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THERMAL REARRANGEMENT OF PYRIDINIUM ANHYDROBASES: MIGRATION OF N-SUBSTITUENTS TO METHINE CARBON†

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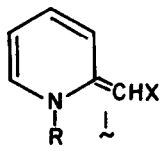
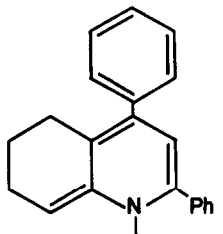
N-Benzyl and N-methyl groups migrate to the methine carbon atom on thermolysis of pyridinium anhydrobases. Cross-over experiments indicate an intermolecular reaction, probably involving homolysis.

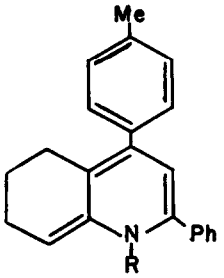
Pyridinium anhydrobases 1 are implicated in many reactions of pyridinium cations.[1] In most cases where X was not an electron-withdrawing group, the free anhydrobase is unstable (for a summary see ref. 2), but we recently found[2] that the fused alicyclic ring in 2 confers considerable stability.



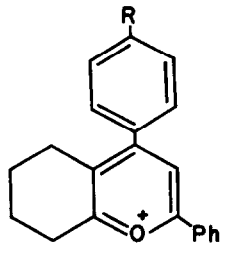
2 R = 4-MeC_6H_4
3 R = Me
4 R = $PhCH_2$



5 R = 4-$MeC_6H_4CH_2$
6 R = Ph

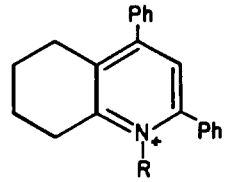


7 R = $PhCH_2$
8 R = 4-$MeC_6H_4CH_2$

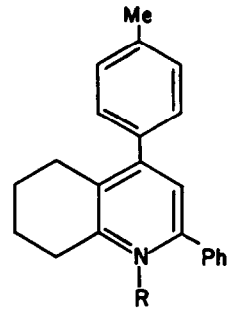


9 R = H
10 R = Me

Reported reactions[2] of pyridinium anhydrobases are all with electrophiles at the exocyclic carbon - emphasizing their enamine character. The recent discovery[3] that pyridinium compounds can undergo facile homolytic loss of the N-substituent led to speculation that radical pathways could occur for anhydrobases. The present paper describes a novel thermal rearrangement of N-alkyl group to the α'-position of anhydrobases which we believe involves a radical path.



11 R = Me
12 R = Pr^n
13 R = Bu^n
14 R = $PhCH_2$
15 R = 4-$MeC_6H_4CH_2$
16 R = Ph
17 R = $PhCH_2CH_2$



18 R = $PhCH_2$
19 R = 4-$MeC_6H_4CH_2$

†Dedicated to the memory of Academician F. Sorm

Preparation of Anhydrobases.- The bicyclic pyrylium 9 was prepared as tetrafluoroborate following Russian work[4] and as triflate.[2] The triflate of 10 was prepared analogously. Pyryliums 9 and 10 gave the corresponding pyridiniums 11-17 and 18-19, respectively, with primary amines (Table 1). These pyridiniums on treatment with NaOEt/EtOH were smoothly converted into the corresponding anhydrobases 4-8 (Table 2). The anhydrobases decompose on attempted crystallisation or on standing and did not give satisfactory analyses: they were characterised by their ^{1}H nmr spectra.

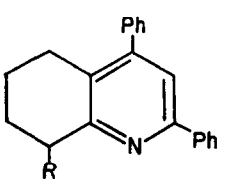
Thermolysis of Anhydrobases.- On heating under reduced pressure at 200-250 °C, the anhydrobases 3-5, 7, 8 and 28 were all converted into isomeric compounds which sublimed in an analytically pure state (Table 3). The structures of these isomeric products were proved to be 20-22, 24, 25 and 29, respectively, by ^{1}H and ^{13}C nmr spectra.

