885. *Pyrone Series. Part IV.*[1] *5-Aryloxy-2-pyrones. The Corresponding 2-Thiopyrones, Pyridones, 1-Hydroxy- and 1-Amino-2-pyridones, and Related 4,5,6-Triphenyl-2-pyrones.*

By Ibrahim El-Sayed El-Kholy, Fathi Kamel Rafla, and Gabra Soliman.

Some 5-aryloxy-2-pyrones have been prepared and their structures determined by alkaline fission. These and 4,5,6-triphenyl-2-pyrone have been converted into 2-thiopyrones, 2-pyridones, 1-methyl-2-pyridones, and 1-amino-2-pyridones. The last three types have been inter-related, and 2-alkoxypyridines have been formed from the 2-pyridones. 1-Hydroxy-2-pyridones have been prepared by the action of hydroxylamine on the pyrones in pyridine. The structures of these compounds are apparent from their infrared and ultraviolet spectra, which are recorded.

In earlier papers[1,2] of this series, we showed that ethyl phenylpropiolate undergoes Michael addition with deoxybenzoins and ω-methoxyacetophenones, giving the corresponding 2-pyrones. We now report that ω-aryloxyacetophenones (I; R = OAr) condense with this acetylenic ester, giving 5-aryloxy-4,6-diphenyl-2-pyrones (II; R = OAr). In distinction from a former series,[2] these aryloxypyrones were not accompanied by the *trans*-isomers of the hypothetical intermediate adducts. Their 2-pyrone structure was determined by fission to *cis*-4-aryloxy-5-oxo-3,5-diphenylpentenoic acids (III; R = OAr) whose esters (IV) were readily cyclised to the pyrones.

Having in our hands three types of trisubstituted 2-pyrones, we have studied the infrared absorption spectra of representative members (II; R = Ph, OMe, or OPh) (see Table 1). Bands in the 1718—1724 cm.$^{-1}$ region are attributable to the 2-pyrone carbonyl stretching frequency, whereas the 1613—1634 and 1577—1592 cm.$^{-1}$ maxima are due to the carbon–carbon double-bond stretching frequencies which characterise the 2-pyrone structure.[3,4] The bands at 1471—1497 and 1441—1458 cm.$^{-1}$ appear to signify the presence of phenyl groups [5a] in these pyrones and other compounds in Table 1.

Like 4,6-diaryl-5-methoxy-2-pyrones,[1] the 5-aryloxy-4,6-diphenyl-2-pyrones as well as 4,5,6-triphenyl-2-pyrone were readily converted by our usual technique into the corresponding 2-thiopyrones (V) in quantitative yield. These are characterised by strong absorption in the range 1109—1111 cm.$^{-1}$ (Table 1) which is attributable to the C=S stretching frequency.[6]

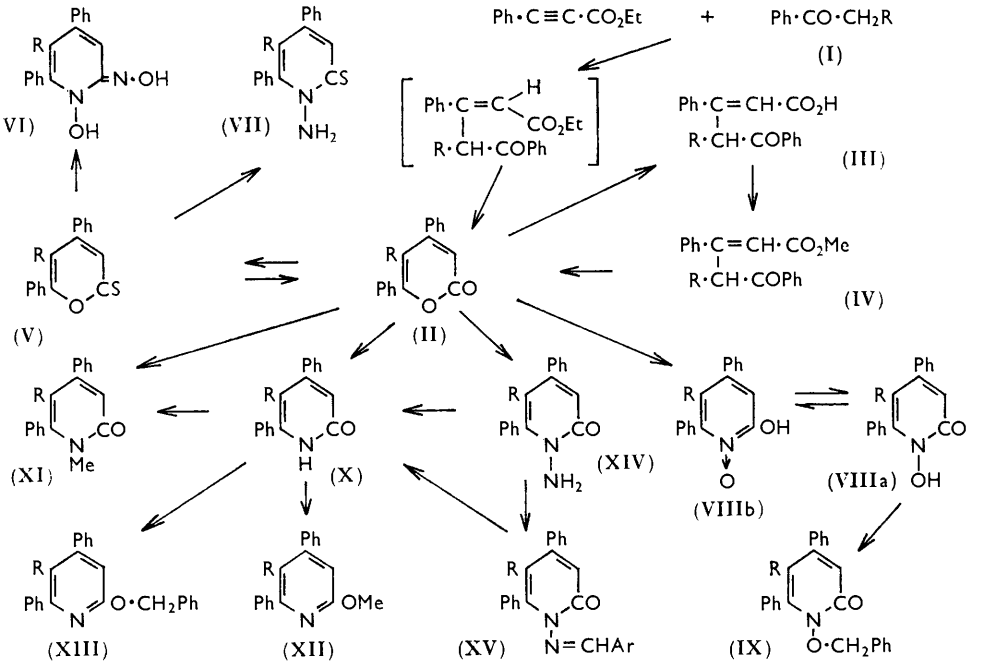
These 2-thiopyrones are converted into the pyrones by hydrogen peroxide in glacial acetic acid, but not by semicarbazide and they are resinified by hydroxylamine or hydrazine hydrate.[1] 4,5,6-Triphenyl-2-thiopyrone reacted with hydroxylamine in a neutral medium and with hydrazine hydrate, giving 1-hydroxy-4,5,6-triphenyl-2-pyridone oxime (VI; R = Ph) and 1-amino-4,5,6-triphenyl-2-thiopyridone (VII; R = Ph), respectively.

5-Methoxy-4,6-diphenyl-2-pyrone (II; R = OMe) was previously shown to react slowly with hydroxylamine in a neutral medium, giving 1-hydroxy-4,6-diphenyl-5-methoxy-2-pyridone (VIII; R = OMe) whereas its thio-analogue (V; R = OMe) was converted into the pyrone. In this paper, however, we report that this pyrone, 5-methoxy-4-phenyl-6-*p*-tolyl-2-pyrone,[1] 5-phenoxy-4,6-diphenyl-2-pyrone, and 4,5,6-triphenyl-2-pyrone give the corresponding 1-hydroxy-2-pyridones (VIIIa or b) on reaction with hydroxylamine in pyridine.

