

Competitive Anion Formation in Pulegone [*p*-Menth-4(8)-en-3-one] Synthesis of Phenylmethylenepyrans

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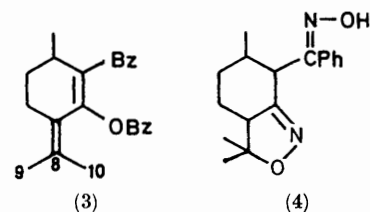
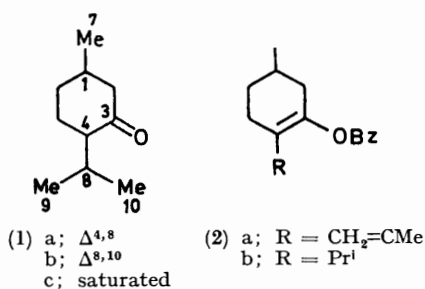
Treatment of (+)-pulegone [*p*-menth-4(8)-en-3-one] with strong base generates various anions which can be quenched with benzoyl chloride. Enolization towards C-4 followed by acylation leads to *p*-mentha-3,8(10)-dien-3-yl benzoate (2a). 2-Benzoyl-*p*-mentha-2,4(8)-dien-3-yl benzoate (3) results from acylation of an enol generated at position 2. The 9,10-dianion reacts with benzoyl chloride to give a diketone, which by cyclization affords 4-benzoylmethylene-5,6,7,8-tetrahydro-7-methyl-2-phenyl-4*H*-chromen (6a). Compound (6a) was identified by an independent synthesis involving treatment of ethyl 4-methyl-2-oxocyclohexanecarboxylate with benzoylmethylene(triphenyl)phosphorane. In addition to 5,6,7,8-tetrahydro-7-methylflavone (9a), 2-(2,6-diphenyl-4*H*-pyran-4-ylidene)-5-methylcyclohexanone (5a) and its isomer (6a) are also formed in equal yields in this reaction.

TREATMENT of (+)-pulegone (1a) with sodium *t*-pentylate in benzene solution in the presence of benzoyl chloride afforded a complex mixture. Initial separation of the products was effected by fractional vacuum distillation which, besides unchanged starting material and a small amount of *t*-pentyl benzoate,¹ furnished fractions (a) and (b), and a residue (c).

Fraction (a) was a slightly yellow liquid identified as *p*-mentha-3,8(10)-dien-3-yl benzoate (2a) on the basis of the following evidence. The u.v. absorption pattern (see Experimental section) is as expected for a heteroannular diene.² Its high intensity indicates the summation of diene and benzoate chromophores. The n.m.r. spectrum shows a signal at δ 1.83 p.p.m. (3H, vinylic 9-H₃) and a doublet for the secondary methyl group at C-1. The only olefinic proton signal is that at δ 4.87 p.p.m. (10-H₂). The mass spectrum shows a molecular ion at *m/e* 256. Whereas alkaline hydrolysis of the benzoate (2a) regenerated a mixture of pulégone (1a) and isopulegone (1b), hydrogenation in the presence of Raney nickel afforded *p*-menth-3-en-3-yl benzoate (2b), identical with a sample prepared directly from

(3) was assigned. Compound (3) exhibits three u.v. absorption maxima in agreement with its highly conjugated nature (see Experimental section). The n.m.r. spectrum is devoid of olefinic signals but shows the presence of two non-equivalent vinylic methyl groups, δ 1.73 (C-9) and 1.76 p.p.m. (C-10). The mass spectrum shows the molecular ion at *m/e* 360. Whereas basic hydrolysis of compound (3) under mild conditions regenerated starting material, more drastic treatment yielded only pulégone (1a).

Treatment of the β -keto-ester (3) with hydroxylamine acetate afforded the isoxazoline derivative (4), characterized by its spectroscopic properties. The mass spectrum shows the molecular ion at *m/e* 286. The absence of a C-8 vinylic methyl signal in the n.m.r. spectrum and the appearance of *gem*-dimethyl signals at δ 1.50 and 1.65 p.p.m. indicates that cyclization has taken place at C-8. In addition, the OH signal at 10.9 p.p.m. (readily exchanged with D₂O) integrates for one proton only. The isoxazoline derivative (4) presumably arises *via*



(+)-menthone (1c). The nature of the C-8 double bond in structure (2a) was also confirmed by ozonization, which gave formaldehyde, identified as its 2,4-dinitrophenylhydrazone and dimedone derivatives.

