404. *Pyrazolidines. Part I. 3-Imino-5-oxo-1,2-diphenylpyrazolidine and Derivatives.*

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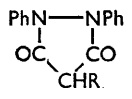
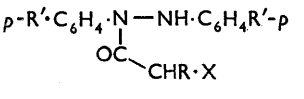
Cyclisation of *N*-cyanoacetylhydrazobenzene or reaction of ethyl cyanoacetate with hydrazobenzene gave 3-imino-5-oxo-1,2-diphenylpyrazolidine. The last compound was best prepared by the action of potassium cyanide on an α-halogenoacylhydrazobenzene. Some reactions of 3-imino-5-oxo-1,2-diphenylpyrazolidine have been studied and it has been converted into the corresponding 3,5-dioxo-compound.

Interest in pyrazolidine derivatives has been stimulated during the last decade by the discovery that phenylbutazone (4-butyl-3,5-dioxo-1,2-diphenylpyrazolidine)[1] (I; R = Bu^n) is of value in the treatment of rheumatoid arthritis and allied conditions. Although a large number of 3,5-dioxo-1,2-diphenylpyrazolidines, substituted in the 4-position or in the phenyl rings or in both, have been described,[1,2] no derivatives have been described in which one of the carbonyl-oxygen atoms in the 1,2-diaryl compounds is replaced by an imino-group.


(I)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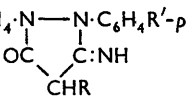

(III)

A possible intermediate for the synthesis of 3-imino-5-oxo-1,2-diphenylpyrazolidine (III; R = R′ = H) is *N*-cyanoacetylhydrazobenzene (II; R = R′ = H, X = CN) and this compound has been mentioned[3] as the product of reaction between hydrazobenzene, cyanoacetic acid, and phosphorus oxychloride in the presence of pyridine. We first examined the reaction of cyanoacetyl chloride with hydrazobenzene in the presence of pyridine and, using 2·5—3 mols. of the acid chloride per mol. of hydrazobenzene, we obtained cyanoacetylhydrazobenzene in *ca.* 30% yield.

N-Cyanoacetylhydrazobenzene (II; R = R′ = H, X = CN) is cyclised to 3-imino-5-oxo-1,2-diphenylpyrazolidine (III; R = R′ = H) when heated with aqueous ethanolic sodium carbonate or, less effectively, by sodium methoxide or ethoxide in the corresponding alcohol. It was also isolated in 9% yield from the mother-liquors of cyanoacetylhydrazobenzene prepared by the acid chloride reaction. Ethyl cyanoacetate with hydrazobenzene in presence of sodium ethoxide gave only an 8% yield of the pyrazolidine (III; R = R′ = H). The most convenient method is reaction of chloroacetylhydrazobenzene[4] with potassium cyanide in aqueous ethanol which gives the pyrazolidine in 57% yield.

4,4′-Dimethylhydrazobenzene was converted into its cyanoacetyl derivative (II; R′ = Me, R = H, X = CN), and the latter when treated with sodium carbonate gave 3-imino-5-oxo-1,2-di-*p*-tolylpyrazolidine which was also prepared in poor yield by base-catalysed interaction between ethyl cyanoacetate and 4,4′-dimethylhydrazobenzene.

Hydrazobenzene with α-chloropropionyl chloride afforded α-chloropropionylhydrazobenzene (II; R = Me, R′ = H, X = Cl); this compound, or α-bromopropionylhydrazobenzene,[5] with aqueous ethanolic potassium cyanide gave 3-imino-4-methyl-5-oxo-1,2-diphenylpyrazolidine (III; R = Me, R′ = H).

[1] B.P. 646,597.

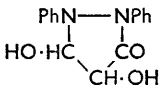
[2] Budziarek, Drain, Macrae, McLean, Newbold, Seymour, Spring, and Stansfield, *J.*, 1953, 3158; Buchi, Ammann, Lieberherr, and Eichenberger, *Helv. Chim. Acta*, 1953, **36**, 75; Pfister and Hafliger, *ibid.*, 1957, **40**, 395; Dens, Hafliger, and Goodwin, *ibid.*, p. 402; U.S.P. 2,700,670, 2,700,671, 2,745,783; Swiss P. 293,925; B.P. 768,813, 769,285, 778,128.