[1] Part III, El-Kholy, Rafla, and Soliman, *J.*, 1959, 2588.
[2] Soliman and El-Kholy, *J.*, 1955, 2911.
[3] Wiley and Slaymaker, *J. Amer. Chem. Soc.*, 1956, **78**, 2393.
[4] Wiley and Esterle, *J. Org. Chem.*, 1957, **22**, 1257.
[5] Bellamy, "The Infra-red Spectra of Complex Molecules," Methuen, London, 1959, pp. (*a*) 69. (*b*) 96, (*c*) 267, (*d*) 205.
[6] Spinner, *J. Org. Chem.*, 1958, **23**, 2037; *J.*, 1960, 1237.

Though these compounds give an intense red colour with ferric chloride, the structure (VIIIa) is preferably assigned to them as they show strong carbonyl absorption at 1650 (±5) cm.$^{-1}$, indicating that *N*-hydroxy-substitution does not affect the characteristic 2-pyridone carbonyl band. The broad band in the region 3030—3145 cm.$^{-1}$ is probably associated with the tautomerism (VIIIa ⟷ b) or strong chelated intramolecular hydrogen bonding in the solid state as well as in solution.[5b] Further, the 1-benzyloxy-ether (IX; R = Ph) obtained by the action of benzyl chloride on 1-hydroxy-4,5,6-triphenyl-2-pyridone in alkali is not susceptible to hydrolysis with hydrochloric acid and shows carbonyl absorption at 1664 cm.$^{-1}$, but the broad absorption in the region 3030—3145 cm.$^{-1}$ is lacking. This conclusion is supported by the ultraviolet absorption maxima recorded in Table 1 which are within the range of other 1-hydroxy-2-pyridones studied by Cunningham *et al.*,[7] Shaw,[8] Adams and Miyano,[9] Wiley and Slaymaker,[3] and Gardner and Katritzky.[10]

Similarly, 1-hydroxy-4,5,6-triphenyl-2-pyridone oxime (VI; R = Ph) has an analogous structure since it is characterised by strong absorption at 1639 cm.$^{-1}$ due to the C=N stretching frequency.[5c]



A new series of 2-pyridones (X) and 1-methyl-2-pyridones (XI) has been obtained from these 5-aryloxy-4,6-diphenyl-2-pyrones and 4,5,6-triphenyl-2-pyrone by the action of ammonia and methylamine, respectively. These pyridones, however, behave as tautomeric systems as they display a red colour with ferric chloride. Accordingly, they yielded 1-methyl-2-pyridones (XI) with methyl iodide and alkali, and 2-methoxypyridines (XII) on treatment with diazomethane in ether–methanol or by the action of methyl iodide on the silver salt. On the other hand, formation of 2-benzyloxy-4,5,6-triphenylpyridine (XIII; R = Ph) by the action of benzyl chloride on the potassium or the silver salt of 4,5,6-triphenyl-2-pyridone is at variance with the general mode of alkylation.[11a]

[7] Cunningham, Newbold, Spring, and Stark, *J.*, 1949, 2091.
[8] Shaw, *J. Amer. Chem. Soc.*, 1949, **71**, 67; Shaw and Lott, *ibid.*, p. 70.
[9] Adams and Miyano, *J. Amer. Chem. Soc.*, 1954, **76**, 3168.
[10] Gardner and Katritzky, *J.*, 1957, 4375.
[11] Elderfield, " Heterocyclic Compounds," Vol. I, John Wiley, Inc., New York, 1950, pp. (*a*) 534, (*b*) 436.

TABLE 1.

Infrared and ultraviolet spectra.

[Infrared spectra ($cm.^{-1}$) of the methoxy-series were measured on a Perkin–Elmer 21 spectrophotometer for a KBr disc. The other compounds were measured with a Perkin–Elmer 137 spectrophotometer for a KBr disc. For solution spectra the thickness was 0·5 mm. Ultraviolet spectra are for ethanol solutions.]

Formula	R	OH or NH stretching	C=O	C=C		*N*-Substn.	Ph group		C=S	U.V. peak ($m\mu$)	(log ε)
2-Pyrones											
II	OMe		1718s	1621s	1577w	—	1490s	1445s	—		
II	OPh		1724s	1634w	1592w	—	1493s	1449m	—		
II	Ph		1721s	1613m	1577w	—	1490s	1449s	—		
2-Thiopyrones											
V	OMe		—	1608s	1572w	—	1497s	1443s	1109s		
V	OPh		—	1618s	1597w	—	1490s	1447s	1111s		
V	Ph		—	1616s	1587m	—	1488s	1445s	1111s		
1-Hydroxy-2-pyridones											
VIII	OMe	3030sb	1645s	1603w	1575w	1553s	1488s	1453s	—		
VIII	OPh	3125sb	1655s	1600w	1585m	1555s	1493s	1458s	—	340	(3·88)
VIII	OPh †	3040sb	1650s	1590w		1538s	1471s		—		
VIII	Ph	3145sb	1655s	1610w	1587m	1531s	1493s	1449s	—	328	(3·83)
VIII	Ph †	3040sb	1647s	1613w	1587w	1531s	1493w	1445w	—		
IX	Ph	—	1664s	1660w	1582w		1481s	1441s	—		
1-Hydroxy-2-pyridone oxime											
VI	Ph		1639s *	1613w	1590w	1555m	1486w	1449s	—	335	(3·76)
2-Pyridones											
X	OMe		1642s	1595s	1575w	—	1490m	1449m	—		
X	OPh		1645s	1600w	1587s	—	1488s	1449s	—	338	(3·94)
X	OPh †	3400m	1650s	1613s	1590s	—	1490s	1449m	—		
X	Ph		1647s	1600w	1572w	—	1493m	1451s	—	330	(3·94)
X	Ph †	3448m	1653s	1605m	1575w	—	1497m	1453m	—		
1-Methyl-2-pyridones											
XI	OPh		1653s	1613w		1515w	1481s	1441w	—	335	(3·85)
XI	Ph		1661s	1608w	1587s	1520m	1493s	1449w	—	325	(3·87)
Pyridines											
XII	OPh		—	1597s		1555s	1493s	1458s	—	312	(3·94)
XII	Ph		—	1597s	1580s	1555s	1497w	1449w	—	305	(3·87)
XIII	Ph		—	1587s		1563s	1493m	1441s	—	308	(4·49)
1-Amino-2-pyridones											
XIV	OMe	3226m	1656s	1608w			1486s	1445m	—		
XIV	OPh	3226m	1658s	1600w	1575w	1558m	1486s	1443w	—	342	(3·88)
XIV	OPh †	3344m	1653s		1575s	1538s	1481m	1443w	—		
XIV	Ph	3215m	1650s	1600w	1580m	1546m	1484s	1443m	—	332	(3·94)
XIV	Ph †	3400m	1650s	1600w	1582m	1543m	1484m	1441m	—		
1-Amino-2-thiopyridone											
VII	Ph	3125m	—	1595s	1577s	1515m	1493s	1449s	1099s		

w = weak; m = medium; s = strong; b = broad.

