIII; R = H) with sodium carbonate afforded 3-methylimino-5-oxo-1,2-diphenylpyrazolidine (IX; R = H), different from 3-imino-4-methyl-5-oxo-1,2-diphenylpyrazolidine (III; R = Me) [2] and giving a red ferric colour indicating that *N*-methylation had been achieved. The alkali-soluble acetate (V; R = H) was also obtained in low yield by the action of acetyl chloride on the imine (III; R = H) in an inert solvent.

† The acetate (I; R = Ac) has $\lambda_{max.}$ (in EtOH) 212 (ε 13,000) and 264 mμ (ε 29,000), $\lambda_{max.}$ (in NaOH 264 mμ (ε 28,000).

[2] McGee, Murdoch, Newbold, Redpath, and Spring, *J.*, 1960, 1989.
[3] Weissberger and Porter, *J. Amer. Chem. Soc.*, 1943, **65**, 2180.

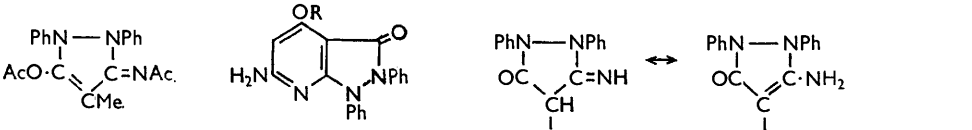
Reaction of the imine (III; R = Me) with acetyl chloride at 0° in the presence of pyridine afforded the alkali-soluble 3-acetylimino-4-methyl-5-oxo-1,2-diphenylpyrazolidine (V; R = Me) which gave a red ferric colour and showed similar ultraviolet properties to (V; R = H). The action of acetic anhydride on the latter gave a neutral diacetate,



(VIII) (IX)

which was also formed by more drastic reaction of (III; R = Me) with acetyl chloride and pyridine, and together with (V; R = Me) by the action of acetic anhydride upon (III; R = Me). Since the diacetate was hydrolysed by sodium carbonate to the monoacetate (V; R = Me), the second acetyl group must have been attached to oxygen and the diacetate therefore has structure (X).

Hydrolysis of the monoacetate (V; R = Me) with sodium hydroxide gave the parent pyrazolidine (III; R = Me). Methylation of the acetate (V; R = Me) with diazomethane afforded compound (VIII; R = Me), hydrolysed to the methylimine (IX; R = Me) by sodium hydroxide. In the 4-methyl series hydrolysis of an *N*-acetyl group requires more drastic conditions than when the 4-position is unsubstituted.



(X) (XI) (XII)

4-Cyanoacetyl-3-imino-5-oxo-1,2-diphenylpyrazolidine (III; R = $CO{\cdot}CH_2{\cdot}CN$) was isomerised by hot aqueous sodium hydroxide or, better, sodium carbonate to an alkali-soluble compound which gave a deep red ferric colour and showed hydrogen-bonded hydroxyl absorption but no cyano-band in the infrared spectrum. We believe that cyclisation has taken place with the formation of 6-amino-2,3-dihydro-4-hydroxy-3-oxo-1,2-diphenylpyrazolo[3,4-*b*]pyridine (XI; R = H); methylation of the latter compound with diazomethane yielded a methyl ether which must be (XI; R = Me) since it was also formed by reaction of (III; R = $CO{\cdot}CH_2{\cdot}CN$) with diazomethane to give 3-imino-4-(1-methoxy-2-cyanovinyl)-5-oxo-1,2-diphenylpyrazolidine (XII), followed by heating to 200°.

Experimental

General directions are given in Part I of this series.

4-Cyanoacetyl-3-imino-5-oxo-1,2-diphenylpyrazolidine.—(*a*) The aqueous sodium hydroxide extract (A) from the preparation of *N*-cyanoacetylhydrazobenzene [2] was acidified (Congo Red) with 2N-hydrochloric acid, and the product isolated by using ether. Crystallisation from methylene chloride–hexane gave *4-cyanoacetyl-3-imino-5-oxo-1,2-diphenylpyrazolidine* (340 mg.) as plates, m. p. 210—211° (Found: C, 67·7; H, 4·5. $C_{18}H_{14}O_2N_4$ requires C, 67·9; H, 4·4%), $\lambda_{max.}$ (in EtOH) 204 (ε 34,000), 231 (ε 25,000) and 270 mμ (ε 21,400), $\nu_{max.}$ 3534, 3257, 2288 (C≡N), 1695 (C=O) and 1653 cm.$^{-1}$ (C=O).

