Improved Methods for Conversion of Primary Amines into Bromides †

By Alan R. Katritzky,* Fatima Al-Omran, Ranjan C. Patel, and Sukhpal S. Thind, School of Chemical Sciences, University of East Anglia, Norwich NR4 7TJ

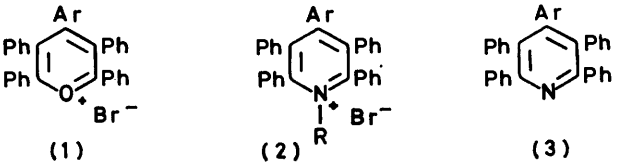
N-Alkyl- and *N*-benzyl-4-*p*-chlorophenyl-2,3,5,6-tetraphenyl- *N*-alkyl- and *N*-benzyl-2,3,4,5,6-pentaphenyl-, and *N*-alkyl- and *N*-benzyl-2,4,6-triphenyl-pyridinium bromides on pyrolysis at 180—220 °C give the corresponding alkyl and benzyl bromides in high yield. 1-Benzyl-5,6-dihydro-2,4-diphenylbenzo[*h*]quinolinium trifluoromethanesulphonate gave benzyl bromide on heating with KBr in dimethylformamide at 100 °C, and n-octyl bromide (80%) was obtained from the corresponding pentacyclic bromide in refluxing acetonitrile.

PRIMARY alkyl- and benzyl-amines can be converted *via* 2,4,6-triphenylpyridinium bromides into the corresponding alkyl and benzyl bromides.[1] The reaction involved pyrolysis at the melting point which ranged up to 250 °C: the yields for the seven examples reported averaged 60%. In view of the synthetic utility of this method (for a comparative survey see ref. 1) we now report improvements in the yield and the achievement of the reaction under milder conditions.

4-Aryl-2,3,5,6-tetraphenyl-pyrylium and -pyridinium Bromides.—2,3,4,5,6-Pentaphenylpyrylium bromide (1a) reacts[1] with primary alkyl and aralkyl amines to give *N*-substituted-2,3,4,5,6-pentaphenylpyridinium bromides (2a), rapidly and in good yield. However, the subsequent pyrolysis of (2a) yielded the corresponding bromides in poorish yields and contaminated with 2,3,4,5,6-pentaphenylpyridine. It was initially believed that the contamination by pentaphenylpyridine was because of the high volatility of this compound (it is now recognised that the high melting points of the pentaphenylpyridinium salts and consequent high temperatures required for the pyrolysis are very relevant, see later). We therefore prepared a series of 4-aryltetraphenylpyrylium bromides (1b—e) (Table 1) to find a suitable leaving group of lower volatility.

The condensation of *o*- and *p*-chloro-, *p*-methyl-, and *p*-methoxy-benzaldehyde with deoxybenzoin in ethanolic potassium hydroxide gave the corresponding pentane-1,5-diones ($\nu_{C=O}$ at *ca.* 1 670 cm^{-1}) which were converted by a previously reported[1] modification of Simalty and Carretto's procedure[2] into the pyrylium bromides (1b—e) (Table 1). These showed ring-stretching bands at 1 600—1 590 cm^{-1}, and (in $CDCl_3$–CF_3CO_2H) complex n.m.r. multiplets in the aromatic region, together with the expected methyl peaks for (1c) and (1d) in the correct integration ratio.

4-(*p*-Chlorophenyl)-, 4-(*p*-tolyl)-, 4-(*p*-methoxyphenyl)-, and 4-(*o*-chlorophenyl)-2,3,5,6-tetraphenylpyridines (3b—e) were obtained from the corresponding pyrylium bromides and ammonia (Table 2): with absolute ethanol as solvent, the pyridines crystallise



a; Ar = Ph
b; Ar = *p*-ClC_6H_4
c; Ar = *p*-MeC_6H_4
d; Ar = *p*-$MeOC_6H_4$
e; Ar = *o*-ClC_6H_4

leaving ammonium bromide in solution. In diethyl ether as solvent, ammonium bromide precipitates leaving the 4-aryl-2,3,5,6-tetraphenylpyridine in solution. Both methods give good yield. The pyridines (3b—e) were characterised by $\nu_{C=C}$ and $\nu_{C=N}$ ring vibrations at 1 630—1 600 cm^{-1} and at 1 580—1 510 cm^{-1}, the former usually the more intense, and C–H deformations at 900—700 cm^{-1}. Rough comparative measurements for the pyridines (3a—e) showed that at 0.6 mm Hg, 2,4,6-triphenylpyridine sublimes at *ca.* 105 °C, pentaphenylpyridine at *ca.* 130 °C, but the 4-(substituted phenyl)-2,3,5,6-tetraphenylpyridines (3b—e) do not sublime at 0.6 mmHg even at 180 °C.