The ^{13}C nmr spectra in the aliphatic region (Table 4) revealed the expected triplets for C-5, C-6, C-7 together with a doublet for C-8. The 8α-CH_2 peak appeared as a triplet together with quartets for the methyl

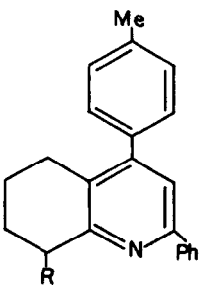
Table 1. Preparation of 2-phenyl-4-aryl-5,6,7,8-tetrahydroquinolinium salts.

Cpd. no.	Substituents 1	4	Anion	Time[a] h	Yield (%)	M.p. (°C)	Crystal[b] form	Analysis Found % C	H	N	S	Molecular formula	Required % C	H	N	S
11	Me	Ph	CF_3SO_3	12	88	113-114	Pl	61.8	5.0	3.1	7.2	$C_{23}H_{22}F_3NO_3S$	61.8	4.9	3.1	7.1
12	Pr^n	Ph	CF_3SO_3	6	92	97-98	Pl[c]	62.5	5.5	2.7	6.9	$C_{25}H_{26}F_3NO_3S$	62.9	5.5	2.9	6.7
13	Bu^n	Ph	CF_3SO_3	12	89	46-48	N Pr[c]	63.9	5.7	2.9	6.5	$C_{26}H_{28}F_3NO_3S$	63.5	5.7	2.9	6.5
14	$PhCH_2$	Ph	CF_3SO_3	4	97	158-159	N	66.3	4.9	2.7	6.1	$C_{29}H_{26}F_3NO_3S$	66.3	5.0	2.7	6.1
15	4-Me-$PhCH_2$	Ph	CF_3SO_3	6	99	156	N	66.6	5.2	2.6	5.8	$C_{30}H_{28}F_3NO_3S$	66.8	5.2	2.6	5.9
15	4-Me-$PhCH_2$	Ph	BF_4	5	97	201-203	Pr	72.8	5.7	3.2	-	$C_{29}H_{28}BF_4N$	73.0	5.7	3.0	-
16	Ph	Ph	CF_3SO_3	12	95	186-188[d]	N	65.5	4.7	2.7	-	$C_{28}H_{24}F_3NO_3S$	65.5	4.7	2.7	-
17	$Ph(CH_2)_2$	Ph	CF_3SO_3	6	94	134	Pl	66.5	5.2	2.6	6.1	$C_{30}H_{28}F_3NO_3S$	66.8	5.2	2.6	5.9
18	$PhCH_2$	p-Tolyl	CF_3SO_3	4	97	162-164	N	66.9	5.2	2.6	6.0	$C_{30}H_{28}F_3NO_3S$	66.8	5.2	2.6	5.9
18	$PhCH_2$	p-Tolyl	BF_4	4	99	229-230	N	72.6	5.9	2.9	-	$C_{29}H_{28}BF_4N$	73.0	5.9	2.9	-
19	4-Me-$PhCH_2$	p-Tolyl	CF_3SO_3	5	96	188-189	N	67.4	5.5	2.5	5.8	$C_{31}H_{30}F_3NO_3S$	67.3	5.4	2.5	5.8
19	4-Me-$PhCH_2$	p-Tolyl	BF_4	12	98	225-227	N	73.1	6.1	2.8	-	$C_{30}H_{30}BF_4N$	73.1	6.1	2.9	-
27	$PhCH_2$	Ph	CF_3SO_3	18	86	157-158	N	66.7	5.3	2.6	5.9	$C_{30}H_{28}F_3NO_3S$	66.8	5.2	2.6	5.9

[a] All reactions were run using CH_2Cl_2 as a solvent at room temperature, unless otherwise indicated. [b] All compounds were recrystallised from absolute ethanol, unless otherwise indicated. [c] Crystallised from absolute ethanol/ether. [d] Also forms microcrystals m.p. 203-205 °C, R.T. Langthorne unpublished work. [e] Reaction was run in refluxing ethanol.



