Reactivity of 3-Amino-, 3-Halogeno-, and 3-Nitro-2-pyrones and Thiopyrones

Ibrahim El-Sayed El-Kholy, Morcos Michael Mishrikey and Hassan Mostafa Fuid-Alla

Chemistry Department, Faculty of Science, Moharram Bey,
Alexandria University, Alexandris, Egypt

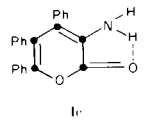
Received February 13, 1974

Substituted pyrrole and furan-2-carboxylic acids were obtained from 3-amino- and 3-halogeno-2-pyrones. The reactions of several substituted 2-pyrones and thiopyrones with different amines and carbonyl reagents were studied.

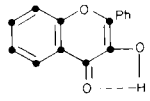
We have previously shown (1) that 4,5,6-triaryl-2-pyrones undergo bromination and nitration in the 3 position. We now report that 4,5,6-triphenyl-2-pyrone (I, R = H; X = O) could be chlorinated and iodinated to give the 3-chloro- (Ia) and the 3-iodo- (Ic) derivatives. The reaction of these 3-halogeno-2-pyrones (Ia and c) with methanolic potassium hydroxide led to the formation of 3,4,5-triphenylfuran-2-carboxylic acid (II) (2). The use of aqueous sodium carbonate raised the yield of II from 30% to 50%.

The validity of the previous reaction as a synthetic route for furan derivatives (3,4) led us to think that if the presence of an amino group at position 3 of the 2-pyrone would lead to the formation of a pyrrole derivative. Accordingly, 3-amino-4,5,6-triphenyl-2-pyrone (Ie) was prepared by reduction of the corresponding 3-nitro derivative (Id) (1) by means of stannous chloride.

The ir spectrum of Ie showed two bands at 3380 and 3484 cm^{-1} for the amino group stretching, and a 2-pyrone carbonyl absorption at 1711 cm^{-1}. This relatively low carbonyl frequency is most probably attributed to hydrogen bonding between the amino group and the 2-pyrone carbonyl, similar to 3-hydroxyflavones (5a).

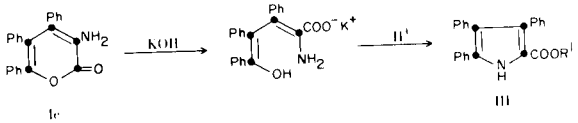


Ie



The aminopyrone (Ie) was further characterised by formation of monoacetyl- (If), monobenzoyl- (Ig), phthalimido- (Ih) and succinimido- (Ii) drivatives. The ir spectra of If and Ig exhibited, besides, the amide carbonyl absroption at 1670-1685 cm^{-1} a split 2-pyrone carbonyl (6) at 1705 and 1730-1736 cm^{-1}. For Ih and Ii the 2-pyrone carbonyl absorption appeared at 1720-1731 cm^{-1}, besides the other two bands at 1735-1752 and 1775-1798 cm^{-1} which characterises the grouping (-CO-N-CO-) (5b).

3,4,5-Triphenylpyrrole-2-carboxylic acid (III, R^1 = H) was obtained by the action of alkali on 3-amino-4,5,6-triphenyl-2-pyrone (Ie). This reaction can be considered as a new route for the synthesis of pyrroles and is thought to proceed as follows:



Ie III

The ir spectrum of the pyrrole methyl ester (III, R^1 = CH_3) showed a sharp band at 3305 cm^{-1} attributed to the pyrrole NH (7), and the ester carbonyl at 1672 cm^{-1}. Also its uv spectrum exhibited two absorption maxima at 254 and 304 nm comparable to other pyrrole esters (8).

Nucleophilic attack leading to ring fission of 2-pyrones would be expected to take place more easy in the presence of an electron-withdrawing group at position 3. Accordingly, 3-nitro-4,5,6-triphenyl-2-pyrone (Id) gave on treatment with cold alkali the pentenoic acid (IV) whose methyl ester could be recyclised to the pyrone (Id). Also, with hydrazine hydrate, the pyrones (Ia-d) reacted smoothly at room temperature forming the corresponding 1-amino-2-pyridones (Va-d, R^2 = NH_2) which were characterised by formation of benzylidene derivatives (Va-d, R^2 = N=CHPh). The ir spectra of V (R^2 = NH_2 and N=CHPh) showed the cyclic amide carbonyl absroption in the region 1640-1680 cm^{-1}. 1-Amino-3-bromo-4,5,6-triphenyl-2-pyridone (Vb, R^2 = NH_2) was further characterised by formation of diacetyl- (Vb, R^2 = NAc_2) and phthalimido- (Vb, R^2 = $N{<}^{CO}_{CO}{>}C_6H_4$) derivatives.

