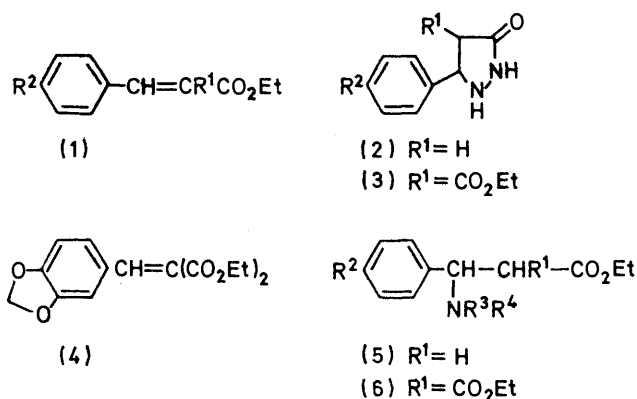


Synthesis of Ethyl 3-Oxopyrazolidine-4-carboxylates

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Ethyl 3-oxopyrazolidine-4-carboxylates are formed in reactions of hydrazine hydrate with $\alpha\beta$ -unsaturated diesters or with β -anilino-diester. The usefulness of the method is limited by the occurrence of other reactions, notably cleavage of the diesters (to malonohydrazide and the appropriate aldehyde azine); ethyl 3-hydroxypyrazole-4-carboxylate derivatives are also produced, subsequent to formation of the oxopyrazolidines.

THE cyclisation of $\alpha\beta$ -unsaturated monoesters (1; $R^1 = H$) by hydrazine to give pyrazolidin-3-ones (2) via a presumed β -substituted intermediate (5; $R^3 = H$, $R^4 = NH_2$) is well known.¹ In contrast to this, the diesters (1; $R^1 = CO_2Et$), which are much less stable and are readily hydrolysed in the presence of bases,^{2,3} are known to be cleaved by hydrazine under various conditions to give malonohydrazide and the appropriate aldehyde azines.⁴⁻⁷



We have now shown that ethyl 5-aryl-3-oxopyrazolidine-4-carboxylates (3) are obtained when the diesters (1; $R^1 = CO_2Et$) are treated with 1 mol. equiv. of hydrazine hydrate at room temperature, but the yields vary considerably according to the nature of the aryl substituent. Thus the compounds (3; $R^2 = NO_2$, NMe_2 , or Cl) were obtained in 72, 31, and 2% yield, respectively; only cleavage products were obtained from the diester (1; $R^1 = CO_2Et$, $R^2 = H$). An H-bonded OH band⁸ at 3320 cm^{-1} in the i.r. spectra of the *p*-nitro- and *p*-chloro-phenyl derivatives suggests that an enolised form of these molecules predominates, with OH hydrogen-bonded to the ester group; this is confirmed by the fact that the saturated ester band at 1720 cm^{-1} in these compounds is poorly defined, as compared with the sharp definition of the corresponding

band in the *p*-dimethylaminophenyl derivative (which has an 'unbonded' CO·NH band at 3240 cm^{-1}).

The possible alternative formulation of (3; $R^2 = NMe_2$) as an open-chain compound (7) is discounted by the finding that the product (m.p. $209\text{--}210^\circ$) obtained by condensing with *p*-dimethylaminobenzaldehyde has the inner salt structure (9) typically formed by pyrazolidinones.⁹⁻¹¹ Its i.r. spectrum is in sharp contrast with that of the known compound¹² (8) (m.p. $158\text{--}159^\circ$), which compound (7) might be expected to yield; there is no NH absorption, and the strong band at 1725 cm^{-1} (saturated ester) contrasts with the unsaturated ester band at 1700 cm^{-1} in the spectrum of (8). [The other pyrazolidinones (3) also form inner salt structures with aromatic aldehydes; in contrast with normal hydrazone formation from hydrazides, prolonged heating with excess of reagent is necessary.] Like the other pyrazolidinones, compound (3; $R^2 = NMe_2$) does not form the 4-methylthiosemicarbazide derivatives typically obtained from free hydrazides on treatment with methyl isothiocyanate. With nitrous acid, it yields a crystalline product (presumably the *N*-nitroso-derivative) but this rapidly decomposes.