20 R = Me
21 R = $PhCH_2$
22 R = 4-$MeC_6H_4CH_2$
23 R = H



24 R = $PhCH_2$
25 R = 4-$MeC_6H_4CH_2$

Table 2. Preparation and physical properties of 1-substituted-2-phenyl-4-aryl-1,5,6,7-tetrahydroquinolines.

Compd. no.	Substituents 1	4	Yield %	M.p. °C	Cryst. form[a]	^{1}H NMR Data 100 MHz: Aromatic multiplet δ	H	C_3(H) δ	C_8(H) δ	CH_2 δ	CH_3 δ	Aliphatic region multiplets[b]
4	$PhCH_2$	Ph	80	123-125	N	7.23-7.32	15	5.14	4.00	4.44	-	1.20-2.60 (5H)
5	p-$MeC_6H_4CH_2$	Ph	97	86	N	7.15-7.70	14	5.20	4.00	4.42	2.40	1.60 (4H), 2.10 (t*, 2H)
6	Ph	Ph	92	85	N	6.9 -7.40	15	5.12	3.74	-	-	1.52 (m, 2H), 2.04 (t*, 2H), 2.40 (t*, 2H).
7	$PhCH_2$	p-Tolyl	88	110-112	M	7.00-7.60	14	5.15	4.01	4.43	2.40	1.40-1.6 (2H), 2.13 (t*, 2H), 2.4 (t*, 2H).
8	p-$MeC_6H_4CH_2$	p-Tolyl	86	85-86	M	7.10-7.30	13	5.13	(d)	4.07	2.33	1.10-1.30 (2H), 2.05 (t*, 2H), 2.4 (t*, 2H).
28	$PhCH_2$	Ph	90	102-103	N[c]	6.70-7.80	15	5.80	-	4.2	2.0	1.54 (2H), 2.23 (4H).

[a] Crystallised from CH_2Cl_2/isopropanol at room temperature, thermally too unstable to give satisfactory analysis; N = needles, M = microcrystals.
[b] t* = distorted triplet; d = signals are hidden within the aliphatic region.
[c] Analysis; Calcd. for $C_{29}H_{27}N$: C, 89.5; H, 6.90; N, 3.6. Found: C, 89.2; H, 7.4; N, 3.6%.

Table 3. 8-Substituted-2-phenyl-4-aryl-5,6,7,8-tetrahydroquinolines, Products of thermolysis of anhydrobases.

Cpd. no.	Substituents 4	8	Reaction Conditions Temp. °C	Pressure mmHg	Time	Yield[a] (%)	M.p. (°C)	Analysis Found, % C	H	N	Molecular Formula	Required, % C	H	N
20	Ph	Me	200	25	5	70	[b]	88.0	6.6	4.7	$C_{22}H_{21}N$	88.3	7.0	4.7
21	Ph	$PhCH_2$	260	25	6	90	45-47	89.4	6.7	3.7	$C_{28}H_{25}N$	89.6	6.7	3.7
22	Ph	4-Me-$PhCH_2$	250	25	4	87	52-53	89.5	7.0	3.7	$C_{29}H_{27}N$	89.5	7.0	3.7
23	Ph	H	260	25	3	89	102-104[c]	88.5	6.8	4.6	$C_{21}H_{19}N$	88.4	6.7	4.9
24	4-Me-Ph	$PhCH_2$	220	0.3	4	85	64-66	89.3	7.0	3.6	$C_{29}H_{27}N$	89.5	6.9	3.6
25	4-Me-Ph	4-Me-$PhCH_2$	220	0.3	3	85	55-56	89.2	7.3	3.5	$C_{30}H_{29}N$	89.3	7.2	3.5
29	Ph	CH_3, $PhCH_2$	220	0.3	4	83	62-64	89.3	7.0	3.6	$C_{29}H_{27}N$	89.5	6.9	3.6

[a] All compounds were obtained as microcrystals, unless otherwise indicated.
[b] Thick oil. [c] Lit. m.p. 103-104 °C, A.M. El-Mowafy, Ph.D. Thesis, University of East Anglia, 1980.

