1,5-Hydride Shifts in Acyclic Systems Containing αβ-Unsaturated Ketones and *p*-Methoxyphenyl Groups

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Acid-catalysed rearrangement of 8-(*p*-hydroxyphenyl)oct-3-en-2-one (4) to [2-(*p*-hydroxyphenyl)cyclohexyl] methyl ketone (10) is shown to involve an intramolecular hydride shift by deuterium labelling: a similar rearrangement is observed for 8-(*p*-hydroxyphenyl)-5,5-dimethyloct-3-en-2-one (3) and its aromatic methyl ether (2) but no analogous products could be isolated from 7-(*p*-methoxyphenyl)hept-3-en-2-one (18) or 7,7-bis-(*p*-methoxyphenyl)hept-3-en-2-one (19) under the same reaction conditions.

INTRAMOLECULAR 1,*n* ($n > 2$) hydride transfer is a common reaction in medium ring and certain polycyclic systems.[1] It is likely that there is an optimum distance between transfer source and terminus in such compounds. The importance, if any, of stereoelectronic factors, which are known to be important in 1,2-hydride shifts has not been assessed.[2]

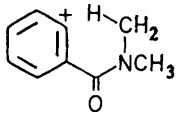
For acyclic systems, 1,*n* ($n > 2$) hydride shifts are less common,[3] but the functionality present in the chain may encourage population of those conformations necessary for such shifts to occur. This is exemplified in the case of (1) from decomposition of the aromatic diazonium salt where the constraint imposed by the benzene ring and carbonyl group enables intramolecular hydride shift to

[1] A. C. Cope, M. M. Martin, and M. A. McKervey, *Quart. Rev.*, 1966, **20**, 119; P. T. Lansbury, J. B. Bieber, F. D. Saeva, and K. R. Fountain, *J. Amer. Chem. Soc.*, 1969, **91**, 399; R. K. Hill and R. M. Carlson, *ibid.*, 1965, **87**, 2772, reference 4; L. Stéhelin, J. Lhomme, and G. Ourisson, *ibid.*, 1971, **93**, 1650.

[2] P. v. R. Schleyer, L. K. M. Lam, D. J. Raber, J. L. Fry, M. A. McKervey, J. R. Alford, B. D. Cuddy, V. G. Keizer, H. W. Geluk, and J. L. M. A. Schlatmann, *J. Amer. Chem. Soc.*, 1970, **92**, 5246.

[3] J. L. Fry and G. J. Karabatsos, in 'Carbonium Ions,' vol. II, eds. G. A. Olah and P. v. R. Schleyer, Wiley-Interscience, New York, 1970; Q. Branca and D. Arigoni, *Chimia*, 1969, **23**, 189.

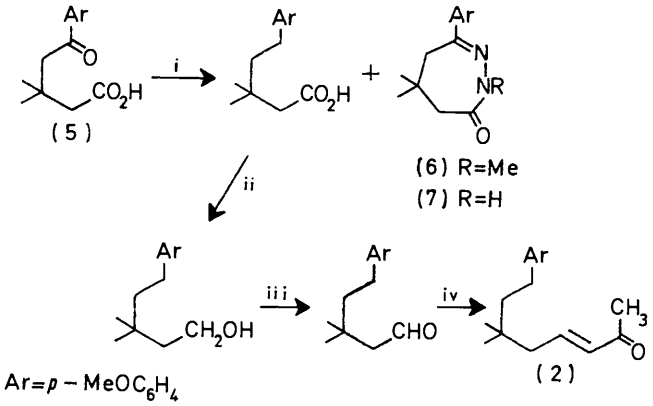
compete with external water for the reactive phenyl cation.[4]



(1)

The present paper is concerned with an acid-catalysed rearrangement of αβ-unsaturated ketones (2)—(4) which is shown to involve a 1,5-hydride shift.[5]

For the synthesis of (2), the route shown in Scheme 1 was followed.



