Reactive Intermediates. Part XXI.[1] Thermal ' Decarboxylation ' of 2,6-Diazatricyclo[5,2,1,$0^{2,6}$]deca-4,8-diene-3,10-diones to Pyrazolo[1,5-*a*]-pyridines[2]

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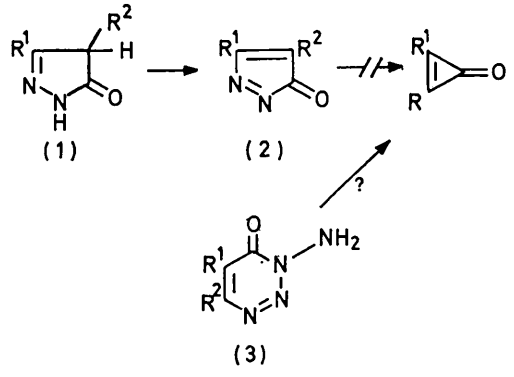
Oxidation of pyrazolin-5-ones (1) in the presence of tetraphenylcyclopentadienone gives high yields of 2,6-diazatricyclo[5,2,1,$0^{2,6}$]deca-4,8-diene-3,10-diones (12). On heating, the latter give pyrazolo[1,5-*a*]pyridines (13) and carbon dioxide formed from two non-adjacent carbonyl groups. A mechanism is proposed for this unusual rearrangement, which is paralleled in the mass spectrometer.

Oxidation of 3,4-diphenyl-Δ^2-pyrazolin-5-one (1; $R^1 = R^2 = Ph$) with lead tetra-acetate in methanol gives methyl *cis*-3-methoxy-2-phenylcinnamate (8), and in ethanol gives ethyl *cis*-3-ethoxy-2-phenylcinnamate.

OXIDATION of 3-aminobenzotriazin-4-one with lead tetra-acetate was shown [3] to proceed by two simultaneous, independent routes involving the loss of 1 mol. equiv. of nitrogen to form indazolone and the loss of 2 mol. equiv. of nitrogen to form benzocyclopropenone. Indazolone, which could be intercepted by dienes, reacted with nucleophiles with subsequent loss of nitrogen but without migration of the carbonyl group. Benzocyclopropenone was extremely reactive towards nucleophiles and could not be isolated; when substituted it gave isomeric pairs of benzoic acid derivatives.

If these reactions are paralleled in the monocyclic series, the five-membered pyrazolones (2) should not collapse to cyclopropenones, whereas the six-membered triazinones (3) should on oxidation give cyclopropenones as isolable products; diphenylcyclopropenone, for example, is stable under the oxidation conditions. Unfortunately no monocyclic 1,2,3-triazinones are known and we have not been able to test whether diphenylcyclopropenone, for example, is formed on oxidation of the triazinone (3; $R^1 = R^2 = Ph$). We have however studied the decomposition of 3,4-disubstituted pyrazol-5-ones (2) and found that, like



(1) (2) (3)

indazolones, these do not collapse with loss of nitrogen to form cyclopropenones.

The pyrazolones (2) are very sensitive to nucleophiles and have not been isolated; they are, however, readily generated under mild conditions by oxidation of pyrazolin-5-ones (1) with lead tetra-acetate.[4]

3-Phenyl- (1; $R^1 = Ph$, $R^2 = H$) [5] and 3,4-diphenyl-Δ^2-pyrazolin-5-one (1; $R^1 = R^2 = Ph$) [6] were prepared by known methods and, as a further check on the intermediacy of cyclopropenones, the isomeric pair of pyrazolinones (1; $R^1 = Ph$, $R^2 = PhCH_2$) and (1; $R^1 = PhCH_2$, $R^2 = Ph$) were also prepared. If the cyclopropenone or any other symmetrical species were an intermediate in the oxidation reaction these two pyrazolinones would give the same products.