(*b*) To a stirred solution of 3-imino-5-oxo-1,2-diphenylpyrazolidine (600 mg.) in dioxan (20 c.c.) and pyridine (5 c.c.) at 0°, cyanoacetyl chloride (1·5 g.) in chloroform (10 c.c.) was added dropwise. After being kept overnight at room temperature the mixture was treated with water (50 c.c.) and extracted with chloroform (3 × 50 c.c.). The combined extracts were washed successively with 2N-hydrochloric acid (3 × 30 c.c.), alkali, and water (30 c.c.) and dried (Na_2SO_4). Removal of the chloroform gave a negligible quantity of gum. The combined alkaline washings were acidified (Congo Red) with 2N-hydrochloric acid, and the product isolated by using chloroform. Crystallisation from acetone–hexane gave 4-cyanoacetyl-3-imino-5-oxo-1,2-diphenylpyrazolidine (350 mg.) as plates, m. p. and mixed m. p. 208—210° (Found: C, 67·9; H, 4·6%). An ethanolic solution of the compound gave a pale brown colour with aqueous ferric chloride.

4-*Acetyl*-3-*imino*-5-*oxo*-1,2-*diphenylpyrazolidine*.—(*a*) 3-Imino-5-oxo-1,2-diphenylpyrazolidine (2·0 g.) was heated on the steam-bath with acetic anhydride (25 c.c.) for 2 hr. The warm solution was treated with water (20 c.c.) and evaporated under reduced pressure. The solid residue was dissolved in chloroform (50 c.c.) and washed with 2N-sodium hydroxide (3 × 30 c.c.) (extract B), then water (30 c.c.), and dried (Na_2SO_4). Removal of the chloroform and crystallisation of the residue from methylene chloride–hexane gave 4-*acetyl*-3-*imino*-5-*oxo*-1,2-*diphenylpyrazolidine* (500 mg.) as needles, m. p. 207—208° (Found: C, 69·8; H, 5·2. $C_{17}H_{15}O_2N_3$ requires C, 69·6; H, 5·2%), $\lambda_{max.}$ (in EtOH) 208 (ε 20,000), 233 (ε 22,500), and 265 mμ (ε 20,000); $\lambda_{max.}$ (in alkali) 235 (ε 17,000) and 264 mμ (ε 15,000), $\nu_{max.}$ 3333, 3175, and 1695 cm.$^{-1}$ (C=O), $\nu_{max.}$ (in $CHCl_3$) 3425, 3268, and 1692 cm.$^{-1}$ (C=O). An ethanolic solution of the compound gave a red colour with aqueous ferric chloride.

(*b*) A stirred solution of 3-imino-5-oxo-1,2-diphenylpyrazolidine (1·0 g.) in pyridine (50 c.c.) and dioxan (25 c.c.) at 0° was treated with pure acetyl chloride (3·0 g.) in dry ether (25 c.c.) during 30 min. The mixture was kept overnight, diluted with water, and extracted with chloroform. The chloroform extract was washed with 2N-sodium hydroxide, then water, dried (Na_2SO_4), and evaporated. The residual solid was crystallised from methylene chloride–hexane, to give 4-acetyl-3-imino-5-oxo-1,2-diphenylpyrazolidine (800 mg.) as needles, m. p. and mixed m. p. 206—208°. No identifiable material was obtained from the alkaline washings.

(*c*) A solution of 4-cyanoacetyl-3-imino-5-oxo-1,2-diphenylpyrazolidine (500 mg.) in ethanol (18 c.c.), water (18 c.c.), and hydrochloric acid (9 c.c.; *d* 1·15) was heated on the steam-bath for 3 hr., then evaporated to dryness under reduced pressure, and the solid residue was treated with 10% aqueous sodium hydrogen carbonate (30 c.c.) and extracted with ether (3 × 30 c.c.). The ethereal extracts were washed with water, dried (Na_2SO_4), and evaporated. Crystallisation of the residue from acetone–hexane gave 4-acetyl-3-imino-5-oxo-1,2-diphenylpyrazolidine (30 mg.) as needles, m. p. and mixed m. p. 206—208°. 4-Acetyl-3-imino-5-oxo-1,2-diphenylpyrazolidine was recovered unchanged (m. p. and mixed m. p. 206—208°) after 4 hr. in boiling 1 : 1 aqueous-ethanolic M-sodium carbonate and after 1 hr. in 4 : 1 80% aqueous-ethanolic 2·5N-sodium hydroxide.

