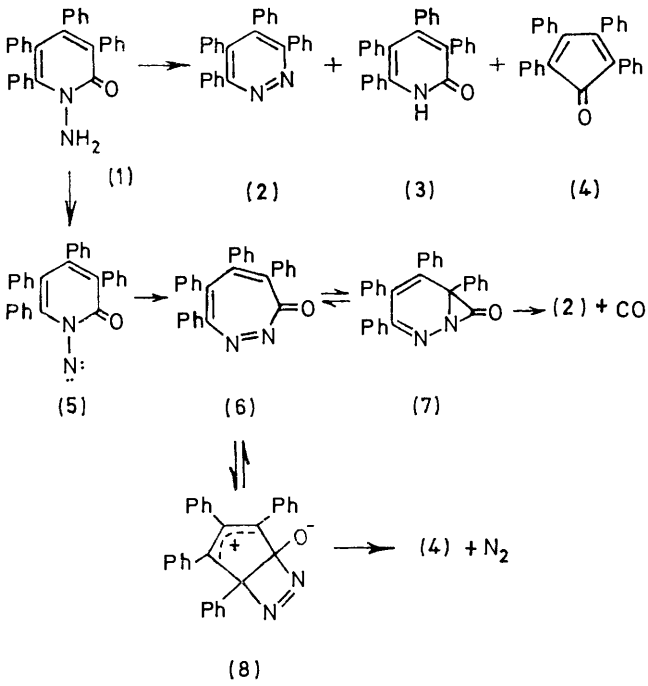
Reactive Intermediates. Part XVIII.[1] An *N*-Aminopyridone-to-Pyridazine Rearrangement; a New Decarbonylation Reaction [2]

By C. W. Rees *† and M. Yelland, Chemistry Department, The University, Leicester LE1 7RH

Oxidation of 1-amino-3,4,5,6-tetraphenyl-2-pyridone with lead tetra-acetate results in loss of carbon monoxide and retention of nitrogen to give 3,4,5,6-tetraphenylpyridazine. This rearrangement is thought to involve ring expansion of the *N*-nitrene to a diazepinone and valence tautomerism of this to give a bicyclic intermediate which extrudes carbon monoxide. This reaction can be suppressed by competitive intermolecular reaction of the nitrene with sulphoxides or with cyclohexene. This pyridone-to-pyridazine rearrangement is observed to a much smaller extent with di- and tri-phenyl-1-amino-2-pyridones, and not at all with 1-amino-2,3-diphenylquinolin-4-one or 5-aminophenanthridin-6-one.

1-AMINO-3,4,5,6-TETRAPHENYL-2-PYRIDONE (1) was prepared by treatment of tetraphenyl-2-pyrone with hydrazine, and also by amination of tetraphenyl-2-pyridone (3) with chloramine. Its identification followed from analytical and spectral data, formation of a benzylidene derivative, and almost quantitative deamination to (3) with nitrous acid.

When the *N*-aminopyridone (1) was oxidised in methylene chloride at room temperature with lead tetra-acetate, gas was evolved and 3,4,5,6-tetraphenylpyridazine (2) (58%) was formed. Thus carbon monoxide rather than nitrogen appears to have been lost from (1); this was confirmed by burning the evolved gas. Oxidative deamination (see later) also occurred to give the pyridone (3) (15%); a small amount of tetraphenyl-



cyclopentadienone (tetracyclone) (4) was also formed, but was consumed during the reaction.

Since in the conversion of the aminopyridone (1) into the pyridazine (2) the exocyclic nitrogen atom becomes incorporated into the ring, it is tempting to suggest that (1) is first dehydrogenated to the *N*-nitrene (5) which undergoes ring expansion to give the diazepinone (6). A few such intramolecular rearrangements of *N*-nitrenes in which the nitrogen atom is retained are known, though these involve the expansion of five- to six-membered rings. Thus oxidation of 1-amino-oxindole with lead tetra-acetate gave cinnolin-3-ol,[3] and base-catalysed decomposition of 1-tosylaminopyrrolidine gave tetrahydropyridazine;[4] in both these reactions the initial product tautomerised to a more stable isomer. The diazepinone (6) is a reactive α-oxo-azo-compound, which can undergo valence tautomerism in a thermally allowed electrocyclic process to give the bicyclic tautomers (7). Carbon monoxide could then be extruded to give the stable, aromatic pyridazine (2). A less favourable valence tautomerism of compound (6) could give the bicyclic system (8), fragmentation of which would provide a route to the small amount of tetracyclone (4) detected in the reaction.

The valence tautomerism (6) ⇌ (7) is isoelectronic with the well known cycloheptatriene–norcaradiene equilibrium.[5] A close analogy for this cycloheptatrienone-to-norcaradienone interconversion is provided by the pyrolysis of tropone to benzene and carbon monoxide, for which the same mechanism is proposed.[6] However, the gas-phase conversion of simple tropones into benzenes requires a temperature of 500° or more, in contrast with our rapid room temperature reaction. The much faster conversion (6) ⟶ (7) ⟶ (2) may be explained partly by the presence of the heterocyclic nitrogen atoms, and partly by the four adjacent phenyl groups. The cycloheptatriene–norcaradiene equilibrium normally lies almost entirely on the side of the heptatriene, though certain structural features can favour the bicyclic structure. One of these is the introduction of three phenyl groups into the cycloheptatriene.[7] A

† *Present address:* The Robert Robinson Laboratories, University of Liverpool, P.O. Box 147, Liverpool L69 3BX.

[1] Part XVII, S. Bradbury, C. W. Rees, and R. C. Storr, preceding paper.

