CROATICA CHEMICA ACTA CCACAA **60** (4) 717—733 (1987)

CCA-1769

YU ISSN 0011-1643
UDC 547.823
Original Scientific Paper

Synthesis of Pyridones and Dihydropyridines from Pyrylium Salts and Nitriles from Adimines

Hassan M. Faid-Allah

Department of Chemistry, Faculty of Science, University of Alexandria, Egypt

Received February 17, 1986

The 4,5,6-triphenyl-2-pyrone I was readily converted to the pyrylium salts II, which under the influence of sodium ethoxide afforded the pyridones III. 4,5,6-Triphenylpyran-2-imine IVa, prepared from I or IIa, was rearranged by sodium ethoxide to the isomeric 2-pyridone IIIa. Bromination of III yielded the 3-bromo-12-pyridones V. Condensation of the aminopyridone VI with aldehydes afforded the aldimine derivatives VIII which on thermolysis formed the nitriles X and the pyridone IX. Reaction of the pyridine-2-thiones XIV with benzyl chloride and ethyl chloroacetate afforded the chlorides XVI and XX, respectively. XX were readily converted to the dihydropyridines XXIII through the zwitterions XXI. Structures were confirmed by spectral data.

Van Allan and Chang[1] have reported that 4,6-diphenyl-2-pyrone reacts with aniline or 2,4-dinitroaniline in the presence of phosphoryl chloride giving the pyran-2-imines. Later S. Afridi and co-workers[2] found that the reaction of 4,6-diphenyl-2-pyrone with aromatic amines in phosphoryl chloride gave 2-arylamino-4,6-diphenylpyrylium chlorides which were converted to the corresponding *N*-aryl-2-pyridones. In the present work the reaction of 4,5,6-triphenyl-2-pyrone[3] I with aromatic amines in phosphoryl chloride at reflux temperature gave yellow crystalline 2-arylamino-4,5,6-triphenylpyrylium chlorides II in 75—90% yield. Using this method, the chlorides IIa-f were prepared; their structures are fully supported by elemental analysis and spectroscopic properties (Table I). The IR spectra of these chlorides II exhibited a C=N absorption in the region 1655—1665 cm^{-1}. Their ^{1}H NMR spectra showed two multiplets in the regions δ 7.3—7.4 and 7.7—8.1. The structure of the chlorides II was further confirmed by their ^{13}C NMR spectra which displayed appropriate peaks corresponding to the expected numbers of carbon atoms for these compounds.

However, the chloride IIa was converted into the free imine IVa by recrystallization from pyridine-methanol. IVa was also prepared from the triphenyl pyrone I following the Van Allan method[1] (see experimental section). The IR spectrum of IVa showed a C=N absorption at 1650 cm^{-1}. Its ^{1}H NMR spectrum exhibited two multiplets at δ 7.3 and 7.8. The ^{13}C NMR spectrum

TABLE I

2-Arylamino-4,5,6-Triphenylpyrylium Chlorides.

Compound No.	Yield	M. P.	Found/%			Elem. Analysis formula	Calc'd/%				Ir/cm^{-1} [a]
	%	°C	C	H	N		C	H	N	C=N	C=C
IIa	90	248	79.6	4.8	3.0	$C_{29}H_{22}ClNO$ (435.8)	79.9	5.0	3.2	1665	1600
IIb	85	250	79.8	5.2	3.1	$C_{30}H_{24}ClNO$ (449.8)	80.1	5.3	3.1	1660	1605
IIc	88	194 (decomp.)	77.0	5.2	3.0	$C_{30}H_{24}ClNO_2$ (465.8)	77.3	5.2	3.0	1660	1602
IId	80	175 (decomp.)	74.1	4.3	3.0	$C_{29}H_{21}Cl_2NO$ (470.3)	74.1	4.5	3.0	1655	1598
IIe	78	240	73.9	4.4	2.9	$C_{29}H_{21}Cl_2NO$ (470.3)	74.1	4.5	3.0	1658	1600
IIf	75	249	72.3	4.3	5.6	$C_{29}H_{21}ClN_2O_3$ (480.8)	72.4	4.4	5.8	1600	1600

[a] Solutions in bromoform.

of IVa showed that the expected numbers of signals correspond to the suggested structure.

On the other hand, when *p*-phenylenediamine was reacted with triphenylpyrone I, the bis-imine XI was isolated directly by recrystallization of the crude product from pyridine.

Furthermore, the chlorides IIa-f were readily converted into the *N*-aryl-2-pyridone derivatives IIIa-f by hot ethanolic sodium ethoxide. This procedure provides a convenient route to the *N*-aryltriphenyl-2-pyridones, which are not easy to prepare from the triphenyl-2-pyrone. The primary product of this base-catalyzed reaction II → III are probably the free imines IV; in a separate experiment 4,5,6,*N*-tetraphenylpyran-2-imine IVa rearranged in hot ethanolic sodium ethoxide to 1,4,5,6-tetraphenyl-2-pyridone IIIa[4]. The rearrangement IV → III presumably occurred by the mechanism proposed by Afridi[2]. The IR spectra of the 2-pyridones IIIa-f (Table III) show an absorption in the region 1654—1658 cm^{-1} which can be attributed to the C=O stretching vibration.

Bromination of the pyridones IIIa-e with bromine in acetic acid afforded the corresponding 3-bromo pyridones Va-e. The IR spectra of the bromo-derivatives exhibited a C=O stretching in the region 1640—1646 cm^{-1} (Table III). The structure of the pyridones II and V was further confirmed from their ^{13}C NMR spectra (Table IV). It exhibited the expected number of signals togather with a carbonyl carbon signal in the region δ 156.8—162.8.

1-Amino-4,5,6-triphenyl-2-pyridone VI[5] was prepared by the action of hydrazine hydrate on the corresponding pyrone I. A series of aldimine derivatives VIIIa-l (Table V) were prepared by the condensation of the amino-2-pyridone VI with aldehydes VII. These aldimines showed a strong 2-pyridone carbonyl absorption[5-7] in the region 1642—1656 cm^{-1}, as well as a C=N stretching of medium intensity in the region 1600—1615 cm^{-1}, similar to those of *N*-benzylidene aniline.[8] The structure of aldimines VIIIa-k was further confirmed by their ^{13}C NMR spectra which exhibited the expected number of signals, as well as C=N and C=O signals in the regions δ 161.6—166.7 and 158.3—159.0, respectively (Table VI).