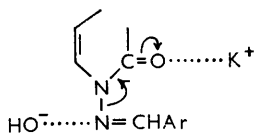
* C=N stretching frequency. † In $CHCl_3$.

Analogously to 2-pyridone [12] which exists predominantly as an amide in the solid state, the polysubstituted 2-pyridones (X) and their *N*-methyl derivatives (XI) are characterised by strong absorption in the region 1661—1642 $cm.^{-1}$ associated with the pyridone carbonyl, and the bands 1613—1595 and 1590—1572 $cm.^{-1}$ are attributed to carbon–carbon double bonds. The broad bands in the region 3—4 μ shown by the pyridones (X) signify N–H · · · O hydrogen bonding in the solid state, whereas the sharp band at 3448, 3400 $cm.^{-1}$ shown by 4,5,6-triphenyl-2-pyridone and 5-phenoxy-4,6-diphenyl-2-pyridone, respectively,

[12] Mason, *J.*, 1957, 4874.

in chloroform is characteristic of NH stretching frequency.[5d] Conversely, the 2-methoxypyridines (XII) and 2-benzyloxy-4,5,6-triphenylpyridine (XIII; R = Ph) do not show carbonyl absorption, and their ultraviolet maxima at 305—312 mμ (log ε 3·87—3·94) are shorter than the corresponding maxima (325—338 mμ, log ε 3·85—3·94) of the isomeric 1-methyl-2-pyridones.[11b]

1-Amino-2-pyridones have been prepared by the action of hydrazine hydrate on 5-aryloxy-2-pyrones and 4,5,6-triphenyl-2-pyrone, as well as on methyl *cis*-4-aryloxy-5-oxo-3,5-diphenylpentenoate (IV; R = OAr) and *cis*-5-oxo-3,4,5-triphenylpentenoate (IV; R = Ph) and related esters. These aminopyridones are characterised by conversion into the pyridones by nitrous acid, diacylation, and formation of arylidene derivatives. Further, the diacylamines are susceptible to stepwise hydrolysis; the arylideneaminopyridones are hydrolysed by concentrated alkali to the pyridone and the corresponding aromatic acid. In response to the approach of the cationic reagent, the =N·N·C=O group appears to be electron-releasing and simultaneously fission of the N–N link takes place with the formation of an aldoxime. The latter appears to undergo elimination of water, giving rise to a nitrile which is susceptible to hydrolysis.



The pyridone structure of these amines (XIV) is evident from their infrared and ultraviolet absorption data (Table 1) which are analogous to those of similarly constituted 1-amino-2-pyridones reported by other workers.[3,13]

Besides the characteristic carbonyl absorption at 1650—1658 cm.$^{-1}$, the 1-aminopyridones, like 1-methyl-2-pyridones and 1-hydroxy-2-pyridones, exhibit absorption at 1515—1558 cm.$^{-1}$ attributable to *N*-substitution (6·47—6·54 μ).[3,13] Further, their chloroform solutions show a medium (3400 cm.$^{-1}$) and a weak band (3280 cm.$^{-1}$) indicating the free amino-group.[5d] In the solid state, however, there is a band at 3226 cm.$^{-1}$. Moreover, the absence of broad absorption in the region 3—4 μ for 1-amino-2-pyridones and 1-methyl-2-pyridones supports the previous views regarding hydrogen bonding in solid *N*-unsubstituted 2-pyridones.

However, 1-amino-4,5,6-triphenyl-2-thiopyridone (VII; R = Ph) is characterised by strong absorption at 1100 cm.$^{-1}$ attributable to the C=S group, but owing to the scarcity of the material, chemical evidence of its structure has not been sought.

Experimental

Light petroleum had b. p. 50—70°.

5-Phenoxy-4,6-diphenyl-2-pyrone.—ω-Phenoxyacetophenone [14] (4·2 g., 1 mol.) and ethyl phenylpropiolate (3·5 g., 1 mol.) were added to an ice-cold suspension of sodium ethoxide (1·4 g., 1 mol.) in ether, and the mixture was kept in the ice-chest for 2 days, then mixed with water. The ethereal solution yielded an oily residue (5·7 g.) from which the pyrone (1·4 g.), m. p. 128°, crystallised. It recrystallised from methanol in yellowish-white prismatic needles, m. p. 131° (Found: C, 81·1; H, 4·7. $C_{23}H_{16}O_3$ requires C, 81·2; H, 4·7%). The alkaline layer yielded phenylpropiolic acid (0·8 g.). This pyrone was recovered unchanged after 8 hr. in boiling ethanol with semicarbazide or hydroxylamine.

cis-*5-Oxo-4-phenoxy-3,5-diphenylpentenoic Acid.*—The foregoing pyrone (1·5 g.) was warmed with 3% methanolic potassium hydroxide (30 ml.), and the solution was diluted with water and extracted with ether. The alkaline solution gave, on acidification and extraction with ether, a yellow oil (1·5 g.) from which the *pentenoic acid* was obtained on treatment with light petroleum. It crystallised from dilute methanol in prisms, m. p. 159° (decomp.) (Found: C, 77·1; H, 5·2. $C_{23}H_{18}O_4$ requires C, 77·1; H, 5·1%).