A new series of 2-pyridones (Va-d, R^2 = H) was obtained by the action of nitrous acid on the 1-amino-2-pyridones (Va-d, R^2 = NH_2) which were also formed by alkaline hydrolysis of the benzylidene derivatives (Va-d, R^2 = N=CHPh). These pyridones, which exhibit lactam-lactim

tautomerism, gave 1-methyl-2-pyridones (Va-c, $R^2 = CH_3$) with methyl iodide and potassium carbonate, while the isomeric 2-methoxypyridines (VIa-c) were exclusively obtained when their silver salts reacted with methyl iodide. Methylation with diazomethane afforded a mixture of 20% Va-c ($R^2 = CH_3$) and *ca.* 40% of VIa-c. The ir spectra of 1-methyl-2-pyridones (V, $R^2 = CH_3$) are characterised by the cyclic amide carbonyl absorption at 1660 cm^{-1} while those of the isomeric 2-methoxypyridines (VI) lack this band and exhibit two absorptions at 1548 and 1572 cm^{-1} attributed to the pyridine ring (5c). Moreover, 2-methoxypyridines (VI) were found to have lower melting points (9) (*cf.* Experimental). However, the 2-pyridones (V, $R^2 = H$) in neutral medium seem to exist predominantly in the lactam form, since their ir spectra exhibited the 2-pyridone carbonyl in the region 1640-1650 cm^{-1} and the NH stretching at 3280-3300 cm^{-1}. Moreover, their electronic spectra (Table I) like those of 1-methyl-2-pyridones (V, $R^2 = CH_3$) - incapable of tautomerism - showed two maxima in the regions 249-256 and 328-339 nm. On the other hand, the 2-methoxypyridines (VI) showed a single maximum in the region 305-310 nm.

TABLE I

Electronis Spectral Data of 2-Pyridones (V) and 2-Methoxypyridines (VI)

No.	R^2	λ max/nm (ε)			
Va	H	256	(11940)	335	(9856)
Vb	H	257	(12310)	336	(11910)
Vc	H	254	(16660)	333	(8674)
Vd	H	250sh	(14300)	337	(6977)
Va	CH_3	249sh	(11990)	328	(9721)
Vb	CH_3	249sh	(11800)	328	(9959)
Vc	CH_3	248sh	(13840)	333	(11090)
Va	OH	251sh	(12810)	339	(5694)
Vb	OH	250sh	(20890)	343	(13620)
Vc	OH	248sh	(19920)	341	(9210)
Va	OCH_3	249sh	(11540)	328	(8658)
Vb	OCH_3	248sh	(13130)	329	(11160)
VIa				305	(11670)
VIb				305	(11260)
VIc				310	(10420)

The pyrones (Ia-c) reacted with hydroxylamine giving the respective 1-hydroxy-2-pyridones (Va-c, $R^2 = OH$) which were converted into the 1-methoxy-2-pyridones