3-*Acetylimino*-5-*oxo*-1,2-*diphenylpyrazolidine*.—(*a*) Alkaline extract B from the reaction between 3-imino-5-oxo-1,2-diphenylpyrazolidine and acetic anhydride was acidified (Congo Red) with 2N-hydrochloric acid. Isolation of the product by chloroform followed by crystallisation from methylene chloride–hexane gave 3-*acetylimino*-5-*oxo*-1,2-*diphenylpyrazolidine* (300 mg.) as needles, m. p. 204—205° (Found: C, 69·6; H, 5·1. $C_{17}H_{15}O_2N_3$ requires C, 69·6; H, 5·2%), $\lambda_{max.}$ (in EtOH) 204 (ε 20,000) and 260 mμ (ε 18,000), $\lambda_{max.}$ (in alkali) 280 mμ (ε 23,000), $\nu_{max.}$ 3100 and 1718 cm.$^{-1}$ (C=O), $\nu_{max.}$ (in $CHCl_3$) 3333, 1733 (C=O) and 1681 cm.$^{-1}$ (C=O). An ethanolic solution of the compound gave a red colour with aqueous ferric chloride.

(*b*) 3-Imino-5-oxo-1,2-diphenylpyrazolidine (1·0 g.) in dioxan (10 c.c.) was heated with acetyl chloride (20 c.c.) on the steam-bath for 2 hr. The cooled solution was diluted with water (50 c.c.) and extracted with chloroform (3 × 50 c.c.). The chloroform extracts were washed with 2N-sodium hydroxide (3 × 30 c.c.), then with water, and dried (Na_2SO_4). The combined alkaline washings were acidified (Congo Red) with 2N-hydrochloric acid, and the product was isolated by using chloroform. Crystallisation from methylene chloride–hexane gave 3-acetylimino-5-oxo-1,2-diphenylpyrazolidine (50 mg.) as needles, m. p. and mixed m. p. 202—204°. Evaporation of the chloroform solution of the neutral material and crystallisation of the residue from methylene chloride–hexane gave back 3-imino-5-oxo-1,2-diphenylpyrazolidine (600 mg.), m. p. and mixed m. p. 221—223°.

3-*Imino*-5-*oxo*-1,2-*diphenylpyrazolidine*.—3-Acetylimino-5-oxo-1,2-diphenylpyrazolidine (100 mg.) in ethanol (7 c.c.) and aqueous 2M-sodium carbonate (7 c.c.) was refluxed for 2 hr. The cooled solution was extracted with chloroform, the chloroform extract evaporated, and the residue crystallised from acetone–light petroleum (b. p. 60—80°), to give 3-imino-5-oxo-1,2-diphenylpyrazolidine (80 mg.) as plates, m. p. and mixed m. p. 221—223°.

3-N-*Acetylmethylamino*-5-*oxo*-1,2-*diphenylpyrazoline*.—A solution of 3-acetylimino-5-oxo-1,2-diphenylpyrazolidine (830 mg.) in methylene chloride (50 c.c.) was treated with large excess of ethereal diazomethane and kept at 0° for 10 days. After removal of excess of diazomethane by treatment with glacial acetic acid the ethereal solution was washed with 2N-aqueous sodium hydroxide to remove unchanged material, then with water, and dried (Na_2SO_4). The ether was removed and the residue crystallised from ethanol–hexane, to give 3-N-*acetylmethylamino*-5-*oxo*-1,2-*diphenylpyrazoline* (55 mg.) as prisms, m. p. 227—228° (Found: C, 70·3; H, 5·3.

$C_{18}H_{17}O_2N_3$ requires C, 70·3; H, 5·6%), $\lambda_{max.}$ (in EtOH) 205 (ε 14,000), 244 (ε 8000), and 281 mμ (ε 7000), $\lambda_{max.}$ (in alkali) 224 (ε 8000) and 260 mμ (ε 14,000), $\nu_{max.}$ 1681 cm.$^{-1}$ (C=O).