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

[3] H. E. Baumgarten, P. L. Creger, and R. L. Zey, *J. Amer. Chem. Soc.*, 1960, **82**, 3977.

[4] D. M. Lemal and T. W. Rave, *J. Amer. Chem. Soc.*, 1965, **87**, 393.

[5] E. Ciganek, *J. Amer. Chem. Soc.*, 1967, **89**, 1454; G. Maier, *Angew. Chem. Internat. Edn.*, 1967, **6**, 402.

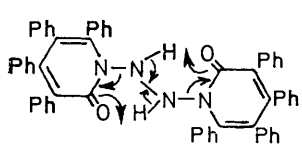
[6] T. Mukai, T. Nakazawa, and T. Shishido, *Tetrahedron Letters*, 1967, 2465.

[7] T. Mukai, H. Kubota, and T. Toda, *Tetrahedron Letters*, 1967, 3581.

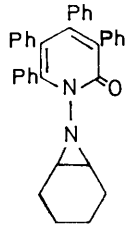
similar factor may be operating here; if the diazepinone exists largely as diazanorcaradienone (7) the overall conversion rate of (6) into (2) will be greatly increased.[8] Furthermore, this could explain the much lower yield of pyridazines from di- and tri-phenylpyridones (see later), since if the diazepinone is not converted rapidly into the diazanorcaradienone it will, as a reactive α-oxo-azo-compound, be rapidly diverted by nucleophiles or by cyclo-addition reactions, possibly to give polymeric products.

The other product of oxidation of the aminopyridone (1) was that of deamination, the pyridone (3) (15%). Such deamination is commonly observed in the lead tetra-acetate oxidation of *N*-amino-lactams. It probably arises by fragmentation of the corresponding tetrazane[9] (9), formed by reaction of the nitrene (5) with another molecule of starting material (1). The two molecules of pyridone, and nitrogen, need not be, and probably are not, formed in the wholly concerted manner shown in (9). Such tetrazanes have recently been isolated from oxidation of *N*-amino-compounds with phenyl iodosoacetate, and shown to undergo the proposed fragmentation readily.[10]

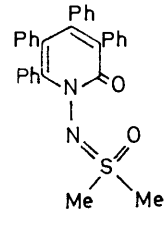
Evidence for the discrete intermediacy of the nitrene (5) in the foregoing reactions was provided by repeating the oxidation of (1) in the presence of cyclohexene and of dimethyl sulphoxide, which react readily with *N*-nitrenes produced under these conditions, to form aziridines[11] and sulphoximides,[12] respectively. When *N*-aminopyridone (1) was oxidised in cyclohexene the nitrene–olefin adduct (10) was indeed formed (25%), in competition with rearrangement to give (2) (21%) and deamination to give (3) (15%). When compound (1)



(9)



(10)



(11)

was oxidised in dimethyl sulphoxide the sulphoximide (11) was formed in high yield (84%), to the exclusion of any significant amount of the other products; this agrees with our general observation that dimethyl sulphoxide is more efficient than olefins as a ' trap ' for *N*-nitrenes.

Similarly, oxidation in the presence of methyl phenyl sulphoxide gave the corresponding sulphoximide in high yield (75%), almost to the exclusion of the pyridazine (4%). Oxidation in the presence of the less reactive diphenyl sulphoxide gave the diphenylsulphoximide (33%), isolated as the monohydrate, together with the pyridazine (2) (34%) and pyridone (3) (*ca.* 10%) in reduced amounts. Oxidation in the presence of diphenyl sulphide however, gave no nitrene–sulphide adduct (a sulphimide); rather less pyridazine and rather more pyridone were formed than in the absence of the sulphide, which was itself largely unchanged (95% recovered).

It is noteworthy that, if the amino-nitrene (5) is the intermediate for formation of the bimolecular products, like (3), (10), and (11), as well as for the unimolecular rearrangement product (2), then dimethyl sulphoxide is a very efficient ' trap ' for this nitrene, reacting with it faster than in any irreversible step on the way to the pyridazine (2). This suggests that the nitrene, or some valence tautomer of it, is a relatively long-lived species. It would thus be intermediate in stability between those *N*-nitrenes which are readily intercepted and do not rearrange, like phthalimidonitrene, and those which fragment or rearrange too fast to be intercepted at all by dimethyl sulphoxide, like benzotriazolyl nitrenes.

Some further evidence for the intermediacy of the *N*-nitrene (5) in the formation of the pyridazine (2) came from pyrolysis of its dimethyl sulphoxide adduct (11). On brief heating of this alone at 270°, dimethyl sulphoxide was formed together with small amounts of tetracyclone and the pyridazine; the major product was the pyridone (3) (43%). The same products were formed in similar yields on heating for longer times at lower temperatures. On boiling in decalin, the sulphoximide (11) gave the pyridazine (21%) and the pyridone (30%) after 4 hr. These reactions (and others to be described in this Series) are considered to involve dissociation of the sulphoximide into dimethyl sulphoxide and the nitrene, which then undergoes the various reactions already described. The higher proportion of pyridone (3) formed in pyrolysis of (11), compared with oxidation of the *N*-amino-pyridone (1), probably results from intramolecular hydrogen transfer from the (active) *S*-methyl groups, since no pyridone was formed when the diphenylsulphoximide (11; Ph for Me) was pyrolysed. This behaviour is paralleled in the vapour-phase flash pyrolysis of several such dimethyl- and diphenyl-sulphoximides, and pyrolysis of a dibenzylsulphoximide has been shown to lead to almost exclusive transfer of the more reactive benzylic hydrogen atoms.[13]