When 3,4-diphenylpyrazolin-5-one (1; $R^1 = R^2 = Ph$) in methylene chloride was added to lead tetra-acetate in methylene chloride, gas was evolved and several other products were formed; only two of these were characterised. A small amount of diphenylacetylene (1·3%) presumably resulted from concerted loss of nitrogen and carbon monoxide from the pyrazol-5-one (2; $R^1 = R^2 = Ph$); diphenylcyclopropenone, which is stable under these conditions, was absent. Another product (8%) was considered to be 2,3,6,7-tetraphenylpyrazolo[1,2-*a*]pyrazole-1,5-dione (4) on the basis of its analysis and comparison of its spectral properties with those of the known indazolo[2,1-*a*]-indazole-6,12-dione (5). The mass spectrum of (4) showed initial loss of carbon monoxide, supported by a metastable peak; the rest of the spectrum was similar to that of (5), showing further loss of carbon monoxide and of nitrogen, with large peaks for diphenylcyclopropenone and diphenylacetylene. The bicyclic compound (4) results, overall, from dimerisation of the pyrazolone (2; $R^1 = R^2 = Ph$) with loss of nitrogen. One mechanism for this would be cycloaddition of one molecule of pyrazolone to a nitrogen-free intermediate formed from another. This intermediate is not diphenylcyclopropenone since the pyrazolone (2; $R^1 = R^2 = Ph$) was found not to react with it, under the experimental conditions. Thus collapse to the stable cyclopropenone is again seen not to be a favourable process.

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[1] Part XX, D. J. Anderson, D. C. Horwell, E. Stanton, T. L. Gilchrist, and C. W. Rees, *J.C.S. Perkin I*, 1972, 1317.

[2] Preliminary communication, C. W. Rees and M. Yelland, *Chem. Comm.*, 1969, 377.

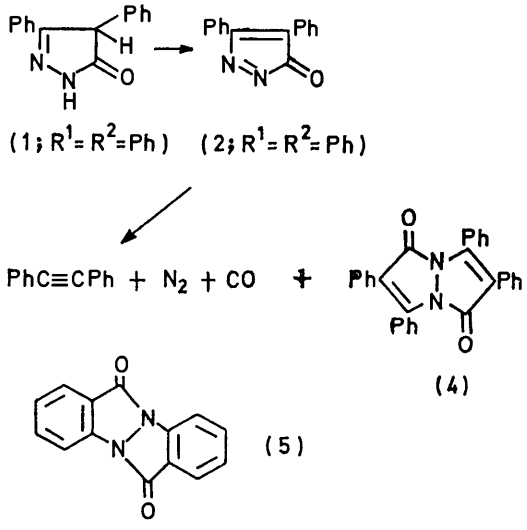
[3] J. Adamson, D. L. Forster, T. L. Gilchrist, and C. W. Rees, *J. Chem. Soc.* (*C*), 1971, 981.

[4] B. T. Gillis and R. Weinkam, *J. Org. Chem.*, 1967, **32**, 3321.

[5] L. A. Carpino, P. H. Terry, and S. D. Thatte, *J. Org. Chem.*, 1966, **31**, 2867; P. E. Gagnon, J. L. Boivin, and R. J. Paquin, *Canad. J. Chem.*, 1953, **31**, 1025.

[6] P. Grünanger and P. Vita Finzi, *Atti. Acad. naz. Lincei*, 1961, **31**, 128; W. O. Gotdfredsen and S. Vangedal, *Acta Chem. Scand.*, 1955, **9**, 1498.

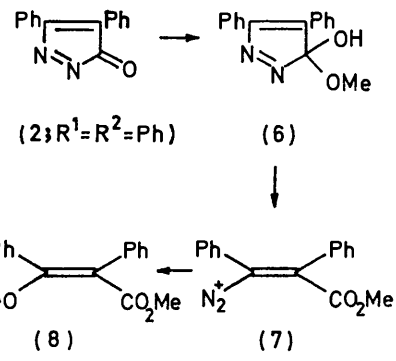
When 4-benzyl-3-phenylpyrazolin-5-one (1; R^1 = Ph, R^2 = $PhCH_2$) and its isomer (1; R^1 = $PhCH_2$, R^2 = Ph) were oxidised similarly, complex mixtures, which could not be resolved chromatographically, were obtained. However, no products common to both reactions were



detected and presumably there was no common intermediate.

