Arab Gulf J. scient. Res. 1(1), pp. 85-97 (1983)

Elimination Reactions of Pyridinium Cations

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ABSTRACT. *N*-Substituted 2,4,6-triphenylpyridinium salts with sodium 2-oxido-4,6-diphenylpyridine give olefins by elimination in fair to good yields. Other attempts to prepare olefins from pyridiniums are discussed.

The conversion of primary aliphatic amines into other functionality *via* pyridinium salts has been reviewed, Katritzky 1980. Most of the reactions have been substitutions with the pyridine as leaving group. Some elimination reactions have been accomplished, notably the preparation of isocyanates (Bapt *et al.* 1976) and carbodiimides (Katritzky *et al.* 1979b). The present paper records our early attempts to prepare olefins by elimination reactions. Positive results are reported for the reaction of 2,4,6-triphenyl-pyridinium salts with sodium 2-oxido-4,6-diphenylpyridine, although we later found that pyrolysis of pentacyclic pyridinium triflates was a preferable method (Katritzky and El-Mowafy 1982).

Pyrolysis of N-*(2-Phenylethyl) Heterocycles*

Attempted bimolecular elimination of 1-(2-phenylethyl)-2,4,6-triphenylpyridinium salt (**la,lb**) with non-hindered bases (pyrolysis with NaOH or NaH in sulpholane) gave only 8% of styrene **3a** (Leddy 1975). Pyrolysis of the *N-n*-octyl derivative **1c** with triphenylpyridine at 160°C for 6hr gave 28% of octene **3b.** Use of pentaphenylpyridine

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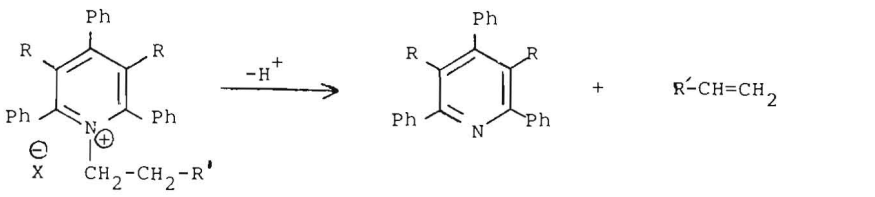
as the leaving group in 1-(2-phenylethyl)-2,3,4,5,6-pentaphenylpyridinium bromide **1d** gave no better results (Leddy 1975).

Similarly pyrolysis of *N*-(2-phenylethyl)phthalimide and of the corresponding 1,8-naphthalimide failed, although the former heated with KOH gave 53% styrene (*cf.* Baumgarten 1968).

BLOCK 1



1 2 3

	R	R'	X
a	H	Ph	ClO_4
b	H	Ph	Cl
c	H	n-C_6H_{13}	BF_4
d	Ph	Ph	Br

a R = H

b R = Ph

a R' = Ph

b R' = n-C_6H_{13}

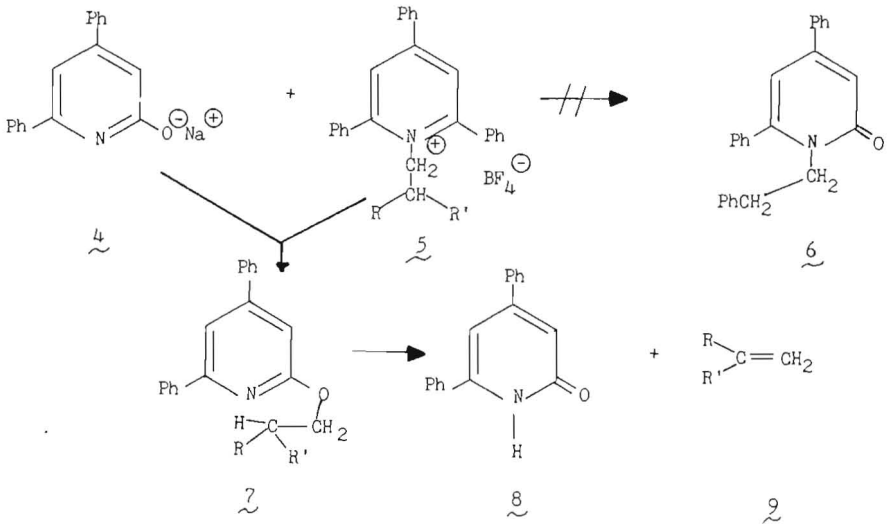
Reactions of N-*Substituted 2,4,6-Triphenylpyridinium Salts with Sodium 2-Oxido-4,6-diphenylpyridine*