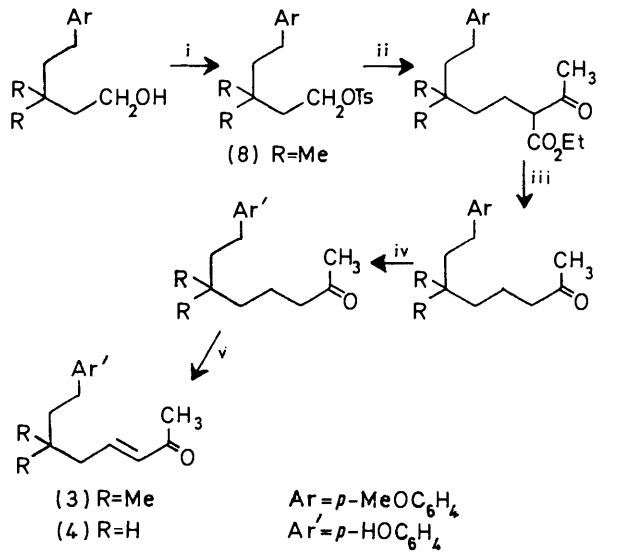
SCHEME 1 *Reagents:* i, Wolff–Kishner, Me_2SO_4, ii, EtOH–H^+ $LiAlH_4$; iii, CrO_3; iv, $Ph_3\overset{+}{P}\overset{-}{C}H{\cdot}COMe$

Wolff–Kishner reduction of (5) was accompanied by partial demethylation of the aromatic methyl ether. Re-methylation using dimethyl sulphate–potassium hydroxide gave the expected acid together with a neutral product (8%). Elemental analysis and the mass spectrum showed that this latter product contained two nitrogen atoms and the n.m.r. spectrum suggested that one of these nitrogen atoms bore a methyl group as shown by the presence of a three-proton singlet at τ 6·75. The available spectroscopic evidence supports the *N*-methyldiazepinone structure (6) for this neutral product. The parent diazepinone (7) was obtained in 51% yield by heating the keto-acid (5) and hydrazine under less vigorous conditions (see Experimental section) and was converted into the *N*-methyl derivative (6) with dimethyl sulphate and sodium hydroxide. Diazepinones of this type have recently been obtained by cyclisation of aroyl acid chlorides, aroyl acids, and aroyl esters with hydrazine.[6]

Ketone (2) showed the expected spectroscopic features with the double bond in the *trans*-configuration (n.m.r.). Attempts to cleave the aromatic methyl ether with hydrobromic acid–acetic acid were thwarted by rearrangement (see below).

The phenolic ketones (3) and (4) were obtained, as shown in Scheme 2. Alkylation of the crystalline tosylate (8) derived from the corresponding alcohol (see Scheme 1), with the sodium salt of ethyl acetoacetate gave the required *C*-alkylation product in 38% yield, the major product being the *O*-alkylated material. Although cleavage of the ethoxycarbonyl and aromatic methyl ether groups proceeded in good yield, αβ-unsaturation was introduced in only 31% yield by the bromination–dehydrobromination sequence. The oily αβ-unsaturated ketone showed the anticipated spectroscopic properties and formed a crystalline 3,5-dinitrobenzoate. A similar procedure provided the αβ-unsaturated ketone (4), both the alkylation (51%) and the bromination–dehydrobromination (40%) steps giving better yields. Again, (4) was adjudged pure by spectroscopy and was characterised by its crystalline *p*-nitrobenzoate.

Heating the αβ-unsaturated ketones (3) and (4) with boron trifluoride–ether complex in benzene gave the crystalline ketones (9) and (10) in 77 and 63% yield, respectively. In the n.m.r. spectrum of (9) the geminal methyl groups appear as two distinct singlets, and both



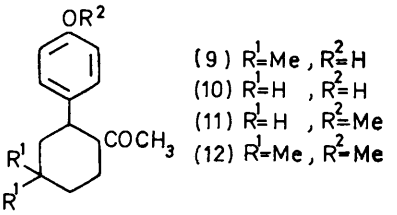
SCHEME 2 *Reagents:* i, TsCl; ii, $MeCO{\cdot}\overset{-}{C}H{\cdot}CO_2Et$; iii, HCl–HOAc; iv, HBr–HOAc; v, $CuBr_2$–$CHCl_3$–EtOAc, LiBr–Li_2CO_3–DMF

(9) and (10) show a two-proton multiplet at τ *ca.* 7·2. A sample identical with (10) was obtained by copper(I) chloride-catalysed addition of *p*-methoxyphenylmagnesium bromide to 1-acetylcyclohexene followed by demethylation of the intermediate ketone (11) with hydrobromic acid–acetic acid. The stereochemistry of (4) is assumed to be *trans* since it was recovered unchanged after treatment with base.[7]