The *methyl ester* was prepared by refluxing a methanol solution of the acid (0·2 g.) containing a few drops of concentrated hydrochloric acid or by the action of ethereal diazomethane. It

[13] Hoegerle, *Helv. Chim. Acta*, 1958, **41**, 539.
[14] Davies and Middleton, *J.*, 1958, 822.

crystallised from methanol in prismatic needles, m. p. 101° (Found: C, 77·1; H, 5·5; OMe, 8·2. $C_{24}H_{20}O_4$ requires C, 77·3; H, 5·4; OMe, 8·3%). It was converted into the pyrone when its ethereal solution was kept with sodium ethoxide at 0° for 4 hr.

4,6-*Diphenyl*-5-p-*tolyloxy*-2-*pyrone* was prepared as above but from ω-*p*-tolyloxyacetophenone,[14] in 25% yield, and crystallised from benzene in yellow elongated prisms, m. p. 162° (Found: C, 81·05; H, 5·0. $C_{24}H_{18}O_3$ requires C, 81·3; H, 5·1%).

cis-5-*Oxo*-3,5-*diphenyl*-4-p-*tolyloxypentenoic acid* was prepared by alkaline fission of the pyrone and crystallised from benzene–light petroleum in prisms, m. p. 155° (decomp.) (Found: C, 77·5; H, 5·4. $C_{24}H_{20}O_4$ requires C, 77·5; H, 5·4%). Its *methyl ester* crystallised from methanol in prisms, m. p. 94° (Found: C, 77·5; H, 5·7; OMe, 7·9. $C_{25}H_{22}O_4$ requires C, 77·7; H, 5·7; OMe, 8·0%).

5-p-*Chlorophenoxy*-4,6-*diphenyl*-2-*pyrone*.—ω-*p*-Chlorophenoxyacetophenone,[15] prepared in 88% yield by refluxing *p*-chlorophenol (15·5 g., 1·2 mol.), phenacyl bromide (20 g., 1 mol.), and potassium carbonate (14 g.) in acetone for 4 hr., crystallised from ethanol in plates, m. p. 101° (Found: C, 68·3; H, 4·55; Cl, 14·3. Calc. for $C_{14}H_{11}ClO_2$: C, 68·3; H, 4·5; Cl, 14·4%). Its *oxime* crystallised from benzene–light petroleum in prismatic plates, m. p. 124° (Found: N, 5·0. $C_{14}H_{12}ClNO_2$ requires N, 5·35%). The *pyrone* was prepared in 25% yield from this ketone in benzene and crystallised from benzene–light petroleum in pale yellow needles, m. p. 162° (Found: C, 73·6; H, 4·1; Cl, 9·2. $C_{23}H_{15}ClO_3$ requires C, 73·7; H, 4·0; Cl, 9·5%).

cis-4-p-*Chlorophenoxy*-5-*oxo*-3,5-*diphenylpentenoic acid* crystallised from benzene–light petroleum in needles, m. p. 162° (decomp.) (Found: C, 70·8; H, 4·5; Cl, 8·7. $C_{23}H_{17}ClO_4$ requires C, 70·3; H, 4·4; Cl, 9·1%). Its *methyl ester* crystallised from light petroleum (b. p. 30—50°) in needles, m. p. 104—105° (Found: C, 70·75; H, 4·95; OMe, 7·5. $C_{24}H_{19}ClO_4$ requires C, 70·8; H, 4·7; OMe, 7·6%).

5-p-*Bromophenoxy*-4,6-*diphenyl*-2-*pyrone*.—ω-p-*Bromophenoxyacetophenone* was prepared in 83% yield from *p*-bromophenol and phenacyl bromide as above and crystallised from ethanol in elongated plates, m. p. 108° (Found: C, 57·4; H, 3·9; Br, 27·5. $C_{14}H_{11}BrO_2$ requires C, 57·7; H, 3·8; Br, 27·5%). Its *semicarbazone* crystallised from ethanol in plates, m. p. 183° (Found: C, 51·4; H, 4·1; N, 11·8; Br, 23·0. $C_{15}H_{14}BrN_3O_2$ requires C, 51·7; H, 4·05; N, 12·1; Br, 23·0%). The *pyrone* was prepared in 26% yield from this ketone in benzene and crystallised from benzene in yellow platelets, m. p. 177° (Found: C, 65·6; H, 3·6; Br, 19·0. $C_{23}H_{15}BrO_3$ requires C, 65·9; H, 3·6; Br, 19·1%).

cis-4-p-*Bromophenoxy*-5-*oxo*-3,5-*diphenylpentenoic acid* crystallised from benzene–light petroleum in needles, m. p. 174° (decomp.) (Found: C, 63·6; H, 3·9; Br, 17·8. $C_{23}H_{17}BrO_4$ requires C, 63·2; H, 3·9; Br, 18·3%). Its *methyl ester* crystallised from light petroleum in needles, m. p. 111° (Found: C, 63·8; H, 4·3; OMe, 6·7. $C_{24}H_{19}BrO_4$ requires C, 63·9; H, 4·2; OMe, 6·8%).

5-p-*Iodophenoxy*-4,6-*diphenyl*-2-*pyrone*.—ω-*p*-Iodophenoxyacetophenone was prepared in 85% yield from *p*-iodophenol and phenacyl bromide and crystallised from ethanol in elongated prisms, m. p. 108° (Found: C, 50·2; H, 3·5; I, 36·8. $C_{14}H_{11}IO_2$ requires C, 49·7; H, 3·3; I, 37·5%). Its *oxime* crystallised from methanol in elongated plates, m. p. 131° (Found: N, 3·7. $C_{14}H_{12}INO_2$ requires N, 4·0%). The *pyrone* was prepared in 24% yield from this ketone in benzene and crystallised from benzene in yellow prisms, m. p. 210° (Found: C, 58·75; H, 3·4; I, 28·05. $C_{23}H_{15}IO_3$ requires C, 59·2; H, 3·2; I, 27·2%).