Sodium 2-oxido-4,6-diphenylpyridine **4** heated with 1-(2-phenylethyl)-2,4,6-triphenylpyridinium tetrafluoroborate **5a** gave styrene (67%). Similarly 1-butyl- and 1-(3-hydroxypropyl)-pyridinium salts (**5b,5c**) gave respectively 32% 1-butene (isolated as the dibromide) and 20% allyl alcohol. Acetaldehyde (19%) and acetone (60%) were obtained when 1-(2-hydroxyethyl)- and 1-(2-hydroxypropyl)-2,4,6-triphenylpyridinium salts (**5d,5e**) were heated with **4,** presumably *via* the corresponding enols.

This method avoids the use of forcing oxidizing conditions involved in the Hofmann deamination (Roberts *et al.* 1977) and the oxidative method of Cope and Trumbell (1960). Furthermore, the reagent is readily obtained (Katritzky *et al.* 1979a) *cf.* use of Ag_2O in other methods (Roberts *et al.* 1977).

The fair yield of styrene obtained from sodium 2-oxido-4,6-diphenylpyridine **4** and the 1-(2-phenylethyl)pyridinium salt **5a** contrasted with the 8% yield obtained by the pyrolysis of 1-(2-phenylethyl)-4,6-diphenyl-2-pyridone **6** and suggests that the *O*-alkylated compound **7** is the intermediate in the former reaction.

BLOCK 2

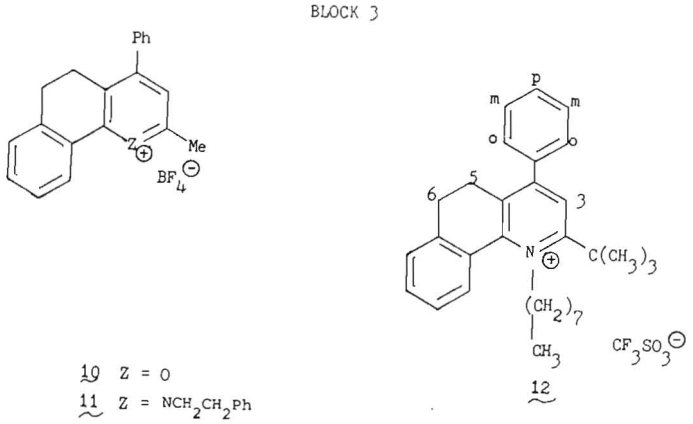


	a	b	c	d	e
R	Ph	Et	CH_2CH_2OH	OH	CH_3
R'	H	H	H	H	OH

Further Attempts to Prepare Olefins

The 2-methylbenzochromylium (Katritzky *et al.* 1981 a) **10** with 2-phenylethylamine afforded the corresponding pyridinium salt **11** in moderate yield, but attempts to oxidize this to analogous pyridone gave mixtures which were difficult to separate.

BLOCK 3

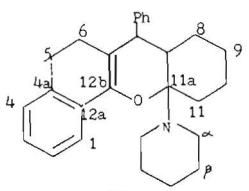


10 Z = O
11 Z = NCH_2CH_2Ph

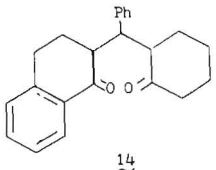
Pyrolysis of the *N*-*n*-octyl tricyclic pyridinium salt **12** with 2,4,6-triphenyl-pyridine

gave a low yield (15%) of 1-, *cis*-2- and *trans*-2-octenes and *n*-octane in the ratio of 59:18:15:8%.

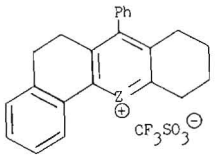
BLOCK 4



13



14

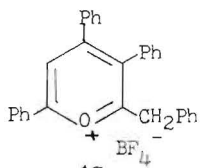


15 Z = O

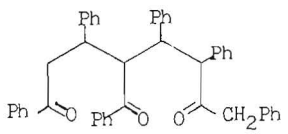
16 Z = NC_6H_{13}-n

Reaction of 1-morpholinocyclohexene with benzylidene-α-tetralone afforded the adduct **13.** The ^{13}C NMR chemical shifts of **13** were assigned aided by off-resonance decoupling measurements and comparison with the literature chemical shifts of dihydropyran (Stothers 1972), morpholine (Johnson and Jankowsky 1972) and the enamine adduct from methyl vinyl ketone and *N,N*-dimethylisobutenylamine (Fleming and Karger 1967). Hydrolysis of adduct **13** gave the 1,5-diketone **14** (Baumgarten 1968) (72%), which gave the-corresponding pyrylium trifluoromethanesulphonate (triflate) **15** smoothly at 20°C with benzylidene-acetophenone as the hydride abstractor. The ^{13}C NMR of **15** was assigned by comparison with those of analogous pyrylium salts (Katritzky *et al.* 1981c).