4-(*p*-Chlorophenyl)-, 4-(*p*-tolyl)-, 4-(*p*-methoxyphenly)-, and 4-(*o*-chlorophenyl)-2,3,5,6-tetraphenyl-pyrylium

TABLE 1

4-Aryl-2,3,5,6-tetraphenylpyrylium bromides

	Starting 1,5-dione													
	Yield			Yield			Crystal	Found (%)				Required (%)		
Compound	(%)	M.p./°C	Lit.[a] m.p./°C	(%)	M.p./°C	Recryst. solvent	form	C	H	Br	Formula [b]	C	H	Br
(1b)	58	240—241	232—235	91	239—242	HCO_2H–Et_2O	Needles	71.7	4.4		$C_{35}H_{24}BrClO{\cdot}0.5H_2O$	71.9	4.3	
(1c)	98	252—253	241—242	72	230—231	EtOH	Needles	75.0	5.0	14.2	$C_{36}H_{26}BrO{\cdot}H_2O$	75.4	5.1	13.9
(1d)	76	245	242	55	230—235	[c]	Prisms	73.4	5.7		$C_{36}H_{27}BrO_2{\cdot}H_2O$	73.3	5.0	
(1e)	78	202—204	196	49	229—230	HCO_2H–HBr	Prisms	71.9	4.1	13.9	$C_{35}H_{26}BrClO{\cdot}0.5H_2O$	71.9	4.3	13.7

[a] P. P. Paranjpe and G. Bagavant, *J. Indian Chem. Soc.*, 1972, **49**, 589. [b] Presence of H_2O inferred from i.r. broad band at 3 300 cm^{-1}. [c] Acetone–light petroleum (1:1).

† Related work has been published in the series ' Heterocycles in Organic Synthesis.'

TABLE 2

4-Substituted 2,3,5,6-tetraphenylpyridines

Compound	Yield (%)	M.p./°C	Crystal form	Solvent	Found (%) C	H	N	Formula	Required (%) C	H	N
(3b)	79	223	Needles	EtOH			2.4	$C_{35}H_{24}ClN$			2.8
(3c)	75	242	Prisms	EtOH			2.9	$C_{36}H_{27}N$			3.0
(3d)	59	204—208	Prisms	Pr^{i}OH	87.9	2.6	3.1	$C_{36}H_{27}NO$	88.3	5.6	2.9
(3e)	87	284—285	Prisms	Pr^{i}OH	85.2	4.8	2.8	$C_{35}H_{24}ClN$	85.1	5.0	2.8

bromides react rapidly with benzylamine in dry dichloromethane or in diethyl ether to give 4-aryl-1-benzyl-2,3,5,6-tetraphenylpyridinium bromides (2b—e; R = $PhCH_2$) in fair to excellent yields (Table 3). The bromide occur at 5.7—5.9 ($CDCl_3$) p.p.m.[3] Thus substitution of the 4-phenyl group, or the introduction of phenyl groups at the 3- and 5-positions, does not affect the chemical shift of the methylene protons.

TABLE 3

4-Aryl-1-benzyl-2,3,5,6-tetraphenylpyridinium bromides

Compound (R = $PhCH_2$)	Yield (%)	M.p./°C	Crystal form [a]	Found (%) C	H	N	Formula	Required (%) C	H	N	Yield (%) of $PhCH_2Br$ [b]
(2b)	75	218—222	Plates	74.1	4.8	2.2	$C_{42}H_{31}BrClN\cdot H_2O$	73.9	4.9	2.0	76
(2c)	73	230—231	Needles [c]	78.7	5.4	2.2	$C_{43}H_{34}BrN\cdot 0.5H_2O$	79.0	5.8	2.1	61
(2d)	82	218—220	Needles	77.9	5.2	2.0	$C_{43}H_{34}BrNO\cdot H_2O$	78.3	5.2	2.1	67
(2e)	96	274	Needles	74.0	5.0	2.1	$C_{42}H_{31}BrClN\cdot H_2O$	73.9	5.2	2.0	

[a] All crystallised from HCO_2H. [b] On thermolysis at the melting point. [c] Br analysis: Found 12.5, required 12. 1%.

crystalline bromides contain water, as shown by the i.r. spectrum and by the analytical figures. The pyrylium-into-pyridinium ring transformation can be monitored by the appearance of medium intensity pyridinium ring-stretching bands at *ca.* 1 600 and 1 570 cm^{-1}. N.m.r. spectra of the 1-benzylpyridinium bromides (2b—e; R = $PhCH_2$) show the CH_2 singlet at δ 5.7 $\pm$ 0.1 p.p.m.: the benzyl methylene singlets in 1-benzyl-2,3,4,5,6-pentaphenyl- and 1-benzyl-2,4,6-triphenyl-pyridinium

The 4-aryl-1-benzyl-2,3,5,6-tetraphenylpyridinium bromides (2b—d; R = $PhCH_2$) on heating at their melting points, yield benzyl bromide in 67—76% yields (Table 3). The 4-chlorophenyl series was chosen for detailed study because of the high yields in the preparations of the pyrylium and pyridinium bromides and of benzyl bromide on pyrolysis without contamination from 4-(4-chlorophenyl)-2,3,5,6-tetraphenylpyridine.