TABLE II

2-Pyridones and 2-Methoxypyridines

No.	R^2	M.p., °C	Formula	Analyses Calcd. C	H	N	X	Found C	H	N	X
Va (a)	NH_2	240	$C_{23}H_{17}ClN_2O$	74.09	4.59	7.51		74.11	5.00	7.51	
Vb	NH_2	273	$C_{23}H_{17}BrN_2O$	66.20	4.11	6.71	19.15	66.00	4.00	6.61	19.32
Vc (a)	NH_2	266	$C_{23}H_{17}IN_2O$	59.49	3.69	6.03	27.33	59.80	3.61	6.02	27.30
Vd	NH_2	230	$C_{23}H_{17}N_3O_3$	72.05	4.45	10.95		71.85	4.41	10.75	
Va	N=CH.Ph	224	$C_{30}H_{21}ClN_2O$	78.16	4.59	6.07		78.52	4.51	6.10	
Vb (b)	N=CH.Ph	232	$C_{30}H_{21}BrN_2O$	71.29	4.18	5.50		70.91	4.23	5.38	
Vc	N=CH.Ph	240	$C_{30}H_{21}IN_2O$	65.20	3.83	5.07		65.00	4.12	5.23	
Vd (b)	N=CH.Ph	258	$C_{30}H_{21}N_3O_3$	76.42	4.49	8.91		76.20	4.80	9.11	
Va (a)	H	285	$C_{23}H_{16}ClNO$	77.20	4.50	3.91		77.30	4.51	3.73	
Vb	H	306	$C_{23}H_{16}BrNO$	68.67	4.01	3.48	19.87	68.80	4.20	3.47	19.52
Vc (a)	H	286	$C_{23}H_{16}INO$	61.48	3.58	3.11	28.24	61.28	3.80	2.91	28.70
Vd	H	285	$C_{23}H_{16}N_2O_3$	74.98	4.37	7.76		75.22	4.21	7.55	
Va	CH_3	238	$C_{24}H_{18}ClNO$	77.51	4.87	3.76		77.80	5.03	4.10	
Vb	CH_3	258	$C_{24}H_{18}BrNO$	69.24	4.35	3.36		69.20	4.22	3.30	
Vc	CH_3	200	$C_{24}H_{18}INO$	62.21	3.91	3.02		62.10	4.00	2.70	
Va (b)	OH	214	$C_{23}H_{16}ClNO_2$	73.89	4.31	3.74		73.89	4.11	3.50	
Vb	OH	266	$C_{23}H_{16}BrNO_2$	66.03	3.85	3.34	19.10	66.11	4.01	3.40	19.13
Vc	OH	225	$C_{23}H_{16}INO_2$	59.37	3.46	3.01		59.62	3.62	3.30	
Va	OCH_3	218	$C_{24}H_{18}ClNO_2$	74.32	4.67	3.61	9.14	74.66	4.70	3.40	8.80
Vb	OCH_3	238	$C_{24}H_{18}BrNO_2$	66.68	4.19	3.24	18.48	66.81	4.22	3.00	18.00
Vc	OCH_3	245	$C_{24}H_{18}INO_2$	60.14	3.78	2.92		60.20	3.39	2.99	
VIa		160	$C_{24}H_{18}ClNO$	77.51	4.87	3.76	9.50	77.50	4.80	3.64	9.30
VIb		168	$C_{24}H_{18}BrNO$	69.24	4.35	3.36	19.19	69.21	4.60	3.70	19.50
VIc		175	$C_{24}H_{18}INO$	62.21	3.91	3.02		62.41	3.70	3.01	

All compounds were crystallised from ethanol unless otherwise stated. (a) Crystallised from benzene-ethanol. (b) Crystallised from methanol.

TABLE III

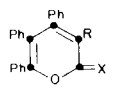
2-Pyrone Phenylhydrazones, Oximes and 1-Methyl-2-thiopyridones

No.	M.P., °C	Solvent	Formula	Analyses Calcd. C	H	N	X	Found C	H	N	X
II	174	C	$C_{29}H_{21}BrN_2O$	70.59	4.28	5.67	16.19	70.90	4.21	5.41	15.90
Im	163	B	$C_{29}H_{21}IN_2O$	64.46	3.90	5.18		64.50	4.01	5.01	
In	260	B-E	$C_{23}H_{16}BrNO_2$	66.03	3.80	3.30		65.80	4.10	3.50	
Io	256	B-E	$C_{23}H_{16}INO_2$	59.37	3.46	3.01		59.20	3.41	2.80	
Vj, $R^2 = CH_3$	206	E	$C_{24}H_{18}BrNS$	66.65	4.19	3.24	7.41 (a)	66.20	4.01	2.90	7.60 (a)
Vk, $R^2 = CH_3$	208	M-B	$C_{24}H_{18}INS$	60.13	3.78	2.92	6.68 (a)	60.11	3.60	3.01	6.73 (a)

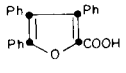
E = ethanol, B = benzene and M = methanol. (a) X = S.

(Va-c, $R^2 = OCH_3$) on reaction with methyl iodide. The ir spectra of both V ($R^2 = OH$) and V ($R^2 = OCH_3$) showed the 2-pyridone carbonyl band in the region 1640-1665 cm^{-1}, besides a broad OH absorption at 3120-3150 cm^{-1} for the former. However, the pyrones (Ia-c) failed to react with phenylhydrazine or with methylamine.