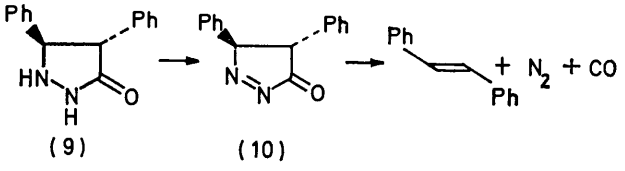
When 3,4-diphenylpyrazolin-5-one (1; R^1 = R^2 = Ph) was oxidised with 1·2 equiv. of lead tetra-acetate in methanol, gas was evolved and methyl *cis*-3-methoxy-2-phenylcinnamate (8) (29%) was isolated. With 2·4 equiv. of oxidant the yield of ester was doubled (58%). The ester was also formed, though in much lower yield (7%), if the methanol was added immediately after oxidation of (1; R^1 = R^2 = Ph) with lead tetra-acetate in methylene chloride. The structure of the ester (8) was confirmed by demethylation with boron tribromide to give methyl 2-benzoylphenylacetate quantitatively; the *cis* stereochemistry follows from the u.v. spectrum, which shows absorptions typical of a *cis*-stilbene derivative. This oxidation of (1; R^1 = R^2 = Ph) presumably involves formation of the pyrazolone (2; R^1 = R^2 = Ph) and rapid nucleophilic addition of methanol to the α-carbonylazo-system to give (6). Compound (6) does not then ring open with loss of nitrogen to give methyl 2-phenylcinnamate since this is inert in the oxidation conditions, and was not detected. Furthermore 2 equiv. of lead tetra-acetate are consumed. So (6) must be oxidised further, possibly to give the diazonium ion (7) as its acetate or lead acetate complex, which is finally solvolysed by methanol. In agreement with this proposal, Carpino [5] has shown that when pyrazolones like (2; R^1 = R^2 = Ph) are generated from the corresponding 4-halogenopyrazolinone and aqueous sodium hydroxide, ring opening is again observed but the nitrogen is replaced by hydrogen to give the simple αβ-unsaturated acid.

Similar oxidation of 3,4-diphenylpyrazolin-5-one (1; R^1 = R^2 = Ph) in ethanol gave ethyl *cis*-3-ethoxy-2-phenylcinnamate (70%). Since pyrazolin-5-ones (1) are readily available, this oxidation in the presence of alcohols probably provides a useful new synthesis of

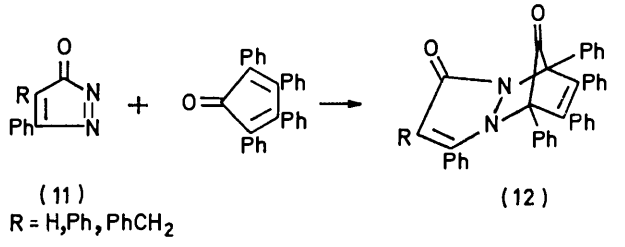


3-alkoxyacrylic esters, though its scope has not been explored.

Oxidation of the fully saturated *trans*-4,5-diphenylpyrazolidin-3-one (9) [7] gave *trans*-stilbene in high yield, in agreement with the literature,[4,8] presumably by concerted loss of nitrogen and carbon monoxide from the α-carbonylazo-intermediate (10). However, this intermediate could not be intercepted with methanol, or with tetraphenylcyclopentadienone (tetracyclone), since in their presence stilbene was again formed in high yield.



As α-azocarbonyl compounds, pyrazolones are highly reactive dienophiles.[4,5] The pyrazolones (11; R = H, Ph, or $PhCH_2$) formed in the above oxidation reactions were readily intercepted with conjugated dienes, particularly tetracyclone, to give yellow Diels-Alder



adducts (12; R = H, Ph, or $PhCH_2$). Similarly, with (11; R = Ph) butadiene gave the simpler adduct, 7,8-diphenylpyrazolo[1,2-*a*]pyridazin-6-one, identical with that formed [5] when the pyrazolone was generated by dehydrochlorination of 4-chloro-3,4-diphenylpyrazolon-5-one with triethylamine.

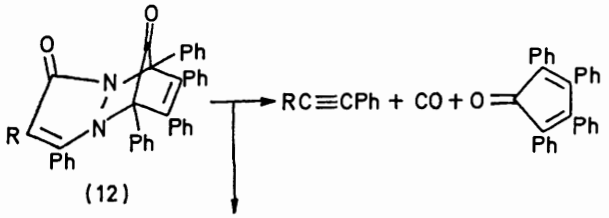
The mass spectra of the tetracyclone adducts showed strong peaks for the parent ion and for tetracyclone,

[7] L. A. Carpino, *J. Amer. Chem. Soc.*, 1958, **80**, 601.
[8] R. H. Kent and J.-P. Anselme, *Canad. J. Chem.*, 1968, **46**, 2322.

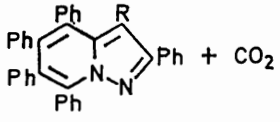
but in each case the first major fragment lost from the parent ion had mass 44, suggesting the loss of carbon dioxide. This was intriguing since the oxygen atoms in the adducts (12) are part of well separated carbonyl groups, and it is not immediately obvious why they should be extruded as carbon *di*oxide. It was therefore of interest to see if the same ' decarboxylation ' occurred thermally.