TABLE 4

Preparation and pyrolysis of 1-substituted 4-(*p*-chlorophenyl)-2,3,5,6-tetraphenylpyridinium bromides (2b)

R	M.p./°C	Yield (%)	Crystal solvent	Crystal form	Found(%) C	H	N	Formula	Required (%) C	H	N	Yield (%) of RBr [a]
Et	239—240	86	HCO_2H	Prisms	71.2	5.1	2.2	$C_{37}H_{29}BrClN\cdot H_2O$	71.6	5.4	2.3	97
Bu^n	272—273	75	EtOH	Prisms	73.9	5.1	2.3	$C_{39}H_{33}BrClN$	74.2	5.3	2.2	75
$Ph(CH_2)_2$	275	88	EtOH	Plates	76.0	4.7	2.0	$C_{43}H_{33}BrClN$	76.0	5.0	2.1	75
p-$MeC_6H_4CH_2$	225—227	73	EtOH	Plates	75.8	4.9	1.9	$C_{43}H_{33}BrClN$	76.1	4.9	2.1	72 [b]
p-$ClC_6H_4CH_2$	234—236	86	EtOH	Prisms	71.3	4.3	2.0	$C_{42}H_{30}BrCl_2N\cdot 0.5H_2O$	71.2	4.7	2.0	79 [c]
Ph	>330	91	HCO_2H	Prisms	76.2	4.7	2.2	$C_{41}H_{29}BrN$	75.8	4.5	2.2	

[a] On pyrolysis at 180—220 °C and 0.5—1.5 mmHg. [b] M.p. 34 °C (lit.,[3] m.p. 34 °C). [c] M.p. 47 °C [lit., 51 °C (' CRC Handbook of Tables for Organic Compound Identification,' ed. Z. Rappoport, Chemical Rubber Co., Cleveland, Ohio, 1967, 3rd edn., p. 59)].

Synthesis and Pyrolysis of 1-*Substituted* 4-(4-*Chloro*-

TABLE 5

Preparation [a] and pyrolysis of 1-substituted 2,3,4,5,6- pentaphenylpyridinium bromides and 1-substituted 2,4,6-triphenylpyridinium bromides

Compound	Series	R	Yield (%)	M.p.(°C)	Lit.[b] Yield (%)	Lit.[b] M.p. (°C)	Cryst. solvent	Cryst. form	Found C	H	N	Formula	Required C	H	N	Yield of RBr (%) [c] *d*	*e*
(2a)	Penta	$PhCH_2$	78	245—246 [b]	60	247	HCO_2H—H_2O	Plates			2.1	$C_{42}H_{33}BrN$			2.2	50	32
(2a)	Penta	Et	64	280	65	280	HCO_2H	Prisms			2.2	$C_{37}H_{30}BrN$			2.4	33	5
(2a)	Penta	$Ph(CH_2)_2$	71	294—295	64	300	EtOH–H_2O	Micro-crystals	80.1	5.4	2.1	$C_{43}H_{34}BrN$	80.1	5.3	2.2	60	21
(2a)	Penta	*p*-$MeC_6H_4CH_2$	89	246			EtOH	Prisms	80.0	5.4	2.1	$C_{43}H_{34}BrN$	79.9	5.3	2.2	74	
(2a)	Penta	*p*-$ClC_6H_4CH_2$	90	245—246			HCO_2H	Prisms	75.5	4.6	2.1	$C_{42}H_{31}BrClN$	75.9	4.7	2.1	76	
(5a)	Tri	$Ph(CH_2)_2$	83	258	81	258 (decomp.)	EtOH–H_2O	Plates	75.4	5.5	2.9	$C_{31}H_{26}BrN$	75.6	5.3	2.9	78	56
(5b)	Tri	*p*-$MeC_6H_4CH_2$	74	115	68	116	EtOH–Et_2O	Needles	70.7	5.4	2.8	$C_{31}H_{26}BrN\cdot 2H_2O$	70.5	5.7	2.6	80	54
(5c)	Tri	*p*-$ClC_6H_4CH_2$	83	129—130	68	130	EtOH–Et_2O	Prisms	67.8	4.9	2.5	$C_{30}H_{23}BrClN\cdot H_2O$	67.9	4.7	2.6	79	44
(5d)	Tri	Et	78	154—157			EtOH–Et_2O	Prisms			18.5 *f*	$C_{25}H_{22}BrN\cdot H_2O$			18.4 *f*	50	

[a] Prepared following procedure described for 4-aryl-1-benzyl-2,3,5,6-tetraphenylpyridinium bromides (see Experimental section). [b] Ref. 1. [c] All characterised by comparison of n.m.r. spectra with authentic sample. [d] Pyrolysis using 2,4,6-triphenylpyridine as a flux at 180—220 °C and 0.5—2.0 mmHg. [e] Pyrolysis without flux at 300 °C and 0.5—2.0 mmHg. *f* Figures for Br analysis.