6-p-*Methoxyphenyl*-5-*phenoxy*-4-*phenyl*-2-*pyrone*.—4-Methoxy-ω-phenoxyacetophenone,[16] m. p. 67°, was prepared in 65% yield by condensation of phenol with ω-bromo-*p*-methoxyacetophenone as above and was freed from 1,2-di-*p*-methoxybenzoylethane [17] by crystallisation from ethanol. The *pyrone* was prepared in 26% yield from the former ketone in ether and crystallised from benzene in yellow needles, m. p. 179° (Found: C, 77·85; H, 5·0. $C_{24}H_{18}O_4$ requires C, 77·8; H, 4·9%).

cis-5-p-*Methoxyphenyl*-5-*oxo*-4-*phenoxy*-3-*phenylpentenoic acid* crystallised from benzene–light petroleum in prisms, m. p. 169° (decomp.) (Found: C, 74·6; H, 5·3. $C_{24}H_{20}O_5$ requires C, 74·2; H, 5·2%).

The 2-*thiopyrones* of Table 2 were prepared by heating the pyrones with phosphorus pentasulphide in toluene for 3—4 hr. and recovered from the medium after washing with ammonium sulphide; they crystallised from benzene–light petroleum.

[15] Wright and Lincoln, *J. Amer. Chem. Soc.*, 1952, **74**, 6301.
[16] Stoermer and Atenstädt, *Ber.*, 1902, **35**, 3565.
[17] Holleman, *Rec. Trav. chim.*, 1891, **10**, 216.

TABLE 2.

2-Thiopyrones (V).

R	M. p.	Form *	Found (%) C	H	S	Formula	Required (%) C	H	S
C_6H_5·O	192°	Prisms	77·85	4·5	8·9	$C_{23}H_{16}O_2S$	77·5	4·5	9·0
p-Me·C_6H_4·O	143	Prisms	77·9	4·8	8·7	$C_{24}H_{18}O_2S$	77·8	4·9	8·7
p-Cl·C_6H_4·O	177	Needles	70·6	3·8	8·2	$C_{23}H_{15}ClO_2S$	70·65	3·9	8·2
p-Br·C_6H_4·O	180	Needles	63·5	3·2	7·3	$C_{23}H_{15}BrO_2S$	63·45	3·5	7·4
C_6H_5	218	Needles	80·7	4·8	9·5	$C_{23}H_{16}OS$	81·1	4·7	9·4
6-*p*-MeO·C_6H_4-5-PhO-4-Ph	185	Needles	74·45	4·7	8·3	$C_{24}H_{18}O_3S$	74·6	4·7	8·3

* All orange-red, except the first which was red.

Action of Hydrogen Peroxide on the 2-Thiopyrones.—When a warm solution of the 2-thiopyrone (0·5 g.) in glacial acetic acid (10 ml.) was treated with 1 ml. of hydrogen peroxide (100-vol.), the initial dark red colour suddenly changed to pale yellow and, on dilution, the corresponding 2-pyrone crystallised.

These 2-thiopyrones were recovered unchanged after being heated with semicarbazide in methanol for 10 hr. and, except when R = Ph, resinous products were obtained from them by the action of hydroxylamine or hydrazine hydrate.

1-*Hydroxy*-4,5,6-*triphenyl*-2-*pyridone Oxime*.—A solution of 4,5,6-triphenyl-2-thiopyrone (0·3 g.) in ethanol (45 ml.) was refluxed with hydroxylamine hydrochloride (0·3 g.) and sodium acetate (0·3 g.) in 2 ml. of water for 4 hr. The *pyridone oxime* (0·3 g.), recovered by concentration and dilution, crystallised from pyridine–methanol in yellow prisms, m. p. 203° (decomp.) (Found: C, 77·8; H, 5·3; N, 8·4. $C_{23}H_{18}N_2O_2$ requires C, 77·9; H, 5·1; N, 7·9%). This gave a green colour with ferric chloride, reduced copper acetate solution and Tollens's reagent, and was recovered unchanged after being heated with hydrochloric acid.

1-*Amino*-4,5,6-*triphenyl*-2-*thiopyridone*.—A mixture of 4,5,6-triphenyl-2-thiopyrone (0·6 g.) and 85% hydrazine hydrate (2·5 ml.) in ethanol (20 ml.) was refluxed for 5 hr. The thiopyrone gradually passed into solution and the mixture became yellow. After dilution and cooling, the 1-*amino-compound* (0·1 g.) separated and crystallised from methanol in yellow plates, m. p. 195° (Found: C, 78·3; H, 5·0; N, 7·9; S, 9·1. $C_{23}H_{18}N_2S$ requires C, 77·9; H, 5·1; N, 7·9; S, 9·05%). It gave with ferric chloride a reddish-brown colour which gradually faded, and it reduced Fehling's solution and Tollens's reagent.

The 2-*pyridones* (X) recorded in Table 3 were prepared in quantitative yield by heating the corresponding pyrones (about 0·7 g.) in sealed tubes with 25% aqueous ammonia (4 ml.) for 3—4 hr. at temperatures within the range of their m. p. These pyridones crystallised from pyridine (P)–methanol (M), benzene (B), or glacial acetic acid (G) in needles, which gave an orange-red colour with ferric chloride and a negative test with titanium trichloride.

TABLE 3.

2-Pyridones (X).

R	M. p.	Solvent	Found (%) C	H	N	Hal	Formula	Required (%) C	H	N	Hal
C_6H_5·O	233°	P–M	81·4	5·0	4·2	—	$C_{23}H_{17}NO_2$	81·4	5·05	4·1	—
p-Me·C_6H_4·O ...	252	P–M	81·5	5·1	4·0	—	$C_{24}H_{19}NO_2$	81·55	5·4	4·0	—
p-Cl·C_6H_4·O ...	241	P–M	73·4	4·1	3·9	9·5	$C_{23}H_{16}ClNO_2$	73·9	4·3	3·75	9·5
p-Br·C_6H_4·O ...	247	P–M	66·2	4·0	3·5	18·6	$C_{23}H_{16}BrNO_2$	66·0	3·9	3·35	19·1
C_6H_5	277	B	85·4	5·2	4·6	—	$C_{23}H_{17}NO$	85·4	5·3	4·3	—

The 1-*methyl*-2-*pyridones* listed in Table 4 of the above-mentioned pyridones were prepared by heating the respective pyrones (about 0·7 g.) with 33% aqueous methylamine in sealed tubes for 3 hr. at 180—190°. They were also prepared by heating the pyridones (about 0·2 g.) with methyl iodide (4 ml.) for 3 hr. at 180—190°. The 1-methyl-2-pyridones crystallised from dilute methanol or benzene–light petroleum (L) and were characterised by giving a brown colour with ferric chloride.