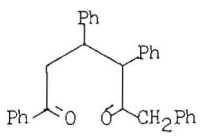
BLOCK 5



17



18



19

The pyrylium **15** with hexylamine gave pyridinium salt **16,** which with sodium methoxide yielded a mixture of starting pyridinium **16** and the corresponding anhydrobase (*cf.* Katritzky *et al.* 1982) as shown by ^{13}C NMR. This mixture on pyrolysis gave *n*-hexane (ca10%).

Dibenzyl ketone with benzylideneacetophenone and CF_3SO_3H gave the triketone **18** instead of **17.** The same reaction at 100°C gave 2,4,6-triphenylpyrylium triflate (Katritzky *et al.* 1980) probably *via* the 1,5-diketone formed by a retro Michael reaction of the triketone **18** (*cf.* Van Allan and Reynolds 1968). The 1,5-diketone **19** was prepared

by treatment of dibenzyl ketone and benzylidene acetophenone with ethanolic sodium hydroxide. Treatment of **19** with trityl tetrafluoroborate gave the pyrylium salt **17.** Further reactions of the latter with amines are still under investigation.

Experimental

Melting points (uncorrected) were determined with a Kofler or a Reichart hot-stage apparatus. IR spectra were measured for $CHBr_3$ or Nujol mulls with Perkin-Elmer 257 instrument. ^1H NMR and ^{13}C NMR spectra were recorded with Perkin-Elmer R 12 (60 MHz) and Jeol FX 100 spectrometers, respectively (Me_4Si as internal standard).

N-*(2-Phenylethyl)-2,4,6-triphenylpyridinium Perchlorate* **1a**

2-Phenylethylamine (1.21 g, 0.010 mol) and 2,4,6-triphenylpyrylium perchlorate (Balaban and Toma 1966) were refluxed in chloroform (50 mL) for 5 hr. Concentration *in vacuo* to 15 mL and addition of ether (200 mL) gave the *product* (4.89 g, 90%) which was crystallised from acetic acid as prisms, mp 260°C; IR (Nujol) 1620 cm^{-1}; ^1H NMR (TFA) δ 2.18 (2 H, t), 4.2 (2 H, t), 6.35 (2 H, m), 7.07 (3 H, m); 7.65 (15 H, m), 7.95 (2 H, s).

Anal. Calcd for $C_{31}H_{26}NClO_4.H_2O$: C, 70.3; N, 2.6; H, 5.3. Found: C, 69.8; N, 2.4; H, 5.0.

N-*(2-Phenylethyl)-2,4,6-triphenylpyridinium Chloride* **1b**

2-Phenylethylamine (7.0 g, 0.06 mol) was added to 2,4,6-triphenylpyrylium chloride, Katritzky *et al.* 1982, Chadwick 1973, (10 g, 0.029 mol) in ethanol while cooling the mixture on an ice bath. The mixture was refulxed for 1hr, cooled and conc. HCl (20 mL) was added. The mixture was cooled for a further 1hr and solvent removed *in vacuo*. The product was crystallised from chloroformether (1:1) to yield the *chloride* (7.43 g, 83%) as colourless solid, mp 205°C; IR (Nujol) 1625 cm^{-1}; ^1H NMR (TFA) δ 2.3 (2 H,m), 4.7 (2 H, m), 6.51 (2 H, m), 7.17 (3 H,m), 7.65 (15 H,m), 8.07 (2 H, s).

Anal Calcd for $C_{31}H_{26}NCl.H_2O$: C, 79.9; N, 3.0; H, 6.0. Found: C, 79.9; N, 2.7; H, 6.1.

Thermolyses of N-*(2-Phenylethyl)-2,4,6-triphenylpyridinium Perchlorate* **1a** *and Chloride* **1b**

The perchlorate **1a** (2.56 g, 0.0050 mol) was triturated with KOH (0.265 g, 0.0050 mol) and the mixture was thermolysed (caution: explosion hazard). To the distillate, 5% vv solution of bromine in CCl_4 (1 mL), (Openshaw 1965), was added to give 1,2-dibromo-1-phenylethane (0.1 g, 8%).

