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# SOME NOVEL t-BUTYLATION REACTIONS IN THE CONVERSION OF PHENYL-SUBSTITUTED 1,5-DIKETONES TO PYRYLIUM SALTS

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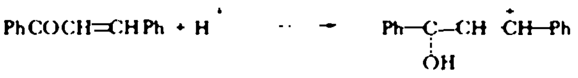
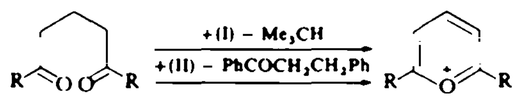
**Abstract**—Phenyl-substituted 1,5-diketones are converted by t-butyl chloride and aluminium chloride into pyrylium salts, in which the γ-phenyl group has been t-butylated.

$$Me_3CCl + AlCl_3 \rightleftharpoons \underset{\text{I}}{Me_3\overset{+}{C}\,\overset{-}{AlCl_4}} \rightleftharpoons Me_2C{=}CH_2 + HCl + AlCl_3$$



$$PhCOCH{=}CHPh + H^+ \longrightarrow Ph{-}\underset{OH}{C}{=}CH\,\overset{+}{C}H{-}Ph$$

II



III IV

In a previous communication,[2] the dehydrogenation of 1,5-diketones to pyrylium salts (III → IV) was described, with t-butyl chloride–aluminium chloride (I)[3] or the conjugate acid of chalcone (II)[4] as hydride ion acceptors in place of the more frequently used triphenylmethyl perchlorate.[5,6] 2,6-Diphenyl-, and 2,4,6-triphenyl-pyrylium cations (IX) were thus obtained. However, in the attempted preparation of the 2,4-diphenyl-5,6,7,8-tetrahydrobenzopyrylium cation (VIII) quite different results were found by the use of the dehydrogenating agents I and II. The perchlorate with the expected structure VIII was obtained exclusively with II. However, in the presence of I, the major product was 2-phenyl-4-*p*-t-butylphenyl-5,6,7,8-tetrahydrobenzopyrylium perchlorate (VI), and the corresponding di-t-butylated pyrylium salt (V) was also formed.

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[1] Applications of Proton Resonance Spectroscopy. Part XXVI. For Part XXV see H.-B. Schröter, D. Neuman, A. R. Katritzky and F. J. Swinbourne, *Tetrahedron* **22**, 2895 (1966).

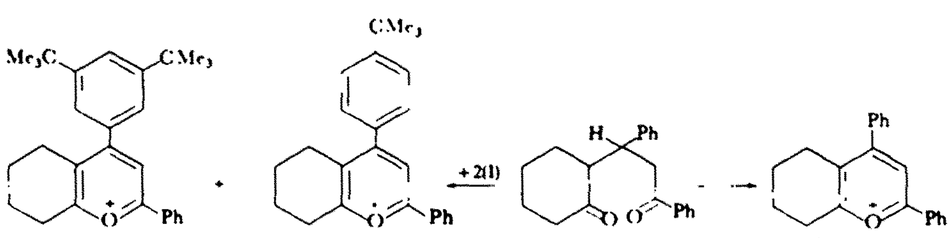
[2] A. T. Balaban, *C.R. Acad. Sci., Paris*, **256**, 4239 (1963).

[3] D. Bryce-Smith and N. A. Perkins, *J. Chem. Soc.* 2320 (1961).

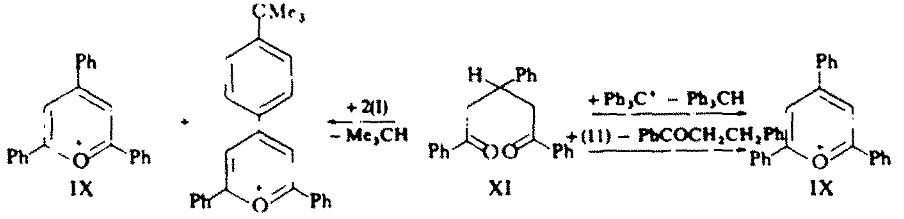
[4] A yellow, crystalline, hygroscopic perchlorate of chalcone ($II^+ClO_4^-$), m.p. 98–100° (from dichloromethane-ligroin) has been prepared (cf. Ref. 5).