When left at room temperature, fraction (b) afforded a crystalline material to which the β -keto-ester structure

initial formation of the benzoyl oxime, followed by hydrolysis of the enol ester linkage. Subsequent reaction of the cyclohexanone conjugated carbonyl group with a second molecule of hydroxylamine then affords structure (4) by internal cyclization.³ The stereochemistry of compound (4) was not established, but in view of the usual behaviour of pulégone derivatives, attack at C-8 would be expected to occur from the β -side.

In contrast to the enol benzoate (2a) obtained *via* enolization towards C-4, the β -keto-ester (3) results

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¹ A. Zaki, *J. Chem. Soc.*, 1928, 983.

² A. E. Gillam and E. S. Stern, 'An Introduction to Electronic Absorption Spectroscopy in Organic Chemistry,' Arnold, London, 1957.

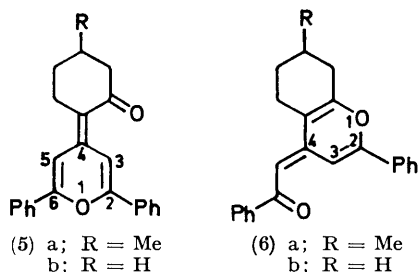
³ See A. H. Blatt, *J. Amer. Chem. Soc.*, 1931, **53**, 1133; S. Kaufmann, L. Tökes, J. W. Murphy, and P. Crabbé, *J. Org. Chem.*, 1969, **34**, 1618; K. Kotera, Y. Takano, A. Matsuura, and K. Kitahonoki, *Tetrahedron*, 1970, **26**, 539, and references cited therein.

from an initial attack of an anion formed at position 2⁴ on benzoyl chloride, followed by esterification of the 3-keto-group, enolized towards C-2. These results conclusively demonstrate the existence of two possible enol forms from pulegone (1a) under these reaction conditions.⁵ Surprisingly, although compound (3) is in fact an enol ester of a β -diketone, as confirmed by the formation of the oxime (4), the expected⁵ tertiary β -diketone, *i.e.* the 4-aryl ketone, was not isolated.

Addition of ether to the distillation residue (c) yielded yellow needles, analysis of which (confirmed by *m/e* 342) corresponded to an empirical formula $C_{24}H_{22}O_2$. This substance presents three intense u.v. maxima and its i.r. spectrum shows a strong band at 1670 cm^{-1} , indicative of a conjugated carbonyl group, besides aromatic absorption and an intense band at 1525 cm^{-1} , attributed to a 4*H*-pyran ring.^{6,7} The n.m.r. spectrum shows two characteristic one-proton signals, at δ 6.19 and 9.0 p.p.m., besides those of the secondary methyl group and ten aromatic protons. None of these protons exchanged with D_2O at room temperature.

Initially, the signal at 9 p.p.m. was attributed to an aldehydic proton. However, all attempts to identify an aldehyde group failed (no reaction with dimedone, silver nitrate, *etc.*). Permanganate oxidation gave *ca.* 30% of benzoic acid as the only identified product. The material was recovered unchanged after either treatment under usual room temperature acetylation conditions or attempted saponification.

On the basis of these data the diphenylpyranylidene-cyclohexanone structure (5a) was tentatively assigned



to this product, although the isomeric structure (6a) would also be compatible with the physical and chemical properties.

A synthesis of compounds (5a) and (6a) was then contemplated.⁸ The sequence chosen was based on reports of the formation of 2,6-diphenylpyrans in

* In a previous study of similar compounds (A. T. Balaban, P. T. Frangopol, A. R. Katritzky, and C. D. Nenitzescu, *J. Chem. Soc.*, 1962, 3889), the authors attributed the 7.6 p.p.m. signal to CO·CH= and the 5.65 p.p.m. signal to the C-3 olefinic proton of the 4*H*-pyran ring. In the light of our data, it seems that these assignments should be reversed.

⁴ For a recent example of enolization towards C-2 in pulegone see Y. Maroni-Barnaud, P. Maroni, and F. Ghozland, *Compt. rend.*, 1969, 268C, 1697.

⁵ J. M. Conia, *Compt. rend.*, 1953, 237, 910; *Bull. Soc. chim. France*, 1954, 943.