Thermolysis of the aldimines VIIIa-j gave rise to the nitriles Xa-k and the pyridone IX.[5] The details are listed in (Table V). Although many reagents are available to effect the conversion of aldehydes to nitriles,[9] the majority are electrophilic in character, or require acidic conditions. Reagent VI offers a useful alternative in cases where thermal lability does not present an additional obstacle.

Moreover, in an earlier publication we described an apparently general method for the conversion of pyridinium-2-carboxylate into pyridine-2-thiones.[10] Here we give two more examples of the above transformation and describe the reaction of some of these 2-thiones with benzyl chloride and ethyl chloroacetate. 2-Ethoxycarbonyl-4,6-diphenylpyrylium tetrafluoroborate[11] on reaction with primary amines gave the pyridinium salts XIIa,b which were hydrolyzed to the betaines XIIIa[12],b[13]. Reaction of sulphur in xylene with the betaines XIIIa,b yielded the pyridine-2-thiones XIVa,b[10]. The esters XIIc,d were similarly prepared and hydrolyzed to the betaines XIIIc,d which were

TABLE II

Preparation of Pyridones

Compound No.	Yield	M. P.	Solvent/crystal form	Found/%						
	%	°C		C	H	N		C	H	N
IIIa	65	279[a]	Chloroform-ether needles	86.8	5.1	3.5	$C_{29}H_{21}NO$ (399)	87.2	5.3	3.5
IIIb	72	135	Methanol/prisms	87.0	5.5	3.3	$C_{30}H_{23}NO$ (413)	87.2	5.6	3.4
IIIc	68	137	Methanol/needles	83.8	5.3	3.1	$C_{30}H_{23}NO_2$ (429)	83.9	5.4	5.3
IIId	78	188 (decomp.)	Benzene/prisms	80.1	4.3	3.0	$C_{29}H_{20}ClNO$ (435.5)	80.3	4.6	3.2
IIIe	75	146	Benzene/needles	80.3	4.5	3.1	$C_{29}H_{20}ClNO$	80.3	4.6	3.2
IIIf	60	300	Chloroform-methanol/needles	78.1	4.3	6.1	$C_{29}H_{20}N_2O_3$ (444)	78.4	4.5	6.3
Va	80	254	Acetic acid/yellowish white needles	72.8	4.1	2.7	$C_{29}H_{20}BrNO$ (478)	72.8	4.2	2.9
Vb	78	226	Benzene-methanol yellowish white prisms	73.1	4.2	2.7	$C_{30}H_{22}BrNO$ (492)	73.2	4.5	2.8
Vc	75	243	Benzene/yellowish white needles	70.8	4.1	3.7	$C_{30}H_{22}BrNO_2$ (508)	70.9	4.3	2.8
Vd	80	212	Benzene-methanol/prisms	67.8	3.7	2.6	$C_{29}H_{19}BrClNO$ (512.5)	67.9	3.7	2.7
Ve	80	292	Acetic acid/prisms	67.5	3.5	2.6	$C_{29}H_{19}BrClNO$ (512.5)	67.9	3.7	2.7

TABLE III

^{1}H NMR and IR Spectral Data of Pyridones

Compound No.	^{1}H NMR[a]	Others	Ir./cm^{-1} [b]	
	ArH		C=O	C=C
IIIa	7.0 (m, 11H), 7.3 (m, 10H)		1658	1600
IIIb	7.1 (m, 10H), 7.3 (m, 10H)	2.3 (s, 3H, CH_3)	1654	1595
IIIc	7.0 (m, 10H), 7.2 (m, 10H)	3.7 (s, 3H, OCH_3)	1656	1598
IIId	6.8 (m, 10H), 7.1 (m, 10H)		1655	1600
IIIe	6.8 (m, 10H), 7.0 (m, 10H)		1655	1595
III	8.2 (m, 2 H), 7.2 (m, 8 H)		1658	1600
IIIf	8.2 (m, 2 H), 7.2 (m, 8 H)		1658	1600
Va	7.0 (m, 10H), 7.0 (m, 10H), 7.3 (m, 10H)		1640	1595
Vb	6.9 (m, 9 H), 7.2 (m, 10H)	2.1 (s, 3H, CH_3)	1645	1600
Vc	7.0 (m, 9 H), 7.3 (m, 10H)	3.8 (s, 3H, OCH_3)	1646	1698
Vd	6.8 (m, 9 H), 7.1 (m, 10H)		1642	1600
Ve	6.7 (m, 9 H), 7.1 (m, 10H)		1645	1600

[a] δ in ppm., soln. in $CDCl_3$.
[b] soln. in $CHBr_3$.

TABLE IV

^{13}C NMR Spectral Data of Pyridones

Compound No.	Arc	C=O	Others
IIIa	154.22, 152.5, 146.2, 139.0, 138.7, 136.6, 134.4, 131.6, 130.6, 129.1, 128.7, 127.7, 127.4, 127.2, 126.1, 120.1	1600	
IIIb	154.0, 146.0, 138.1, 137.5, 131.6, 131.2, 130.6, 129.3, 128.7, 128.1, 127.7, 127.1, 126.0, 122.9, 121.5, 119.9, 118.9	162.6	21.0(CH_3)
IIIc	162.8, 154.0, 147.0, 138.7, 134.5, 131.6, 131.2, 130.6, 129.9, 128.7, 128.2, 128.1, 127.7, 127.3, 127.1, 125.9, 124.3, 119.9	162.8	55.2(OCH_3)
IIId	154.2, 146.9, 138.4, 137.4, 136.1, 133.9, 133.4, 131.3, 130.4, 130.2, 128.7, 128.5, 127.5, 127.2, 127.1, 125.9, 120.4, 119.8	162.0	
IIIe	154.5, 138.5, 137.1, 136.3, 133.7, 132.6, 131.5, 130.8, 130.5, 129.7, 129.4, 128.8, 128.6, 127.6, 127.1, 126.1, 119.9	161.4	
IIIf	154.5, 147.1, 142.8, 139.8, 138.6, 136.3, 134.0, 131.6, 130.6, 129.5, 128.7, 127.8, 127.7, 127.4, 126.1, 122.7, 120.0	161.4	
Va	154.2, 147.9, 139.2, 138.9, 136.4, 133.9, 131.4, 130.5, 128.9, 128.6, 128.4, 127.9, 127.7, 127.2, 127.1, 126.1	157.0	
Vb	154.0, 146.1, 139.9, 137.8, 136.4, 133.8, 131.3, 130.4, 129.2, 128.4, 127.6, 127.6, 127.3, 127.1, 126.1, 125.4, 121.5	156.8	21.0(CH_3)
Vc	154.1, 146.38, 138.1, 135.4, 132.9, 131.5, 130.8, 130.1, 129.8, 128.7, 128.5, 128.3, 127.7, 127.4, 127.0, 126.8, 126.1	159.7	56.3(OCH_3)
Vd	154.2, 145.6, 138.7, 137.6, 136.1, 133.5, 131.3, 130.4, 130.0, 128.8, 128.4, 127.9, 127.7, 127.4, 127.1, 126.3	159.7	
VI	152.0, 145.1, 138.6, 136.1, 132.9, 131.5, 129.6, 128.7, 128.5, 128.0, 127.7, 127.2, 126.1, 117.0.	159.1	