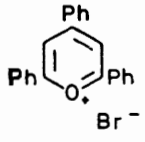
phenyl)-2,3,5,6-*tetraphenylpyridinium Bromides*.—4-(4-Chlorophenyl)-2,3,5,6-tetraphenylpyrylium bromide with primary amines gave the pyridinium bromides in good yield (Table 4). The alkyl and benzyl amines reacted at 20 °C in 2—3 h in CH_2Cl_2, but aniline required heating in super-dry ethanol for 12 h.

1-Substituted 4-(4-chlorophenyl)-2,3,5,6-tetraphenylpyridinium bromides (2b) on pyrolysis with an equal weight of 2,4,6-triphenylpyridine and KBr (1.0 g) at 180—220 °C yielded the corresponding alkyl and benzyl bromides (72—97%) (Table 4), although pyrolysis of 4-(4-chlorophenyl)-1,2,3,5,6-pentaphenylpyridinium bromide failed.

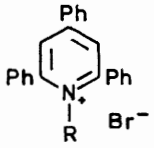
Pyrolysis of 1-*Substituted* 2,3,4,5,6-*Pentaphenylpyridinium Bromides*.—Evidently, 2,4,6-triphenylpyridine as flux lowers the reaction temperature. To show that previous contamination of alkyl bromides by 2,3,4,5,6-pentaphenylpyridine was due to high pyrolysis temperatures (>300 °C) rather than to the volatility of this pyridine, we re-examined 1-substituted 2,3,4,5,6-pentaphenylpyridinium bromides, which were prepared in dichloromethane at 20 °C (Table 5). Pyrolysis with 2,4,6-triphenylpyridine and KBr as flux at 180—220 °C for 3—4 h yielded the pure alkyl and aralkyl bromides (see Table 5) in yields considerably better than those previously reported.[1]

Synthesis and Pyrolysis of 1-*Substituted* 2,4,6-*Triphenylpyridinium Bromides*.—The conversion of 2,4,6-triphenylpyrylium bromide (4) into the corresponding pyridinium salt (CH_2Cl_2 at 20 °C) was slower than that for the pentaphenyl analogues; a typical reaction time was 6 h. These pyridinium bromides were obtained in higher yields than previously reported.[3] Pyrolysis of these compounds (5a—d) with 2,4,6-triphenylpyridine and KBr as flux at 180—200 °C gives the alkyl bromides (Table 5) in yields superior to those previously reported.

Synthesis and Transformation of 1-*Substituted Benzoquinolinium and Dibenzoacridinium Bromides*.—The standard method for the preparation of pyrylium bromides[4] was applied to the tricyclic (8) and pentacyclic (10) series; the corresponding diketones (12)[5] and (13) (obtained from the pentacyclic pyrylium tetrafluoroborate[6]) reacted smoothly with hydrogen bromide. 5,6-Dihydro-2,4-diphenylbenzo[*h*]-chromenylium bromide (8) and 5,6,8,9-tetrahydro-7-phenyl-dibenzo[*c*,*h*]xanthylium bromide (10) with aromatic amines in high yields in absolute ethanol and dimethylformamide respectively give the corresponding *N*-aryl quaternary salts (14) and (15) (Table 6).

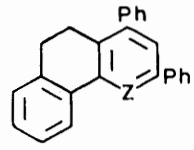


(4)

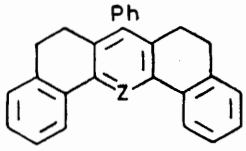


(5)

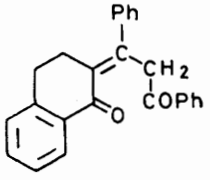
a; R = $Ph[CH_2]_2$
b; R = p-$MeC_6H_4CH_2$
c; R = p-$ClC_6H_4CH_2$
d; R = Et



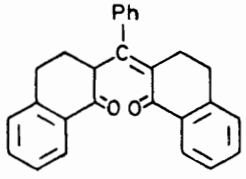
(6) Z = N
(7) Z = N^+CH_2Ph; $CF_3SO_3^-$
(8) Z = O^+; Br^-
(9) Z = O^+; $CF_3SO_3^-$



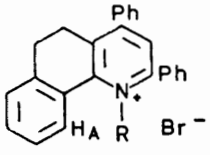
(10) Z = O^+; Br^-
(11) Z = N



(12)

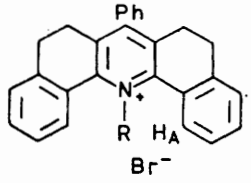


(13)