[3] Girod, Delley, and Hafliger, *Helv. Chim. Acta*, 1957, **40**, 408.

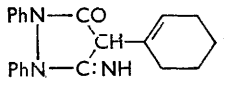
[4] Goldschmidt, *Annalen*, 1924, **437**, 194.

[5] Bischoff, *Ber.*, 1898, **31**, 3241.

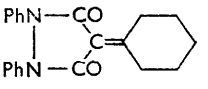
N-Cyanoacetylhydrazobenzene is unaffected by refluxing acetic anhydride for 1 hr. It is insoluble in aqueous mineral acid and aqueous sodium hydroxide, as is 3-imino-5-oxo-1,2-diphenylpyrazolidine. Diazomethane does not react with *N*-cyanoacetylhydrazobenzene or 3-imino-5-oxo-1,2-diphenylpyrazolidine; the latter and the other imino-oxo-compounds described in this paper give red colours with ferric chloride. The position or intensity of the longer-wavelength ultraviolet maximum of 3-imino-5-oxo-1,2-diphenylpyrazolidine is substantially the same in neutral, acid, or alkaline solution; *N*-cyanoacetylhydrazobenzene shows a bathochromic shift from neutral to alkaline solution.



(IV)



(V)



(VI)

Heating 3-imino-5-oxo-1,2-diphenylpyrazolidine or *N*-cyanoacetylhydrazobenzene with aqueous-ethanolic hydrochloric acid gave a mixture of *N*-carboxyacetylhydrazobenzene (II; R = R′ = H, X = CO_2H), its ethyl ester, and a smaller amount of 3,5-dioxo-1,2-diphenylpyrazolidine (I; R = H). The acid (II; R = R′ = H, X = CO_2H), which was thermally decarboxylated to *N*-acetylhydrazobenzene (II; R = R′ = X = H), was converted into its ester by diazoethane, and the ester was cyclised by ethanolic sodium ethoxide to 3,5-dioxo-1,2-diphenylpyrazolidine. 3,5-Dioxo-1,2-diphenylpyrazolidine was partly converted into *N*-carboxyacetylhydrazobenzene by a hot aqueous dioxan solution of hydrochloric acid; replacement of aqueous dioxan by ethanol gave a mixture of the acid (II; R = R′ = H, X = CO_2H) and its ethyl ester.

Tsumaki [6] obtained an acidic compound, $C_{15}H_{14}O_3N_2$, m. p. 160—162° with decomp., as a by-product from the action of malonyl chloride on hydrazobenzene (the major product was 3,5-dioxo-1,2-diphenylpyrazolidine) or by the action of dilute hydrochloric acid on a chloroform–ethanol solution of 3,5-dioxo-1,2-diphenylpyrazolidine. He formulated this as (IV), in preference to (II; R = R′ = H, X = CO_2H). Since *N*-carboxyacetylhydrobenzene melts at 133—134° (decomp.) and *N*-acetylhydrazobenzene has m. p. 161—162° we believe that Tsumaki's product was probably (II; R = R′ = H, X = CO_2H) and that his melting-point determination method resulted in slow decomposition of the compound to *N*-acetylhydrazobenzene. When 3-imino-5-oxo-1,2-diphenylpyrazolidine (III; R = R′ = H) is heated with cyclohexanone a colourless compound $C_{21}H_{21}ON_3$ is obtained which we consider to be 4-cyclohexenyl-3-imino-5-oxo-1,2-diphenylpyrazolidine (V). Cyclohexanone and 3,5-dioxo-1,2-diphenylpyrazolidine give the yellow cyclohexylidene derivative [1] (VI). The lack of conjugation between the double bond and the heterocyclic system in (V) is apparent from its ultraviolet spectrum which shows a maximum at 255 mμ [cf. (III; R = R′ = H) with maximum at 256 mμ] whereas (VI) absorbs at 360 and 372 mμ. The compound (V) was hydrogenated to the cyclohexyl derivative (III; R = C_6H_{11}, R′ = H) which in aqueous-ethanolic acid afforded 4-cyclohexyl-3,5-dioxo-1,2-diphenylpyrazolidine [1] (I; R = C_6H_{11}), the reduction product of (VI).