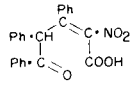
While 3-iodo-4,5,6-triphenyl-2-pyrone (Ic) reacted with phosphorus pentasulphide giving the corresponding 2-thiopyrone (Ik), 3-chloro- (Ia) and 3-nitro- (Id) derivatives failed to give their thioanalogues. The ir spectrum of Ik showed the thiocarbonyl absorption at 1100 cm^{-1} (10) and could be converted into the pyrone Ic by the action of hydrogen peroxide.



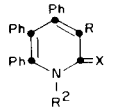
I



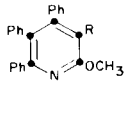
II



IV



V



VI

	R	X
a:	Cl	O
b:	Br	O
c:	I	O
d:	NO_2	O
e:	NH_2	O
f:	NHAc	O
g:	NHCOPh	O
h:		O
i:		O
j:	Br	S
k:	I	S
l:	Br	N.NHPh
m:	I	N.NHPh
n:	Br	NOH
o:	I	NOH

The fact that 2-thiopyrones are more reactive than 2-pyrones (II) was illustrated by their behaviour towards nucleophilic reagents. Thus with phenylhydrazine the 2-thiopyrones (Ij and k) readily gave the corresponding phenylhydrazones (II and m). Their ir spectra showed a strong C=N absorption at 1595 cm^{-1} and NH stretching at 3405 cm^{-1}.

The 2-thiopyrones (Ij and k) afforded with hydroxylamine the corresponding oximes (In and o). These oximes were differentiated from their isomeric 1-hydroxy-2-pyridones (Vb and c, $R^2 = OH$) by lack of the 2-pyridone carbonyl absorption and by exhibiting a strong C=N band at 1620 cm^{-1}, besides a broad OH absorption at 3280-3360 cm^{-1}. Also, these oximes (In and o) underwent acid hydrolysis to the corresponding 2-pyrones. Moreover, the thiopyrones (Ij and k) gave with methylamine the respecgive 1-methyl-2-thiopyridones (Vj and k, $R^2 = CH_3$) whose ir spectra showed the thiocarbonyl band at 1100 cm^{-1} (10).

EXPERIMENTAL

Analyses were performed by Microanalysis Unit, Faculty of Science, Cairo University, Cairo. Ir spectra were measured with a Unicam SP 200 spectrophotometer in potassium bromide pellets or in nujol, and electronic spectra were measured using ethanol solutions with a Unicam SP 800 spectromoter.

3-Chloro-4,5,6-triphenyl-2-pyrone (Ia).

Chlorine gas was passed into a solution of 4,5,6-triphenyl-2-pyrone (1 g.) in chloroform (20 ml.) in the presence of ferric chloride (0.5 g.) for 7 minutes. Compound Ia crystallised as needles (ethanol), m.p. 185°; ν max 1739 (CO) cm^{-1}; λ max 251 and 338 nm (ϵ 14,950 and 8,047).

Anal. Calcd. for $C_{23}H_{15}ClO_2$: C, 76.96; N, 4.21; Cl, 9.88. Found: C, 76.70; H, 4.40; Cl, 10.21.

3-Iodo-4,5,6-triphenyl-2-pyrone (Ic).

4,5,6-Triphenyl-2-pyrone (1 g.) in chloroform (20 ml.) was refluxed with iodine (0.4 g.) and fuming nitric acid (d, 1.5; 0.3 ml.) for 1 hour. After evaporation and treatment with light petroleum

(b.p. 50-70°), Ic (1 g.) was obtained which crystallised as yellow needles (benzene), m.p. 205°; ν max 1722 (CO) cm^{-1}; λ max 233-240 and 253 nm (ϵ 13,590 and 14,790).

Anal. Calcd. for $C_{23}H_{15}IO_2$: C, 61.35; H, 3.35; I, 28.18. Found: C, 61.30; H, 3.21; I, 28.50.

3,4,5-Triphenyl-2-furoic Acid (II).

A solution of Ia-c (1 g.) in ethanol (20 ml.) was refluxed with 10% aqueous sodium carbonate (10 ml.) for 20 minutes. The solution was cooled, acidified with 10% sulphuric acid and extracted with ehter which afforded after drying (sodium sulfate) and evaporation the acid II (0.4 g.), m.p. and mxied m.p. 166° dec., (2).