2-*Methoxy*-5-p-*phenoxy*-4,6-*diphenylpyridine* (XII; R = OPh).—The dry silver salt of 5-phenoxy-4,6-diphenyl-2-pyridone, prepared by addition of a 66% soiution of aqueous silver nitrate (5 ml.) to a solution of the pyridone (0·7 g.) in 5·5% methanolic potassium hydroxide

(20 ml.), was refluxed with methyl iodide for 4 hr. After filtration of silver iodide, the *methoxypyridine* (0·7 g.) was recovered from the filtrate and crystallised from ethanol in needles, m. p. 107—108°, which gave a negative ferric chloride test (Found: C, 81·6; H, 5·4; N, 4·15; OMe, 8·9. $C_{24}H_{19}NO_2$ requires C, 81·55; H, 5·4; N, 4·0; OMe, 8·8%). This pyridine was also obtained by the action of diazomethane on the pyridone in ether–methanol.

TABLE 4.

1-Methyl-2-pyridones (XI).

R	M. p.	Appearance	Solvent	Found (%) C	H	N	Formula	Required (%) C	H	N
C_6H_5·O	167°	Needles	M	81·6	5·5	4·0	$C_{24}H_{19}NO_2$	81·55	5·4	4·0
p-Me·C_6H_4·O ...	180	Yellow needles	M	81·6	5·65	3·7	$C_{25}H_{21}NO_2$	81·7	5·8	3·8
p-Cl·C_6H_4·O	200	Needles	M	74·7	4·7	3·6	$C_{24}H_{18}ClNO_2$ [a]	74·3	4·7	3·6
p-Br·C_6H_4·O	209	Prisms	B–L	67·2	4·2	3·0	$C_{24}H_{18}BrNO_2$ [b]	66·7	4·2	3·2
C_6H_5	189	Needles	M	85·7	5·5	4·0	$C_{24}H_{19}NO$	85·4	5·7	4·15

[a] Cl: Found, 8·55. Reqd., 9·1%. [b] Br: Found, 19·1. Reqd., 18·5%.

2-*Methoxy*-4,5,6-*triphenylpyridine* (XII; R = Ph) was prepared from the dry silver salt of 4,5,6-triphenyl-2-pyridone and crystallised from ethanol in needles, m. p. 144—145° (Found: C, 85·3; H, 5·4; N, 4·3; OMe, 9·4. $C_{24}H_{19}NO$ requires C, 85·4; H, 5·7; N, 4·15; OMe, 9·2%). The ethanolic mother liquor yielded traces of 1-methyl-4,5,6-triphenyl-2-pyridone, m. p. and mixed m. p. 188—189°. The action of diazomethane on this pyridone in ether–methanol gave only the 2-methoxypyridine.

Other Alkylations.—(a) A mixture of 4,5,6-triphenyl-2-pyridone (0·3 g.), potassium hydroxide (0·7 g.), and methyl iodide (20 ml.) was refluxed for 2 hr. and filtered. When the residue recovered by evaporation of the filtrate was dissolved in hot methanol, 2-methoxy-4,5,6-triphenylpyridine (0·07 g.), m. p. 144—145°, crystallised. The mother liquor yielded, on dilution, 1-methyl-4,5,6-triphenyl-2-pyridone (0·2 g.) which crystallised from dilute methanol in needles, m. p. and mixed m. p. 189°.

(b) 2-*Benzyloxy*-4,5,6-*triphenylpyridine* (XIII; R = Ph) was obtained when a solution of 4,5,6-triphenyl-2-pyridone (0·3 g.) in absolute ethanol (20 ml.) containing sodium ethoxide (0·3 g. of sodium) was refluxed with benzyl chloride (1·7 g.) for 2 hr. When the filtrate was diluted with water, the benzyloxypyridine (0·2 g.) was recovered and crystallised from methanol in needles, m. p. 150°, which gave a negative ferric chloride test (Found: C, 87·0; H, 5·5; N, 3·7. $C_{30}H_{23}NO$ requires C, 87·1; H, 5·6; N, 3·4%). It was also prepared in 70% yield when the silver salt of 4,5,6-triphenyl-2-pyridone (0·9 g.) was refluxed with benzyl chloride (3 g.) in dry benzene for 3 hr.

1-*Hydroxy*-5-*phenoxy*-4,6-*diphenyl*-2-*pyridone* was prepared when 5-phenoxy-4,6-diphenyl-2-pyrone (0·5 g.) was refluxed with hydroxylamine hydrochloride (0·5 g.) in pyridine (12 ml.) for 5 hr., and recovered by dilution with water. It crystallised from benzene in needles, m. p. 224—225°, which gave a red colour with ferric chloride but did not reduce Tollens's reagent (Found: C, 77·85; H, 4·8; N, 4·1. $C_{23}H_{17}NO_3$ requires C, 78·0; H, 4·8; N, 3·9%).

1-*Hydroxy*-4,5,6-*triphenyl*-2-*pyridone* was prepared from 4,5,6-triphenyl-2-pyrone as above and crystallised from benzene–light petroleum in plates, m. p. 232—233° (Found: C, 81·7; H, 5·1; N, 4·15. $C_{23}H_{17}NO_2$ requires C, 81·4; H, 5·05; N, 4·1%).

1-*Hydroxy*-5-*methoxy*-4-*phenyl*-6-p-*tolyl*-2-*pyridone* was prepared in 20% yield when 5-methoxy-4-phenyl-6-*p*-tolyl-2-pyrone (1 g.) was refluxed with hydroxylamine hydrochloride (1 g.) in pyridine (20 ml.) for 5 hr. The mixture was poured into water, and the product crystallised from methanol; the unchanged pyrone was recovered, leaving the pyridone in the mother liquor. The *pyridone* was recovered by dilution and crystallised from benzene–light petroleum in elongated plates, m. p. 195—196° (Found: C, 74·4; H, 5·6; N, 4·5. $C_{19}H_{17}NO_3$ requires C, 74·25; H, 5·6; N, 4·6%).