When the adduct (12; R = Ph) was sublimed at 210° and 0·1 torr it gave diphenylacetylene (4%), tetracyclone (35%), and a colourless crystalline compound, $C_{43}H_{30}N_2$ (35%), highly fluorescent in u.v. light, which from spectral and analytical data, and its striking chemical inertness, was assigned the hexaphenylpyrazolopyridine structure (13; R = Ph). Its very simple i.r. spectrum, its u.v. spectrum, and its mass spectral fragmentation accord with the highly stable 10 π-electron aromatic system, and agree with data reported for other pyrazolo[1,5-*a*]pyridines.[9] Further evidence for the pyrazolopyridine structure was provided by the pyrolysis of adduct (12; R = H). In the n.m.r. spectrum of the product (13; R = H), the lone 3-proton appeared as a singlet at τ 3·3. Bromination of this product gave a monobromo-derivative (13; R = Br) in the spectrum of which this signal had disappeared. The high reactivity of the 3-position in pyrazolo[1,5-*a*]pyridine towards electrophilic attack was suggested by electron-density calculations by Paudler and Dunham, and confirmed by its ready conversion into the 3-bromo-derivative.[9c]

In the pyrolysis of (12; R = Ph), diphenylacetylene and tetracyclone presumably arose by a retro-Diels-Alder reaction; again the acetylene is formed, together with carbon monoxide and nitrogen, in only low yield

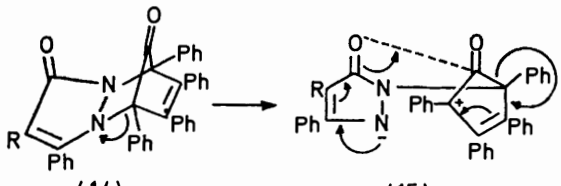


(12)



(13)

from the pyrazolone (11; R = Ph). In the pyrolysis of (12; R = H) carbon monoxide was detected by burning the evolved gas, and carbon dioxide was detected separately, by passing the gas through lime water. In this example, tetracyclone (34%) and the pentaphenylpyrazolopyridine (13; R = H) (44%) were obtained. In a large-scale experiment, pentaphenylbenzene (7%) was also isolated; its formation is readily explained in terms of initial generation of tetracyclone and phenylacetylene, as above, and a Diels-Alder reaction between them, followed by extrusion of carbon monoxide to give the aromatic system.



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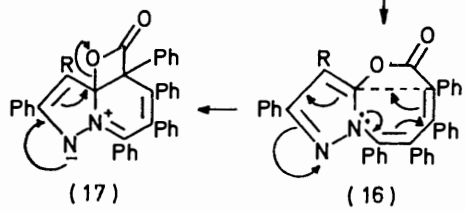

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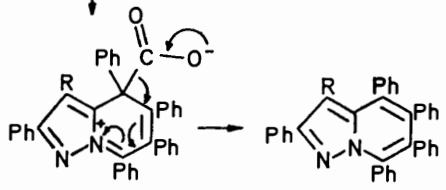

(18) (13)

Similar pyrolysis of the adduct (12; R = $PhCH_2$) at 230° and 0·1 torr gave the pyrazolopyridine (13; R = $PhCH_2$) (27%) and tetracyclone (41%).

The bridging carbonyl group in the adducts (12) could not be extruded as carbon monoxide preferentially, by more gentle heating in the solid state or in solution. This only served to decrease the rate of ' decarboxylation '. Presumably the bicyclic structure which would result from decarbonylation is not a sufficiently stabilised, aromatic system. Unfortunately the adducts (12) were not volatile enough for their thermal decomposition in the gas phase to be studied. Attempted photolysis of the adduct (12; R = Ph) gave only a small amount of tetracyclone and a complex mixture of other products containing the pyrazolopyridine (13; R = Ph).

The mechanism of this unusual and unexpected rearrangement has not been studied in detail; we suggest the following as a reasonable pathway. Heterolytic C–N bond fission (14), the first part of a stepwise retro-Diels-Alder reaction, would give the stabilised zwitterion (15) in which nucleophilic attack by the pyrazolone oxygen on the other carbonyl group becomes possible; neutralisation of charges would then give the bicyclic lactone (16). However, the initial bond fission could be homolytic rather than heterolytic to give a diradical

[9] (*a*) J. D. Bower and G. R. Ramage, *J. Chem. Soc.*, 1957, 4506; (*b*) J. D. Bower, *ibid.*, p. 4510; (*c*) W. N. Paudler and D. E. Dunham, *J. Heterocyclic Chem.*, 1965, **2**, 410; (*d*) V. Boekelheide and N. A. Fedoruk, *J. Org. Chem.*, 1968, **33**, 2062; (*e*) K. T. Potts, U. P. Singh, and J. Bhattacharyya, *ibid.*, p. 3766.