From the reaction of hydrazine hydrate with two other $\alpha\beta$ -unsaturated diesters (1; $R^1 = CO_2Et$, $R^2 = Me$) and (4) the cyclic products isolated (along with cleavage products) were identified as the hydrazine salts of ethyl 3-hydroxypyrazole-4-carboxylates (10). Some β -substituted diesters (6) have also been examined as starting materials. β -Phenylhydrazino-derivatives (6; $R^3 = H$, $R^4 = NHPH$) are themselves unstable and decompose to aldehyde phenylhydrazones.¹³ The availability of the β -anilino-compounds (6; $R^3 = H$, $R^4 = Ph$) is limited,¹⁴ and cleavage in the presence of hydrazine hydrate also occurs to some extent, but from two of them ($R = Cl$ or Me) it was possible to isolate the hydrazine salt of the appropriate ethyl 3-hydroxypyrazole-4-carboxylate derivative (10). The only other β -substituted diester examined was the piperidino-

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¹⁰ J. C. Howard, G. Geker, and P. H. L. Wei, *J. Org. Chem.*, 1963, **28**, 868.

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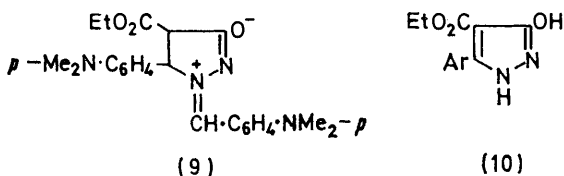
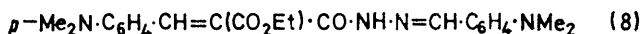
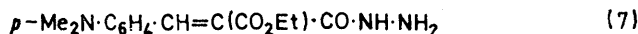
⁵ W. Gustowski and T. Urbanski, *Roczniki Chem.*, 1963, **37**, 437.

⁶ C. N. O'Callaghan and D. Twomey, *Proc. Roy. Irish Acad.*, 1964, **63B**, 217.

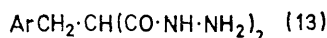
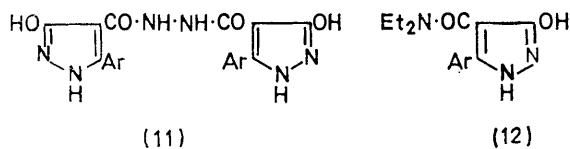
⁷ H. Brauniger and K. Breuer, *Pharm. Zentralhalle*, 1968, **107**, 579.

derivative (6; $R^3R^4 = [CH_2]_5$, $R^2 = Cl$), from which the main product obtained was the piperidine salt of (10; $Ar = C_6H_4Cl-p$).

Evidence for the structure of the various pyrazole hydrazine salts was provided by the ease with which



hydrazine was removed by dilute mineral acid, by aldehydes (which incorporated it into azines), and by methyl isothiocyanate [which incorporated it into NN' -bis(methylthiocarbamoyl)hydrazine¹⁵] with liberation of the free pyrazole in each case. The pyrazoles are stable compounds which do not react with aldehydes; a feature of their i.r. spectra is a highly characteristic ester band at *ca.* 1660 cm^{-1} analogous to the similar band displayed by salicylates.^{8,16} The pyrazoles are readily reconverted into salts in the presence of hydrazine, and form similar salts with other bases, *e.g.* diethylamine and triethylamine. When the pyrazole hydrazine salts are heated to their m.p.s (*ca.* 180°), *sym*-diacylhydrazines (11) are formed;¹⁷ in the case of the diethylamine salt, diacylation is not possible and only the simple diethylamide (12) is formed.