⁶ K. Nakanishi, 'Infrared Absorption Spectroscopy,' Holden-Day, San Francisco, 1964, p. 204.

⁷ J. Wolinsky and H. Schoen Hauer, *J. Org. Chem.*, 1969, 34, 3169.

reactions of arylmethylenetriphenylphosphoranes with ketens generated from β -keto-esters.⁹

A pilot reaction performed with ethyl 2-oxocyclohexanecarboxylate (7b) and benzoylmethylene(triphenyl)phosphorane (8) gave, besides triphenylphosphine oxide, three substances instead of the expected two products.⁹ The first a white crystalline material, M^+ 226, was shown to have the empirical formula $C_{15}H_{14}O_2$. The u.v. and n.m.r. properties (see Experimental section) are in agreement with the 5,6,7,8-tetrahydroflavone structure (9b).¹⁰ Besides the aromatic signals at δ *ca.* 7.4–7.8 p.p.m., the n.m.r. spectrum shows a sharp singlet at 6.7 p.p.m. (vinylic 3-H).¹¹

The 2-(2,6-diphenyl-4*H*-pyran-4-ylidene)cyclohexanone structure (5b) was assigned to the second substance, a yellow crystalline material, $C_{23}H_{20}O_2$, M^+ 328. The n.m.r. spectrum shows signals for eight alicyclic protons between δ 1.6 and 2.75 p.p.m., and the olefinic proton at C-5 of the pyran gives rise to a doublet¹² by coupling with the C-3 proton, at δ 6.65 p.p.m. (J *ca.* 2 Hz). A second doublet¹² at 8.9 p.p.m. (J *ca.* 2 Hz) is attributed to the pyran vinylic proton at C-3, deshielded by the cyclohexanone carbonyl group.

Structure (6b) is assigned to the third compound, also a yellow crystalline material, shown by analytical and mass spectral data to be an isomer of (5b). Its n.m.r. spectrum shows signals at δ 6.2 (CO·CH=) and 9.0 p.p.m. (C-3 proton, deshielded by the carbonyl grouping). The coupling constant between these protons is very small (0.5 Hz), as expected in such cases.¹³ *

To check that isolation of the product (6b) did not simply reflect the instability of the tetrahydroflavone, a sample of compound (9b) was subjected to the foregoing alkylation conditions with the phosphorane derivative (8), and was recovered unchanged.

These results conclusively demonstrate the existence of three discrete intermediates during the reaction of the ester (7b) with the phosphorane (8), two of which give rise to the isomeric cyclization products (5b) and (6b). A careful examination of the mechanism of the reaction indicates that under such experimental conditions, one could in fact anticipate the formation of three distinct products.⁸

Accordingly, a similar reaction between ethyl 4-methylcyclohexanecarboxylate (7a) and the phosphorane (8) was attempted. In addition to triphenylphosphine oxide, in this case also three products

⁸ For a preliminary communication and a reaction mechanism see P. Crabbé, E. Díaz, J. Haro, G. Pérez, D. Salgado, and E. Santos, *Tetrahedron Letters*, 1970, 5069.

⁹ H. Strzelecka and M. Simalty-Siemiatycki, *Compt. rend.*, 1965, 260, 3989; M. Simalty, H. Strzelecka, and M. Dupré, *ibid.*, 1968, 266C, 1306; H. Strzelecka, M. Dupré, and M. Simalty, *Tetrahedron Letters*, 1971, 617.

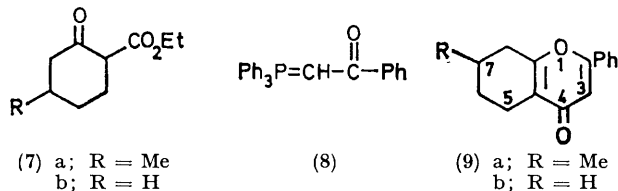
¹⁰ R. J. Light and C. R. Hauser, *J. Org. Chem.*, 1960, 25, 538.

¹¹ T. J. Mabry, J. Kagan, and H. Rösler, 'Nuclear Magnetic Resonance Analysis of Flavonoids,' The University of Texas Publications, No. 6418, Austin, 1964.