[5] P. Pfeiffer and H. Kleu, *Ber. Dtsch. Chem. Ges.* **66**, 1058 (1933).

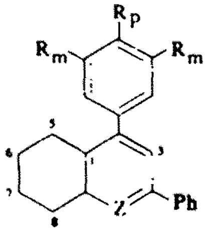
[6] M. Siemiatycki and R. Fugnitto, *Bull. Soc. Chim. Fr.* 538 (1961).



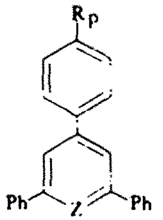
V VI VII VIII



IX X XI IX



XII



XIII

Similarly, treatment of 1,3,5-triphenyl-1,5-pentanedione (XI) with aluminium chloride in t-butyl chloride gave, in addition to 2,4,6-triphenylpyrylium perchlorate (IX) [the only product formed using trityl perchlorate[6] or the chalcone cation II], the t-butylphenylpyrylium perchlorate (X). The pyrylium perchlorates (V, VI, VIII and X) were all converted by aqueous ammonia to the corresponding pyridines (or tetrahydroquinolines), which were characterized as picrates.

The structures of compounds V, VI and VIII follow from (a) elementary analyses of the perchlorates and the derived pyridines, (b) permanganate oxidations which yielded benzoic acid (from VIII) and benzoic and *p*-t-butylbenzoic acid (from VI), and (c) the spectral data discussed below.

It is known that the nitration of 2,4,6-triphenylpyrylium perchlorate results in the *meta*-substitution of the 2- and 6-phenyl groups, but in the *para*-substitution of the 4-phenyl ring;[7a] similarly in benzopyrylium salts a 3-phenyl group is nitrated in the *para*-, and a 2-phenyl in the *meta*- position.[7b] Experiments were therefore designed to ascertain whether the t-butylations occurred before or after the dehydrogenation and cyclization of the 1,5-diketones to the pyrylium cations. The pyrylium cation VIII is not t-butylated to VI on treatment with I, which indicates that the diketone VII is t-butylated at the non-deactivated phenyl group *before* cyclization to VIII.

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[7] [a] C. G. Le Fèvre and R. Le Fèvre, *J. Chem. Soc.* 2894 (1932); [b] R. L. Shriner and R. B. Moffett, *J. Am. Chem. Soc.* **61**, 1474 (1939).

TABLE 1. PROTON CHEMICAL SHIFTS (P.P.M. ON $\tau$ SCALE) FOR PYRYLIUM PERCHLORATES AND PYRIDINES

| Type | Z | $R_p$ | $R_m$ | Solvent | 3-H | 2-Phenyl | | 4-Phenyl | 8-$CH_2$ | 5-$CH_2$ | 6,7-$(CH_2)_2$ | $Bu^t$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | o-H | m, p-H | | | | | |
| XII | $O^+$ | H | H | $SO_2$ | 1·68 s | 1·65 m | ca. 2·2 m | ca. 2·55 | 6·54 (3, $J$ = 6) | 6·98 (3, $J$ = 6) | 7·9 m | — |
| | $O^+$ | $Bu^t$ | H | $SO_2$ | 1·70 s | 1·67 m | ca. 2·2 m | ca. 2·2 m | 6·55 (3, $J$ = 6) | 6·93 (3, $J$ = 6) | 7·9 m | 8·66 s |
| | $O^+$ | H | $Bu^t$ | $SO_2$ | 1·71 s | 1·69 m | ca. 2·2 | o-2·45 (2, $J$ = 1·8)<br>p-ca. 2·2 | 6·55 (3, $J$ = 6) | 6·98 (3, $J$ = 6) | 8·0 m | 8·57 s |
| | N | H | H | $CDCl_3$ | ca. 2·55 | 1·96 m | ca. 2·55 | ca. 2·2 m | 6·86 (3, $J$ = 6) | 7·31 (3, $J$ = 6) | 8·15 m | — |
| | N | $Bu^t$ | H | $CDCl_3$ | 2·60 s | 1·97 m | ca. 2·5 m | ca. 2·5 | 6·88 (3, $J$ = 6) | 7·29 (3, $J$ = 6) | 8·13 m | 8·60 s |
| | N | H | $Bu^t$ | $CDCl_3$ | 2·50 s | 1·94 m | ca. 2·5 m | o-2·74 (2, $J$ = 1·6)<br>p-ca. 2·5 m | 6·85 (3, $J$ = 6) | 7·30 (3, $J$ = 6) | 8·12 m | 8·63 s |
| XIII | $O^+$ | $Bu^t$ | H | $SO_2$ | 1·28* | 1·6 m | ca. 2·1 m | ca. 2·1 m | | — | — | 8·54 s |

s = singlet; m = multiplet; figures in brackets give multiplicity and spin-spin coupling constants in c/s.