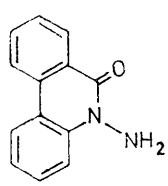
Photolysis of these sulphoximides is similarly thought to cause dissociation into the sulphoxide and the nitrene, and u.v. irradiation of compound (11) in cyclohexene gave the aziridine (10), identical with that formed by oxidation of the *N*-amino-pyridone (1) in cyclohexene. To our surprise, the sulphoximide (11) was unchanged on irradiation in the absence of cyclohexene; no pyridazine

[8] J. A. Berson, P. W. Grubb, R. A. Clark, D. R. Hartter, and M. R. Willcott, *J. Amer. Chem. Soc.*, 1967, **89**, 4076.
[9] L. Hoesch and A. S. Dreiding, *Chimia* (*Switz.*), 1969, **23**, 405.
[10] D. J. Anderson, T. L. Gilchrist, and C. W. Rees, *Chem. Comm.*, 1971, 800.
[11] D. J. Anderson, T. L. Gilchrist, D. C. Horwell, and C. W. Rees, *J. Chem. Soc.* (*C*), 1970, 576.
[12] D. J. Anderson, T. L. Gilchrist, D. C. Horwell, and C. W. Rees, *Chem. Comm.*, 1969, 146.
[13] T. L. Gilchrist, C. W. Rees, and E. Stanton, *Chem. Comm.*, 1971, 801.

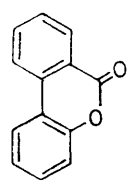
was formed, and again this could result from the avidity of dimethyl sulphoxide for the nitrene.

Attempted extension of this pyridone-to-pyridazine rearrangement to simpler 1-amino-2-pyridones was not very successful. Oxidation of 1-amino-4,6-diphenyl-2-pyridone, exactly as described for (1), did give 3,5-diphenylpyridazine but in considerably lower yield (12%). Oxidation of 1-amino-4,5,6-triphenyl-2-pyridone similarly gave 3,4,5-tiphenylpyridazine in low yield (7%), but in this case a large amount (58%) of the deaminated material was formed; this was identical with the product obtained by nitrous acid deamination of the starting material. Oxidation of 1-amino-6-methyl-3,4,5-triphenyl-2-pyridone, however, gave no pyridazine, but only deaminated product (25%). A possible factor contributing to this variation of products with structure was mentioned earlier.

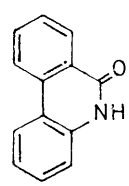
The similar oxidation of 5-aminophenanthridone (12) was also briefly investigated. By analogy this would be expected to give benzo[*c*]cinnoline by elimination of carbon monoxide from the seven-membered α-oxo-azo-intermediate, and possibly some fluorenone by analogy with the formation of tetracyclone. However, oxidation of (12) gave dibenzo[*b*,*d*]pyran-6-one (13) (31%) and phenanthridone (14) (43%); no benzo[*c*]cinnoline or



(12)



(13)

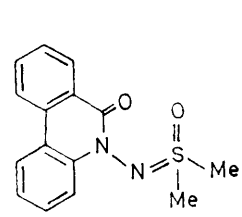


(14)

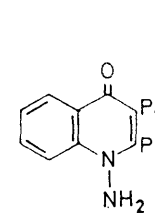
fluorenone could be detected. Formation of the dibenzopyranone from (12) requires 2 mol. of lead tetra-acetate and on increasing the amount of oxidant to 4 mol. the yield was increased (to 70%). The proposed mechanism of ring expansion of the nitrene and valence tautomerism of the diazepinone would here require the disruption of the aromaticity of both benzene rings of (12) and so perhaps it is not surprising that benzo[*c*]-cinnoline is not formed. The deamination reaction could proceed *via* the tetrazane as already proposed. Formation of the dibenzopyranone is a new reaction which had no counterpart in the aminopyridone oxidations, where the corresponding 2-pyrones were not formed. One rationalisation of its formation would be oxidation of *N*-aminophenanthridone to *N*-nitrosophenanthridone and isomerisation of the latter to biphenyl-2-diazonium-2′-carboxylate, which would rapidly ring close, with loss of nitrogen, to give dibenzopyran.

Oxidation of *N*-aminophenanthridone (12) in dimethyl sulphoxide gave the sulphoximide (15) in high yield. Pyrolysis of this at 200° and 0·1 Torr gave phenanthridone (50%) only; vapour-phase flash pyrolysis at 400° and 0·01 Torr gave phenanthridone (80%) much more cleanly, together with a little fluorenone (10%), presumably formed by an unfavourable extrusion of nitrogen from the nitrene, either directly or *via* the diazepinone.

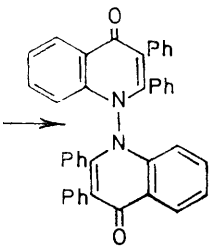
Finally, the generation of an analogously substituted *N*-nitrene in the 4-pyridone series was studied to see if a more stable ring-expanded intermediate could be isolated, since here extrusion of carbon monoxide would require the breaking of two C–C bonds. The 1-aminoquinolin-4-one (16) was therefore oxidised exactly as



(15)



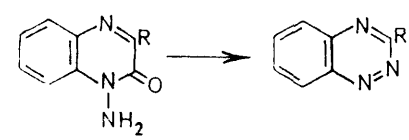
(16)



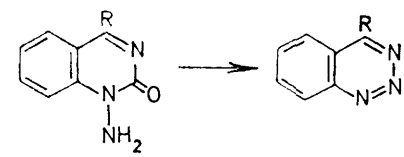
(17)

for the pyridones; however, apart from the formation of a small amount of deaminated product (11%) the reaction took an entirely different course to give 2,2′,3,3′-tetraphenyl-1,1′-bi-4-quinolone (17) as the major product (63%). The structure of (17) was confirmed by quantitative cleavage to 2,3-diphenylquinolin-4-one by zinc and acetic acid. This dimeric type of product, (17), is very rare in the oxidation of *N*-amino-heterocyclic compounds or indeed of 1,1-disubstituted hydrazines generally. It could possibly arise from an unusually easy loss of nitrogen from the corresponding tetrazene, $R_2N{-}N{=}N{-}NR_2$, formed initially.