Presumably the production of pyrazole salts takes place subsequent to pyrazolidinone formation and depends on the stability of the latter. The *p*-chlorophenyl derivative (3; $R^2 = Cl$) has in fact been isolated during the preparation from (6; $R^2 = Cl$, $R^3 = H$, $R^4 = Ph$) of the hydrazine salt of (10; $Ar = C_6H_4Cl-p$) and, by an oxidative effect,^{18,19} is converted into the latter. Similarly, compound (3; $R^2 = NMe_2$) is converted into the hydrazine salt of (10; $Ar = C_6H_4\cdot NMe_2-p$), but in this case salt formation is accompanied

by hydrolysis and production of *p*-dimethylaminobenzaldehyde azine, and it is necessary to perform the reaction at low temperatures. [Ethyl 3-oxopyrazolidine-4-carboxylates do not undergo oxidation when exposed to air or recrystallised; when suspended in acid solution, however, compound (3; $R^2 = Cl$) slowly dissolved with formation of (10; $Ar = C_6H_4Cl-p$).]

The dihydrazide (13; $Ar = C_6H_4\cdot NO_2-p$), which forms a bis-(4-methylthiosemicarbazide) derivative with methyl isothiocyanate, can be isolated from the reaction of compound (3; $R^2 = NO_2$) with hydrazine hydrate. A similar dihydrazide (13; $Ar = C_6H_4Cl-p$) has been obtained in low yield during the preparation of the piperidine salt of (10; $Ar = C_6H_4Cl-p$).

EXPERIMENTAL

I.r. spectra were determined for Nujol mulls.

Ethyl 5-(4-Dimethylaminophenyl)-3-oxopyrazolidine-4-carboxylate (3; $R^2 = NMe_2$).—A mixture of ethyl α -ethoxy-carbonyl-4-dimethylaminocinnamate (5.8 g) and hydrazine hydrate (1.0 g) in ethanol (50 ml) was stirred at room temperature for 3 h, then stored at -10° overnight. The flocculent yellow product which separated was collected, dried, and recrystallised from benzene. Repeated extraction with light petroleum (b.p. 80–100°) left undissolved a crystalline product, m.p. 154° (1.7 g) (Found: C, 61.0; H, 6.9; N, 15.1. $C_{14}H_{19}N_3O_3$ requires C, 60.7; H, 6.9; N, 15.2%), ν_{max} 3240, 1720, 1685, and 1610 cm^{-1} .

The petroleum-soluble material was recovered and identified as *p*-dimethylaminobenzaldehyde azine, identical (m.p. and mixed m.p.²⁰ 250–253°; i.r. spectrum) with authentic material.

Similarly prepared were *ethyl 5-(4-nitrophenyl)-3-oxopyrazolidine-4-carboxylate* (3; $R^2 = NO_2$), m.p. 193–194° (from ethanol) (Found: C, 51.8; H, 4.7; N, 15.3. $C_{12}H_{13}N_3O_5$ requires C, 51.6; H, 4.7; N, 15.1%), ν_{max} 3320, 3200, 1720, and 1670 (not fully resolved) cm^{-1} , and *ethyl 5-(4-chlorophenyl)-3-oxopyrazolidine-4-carboxylate* (3; $R^2 = Cl$), mp. 155–156° (from benzene) (Found: C, 53.8; H, 4.9; Cl, 13.3; N, 10.7; OEt, 16.6. $C_{12}H_{13}ClN_3O_3$ requires C, 53.6; H, 4.8; Cl, 13.2; N, 10.4; OEt, 16.8%), ν_{max} 3320, 3200, 1720, and 1670 (not fully resolved) cm^{-1} .

1-(4-Dimethylaminobenzylidene)-5-(4-dimethylaminophenyl)-4-ethoxycarbonyl- Δ^2 -pyrazolinium-3-olate (9).—The pyrazolidinone ester (3; $R^2 = Me_2N$) (277 mg) and 4-dimethylaminobenzaldehyde (298 mg) were heated for 3 h on a steam-bath. Next day, the solvent was removed at 35° *in vacuo*, and the residue was washed with benzene, leaving a pale yellow compound, m.p. 209–210° (from ethanol) (240 mg) (Found: C, 67.5; H, 6.9; N, 13.4. $C_{23}H_{28}N_4O_3$ requires C, 67.6; H, 6.9; N, 13.7%), ν_{max} 1720, 1630, and 1590 cm^{-1} .