1-n-*Octyl-2,4,6-triphenylpyridinium Tetrafluoroborate* **1c**

To 2,4,6-triphenylpyrylium tetrafluoroborate (Lombard and Stephan 1958), (5.0 g, 0.013 mol) suspended in ethanol (25mL), *n*-octylamine (4.2 mL, 0.025 mol) was

added and the mixture stirred at 20°C for 12 hr. The resulting solution was concentrated *in vacuo* to 10 mL and added dropwise to vigorously stirred ether (100 mL). The resulting crystals were filtered off and washed with ether to give *salt* **1c** (4.0 g, 63%). It crystallised from ethanol as prisms, mp 153-155°C; IR ($CHBr_3$) 1620 cm^{-1}; ^1H NMR ($CDCl_3$ / TFA) δ 0.98-1.70 (15 H, m), 4.05-4.60 (2 H, m), 7.2-7.89 (15 H, m), and 7.92 (2 H, s).

Anal. Calcd for $C_{31}H_{34}BF_4N$: C, 73.4; H, 6.8; N, 2.8. Found: C, 73.6: H, 6.7; N, 2.8.

*Thermolysis of 1-*n*-Octyl-2,4,6-triphenylpyridinium Tetrafluoroborate* **1c**

Salt **1c** (4.0 g, 0.0079 mol) and 2,4,6-triphenylpyridine (3.0 g) were dried, mixed, ground finely and thermolysed at 160°C (200 mm) for 6 hr. The temperature was then raised to 220-240°C at 100 mm for 2 hr. Octene (250 mg, 28%) collected in a receiver cooled with liquid nitrogen. IR and ^1H NMR spectra were identical to those of an authentic sample (The Sadtler Standard Spectra 1975).

N-*(2-Phenylethyl)-1,8-naphthalimide*

1,8-Naphthalic anhydride (19.8 g, 0.1 mol) and 2-phenylethylamine (12.1 g, 0.10 mol) in ethanol (1 L) were heated under reflux for 12 hr. The product which crystallised out on cooling was recrystallised from ethanol to yield the *naphthalimide*, 23.5 g (78%) as colourless needles, mp 133°C; IR (Nujol) 1690, 1655, 1614, 1599 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.92 (2 H, m), 4.35 (2 H, m), 7.25 (5 H, m), 7.7 (2 H, d, J=4.1 Hz), 8.12 (2H, d, J=4.5 Hz), 8.52 (2H, d, J = 3.8 Hz).

Anal. Calcd for $C_{20}H_{15}NO_2$; C, 79.7; H, 5.0; N, 4.7. Found: C, 79.4; H, 5.2; N, 4.7.

N-*(2-Phenylethyl)-2,4,6-triphenylpyridinium Tetrafluoroborate* **5a**

2-Phenylethylamine (1.21 g, 0.010 mol) was added to 2,4,6-triphenylpyrylium tetrafluoroborate, Lombard and Stephan 1958, (3.96 g, 0.010 mol) in chloroform (50 mL) and the mixture was stirred at 20°C for 24 hr. Solvent was removed *in vacuo;* ether triturations (200 mL) afforded the salt **5a** (3.83 g, 77%) which crystallised from water/acetone (3:1) as colourless prisms, mp 271°C; IR 1625 cm^{-1}; ^1H NMR (TFA) δ 2.72 (2 H, t), 4.81 (2 H, t), 6.45 (2 H, m), 7.15 (3 H, m), 7.66 (15 H, m), 8.06 (2 H, s).

Anal. Calcd for $C_{31}H_{26}BF_4N.H_2O$: C, 72.0; N, 2.7; H, 5.4. Found: C, 72.6; N, 2.8; H, 5.1.

N-*Substituted-2,4,6-triphenylpyridinium Tetrafluoroborates* **5b-5e**

These compounds were prepared according to literature procedures (Katritzky *et al.* 1981 b).

Sodium 2-Oxido-4,6-diphenylpyridine

A mixture of 4,6-diphenyl-2-pyridone, El-Kholy *et al.* 1970, (2.47 g, 0.010 mol) and NaOH (0.4 g, 0.010 mol) in ethanol (50 mL) was evaporated to dryness. The resultant solid was used in the olefin synthesis.