[a] δ in ppm, soln. in $CDCl_3$.

TABLE V

Conversion of Aldehydes into Nitriles

R′	Aldimine VIII Yield %	Aldimine VIII M.p. °C	Solvent/crystal form	Found/% C	Found/% H	Found/% N	Elem. Analysis formula	Calc'd/% C	Calc'd/% H	Calc'd/% N	Pyrolysis temp./°C	Nitrile X[a] yield/%
C_6H_5	95	159[b]	Methanol/yellow needles									
o-HOC_6H_4	90	130[c]	Methanol/yellow plates								200	85
p-HoC_6H_4	92	266[d]									185	82
p-$O_2NC_6H_4$	90	212[e]	Benzene-pet. ether/yellow needles								210	80
p-$CH_3C_6H_4$	95	205	Methanol/yellow needles	84.5	5.5	6.4					225	75
p-$CH_3OC_6H_4$	95	209[f]	Methanol/yellow needles				$C_{30}H_{24}N_2O$ (440)	84.5	5.5	6.4	220	80
p-ClC_6H_4	90	186	Methanol/pale yellow needles	78.1	4.8	6.3	$C_{30}H_{21}ClN_2O$ (460.5)	78.2	4.6	6.1	220	70
2-Thenyl	80	195	Methanol/yellow prisms	77.7	4.5	6.6	$C_{28}H_{20}N_2OS$ (432)	77.8	4.6	6.5	220	68
2-Pyridyl	75	198	Methanol/pale yellow needles	81.6	4.7	9.6	$C_{29}H_{21}N_3O$ (427)	81.5	4.9	9.8	220	65
4-Pyridyl	80	185	Methanol/pale yellow needles	81.4	4.8	9.8	$C_{29}H_{21}N_3O$ (427)	81.5	4.9	9.8	220	67
2-Furyl	80	184[g]	Methanol/yellow plates									
3-Methyl-2-pyridyl	80	205	Methanol/yellow needles	81.3	5.1	9.3	$C_{30}H_{23}N_3O$	81.6	5.2	9.5	220	65

[a] Solid nitriles had m. p. in agreement with lit. values; liquids were identified by IR Spectral comparisons with authentic material. [b] Lit. [16] 158 °C. [c] Lit. [16] 128 °C. [d] Lit. [16] 267 °C. [e] Lit. [16] 210 °C. [f] Lit. [16] 209 °C. [g] Lit. [5] 183 °C.

TABLE VI

NMR[a] *Spectral Data of Aldimines VIII*

R′	Ar*H* (m)	^{1}H NMR	N=CH (s,1H)	Others (s,3H)	N=CH	C=O	^{13}C NMR Ar*C*	Others
C_6H_5	7.4 (10H),	7.0 (11H)	9.4		164.0	158.6	152.4, 146.0, 142.5, 138.6, 136.1, 133.9, 131.6, 130.6, 130.1, 129.2, 128.7, 127.8, 127.1, 126.0, 119.9.	
p-$NO_2C_6H_4$	8.2 (2H)[b], 7.0 (10H)	7.2 (8H),	9.5		166.3	159.0	153.3, 148.0, 143.5, 138.9, 136.2, 143.0, 131.7, 130.7, 130.2, 129.3, 128.8, 127.9, 127.3, 126.3, 120.0.	
p-$CH_3C_6H_4$	7.55 (2H), 7.0 (6H)	7.2 (12H),	9.1	2.3 (CH_3)	166.7	158.4	152.4, 146.0, 142.4, 138.5, 136.1, 133.9, 131.6, 130.4, 130.0, 129.2, 128.7, 127.6, 127.2, 126.0, 119.7.	21.5 (CH_3)
p-$CH_3OC_6H_4$	7.5 (2T), 7.0 (6H)	7.1 (12H)	9.2	3.8 (OCH_3)	165.8	158.5	152.3, 146.2, 142.8, 138.0, 136.3, 133.8, 131.6, 130.3, 128.8, 127.6, 127.3, 126.1, 119.6.	55.3 (OCH_3)
p-ClC_6H_4	7.5 (4H), 6.9 (6H)	7.2 (10H),	9.2		164.5	158.5	152.6, 146.9, 138.5, 137.9, 136.1, 134.7, 133.9, 131.6, 130.4, 129.7, 128.8, 128.0, 127.7, 127.3, 126.1, 119.8, 117.0.	