¹² Coupling between the olefinic protons at C-3 and C-5 in a γ -pyrone has been reported: J. Jonas, W. Derbyshire, and H. S. Gutowsky, *J. Phys. Chem.*, 1965, 69, 1; see also ref. 13.

¹³ M. Dupré, M. L. Filleux-Blanchard, M. Simalty, and H. Strzelecka, *Compt. rend.*, 1969, 268C, 1611.

could be separated by chromatography. As anticipated, the first white crystalline compound shows spectral data (see Experimental section) as expected for the 7-methyltetrahydroflavone (9a). The physical pro-



erties of the second substance, a yellow crystalline product, fully support the 2,6-diphenylpyran structure (5a). The third product was the phenylpyran (6a), identical (except for optical properties) with the yellow substance isolated from the reaction of pulegone (1a) with benzoyl chloride. This establishes its structure unambiguously. Besides the typical i.r. and u.v. properties (see Experimental section), the vinyl proton signal at δ 9.0 p.p.m. in the n.m.r. spectrum of (6a) allows one to exclude the alternative structure (5a). The strong deshielding of the vinylic proton at C-3 in compound (6a), attributed to the carbonyl group, thus establishes the configuration of the C-4 double bond. Finally, although isomeric, compounds (5a) and (6a) show markedly different fragmentation patterns under electron impact (see Experimental section).

With the structure (6a) firmly established, it seems that in the reaction of pulegone (1a) with benzoyl chloride in strong alkaline medium, condensation of a 9,10-dianion with the benzoyl group occurs, followed by cyclization of the resulting 1,5-diketone, involving the enol form of the cyclohexanone.^{7,8}

EXPERIMENTAL

Microanalyses were performed by Dr. A. Bernhardt, Mühlheim, Germany. M.p.s were determined with a Kofler-Thomas apparatus. Optical rotations were taken for solutions in chloroform between 16 and 22° (1 dm tube). I.r. spectra were taken with a Perkin-Elmer model 21, instrument (NaCl prism). U.v. spectra were obtained with a Beckman DU spectrophotometer. Unless otherwise stated, n.m.r. spectra were recorded at 60 MHz for 5–8% w/v solutions in deuteriochloroform containing tetramethylsilane as internal reference. Coupling constants are accurate to ± 1 Hz. The mass spectra were obtained with an Atlas CH-4 spectrometer.

Reaction of (+)-Pulegone (1a) with Benzoyl Chloride.—(+)-Pulegone (1a) (Givaudan Corp., Clifton, New Jersey) (61 g) was dissolved in anhydrous benzene (220 ml). 2.4 N-Sodium t-pentylate in benzene solution (0.2 mol) was then added with stirring. The mixture was stirred for 20 min at room temperature, during which time it turned orange-red. Freshly distilled benzoyl chloride (59.2 g, 0.2 mol) dissolved in anhydrous benzene (340 ml) was added with vigorous agitation. When the mixture had cooled to room temperature, aqueous 20% hydrochloric acid (500 ml) was added. The organic layer was separated,

washed with 15% sodium carbonate-water and then with water until neutral, dried, filtered, and concentrated. The residue was distilled under vacuum, yielding unchanged pulegone (31%, 24.6 g) and four other fractions: (i) a volatile fraction (7%), b.p. 125–130° at 22 mmHg, λ_{\max} 229 nm (log ϵ 4.02), ν_{\max} 1725, 1610, 1580, and 710 cm^{-1} , δ 0.96 (t, J 7 Hz, CH_3 of Et), 1.52 (2 \times Me), 1.9 (q, J 7 Hz, CH_2 of Et), and 7.2–8.0 p.p.m. (5 aromatic H). That this liquid was t-pentyl benzoate was confirmed by g.l.c., i.r., and n.m.r. comparison with an authentic sample.¹ The 8-benzoyloxymenthone structure was previously⁸ assigned in error to this distillation fraction, which was contaminated with (+)-pulegone (1a) so that the mass spectrum gave two major peaks, m/e 122 (benzoic acid) and 152 (pulegone).

(ii) Fraction (a) consisted of the pale yellow *p*-mentha-3,8(10)-dien-3-yl benzoate (2a) (37%), b.p. 85–87° at 0.2 mmHg, $[\alpha]_D +44^\circ$, λ_{\max} 231 nm (log ϵ 4.23), ν_{\max} 1730, 1120, and 710 cm^{-1} , δ 1.03 (d, J 6 Hz, 1-Me), 1.83 (9-Me), 4.87 (C=CH₂), and 7.45 and 8.05 p.p.m. (5 aromatic H), m/e 256 (M^+) (Found: C, 79.65; H, 7.7; O, 12.65. $\text{C}_{17}\text{H}_{20}\text{O}_2$ requires C, 79.65; H, 7.85; O, 12.5%).