Analogous derivatives, prepared in the same way from salicylaldehyde and the appropriate pyrazolidinones, are listed in the Table. Typically the compounds have ν_{max} 1720, 1630, and 1590 cm^{-1} .

Hydrazine Salts of 5-Substituted Derivatives of Ethyl

¹⁵ S. L. Janniah and P. C. Guha, *J. Indian Inst. Sci.*, 1933, **16A**, 11.

¹⁶ R. R. Hampton and J. E. Newell, *Analyt. Chem.*, 1949, **21**, 914.

¹⁷ P. A. S. Smith, 'Open-chain Nitrogen Compounds,' Benjamin, New York, 1966, vol. 2, p. 177.

¹⁸ A. Giner-Sorolla and A. Bendich, *J. Org. Chem.*, 1966, **31**, 4239.

¹⁹ D. A. Armitage, M. J. Clark, and A. C. Kinsey, *J. Chem. Soc. (C)*, 1971, 3867.

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3-Hydroxypyrazole-4-carboxylate.—(a) Addition of hydrazine hydrate to ethyl α -ethoxycarbonyl-3,4-methylenedioxycinnamate and ethyl α -ethoxycarbonyl-4-methylcinnamate, respectively, under the conditions described for the preparation of the pyrazolidinone (3; R² = NMe₂) yielded the *hydrazine salt of ethyl 3-hydroxy-5-(3,4-methylenedioxyphenyl)pyrazole-4-carboxylate*, m.p. 172° (resolidifying 182°) (27%) (Found: C, 50.6; H, 5.3; N, 18.2. C₁₃H₁₂N₂O₅.N₂H₄ requires C, 50.6; H, 5.2; N, 18.2%), and the *hydrazine salt of ethyl 3-hydroxy-5-(4-tolyl)pyrazole-4-carboxylate*, m.p. 169—171° (resolidifying immediately) (2%) (Found: C, 56.6; H, 6.6; N, 19.7. C₁₃H₁₄N₂O₄.N₂H₄ requires C, 56.1; H, 6.6; N, 20.1%).

(b) Ethyl 3-anilino-2-ethoxycarbonyl-3-(4-chlorophenyl)propionate²¹ (3.75 g) in ethanol (100 ml) was shaken at room temperature with hydrazine hydrate (1.0 g) for 3 h. Next day, the *hydrazine salt of ethyl 5-(4-chlorophenyl)-3-hydroxypyrazole-4-carboxylate* separated; it crystallised

4-carboxylate (m.p. and mixed m.p. 155°; 0.3 g) separated. The benzene-insoluble residue was *p-chlorobenzylmalonohydrazide* (13; Ar = C₆H₄Cl-*p*), m.p. 235—236° (Found: C, 46.9; H, 5.1; Cl, 13.9; N, 21.8. C₁₀H₁₃ClN₄O₂, requires C, 46.8; H, 5.1; Cl, 13.8; N, 21.8%), ν_{\max} 3260, 1655, 1635, and 1510 cm⁻¹. [The *bis-salicylidenehydrazone* of this compound, prepared by heating in ethanol with 2 equiv. of salicylaldehyde, had m.p. 228—230° (Found: C, 61.5; H, 4.6; Cl, 8.1; N, 12.0. C₂₄H₂₁ClN₄O₄ requires C, 62.0; H, 4.5; Cl, 7.6; N, 12.1%) and *p-chlorobenzylmalono-(4-methylthiosemicarbazide)*, prepared by heating the dihydrazide in ethanol with excess of methyl isothiocyanate, had m.p. 219—221° (Found: C, 41.3; H, 4.9; Cl, 8.4; N, 21.2; S, 15.8. C₁₄H₁₉ClN₄O₂S₂ requires C, 41.7; H, 4.7; Cl, 8.8; N, 20.9; S, 15.9%).] Evaporation of the ethanol from the original mother liquor left a partly crystalline residue which, when recrystallised from methanol and from benzene, yielded the *piperidine salt of*