Table VI to be continued

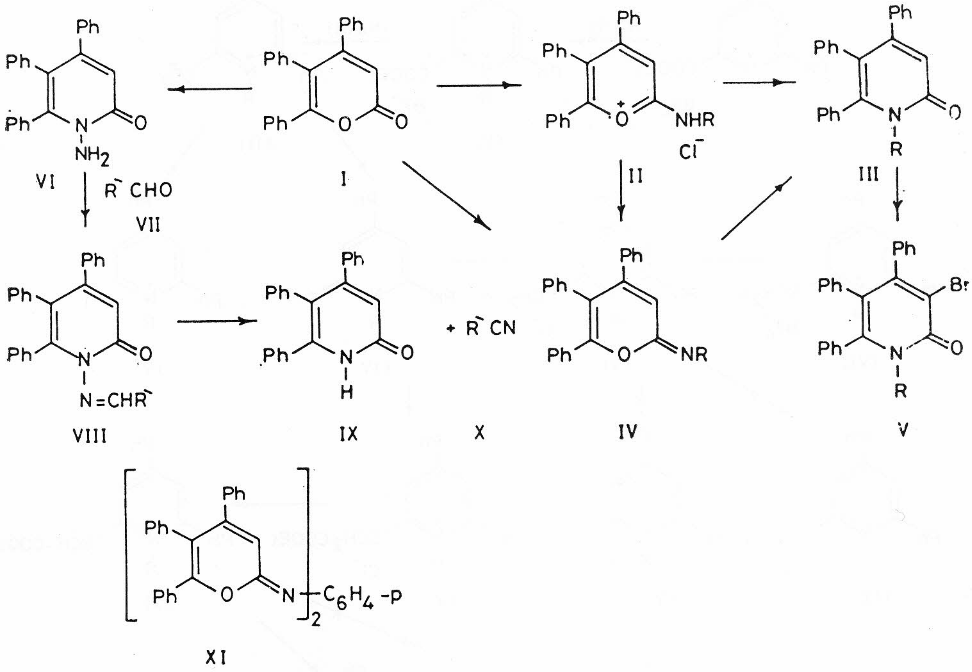
Table VI continued

R′	Ar*H* (m)	^{1}H NMR	N=CH (s,1H)	Others (s,3H)	N=CH	C=O	^{13}C NMR ArC	Others
	7.4 (4H), 6.4 (7H)	7.2 (8H),	9.4		159.3	158.7	152.4, 146.2, 138.5 137.6, 136.1, 133.9, 131.6, 131.0, 130.4, 129.6, 128.7, 127.9, 127.6, 127.2, 126.8, 126.0, 125.6, 119.6.	
2-Pyridyl	7.6 (2H), 6.9 (6H),	7.2 (11H), 8.7 (1H)[c]	9.4		166.3	158.3	152.7, 152.2, 149.5, 145.9, 138.4, 136.4, 136.3, 133.9, 131.6, 130.4, 128.7, 127.7, 127.3, 126.8, 126.1, 125.3, 121.3, 119.9.	
4-Pyridyl	7.3 (3H), 6.9 (6H),	7.2 (9H), 8.6 (2H)[c]	9.5		161.6	158.9	153.0, 150.2, 146.4, 140.5, 138.2, 135.9, 134.5, 131.5, 130.3, 128.7, 127.8, 127.7, 126.3, 121.7, 120.0.	

[a] δ in ppm., J = coupling constant in Hz, soln. in $CDCl_3$; [b] d J = 3Hz; [c]d, J = 3Hz, α-H of pyridine.

characterized spectroscopically (see Experimental). The pyridinium betaines XIIIc,d were smoothly converted by sulphur into the corresponding pyridine-2-thiones XIVc,d (Scheme 2).

Scheme 1



R

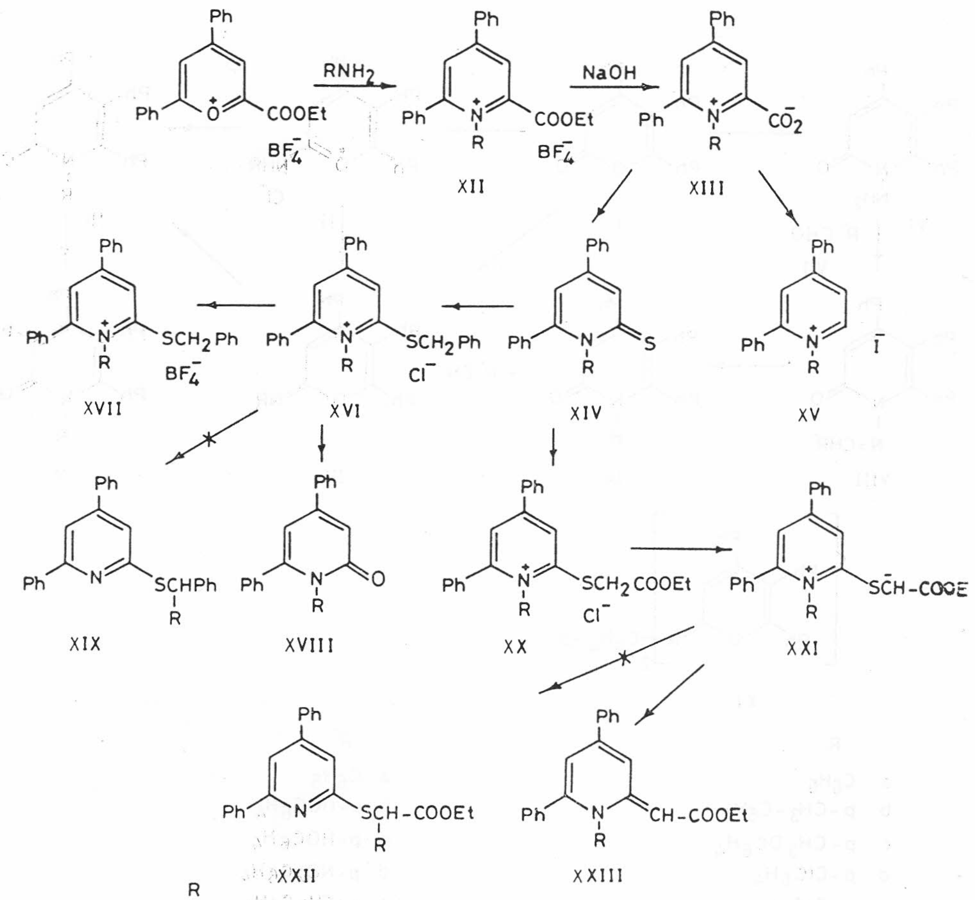
- a C_6H_5
- b p-CH_3-C_6H_4
- c p-$CH_3OC_6H_4$
- d p-ClC_6H_4
- e o-ClC_6H_4
- f p-$NO_2C_6H_4$

R`

- a C_6H_5
- b o-HOC_6H_4
- c p-HOC_6H_4
- d p-$NO_2C_6H_4$
- e p-$CH_3C_6H_4$
- f p-$CH_3OC_6H_4$
- g p-ClC_6H_4
- h 2-Thenyl
- i 2-pyridyl
- j 4-pyridyl
- k 2-Furyl
- l 3-Methyl-2-pyridyl

Infrared spectra of the pyridine-2-thiones XIVc,d showed a characteristic[14,15] strong thiocarbonyl absorption at 1150—1160 cm^{-1} and the absence of the carbonyl absorption was found in XIII at 1650 cm^{-1}. Their ^1H NMR spectra exhibited two doublets at δ 8.1—8.6 and 6.8—6.9 for H-3 and H-5, respectively.