intermediate analogous to (15). The lactone (16) can now lose carbon dioxide by, first, the extended pericyclic process shown [arrows in (16)], which is facilitated by the terminal nucleophilic and electrophilic nitrogen atoms, followed by the reverse process [arrows in (17) and (18)], in which carbon dioxide is extruded to form the very stable aromatic system (13). Nothing is known about the timing of these steps. For example, the final reaction, (16) ⟶ (13), could occur stepwise through the zwitterion (18). Similarly the initial conversion of (14) into (16) could be an entirely concerted rearrangement.

EXPERIMENTAL

For general directions see Part XVIII.[10]

General Procedure for the Oxidations.—A solution of the pyrazolinone in dry methylene chloride (20 ml per mmol) was added dropwise over 15 min to a stirred solution of lead tetra-acetate (1·2 mmol per mmol of pyrazolinone) in methylene chloride (50 ml per mmol of lead tetra-acetate) at room temperature. Stirring was continued until the reaction was complete (t.l.c.). The mixture was filtered, the filtrate was evaporated, and the residue was subjected to column chromatography.

Oxidation of 3,4-*Diphenyl-*Δ^2*-pyrazolin-5-one* (1; $R^1 = R^2$ = Ph).—(a) *Alone.* The pyrazolinone [6] (1·9 g, 8 mmol) was oxidised as above. The solution darkened and gas was evolved. Chromatography on silica gel with ether–petroleum gave: (i) diphenylacetylene (1·3%), m.p. and mixed m.p. 57—58°, identical (i.r. spectrum) with an authentic specimen; (ii) crystals (17 mg), m.p. 260—262°, fluorescent in u.v. light, *m/e* 414, 307, 281, 206, 178, 165, 127, 105, and 77; (iii) 2,3,6,7-*tetraphenylpyrazolo*[1,2a]-*pyrazole*-1,5-*dione* (4) (8%), m.p. 272—274° (needles from ethanol) (Found: C, 81·8; H, 4·5; N, 6·3%; *m/e* 440. $C_{30}H_{20}N_2O_2$ requires C, 81·8; H, 4·5; N, 6·4%; *M*, 440), $\lambda_{max.}$ 262 nm (log ε 4·39), $\nu_{max.}$ 1725, 1635, 1610, 1585, 1515, 1465, 1450, 1390, 1370, and 765 cm^{-1}, *m/e* 440, 412, 385·78 (metastable), 356, 220, 206, 178, 105, and 77; and (iv) a bright yellow fluorescent compound which could not be purified; its poorly resolved i.r. spectrum showed a broad carbonyl band at 1729 cm^{-1}. No diphenylcyclopropenone was detected (t.l.c.).

(b) *In the presence of diphenylcyclopropenone.* The pyrazoline (120 mg, 0·5 mmol) was oxidised as above in the presence of diphenylcyclopropenone (103 mg, 0·5 mmol). The mixture was filtered after 2 h and the methylene chloride solution extracted with 65% sulphuric acid (4 × 10 ml). The acid extract was poured into iced water and the aqueous solution extracted with methylene chloride; the organic solution was washed with water, dried, and evaporated to give diphenylcyclopropenone (96%).

(c) *In methanol.* The pyrazolinone (0·5 g) in dry methanol (50 ml) was added dropwise to a stirred suspension of lead tetra-acetate (1·2 g) in methanol (100 ml) at room temperature. Stirring was continued overnight. The suspension was filtered and the filtrate evaporated on silica gel and chromatographed with ether–petroleum to give *methyl* cis-3-*methoxy*-2-*phenylcinnamate* (29%), m.p. 81—82° (after sublimation) (Found: C, 75·9; H, 6·1%; *m/e* 268. $C_{17}H_{16}O_3$ requires C, 76·2; H, 6·0%; *M*, 268), $\nu_{max.}$ 1710, 1620, 1600, 1580, 1500, 1310, 1300, 1212, 1100, 1070, 1045, 768, 743, 712, and 698 cm^{-1}, $\lambda_{max.}$ (EtOH) 225 (ε 12,000) and 280 (11,000) nm, τ 6·68 (3H, s), 6·60 (3H, s), and 2·62—2·8 (10H, m), *m/e* 268, 237, 221, 194, 179, 165, 105, 92, and 77. Treatment of the ester with boron tribromide in methylene chloride gave methyl 2-benzoylphenylacetate (100%), m.p. 72—74° (lit.,[11] 74°).