Thermolysis of N-*(2-Phenylethyl)-2,4,6-triphenylpyridinium Tetrafluroborate* **5a**

Salt **5a** (4.99 g, 0.010 mol) and 4,6-diphenyl-2-pyridone **4** (sodium salt) 2.69 g, 0.01 mol) were dried and thermolysed to yield styrene (0.7 g, 67%) which was characterised by IR spectroscopy, n_D^{18} 1.5563, (n_D^{20} 1.5458).

Thermolysis of N-n-*butyl-2,4,6-triphenylpyridinium Tetrafluroborate* **5b**

A dried mixture of **5b** (3.29 g, 0.0074 mol) and pyridone **4** (2.0 g, 0.0074 mol) was thermolysed. The effluent gases were passed through bromine in CCl_4 (25%, vv, 20 mL). Solvent was removed *in vacuo* and the resultant liquid distilled at atmospheric pressure to yield 1,2-dibromobutane (0.5 g, 32%), bp 170°C (lit. 160°C), which was characterised by ^1H NMR spectroscopy.

Thermolysis of N-*(2-Hydroxyethyl)-2,4,6-triphenylpyridinium Tetrafluoroborate* **5c**

The thermolysis was conducted as above. The product was dissolved in pet. ether (30-40°C, 10 mL), dried ($MgSO_4$), filtered and the solvent removed *in vacuo* to yield allyl alcohol (0.05 g, 20%), characterized by IR spectroscopy.

Thermolysis of N-*Hydroxymethyl-2,4,6-triphenylpyridinium Tetrafluoroborate* **5d**

Salt **5d** (2.195 g, 0.0050 mol) and pyridone **4** (1.35 g, 0.0050 mol) were thermolysed at reduced pressure (2mm/Hg, 190°C) for 30 min. The product acetaldehyde (0.03, 19%), was characterised by IR spectroscopy.

Thermolysis of N-*(2-Hydroxypropyl)-2,4,6-triphenylpyridinium Tetrafluoroborate* **5e**

Dried **5e** (1.62 g, 0.0037 mol) and **4** (1.0 g, 0.0037 mol) were pyrolysed under reduced pressure at the melting point. The product was dried ($MgSO_4$) and distilled at 760 mm to yield acetone (0.15 g, 60%), characterised as the 2,4-dinitrophenylhydrazone, mp 122°C (lit., 128°C).

N-*(2-Phenylethyl)-4,6-diphenyl-2-pyridone* **6**

4,6-Di-phenyl-2-pyrone, Arndt and Eistert 1925, (2.48 g, 0.010 mol), 2-phenylethylamine (12.1 g, 0.10 mol) and ethanol (50 mL) were heated under reflux for 16 hr. The mixture was cooled, diluted with water (100 mL) and extracted into $CHCl_3$ (3 × 5 mL). The $CHCl_3$ extract was dried ($MgSO_4$), filtered and the solvent removed *in vacuo*. The product precipitated from the resultant yellow oil with petroleum ether (30-40°C, 100 mL) and collected by filteration. Crystallisation from ethanol gave the *pyridone* **6** (2.2 g, 63%) as colourless needles, mp 155°C; IR ($CHCl_3$) 1655 cm^{-1}; ^1H

NMR ($CDCl_3$) δ 2.92 (2 H, m), 4.15 (2 H, m), 6.33 (2 H, m), and 6.75-7.75 (15 H, m).

Anal. Calcd for $C_{25}H_{21}NO$: C, 85.5; H, 6.0; N, 4.0. Found: C, 85.1; H, 6.0; N, 3.9.

Thermolysis of N-*(2-Phenylethyl)-4,6-diphenyl-2-pyridone* **6**

Dried *N*-(2-phenylethyl)-4,6-diphenyl-2-pyridone (2.0 g, 0.006 mol) was thermolysed under vacuum using a dry ice/acetone trap to yield styrene (0.05 g, 8%), characterised by IR spectroscopy.