Table 4. ^{13}C Chemical shifts of the aliphatic region of 8-substituted-2,4-diaryl-5,6,7,8-tetrahydroquinoline [a]

Compd.	Aliphatic Ring Carbons [b] C_5 (t)	C_6 (t)	C_7 (t)	C_8 (d)	CH_2 (t)	8-Me (q)	4-Me (q)
21	41.6	27.1	27.8	43.3	20.4	-	-
22	41.2	27.0	27.7	43.3	20.3	21.0	-
24	41.6	27.1	27.8	43.3	20.4	-	21.2
25	41.2	27.0	27.8	43.3	20.4	21.0	21.2
29	48.0	29.4	34.0	41.7 [e]	19.0	8-CH_3	29.4
23 [c]	31.4	27.5	27.5	36.7	-	-	-
20 [d]	31.3	20.6	27.8	36.3	-	-	-

[a] Spectra were run at room temperature on a JEOL FX-100 at 25.0 MHz using $CDCl_3$ as internal reference. Typical conditions were: 5KHz width; 8 K data; pulse width 9 μ sec with a repetition time of 1 sec. [b] in ppm; d = doublet; t = triplet; q = quartet. [c] Spectrum was recorded in dmso-d_6. [d] CH_3 = 21.9 ppm. [e] singlet

groups. The ^1H nmr spectra (Table 5) showed the expected signals: the benzylic protons were non equivalent and appeared as the AB peaks of ABX multiplets: in 29 the benzylic protons form a simple AB quartet with a typical J_{gem} value.

This rearrangement does not occur

Table 5. ^1H NMR spectral data of 2-phenyl-4-aryl-8-substituted-5,6,7,8-tetrahydroquinoline

Cpd. no.	Substituents C_4	C_8	Aliphatic mult. δ	H	CH_3 8-CH_3 δ	Benzylic [c] protons H_A	H_X	H_8	Aromatic mult. δ	H
20	Ph	CH_3	2.60-2.20	4	1.52 [a]	-	-	3.10	7.0 -7.60	9
			2.6	3	2.34 [e]				7.98-8.07	2
21 [b]	Ph	$PhCH_2$	1.60-1.75	2					7.24-7.55	14
			1.80-2.85	2	-	2.88	3.91	3.40	8.13-8.17	2
			2.70	2						
22	Ph	p-xylyl	1.40-2.05	4	2.34 [e]	2.84	3.84	3.35	7.10-7.70	13
			2.48-2.8	2	-				8.0 -8.20	2
24	p-tolyl	$PhCH_2$	1.40-2.00	2	2.42 [f]	2.84	3.80	3.32	7.20-7.60	13
			2.60-2.78	2	-				8.00-8.18	2
25	p-tolyl	p-xylyl	1.40-2.0	4	3.36 [f]	2.80	3.80	3.30	7.00-7.60	11
			2.48-2.68	2	2.28 [e]				7.94-8.10	2
28	Ph	Me, $PhCH_2$	1.62-2.57	6	1.49 [g]	3.22 [d]	3.42 [d]	-	7.10-7.60	14
									8.00-8.20	2

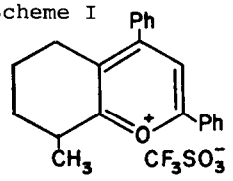
[a] 8-Me, d, J = 6.9 Hz. [b] Spectrum was recorded on 300 MHz NIC spectrometer. [c] J_{AX} = 13.5 Hz, J_{MX} = 4.0 Hz and J_{AM} = 10.6 Hz. [d] AB quartet, J_{AB} = 13 Hz. [e] 8'-Me. [f] 4'-Me. [g] 8-Me.

for N-aryl compounds: anhydrobase 6 on pyrolysis under the same conditions lost completely the N-phenyl group and formed the known tetrahydroquinoline 23.