3-Amino-4,5,6-triphenyl-2-pyrone (Ie).

A solution of Id (1 g.) in ethanol (20 ml.) was refluxed with tin (5 g.) and concentrated hydrochloric acid (30 ml.) for one hour, poured into water and extracted with ether. The ethereal solution after washing with water,.drying (sodium sulfate) and evaporation afforded Ie (0.8 g.) which crystallised as yellow prismatic needles (ethanol), m.p. 200°; ν max 1711 (CO), 3484, 3380 (NH_2) cm^{-1}; λ max 234, 271 and 350 nm (ϵ 15,200, 13,250 and 14,670).

Anal. Calcd. for $C_{23}H_{17}NO_2$: C, 81.39; H, 5.05; N, 4.12. Found: C, 81.71; H, 4.78; N, 4.12.

3-Acetylamino-4,5,6-triphenyl-2-pyrone (If).

This compound was obtained (80% yield) by refluxing Ie in acetic acid with acetic anhydride and sodium acetate for 3 hours. It gave plates (methanol), m.p. 197°; ν max 1705, 1730 (CO 2-pyrone), 1685 (CO amide) and 3380-3410 (NH) cm^{-1}.

Anal. Calcd. for $C_{25}H_{19}NO_3$: C, 78.72; H, 5.02; N, 3.67. Found: C, 78.95; H, 5.21; N, 3.83.

This acetate was hydrolysed to Ie on refluxing its ethanolic solution with hydrochloric acid for 2 hours.

3-Benzoylamino-4,5,6-triphenyl-2-pyrone (Ig).

This compound was prepared (70% yield) be keeping Ie and benzoyl chloride overnight at room temperature. It gave needles (methanol), m.p. 215°; ν max 1705, 1737 (CO 2-pyrone), 1670 (CO amide) and 3380-342obr (NH) cm^{-1}.

Anal. Calcd. for $C_{30}H_{21}NO_3$: C, 81.24; H, 4.77; N, 3.16. Found: C, 81.30; H, 4.61; N, 3.00.

3-Phthalimido-4,5,6-triphenyl-2-pyrone (Ih).

This compound was prepared (90% yield) be heating Ie with phthalic anhydride at 190-200° for 10 minutes. It gave prismatic needles (methanol), m.p. 250°; ν max 1731 (CO 2-pyrone), 1752, 1798 (CO-N-CO) cm^{-1}.

Anal. Calcd. for $C_{31}H_{19}NO_4$: C, 79.30; H, 4.08; N, 2.98. Found: C, 78.95; H, 3.81; N, 3.01.

3-Succinimido-4,5,6-triphenyl-2-pyrone (Ii).

This compound was obtained (80% yield) by heating Ie with succinic anhydride at 185-195° for 10 minutes. It gave needles (ethanol), m.p. 221°; ν max 1720 (CO 2-pyrone) and 1735, 1775 (CO-N-CO) cm^{-1}.

Anal. Calcd. for $C_{27}H_{19}NO_4$: C, 76.95; H, 4.54; N, 3.32. Found: C, 76.75; H, 4.66; N, 2.90.

3,4,5-Triphenylpyrrole-2-carboxylic Acid (III, R^1 = H).

Compound Ie (0.5 g.) was refluxed with 5% methanolic potassium hydroxide (20 ml.) for 10 minutes. After dilution with water and extraction with ether, the alkaline aqueous solution yielded the acid (III, R^1 = H) (0.3 g.) on acidification. It gave needles (ethanol), m.p. 222° dec.; ν max 1648 (CO) and 3422 (NH) cm^{-1}; λ max 254 and 303 nm (ϵ, 21,210 and 16,870).

Anal. Calcd. for $C_{23}H_{17}NO_2$: C, 81.39; H, 5.05; N, 4.13. Found: C, 81.40; H, 5.13; N, 3.82.

Its methyl ester (III, R^1 = CH_3) prepared by diazomethane gave needles (benzene-methanol mixture), m.p. 220°; ν max 1672 (CO ester) and 3305 (NH) cm^{-1}; λ max 254, and 304 nm (ϵ, 20,690 and 18,650).

Anal. Calcd. for $C_{24}H_{19}NO_2$: C, 81.56; H, 5.42; N, 3.96. Found: C, 81.50; H, 5.40; N, 3.66.