Thus the rearrangement of *N*-aminopyridones to pyridazines is apparently of limited scope, and indeed the unsubstituted compounds, 1-amino-2-pyridone and 1-aminoquinolin-2-one, gave none of the rearrangement product (pyridazine or cinnoline).[14] However, this rearrangement may well prove to be quite general, and



(18)



(19)

synthetically useful in other heterocyclic systems, since we have recently found that the oxidation of 1-aminoquinoxalin-2-ones (18) and of 1-aminoquinazolin-2-ones

[14] D. C. Horwell, unpublished work.

(19) provides attractive routes to 1,2,4- and 1,2,3-benzotriazines, respectively.[15]

EXPERIMENTAL

U.v. spectra are for solutions in absolute ethanol, i.r. spectra for Nujol mulls, and ^1H n.m.r. spectra (Varian A60) for solutions in deuterichloroform. Chromatography refers to columns of silica gel (MFC; B.D.H.) or alumina pH 7—7·5, prepared by deactivation of basic alumina (Spence type H) with 10% by weight of 20% acetic acid. Solvents used in oxidations were anhydrous. Lead tetra-acetate was dried by suction and stored over sulphuric acid. Petroleum refers to light petroleum, b.p. 40—60°.

1-*Amino*-3,4,5,6-*tetraphenyl*-2-*pyridone* (1).—(*a*) 3,4,5,6-Tetraphenyl-2-pyrone[16] (5 g.) and hydrazine hydrate (99%; 10 ml.) were heated under reflux in ethanol (100 ml.) for 18 hr. The solution was cooled, poured into water (400 ml.), and on addition of concentrated hydrochloric acid (20 ml.) the crude product precipitated. Chromatography on neutral alumina, followed by crystallisation from benzene–petroleum (1 : 1), gave the *pyridone* (1) (35%), m.p. 187—188° (Found: C, 81·7; H, 5·3; N, 6·7%; *m/e* 414. $C_{29}H_{22}N_2O$ requires C, 81·6; H, 5·3; N, 6·8%; *M*, 414), $\lambda_{max.}$ 337 (log ε 4·03) and 218 nm. (4·34), $\nu_{max.}$ 3170, 3050, 1625, 1595, 1580, 1550, 750, 740, and 700 cm.$^{-1}$, τ 4·46br (2H, s) and 2·77—3·16 (20H, m), *m/e* 414, 397, 296, 192, and 178.

(*b*) Sodium hydride (50% emulsion; 0·26 g.) was added to 3,4,5,6-tetraphenyl-2-pyridone[17] (2·0 g.) in methylene chloride (100 ml.). The mixture was refluxed for 3 hr. then cooled to 20°, and chloramine (0·4 g.) in ether (36 ml.) was added. After being stirred at 20° for 46 hr. the mixture was filtered and the residue washed with ether. Evaporation and crystallisation from benzene–petroleum gave the *N*-aminopyridone (50%), m.p. and mixed m.p. 187—188°, identical (spectra) with the product from (*a*). The *benzylidene derivative* (65% yield) of the *N*-aminopyridone (0·12 g.) was prepared by heating for 3 hr. with benzaldehyde (0·4 ml.) in ethanol (6 ml.) containing a trace of acetic acid. Crystallisation from ethanol gave yellow needles, m.p. 204—205° (Found: C, 86·0; H, 5·3; N, 5·6. $C_{36}H_{26}N_2O$ requires C, 86·1; H, 5·2; N, 5·6%), $\nu_{max.}$ 1640, 1600, 1595, 1520, 1490, 1450, 1080, 1030, 750, 720, and 700 cm.$^{-1}$.

Deamination of 1-*Amino*-3,4,5,6-*tetraphenyl*-2-*pyridone*.—Sodium nitrite (17 mg.) in water (0·2 ml.) was added to a solution of the *N*-aminopyridone (100 mg.) in acetic acid (3 ml.) and water (0·5 ml.) at 0°. After 1 hr. the separated solid was collected and crystallised from methylene chloride–petroleum (1 : 3) to give 3,4,5,6-tetraphenyl-2-pyridone (95%), m.p. and mixed m.p. 271—272°.

1-*Amino*-4,6-*diphenyl*-2-*pyridone*.— 4,6-Diphenyl-2-pyrone[18] (1·0 g.) in ethanol (60 ml.) was treated with hydrazine hydrate (25%; 10 ml.) and the mixture was refluxed for 8 hr. On pouring into water (150 ml.) containing a little concentrated hydrochloric acid a precipitate formed; this was collected and crystallised from benzene–methylene chloride to give the *aminopyridone* (35%), m.p. 164—165° (Found: C, 77·8; H, 5·4; N, 10·8. $C_{17}H_{14}N_2O$ requires C, 77·8; H, 5·4; N, 10·8%), $\lambda_{max.}$ 335 (log ε 3·95), 275 (4·04), and 249 nm. (4·30), $\nu_{max.}$ 3400, 3300, 1640, 1595, 1570, 1545, 1505, 1215, 1060, 1020, 860, 810, 780, 760, and 695 cm.$^{-1}$, τ 4·72br (2H, s), 3·56 (1H, d), 3·15 (1H, d), and 2·5br (10H, s).