Experimental

Infrared spectra were determined for Nujol suspensions unless otherwise stated. Where two compounds are claimed to be identical, the identity was confirmed by infrared comparison (Nujol). Ultraviolet spectra in alkali were determined in a mixture of equal parts of 2N-sodium hydroxide and ethanol, and in acid were obtained by using equal parts of 2N-hydrochloric acid and ethanol.

N-Cyanoacetylhydrazobenzene.—Lacking experimental details we were unable to reproduce the recorded method; [3] the following technique was used. A stirred solution of hydrazobenzene (13·8 g.) in chloroform (300 c.c.) and pyridine (100 c.c.) was treated at −10° with

[6] Tsumaki, *Bull. Chem. Soc. Japan*, 1931, **6**, 1.

freshly prepared cyanoacetyl chloride [7,8] (21·5 g., 3 mols.) in chloroform (75 c.c.) during 1 hr. The mixture was allowed to attain room temperature during 3 hr., then kept overnight and poured into water (500 c.c.). The chloroform layer was washed with water (100 c.c.), 2N-hydrochloric acid (3 × 150 c.c.), 2N-sodium hydroxide (3 × 150 c.c.) (extract A), and water and dried (Na_2SO_4). Evaporation of the chloroform and crystallisation of the residue from ethanol gave *N*-cyanoacetylhydrazobenzene (5·4 g., 29%) as plates, m. p. 172—173° (lit.,[3] m. p. 172—173°) (Found: C, 71·5; H, 5·1. Calc. for $C_{15}H_{13}ON_3$: C, 71·7; H, 5·2%), $\lambda_{max.}$ (in EtOH) 208 (ε 16,000) and 237 mμ (ε 18,000), $\lambda_{max.}$ (in alkali) 254 mμ (ε 23,900), $\lambda_{max.}$ (in acid) 205 (ε 36,000) and 236 mμ (ε 24,000), $\nu_{max.}$ 3306 (NH), 2245 (CN), and 1667 cm.$^{-1}$ (CO).

3-*Imino*-5-*oxo*-1,2-*diphenylpyrazolidine*.—(*a*) Concentration of the ethanolic mother-liquors from cyanoacetylhydrazobenzene yielded 3-*imino*-5-*oxo*-1,2-*diphenylpyrazolidine* (1·6 g., 9%) as plates, m. p. 222—223°; it was sublimed at 200°/0·5 mm. for analysis (Found: C, 71·45; H, 5·2. $C_{15}H_{13}ON_3$ requires C, 71·7; H, 5·2%), $\lambda_{max.}$ (in EtOH) 206 (ε 17,000) and 254 mμ (ε 23,000); $\lambda_{max.}$ (in alkali) 225 (ε 61,000) and 255 mμ (ε 22,000); $\lambda_{max.}$ (in acid) 206 (ε 19,000) and 252 mμ (ε 22,000), $\nu_{max.}$ 3333 (NH), 1675 (CO), and 1639 cm.$^{-1}$.

(*b*) *N*-Cyanoacetylhydrazobenzene (500 mg.) in ethanol (18 c.c.) and aqueous 2M-sodium carbonate (18 c.c.) was refluxed for 4 hr. The cooled solution was diluted with water (50 c.c.) and extracted with chloroform (3 × 50 c.c.), and the combined extracts were washed with water and dried (Na_2SO_4). Evaporation of the chloroform and crystallisation of the residue from ethanol gave 3-imino-5-oxo-1,2-diphenylpyrazolidine (400 mg., 80%), m. p. and mixed m. p. 220—222° (Found: C, 71·7; H, 5·3%).

(*c*) A solution of *N*-cyanoacetylhydrazobenzene (225 mg.) in ethanolic sodium ethoxide (from sodium, 20 mg., and ethanol, 15 c.c.) was refluxed for 3 hr., cooled, diluted with water, and the product isolated by chloroform. Crystallisation from methylene chloride–hexane gave 3-imino-5-oxo-1,2-diphenylpyrazolidine (75 mg.) as prisms, m. p. and mixed m. p. 220—222° (Found: C, 71·7; H, 5·2%). A similar yield was obtained on using methanolic sodium methoxide.