(iii) Fraction (b) consisted of a coloured viscous liquid (15%), b.p. 126–150° at 0.2 mmHg. At room temperature, white crystals were obtained which furnished 2-benzoyl-*p*-mentha-2,4(8)-dien-3-yl benzoate (3), m.p. 110–111° (from ether-hexane), $[\alpha]_D -149^\circ$, λ_{\max} 237, 284, and 308 nm (log ϵ 4.46, 3.79, and 3.80), ν_{\max} 1730, 1650, 1270, and 710 cm^{-1} , δ 1.08 (d, J 7 Hz, 1-Me), 1.73 (9-Me), 1.76 (10-Me), and 7–8 p.p.m. (10 aromatic H), m/e 360 (M^+) (Found: C, 79.95; H, 6.75; O, 13.45. $\text{C}_{24}\text{H}_{24}\text{O}_3$ requires C, 79.95; H, 6.7; O, 13.3%).

(iv) The distillation residue constituted fraction (c); when ether was added to this residue and the flask was left overnight, long deep yellow crystals were produced (9% of the total reaction mixture), which afforded 4-benzoylmethylene-5,6,7,8-tetrahydro-7-methyl-2-phenyl-4H-chromen (6a), m.p. 166–167° (from chloroform-hexane), $[\alpha]_D +85^\circ$, λ_{\max} 233, 295, and 408 nm (log ϵ 4.18, 4.19, and 4.50), ν_{\max} 1670, 1600, 1525, 710, and 690 cm^{-1} , δ 1.10 (d, J 7 Hz, Me), 6.19 (d, J 0.5 Hz, CO-CH=), 9.0 (d, J 0.5 Hz, 3-H), and 7.4–8.0 p.p.m. (10 aromatic H), m/e 342 (M^+) (Found: C, 84.15; H, 6.35; O, 9.5. $\text{C}_{24}\text{H}_{22}\text{O}_2$ requires C, 84.15; H, 6.45; O, 9.35%).

Catalytic Hydrogenation of the Enol Benzoate (2a).—The ester (2a) (2 g) in ethanol (25 ml) was reduced with hydrogen over Raney nickel (uptake 170 ml in 3 h) to give *p*-mentha-3-en-3-yl benzoate (2b), b.p. 89° at 0.3 mmHg, $[\alpha]_D +47^\circ$, λ_{\max} 231 and 270 nm (log ϵ 4.14 and 3.60), ν_{\max} 1720, 1685, and 710 cm^{-1} , δ 0.92 (d, J 7 Hz, 1-, 9-, and 10-Me), 2.75 (8-H), and 7.45–8.05 p.p.m. (5 aromatic H) (Found: C, 78.8; H, 8.5. $\text{C}_{17}\text{H}_{22}\text{O}_2$ requires C, 79.05; H, 8.6%), identical with material prepared from (+)-menthone (1c) and benzoyl chloride in benzene in the presence of a trace of toluene-*p*-sulphonic acid.

Hydrolysis of the Enol Benzoate (2a).—Acidic hydrolysis provided only (+)-pulegone (1a), in almost quantitative yield. Basic hydrolysis (1% KOH in ethanol) yielded a mixture of pulegone (1a) (70%) and isopulegone (1b) (30%).

Attempted Hydrolysis of the β -Keto-ester (3).—Treatment with ethanolic 10% sodium hydrogen carbonate at room temperature for 5 days produced no change. Treatment with methanolic 10% sodium hydrogen carbonate at reflux temperature for a short time yielded 80% (+)-pule-

gone (1a). Other reaction conditions also provided (1a) in almost quantitative yields.