(14)

a; R = $PhCH_2$
b; R = m-MeC_6H_4
c; R = Ph
d; R = p-MeC_6H_4
e; R = 2-Pyridyl



(15)

a; R = Me
b; R = Ph
c; R = m-MeC_6H_4
d; R = p-MeC_6H_4
e; R = p-$MeOC_6H_4$
f; R = $Ph[CH_2]_2$
g; R = $Me[CH_2]_7$

Table 7 records the ^1H n.m.r. spectra of these compounds; the chemical shifts of both series are closely analogous to those of the corresponding trifluoromethanesulphonates.[7] However in all cases peaks due to the recrystallisation solvent are observed. Heating these pyridinium salts at 75 °C (0.5 mmHg) failed to remove the occluded solvent. Pyrolysis of the *N*-aryl tri- and penta-cyclic pyridinium salts gave HBr and polymer, but no aryl bromides.

Attempted preparation of *N*-benzyl-5,6-dihydro-2,4-diphenylbenzo[*h*]quinolinium bromide gave the substituted pyridine (6); evidently nucleophilic attack by bromide had already occurred. That the *N*-benzyl system is indeed a highly reactive system was proved

by heating its trifluoromethanesulphonate (7) salt with KBr in dimethylformamide at 100 °C: benzyl bromide was isolated in 60% yield.

Other work has shown the superiority of the tricyclic (6) and especially the pentacyclic (11) systems as leaving groups.[6] In confirmation we showed that the *N*-octyl pentacyclic bromide was transformed into n-octyl bromide (80%) at 81 °C in refluxing acetonitrile. These mild conditions would appear to be the method of choice for the conversion of amines into bromides.

EXPERIMENTAL

I.r. and ^{1}H n.m.r. spectra were recorded on Perkin-Elmer 257 and R12 instruments respectively; solutions in $CDCl_3$ with trifluoroacetic acid as internal standard were used to obtain the n.m.r. spectra. M.p.s were obtained on a Kofler hot-stage apparatus. The sublimation temperatures of the pentaphenylpyridines were estimated at 0.2 mmHg, the temperature being raised by 40 °C per hour: the temperature at which sublimation first occurred was noted.

The following compounds were prepared by literature methods: 2,4,6-triphenylpyridine, m.p. 139 °C (lit.,[8] 139 °C); 1,3,5-triphenylpent-3-ene-1,5-dione, m.p. 119 °C (lit.,[9] 119 °C); 2,4,6-triphenylpyrylium bromide, m.p. 242—245 °C (lit.,[2] 247 °C); and 3,4-dihydro-2-(3-oxo-1,3-diphenylpropylidene) naphthalen-1(2*H*)-one (12), m.p. 138—139 °C (lit.,[5] 138—139 °C).

General Procedure for Preparation of 3-*Aryl*-1,2,4,5-*tetraphenylpentane*-1,5-*diones*.—Deoxybenzoin (25 mmol) and the appropriate substituted benzaldehyde (12 mmol) in ethanolic KOH (2.0 g in 50 ml EtOH) was stirred for 3 d at 25 °C. The resulting white suspension was filtered to give the white powdery 1,5-dione, which was crystallised from hot HOAc (see Table 1).

4-*Aryl*-2,3,5,6-*tetraphenylpyrylium Bromides* (1a—e).—To the appropriate 3-aryl-1,2,4,5-tetraphenylpentane-1,5-dione (10 mmol) in glacial HOAc (300 ml) at 100 °C was added dropwise bromine (10 mmol) in HOAc (15 ml). The resulting red solution was heated at 100 °C for 10 h. On cooling, yellow crystals of the pyrylium bromide were deposited. Further crops were obtained by the addition of Et_2O to the mother-liquors (see Table 1).

4-*Aryl*-2,3,5,6-*tetraphenylpyridines* (3a—e).—The appropriate 4-aryl-2,3,5,6-tetraphenylpyrylium bromide (1) (1 g) was heated in EtOH (10 ml) with an excess of ammonia solution (*d* 0.88) for 10 min. On cooling, the 4-aryl-2,3,5,6-tetraphenylpyridines (3) separated and were recrystallised from absolute EtOH (Table 2).

TABLE 6

N-Substituted 5,6-dihydro-2,4-diphenylbenzo[*h*]quinolinium and *N*-substituted 5,6,8,9-tetrahydro-7-phenyldibenzo[*c*,*h*]-acridinium bromides