5,6-Dihydro-2-methyl-1-(2-phenylethyl)-4-phenylbenzo [h] *quinolinium Tetrafluoroborate* **11**

2-Phenylethylamine (1 mL) was added to a well stirred suspension of 5,6-dihydro-2-methyl-4-phenylnaphtho [1.2 *b*] pyrylium (Katritzky *et al.* 1981a) **10** (1.9 g, 0.0053 mol) in magnesium-dried ethanol (20 mL). The mixture was stirred for 24 hr and then refluxed for one hour. Ether trituration (100 mL) afforded a gum which was worked with dry ethanol (5 mL) and triturated with more ether. The gum was vigorously stirred under ether at 20°C for 96 hr. The resulting crystals were filtered off and washed with ether to give *salt* **11** (1.5 g, 62%) which crystallised from ethanol as white prisms, mp 129-135°C; IR ($CHBr_3$) 1620 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.10-3.10 (6 H, m), 3.12 (3 H, s), 5.14 (2 H, m), 6.70 (2. H, m), 7.08-7.80 (13 H, m).

Anal. Calcd for $C_{28}H_{26}BF_4N$: C, 72.6; H, 5.7; N, 3.0. Found: C, 72.6; H, 5.7; N, 2.8.

2-tert-*Butyl-5,6-dihydro-1*-n-*octyl-4-phenylbenzo* [h] *quinolinium Triflate* **12**

n-Octylamine (0.36 mL, 0.0022 mol) was added to a suspension of 2-*tert*-butyl-5,6-dihydro-4-phenylnaphtho [1.2-*b*] pyrylium, Thind 1979, (500 mg, 0.0011 mol) in dried ether (15 mL). The mixture was stirred at 20°C for 72 hr, after which an oil separated. Solvent was decanted and fresh ether was added and then decanted. The resulting oil was dried at 20°C, 0.1 mm and characterised as such; IR ($CHBr_3$) 1610 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.70-1.55 (15 H, m), 1.76 (9 H, m), 2.85 (4 H, m), 5.32 (2 H, m), 7.56 (8 H, m), 7.77 (1 H, s), 8.10 (1 H, m); ^{13}C NMR ($CDCl_3$) δ 14.0 ($C_{8'}$), 22.4 ($C_{7'}$), 26.1 ($C_{3'}$), 26.8 (C_6), 28.4 (C_5,$C_{5'}$), 28.6 ($C_{4'}$), 29.0 ($C_{6'}$), 31.4 ($C_{2'}$ C_β), 38.9 (C_α), 57.5 ($C_{1'}$), 125.8 (C_3), 128.0 (C_m), 128.2* (C_{4a}, C_7), 128.6* (C_g, C_p), 129.2 (C_o), 130.5 (C_8), 132.7 (C_{10}), 135.5 (C_i), 137.9 ($C_{10\alpha}$), 141.1 (C_{6a}), 155.5 (C_4), 156.5 (C_{10b}), 164.3 (C_2).

Anal. Calcd for $C_{32}H_{40}F_3NO_3S.2H_2O$: C, 62.8; H, 7.3; N, 2.3. Found: C, 63.1; H, 7.1; N, 2.7.

* The asterisk denotes ambiguity

Thermolysis of 2-tert-*Butyl-5,6-dihydro- 1*-n- *octyl-4-phenylbenzo* [h] *quinolinium Triflate* **12**

Salt **12** (3 g, 0.0051 mol) and 2,4,6-triphenyl-pyridine (1.6 g, 0.0052 mol) were mixed in a thermolysis apparatus and dried for 1hr (40°C, 10 mm). The thermolysis trap was then cooled with liquid nitrogen and the temperature was raised to and maintained at 120°C (300 mm) for 2 hr, and then up to 160°C (300 mm) for 20 min. The product was then collected to give a mixture (60 mg, 10%) of 1-,*trans*-2- and *cis*-2-octenes in addition to *n*-octane (as shown by ^{13}C NMR and GLC studies). The gas chromatogram of the mixture (C 20M, 40°C, flow 18 mL/min) showed the ratio of the above mixture to be 59.3:17.9:14.9:7.9%, respectively.

5,6,7a,8,9,10,11,11a(7 H)*Octahydro-11a-morpholino-4-phenylbenzo* [c] *xanthene* **13**