1-*Amino*-4,5,6-*triphenyl*-2-*pyridone*.—Hydrazine hydrate (25%; 10 ml.) was added to 4,5,6-triphenyl-2-pyrone[19] (1·0 g.) in ethylcellosolve (60 ml.) and the mixture was stirred at 80° for 16 hr. The solvent was evaporated off and the residue crystallised from ethanol to give the aminopyridone (36%), m.p. 197° (lit.,[19] 199°). Treatment of this *N*-amino-compound with sodium nitrite in acetic acid at 0° gave 4,5,6-triphenyl-2-pyridone (82%), m.p. 278—279° (lit.,[20] 277°).

1-*Amino*-6-*methyl*-3,4,5-*triphenyl*-2-*pyridone*.— 6-Methyl-3,4,5-triphenyl-2-pyridone was aminated with chloramine as described for the tetraphenylpyridone, to give the N-*amino-compound* (12%), m.p. 238—240° (decomp.) (Found: C, 85·7; H, 5·9; N, 8·2. $C_{24}H_{20}N_2O$ requires C, 85·7; H, 5·9; N, 8·3%), $\lambda_{max.}$ 231 (log ε 4·33), 250 (4·16), and 331 nm. (3·90), $\nu_{max.}$ 3300, 3190, 1640, 1600, 1575, 1545—1530, 1490, 1440, 1075, 1010, 760, and 700 cm.$^{-1}$.

1-*Amino*-2,3-*diphenylquinolin*-4-*one* (16).—Sodium hydride (0·9 g., 20 mmoles) was added to a suspension of 2,3 diphenylquinolin-4-one[21] (4·2 g., 15 mmoles) in methylene chloride (50 ml.). The mixture was refluxed for 20 hr., then cooled to 20°, and chloramine (2·3 g., 45 mmoles) in ether (235 ml.) was added. After being stirred for 20 hr., the mixture was filtered and the residue washed with methylene chloride. Evaporation of the filtrates to a small volume and addition of petroleum gave the *amino-quinolone* (18%), m.p. 218—219° (from aqueous ethanol) (Found: C, 80·3; H, 5·2; N, 8·6. $C_{21}H_{16}N_2O$ requires C, 80·7; H, 5·1; N, 8·9%), $\lambda_{max.}$ 254 (log ε 4·41) and 342 nm. (4·08), $\nu_{max.}$ 3330, 3200, 1630, 1610, 1600, 1590, 1550, 1440, 1325, 1165, 1140, 1030, 960, 890, 860, 750, and 700 cm.$^{-1}$, τ 5·52 (2H, s) and 2·75—2·95 (14H, m).

5-*Aminophenanthridin*-6-*one* (12).—Sodium hydride (50% emulsion; 0·6 g.) was added to a suspension of phenanthridone (1·5 g.) in methylene chloride (50 ml.) and the mixture was refluxed for 3 hr. Chloramine (0.63 g.) in ether (60 ml.) was added to the suspension at 20° and stirring was continued overnight. The mixture was filtered and the residue washed with methylene chloride. Evaporation of the filtrates and crystallisation from benzene–petroleum (2 : 1) gave the *aminophenanthridone* as pale fawn needles, m.p. 175—176° (Found: C, 74·3; H, 4·8; N, 13·3%; *m/e* 210. $C_{13}H_{10}N_2O$ requires C, 74·3; H, 4·8; N, 13·3%; *M*, 210), $\lambda_{max.}$ 239 (log ε 4·53), 260 (4·33), 325 (3·82), and 335 nm. (3·81), $\nu_{max.}$ 3300, 3195, 1630, 1600, 1575, 1350, 1175, 950, and 730 cm.$^{-1}$, τ 4·98 (2H, s) and 1·6—2·85 (8H, m), *m/e* 210, 195, 181, 166, 152, 140, and 105. Phenanthridone (0·8 g.) was recovered from the insoluble residue. Treatment of the *N*-aminophenanthridone with sodium nitrite in acetic acid gave phenanthridone (88%), m.p. and mixed m.p. 290—291°.

Oxidation of 1-*Amino*-3,4,5,6-*tetraphenyl*-2-*pyridone* (1).—(a) *Alone*. Lead tetra-acetate (0·2 g.) was added during 2 min. to a stirred solution of the *N*-amino-compound (0·1 g.) in methylene chloride (25 ml.) at 20°. Gas was evolved and the solution became pink; tetracyclone could

[15] B. Adger, C. W. Rees, A. A. Sale, and R. C. Storr, *Chem. Comm.*, 1971, 695.
[16] R. Putter and W. Dilthey, *J. prakt. Chem.*, 1937, **149**, 183.
[17] J. F. M. Wajon and J. F. Arens, *Rec. Trav. chim.*, 1957, **76**, 65.
[18] F. Arndt and B. Eistert, *Ber.*, 1925, **58**, 2318.
[19] G. Soliman and I. El-Sayed El-Kholy, *J. Chem. Soc.*, 1955, 2911.
[20] I. El-Sayed El-Kholy and G. Soliman, *J. Chem. Soc.*, 1961, 4490.
[21] B. K. Singh and J. K. Mazumdar, *J. Chem. Soc.*, 1919, **115**, 823.