5-Aryl-4-ethoxycarbonyl-1-(2-hydroxybenzylidene)- Δ^2 -pyrazolinium-3-olates

5-Ar	M.p. (°C)	Found (%)				Formula	Required (%)			
		C	H	Cl	N		C	H	Cl	N
<i>p</i> -C ₆ H ₄ .NMe ₂	173—175	66.2	6.0		10.8	C ₂₁ H ₂₃ N ₃ O ₄	66.1	6.0		11.0
<i>p</i> -C ₆ H ₄ Cl	198—199	61.4	4.7	9.6	7.3	C ₁₉ H ₁₇ ClN ₃ O ₄	61.2	4.6	9.5	7.5
<i>p</i> -C ₆ H ₄ .NO ₂	204	59.1	4.6		10.9	C ₁₉ H ₁₇ N ₃ O ₆	59.5	4.4		11.0

from ethanol as *needles*, m.p. 179—181° (resolidifying immediately) (Found: C, 48.5; H, 5.0; Cl, 11.8; N, 18.6. C₁₂H₁₁ClN₂O₃.N₂H₄ requires C, 48.2; H, 5.0; Cl, 11.9; N, 18.8%). The mother liquor was cooled to -10° and a small quantity of ethyl 5-(4-chlorophenyl)-3-oxopyrazolidine-4-carboxylate separated. This was collected and the remaining mother liquor was evaporated to dryness; the solid residue, extracted in turn with light petroleum, benzene, and ethanol, yielded, respectively, small quantities of *p*-chlorobenzaldehyde azine (m.p. and mixed m.p.²² 208°), the pyrazolidinone (total yield 185 mg, 7%), and the hydrazine salt (total yield 1.11 g, 37%) already described. (When 1 mol. equiv. of hydrazine hydrate was used instead of 2, the same products were obtained but the yields were only about one-third.)

Similarly, from ethyl 3-anilino-2-ethoxycarbonyl-3-(4-tolyl)propionate,¹⁴ the hydrazine salt of ethyl 3-hydroxy-5-(4-tolyl)pyrazole-4-carboxylate was obtained (28%).

Typically the i.r. spectra of these pyrazole hydrazine salts have ν_{\max} 3280, 3120, 2580 (diffuse), 1660, and 1590 cm⁻¹.

Ethyl 2-ethoxycarbonyl-3-piperidino-3-(4-chlorophenyl)propionate, prepared by heating *p*-chlorobenzaldehyde (14.1 g) with diethyl malonate (16.0 g) and piperidine (7.5 g) in ethanol (50 ml) at 80° for 1 h (yield 11.5 g, 31%), had m.p. 94° (from ethanol) (Found: C, 62.5; H, 7.3; Cl, 10.2; N, 3.5. C₁₉H₂₆ClNO₄ requires C, 62.0; H, 7.1; Cl, 9.7; N, 3.8%).

Reaction of Ethyl 2-Ethoxycarbonyl-3-piperidino-3-(4-chlorophenyl)propionate with Hydrazine Hydrate.—Hydrazine hydrate (1.0 g) was added to a solution of the diester (7.4 g) in ethanol (100 ml). The mixture was stored at room temperature for 4 h and then at -10° overnight. The solid which separated was extracted with benzene, from which ethyl 5-(4-chlorophenyl)-3-oxopyrazolidine-

ethyl 5-(4-chlorophenyl)-3-hydroxypyrazole-4-carboxylate, m.p. 186—188° (0.8 g) (Found: C, 57.7; H, 6.5; Cl, 10.1; N, 11.7. C₁₂H₁₁ClN₂O₃.C₅H₁₁N requires C, 58.0; H, 6.3; Cl, 10.1; N, 11.9%). (Dilute mineral acid converted the salt into the parent pyrazole, from which the salt was readily regenerated by addition of piperidine at room temperature.)

In a repeat of the experiment, only the pyrazolidinone and the piperidine salt of the pyrazole were obtained.