When the oxidation was repeated with more lead tetra-acetate (2·4 g) the yield of ester was 58%.

The pyrazolinone was oxidised in methylene chloride as described in (a), but as soon as the addition to the oxidant was complete methanol was added. The colour of the mixture changed from brown to orange and gas was evolved. Chromatography gave methyl 3-methoxy-2-phenylcinnamate (7%).

Methyl 2-phenylcinnamate was recovered (99%) after treatment with lead tetra-acetate in methanol at room temperature overnight.

(d) *In ethanol.* Oxidation as in (c) but in dry ethanol gave, after chromatography on silica gel, *ethyl* cis-3-*ethoxy*-2-*phenylcinnamate* (36%), m.p. 46—48° (Found: C, 77·5; H, 6·8%; *m/e* 296. $C_{19}H_{20}O_3$ requires C, 77·8; H, 6·8%; *M*, 296), $\nu_{max.}$ 1710, 1620, 1600, 1212, 1100, 743, 712, and 698 cm^{-1}, $\lambda_{max.}$ (EtOH) 225 (ε 10,000) and 280 nm (10,000) *m/e* 296, 267, 251, 206, and 178. When the oxidation was repeated with more lead tetra-acetate (4·8 g) the yield of ester was 70%.

(e) *In the presence of tetracyclone.* The pyrazolinone (1·5 g) in methylene chloride (150 ml) was added dropwise to a stirred mixture of lead tetra-acetate (4 g) and tetracyclone (3·5 g) in methylene chloride (150 ml) during 1 h at room temperature. The mixture was stirred overnight and filtered, and the residue was washed with methylene chloride. The filtrates were evaporated on silica gel and chromatographed to give tetracyclone (40% recovery), and yellow needles (from benzene) of 1,4,5,7,8,9-*hexaphenyl*-2,6-*diazatricyclo*[5,2,1,$0^{2,6}$]*deca*-4,8-*diene*-3,10-*dione* (12; R = Ph) (62%), m.p. 227·5—228·5° (Found: C, 85·0; H, 4·9; N, 4·5%; *m/e* 618. $C_{44}H_{30}N_2O_2$ requires C, 85·4; H, 4·9; N, 4·5%; *M*, 618), $\nu_{max.}$ 1715, 1605, 1590, 1570, 740, 730, and 690 cm^{-1}, τ 2·3—3·3br (m, aromatic H only), *m/e* 618(*M*), 574 (*M* − CO_2), 384 (tetracyclone), and 178 (tolan).

The adduct (12; R = Ph) was also prepared as follows. 4-Chloro-3,4-diphenyl-Δ^2-pyrazolin-5-one [5] (0·27 g) and tetracyclone (0·96 g) were suspended in dry ether (50 ml) at 0°. Triethylamine (0·15 ml) was added and the mixture was stirred at 0° for 3 h and filtered; the filtrate was evaporated and the residue chromatographed to give the adduct (12; R = Ph) (44%), m.p. and mixed m.p. 225—227°.

(f) *In the presence of buta*-1,3-*diene.* The pyrazolinone (1·18 g) in methylene chloride (20 ml) was added dropwise at 0° to a stirred suspension of lead tetra-acetate (3·5 g) in methylene chloride (50 ml) through which a slow stream of butadiene was bubbling. The mixture was stirred at 0° for 1 h, then filtered, and the filtrate was evaporated. The residue was extracted with ether; evaporation of the extract gave pale yellow needles, m.p. 186—187° (lit.,[5] 187—189°) (from benzene–petroleum) of 7,8-diphenylpyrazolo-[1,2*a*]pyridazin-6-one (45%) (Found: C, 79·1; H, 5·7; N, 9·8. Calc. for $C_{19}H_{16}N_2O$: C, 79·2; H, 5·6; N, 9·7%), $\lambda_{max.}$ 210 (log ε 4·34) and 300 nm (4·00), $\nu_{max.}$ 1670, 1640, 1600, 740, 700, and 655 cm^{-1}, τ 6·23br (2H, s), 5·61br (2H, s), and 2·62 (10H, m).

Oxidation of Other Pyrazolinones.—(a) 4-*Benzyl*-3-*phenyl*-

[10] C. W. Rees and M. Yelland, *J.C.S. Perkin I*, 1972, 77.
[11] E. P. Kohler, *J. Amer. Chem. Soc.*, 1924, **46**, 1743.