be detected (t.l.c.) at the beginning of the oxidation but it slowly disappeared. After stirring for 1 hr. [no starting material could then be detected (t.l.c.)], glycerol (1 drop) was added, and the mixture was adsorbed on neutral alumina. Elution with ether–petroleum gave 3,4,5,6-tetraphenylpyridazine (54 mg., 58%), which crystallised from ether–petroleum (1 : 2) as pale yellow needles, m.p. and mixed m.p. 195—196° (lit.,[22] 196—197°) (Found: C, 87·3; H, 5·2; N, 7·3%; *m/e* 384. Calc. for $C_{28}H_{20}N_2$: C, 87·5; H, 5·2; N, 7·3%; *M*, 384), i.r. spectrum identical with that of a specimen prepared by the method of Carboni and Lindsay.[22] Elution with ether gave 3,4,5,6-tetraphenyl-2-pyridone (18 mg., 15%), m.p. and mixed m.p. 270—272° (lit.,[17] 272—273°).

(b) *In dimethyl sulphoxide.* Lead tetra-acetate (1·1 g.) was added during 2 min. to a stirred solution of the *N*-aminopyridone (0·9 g.) in dry dimethyl sulphoxide (30 ml.). After 1 hr. the mixture was poured into water (200 ml.) and the precipitate was collected, washed with warm water, and dried. The solid was finely ground and extracted with boiling chloroform (100 ml.). The chloroform solution was evaporated to 10 ml. and petroleum was added to give a slight turbidity. Storage at 0° for 12 hr. gave SS-*dimethyl*-N-(1,2-*dihydro*-2-*oxo*-3,4,5,6-*tetraphenyl*-1-*pyridyl*)*sulphoximide* (11) (0·9 g., 84%), m.p. 247—248° (decomp.) (from methylene chloride–petroleum) (Found: C, 75·7; H, 5·3; N, 5·6; S, 6·2%; *m/e* 496. $C_{31}H_{26}N_2O_2S$ requires C, 75·7; H, 5·3; N, 5·7; S, 6·5%; *M*, 496), $\lambda_{max.}$ 340 (log ε 3·98) and 223 nm. (4·57), $\nu_{max.}$ 1630, 1580, 1560, 1215, 1040—1025 (doublet, S=O), 860, 750, and 700 cm.$^{-1}$, τ 6·93 (6H, s) and 2·82—3·18 (20H, m), *m/e* 496, 425, 412, 398, 382, 356, 278, 265, and 178.

(c) *In the presence of methyl phenyl sulphoxide.* Lead tetra-acetate (0·8 g.) was added to a solution of the *N*-aminopyridone (0·7 g.) and methyl phenyl sulphoxide (1·8 g.) in methylene chloride (40 ml.). The mixture was stirred for 12 hr. and then chromatographed on neutral alumina. Ether–petroleum (2 : 3) eluted 3,4,5,6-tetraphenylpyridazine (25 mg.), and ether–petroleum (3 : 1) eluted S-*methyl*-S-*phenyl*-N-(1,2-*dihydro*-2-*oxo*-3,4,5,6-*tetraphenyl*-1-*pyridyl*)*sulphoximide* (0·7 g., 75%), m.p. 216—222° (from ethanol; m.p. unaltered after further recrystallisation) (Found: C, 78·0; H, 5·3; N, 5·1; S, 5·8. $C_{36}H_{28}N_2O_2S$ requires C, 78·2; H, 5·1; N, 5·1; S, 5·8%), $\lambda_{max.}$ 342 (log ε 4·06), 259 (4·16), and 238 nm. (4·35), $\nu_{max.}$ 1645, 1600, 1585, 1570, 1520, 1490, 1305, 1220, 1175, 1010, 995, 960, 760, and 700 cm.$^{-1}$, τ 6·15 (3H, s) and 2·0—3·3 (25H, m).

(d) *In the presence of diphenyl sulphoxide.* The *N*-aminopyridone (0·5 g.) and diphenyl sulphoxide (1·0 g.) were dissolved in methylene chloride (20 ml.). Lead tetra-acetate was added, with stirring, during 2 min. After 1 hr. the mixture was adsorbed on silica gel. Ether–petroleum mixtures eluted: (i) 3,4,5,6-tetraphenylpyridazine (125 mg. 34%), m.p. and mixed m.p. 194°; (ii) diphenyl sulphoxide (0·8 g.); and (iii) SS-*diphenyl*-N-(1,2-*dihydro*-2-*oxo*-3,4,5,6-*tetraphenyl*-1-*pyridylsulphoximide monohydrate* (0·25 g., 33%). Recrystallisation from ethanol gave plates, m.p. 154°, which solidified at 169—170° and remelted at 220—221° (Found: C, 77·9; H, 5·1; N, 4·4; S, 5·0. $C_{41}H_{30}N_2O_2S,H_2O$ requires C, 77·8; H, 5·1; N, 4·4; S, 5·1%), $\lambda_{max.}$ 237 (log ε 4·52), 264 (4·3), 275 (4·16), and 349 nm. (4·03), $\nu_{max.}$ 3500 (OH), 1640, 1590, 1570, 1470, 1310, 1240, 1180, 1000, 955, 868, 765, and 750 cm.$^{-1}$, τ 6·57 (2H, s) and 2·1—3·2 (30H, m). After heating the sulphoximide monohydrate at its m.p. for 30 sec. and cooling, the i.r. band at 3500 cm.$^{-1}$ and the singlet at τ 6·57 in the n.m.r. spectrum had disappeared. Finally, (iv) 3,4,5,6-tetraphenyl-2-pyridone (50 mg.), contaminated with the sulphoximide, was eluted.