(*d*) A solution of sodium ethoxide in ethanol (from sodium 4·5 g., and dry ethanol, 90 c.c.) was treated successively with ethyl cyanoacetate (10·6 g.) and hydrazobenzene (18 g.), and the mixture refluxed for 17 hr. in nitrogen (bath-temp., 115—125°; internal temp. 86—88°). Ethanol (60 c.c.) was removed by distillation at atmospheric pressure, the internal temperature rising to 126°. The mixture was cooled and treated with ether (250 c.c.) and water (250 c.c.) with stirring and shaking, and the insoluble material (1·0 g.) separated (aqueous phase B, and an ether phase C). The pale yellow solid, which had the properties of a sodium salt, was treated with hydrochloric acid (*d* 1·15), and the aqueous suspension extracted with chloroform. The chloroform extract was washed with water, dried, and evaporated. The residue crystallised from ethanol, to give 3-imino-5-oxo-1,2-diphenylpyrazolidine (0·55 g.) as plates, m. p. and mixed m. p. 220—222°; it was sublimed *in vacuo* (Found: C, 71·7; H, 5·2%). Phase C was dried (Na_2SO_4) and evaporated and the reddish solid crystallised from chloroform–methanol to give hydrazobenzene (9·37 g.) as plates, m. p. 126—128° [washed with light petroleum (b. p. 60—80°) to remove the orange colour]. Evaporation of the light petroleum washings yielded azobenzene (2·5 g.), m. p. 67°. The aqueous alkaline phase B gradually deposited solid (1·0 g.), m. p. 222°. Evaporation of the mother-liquor to one-third of its bulk under reduced pressure gave a second crop (0·3 g.), m. p. 220°, and from the mother-liquor a third crop (0·3 g.), m. p. 210—220°, was isolated by means of chloroform. Combination of the three crops and crystallisation from ethanol yielded 3-imino-5-oxo-1,2-diphenylpyrazolidine, m. p. and mixed m. p. 220—222°. Acidification of the aqueous alkaline liquor with 2N-hydrochloric acid precipitated a brown solid (2·2 g.), m. p. 300°, which could not be crystallised and was not further examined.

(*e*) A solution of chloroacetylhydrazobenzene [4] (1·5 g.) in ethanol (25 c.c.) was refluxed with potassium cyanide (2·5 g.) in water (15 c.c.) for 7 hr. The solution was diluted with water (50 c.c.) and extracted with chloroform (3 × 50 c.c.). The combined chloroform extracts were washed with water (2 × 25 c.c.), dried (Na_2SO_4), and evaporated. Crystallisation of the residue from chloroform–ethanol gave 3-imino-5-oxo-1,2-diphenylpyrazolidine (0·8 g., 57%), m. p. and mixed m. p. 221—222°.

N-*Cyanoacetyl*-4,4′-*dimethylhydrazobenzene*.—To a stirred solution of 4,4′-dimethylhydrazobenzene (9·2 g.) in chloroform (150 c.c.) and pyridine (50 c.c.), cooled in an ice-bath, a solution

[7] Schroeter and Zink, *Ber.*, 1938, **71**, 675.
[8] Weissberger and Porter, *J. Amer. Chem. Soc.* 1943, **65**, 52.

of cyanoacetyl chloride (15·6 g.) in chloroform (40 c.c.) was added dropwise in 1 hr. The cooling bath was removed and the stirring continued for a further 2 hr. The solution was treated with water, and the chloroform layer washed successively with 3N-hydrochloric acid, water, 3N-sodium hydroxide, and water and dried (Na_2SO_4). The chloroform solution was evaporated under reduced pressure and the residue crystallised from chloroform–methanol, giving 4,4′-dimethylhydrazobenzene (1·0 g.), m. p. and mixed m. p. 132—134°. Concentration of the mother-liquor gave crystals which were digested with cold benzene, and the residue was separated. Recrystallisation from acetone–methanol gave *N*-cyanoacetyl-4,4′-dimethylhydrazobenzene (2·8 g.) as needles, m. p. 144—145° (Found: C, 73·4; H, 6·0. $C_{17}H_{17}ON_3$ requires C, 73·1; H, 6·1%). $\lambda_{max.}$ (in EtOH) 209 (ε 20,000) and 238 mμ (ε 21,000), $\lambda_{max.}$ (in alkali) 225 (ε 66,000) and 254 mμ (ε 30,000), $\lambda_{max.}$ (in acid) 207 (ε 23,000) and 238 mμ (ε 19,600), $\nu_{max.}$ 3333 (NH), 2273 (C≡N), and 1692 cm.$^{-1}$ (C=O).