Scheme 2



R
a- C_6H_5
b- p-$CH_3C_6H_4$
c- p-ClC_6H_4
d- α-naphthyl

Decarboxylation of XIIId with HI—H_2O gave the iodide XVd. The IR spectrum showed loss of CO_2Et (at ca. 1750 cm^{-1}) and the ^1H NMR spectrum exhibited the H-2 signal as a downfield doublet at δ 9.2.

Reaction of the pyridine-2-thiones XIVa,b with benzyl chloride afforded the chlorides XIVa,b which on stirring with fluoroboric acid yielded the tetrafluoroborate salts XVIIa,b.

TABLE VII

^{1}H NMR and IR Spectral Data of Pyridinium Salts and Dihydropyridines

Compound No.	CH_3 (3H, t) ($J=4$)	^{1}H NMR CH_2 (2H, q) $J=4$	H-3 (1H, d) ($J=2$)	H-5 (1H, d) ($J=2$)	ArH and $CH=$ (m)	IR/cm^{-1} [b] C=O	IR/cm^{-1} [b] Pyridinium	IR/cm^{-1} [b] BF_4^-
XVIa		4.9[c]	d	d	7.1—8.4 (22H)		1620	1050
XVIb	2.3[c]	5.0[c]	d	d	7.2—8.4 (21H)		1620	1050
XVIIa	2.4	4.5	d	d	6.9—8.2 (22H)		1615	1050
XVIIb	2.5	4.5	d	d	7.0—8.2 (21H)		1610	1050
XXa	1.3	4.1, 4.5[c]	8.7	d	7.2—8.3 (16H)	1730	1610	
XXb	1.2, 2.3[c]	4.2, 4.4[c]	8.6	d	7.1—8.3 (15H)	1730	1613	
XXIa[e]	1.2	4.0	d	d	6.7—8.1 (17H)	1675	1618	
XXIb[e]	1.3, 2.3[c]	4.2	d	d	6.9—8.3 (16H)	1670	1615	
XXIII	1.3	4.2	9.0	6.3	7.0—7.9 (16H)	1725		
XXIII	1.2, 2.2[c]	4.1	8.8	6.4	6.8—7.8 (15H)	1722		

[a] δ in ppm, J = coupling constant in Hz, solutions in deuterochloroform

[b] Solutions in bromoform. [c] s

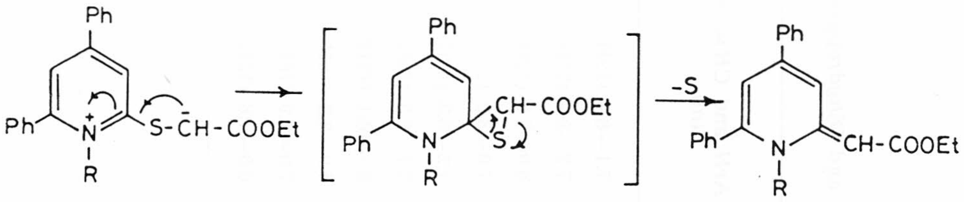
[d] overlap with Aromatic protons

[e] δ 4.1 (1H, s, CH—COOEt).

Reaction of XVIb with sodium ethoxide yielded the corresponding 2-pyridone XVIIIb[14] instead of the rearranged product XIXb.

On the other hand, reaction of the pyridine-2-thiones XIVa,b with ethyl chloroacetate afforded the pyridinium esters XXa,b. These, upon treatment with aqueous sodium hydroxide, yielded the zwitterions XXIa,b which readily lost sulphur during crystallization to give the esters XXIIIa,b instead of the expected products XXII. A possible mechanism for the formation of XXIII is shown in (Scheme 3). It involves an intramolecular charge neutralization of the betaine XXI yielding the intermediate thiiran XXIV. This three-membered thiiran could then lose sulphur to give the product XXIII. The IR spectra of the esters XXIIII showed a carbonyl absorption at 1722—1725 cm^{-1}. Their ^1H NMR spectra exhibited two doublets at δ 8.8—9.0 and 6.3—6.4 for H-3 and H-5, respectively.

Scheme 3



XXI XXIV XXIII

The ^{13}C NMR spectra of the esters XXIIIa,b showed the presence of a total of 21 (22 for XXIIIb) signals, of which 19 lie in the region expected for sp^2 hybridized carbon atoms and 2 (3 for XXIIIb) in the region expected for sp^3 hybridized. The aliphatic carbon atoms are for the CH_2 and CH_3 groups. Of the sp^2 hybridized carbon signals 7 (8 for XXIIIb) are quaternary and 12 (11 for XXIIIb) are methines. The number of signals of each type corresponds to those expected for structure XXIII (Table VIII) (Figure (1).

TABLE VIII

^{13}C NMR[a] Spectral Data of Dihydropyridines

Compound No.	Aliphatic *C*		Aromatic *C* and CH=		C=O
	CH_3	CH_2	Quaternary *C*	Methine *C*	
XXIIIa	14.7	58.2	168.7, 156.1, 148.8, 139.7, 137.6, 135.9	130.6, 129.8, 129.7, 129.2, 129.1, 129.0, 128.9, 128.7, 128.4, 128.2, 127.7, 126.6	172.7
XXIIIb	14.8, 21.1	58.2	168.8, 156.3, 148.7, 138.4, 137.7, 137.2, 136.1	130.4, 129.9, 129.5, 129.2, 129.0, 128.9, 128.7, 128.3, 128.1, 127.7, 126.6	172.6

[a] δ in ppm., solutions in deuterochloroform.