Mechanism of the Rearrangement.- To ascertain the intra- or intermolecularity of this rearrangement we pyrolysed a mixture of the two anhydrobases 4 and 8. For an intramolecular reaction, we expect only two products 21 and 25. However, if the reaction is intermolecular we expect, in addition, the formation of 22 and 24.

The sublimate for pyrolysis of 4 + 8 was examined by GC-MS. For standardization, the MS of the four possible products 21, 22, 24, 25 were first elucidated on the pure compounds: these products gave similar degradation patterns as shown in Scheme I and Table 6. In each case the molecular ion lost the 8-benzyl substituent to give 30 or 31 as the base peak; further loss of phenyl now afforded 32 or 33. The other main fragmentation involves loss of H to 34-37 which then lost ethylene to 38-41.

Scheme I



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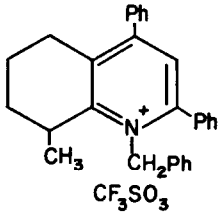

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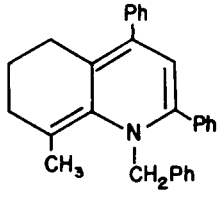

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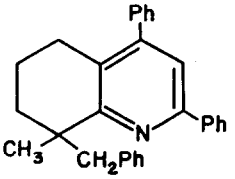

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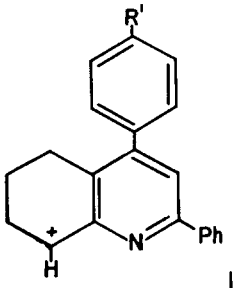
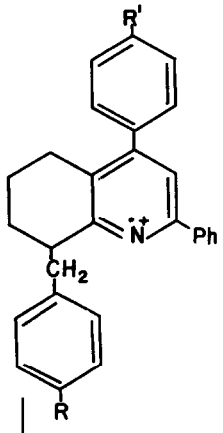


30 R = H
31 R' = Me

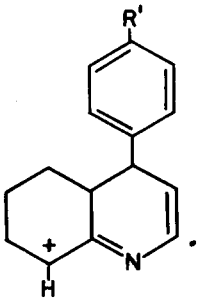
$-8\,\dot{C}H_2C_6H_4R$



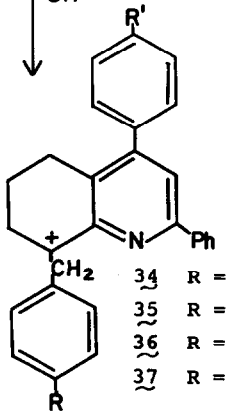
21 R = R' = H
22 R = Me, R' = H
24 R = H, R' = Me
25 R = R' = Me