Δ^2-*pyrazolin-5-one* (I; R^1 = Ph, R^2 = $PhCH_2$) *and* 3-*benzyl-4-phenyl-*Δ^2-*pyrazolin-5-one* (1; R′ = $PhCH_2$, R^2 = Ph). The two pyrazolinones [5] were oxidised separately with lead tetra-acetate in methylene chloride as before. Each reaction gave a complex mixture of products (t.l.c.) but no product common to both was detected. Attempted resolution of the mixtures by column chromatography was unsuccessful.

(b) 4-*Benzyl-3-phenyl-*Δ^2-*pyrazolin-5-one in the presence of tetracyclone*. The pyrazolinone was oxidised as described in (e) to give the adduct, 4-*benzyl*-1,5,7,8,9-*pentaphenyl*-2,6-*diazatricyclo*[5,2,1,$0^{2,6}$]*deca*-4,8-*diene*-3,10-*dione* (12; R = $PhCH_2$) (53%) as pale yellow needles from benzene, m.p. 174—175° (Found: C, 85·3; H, 5·0; N, 4·4%; *m/e* 632. $C_{45}H_{32}N_2O_2$ requires C, 85·4; H, 5·1; N, 4·4%; *M*, 632), $\nu_{max.}$ 1730, 1625, 1590, 730, 705, and 695 cm^{-1}, τ 8·70—8·93 (2H, m) and 2·65—2·95 (30H, m), *m/e* 632 (*M*), 588 (*M* − CO_2), and 384 (tetracyclone).

(c) 3-*Phenyl-*Δ^2-*pyrazolin-5-one* [5] *in the presence of tetracyclone*. The pyrazolinone was oxidised as described in (e) to give the adduct, 1,5,7,8,9-*pentaphenyl*-2,6-*diazatricyclo*-[5,2,1,$0^{2,6}$]*deca*-4,8-*diene*-3,10-*dione* (12; R = H) (63%) as yellow needles from benzene–petroleum (1 : 1), m.p. 225·5—223° (Found: C, 85·3; H, 4·8; N, 5·2%; *m/e* 542. $C_{38}H_{26}N_2O_2$ requires C, 84·1; H, 4·8; N, 5·2; *M*, 542), $\nu_{max.}$ 1740, 1570, 1600, 745, 700, and 690 cm^{-1}, τ 4·03 (1H, s) and 2·10—3·35 (25H, m), *m/e* 542 (*M*), 514 (*M* − CO), 498 (*M* − CO_2), and 384 (tetracyclone).

Oxidation of 4,5-*Diphenylpyrazolidin-3-one* [5] (9).—(a) *Alone*. The pyrazolidinone (0·476 g) in methylene chloride (5 ml) was added dropwise to lead tetra-acetate (3·0 g) in methylene chloride (15 ml). Gas was evolved immediately. The mixture was stirred for 1 h, glycerol (1 drop) was added, and the insoluble residue was filtered off. The filtrate was evaporated to dryness and extracted with ether. Evaporation gave *trans*-stilbene (72%), m.p. and mixed m.p. 125—126°, identical (i.r. spectrum) with an authentic specimen.

A similar oxidation in methanol gave *trans*-stilbene (67%), with no evidence for ester products.

(b) *In the presence of tetracyclone*. Oxidation of the pyrazolidinone as before in the presence of an excess of tetracyclone gave, after chromatography, *trans*-stilbene (77%), unchanged tetracyclone (87%), and the adduct (12; R = Ph) (1%), m.p. and mixed m.p. 226—227°, identical with that obtained from 3,4-diphenyl-Δ^2-pyrazolin-5-one.

Pyrolysis of the Adducts (12).—*Adduct* (12; R = Ph). (*a*) This adduct (200 mg) was sublimed at 210° and 0·1 Torr for 16 h. Tolan (4%), m.p. and mixed m.p. 58—59°, was collected from the walls of the tube. The remaining sublimate was chromatographed on silica gel to give tetracyclone (35%), m.p. and mixed m.p. 218—220°, and 2,3,4,5,6,7-*hexaphenylpyrazolo*[1,5a]*pyridine* (13; R = Ph) (35%), m.p. 272·5—273·5° (Found: C, 90·2; H, 5·1; N, 4·9%; *m/e* 574. $C_{43}H_{30}N_2$ requires C, 89·9; H, 5·2; N, 4·9%; *M*, 574), $\lambda_{max.}$ 258 (log ε 4·43), 274 (4·43), and 325 nm (3·60), $\nu_{max.}$ 1610, 1575, 1490, 1062, 1020, 773, 753, and 700 cm^{-1}, τ 2·5—3·1 (m, aromatic protons only), *m/e* 574 (*M*) and 471 (*M* − PhCN).