3-*Methylimino*-5-*oxo*-1,2-*diphenylpyrazolidine*.—A solution of 3-*N*-acetylmethylamino-5-oxo-1,2-diphenylpyrazoline (23 mg.) in ethanolic 2M-sodium hydroxide (5 c.c.) was refluxed for 2 hr. The cooled solution was diluted with water (20 c.c.) and extracted with chloroform (2 × 20 c.c.). The dried (Na_2SO_4) chloroform extract was evaporated and the residue crystallised from methylene chloride–hexane, to give 3-*methylimino*-5-*oxo*-1,2-*diphenylpyrazolidine* (15·3 mg.) as needles, m. p. 178—179° (Found: C, 72·09; H, 5·56. $C_{16}H_{15}ON_3$ requires C, 72·43; H, 5·7%), $\lambda_{max.}$ (in EtOH) 210 (ε 13,000) and 256 mμ (ε 22,000), $\lambda_{max.}$ (in alkali) 256 mμ (ε 27,000), $\lambda_{max.}$ (in acid) 208 (ε 18,000) and 266 mμ (ε 18,000), $\nu_{max.}$ (in $CHCl_3$) 3425 (NH) and 1667 cm.$^{-1}$ (C=O). An ethanolic solution of the compound gave a red colour with aqueous ferric chloride.

3-*Acetylimino*-4-*methyl*-5-*oxo*-1,2-*diphenylpyrazolidine*.—(*a*) A stirred solution of 3-imino-4-methyl-5-oxo-1,2-diphenylpyrazolidine (1·0 g.) in dioxan (25 c.c.) and pyridine (5 c.c.) at 0° was treated in 30 min. with acetyl chloride (3 c.c.) in ether (20 c.c.). After 2 hr. the mixture was diluted with chloroform, and washed with 2N-hydrochloric acid, water, and 2N-sodium hydroxide; the alkaline washings, on acidification, isolation through chloroform, and crystallisation from methanol, gave 3-*acetylimino*-4-*methyl*-5-*oxo*-1,2-*diphenylpyrazolidine* (250 mg.) as plates, m. p. 189° (Found: C, 70·1; H, 5·8. $C_{18}H_{17}O_2N_3$ requires C, 70·3; H, 5·6%), $\lambda_{max.}$ (in EtOH) 205 (ε 23,000), 242 (ε 19,600), and 276 mμ (ε 13,500), $\lambda_{max.}$ (in alkali) 272 (ε 24,400), $\nu_{max.}$ 3333, 3106 (NH), 1681 cm.$^{-1}$ (C=O). An ethanolic solution of the compound gave a red colour with aqueous ferric chloride. Evaporation of the chloroform solution of the neutral fraction gave 3-imino-4-methyl-5-oxo-1,2-diphenylpyrazolidine (500 mg.), m. p. and mixed m. p. 180°.

(*b*) 3-Imino-4-methyl-5-oxo-1,2-diphenylpyrazolidine (2·1 g.) was heated on the steam-bath for 3 hr. with acetic anhydride (20 c.c.). The cooled solution was treated with water (20 c.c.) and evaporated to dryness under reduced pressure. The solid residue was taken up in chloroform (50 c.c.) and washed with 2N-sodium hydroxide (3 × 30 c.c.), then water, and dried (Na_2SO_4). Acidification of the combined alkaline phases and isolation by means of chloroform gave 3-acetylimino-4-methyl-5-oxo-1,2-diphenylpyrazolidine (850 mg.), separating from tetrahydrofuran–hexane as prisms, m. p. and mixed m. p. 188—189°. 3-Acetylimino-4-methyl-5-oxo-1,2-diphenylpyrazolidine dissolved in aqueous sodium carbonate but was recovered unchanged on acidification after 2 hours' refluxing. When a solution of the compound (250 mg.) in aqueous 5% sodium hydroxide (30 c.c.) was refluxed for 5 hr. the neutral fraction yielded 3-imino-4-methyl-5-oxo-1,2-diphenylpyrazolidine (150 mg.), m. p. and mixed m. p. 180°, and the acid fraction unchanged acetyl compound (80 mg.), m. p. and mixed m. p. 189°.