Compound	Series	Yield [a] (%)	M.p./°C	Found (%) C	H	N	Br	Formula	Required (%) C	H	N	Br
(14b)	Tricyclic	88	274—276	73.8	5.9	2.5	14.7	$C_{32}H_{26}BrN\cdot EtOH$	74.2	5.9	2.5	14.5
(14c)	Tricyclic	84	163—165			3.0		$C_{31}H_{24}BrN$			2.9	
(14d)	Tricyclic	92	290—291	73.8	5.8	2.8	14.3	$C_{32}H_{26}BrN\cdot EtOH$	74.2	5.9	2.5	14.5
(14e)	Tricyclic	95	293—295			6.0		$C_{30}H_{23}BrN_2$			5.7	
(15a)	Pentacyclic	66	155			3.1		$C_{28}H_{24}BrN$			3.1	
(15b)	Pentacyclic	68	292—293	74.2	5.7	2.6	14.3	$C_{33}H_{26}BrN\cdot EtOH$	74.7	5.7	2.5	14.2
(15c)	Pentacyclic	55	293—294	74.3	5.4	3.0	14.3	$C_{34}H_{28}BrN\cdot 0.5MeOH$	74.7	5.2	2.6	14.6
(15d)	Pentacyclic	67	304—305			2.9	14.6	$C_{34}H_{28}BrN\cdot MeOH$			2.5	14.2
(15e)	Pentacyclic	78	291—292	74.6	5.1	2.4	14.8	$C_{34}H_{28}BrNO$	74.7	5.2	2.6	14.6
(15f)	Pentacyclic	62	159			2.5		$C_{35}H_{30}BrN$			2.6	
(15g)	Pentacyclic	80	140	76.1	7.0	2.5	14.4	$C_{35}H_{38}BrN$	76.1	6.9	2.5	14.5

[a] All compounds crystallised as prisms from EtOH.

TABLE 7

^{1}H N.m.r. data (δ) for *N*-substituted 5,6-dihydro-2,4-diphenylbenzo[*h*]quinolinium and *N*-substituted 5,6,8-9-tetrahydro-7-phenyldibenzo[*c*,*h*]acridinium bromide

Compound	Aromatic protons	Proton H_A	$-CH_2-CH_2-$	Alkyl substituent
(14b)	7.8—6.8 (18 H, m)	6.8—6.5 (1 H, d, *J* 8—9 Hz)	2.9 (4 H, br s)	2.46 (3 H, s)
(14c)	7.9—6.8 (19 H, m)	6.8—6.6 (1 H, d, *J* 8—9 Hz)	2.9 (4 H, br s)	
(14d)	7.8—6.8 (18 H, m)	6.8—6.5 (1 H, d, *J* 8—9 Hz)	2.9 (4 H, br s)	2.5 (3 H, s)
(14e)	9—8.8 (1 H, d, *J* 6—7 Hz), 8.7—8.3 (2 H, m, *J*, 6—7 Hz), 8.21 (1 H, s), 7.9—7.0 (16 H, m)	7—6.7 (1 H, d, *J* 8—9 Hz)	3.9—3.0 (4 H, m)	
(15a)	7.8—7.2 (11 H, m)	8.4—8 (2 H, m) [a]	2.9 (8 H, br s)	4.6 (3 H, s)
(15b)	7.8—6.8 (16 H, m)	6.8—6.6 (2 H, d, *J* 8—9 Hz)	2.9 (8 H, br s)	2.5 (3 H, s)
(15c)	7.8—6.8 (15 H, m)	6.8—6.5 (2 H, d, *J* 8—9 Hz)	2.9 (8 H, br s)	2.5 (3 H, s), 4.05 (3 H, s, MeOH)
(15d)	7.8—6.8 (15 H, m)	6.8—6.5 (2 H, d, *J* 8.6 Hz)	2.9 (8 H, br s)	2.5 (3 H, s), 4.1 (3 H, s, MeOH)
(15e)	7.9—6.9 (15 H, m)	6.8—6.6 (2 H, d, *J* 7—8 Hz)	2.9 (8 H, br s)	3.0 (3 H, s, MeOH)
(15f)	7.9—7.0 (16 H, m)	8.3—7.9 (2 H, m) [a]	2.6 (8 H, br s)	6.9—6.7 (2 H, dd), 6.1—5.7 (2 H, dd)
(15g)	7.9—7.1 (11 H, m)	8.3—8.0 (2 H, m) [a]	2.9 (8 H, br s)	5.5—(2 H, t, *J* 7—8 Hz), 2.8—0.7 (15 H, m)

[a] Proton H_A is deshielded in *N*-alkyl substituents, and shielded by the aryl group.

4-*Aryl*-1-*benzyl*-2,3,5,6-*tetraphenylpyridinium Bromides* (2a—e; R = $PhCH_3$).—The appropriate 4-aryl-2,3,5,6-tetraphenylpyrylium bromide (1 mmol) and benzylamine (1.2 mmol) were stirred at 25 °C for 6 h in either CH_2Cl_2 or Et_2O (5 ml). The 4-aryl-1-benzyl-2,3,5,6-tetraphenylpyridinium bromides were filtered off and washed with Et_2O (Table 3). 1-Substituted-4-(4-chlorophenyl)-2,3,5,6-tetraphenylpyridinium bromides (2b) (Table 4) and the tri- and penta-phenylpyridinium bromides (Table 5) were prepared following the same procedure.