3,3a,4,5,6,7-Hexahydro-7-(α -hydroxyiminobenzyl)-3,3,6-trimethyl-2,1-benzisoxazole (4).—Sodium acetate (1 g) and hydroxylamine hydrochloride (0.944 g) dissolved in ethanol (20 ml) were heated at reflux temperature. After cooling, the sodium chloride which precipitated was filtered off. To the clear solution of hydroxylamine acetate, the keto-ester (3) (1 g) in ethanol (25 ml) was added. The mixture was refluxed gently for 70 h. The solution, concentrated to half its volume, was then poured into ice-water. The product which precipitated was filtered off, washed, and dried to yield the *oxime* (4) (420 mg), m.p. 313—315° (from ethanol), $[\alpha]_D +143^\circ$, λ_{\max} 282 nm (log ϵ 3.82), ν_{\max} 3500, 1580, 960, 800, 750, and 700 cm^{-1} , δ 1.0 (d, J 7 Hz, 6-Me), 1.50 (3-Me), 1.65 (3-Me), 3.45 (3a-H), 3.60 (1-H), 7.25—7.9 (5 aromatic H), and 10.9 p.p.m. (N-OH), m/e 286 (M^+) and 285 ($M^+ - H$) (Found: C, 71.1; H, 7.6; N, 9.6. $\text{C}_{17}\text{H}_{22}\text{N}_2\text{O}_2$ requires C, 71.3; H, 7.75; N, 9.8%).

Potassium Permanganate Oxidation of the Chromen (6a).—Compound (6a) (0.05 g) in glacial acetic acid (50 ml) was treated with potassium permanganate (2.5 g) in water. The acidic fraction was separated under alkaline conditions. Neutralization, washing with water, and isolation by the usual procedure gave benzoic acid (150 mg), m.p. 120—122°. The neutral fraction did not lead to any identified material.

Ozonization of the Enol Benzoate (2a).—Compound (2a) (1 g) in chloroform (5 ml) was treated at -30° with ozone for 1.5 h. After passing through the chloroform solution the stream of gas was trapped in ethanol containing dimedone. Crystalline material precipitated was filtered off and recrystallized (m.p. 189°). It was identical (mixed m.p.) with an authentic sample of the dimedone condensation compound of formaldehyde. In a similar manner, formaldehyde was identified through its 2,4-dinitrophenylhydrazone, m.p. 165°. Hydrolysis of the ozonolysis product with water was followed by extraction, leading to benzoic acid (0.3 g), m.p. 120—121°, identified by comparison with an authentic sample.

Reaction of Ethyl 4-Methylcyclohexanecarboxylate (7a) with Benzoylmethylene(triphenyl)phosphorane (8).—To a solution of the ester (7a)¹⁴ (1.84 g) in anhydrous xylene (150 ml), the phosphorane (8) (7.6 g)¹⁵ was added. The mixture was refluxed gently under nitrogen with stirring for 10 days. The reaction was followed by t.l.c. and stopped when all the β -keto-ester (7a) had reacted. The mixture was cooled to room temperature and concentrated under reduced pressure to half its volume. The crystalline material [unchanged (8)] was filtered off and washed with ether. The organic solution was evaporated to dryness and the residue was dissolved in benzene. Chromatography over Florisil (800 g) gave, on elution with benzene, the phenylchromen (6a) (8%), m.p. 167—168° (from acetone-ether), m/e 342 (M^+), 299 ($M^+ - \text{C}_3\text{H}_7$), 265 ($M^+ - 77$), 237 ($M^+ - 105$), 105 ($\text{C}_6\text{H}_5\text{-C}\equiv\text{O}^+$), and 77 (C_6H_5^+), identical (except for a slight difference in m.p. and for the absence of optical activity), with the substance obtained from (+)-pulegone (1a) (i.r., u.v., n.m.r., and mass spectra and t.l.c.).

Further elution of the column with benzene-chloroform (9:1) furnished a product which was purified by pre-

parative t.l.c. on silica gel. 2-(2,6-Diphenyl-4H-pyran-4-ylidene)-5-methylcyclohexanone (5a) (9%), recrystallized from acetone-ether, had m.p. 172—173°, λ_{\max} 221, 244, 280—285sh, 306—308, and 408 nm (log ϵ 4.30, 4.17, 4.05, 4.19, and 4.38), ν_{\max} 1660, 1610, 1580, 1500, and 690 cm^{-1} , δ 1.02 (d, J 6 Hz, 5-Me), 6.65 (d, J 2 Hz, pyran 5-H), 7.3—8.0 (10 aromatic H), and 8.9 p.p.m. (d, J 2 Hz, pyran 3-H), m/e 342 (M^+), 299 ($M^+ - \text{C}_3\text{H}_7$), 259 (base peak, $M^+ - \text{C}_5\text{H}_7\text{O}$), 105 ($\text{C}_6\text{H}_5\text{-C}\equiv\text{O}^+$), and 77 (C_6H_5^+) (Found: C, 84.35; H, 6.5; O, 9.2. $\text{C}_{24}\text{H}_{22}\text{O}_2$ requires C, 84.15; H, 6.45; O, 9.35%).