$-2\cdot\dot{P}h$

$-8H$

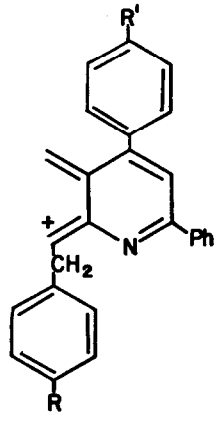


32 R' = H
33 R' = Me



34 R = R' = H
35 R = Me, R' = H
36 R = H, R' = Me
37 R = R' = Me

$-C_2H_4$



38 R = R' = H
39 R = Me, R' = H
40 R = H, R' = Me
41 R = R' = Me

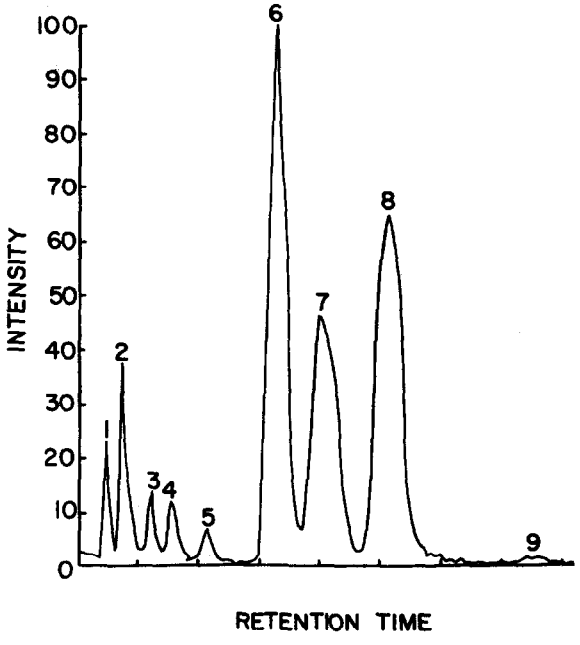
Table 6. Mass spectral fragmentation pattern of individual compounds.

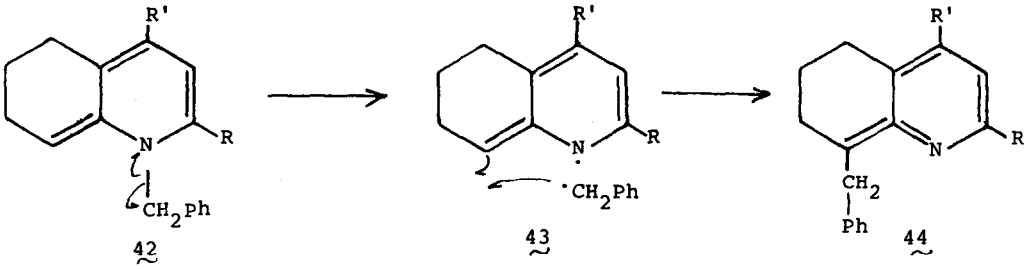
Ion	Position[a]	21 Str.[b]	21 m/e	21 I[b] (%)	22 Str.[b]	22 m/e	22 I[b] (%)	24 Str.[b]	24 m/e	24 I[b] (%)	25 Str.[b]	25 m/e	25 I[b] (%)
M	-	21	375	82.7	22	389	61.0	24	389	90.8	25	403	85.6
M-H	8	34	374	38.4	35	388	24.1	36	388	42.2	37	462	41.6
M-C_2H_5	6,7,8	38	347	16.0	39	361	21.2	40	361	14.6	41	375	16.6
M-Ph	2	-	298	11.6	-	312	1.5	-	312	8.1	-	312	9.6
M-CH_2Ph-R	8	30	284	100.0	30	284	100.0	31	298	100.0	31	298	100.0
M-CH_2PhR-PhR	8,2	32	207	12.1	32	207	2.4	33	207	16.2	33	207	8.0
R-$PhCH_2$	8		91	28.5	-	105	36.1	-	91	22.3	-	105	22.4

[a] Position indicates from where the fragment has been lost. [b] Str. = Structure, I = Intensity.

The GC spectrum (see Fig. 1 and Table 7) gave five major peaks (minor peaks nos. 3,4,5 and 9 are trace contaminants). Peaks 6 and 8 are for the expected products 21 and 25 respectively, which result from the separate pyrolysis of compounds 4 and 8. Products 21 and 25 are formed in nearly equal amounts The "cross over" products 22 and 24 possess nearly equal retention times and together compose peak 7. The MS from peak 7 was found to be identical with a superposition of the MS from compounds 22 and 24. The formation of substantial amounts of 22 and 24 clearly indicates an intermolecular pathway. The ratio of the "cross over" products (22 +24) to those which would be obtained through an intramolecular pathway (21+25) is ca. 1:3 (cf. Table 7). If the reaction had been completely random, a 1:1 ratio would be expected. Hence these results suggest that although the benzyl N-bond breaks (cf. 42) to give a radical pair (43), the benzyl radicals tend to be trapped more rapidly by the β-carbon of the same molecule to give 44. This explains the distribution ratios of the products in Table 7. Peaks 1 and 2 are probably due to traces of quinolines 23 and 45 respectively, the corresponding MS data are presented in Table 8.