General Procedure for Pyrolysis.—The pyridinium bromide was heated with the same weight of 2,4,6-triphenylpyridine as a flux at 200—220 °C and 0.5—1.5 mmHg for 1—2 h. The alkyl bromide was collected in a receiver cooled by liquid nitrogen and characterised by i.r. and ^1H n.m.r. spectroscopy (Tables 3, 4, and 5).

3,4-*Dihydro*-2-[α-(1,2,3,4-*tetrahydro*-1-*oxo*-2-*naphthyl*)-*benzylidene*]*naphthalen*-1(2H)-*one* (13).—5,6,8,9-Tetrahydro-7-phenyldibenzo[*c*,*h*]xanthylium tetrafluoroborate (10 g, 0.02 mol) was suspended in boiling absolute EtOH (120 ml). NaOH (2 g, 0.047 mol) in water (10 ml) was added dropwise until a permanent colour change was observed. On cooling, the title compound (13) separated out (8.1 g, 96%). Recrystallisation from EtOH gave *plates*, m.p. 68 °C (Found: C, 85.6; H, 5.9; $C_{27}H_{22}O_2$ requires C, 85.7; H, 5.8%); $\nu_{max.}$ ($CHBr_3$) 2 940m, 2 900m, 2 840m, 1 680s, 1 645m, 1 600m, 1 492s, 1 453ms, 1 428m, 1 362s, 1 335ms, 1 325vs, 1 315m, 1 300s, 1 280w, 1 240w, 1 220w, 1 100m, 1 070ms, 1 045m, 1 032m, 1 012m, 930ms, 890w, 878w, 838m, 818w, and 770vs cm^{-1}; δ($CDCl_3$) 7.85 (2 H, m), 7.30 (11 H, m), and 2.70 (9 H, m).

5,6-*Dihydro*-2,4-*diphenylbenzo*[h]*chromenylium Bromide* (8).— 3,4-Dihydro-2-(3-oxo-1,3-diphenylpropylidene)-naphthalen-1(2*H*)-one (12) (20 g, 0.06 mol) was dissolved in hot absolute EtOH (100 ml) and an excess of HBr (6.2 g, 0.08 mol) added. Cooling gave the *chromenylium bromide* (8) as yellow prisms (22.3 g, 90%) (from EtOH), m.p. 268—269 °C (Found: C, 72.1; H, 4.9; Br, 19.1. $C_{25}H_{19}BrO$ requires C, 72.3; H, 4.6; Br, 19.2%); $\nu_{max.}$ ($CHBr_3$) 1 612s, 1 598s, 1 492vs, 1 472vs, 1 442s, 1 423s, 1 385s, 1 343w, 1 324w, 1 303w, 1 280w, 1 245m, 1 215ms, 1 190w, 1 173m, 998w, 932w, 875w, 822w, 788ms, 779m, 765ms, 745s, 730w, and 702ms cm^{-1}; δ(CF_3CO_2H) 8.3 (4 H, m), 7.65 (11 H, m), and 3.2 (4 H, m).

3,4-Dihydro-2-[α-(1,2,3,4-tetrahydro-1-oxo-2-naphthyl)-benzylidene]naphthalen-1(2*H*)one (13) and HBr similarly gave 5,6,8,9-*tetrahydro*-7-*phenyldibenzo*[c,h]*xanthylium bromide* (10) (89%) as needles, m.p. 292—293 °C (from isopropyl alcohol) (Found: C, 73.2; H, 4.7; Br, 18.3. $C_{27}H_{21}BrO$ requires C, 73.5; H, 4.8; Br, 18.1%); $\nu_{max.}$ ($CHBr_3$) 1 612s, 1 602s, 1 563s, 1 475s, 1 415s, 1 400m, 1 210m, 1 198m, 890m, 803m, 785ms, 760s, and 694s cm^{-1}.

N-*Arylbenzoquinolinium* (14b—e) *and* N-*Aryltetrahydrodibenzoacridinium* (15b—e) *Bromides*.—These compounds were prepared by treating the respective pyrylium salt (8) or (10) (10 mmol) with the appropriate primary amine in hot EtOH (10 ml). Cooling and diluting with Et_2O gave the quinolinium and acridinium bromides (Table 6).

N-*Alkyl*-5,6,8,9-*tetrahydro*-7-*phenyldibenzo*[c,h]*acridinium Bromides* (15a, f, *and* g).—The pyrylium bromide (10) (2 g) was treated with the appropriate primary amine in Et_2O (20 ml) at 20 °C for 12 h. The pure crystalline bromides (Table 6) were filtered off and washed with Et_2O.