Procedure A

1-Morpholinocyclohexene (9 g, 0.054 mol) and 2-benzylidene -α- tetralone (10 g, 0.045 mol) were refluxed in sodium-dry toluene (100 mL) for 20 hr (over activated molecular sieves) under an atmosphere of nitrogen. The reaction mixture was then filtered and toluene was removed *in vacuo* at 100°C. The residue was triturated with acetonitrile (25 mL) and the resulting precipitate was filtered to give the *enamine adduct* **13** (17.4 g, 96%) which crystallised from ethyl acetate as white prisms, mp 175-176°C; IR ($CHBr_3$) 1665 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.10-2.16 (10 H, m), 2.18-2.42 (1 H, m), 2.50-2.98 (5 H, m), 3.20-3.80 (5 H, m), 6.82-7.30 (8 H, m), 7.44-7.60 (1 H, m); ^{13}C NMR ($CDCl_3$) δ 22.7 (t, C_9), 25.8* (C_{10}), 26.3* (C_6, C_8), 28.4* (t, C_5), 40.8 (d, C_7), 44.5 (t, C_{11}, C_α), 45.1 (C_{7a}), 67.3 (t, C_β), 91.0 (s, C_{11a}), 107.1 (s, C_{6a}), 121.3 (d, C_1), 126.2 (d, C_3, C_p), 126.9 (d, C_o), 128.2* (d, C_m), 129.1* (d, C_2, C_4), 132.3 (s, C_{4a}), 136.2 (s, C_i), 143.3 (s, C_{12b}), 144.1 (s, C_{12a}).

Anal. Calcd for $C_{27}H_{31}NO_2$: C, 80.8; H, 7.8; N, 3.5. Found: C, 80.8; H, 7.9; N, 3.4.

Procedure B

Cyclohexanone (5 g, 0.051 mol) and morpholine (5.77 g, 0.066 mol) were refluxed in toluene (100 mL) with azeotropic removal of water for 10 hr. 2-Benzylidene-α-tetralone (5 g, 0.045 mol) was added and the mixture was refluxed for a further 23 hr (over activated molecular seives). Filteration and removal of toluene *in vacuo* gave an oily residue which crystallised upon trituration with acetonitrile (25 mL) to give **13** (14.2 g, 79%).

Hydrolysis of Enamine Adduct **13**

Compound **13** (6.4 g, 0.016 mol) was refluxed in acetic acid (25 mL) and H_2O (1 mL) at 100°C for 3 hr. The mixture was then left standing at room temperature for 12 hr and the resulting crystals were filtered to give a first crop of the 1,5-diketone **14** (2.9 g). Concentration of solvent afforded a second crop of **14** (0.91 g) leading to total yield of 3.81 (72%). It was crystallized from AcOH, mp 154-165°C (Baumgarten 1968, 154-165°C).

5,6,8,9,10,11-Hexahydro-7-phenylbenzo [c] *xanthylium Triflate* **15**

The 1,5-diketone **14** (3 g, 0.0090 mol) and benzylideneacetophenone (1.88 g, 0.0090 mol) were dissolved in dry ether (50 mL). Triflic acid (0.8 mL) was added dropwise and the mixture was stirred at 20°C for 30 min. The crystals which separated were filtered off to give *salt* **15** (3.79 g, 91%), mp 163-168°C (decomp.) (with no further purification); IR 1620 cm^{-1}; ^1H NMR (TFA) 1.50-2.42 (4 H, m), 2.46-2.80 (2 H, m), 2.96 (4 H, m), 3.10-3.50 (2 H, m); ^{13}C NMR (DMSO-d_6) 20.1 (C_9), 20.6 (C_{10}), 23.8 (C_5), 25.5 (C_6), 25.9 (C_8), 28.9 (C_{11}), 25.9 (C_8), 125.5 (C_{6a}), 126.0* (C_2, C_4), 128.1* (C_m), 129.1* (C_1, C_o), 129.4* (C_{12b}), 130.1* (C_p), 131.3* (C_{7a}), 132.7* (C_i), 135.2 (C_3), 141.5 (C_{4a}), 166.1 (C_{12a}), 166.3 (C_7), 173.7 (C_{11a}).

Anal. Calcd for $C_{24}H_{21}F_3O_4S$: C, 62.3; H, 4.6; S, 6.9. Found C, 62.2; H, 4.7; S, 6.7.

*Thermolysis of 5,6,8,9,10,12-Hexahydro-*1-n-*hexyl-4-phenylbenzo* [c]*-acridine*

A mixture of pyrylium **15** (3 g, 0.0065 mol) and *n*-hexylamine (0.99 g, 0.0098 mol) in dried ether (50 mL) was stirred at room temperature for 20 hr. Ether was decanted and the oily residue was washed with fresh ether (2×10 mL) to give salt **16** as gum (2.13 g, 60%) which could not be crystallised; IR ($CHBr_3$) 1610 cm^{-1}; ^1H NMR ($CDCl_3$) 0.9-2.15 (15 H, m), 2.2-3.0 (6 H, m), 3.1-3.5 (2 H, m), 5.1 (2 H, m), 7.0-8.8 (8 H, m), 2.0 (1 H, m). Salt **16** (2.13 g, 0.0039 mol) was added to a solution of sodium hydride (94 mg, 0.0039 mol) in methanol (10 mL). The mixture was stirred at 20°C for 1hr and then ether (60 mL) was added and the organic layer was washed with H_2O (3×10 mL) dried ($MgSO_4$) and ether was removed *in vacuo*. The resulting crude residue was thermolysed at 160°C (300 mm) for 4 hr. The product (9%) was identified by ^{13}C NMR spectroscopy as *n*-hexane.