3-*Imino*-5-*oxo*-1,2-*di*-p-*tolylpyrazolidine*.—(*a*) Under the conditions described for the cyclisation of *N*-cyanoacetylhydrazobenzene with sodium carbonate, *N*-cyanoacetyl-4,4′-dimethylhydrazobenzene (1 g.) gave 3-*imino*-5-*oxo*-1,2-*di*-p-*tolylpyrazolidine* (800 mg.) which separated from acetone–hexane as needles, m. p. 212—213° (Found: C, 72·9; H, 5·9. $C_{17}H_{17}ON_3$ requires C, 73·1; H, 6·1%), $\lambda_{max.}$ (in EtOH) 207 (ε 25,000) and 254 mμ (ε 29,500), $\lambda_{max.}$ (in alkali) 254 mμ (ε 52,000), $\lambda_{max.}$ (in acid) 209 (ε 28,000) and 250 mμ (ε 30,000), $\nu_{max.}$ 3390, 3185 (NH), 1675 and 1647 cm.$^{-1}$ (C=O). An ethanolic solution of the compound gave a red colour with aqueous ferric chloride.

(*b*) A mixture of ethyl cyanoacetate (10·6 g.), 4,4′-dimethylhydrazobenzene (21 g.), and ethanolic sodium ethoxide (from 4·8 g. of sodium and 150 c.c. of dry ethanol) was refluxed for 17 hr. in nitrogen. The mixture was separated as described for the similar preparation of 3-imino-5-oxo-1,2-diphenylpyrazolidine, into an ethereal phase, an interfacial solid, and an aqueous-alkaline phase. The dried (Na_2SO_4) ethereal phase was evaporated to a bright orange solid which was triturated with light petroleum (b. p. 40—60°), and the residue crystallised from chloroform–light petroleum (b. p. 40—60°) to give 4,4′-dimethylhydrazobenzene (10·6 g.) as plates, m. p. and mixed m. p. 128°. The combined light petroleum washings on concentration yielded 4,4′-dimethylazobenzene (6·1 g.) as orange blades, m. p. and mixed m. p. 142°.

The interfacial solid was combined with further solid which slowly separated from the aqueous alkaline phase and crystallised from chloroform–light petroleum (b. p. 40—60°), to give 3-imino-5-oxo-1,2-di-p-tolylpyrazolidine (1·2 g.) as needles, m. p. and mixed m. p. 213°.

The aqueous phase was continuously extracted with chloroform for 5 hr. Removal of the chloroform gave uncrystallisable material. The aqueous alkaline solution on acidification with hydrochloric acid (*d* 1·15) gave a brown solid (1·8 g.), m. p. *ca.* 320°, which could not be recrystallised.

N-α-*Chloropropionylhydrazobenzene*.—α-Chloropropionyl chloride (40 g.) in chloroform (30 c.c.) was added dropwise to an ice-cooled solution of hydrazobenzene (25 g.) in chloroform (300 c.c.) and pyridine (100 c.c.), with stirring, in 1 hr. The ice-bath was then removed and stirring continued for a further 2 hr. The solution was washed with 2N-hydrochloric acid (500 c.c.), then water (300 c.c.), and dried (Na_2SO_4). Concentration, cooling, and crystallisation of the precipitated solid from ethanol gave α-*chloropropionylhydrazobenzene* (40 g.) as prisms, m. p. 149° (Found: C, 65·22; H, 5·9. $C_{15}H_{15}ON_2Cl$ requires C, 65·5; H, 5·5%), $\lambda_{max.}$ (in EtOH) 206 (ε 28,000) and 238 mμ (ε 20,000), $\nu_{max.}$ 3250 (NH) and 1642 cm.$^{-1}$ (C=O).