5-*Acetoxy*-3-*acetylimino*-4-*methyl*-1,2-*diphenylpyrazoline*.—(*a*) The chloroformic neutral fraction from the action of acetic anhydride on 3-imino-4-methyl-5-oxo-1,2-diphenylpyrazolidine was evaporated to dryness and the residue crystallised from tetrahydrofuran–hexane, to give 3-imino-4-methyl-5-oxo-1,2-diphenylpyrazolidine (400 mg.), m. p. and mixed m. p. 179—180°, as the less soluble component. Concentration of the mother-liquors gave 5-*acetoxy*-3-*acetylimino*-4-*methyl*-1,2-*diphenylpyrazoline* (40 mg.) which separated from chloroform as prisms, m. p. 166—167° (Found: C, 68·2; H, 5·2. $C_{20}H_{19}O_3N_3$ requires C, 68·75; H, 5·5%), $\lambda_{max.}$ (in EtOH) 209 (ε 18,000), 246 (ε 12,000), and 286 mμ (ε 12,000), $\lambda_{max.}$ (in alkali) 228 (ε 49,000) and 278 mμ (ε 17,000), $\lambda_{max.}$ (in acid) 203 (ε 14,000), 210 (ε 11,000), 257 mμ (ε 15,000), $\nu_{max.}$ 1725, 1710, and 1667 cm.$^{-1}$ (C=O).

(*b*) A solution of 3-imino-4-methyl-5-oxo-1,2-diphenylpyrazolidine (1·0 g.) in chloroform (25 c.c.) and pyridine (5 c.c.) was treated without cooling with a solution of acetyl chloride (6 c.c.) in chloroform (25 c.c.). The hot solution was then refluxed for 5 min., cooled, and washed successively with 2N-hydrochloric acid, water, and 3N-sodium hydroxide, the last extract yielding no product on acidification and extraction. After being washed with water, the chloroform solution was dried (Na_2SO_4) and evaporated, and the residue crystallised from chloroform to give 5-acetoxy-3-acetylimino-4-methyl-1,2-diphenylpyrazoline (700 mg.) as prisms, m. p. and mixed m. p. 167°.

(*c*) 3-Acetylimino-4-methyl-5-oxo-1,2-diphenylpyrazolidine (200 mg.) was heated with acetic anhydride (5 c.c.) on the steam-bath for 1 hr. The solution was diluted with water, and the product isolated through chloroform, to give 5-acetoxy-3-acetylimino-4-methyl-5-oxo-1,2-diphenylpyrazoline (150 mg.) as prisms, m. p. and mixed m. p. 167°, from chloroform. 5-Acetoxy-3-acetylimino-4-methyl-1,2-diphenylpyrazoline (250 mg.) in ethanol (10 c.c.) and

aqueous 2M-sodium carbonate (10 c.c.) was refluxed for 1 hr. Acidification and isolation through chloroform gave 3-acetylimino-4-methyl-5-oxo-1,2-diphenylpyrazolidine (200 mg.), m. p. and mixed m. p. 189°.

3-N-*Acetylmethylamino*-4-*methyl*-5-*oxo*-1,2-*diphenylpyrazoline*.—3-Acetylimino-4-methyl-5-oxo-1,2-diphenylpyrazolidine (500 mg.) was treated with ethereal diazomethane as described for the preparation of 3-*N*-acetylmethylamino-5-oxo-1,2-diphenylpyrazoline. Crystallisation of the product from acetone–light petroleum (b. p. 60—80°) gave 3-N-*acetylmethylamino*-4-*methyl*-5-*oxo*-1,2-*diphenylpyrazoline* (400 mg.) as prisms, m. p. 123° (Found: C, 71·4; H, 6·2. $C_{19}H_{19}O_2N_3$ requires C, 71·0; H, 6·0%), $\nu_{max.}$ 1667 and 1650 cm.$^{-1}$ (C=O).

3-*Methylimino*-4-*methyl*-5-*oxo*-1,2-*diphenylpyrazolidine*.—A solution of the foregoing acetyl derivative (150 mg.) in ethanol (5 c.c.) and 5% aqueous potassium hydroxide (5 c.c.) was refluxed for 5 hr., cooled, acidified with 2N-hydrochloric acid, and extracted with chloroform, and the chloroform extract was washed with water, dried (Na_2SO_4), and evaporated. Crystallisation of the residue from methanol gave 3-*methylimino*-4-*methyl*-5-*oxo*-1,2-*diphenylpyrazolidine* (100 mg.) as prisms, m. p. 208° (Found: C, 73·4; H, 6·2. $C_{17}H_{17}ON_3$ requires C, 73·5; H, 5·8%), $\nu_{max.}$ 3210, 3000 (both OH or NH) and 1660 cm.$^{-1}$ (C=O).