(e) *In the presence of diphenyl sulphide.* Lead tetra-acetate was added during 2 min. to a stirred solution of the *N*-aminopyridone (0·5 g.) and diphenyl sulphide (1·0 g.) in methylene chloride (20 ml.). After being stirred for 16 hr. the mixture was chromatographed on neutral alumina to give 3,4,5,6-tetraphenylpyridazine (20%), m.p. and mixed m.p. 194—195°, and 3,4,5,6-tetraphenyl-2-pyridone (48%), m.p. and mixed m.p. 268—270°. Diphenyl sulphide (95%) was recovered.

(f) *In the presence of cyclohexene.* The *N*-aminopyridone (1·0 g.) was dissolved in methylene chloride (5 ml.) and cyclohexene (25 ml.) was added. Lead tetra-acetate was added with stirring during 2 min. and after 1 hr. the mixture was adsorbed on neutral alumina. Ether–petroleum mixtures eluted: (i) tetracyclone (1 mg.), m.p. and mixed m.p. 216—218°; (ii) 3,4,5,6-tetraphenylpyridazine (21%), m.p. and mixed m.p. 195—196°; (iii) 7-(1,2-*dihydro*-2-*oxo*-3,4,5,6-*tetraphenyl*-1-*pyridyl*)-7-*azabicyclo*[4,1,0]*heptane* (10) (25%), m.p. 219—221° (from ethanol) (Found: C, 85·1; H, 6·2; N, 5·6%; *m/e* 494. $C_{35}H_{30}N_2O$ requires C, 85·0; H, 6·1; N, 5·6%; *M*, 494), $\lambda_{max.}$ 227 (log ε 4·33) and 342 nm (4·07), $\nu_{max.}$ 1630, 1600, 1580, 1570, 1495, 1230, 1180, 1165, 1080, 1030, 780, 760, and 700 cm.$^{-1}$, τ 7·34 (2H, s), 8·75 (8H, m), and 3·0 (20H, m), *m/e* 494, 399, 398, 178, and 77; and (iv) 3,4,5,6-tetraphenyl-2-pyridone (15%), m.p. and mixed m.p. 270—272°.

Pyrolysis of the Dimethylsulphoximide (11).—(a) *Alone.* The sulphoximide (120 mg.) was heated at 270° in an open glass sublimation tube for 10 min. Dimethyl sulphoxide (4·5 mg.) distilled up the tube and was collected. Chromatography of the residue on neutral alumina gave tetracyclone (4%), 3,4,5,6-tetraphenylpyridazine (5%), and 3,4,5,6-tetraphenyl-2-pyridone (43%). Sublimation of the sulphoximide at 205° and 0·1 Torr for 18 hr. and then at 250° and 0·1 Torr for 4 hr. gave the same products in approximately the same yields.

(b) *In decalin.* The sulphoximide (250 mg.) was heated in dry decalin (10 ml.) at 194° for 4 hr. The solvent was distilled off and the residue chromatographed on neutral alumina to give a trace of tetracyclone, 3,4,5,6-tetraphenylpyridazine (21%), and 3,4,5,6-tetraphenyl-2-pyridone (30%).

Photolysis of the Sulphoximide (11).—(a) *Alone.* The sulphoximide in methylene chloride–acetonitrile–acetone (1 : 1 : 0·1) was irradiated in a quartz tube in a Rayonet Photochemical Reactor for 3 days. Negligible change occurred (t.l.c.), the only product being a minor amount of tetraphenyl-2-pyridone.

(b) *In the presence of cyclohexene.* The sulphoximide in a mixture of benzene, methylene chloride, acetone, and cyclohexene (1 : 1 : 0·1 : 2) was photolysed as in (a) for 9 hr. Chromatography on neutral alumina gave the pyridylazabicycloheptane (10) (35%), m.p. and mixed m.p. 219—220°, and 3,4,5,6-tetraphenyl-2-pyridone (26%), m.p. and mixed m.p. 270—272°.

Oxidation of 1-*Amino*-4,6-*diphenyl*-2-*pyridone.*—Lead tetra-acetate (600 mg.) was added to a solution of the *N*-aminopyridone (300 mg.) in methylene chloride (100 ml.) and the mixture was stirred for 12 hr. Chromatography

[22] R. A. Carboni and R. V. Lindsey, *J. Amer. Chem. Soc.*, 1959, **81**, 4342.

on neutral alumina gave 3,5-diphenylpyridazine (12%), m.p. 142—143° (lit.,[23] 147—148°) (Found: C, 82·6; H, 5·2; N, 12·0%; *m/e* 232. Calc. for $C_{16}H_{12}N_2$: C, 82·7; H, 5·2; N, 12·1%; *M*, 232), $\nu_{max.}$ 1595, 1580, 1500, 1410, 1080, 910, 770, 745, and 695 cm.$^{-1}$, *m/e* 232, 203, 173, 171, 129, 102, and 76.

Oxidation of 1-*Amino*-4,5,6-*triphenyl*-2-*pyridone*.—Lead tetra-acetate (670 mg.) was added to a solution of the *N*-aminopyridone (500 mg.) in methylene chloride (50 ml.) and the mixture was stirred for 16 hr. Chromatography on neutral alumina gave, on elution with ether–petroleum mixtures, 3,4,5-*triphenylpyridazine* (7%), pale yellow crystals, m.p. 254—255° (Found: C, 86·2; H, 4·9; N, 9·2. $C_{22}H_{16}N_2$ requires C, 86·0; H, 4·9; N, 9·1%), $\lambda_{max.}$ 253 (log ε 4·34) and 280sh nm. (4·05), $\nu_{max.}$ 1660, 1555, 1500, 1340, 1320, 1080, 1035, 755, and 710—700 cm.$^{-1}$, and 4,5,6-triphenyl-2-pyridone (58%), m.p. and mixed m.p. 276—277° (lit.,[20] 277°).