* doublet, with $J$ = 1 c/s.

## DISCUSSION OF SPECTRA

The NMR spectra of the compounds of types XII and XIII are recorded in Table 1, and the spectra of the pyridines are shown in Figs 1–3. Integrations were carried out for all spectra and the areas so determined.

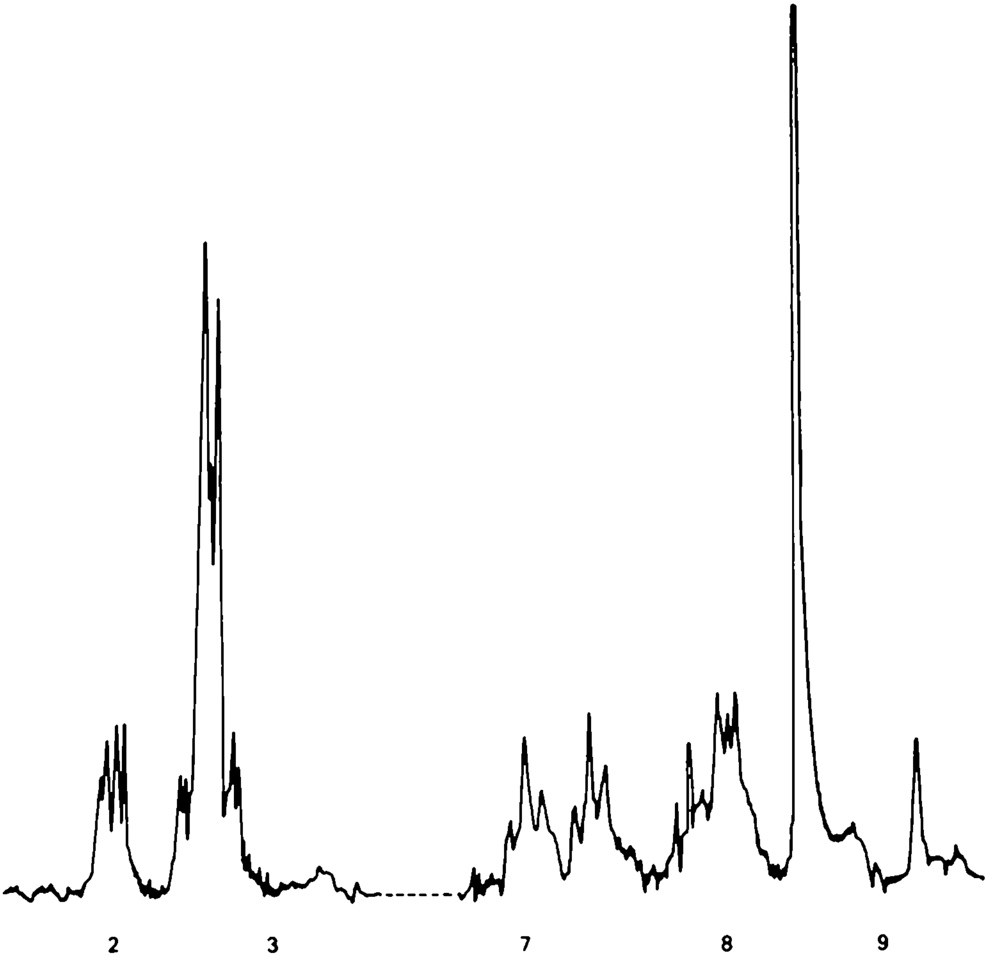

FIG. 1. The NMR spectrum at 60 Mc/s of 2-phenyl-4-(4'-t-butylphenyl)-5.6.7.8-tetrahydroquinoline in $CDCl_3$

For all the compounds containing a fused cyclohexeno-ring, the ring methylene groups were found at characteristic positions. The 8-$CH_2$ group absorbed at lowest field (6·54–6·55 τ for the pyrylium salts, 6·85–6·88 τ for the pyridines), and disclosed a triplet structure due to coupling with the adjacent 7-methylene group. The 5-position methylene, likewise a triplet, absorbed at 6·93–6·98 τ for the pyrylium salts and at 7·29–7·31 τ for the pyridines. The 6- and 7-methylenes formed unresolved multiplets centred near 7·9 τ for the pyrylium salts and 8·1 τ for the pyridines.