Figure 1





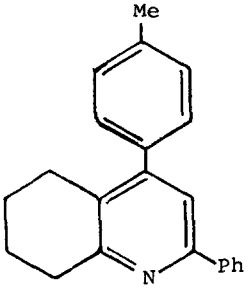


Table 7. GC Data for pyrolysis of mixture of 4 and 8 (cf. Fig. 1).

PK. No.	Compound No.	R.T. (sec)	Area
1	23	190	2.96
2	42	224	7.13
3	*	293	2.77
4	*	334	3.06
5	*	416	2.16
6	21	574	40.82
7	22 + 24	670	27.50
8	25	827	38.96
9	*	1136	1.31

* Unknown background

Table 8. Major mass spectral fragmentation pattern of quinolines 23 and 42.

Ion	Position from which fragment is lost	Cpd. 23 m/e	Cpd. 23 Intensity	Cpd. 42 m/e	Cpd. 42 Intensity
M	-	285	77.5	299	83.0
M-H	8	284	100.0	298	100.0
M-15	4	-	-	284	16.1
M-29	6,7,8	256	9.9	270	7.3
M-207	2 or 4	77	8.6	222	7.8

EXPERIMENTAL

The ^{1}H NMR spectra were recorded on a Varian HA-100 and a Jeol FX-100 spectrometers at 100 MHz, ^{13}C nmr spectra were recorded on a Jeol FX-100 spectrometer at 25.0 MHz using tetramethylsilane as internal standard for ^{1}H nmr or $CDCl_3$ for ^{13}C spectra. Ir spectra were obtained on a Perkin-Elmer

297 and 283B spectrophotometers, in $CHBr_3$ solutions. GC/MS spectra were obtained on an AEI MS 30 instrument equipped with a DS-55 data system. M.p.'s were recorded on a Reichert hot stage microscope and are uncorrected.

The following compounds were prepared according to the literature procedures quoted: 1,3-diphenyl-1-(oxocyclohexyl)-propan-3-one, m.p. 147-149 °C (lit.[5] m.p. 148-149 °C); 2,4-diphenyl-5,6,7,8-tetrahydrochromylium both as triflate m.p. 183-184 °C (lit.[2] m.p. 182-183 °C), and as tetrafluoroborate, m.p. 213-214 °C (lit.[4] m.p. 212-214 °C).

1-Phenyl-3-(p-tolyl)-3-(oxocyclohexyl)-propan-3-one was prepared following the procedure reported[5] for the preparation of 1,3-diphenyl-1-(oxocyclohexyl)-propan-3-one (80%), m.p. 140-141 °C; ν (cm-1) 1690 m, 1440 s; δ($CDCl_3$) 1.0-2.0 (m, 4 H), 2.24 (s, 3 H), 2.32-3.72 (m, 4 H), 7.0-8.0 (m, 9 H). Anal. Calcd. for $C_{22}H_{24}O_2$: C, 82.5; H, 7.5. Found: C, 82.5; H, 7.4%.

2-Phenyl-4-(p-tolyl)-5,6,7,8-tetrahydrochromenylium triflate 10 was prepared according to literature procedure.[2] To a mixture of 4-methylbenzoalacetophenone (30.0 g, 13.5 mmol) and cyclohexanone (6.6 g, 6.8 mmol) in 150 ml of absolute ether was added trifluoromethanesulphonic acid dropwise (6 ml). The mixture was stirred at room temperature for 2 h to give a solid material which was filtered off, washed with ether and recrystallised from ethanol to give pyrylium 10 (10.7 g, 35%) as prisms, m.p. 185-187 °C; ν 1620 s, 1600 s, 1500 s, 1475 s, 1270 b, 1030 s cm^{-1}. δ($CDCl_3$/TFA) 1.67-2.33 (m, 4 H), 2.50 (s, 3 H), 2.90 (t*, 2 H), 3.30 (t*, 2 H), 7.30-7.80 (m, 7 H), 8.00-8.23 (m, 3 H). Anal. Calcd for $C_{23}H_{18}F_3O_4S$: C, 61.3; H, 4.7; S, 7.2. Found: C, 61.2; H, 4.7; S, 7.1%.