Oxidation of 1-*Amino*-6-*methyl*-3,4,5-*triphenyl*-2-*pyridone*.—Oxidation with lead tetra-acetate in methylene chloride as just described gave 6-methyl-3,4,5-triphenyl-2-pyridone (25%), m.p. 308—310°, as the only crystalline product.

Oxidation of 1-*Amino*-2,3-*diphenylquinolin*-4-*one* (16).—The *N*-aminoquinolone (500 mg.) was similarly oxidised with lead tetra-acetate in methylene chloride. Chromatography on silica gel gave, on elution with ether–petroleum, 2,2′,3,3′-*tetraphenyl*-1,1′-*bi*-4-*quinolone* (17) (63%), m.p. 158·5—159° (pale yellow needles from aqueous ethanol) [Found: C, 85·4; H, 4·7; N, 4·9%; *M*, (osmometer) 600. $C_{42}H_{28}N_2O_2$ requires C, 85·1; H, 4·7; N, 4·7%; *M*, 592], $\lambda_{max.}$ 248 (log ε 4·76) and 322 nm. (3·92), $\nu_{max.}$ 1620, 1580, 1570, 1120, 965, 770, 710, and 700 cm.$^{-1}$, *m/e* 296, 278, 267, 147, 146, 145, and 138. Elution with ether gave 2,3-diphenylquinolin-4-one (11%), m.p. 333—334° (lit.,[24] 333°).

Reductive Cleavage of the Biquinolone (17).—Zinc dust (200 mg.) was added to a refluxing solution of the dimer (40 mg.) in acetic acid (5 ml.) and heating was continued for 1 hr. The suspension was filtered hot and the filtrate was diluted with water (2 ml.) causing slow separation of 2,3-diphenylquinolin-4-one (38 mg., 97%), m.p. and mixed m.p. 333°, i.r. spectrum identical with that of an authentic specimen.

Oxidation of 5-*Aminophenanthridin*-6-*one* (12).—(a) *Alone*. The amino-compound (50 mg.) in methylene chloride (20 ml.) was added dropwise to a suspension of lead tetra-acetate (150 mg.) in methylene chloride (20 ml.), with stirring. After 16 hr. the mixture was chromatographed on silica gel to give dibenzo[*b*,*d*]pyran-6-one (31%), m.p. and mixed m.p. 92—92·5°, and phenanthridone (43%), m.p. and mixed m.p. 288—290°. Fluorenone was unchanged under these conditions.

(b) *In dimethyl sulphoxide*. Oxidation of the amino-compound (250 mg.) in dimethyl sulphoxide as before gave SS-*dimethyl*-N-(5,6-*dihydro*-6-*oxophenanthridin*-5-*yl*) *sulphoximide* (15) (73%), m.p. 211—212° (decomp.) (Found: C, 62·8; H, 4·8; N, 9·4; S, 10·9. $C_{15}H_{14}N_2O_2S$ requires C, 62·9; H, 4·9; N, 9·8; S, 11·2%), $\nu_{max.}$ 1655, 1620, 1320, 1310, 1200, 1070, 1050, 960, 870, 745, and 725 cm.$^{-1}$, τ 6·62 (6H, s) and 1·75—2·7 (8H, m).

Pyrolysis of this sulphoximide at 200° and 0·1 Torr for 4 hr. gave phenanthridone (50%); no fluorenone or benzo[*c*]-cinnoline was detected (t.l.c.). Vapour-phase flash pyrolysis at 400° and 0·01 Torr was much cleaner and gave some fluorenone (10%) and phenanthridone (80%).[13]

3,3′,4,4′,5,5′,6,6′-*Octaphenyl*-1,1′-*bi*-2-*pyridone*.— Lead tetra-acetate (1·0 g.) was added to 3,4,5,6-tetraphenyl-2-pyridone (1·0 g.) in methylene chloride (40 ml.) and the mixture was stirred for 4 hr. Adsorption on neutral alumina and elution with ether–petroleum gave the *bipyridone* (11%), m.p. 244—245° (from ethanol) (Found: C, 87·4; H, 5·1; N, 3·5. $C_{58}H_{40}N_2O_2$ requires C, 87·4; H, 5·0; N, 3·5%), $\lambda_{max.}$ 236 (log ε 4·54), 255 (4·48), 275 (4·42), and 300 nm. (4·30), $\nu_{max.}$ 1660, 1630, 1575, 1555, 1480, 1440, 1400, 1360, 1330, 1270, 1220, 1190, 1150, 1100, 1050, 965, 790, 760, 750, and 700 cm.$^{-1}$. Treatment of this compound with zinc dust in boiling acetic acid for 5 hr. gave 3,4,5,6-tetraphenyl-2-pyridone (62%), m.p. and mixed m.p. 272—273°.

We thank Imperial Chemical Industries, Ltd., Dyestuffs Division, for secondment of M.Y., and Drs. T. L. Gilchrist and R. C. Storr for discussion.

[1/852 *Received, May 26th,* 1971]

[23] K. Almström, *Annalen*, 1913, **403**, 135.
[24] W. R. Vaughan and I. S. Covey, *J. Amer. Chem. Soc.*, 1958, **80**, 2197.