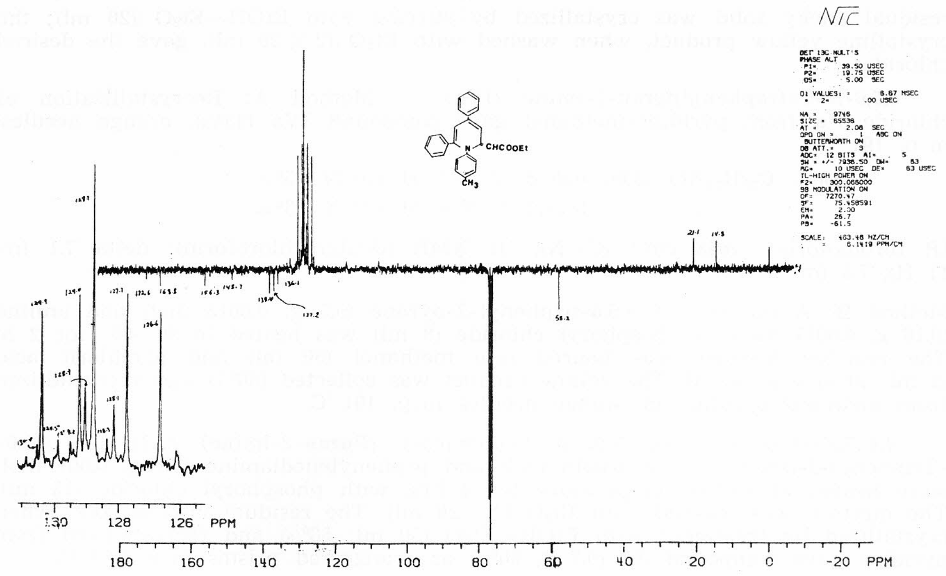


Figure 1.

TABLE IX

Preparation Details for Pyridinium Chlorides

Compound No.	Yiled/%	M. P./°C	Solvent/crystal form	Found/% C	Found/% H	Found/% N	Elem. Analysis formula	Calc'd/% C	Calc'd/% H	Calc'd/% N
XVIa	95	167	Ethanol- -benzene/needles	77.5	5.2	2.9	$C_{28}H_{26}ClNO_2S$ (465.8)	70.7	5.5	2.9
XVIb	98	178	Ethanol- -ether/needles	77.6	5.5	2.9	$C_{31}H_{26}ClNS$ (479.8)	77.6	5.4	2.9
XXa	94	175	Benzene- -methanol/needles	70.0	5.3	2.8	$C_{27}H_{24}ClNO_2S$ (461.8)	70.2	5.2	3.0
XXb	95	138	Benzene- -methanol/needles	70.5	5.8	2.7	$C_{28}H_{26}ClNO_2S$ (475.8)	70.7	5.5	2.9

EXPERIMENTAL

^{1}H NMR spectra were recorded on a Varian EM 360L spectrometer using tetramethyl silane as internal standard. ^{13}C NMR spectra were obtained on a Nicolet 300NT spectrometer. Ir. spectra were obtained using sodium chloride plates on a Perkin-Elmer 297 spectrometer as solutions in bromoform. Melting points were measured on a kofler hot stage apparatus and are uncorrected.

The following compounds were prepared using literature methods: I [m. p 247 °C, Lit. 3, 246°]; VI [m. p. 200 °C, Lit. 3, 199°]; XIVa (m. p. 192 °C, Lit. 10, m. p. 193 °C); XIVb (m. p. 232 °C, Lit. 10, 231 °C).

2-Arylamino-4,5,6-triphenylpyrylium Chlorides (IIa-f) (Table I). — 4,5,6-Triphenyl-2-pyrone (0.5 g., 0.0015 mol) and the appropriate arylamine (0.0017 mol) in phosphoryl chloride (15 ml) were heated under reflux for 8 h. After cooling the mixture was extracted with Et_2O (4 × 30 ml) and the extracts discarded. The residual sticky solid was crystallized by stirring with EtOH—Et_2O (20 ml); the crystalline yellow product, when washed with Et_2O (2 × 20 ml), gave the desired chlorides.

4,5,6-N-Tetraphenylpyran-2-imine (IVa). — Method A: Recrystallization of chloride IIa from pyridine-methanol gave compound IVa (45%), orange needles, m. p. 191 °C.

Anal. $C_{29}H_{21}NO$ (399) calc'd: C 87.2; H 5.3; N 3.5%,
found: C 87.0; H 5.2; N 3.3%.

IR (bromoform): 1648 cm^{-1} (C=N), ^1H NMR (deuterochloroform): delta 7.1 (m, 11 H), 7.3 (m, 10 H).

Method B: A mixture of 4,5,6-triphenyl-2-pyrone (0.5 g, 0.0015 mol) and aniline (0.16 g, 0.0017 mol) in phosphoryl chloride (8 ml) was heated to 90—95° for 2 h. The reaction mixture was poured into methanol (50 ml) and perchloric acid (2 ml, 70%) was added. The yellow product was collected (50%) and recrystallized from methanol-pyridine in orange needles m. p. 191 °C.

*4,4',5,5',6,6'-Hexaphenyl-*N,N'-p-*phenylenebis (Pyran-2-imine) (XI):* — 4,5.6-Triphenyl-2-pyrone (0.5 g, 0.0015 mol) and *p*-phenylenediamine (0.1 g, 0.001 mol) were heated at reflux temperature for 4 hrs. with phosphoryl chloride (15 ml). The mixture was washed with Et_2O (2 × 20 ml). The residual viscous solid when crystallized by treatment with EtOH—Et_2O (50 ml; 50%) and recrystallized from pyridine gave compound XI (0.7 g, 60%) as orange-red prisms m. p. 244 °C.

Anal. $C_{52}H_{36}N_2O_2$ (720) calc'd: C 86.7; H 5.0; N 3.9%,
found: C 86.5; H 4.8; N 3.7%.

IR (bromoform): 1658 cm^{-1} (C=N), 1600 (C=C).

1-Aryl-4,5,6-triphenyl-2-pyridones IIIa-f (Table II). — The chlorides IIIa-f (0.001 mol) and NaOEt (0.005 mol) in ethanol (20 ml) were heated under reflux for 10 h. After cooling, the reaction mixture was poured into ice-cold water and the solid product collected and extracted with chloroform. Evaporation left a residue which, on treatment with ethanol, gave the pyridone derivatives.

3-Bromo-1-aryl-4,5,6-triphenyl-2-pyridones V (Table II). — A solution of bromine (0.0012 mol) in acetic acid (5 ml) was added slowly with stirring to a hot solution of the appropriate 1-aryl-4,5,6-triphenyl-2-pyridone (0.001 mol) in acetic acid (10 ml). The reaction mixture was then refluxed for 1 h. and then poured into ice-cold water. The solid products were collected, washed with water and crystallized from the appropriate solvent.