Reaction of Benzylideneacetophenone with Dibenzyl Ketone at 20°C

Benzylideneacetophenone (2 g, 0.0096 mol) and dibenzyl ketone (10 g, 0.0048 mol) were mixed in dry ether (50 mL). Triflic acid (0.4 mL) was added dropwise and the mixture was left stirring at 20°C for 30 min. The crystals which separated were filtered off and washed with ether to give *5,6-dibenzyl-1,3,4,6-tetraphenylheptan-2-one* **18** (1.5 g, 50%). It crystallised from AcOH/EtOH as colourless prisms, mp 203-204°C; IR 1720, 1680 cm^{-1}; ^1H NMR, not resolved.

Anal. Calcd for $C_{45}H_{38}O_3$: C, 86.2; H, 6.1. Found: C, 85.8; H, 6.2.

Reaction of Benzylideneacetophenone with Dibenzyl Ketone at 100°C

Benzylideneacetophenone (2 g, 0.0096 mol) and dibenzyl ketone (1 g, 0.0048 mol) were melted at 100°C. Triflic acid (0.4 mL) was added and the mixture was heated at 100°C for 4 hr. Ethanol (5 mL) was added and the mixture was refluxed for a further 15 min. Ether trituration (100 mL) afforded a pyrylium which was identified by its spectral data as 2,4,6-triphenylpyrylium triflate (18%), mp 257-259°C (Katritzky *et al.* 1980, 257-259°C).

1,3,4,6-Tetraphenylhexan-1,5-dione **19**

Benzylideneacetophenone (1 g, 0.0048 mol) and dibenzyl ketone (1 g, 0.0048 mol) were dissolved in hot ethanol (5 mL). The mixture was added to a solution of sodium hydroxide (0.2 g) in ethanol (25 mL) to which was added a few drops of water. The reaction mixture was stirred vigorously for 3 min at 20°C. A few more drops of H_2O were added and the precipitate was filtered off immediately and washed with EtOH (5 mL) to give **21** (1.5 g, 75%). It crystallised from EtOH/AcOH mixture as prisms, mp 189-190°C (Gorrichon-Guigon and Maroni-Barnaud 1973, mp 144-146°C); IR ($CHBr_3$) 1720, 1680 cm^{-1}.

Anal. Calcd for $C_{30}H_{26}O_2$: C, 86.1; H, 6.3. Found: C, 86.00; H, 6.3.

2-Benzyl-3,4,6-triphenylpyrylium Tetrafluoroborate **17**

1,5-Diketone **19** (2 g, 0.0048 mol) and trityl tetrafluoroborate (2 g, 0.0061 mol) were heated in Ac_2O (5 mL) at 100°C for 30 min. One drop of H_2O was added and the mixture was triturated with ether (100 mL) to give *Pyrylium* **17** (1.6 g, 69%) which crystallised from acetic acid as yellow prisms, mp 236-240°C (decomp.); IR ($CHBr_3$) 1610 cm^{-1}; ^1H NMR (TFA) δ 4.5 (2 H, m), 7.1-7.9 (18 H, m), 8.0-8.3 (2 H, m), 8.44 (1 H, s).

Anal. Calcd for $C_{30}H_{23}BF_4O$: C, 74.1; H, 4.8. Found: C, 73.6; H, 4.5.

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(Received 9/6/1982;
in revised form 23/11/1982)

تفاعلات إزالة كاتيونات البيريدينيوم

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تعطى أملاح البيريدينيوم ثلاثي الفنيل ٢،٤،٦ المستبدلة النيتروجين مع ٢ ـ أكسيدو بيريدين الصوديوم، ثنائي الفنيل ٤، ٦ أوليفينات بالإزالة مع إنتاج يترواح بين المعتدل والوفير. يناقش البحث محاولات تحضير الأوليفينات من البيريدينيومات.