This ester (III, R^1 = CH_3) was hydrolysed to the acid (III, R^1 = H) on refluxing with 5% methanolic potassium hydroxide for 2 hours, but was recovered unchanged after refluxing with hydrochloric acid in ethanol for 1 hour.

2-Nitro-3,4,5-triphenyl-5-oxopent-2-enoic Acid (IV).

The pyrone Id (1 g.) was kept with 5% methanolic potassium hydroxide (20 ml.) at room temperature for 10 minutes. After dilution with water and extraction with ether, the aqueous alkaline solution gave the acid IV (0.6 g.) on acidification. It gave needles (methanol), m.p. 106° dec.

Anal. Calcd. for $C_{23}H_{17}NO_5$: C, 71.31; H, 4.42; N, 3.61. Found: C, 71.21; H, 4.33; N, 3.45.

Esterification of IV with diazomethane gave an oily ester which when treated with sodium methoxide afforded the pyrone Id, m.p. and mixed m.p. 171° dec. (1).

1-Amino-2-pyridones (Va-d, R^2 = NH_2) (Table II).

These compounds were prepared (60% yield) by keeping a suspension of Ia-d (0.5 g.) in ethanol (5 ml.) with 98% hydrazine hydrate (1 ml.) overnight.

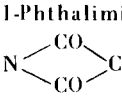
1-Benzylideneamino-2-pyridones (Va-d, R^2 = N=CHPh) (Table II).

These compounds were prepared by heating the 1-amino-2-pyridones (Va-d, R^2 = NH_2) with benzaldehydr in dry benzene for 30 minutes. These benzylidene derivatives were converted to the corresponding 2-pyridones (Va-d, R^2 = H) when refluxed with 15% ethanolic potassium hydroxide for 2 hours.

1-Diacetylamino-3-bromo-4,5,6-triphenyl-2-pyridone (Vb, R^2 = NHc_2).

This compound was obtained by refluxing the amino-pyridone (Vb, R^2 = NH_2) in pyridine with acetic anhydride for 3 hour. It gave needles (benzene-light petroleum b.p. 50-70°), m.p. 220°.

Anal. Calcd. for $C_{27}H_{21}BrN_2O_3$: C, 64.68; H, 4.22; N, 5,58. Found: C, 64.62; H, 4.33; N, 6.00.

1-Phthalimido-3-bromo-4,5,6-triphenyl-2-pyridone (Vb, R^2 = ).

This compound was prepared by fusing the amino-pyridone (Vb, R^2 = NH_2) and phthalic anhydride at 200-210°. It gave needles (ethanol), m.p. 263°; ν max 1670 (CO pyridone) and 1750, 1795 (CO-N-CO) cm^{-1}.

Anal. Calcd. for $C_{31}H_{19}BrN_2O_3$: C, 68.01; H, 3.50; N, 5.11. Found: C, 68.02; H, 3.60; N, 5.29.

2-Pyridones (Va-d, R^2 = H) (Table II).

These compounds were prepared (50-70% yield) by treating a solution of the amino-pyridones (Va-d, R^2 = NH_2) in acetic aicd (8 ml.) with aqueous sodium nitrite (0.5 g.) and then pouring into ice-cold water.

1-Methyl-2-pyridones (Va-c, R^2 = CH_3) (Table II).

These compounds were prepared (80% yield) by refluxing a solution of the pyridones (Va-c, R^2 = H) (0.5 g.) in acetone (20 ml.) with methyl iodide (10 ml.) and anhydrous potassium carbonate (2 g.) for 5 hours.

2-Methoxypyridines (VIa-c) (Table II).

A solution of the pyridones (Va-c, R^2 = H) (0.7 g.) in 10% ethanolic potassium hydroxide (15 ml.) was treated with aqueous silver nitrate (20 ml.) and the black silver oxide-silver salt mixture filtered and dried. The methoxypyridines (VIa-c) were obtained (65% yield) after refluxing the powdered mass with methyl iodide (15 ml.) for 3 hours, filtering, extracting the residue with boiling methanol and evaporating the solvent.

Action of Diazomethane on the 2-Pyridones (Va-c, R^2 = H).