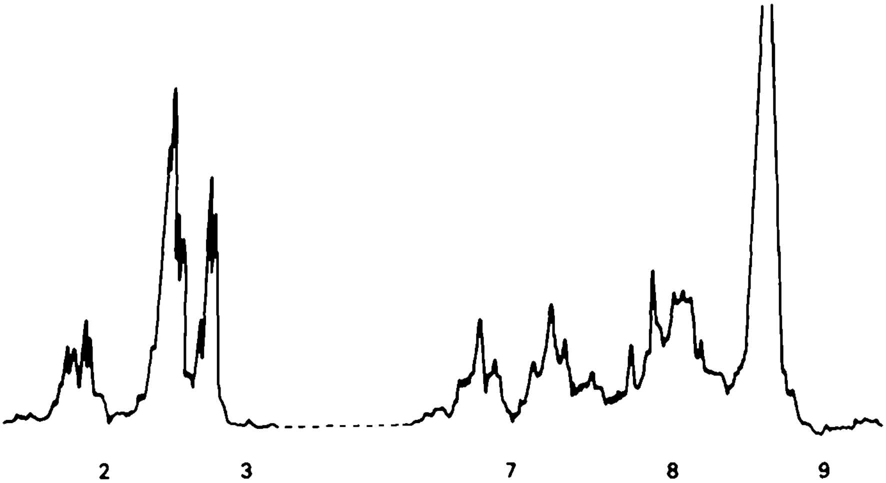

FIG. 2 The NMR spectrum at 60 Mc/s of 2-phenyl-4-(3',5'-di-t-butyl)-5,6,7,8-tetrahydroquinoline in $CDCl_3$.