The corresponding BF_4 salt was prepared following the Russian procedure[4] with modification where Ac_2O was used as a hydride abstractor instead of the chalcone. A mixture of 3-phenyl-1-(p-tolyl)-1-(oxocyclohexyl)-propan-3-one (10 g, 31.3 mmol) and Ac_2O (3.2 g, 31.3 mmol) was stirred at 100 °C for 5 min. Borontrifluoride etherate (10.0 g, 45%) was added dropwise and the mixture was refluxed at 20 °C for 15 min. After cooling 20 ml of ethanol were added followed by 400 ml of ether to afford the pyrylium salt 10, recrystallised from acetonitrile-ether (7.9 g, 65%), m.p. 198-201 °C; Ir ν 1620 s, 1050 b; δ 1.70 (m, 2 H), 2.22 (s, 3 H), 2.70 (t*, 2 H), 3.10 (t*, 2 H), 7.10-7.50 (m, 8 H), 7.80-7.90 (m, 2 H). Anal. Calcd for $C_{22}H_{21}BF_4O$: C, 68.0; H, 5.4. Found: C, 67.9, H, 5.4%.

General Procedure for the preparation of 1-Substituted-2,4-diaryl-5,6,7,8-tetrahydroquinolinium BF_4 and CF_3SO_3 (11-19 and 27).- To a suspension of the chromenylium salt (5 mmol) in CH_2Cl_2 (20 ml) at 25 °C was added the amine (5.2 mmol). The red solution was stirred for appropriate time (Table 1). After concentration of the orange solution in vacuo (25 mmHg), the residue was triturated with ether (500 ml) to give after filtration the quinolinium salt, recrystallised from absolute EtOH. See Table 1 for physical data.

General Method for the Reaction of 2,4-Diaryl-5,6,7,8-tetrahydroquinolinium salts with sodium ethoxide.- To a solution of the quinolinium salt (2 mmol) in absolute EtOH (15 ml), NaH (2.2 mmol) was added carefully at room temperature. After 5-15 min the anhydrobases 2-8 and 28 were precipitated as orange and yellow solids respectively. They were filtered off and washed with 95% cold EtOH (5 ml) (80-90%). Attempted recrystallisation of these anhydrobases resulted in decomposition. See Table 2 for ^1H nmr data.

Thermolysis of Anhydrobases.- 400 mg of a well dried anhydrobase were heated to 180 °C in a cold finger tube for 5 min after which vacuum was applied and temperature raised. The sublimate was collected on a cold finger. See Table 3 for reaction conditions and analyses; Tables 4 and 5 for ^{13}C and ^1H nmr chemical shifts respectively.

2,4-Diphenyl-8-methyl-5,6,7,8-tetrahydrochromenylium triflate 26.- A mixture of benzalacetophenone (5 g, 2.4 mmol), 2-methylcyclohexane (1.80 g, 1.6 mmol) and trifluoromethanesulfonic acid (4.6 g, 2.4 mmol) was heated on a steam bath for 2 h. The mixture was cooled to room temperature, triturated with ether (200 ml) and stirred vigorously for 8 h to give a yellow solid which was filtered off and recrystallised from absolute ethanol as microcrystals (1.5 g, 21%); m.p. 130-133 °C; Ir, ν 1615 s, 1270 b, 1030 s cm^{-1}; δ($CDCl_3$) 1.61 (d, 3 H, J = 7 Hz), 1.82 (m, 3 H), 2.18 (m, 1 H), 2.88 (m, 2 H), 3.5 (m, 1 H), 7.4-8.4 (m, 11 H). Anal. Calcd for $C_{23}H_{18}F_3SO_4$: C, 61.3; H, 4.7; S, 7.2. Found C, 61.4; H, 4.8; S, 7.2%.

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t* = refers to distorted triplet

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