1-Hydroxy-5-methoxy-4,6-diphenyl-2-pyridone, m. p. and mixed m. p.[1] 211°, was prepared from the pyrone by the same method.

1-*Benzyloxy*-4,5,6-*triphenyl*-2-*pyridone* (IX; R = Ph).—1-Hydroxy-4,5,6-triphenyl-2-pyridone (0·7 g.) was added to a solution of sodium (0·1 g.) in ethanol (30 ml.) and refluxed with

benzyl chloride (0·5 g.) for 4 hr. The mixture was diluted with water and extracted with ether, and the ethereal solution distilled. The residual 1-benzyloxy-2-pyridone (0·4 g.) crystallised from dilute methanol in pale yellowish prismatic plates, m. p. 174—175°, which gave a negative ferric chloride test (Found: C, 83·7; H, 5·4; N, 3·25. $C_{30}H_{23}NO_2$ requires C, 83·9; H, 5·4; N, 3·3%). This 1-benzyloxypyridone (0·1 g.) was recovered unchanged after being heated with methanol (5 ml.) containing 5 drops concentrated hydrochloric acid for 30 min.

1-*Amino-5-phenoxy-4,6-diphenyl-2-pyridone* (XIVa; R = OPh).—5-Phenoxy-4,6-diphenyl-2-pyrone (0·7 g.) was refluxed with 25% hydrazine hydrate (7 ml.) for 4 hr. and, after dilution, the *aminopyridone* was recovered in 80% yield. It crystallised from dilute methanol in needles, m. p. 181° (Found: C, 77·4; H, 5·25; N, 7·8. $C_{23}H_{18}N_2O_2$ requires C, 77·9; H, 5·1; N, 7·9%). It reduces Fehling's solution and Tollens's reagent and gives a green colour with ferric chloride. This aminopyridone was also prepared in 70% yield when a solution of methyl *cis*-5-oxo-4-phenoxy-3,5-diphenylpentenoate (0·3 g.) in ethanol (15 ml.) was refluxed with 85% hydrazine hydrate (2 ml.) for 2 hr.

Action of Nitrous Acid.—A solution of the aminopyridone (0·7 g.) in glacial acetic acid (30 ml.) was treated (dropwise) with a solution of sodium nitrite (1·5 g.) in water (12 ml.). When the mixture was heated to boiling, diluted, and cooled, 5-phenoxy-4,6-diphenyl-2-pyridone, m. p. and mixed m. p. 235°, was obtained.

1-*Diacetylamino-5-phenoxy-4,6-diphenyl-2-pyridone* was prepared when the foregoing aminopyridone (0·6 g.) was heated with acetic anhydride (6 ml.) in pyridine (10 ml.) for 3 hr. It crystallised from methanol in needles, m. p. 158° (Found: C, 74·2; H, 5·2; N, 6·5. $C_{27}H_{22}N_2O_4$ requires C, 73·9; H, 5·1; N, 6·4%). When this diacetate (0·2 g.) in ethanol (20 ml.) containing hydrochloric acid (2 ml.) was refluxed for 30 min., the aminopyridone was recovered after dilution and neutralisation.

1-*Monoacetylamino-5-phenoxy-4,6-diphenyl-2-pyridone* was prepared when the foregoing diacetate (0·3 g.) was refluxed with 5% methanolic potassium hydroxide (10 ml.) for 2 hr. It separated after dilution and acidification, and crystallised from chloroform–light petroleum in needles, m. p. 234° (Found: C, 75·8; H, 4·9; N, 7·4. $C_{25}H_{20}N_2O_3$ requires C, 75·7; H, 5·1; N, 7·1%). It was soluble in aqueous sodium hydroxide, was hydrolysed to the free amine by methanolic hydrochloric acid, and did not give a colour with ferric chloride.

1-*Acetyl-1-methylamino-5-phenoxy-4,6-diphenyl-2-pyridone.*—A solution of 1-monoacetylamino-5-phenoxy-4,6-diphenyl-2-pyridone (0·4 g.) in 2% aqueous potassium hydroxide (100 ml.) was treated with dimethyl sulphate (4 ml.) with shaking. The desired *compound* was separated from the alkaline medium and crystallised from dilute methanol in aggregate plates, m. p. 173° (Found: C, 75·85; H, 5·2; N, 6·9; NMe, 6·8. $C_{26}H_{22}N_2O_3$ requires C, 76·1; H, 5·4; N, 6·8; NMe, 7·1%). It was recovered unchanged after 2 hr. with 3% methanolic potassium hydroxide or hydrochloric acid in boiling ethanol.

1-*Dibenzoylamino-5-phenoxy-4,6-diphenyl-2-pyridone.*—The foregoing 1-amino-2-pyridone (0·5 g.) was refluxed with benzoyl chloride (1 ml.) and anhydrous sodium carbonate (2 g.) in dry chloroform for 2 hr. The *product* recovered from the solvent was treated with cold methanol and then crystallised from benzene–light petroleum in prismatic needles, m. p. 219° (decomp.) (Found: C, 79·2; H, 4·8; N, 5·25. $C_{37}H_{26}N_2O_4$ requires C, 79·0; H, 4·7; N, 5·0%).

1-*Monobenzoylamino-5-phenoxy-4,6-diphenyl-2-pyridone.*—This *amide* was prepared by heating the dibenzoyl derivative (0·3 g.) (*a*) with methanolic potassium hydroxide as for the diacetate or (*b*) in methanol (60 ml.) containing hydrochloric acid (2 ml.) for 1 hr. It crystallised from chloroform–light petroleum in aggregate needles, m. p. 242° (Found: C, 78·5; H, 4·8; N, 5·9. $C_{30}H_{22}N_2O_3$ requires C, 78·6; H, 4·8; N, 6·1%). This derivative was also prepared by refluxing benzoyl chloride with a dry chloroform solution of the aminopyridone in presence of anhydrous potassium carbonate for 3 hr.