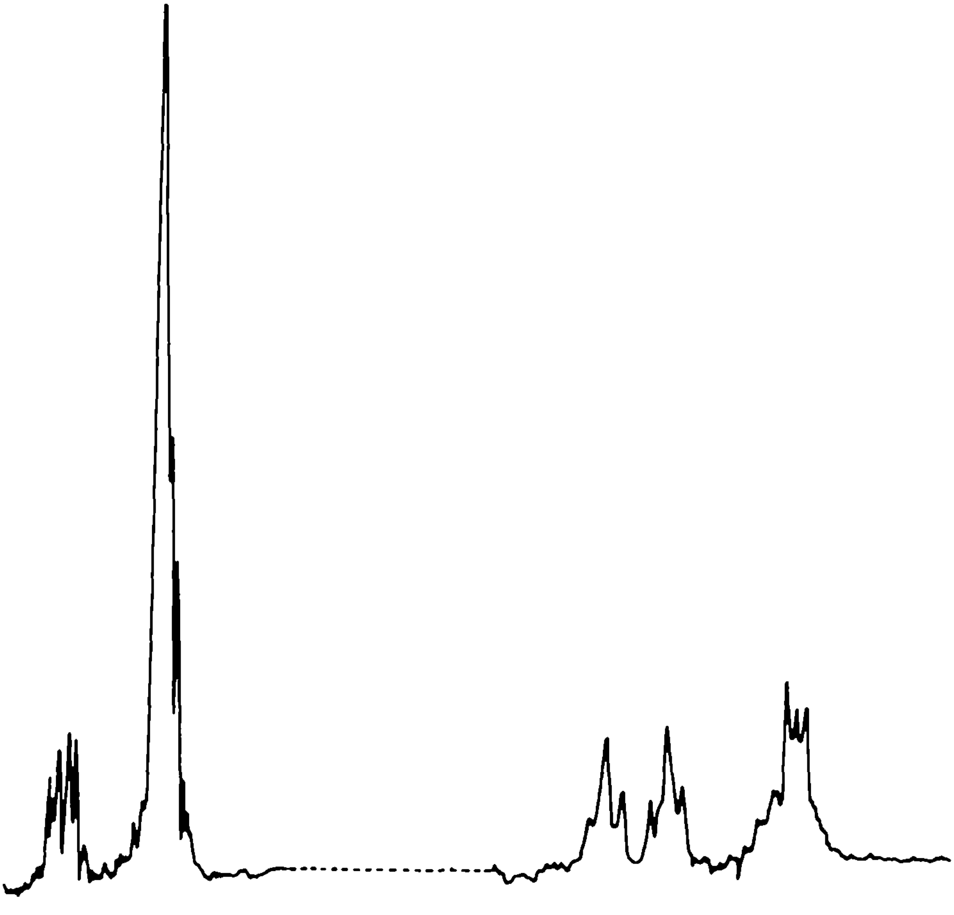

FIG. 3. The NMR spectrum at 60 Mc/s of 2,4-diphenyl-5,6,7,8-tetrahydroquinoline in $CS_2$.

The t-butyl groups showed as singlets in the range 8·54–8·66 τ for all the compounds. The singlet structure for the derivatives containing two t-butyl groups indicates that these groups are similarly placed.

The aromatic proton region is frequently complex, but several interesting features could be discerned therein. All the compounds disclosed a two-proton multiplet at low field, which was assigned to the *ortho*-protons of the 2-phenyl group. The general shape of the spin-coupling within this multiplet did not alter throughout the series, indicating the no t-butyl groups were substituted in the 2-phenyl ring. For the pyrylium salts, the singlet due to the 3-position hetero-ring proton was superimposed on this multiplet (cf. Ref. 8); for the pyridines this proton was found as a singlet at 2·5–2·6 τ (cf. for pyridine itself, the β-proton is quoted[9] at 2·4 τ).

The remaining protons of the 2-phenyl group, and the protons of the 4-phenyl group generally formed a more or less complex multiplet, centred at ca. 2·2 τ for the pyrylium salts and ca. 2·5 τ for the pyridines. However, in the di-t-butyl derivatives two-proton doublets were found at 2·45 τ ($J$ = 1·8 c/s) and 2·74 τ ($J$ = 1·6 c/s) for the pyrylium salt and the pyridine respectively. This can only be explained by 3′, 5′-substitution of the 4-phenyl group by t-butyl groups: the up-field chemical shift for the 2′- and 6′-protons is a consequence of the t-butyl group *para* to each of them, as found by Bovey *et al.*[10]

IR maxima for the pyrylium perchlorates are recorded in Table 2. The pyrylium ring bands are in agreement with those previously found.[11] The benzene ring vibrations indicate (a) the presence of a mono-substituted benzene ring in all cases and (b) the presence of a *para*-substituted benzene ring in compound VIII.

UV spectra (Table 3) confirm that the pyrylium salts (V, VI and VIII) all have the same chromophoric system as that of 2,4-diphenyl-6-methylpyrylium perchlorate.

## EXPERIMENTAL

M.ps are uncorrected. The IR spectra were recorded with a Jena UR-10, apparatus, UV and visible spectra with an Optica CF4 instrument, and NMR spectra with a Perkin-Elmer permanent magnet instrument operating at 60 Mc/s.

*Dehydrogenation and t-butylation of* 3-(2′-*oxocyclohexyl*)-1,3-*diphenylpropane*-1-*one*[12] (VII) *with t-butyl chloride and aluminium chloride.* Powdered $AlCl_3$ (25 g) was added with stirring at 0–10° to a suspension of the diketone (18 g) in dry t-butyl chloride (150 ml). Stirring was then continued for 4 hr (evolution of HCl) and the clear soln kept overnight. EtOH (50 ml) was cautiously added, and the mixture was extracted with cold 2% HClaq (3 × 70 ml). The combined aqueous extracts were treated with excess perchloric acid to yield an orange ppt of pyrylium perchlorates (12 g), m.p. 190–195°. Recrystallization from hot EtOH (50 ml) gave 2-*phenyl*-4-(4′-*t-butylphenyl*)-5,6,7,8-*tetrahydrobenzopyrylium perchlorate* as pale yellow prisms (7 g), m.p. 221°, by filtration after 15–20 min. (Found: C, 67·6; H, 6·3. $C_{25}H_{27}ClO_5$ requires: C, 67·7; H, 6·1%.)