*Rearrangement of 4,5,6,*N*-tetraphenyl-2-imine (IVa):* — Sodium (0.3 g) was dissolved in EtOH (20 ml) and compound IVa (1.5 g; 0.0045 mol) was added to the solution, which was then heated under reflux for 8 h. After cooling, the solution was poured into ice-cold water, and extracted with chloroform. Evaporation left a residue which on treatment with ethanol gave 1,4,5,6-tetraphenyl-2-pyridone IIIa (0.95, 63%). Recrystallization from chloroform-ethanol afforded needles m. p. 279 °C identical with those prepared from the 2-anilino-4,5,6-triphenylpyrylium chloride (IIa).

1-Arylideneamino-4,5,6-triphenyl-2-pyridone VIII (Table V) — A solution of the appropriate aldehyde (0.0012 mol) and the aminopyridone (0.001 mol) in ethanol (6 ml) was heated on the water-bath for 3 h. The residue was then treated with methanol to give the corresponding aldimines VIII which crystallized from the appropriate solvent.

Preparation of nitriles: (Table V). — Aldimine VII (1 g) was heated at the appropriate temperature in vacuo (12 Torr) for 1 h, collecting the nitrile as distillate in a trap cooled in liquid nitrogen. The 4,5,6-triphenyl-2-pyridone remained in the pyrolysis flask. For details see Table V.

2-Ethoxycarbonyl-4,6-diphenyl-1-substituted pyridinium tetrafluoroborate XIIc, d. — A suspension of 2-ethoxycarbonyl-4,6-diphenylpyrilium tetrafluoroborate[11]

(2 g, 0.005 mol) in dichloromethane (40 ml) was stirred with the appropriate amine (0.0052 mol) for 8 hours at 25 °C. After concentration, the residue was triturated with ether (100 ml) to give white crystals of pyridinium salts which were crystallized from alcohol as needles.

XIIc: yield 70%, m. p. 200 °C.

Anal. $C_{26}H_{21}BClF_4NO_2$ (501.8) calc'd: C 62.2; H 4.2; N 2.8%;
found: C 62.1; H 4.0; N 2.7%.

IR ($CHBr_3$) 1748 (C=O), 1622 (pyridinium); 1050 cm^{-1} (BF_4^-).

XIId: yield 86%; m. p. 212 °C.

Anal. $C_{30}H_{24}BF_4NO_2$ (517.3) calc'd: C 69.7; H 4.7; N 2.7%;
found: C 69.7; H 4.7; N 2.7%.

IR ($CHBr_3$): 1745 (C=O); 1625 (pyridinium): 1050 cm^{-1} (BF_4^-).

^1H NMR (deuterochloroform): delta 0.6 (3H, t, $J = 4Hz$, CH_3); 4.0 (2H, q, $J = 4Hz$, CH_2), 7.0—8.8 (19H, m, ArH, H-3 and H-5).

Pyridinium Betaines XIIIc, d. — A suspension of the pyridinium salt XIIc or d (0.01 mol) in water was stirred with aqueous sodium hydroxide (0.0175 mol) for 24 hours. The white solid was filtered off, washed with water (100 ml) and ether (50 ml) to give the betaine as microcrystals (nosatisfactory analysis was obtained due to decomposition during crystallization).

XIIIc: yield 62%; m. p. 102 °C.

IR ($CHBr_3$): 1655 (C=O); 1620 cm^{-1} (pyridinium).

XIIId: yield 78%; m. p. 105 °C.

IR ($CHBr_3$): 1650 (C=O); 1625 cm^{-1} (pyridinium). ^1H NMR (deuterochloroform): delta 7.0—8.5 (19H, m, ArH, H-3 and H-5).

Pyridine-2-thiones XIVc, d. — The betaine XIIIa or b (0.005 mol) in xylene (50 ml) was refluxed with sulphur (0.01 mol) for 2 hours. After washing with 10% aqueous ammonium sulphide (50 ml), water (200 ml), and drying with magnesium sulphate followed by evaporation of the solvent, the residue was boiled with a mixture of methanol (30 ml) and benzene (20 ml), the pyridine-2-thiones were separated out and recrystallized from methanol as yellow needles.

XIVc: yield 25%; m. p. 20 °C.

Anal. $C_{23}H_{16}ClNS$ (373.8) calc'd: C 73.9; H 5.9; N 3.7%;
found: C 73.8; H 5.7; N 3.7%.

IR ($CHBr_3$): 1160 cm^{-1} (C=S)

^1H NMR (deuterochloroform): delta 6.8 (1H, d, $J = 2Hz$, H-5); 7.0—7.9 (15H, m, ArH); 8.1 (1H, d, $J = 2Hz$, H-3).

XIV: 45%, m. p. 250 °C.

Anal. $C_{27}H_{19}NS$ (389.4) calc'd: C 83.3; H 4.9; N 3.6%;
found: C 83.0; H 4.7; N 3.4%.

IR ($CHBr_3$): 1150 cm^{-1} (C=C).

^1H NMR (deuterochloroform): delta 7.0—9.2 (19H, m, ArH, H-3 and H-5).

4,6-Diphenyl-1-naphthylpyridinium iodide XVd. — was obtained by refluxing 4,6-diphenyl-1-nephthylpyridinium-2-carboxylate (1.5 g; 0.0037 mol) with aqueous HI (65%; 1.2 g, 0.061 mol) in tetrahydrofuran (50 ml) for 4 hours to yield yellow crystals (washed with ether). Recrystallization from absolute ethanol gave yellow needles, 1.6 g (89%); m. p. 280 °C.

Anal. $C_{27}H_{20}IN$ (485.4) calc'd: C 66.8; H 4.2; N 2.9%,
found: C 67.0; H 4.2; N 2.8%.

IR ($CHBr_3$): 1620 cm^{-1} (pyridinium). ^1H NMR (deuterochloroform): delta 9.2 (1H, d, $J = 4Hz$, H-2); 7.0—8.8 (19H, m, ArH, H-3 and H-5).

Pyridinium chlorides XVIa, b and XXa, b (Tables VII and IX). — The thiopyridine XIVa or b (0.001 mol) was stirred with the appropriate chloride (2 ml) for 12 hours at room temperature. The reaction mixture was then treated with ether, and the solid which separated out was recrystallized from the approporiate solvent.