3-*Imino*-4-(1-*methoxy*-2-*cyanovinyl*)-5-*oxo*-1,2-*diphenylpyrazolidine*.—A solution of 4-cyanoacetyl-3-imino-5-oxo-1,2-diphenylpyrazolidine (730 mg.) in methylene chloride (30 c.c.) was treated with an excess of ethereal diazomethane, kept overnight, washed with 2N-sodium hydroxide (2 × 50 c.c.), then water, dried (Na_2SO_4), and evaporated. Crystallisation of the residue from acetone–hexane gave 3-*imino*-4-(2-*cyano*-1-*methoxyvinyl*)-5-*oxo*-1,2-*diphenylpyrazolidine* (300 mg.) as needles, m. p. 183—185°, resolidifying and remelting at 265—270° (Found: C, 68·5; H, 5·0. $C_{19}H_{16}O_2N_4$ requires C, 68·7; H, 4·85%), $\lambda_{max.}$ (in EtOH) 207 (ε 24,000), 297 mμ (ε 33,000), $\lambda_{infl.}$ 260 mμ (ε 23,000), $\nu_{max.}$ 3333 (NH), 2222 (C≡N), and 1656 cm.$^{-1}$ (C=O).

Use of diazoethane led to 3-*imino*-4-(2-*cyano*-1-*ethoxyvinyl*)-5-*oxo*-1,2-*diphenylpyrazolidine*, m. p. 162—163° (Found: C, 69·2; H, 5·6. $C_{20}H_{18}O_2N_4$ requires C, 69·35; H, 5·2%).

6-*Amino*-2,3-*dihydro*-4^1-*hydroxy*-3-*oxo*-1,2-*diphenylpyrazolo*[3,4-b]*pyridine*.—(*a*) 4-Cyanoacetyl-3-imino-5-oxo-1,2-diphenylpyrazolidine (1·02 g.) was heated on the steam-bath with aqueous M-sodium carbonate (30 c.c.) for 2 hr. The cooled solution was extracted with chloroform, and the extract rejected. The aqueous phase was acidified (Congo Red) with 2N-hydrochloric acid and extracted with chloroform. A solid which separated at the interface was collected. The chloroform extract was washed with water, dried (Na_2SO_4), and evaporated. The residue was combined with the solid from the interface and crystallised from tetrahydrofuran–hexane, to give the *pyrazolopyridine* (550 mg.) as prisms, m. p. 289—290° (Found: C, 67·5; H, 4·7. $C_{18}H_{14}O_2N_4$ requires C, 67·9; H, 4·4%), $\lambda_{max.}$ (in EtOH) 208 (ε 23,000), 230 (ε 18,000) and 284 mμ (ε 28,000), $\lambda_{max.}$ (in alkali) 233 (ε 24,600), 238 (ε 24,600), and 272 (ε 28,600), $\lambda_{infl.}$ 295 mμ (ε 16,000), $\nu_{max.}$ 3425, 3155 (OH), and 1667 cm.$^{-1}$ (C=O). An ethanolic solution of the compound gave a deep red colour with aqueous ferric chloride.

(*b*) A solution of 4-cyanoacetyl-3-imino-5-oxo-1,2-diphenylpyrazolidine (450 mg.) in aqueous N-sodium hydroxide (25 c.c.) was heated on the steam-bath for 1 hr. Acidification of the cooled solution, isolation by ether, and crystallisation from chloroform–ethanol gave the pyrazolopyridine (40 mg.) as plates, m. p. and mixed m. p. 288—290°.

6-*Amino*-2,3-*dihydro*-4-*methoxy*-3-*oxo*-1,2-*diphenylpyrazolo*[3,4-b]*pyridine*.—(*a*) The foregoing compound (200 mg.) in acetone (30 c.c.) was treated with an excess of ethereal diazomethane overnight. Working up as usual gave the *ether* (120 mg.) as needles (from chloroform–methanol), m. p. 272—273° (Found: C, 68·9; H, 4·8. $C_{19}H_{16}O_2N_4$ requires C, 68·7; H, 4·8%), $\lambda_{max.}$ (in EtOH) 206 (ε 28,000), 230 (ε 18,000), and 288 mμ (ε 28,000), $\nu_{max.}$ 3247, 3145 (both NH) and 1681 cm.$^{-1}$ (C=O), $\nu_{max.}$ (in $CHCl_3$) 3333 (NH) and 1692 cm.$^{-1}$ (C=O).

(*b*) 3-Imino-4-(2-cyano-1-methoxyvinyl)-5-oxo-1,2-diphenylpyrazolidine (50 mg.) was heated at 200° for 30 min. After cooling, the solidified melt crystallised from chloroform–methanol, to give the methoxypyrazolopyridine (20 mg.) as needles, m. p. and mixed m. p. 271—273°.

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