A suspension of the pyridones (Va-c, R^2 = H) in ether was treated with ethereal diazomethane and the reaction mixture was kept overnight at room temperature. After removal of the solvent, the methylation product was subjected to fractional crystallisation from methanol, when 2-methoxypyridines (VIa-c; 40%) separated out first and from the mother liquor, 1-methyl-2-pyridones (Va-c, R^2 = CH_3; 20%) were obtained.

1-Hydroxy-2-pyridones (Va-c, R^2 = OH) (Table II).

These compounds were prepared (40-45% yield) by refluxing a solution of Ia-c (1 g.) in pyridine (10 ml.) with hydroxylamine hydrochloride (0.7 g.) in water (4 ml.) for 5 hours.

1-Methoxy-2-pyridones (Va-c, R^2 = OCH_3) (Table II).

These compounds were prepared (45-50% yield) by refluxing a solution of the hydroxy-pyridones (Va-c, R^2 = OH) (0.5 g.) in acetone (20 ml.) with methyl iodide (10 ml.) and anhydrous potassium carbonate (2 g.) for 5 hours.

3-Iodo-4,5,6-triphenyl-2-thiopyrone (Ik).

This compound was prepared (80% yield) by refluxing a solution of Ic (1 g.) in dry toluene (15 ml.) with phosphorus pentasulphide (3 g.) for 4 hours. It gave red needles (benzene-light petroleum b.p. 50-70°), m.p. 220°; ν max 1100 (CS) cm^{-1}; λ max 300 and 426 nm (ϵ, 15,970 and 9,712).

Anal. Calcd. for $C_{23}H_{15}IOS$: C, 59.24; H, 3.24; I, 27.22; S, 6.86. Found: C, 59.20; H, 3.11; I, 27.60; S, 7.20.

2-Pyrone Phenylhydrazones (Il and m) (Table III).

These compounds were obtained (55-60% yield) by refluxing a suspension of Ij and k (0.5 g.) in ethanol (20 ml.) with phenylhydrazine (1 ml.) for 2 hours. These phenylhydrazones were hydrolysed to the pyrones Ib and c when their ethanolic solutions were refluxed with hydrochloric acid for one hour.

2-Pyrone Oximes (In and o) (Table III).

The oximes were prepared (60% yield) by refluxing a suspension of Ij and k (0.5 g.) in ethanol (20 ml.) with hydroxylamine hydrochloride (0.5 g.) and sodium acetate (0.5 g.) in water (4 ml.) for 2 hours. They were hydrolysed to the pyrones Ib and c when refluxed with ethanolic hydrochloric acid for 30 minutes.

1-Methyl-2-thiopyridones (Vj and k, R^2 = CH_3) (Table III).

These compounds were obtained (40% yield) by refluxing a suspension of Ij and k (0.5 g.) in ethanol (20 ml.) with methylamine hydrochloride (0.5 g.) and sodium acetate (0.5 g.) in water (4 ml.) for 5 hours.

REFERENCES

(1) I. E. El-Kholy, F. K. Fafla and M. M. Mishrikey, *J. Chem. Soc. (C)*, 1950 (1969).

(2) I. E. El-Kholy and F. K. Rafla, *J. Chem. Soc.*, 5297 (1962).

(3) W. Broy and R. Mayer, *Z. Chem.*, **3**, 150 (1963).

(4) D. L. Dare, I. D. Entwistle and R. A. W. Johnston, *J. Chem. Soc. Perkin I*, 1130 (1973).

(5) L. J. Bellamy "The Infrared Spectra of Complex Molecules", London, Methuen and Co. Ltd., 1964, pp. (a) 144, (b) 221 and (c) 279.

(6) R. N. Jones and B. Gallagher, *J. Am. Chem. Soc.*, **81**, 5242 (1959).

(7) A. Fujino and M. Yamaguchi, "IR Spectra", Vol. 6, (1959), p. 61.

(8) "Spectrophotometric Identification of Organic Compounds," Wiley, USA, 1967, p. 167.

(9) R. C. Elderfield "Heterocyclic Compounds", Vol. 1, 1950, p. 536.

(10) E. Spinner, *J. Org. Chem.*, **23**, 2037 (1958); *J. Chem. Soc.*, 1237 (1960).

(11) G. Soliman and I. El-Sayed El-Kholy, *ibid.*, 1755 (1955); A. R. Katritzky and A. J. Boulton "Advances in Heterocyclic Chemistry" Vol. 8, 1967, p. 269.