The filtrate from the above recrystallization deposited, on longer standing and scratching, (3 g) which separated from EtOH as orange needles, m.p. 244°. This compound was characterized as the quinoline, see below.

2-*Phenyl*-4-(4′-*t-butylphenyl*)-5,6,7,8-*tetrahydroquinoline.* The pyrylium salt (0·5 g) was treated with ether (10 ml) and N $NH_4OH$ (8 ml). After complete dissolution, the ethereal soln was extracted with

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[8] A. T. Balaban, G. R. Bedford and A. R. Katritzky, *J. Chem. Soc.* 1646 (1964).

[9] Varian Spectra Catalogue I, No 96.

[10] F. A. Bovey, F. P. Hood, III, E. Pier and H. E. Weaver, *J. Am. Chem. Soc.* 87, 2060 (1965).

[11] A. T. Balaban, G. D. Mateescu and M. Elian, *Tetrahedron*, 18, 1083 (1962).

[12] C. F. H. Allen and H. R. Sallans, *Canad. J. Research*, 9, 574 (1933).

TABLE 2. IR SPECTRA MAXIMA (CM$^{-1}$) FOR PYRYLIUM PERCHLORATES

| Compound | Py-8a | Ph | Ph | Py-8b | Py-19a | Ph | Ph | Ph |
|---|---|---|---|---|---|---|---|---|
| VIII | 1619 | 1600 | 1585 | 1503 | 1480 | — | 781<br>730 | 685 |
| VI | 1627 | 1620<br>1612 | 1585 | 1510 | 1481 | 889<br>837 | 775 | 685 |
| V | 1614 | 1600 sh | 1580 | 1505 | 1470 | 880 | 781 | 689 |

sh = shoulder

TABLE 3. UV SPECTRAL MAXIMA (mμ) FOR PYRYLIUM PERCHLORATES

| Compound | AcOH Solvent[a] | | | | | | $CH_2Cl_2$ Solvent | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | $\lambda_{max}$ | log ε | $\lambda_{max}$ | log ε | $\lambda_{max}$ | log ε | | | | | | | | |
| VIII | 254 | 4·17 | 3·40[b] | | 368 | 4·41 | 256 | 4·13 | 266[b] | 3·94 | 339[b] | 4·14 | 377 | 4·41 |
| VI | 254 | 4·17 | | | 368 | 4·44 | 256 | 4·15 | 266[b] | 4·08 | | | 379 | 4·43 |
| V | | | | | | | 256 | | 266[b] | | | | 376 | |
| 2,4-Diphenyl-6-methyl-pyrylium perchlorate | 254 | 4·16 | 338 | 4·37 | 374 | 4·46 | 248 | 4·30 | 346 | 4·32 | | | 380 | 4·42 |

[a] Except last compound which is in $H_2O$. [b] Shoulder.

10% HCl aq. The aqueous layer was treated with NaOH aq and the ppt recrystallized to yield the *quinoline* (68%) as long rods, m.p. 139° (from aqueous EtOH). (Found: C, 88·2; H, 8·2; N, 4·1. $C_{25}H_{27}N$ requires: C, 87·9; H, 8·0; N, 4·1%.) The *picrate* formed needles, m.p. 189° (from dilute EtOH). (Found: C, 65·4; H, 5·3; N, 10·1. $C_{31}H_{30}N_4O_7$ requires: C, 65·3; H, 5·3; N, 9·8%.)

*2-Phenyl-4-(3',5'-di-t-butylphenyl)-5,6,7,8-tetrahydroquinoline* was prepared similarly as prisms, m.p. 195–197° (from EtOH). (Found: C, 87·0, 87·6; H, 8·7; N, 3·4. $C_{29}H_{35}N$ requires: C, 87·6; H, 8·9; N, 3·5%.)