5,6-*Dihydro*-2,4-*diphenylbenzo*[h]*chromenylium Trifluoromethanesulphonate* (9).—Chalcone (20.8 g, 0.1 mol) was warmed to its melting point on a steam-bath. α-Tetralone (11.7 g, 0.08 mol) and trifluoromethanesulphonic acid (12 g, 0.08 mol) were added with mechanical stirring. The temperature was raised to 90 °C. After 4 h, the reaction mixture was cooled to 30 °C and Et_2O (200 ml) added. The yellow crystalline *trifluoromethanesulphonate* (9) formed was filtered off (29.8 g, 75%) and recrystallised from glacial HOAc as prisms, m.p. 276 °C (Found: C, 64.8; H, 3.9; S, 6.6. $C_{26}H_{19}F_3SO_4$ requires C, 64.5; H, 4.0; S, 6.6%); $\nu_{max.}$ ($CHBr_3$) 1 615s, 1 600ms, 1 575m, 1 495m, 1 475ms, 1 450m, 1 435m, 1 425m, 1 390m, 1 270vs, 1 228m, 1 195w, 1 035s, 1 000m, 885m, 829m, 795ms, 770ms, 755m, and 750ms cm^{-1}; δ(CF_3CO_2H) 8.3 (4 H, m), 7.65 (11 H, m), and 3.15 (4 H, m).

1-*Benzyl*-5,6-*dihydro*-2,4-*diphenylbenzo*[h]*quinolinium Trifluoromethanesulphonate* (7).—The pyrylium salt (9) (3.0 g, 0.006 mol) was stirred with benzylamine (0.75 g, 0.007 mol) in CH_2Cl_2 (15 ml). After 5 min a catalytic quantity of glacial HOAc was added. After 15 min the solution was cooled to 0 °C and Et_2O (50 ml) added. The precipitated compound (7) (3.2 g, 90%) was collected and recrystallised from absolute EtOH as *needles*, m.p. 133 °C; (Found: C, 68.8; H, 4.4; N, 2.5; S, 5.6. $C_{33}H_{26}F_3NO_3S$ requires C, 69.1; H, 4.6; N, 2.4; S, 5.6%); $\nu_{max.}$ 1 612s, 1 598ms, 1 572m, 1 535ms, 1 497m, 1 468w, 1 453m, 1 420m, 1 395m, 1 365w, 1 260vs, 1 222s, 1 205w, 1 028vs, 1 010w, 998w, 895m, 790s, and 750s cm^{-1}; δ(CF_3CO_2H) 8.05 (1 H, m), 7.45 (17 H, m), 6.45 (2 H, m), 6.20 (2 H, s), and 2.95 (4 H, br s).

Displacement Reactions in Solution.—(a) *With* KBr *in* $HCONMe_2$. The trifluoromethanesulphonate (7) (2.5 g, 0.004 mol) was heated in $HCONMe_2$ (20 ml) at 120 °C for 6 h with KBr (1 g, 0.01 mol). The mixture was poured into water at 0 °C and extracted with Et_2O, and again washed with water. The ethereal extract was dried (Na_2SO_4). Anhydrous HCl gas was passed through the solution to remove the quinoline (6) as the hydrochloride. Filtration and removal of solvent from the filtrate gave benzyl bromide (0.48 g, 60%), characterised by its i.r. spectrum. The ^1H n.m.r. spectrum showed contamination by the quinoline (6) (<5%) which could be removed by distillation.

(b) *In* MeCN. 5,6,8,9-Tetrahydro-14-octyl-7-phenyldibenzo[*c*,*h*]acridinium bromide (15g) (1.5 g, 2.7 mmol) was refluxed in MeCN (15 ml) for 4 h. The solution was cooled at 0 °C for 6 h. The crystallised acridine was removed by filtration. Removal of solvent and distillation of the residue at 10 mmHg gave n-octyl bromide (0.37 g, 80%), characterised by i.r. and ^1H n.m.r. comparison with an authentic sample, and homogeneous by g.l.c.

[9/1743 *Received*, 30*th October*, 1979]

REFERENCES

1 A. R. Katritzky, U. Gruntz, A. A. Ikizler, D. H. Kenny, and B. P. Leddy, *J.C.S. Perkin I*, 1979, 436.
2 M. Simalty and J. Carretto, *Bull. Soc. chim. France*, 1966, 2959.
3 B. P. Leddy, Ph.D. Thesis, University of East Anglia, 1977.
4 A. T. Balaban, C. N. Rentea, and M. Bacescu-Roman, *Rev. Roum. Chim.*, 1965, **10**, 865.
5 A. R. Katritzky and S. S. Thind, *J.C.S. Perkin I*, 1980, 865.
6 A. R. Katritzky and S. S. Thind, following paper.
7 A. R. Katritzky, A. M. El-Mowafy, L. Marzorati, R. C. Patel, and S. S. Thind, in preparation.
8 M. Weiss, *J. Amer. Chem. Soc.*, 1952, **74**, 200.
9 R. Hubaut and J. Landais, *Bull. Soc. chim. France*, 1975, 2147.