3-*Imino*-4-*methyl*-5-*oxo*-1,2-*diphenylpyrazolidine*.—(*a*) A solution of α-bromopropionylhydrazobenzene [5] (2·5 g.) and potassium cyanide (3·0 g.) in ethanol (25 c.c.) and water (8 c.c.) was refluxed for 5 hr. The cooled solution was diluted with water, and the product isolated by using chloroform. 3-*Imino*-4-*methyl*-5-*oxo*-1,2-*diphenylpyrazolidine* (1·0 g.) separated from chloroform as plates, m. p. 180° (Found: C, 72·1; H, 5·45. $C_{16}H_{15}ON_3$ requires C, 72·4; H, 5·7%), $\lambda_{max.}$ (in EtOH) 206 (ε 22,000) and 264 mμ (ε 25,000), $\lambda_{max.}$ (in alkali) 263 mμ (ε 19,500), $\nu_{max.}$ 3874 (NH), 3278 (OH), and 1640 cm.$^{-1}$ (CO). The compound gave a red colour in ethanol with aqueous ferric chloride.

(*b*) α-Chloropropionylhydrazobenzene (12 g.) likewise gave the pyrazolidine (5·0 g.), m. p. and mixed m. p. 180°.

N-*Carboxyacetylhydrazobenzene*.—(*a*) A solution of *N*-cyanoacetylhydrazobenzene (500 mg.) in ethanol (18 c.c.) water (18 c.c.) and hydrochloric acid (1 c.c.; *d* 1·15) was refluxed for 1 hr. The solution was separated into an ethereal neutral fraction (D) and an alkali-soluble fraction. Acidification of the alkaline solution gave a product which was isolated in ether and crystallised

from methylene chloride–hexane, to yield N-*carboxyacetylhydrazobenzene* (300 mg.) as needles, m. p. 133—134° (decomp.) (Found: C, 66·32; H, 5·4. $C_{15}H_{14}O_3N_2$ requires C, 66·65; H, 5·2%), $\lambda_{max.}$ (in EtOH) 208 (ε 17,000) and 236 mμ (ε 14,500), $\nu_{max.}$ 3390—3175 (NH), 1724 (CO) cm.$^{-1}$.

(*b*) A solution of 3-imino-5-oxo-1,2-diphenylpyrazolidine (220 mg.) in ethanol (9 c.c.), water (9 c.c.), and hydrochloric acid (0·5 c.c.; *d* 1·15) was refluxed for 1 hr. The solution was separated by means of ether into a neutral fraction E and an acid fraction which crystallised from methylene chloride–hexane, to give *N*-carboxyacetylhydrazobenzene (100 mg.) as needles, m. p. and mixed m. p. 133—134° (decomp.).

(*c*) A solution of 3,5-dioxo-1,2-diphenylpyrazolidine (1·0 g.) in dioxan (20 c.c.) and 2N-hydrochloric acid (0·5 c.c.) was kept at room temperature for 6 days with occasional shaking. Water was added and the solution was extracted with chloroform, and the combined chloroform extracts were washed with aqueous sodium hydrogen carbonate, aqueous sodium hydroxide, and water, and dried (Na_2SO_4). From the sodium hydrogen carbonate solution by acidification and isolation with ether, *N*-carboxyacetylhydrazobenzene (260 mg.), m. p. and mixed m. p. 130—132°, was obtained, crystallising from methylene chloride–hexane as needles. The sodium hydroxide extract, on acidification, yielded 3,5-dioxo-1,2-diphenylpyrazolidine (450 mg.), m. p. and mixed m. p. 175—178°. Crystalline material was not isolated from the neutral fraction.

N-*Acetylhydrazobenzene*.—*N*-Carboxyacetylhydrazobenzene (150 mg.) was heated for 15 min. at 140°. The cooled mass was dissolved in ether, and the ethereal solution washed with 2N-aqueous sodium hydroxide, then water, and dried (Na_2SO_4). The ethereal solution was evaporated and the residue crystallised from chloroform–ethanol, to give *N*-acetylhydrazobenzene (60 mg.) as needles, m. p. and mixed m. p. 161—162° (lit.,[9] m. p. 159°).

N-*Ethoxycarbonylacetylhydrazobenzene*.—(*a*) *N*-Carboxyacetylhydrazobenzene (30 mg.) was added to an excess of ethereal diazoethane, and the solution kept overnight at room temperature. Removal of the solvent and crystallisation of the residue from methylene chloride–hexane gave N-*ethoxycarbonylacetylhydrazobenzene* (20 mg.) as needles, m. p. 98—100° (Found: C, 68·4; H, 5·7. $C_{17}H_{18}O_3N_2$ requires C, 68·4; H, 6·1%), $\lambda_{max.}$ (in EtOH) 208 (ε 26,400) and 236 mμ (ε 18,000), $\nu_{max.}$ 3333 (NH) and 1739 cm.$^{-1}$ (ester C=O).