(*b*) The adduct (100 mg) was stirred in *o*-dichlorobenzene (2 ml) at 180° for 2 h. ' Decarboxylation ' occurred slowly (t.l.c.). After 28 h *ca.* 40% of the adduct had decomposed to give tetracyclone and the pyrazolopyridine (13; R = Ph). There was no evidence (t.l.c.) for the formation of a decarbonylation product.

(*c*) ' Decarboxylation ' of the adduct in 1,2,4-trichlorobenzene at 220° was complete after 4 h. The mixture was cooled and poured into ether. The precipitate crystallised from benzene to give the pyrazolopyridine (13; R = Ph) (45%), m.p. and mixed m.p. 272—273°.

Adduct (12; R = $PhCH_2$). This adduct (200 mg) was sublimed at 230° and 0·1 Torr for 16 h. Chromatography of the sublimate on silica gel gave tetracyclone (41%), m.p. and mixed m.p. 218—219°, and 3-*benzyl*-2,4,5,6,7-*pentaphenylpyrazolo*[1,5a]*pyridine* (13; R = $PhCH_2$) (27%), m.p. 204—205° (Found: C, 89·5; H, 5·5; N, 4·7%; *m/e* 588. $C_{44}H_{32}N_2$ requires C, 89·8; H, 5·4; 4·8%; *M*, 588), $\nu_{max.}$ 1610, 1580, 1525, 1500, 1440, 1075, 1030, 775, 760, 745, 710, and 695 cm^{-1}, *m/e* 588 (*M*), 511 (*M* − Ph) and 497 (*M* − $PhCH_2$).

Adduct (12; R = H). This adduct (500 mg) was heated at 260° (bath temp.). It melted and turned red, and carbon dioxide (lime water test) was evolved. After 1 h the residue was chromatographed on silica gel to give tetracyclone (34%), m.p. 218—220°, and 2,4,5,6,7-*pentaphenylpyrazolo*[1,5a]*pyridine* (13; R = H) (44%), as crystals from benzene–petroleum (1 : 5), m.p. 300—301° (Found: C, 88·9; H, 5·2; N, 5·6%; *m/e* 498. $C_{37}H_{26}N_2$ requires C, 89·1; H, 5·2; N, 5·6%; *M*, 498), $\lambda_{max.}$ (dioxan) 286 (log ε 4·47) and 324 nm (4·00), $\nu_{max.}$ 1605, 1580, 1535, 1490, 1275, 1080, 1030, 765, 750, 705, and 695 cm^{-1}, τ 3·3 (1H, s, aromatic), 3·1 (10H, s, aromatic), and 2·65—2·8 (15H, m, aromatic), *m/e* 498 (*M*), 394 (*M* − H − PhCN), 317, 289, 248, 202, 200, 199, 181, 131, and 103 (PhCN).

A repeat experiment with this adduct (1·8 g) also gave pentaphenylbenzene (7%) after chromatography; m.p. 248—249° (lit.,[12] 246°) (Found: C, 94·4; H, 5·9%; *m/e* 458. Calc. for $C_{35}H_{26}$. C, 94·3; H, 5·7%; *M* 458), $\nu_{max.}$ 1600, 1575, 1490, 1080, 1035, 907, 780, 766, 730, and 700 cm^{-1}, τ 2·4 (1H, s, aromatic) and 2·84—3·1 (25H, m, aromatic).

3-*Bromo*-2,4,5,6,7-*pentaphenylpyrazolo*[1,5-a]*pyridine*.—Pentaphenylpyrazolo[1,5-a]pyridine (13; R = H) (50 mg) was dissolved in ethylcellosolve–acetic acid (1 : 1; 20 ml) and bromine (1 drop) was added. After 16 h the addition of water (5 ml) caused slow crystallisation of the *bromo-compound* (84%), m.p. 302—303° (Found: C, 77·0; H, 4·5; N, 4·9. $C_{37}H_{25}BrN_2$ requires C, 77·0; H, 4·3; N, 4·9%), $\nu_{max.}$ 1600, 1590, 1475, 1270, 1070, 1025, 770, 750, 710, and 700 cm^{-1}, τ 3·1 (10H, s, aromatic) and 2·72 (15H, m, aromatic), *m/e* 578, 576, 532, 498, 395, 219, and 178.

We thank Imperial Chemical Industries, Ltd., Organics Division, for secondment of M. Y., and Dr. T. L. Gilchrist for discussion.

[2/1969 *Received*, 17*th August*, 1972]

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