Liberation of Pyrazoles from their Hydrazine Salts.—The hydrazine salt of ethyl 5-(4-chlorophenyl)-3-hydroxypyrazole-4-carboxylate (597 mg) in ethanol (50 ml) was warmed with salicylaldehyde (0.6 ml) at 80° for 10 min and then stored at room temperature for 3 h. Salicylaldehyde azine (m.p. and mixed m.p.²³ 213°) which had begun to separate during heating, was collected (450 mg, 94%). The mother liquor was evaporated to dryness at 35°, leaving a crystalline *solid*, m.p. 170—171° (from methanol) (501 mg, 94%) (Found: C, 54.1; H, 4.1; Cl, 13.5; N, 10.5; OEt, 16.6. C₁₂H₁₁ClN₂O₃ requires C, 54.0; H, 4.1; Cl, 13.5; N, 10.5; OEt, 16.9%), ν_{\max} 3400, 3220w, 1680, 1630w, and 1590 cm⁻¹. When 2N-hydrochloric acid was added to an ethanolic solution of the hydrazine salt, the same compound was obtained in 98% yield, following removal of the solvent and washing with water. Similarly, when methyl isothiocyanate (300 mg) was refluxed for 30 min with the hydrazine salt (597 mg) in ethanol (20 ml), *NN'*-bis(thiocarbamoyl)hydrazine (235 mg, 66%),¹⁵ identical (m.p. and mixed m.p. 211—213°; i.r. spectrum) with authentic material, was produced, and the free pyrazole (339 mg, 64%) was recovered from the residues.

Ethyl 3-hydroxy-5-(4-tolyl)pyrazole-4-carboxylate, m.p. 178—181° (Found: C, 63.6; H, 5.9; N, 11.6. C₁₃H₁₄N₂O₃ requires C, 63.4; H, 5.7; N, 11.4%), and *ethyl 3-hydroxy-*

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5-(3,4-methylenedioxyphenyl)pyrazole-4-carboxylate, m.p. 185—186° (Found: C, 56.9; H, 4.5; N, 10.2. $C_{13}H_{12}N_2O_5$ requires C, 56.5; H, 4.3; N, 10.1%), were obtained similarly from their hydrazine salts.

Conversion of Ethyl 5-(4-chlorophenyl)-3-hydroxypyrazole-4-carboxylate into its Salts.—Hydrazine hydrate (0.1 ml) was added to a solution of ethyl 5-(4-chlorophenyl)-3-hydroxypyrazole-4-carboxylate (267 mg) in ethanol (40 ml). Crystallisation began almost immediately, and after 1 h the hydrazine salt (268 mg, 90%), identical (m.p. and mixed m.p. 179—181°; i.r. spectrum) with authentic material, was collected. The diethylamine salt, prepared in similar fashion, was purified by washing with cold water and recrystallisation from ethanol and from benzene. The product melted at 165° (resolidifying at higher temperatures) (Found: C, 56.5; H, 6.6; Cl, 10.6; N, 12.2. $C_{12}H_{11}ClN_2O_3 \cdot C_4H_{11}N$ requires C, 56.6; H, 6.5; Cl, 10.5; N, 12.4%). The triethylamine salt, prepared in the same way, m.p. 102—105° (with effervescence), was hygroscopic and contained 1.5 mol. equiv. water (Found: C, 54.7; H, 7.1; Cl, 9.2; N, 10.6. $C_{12}H_{11}ClN_2O_3 \cdot C_6H_{15}N \cdot 1.5H_2O$ requires C, 54.8; H, 7.3; Cl, 9.0; N, 10.6%).

NN'-Bis-[5-(4-chlorophenyl)-3-hydroxypyrazol-4-ylcarbonyl]hydrazine.—The hydrazine salt of ethyl 5-(4-chlorophenyl)-3-hydroxypyrazole-4-carboxylate (597 mg) was heated on an oil-bath to 185°. The product had m.p. 288—289° (from dimethylformamide-ethanol) (380 mg, 80%) (Found: C, 50.6; H, 3.0; Cl, 14.6; N, 17.8. $C_{20}H_{14}Cl_2N_6O_4$ requires C, 50.7; H, 3.0; Cl, 15.0; N, 17.8%). *NN'-Bis-[5-(4-tolyl)-3-hydroxypyrazol-4-ylcarbonyl]hydrazine* (hygroscopic), m.p. 288—289° (Found: C, 59.4; H, 4.8; N, 19.3. $C_{22}H_{20}N_6O_4 \cdot 0.5H_2O$ requires C, 59.9; H, 4.8; N, 19.0%), and *NN'-bis-[3-hydroxy-5-(3,4-methylenedioxyphenyl)pyrazol-4-ylcarbonyl]hydrazine* (hygroscopic), m.p. 288° (Found: C, 52.8; H, 3.6; N, 17.2. $C_{22}H_{16}N_6O_8 \cdot 0.5H_2O$ requires C, 52.7; H, 3.4; N, 16.8%), were prepared in the same way.