1-*Benzylideneamino-5-phenoxy-4,6-diphenyl-2-pyridone.*—A solution of benzaldehyde (0·5 g.) and the aminopyridone (0·4 g.) in ethanol (2 ml.) was heated on the water-bath for 2 hr. The residue was then extracted with ethanol and, after dilution with water, the *benzylidene derivative* separated. It crystallised from benzene in yellow needles, m. p. 236° (Found: C, 81·4; H, 5·1; N, 6·1. $C_{30}H_{22}N_2O_2$ requires C, 81·4; H, 5·0; N, 6·3%).

The benzylidene derivative (0·7 g.) was refluxed with 20% ethanolic potassium hydroxide (20 ml.) for 4 hr., during which ammonia was evolved. On dilution with water, 5-phenoxy-4,6-diphenyl-2-pyridone (0·45 g.) was recovered and crystallised from pyridine–methanol in needles, m. p. and mixed m. p. 233°. When the alkaline solution was extracted with chloroform,

acidified, and again extracted with chloroform, benzoic acid (m. p. and mixed m. p. 121°) was obtained. This benzylidene derivative (0·15 g.) was not hydrolysed by boiling hydrochloric acid (3 ml.) in methanol (80 ml.) for 3 hr.

1-*Furfurylideneamino*-5-*phenoxy*-4,6-*diphenyl*-2-*pyridone*.—This *derivative* was prepared from the aminopyridone and furfuraldehyde and crystallised from benzene–light petroleum in yellow needles, m. p. 195—196° (Found: C, 77·9; H, 4·6; N, 6·2. $C_{28}H_{20}N_2O_3$ requires C, 77·8; H, 4·7; N, 6·5%). It was hydrolysed to the pyridone and furoic acid, m. p. and mixed m. p. 131°, by boiling ethanolic potassium hydroxide.

Analogously, the 1-*amino*-2-*pyridones* (XIVb—f) (Table 5) were prepared from the pyrones (II) in about 70% yield and crystallised from suitable solvents. Therefrom, the diacetates,

TABLE 5.

1-Amino-2-pyridones (XIVb—f) and their derivatives.

				Found (%)				Required (%)		
	R	M. p.	Solvent †	C	H	N	Formula	C	H	N
b	*p*-Me·C_6H_4·O	202°	E	78·0	5·3	7·65	$C_{24}H_{20}N_2O_2$	78·2	5·5	7·6
b	diacetyl	164	Dil. M	73·8	5·4	6·2	$C_{28}H_{24}N_2O_4$	74·3	5·35	6·2
b	monoacetyl	258	C–L	75·75	5·4	6·8	$C_{26}H_{22}N_2O_3$	76·1	5·4	6·8
b	acetyl-methyl ...	176 [a]	Dil. M	76·2	5·65	6·5	$C_{27}H_{24}N_2O_3$	76·4	5·7	6·6
b	dibenzoyl	198 *	B–L	79·1	4·8	4·9	$C_{38}H_{28}N_2O_4$	79·2	4·9	4·9
b	monobenzoyl	150 *	B–L	78·7	5·0	5·8	$C_{31}H_{24}N_2O_3$	78·8	5·1	5·9
b	benzylidene	246 [b]	C–L	81·8	5·1	6·1	$C_{31}H_{24}N_2O_2$	81·5	5·3	6·1
b	furfurylidene	220 [b]	C–L	78·3	4·85	6·4	$C_{29}H_{22}N_2O_3$	77·8	5·0	6·3
c	*p*-Cl·C_6H_4·O	203	M	71·1	4·5	7·4	$C_{23}H_{17}ClN_2O_2$ [c]	71·05	4·4	7·2
c	diacetate	159	Dil. M	68·3	4·55	5·8	$C_{27}H_{21}ClN_2O_4$	68·55	4·5	5·9
c	furfurylidene	216 [b]	B–L	71·9	4·1	5·9	$C_{28}H_{19}ClN_2O_3$	72·0	4·1	6·0
d	*p*-Br·C_6H_4·O	222	E	63·7	3·95	6·5	$C_{23}H_{17}BrN_2O_2$ [d]	63·7	4·0	6·5
d	diacetyl	160	Dil. M	62·4	4·3	5·3	$C_{27}H_{21}BrN_2O_4$	62·65	4·1	5·4
e	C_6H_5	199	B–L	81·6	5·4	8·35	$C_{23}H_{18}N_2O$	81·6	5·4	8·3
e	diacetyl	167	Dil. M	76·5	5·1	6·7	$C_{27}H_{22}N_2O_3$	76·7	5·25	6·6
e	monoacetyl	246 [a]	Dil. M	78·7	5·15	7·4	$C_{25}H_{20}N_2O_2$	78·9	5·3	7·4
e	dibenzoyl	272 *	E	80·9	4·8	5·3	$C_{37}H_{26}N_2O_3$	81·3	4·8	5·1
e	monobenzyl	252	B–L	81·4	5·2	6·4	$C_{30}H_{22}N_2O_2$	81·4	5·0	6·3
e	benzylidene	158 [b]	M	84·3	5·3	6·65	$C_{30}H_{22}N_2O$	84·5	5·2	6·6
e	furfurylidene	183 [b]	E	80·75	4·8	6·9	$C_{28}H_{20}N_2O_2$	80·7	4·8	6·7
f	OMe [1]	186								
f	diacetyl	128	M	68·9	5·45	7·7	$C_{22}H_{20}N_2O_4$	68·6	5·4	7·45
f	benzylidene	164 [b]	B–L	79·25	5·15	7·2	$C_{25}H_{20}N_2O_2$	78·9	5·3	7·4

* With decomp. † E = ethanol; C = chloroform; other solvents as indicated before.
[a] Plates; the others formed needles. [b] Yellow. [c] Cl: Found, 9·0. Reqd., 9·1%. [d] Br: Found, 18·4. Reqd., 18·45%.

monoacetates, dibenzoates, monobenzoates, and benzylidene and furfurylidene derivatives have been prepared. Compound (XIVe) was also prepared from ethyl *trans*-β-desylcinnamate, methyl *cis*-β-desylcinnamate, or methyl β-benzoyl-αβ-diphenylacrylate, and (XIVf) from methyl *cis*-4-methoxy-5-oxo-3,5-diphenylpentenoate by the action of hydrazine hydrate.

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