(*b*) Removal of ether from neutral fraction D of the hydrolysis product from *N*-cyanoacetylhydrazobenzene and crystallisation of the residue from methylene chloride–hexane gave *N*-ethoxycarbonylacetylhydrazobenzene (150 mg.) as needles, m. p. and mixed m. p. 99—100°.

(*c*) Neutral fraction E from the action of aqueous-ethanolic hydrochloric acid on 3-imino-5-oxo-1,2-diphenylpyrazolidine was crystallised from methylene chloride–hexane to give *N*-ethoxycarbonylacetylhydrazobenzene as needles, m. p. and mixed m. p. 97—98°.

(*d*) A solution of 3,5-dioxo-1,2-diphenylpyrazolidine (500 mg.) in ethanol (18 c.c.), water (18 c.c.) and hydrochloric acid (1 c.c.; *d* 1·15) was refluxed for 1 hr. The cooled solution was separated in the usual way into neutral and alkali-soluble fractions. The neutral fraction crystallised from methylene chloride–hexane, to give *N*-ethoxycarbonylacetylhydrazobenzene (80 mg.) as needles, m. p. and mixed m. p. 97—99°. *N*-Carboxyacetylhydrazobenzene, m. p. and mixed m. p. 130—132° (decomp.), was obtained from the acidic fraction together with starting material, m. p. and mixed m. p. 175—178°.

3,5-*Dioxo*-1,2-*diphenylpyrazolidine*.—(*a*) *N*-Ethoxycarbonylacetylhydrazobenzene (50 mg.) was added to a solution of sodium ethoxide prepared from sodium (40 mg.) and ethanol (15 c.c.), and the mixture refluxed for 2 hr. and evaporated to dryness under reduced pressure. The residue was diluted with water (25 c.c.), acidified with hydrochloric acid (*d* 1·15), and extracted with ether (3 × 30 c.c.). The combined ethereal extracts were washed with water, dried (Na_2SO_4), and evaporated. Crystallisation of the residue from ethanol gave 3,5-dioxo-1,2-diphenylpyrazolidine (30 mg.) as plates, m. p. and mixed m. p. 178—179°.

(*b*) Concentration of the methylene chloride–hexane mother-liquor from the crystallisation of the specimen of *N*-carboxyacetylhydrazobenzene obtained from *N*-cyanoacetylhydrazobenzene gave 3,5-dioxo-1,2-diphenylpyrazolidine (20 mg.) which separated from ethanol as plates, m. p. and mixed m. p. 175—178°.

(*c*) A solution of 3-imino-5-oxo-1,2-diphenylpyrazolidine (1·2 g.) in ethanol (20 c.c.), water (20 c.c.), and hydrochloric acid (2 c.c.; *d* 1·15) was refluxed for 1 hr. The solution was diluted with water (50 c.c.) and extracted with chloroform. The chloroform extract was washed with

[9] Stern, *Ber.*, 1884, **17**, 379.

aqueous sodium hydrogen carbonate, aqueous sodium hydroxide, and water and dried (Na_2SO_4). Acidification of the sodium hydroxide solution and extraction with chloroform gave 3,5-dioxo-1,2-diphenylpyrazolidine (100 mg.; plates from chloroform–ethanol), m. p. and mixed m. p. 177—178°. *N*-Carboxyacetylhydrazobenzene (480 mg.), m. p. and mixed m. p. 130—132° (decomp.), was obtained as needles by acidification of the sodium hydrogen carbonate washings. Evaporation of the chloroform yielded *N*-ethoxycarbonylacetylhydrazobenzene (80 mg.), m. p. and mixed m. p. 96—98°.