5-(4-Chlorophenyl)-NN-diethyl-3-hydroxypyrazole-4-carboxamide, m.p. 250—254° (from ethanol), was obtained when the diethylamine salt of ethyl 5-(4-chlorophenyl)-3-hydroxypyrazole-4-carboxylate was heated to 195° (Found: C, 57.2; H, 5.4; Cl, 12.0; N, 14.3. $C_{14}H_{16}ClN_3O_2$ requires C, 57.2; H, 5.5; Cl, 12.1; N, 14.3%).

Conversion of Pyrazolidinones into Pyrazoles.—(a) Hydrazine hydrate (0.1 ml) was added to a solution of ethyl

5-(4-chlorophenyl)-3-oxopyrazolidine-4-carboxylate (400 mg) in ethanol (40 ml) and the solution was stored overnight. The product which crystallised was identified (m.p. and mixed m.p. 179—181°; i.r. spectrum) as the hydrazine salt of ethyl 5-(4-chlorophenyl)-3-hydroxypyrazole-4-carboxylate (198 mg, 45%).

(b) Hydrazine hydrate (0.1 ml) was added to a solution of ethyl 5-(4-dimethylaminophenyl)-3-oxopyrazolidine-4-carboxylate (277 mg) in ethanol (15 ml). After 1 h at -10° , crystallisation [m.p. 171—173° (with resolidification) (40 mg)] was induced by scratching. As attempted recrystallisation of the product caused decomposition, with *p*-dimethylaminobenzaldehyde azine (m.p. and mixed m.p.²⁰ 250—253°) among the products, the material was purified by washing with warm benzene (Found: C, 54.7; H, 7.1; N, 22.3. $C_{14}H_{17}N_3O_3 \cdot N_2H_4$ requires C, 54.7; H, 6.8; N, 22.8%).

(c) When a suspension of ethyl 5-(4-chlorophenyl)-3-oxopyrazolidine-4-carboxylate (269 mg) in hydrochloric acid (2*N*; 10 ml) was stored at room temperature for 3 days with occasional shaking, the solid gradually dissolved. After removal of the solvent *in vacuo*, the residue was recrystallised from methanol and identified (m.p. and mixed m.p. 170—171°) as ethyl 5-(4-chlorophenyl)-3-hydroxypyrazole-4-carboxylate (140 mg, 53%).

p-Nitrobenzylmalonohydrazide.—A large excess (0.7 ml) of hydrazine hydrate was added to a suspension of ethyl 5-(4-nitrophenyl)-3-oxopyrazolidine-4-carboxylate (279 mg) in ethanol (20 ml), which was then stored overnight. The product (85 mg) had m.p. 196—197° (from ethanol) (Found: C, 44.9; H, 5.0; N, 26.2. $C_{10}H_{13}N_5O_4$ requires C, 44.9; H, 4.9; N, 26.2%). The *bis*-(4-methylthiosemicarbazide) had m.p. 220—221° (from ethanol) (Found: C, 40.3; H, 4.7; N, 23.9; S, 15.5. $C_{14}H_{19}N_7O_4S_2$ requires C, 40.7; H, 4.6; N, 23.7; S, 15.5%).

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The m.p. recently recorded for *p*-chlorobenzylmalonohydrazide (H. N. Al-Jallo, A. Al-Khashab, and I. G. Sallomi, *J. C. S. Perkin I*, 1972, 1022) appears to refer to a different compound.

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