Elution of the column with benzene-chloroform (8:2) afforded white crystalline 5,6,7,8-tetrahydro-7-methylflavone (9a) (59%), m.p. 134—135° (from benzene-hexane), λ_{\max} 229 and 274—275 nm (log ϵ 4.15 and 4.40), ν_{\max} 1670, 1630, and 1600 cm^{-1} , δ 1.1 (d, J 6 Hz, 7-Me), 6.7 (3-H), and 7.45—7.75 p.p.m. (5 aromatic H), m/e 240 (M^+) (Found: C, 80.1; H, 6.9; O, 13.0. $\text{C}_{18}\text{H}_{16}\text{O}_2$ requires C, 79.95; H, 6.7; O, 13.3%).

Finally, elution with benzene-chloroform (2:8) gave triphenylphosphine oxide (0.53 g) (m.p. 149—152°) and the phosphorane (8) (3.12 g) (m.p. 181°).

Reaction of Ethyl Cyclohexanecarboxylate (7b) with Benzoylmethylene(triphenyl)phosphorane (8).—To a solution of the ester (7b)¹⁴ (2.55 g) in anhydrous xylene (110 ml), the phosphorane (8)¹⁵ (11.4 g) was added. The mixture was heated at reflux temperature, under nitrogen, for 8 days. After work-up as before the crude material was chromatographed over Florisil.

Elution with benzene gave a mixture of two yellow compounds, separated by preparative silica gel t.l.c. (i) 4-Benzoylmethylene-5,6,7,8-tetrahydro-2-phenyl-4H-chromen (6b) (8%) had m.p. 130—131° (from acetone-ether) λ_{\max} 234, 294, and 408 nm (log ϵ 4.18, 4.19, and 4.50), ν_{\max} 1660, 1590, 1520, 715, and 690 cm^{-1} , δ 6.2 (d, J 0.5 Hz, CO-CH=), 7.35—8.1 (10 aromatic H), and 9.0 p.p.m. (d, J 0.5 Hz, 3-H), m/e 328 (M^+) (Found: C, 83.95; H, 6.1; O, 9.95. $\text{C}_{23}\text{H}_{20}\text{O}_2$ requires C, 84.1; H, 6.15; O, 9.75%). (ii) 2-(2,6-Diphenyl-4H-pyran-4-ylidene)cyclohexanone (5b) (14%) had m.p. 174—175° (from acetone-ether) λ_{\max} 221, 244, 280—284sh, 308, and 408 nm (log ϵ 4.28, 4.17, 4.06, 4.19, and 4.38), ν_{\max} 1650, 1600, 1575, 1500, 695, and 680 cm^{-1} , δ 6.65 (d, J 2 Hz, pyran 5-H), 7.3—8.0 (10 aromatic H), and 8.9 p.p.m. (d, J 2 Hz, pyran 3-H), m/e 328 (M^+) (Found: C, 84.05; H, 6.15; O, 9.8. $\text{C}_{23}\text{H}_{20}\text{O}_2$ requires C, 84.1; H, 6.15; O, 9.75%).

Further elution of the column, with chloroform, gave 5,6,7,8-tetrahydroflavone (9b)¹⁰ (55%), m.p. 124—125°, λ_{\max} 229 and 274—275 nm (log ϵ 4.17 and 4.41), ν_{\max} 1660, 1625, and 690 cm^{-1} , δ 6.7 (3-H) and 7.4—7.8 p.p.m. (5 aromatic H), m/e 226 (M^+) (Found: C, 79.45; H, 6.35; O, 14.2. Calc. for $\text{C}_{15}\text{H}_{14}\text{O}_2$: C, 79.6; H, 6.25; O, 14.15%).

Triphenylphosphine oxide (3.6 g) and the phosphorane (8) (1.8 g) were identified in the final chromatography fractions.

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