4-Cyclohexenyl-3-imino-5-oxo-1,2-diphenylpyrazolidine.—(*a*) 3-Imino-5-oxo-1,2-diphenylpyrazolidine (1·0 g.) was refluxed with cyclohexanone (10 c.c.) for 1 hr. The solution was evaporated to dryness under reduced pressure and the residue crystallised from ethanol–light petroleum (b. p. 60—80°), to give *4-cyclohexenyl-3-imino-5-oxo-1,2-diphenylpyrazolidine* (1·0 g.) as prisms, m. p. 188—189° (Found: C, 75·8; H, 6·0. $C_{21}H_{21}ON_3$ requires C, 76·1; H, 6·4%), $\lambda_{max.}$ (in EtOH) 205 (ε 29,000) and 255 mμ (ε 22,000), $\lambda_{max.}$ (in alkali) 288 (ε 6300) and 254 mμ (ε 24,000), $\nu_{max.}$ 3356 (NH) and 1664 cm.$^{-1}$ (CO). An ethanolic solution of the compound gave a reddish-brown colour with aqueous ferric chloride.

(*b*) Cyanoacetylhydrazobenzene (500 mg.) was refluxed for 6 hr. with cyclohexanone (10 c.c.). Crystallisation of the product, isolated as described in the preceding experiments, from chloroform–methanol gave 4-cyclohexenyl-3-imino-5-oxo-1,2-diphenylpyrazolidine (30 mg.) as prisms, m. p. and mixed m. p. 185—186°.

4-Cyclohexyl-3-imino-5-oxo-1,2-diphenylpyrazolidine.—A solution of 4-cyclohexenyl-3-imino-5-oxo-1,2-diphenylpyrazolidine (1·0 g.) in ethyl acetate (250 c.c.) was shaken with hydrogen at room temperature and atmospheric pressure in the presence of platinum from Adams catalyst (500 mg.). When absorption was complete (*ca.* 2 hr.) the filtered solution was evaporated to dryness under reduced pressure and the residue crystallised from methylene chloride–hexane, to give *4-cyclohexyl-3-imino-5-oxo-1,2-diphenylpyrazolidine* (1·0 g.) as needles, m. p. 223—225°, (Found: C, 75·2; H, 6·8; N, 12·9. $C_{21}H_{23}ON_3$ requires C, 75·6; H, 6·95; N, 12·6%), $\lambda_{max.}$ (in EtOH) 204 (ε 24,000) and 262 mμ (ε 25,000), $\lambda_{max.}$ (in alkali) 223 (ε 45,000) and 263 mμ (ε 19,000), $\nu_{max.}$ 3226, 3106, and 1618 cm.$^{-1}$ (C=O). An ethanolic solution of the compound gave a reddish-brown colour with aqueous ferric chloride.

4-Cyclohexyl-3,5-dioxo-1,2-diphenylpyrazolidine.—(*a*) A solution of 4-cyclohexylidene-3,5-dioxo-1,2-diphenylpyrazolidine [1] (400 mg.) in ethyl acetate (40 c.c.) was shaken at room temperature and atmospheric pressure with hydrogen and platinum from Adams catalyst (140 mg.) until absorption was complete (*ca.* 1 hr.). The filtered solution was evaporated under reduced pressure and the residue crystallised from chloroform–methanol, to give 4-cyclohexyl-3,5-dioxo-1,2-diphenylpyrazolidine (350 mg.) as needles, m. p. 176—178° (lit.,[1] m. p. 177°) $\lambda_{max.}$ (in EtOH) 207 (ε 19,000) and 268 mμ (ε 22,000), $\lambda_{max.}$ (in alkali) 270 mμ (ε 23,000), $\nu_{max.}$ 1754 and 1730 cm.$^{-1}$ (both C=O). An ethanolic solution of the compound gave no colour with aqueous ferric chloride.

(*b*) A solution of 4-cyclohexyl-3-imino-5-oxo-1,2-diphenylpyrazolidine (740 mg.) in ethanol (20 c.c.), water (20 c.c.), and hydrochloric acid (2 c.c.; *d* 1·15) was refluxed for 1 hr., then cooled and extracted with chloroform (3 × 40 c.c.), and the combined extracts were washed with 2N-sodium hydroxide (2 × 50 c.c.), then water and dried (Na_2SO_4). Removal of the chloroform and crystallisation of the residue from chloroform–methanol gave unchanged material (300 mg.), m. p. and mixed m. p. 220—222°. Acidification of the combined alkaline washings with 2N-hydrochloric acid (Congo Red) and isolation of the product by chloroform gave 4-cyclohexyl-3,5-dioxo-1,2-diphenylpyrazolidine (100 mg.), m. p. and mixed m. p. 174—176°.

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