Pyridinium tetrafluoroborates XVIIa, b (Table VII). — The chloride XVIa or b (0.6 g, 0.002 mol) was stirred with fluoroboric acid (10 ml) for 24 hours. The reaction mixture was then triturated with ether (10 ml) to give white crystals of the corresponding pyridinium tetrafluoroborate which was recrystallized from ethanol-ether as needles.

XVIIa: yield 98%, m. p. 160 °C.

Anal. $C_{30}H_{24}BF_4NS$ (517.3) calc'd: C 69.6; H 4.6; N 2.7%;
found: C 69.4; H 4.7; N 2.6%.

XVIIb: yield 95%, m. p. 165 °C.

Anal. $C_{31}H_{26}BF_4NS$ (531.3) calc'd: C 70.0; H 4.9; N 2.6%;
found: C 69.8; H 5.0; N 2.6%.

*4,6-Diphenyl-*N*-(p-tolyl)-2-pyridone XVIIIb*[14]: Sodium (0.3 g, 0.013 mol) was dissolved in ethanol (20 ml) and the chloride XVIb (1 g, 0.002 mol) was added to the solution, which was then stirred for 15 minutes. The reaction mixture was then poure into water and the solid which separated was collected and recrystallized from ethanol to give 4,6-diphenyl-*N*-(*p*-tolyl)-2-pyridone (0.3 g, 43%), needles, m. p. 241 °C (Lit.[14], m. p. 243—246 °C).

Zwitter ions XXIa, b (Table VII): A suspension of XXa or b in 0.25 M NaOH (20 ml) was stirred at room temperature for 24 hours. The reaction mixture was then filtered, washed with water (200 ml), ether (50 ml), and dried in vacuo to give a crystalline yellow solid of XXI.

XXIa: yield 90%; m. p. 175 °C.

Anal. $C_{27}H_{23}NSO_2$ (425.3) calc'd: C 76.3; H 5.4; N 3.3%;
found: C 76.0; H 5.3; N 3.3%.

XXIb: yield 88%; m. p. 170 °C.

Anal. $C_{28}H_{25}NSO_2$ (439.3) calc'd: C 76.6; H 5.7; N 3.2%;
found: C 76.5; H 5.6; N 3.0%.

Dihydropyridines XXIIIa, b (Tables VII and VIII): The zwitter ion XXI a or b was heated with ethanol for 30 minutes. The solution was then concentrated and the solid which separated out was recrystallized from ethanol to give the dihydropyridine derivative.

XXIIIa: yield 75%; m. p. 200 °C.

Anal. $C_{27}H_{23}NO_2$ (393.5) calc'd: C 82.4; H 5.9; N 3.5%;
found: C 82.3; H 6.2; N 3.5%.

XXIIIb: yield 78%; m. p. 215 °C.

Anal $C_{28}H_{25}NO_2$ (407.5) calc'd: C 82.5; H 6.2; N 3.4%;
found: C 82.3; H 6.2; N 3.5%.

REFERENCES

1. J. A. Van Allan and C. S. Chang, *J Heterocyclic Chem.* **11** (1974) 1065.
2. A. S. Afridi, A. R. Katritzky, and C. A. Ramsdem, *J. Chem. Soc. Perkin I,* (1977) 1436.
3. G. Soliman and I. El-S. El-Kholy, *J. Chem. Soc.* (1955) 2911.
4. K. T. Potts, J. Baum, and E. Houghton, *J. Org. Chem.* **41** (1976) 818.
5. I. El-S. El-Kholy, F. K. Rafla, and G. Soliman, *J. Chem. Soc.* (1961) 4490.
6. R. H. Wiley and S. C. Slaymaker, *J. Amer. Chem. Soc.* **78** (1956) 2393.
7. S. F. Mason, *J. Chem. Soc.* (1957) 3874.
8. L. E. Clougherty, J. A. Sousa, and G. M. Wyman, *J. Org. Chem.* **22** (1957) 462.
9. I. T. Harrison and S. Harrison, *Compendium of Organic Synthetic Methods,* vol. 1, p. 461, Wiley-Interscience, New York 1971.
10. Alan R. Katritzky and Hassan M. Faidallah, *Synthesis* (1983) 149.
11. Alan R. Katritzky, A. Chermprapai, R. C. Patel, and A. Tarraga-Tomas, *J. Org. Chem.* **47** (1982) 492.
12. Alan R. Katritzky, R. Awartani, and R. C. Patel, *J. Org. Chem.* 47 (1982) 498.
13. A. J. Cozens, *M. Sc. Thesis,* University of East Anglia, Norwich, England, 1980.
14. A. S. Afridi, A. R. Katritzky, and C. A. Ramsden, *J. Chem. Soc. Perkin Trans.* **1** (1977) 1436.
15. R. Lawrence and E. S., Waight, *J. Chem. Soc. B* (1968) 1.
16. I. El-S. El-Kholy and F. K. Rafla, *J. Chem. Soc.* (1969) 974.

SAŽETAK

Sinteza piridona i dihidropiridina iz pirilijevih soli, te nitrila iz aldimina

Hasan M. Faid-Allah

Pirilijeve soli (*II*) dobivene iz 4,5,6-trifenil-2-pirona (*I*) daju u reakciji s natrij-etoksidom piridone (*III*). 4,5,6-trifenilpiran-2-imin (*IVa*) bilo je moguće pripraviti iz spoja *I* ili *IIa,* a pregradnjom *IVa* uz natrij-etoksid dobiven je izomerni 2-piridon *IIIa.* Bromiranjem spojeva *III* dobiveni su odgovarajući 3-brom-2-piridoni *V.* Kondenzacijom aminopiridona *VI* s aldehidima pripravljeni su aldimini *VIII,* koji su termolizom dali nitrile *X* i piridone *IX.* Reakcijom piridin-2-tiona *XIV* s benzil-kloridom i etilkloracetatom pripravljeni su kloridi *XVI* i *XX.* Spojevi *XX* prevedeni su u baznom mediju u dipolarne ione *XXIa, b,* a ti su kemičkom eliminacijom dali dihidropiridine *XXIIIa, b.*

Struktura svih do sada neopisanih spojeva potvrđena je elementnom analizom IR i ^{1}H-NMR spektrima.