*2,4-Diphenyl-5,6,7,8-tetrahydroquinoline.* Compound VII (3·2 g) and chalcone (2·2 g) were heated with $H_2SO_4$ (4 ml) at 100° for 1 hr with stirring, then EtOH (10 ml) was added, followed by excess of perchloric acid. Ether (25 ml) was added to complete the precipitation, and the sparingly soluble orange-coloured VIII was recrystallized from EtOH as needles, m.p. 222° (lit.,[12] 214°). (Found: C, 65·5; H, 5·0. Calc. for $C_{21}H_{19}ClO_5$: C, 65·2; H, 5·0%.) This perchlorate on treatment with ammonia as above afforded the *quinoline* as short prisms, m.p. 106–107° (from MeOH). (Found: C, 88·3; H, 6·9; N, 4·8. $C_{21}H_{19}N$ requires: C, 88·4; H, 6·7; N, 4·9%.) The *picrate* formed rhombic plates with diagonal ribs, m.p. 200°. (Found: C, 63·2; H, 4·6; N, 11·1. $C_{27}H_{22}N_4O_7$ requires: C, 63·0; H, 4·3; N, 10·9%.)

*Oxidation of 2,4-diaryl-5,6,7,8-tetrahydrobenzopyrylium perchlorates.* $KMnO_4$ (4 g) in water (100 ml) was refluxed with stirring with 2-phenyl-4-t-butylphenyl-5,6,7,8-tetrahydrobenzopyrylium perchlorate (0·5 g) for 2 hr. EtOH was added to destroy excess $KMnO_4$, and the filtered soln was acidified with HCl to yield *p*-t-butylbenzoic acid, m.p. 164–166° (from n-heptane) (lit.,[13] 163–165°). (Found: C, 74·4; H, 8·1. Calc. for $C_{11}H_{11}O_2$: C, 74·1; H, 7·9%.) The NMR spectrum (in $CCl_4$) showed the $CMe_3$ band at 8·67 τ, the COOH peak at −2·65 τ, and the AA'BB' quadruplet of the four aromatic protons at 1·98, 2·60 τ (*J* = 8 c/s).

Similar oxidation of 2,4-diphenyl-5,6,7,8-tetrahydrobenzopyrylium perchlorate gave only benzoic acid (m.p. and mixed m.p.) on acidification of the aqueous soln and extraction with ether.

*Attempted t-butylation of 2,4-diphenyl-5,6,7,8-tetrahydrobenzopyrylium perchlorate.* Powdered $AlCl_3$ (6 g) was slowly added to a suspension of the perchlorate (3 g) in t-butyl chloride (60 ml). HCl was evolved, and the perchlorate mostly dissolved to a red soln. After heating at 100° for 3 hr, EtOH was added with cooling, and the filtered soln ether-extracted. Treatment of the aqueous-ethanolic layer with perchloric acid gave only the starting perchlorate.

*Dehydrogenation and t-butylation of 1,3,5-triphenyl-1,5-pentane dione.*[14] Powdered $AlCl_3$ (6 g) was added to a suspension of diketone (7 g) in t-butyl chloride (60 ml) with stirring and cooling. An insoluble complex formed. The mixture was refluxed (water-bath) with a stirring for 2 hr, then EtOH (60 ml) was introduced and the mixture was again refluxed till a clear soln resulted. Ether (100 ml) was then added and the whole extracted with 2% HCl aq (2 × 30 ml). The combined aqueous layers were treated with perchloric acid, and the oily ppt was recrystallized successively from EtOH and AcOH, yielding *2,6-diphenyl-4-t-butylphenylpyrylium perchlorate* which formed yellow needles, m.p. 245°. (Found: C, 69·6; H, 5·5. $C_{27}H_{25}ClO_5$ requires: C, 69·8; H, 5·4%.)

Reaction with aqueous ammonia and ether converted this perchlorate into 2,6-diphenyl-4-(4'-t-butylphenyl)pyridine which was characterized as a *picrate*, yellow conglomerates, m.p. 178°. (Found: C, 66·8; H, 4·9; N, 9·7. $C_{33}H_{28}N_4O_7$ requires: C, 66·9; H, 4·8; N, 9·5%.)

*Acknowledgement*—This work was carried out during the tenure (by B.M.S.) of an S.R.C. Advanced Course Studentship.

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[13] J. R. B. Boocock and W. J. Hickinbottom, *J. Chem. Soc.* 2587 (1961); C. S. Marvel *et al.*, *J. Am. Chem. Soc.* **66**, 914 (1944); N. Mori, *Bull. Chem. Soc. Japan*, **34**, 1567 (1961); R. L. Huang and Oon-Keong Yeo, *J. Chem. Soc.* 3190 (1959).

[14] St. von Kostanecki and G. Rossbach, *Ber. Dtsch. Chem. Ges.* **29**, 1488 (1896).