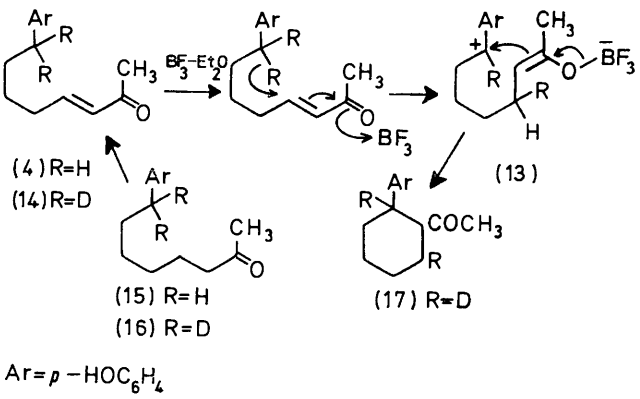
The conversion of (3) into (9) was also effected by other acid catalysts including toluene-*p*-sulphonic acid, and hydrobromic acid–acetic acid but the yield was inferior to that obtained with boron trifluoride–ether complex–benzene. Rearrangement of the aromatic methyl ether

[4] T. Cohen, C. H. McMullen, and K. Smith, *J. Amer. Chem. Soc.*, 1968, **90**, 6866.
[5] R. S. Atkinson, *Chem. Comm.*, 1969, 735.
[6] C.-G. Wermuth and J.-J. Koenig, *Angew. Chem. Internat. Edn.*, 1972, **11**, 152; I. Sataty, *Tetrahedron*, 1972, **28**, 2307; J.-J. Koenig and C.-G. Wermuth, *Tetrahedron Letters*, 1973, 603.
[7] H. E. Zimmerman, *J. Amer. Chem. Soc.*, 1957, **79**, 6554.

(2) to the ketone (12) was accomplished using 70% perchloric acid in 43% yield. Methylation of the phenolic ketone (9) with dimethyl sulphate–potassium carbonate gave a sample identical with this *p*-methoxyphenyl ketone (12).



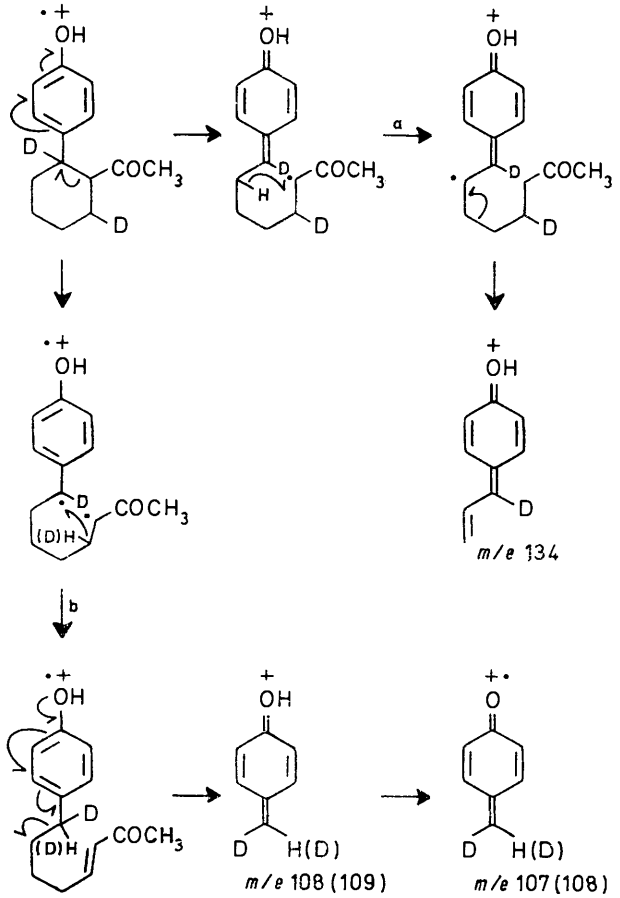
A reasonable mechanism for this rearrangement, illustrated for the case of (4) (Scheme 3) includes a 1,5-hydride shift within the molecule, assisted by co-ordination of the boron trifluoride to the carbonyl oxygen and the stability of the resulting anisylic carbonium ion (13)



SCHEME 3

To test this mechanism, the [8,8-$^2H_2$]-αβ-unsaturated ketone (14) has been prepared by catalytic exchange of the anisylic protons in (15) in the presence of deuterium followed by the bromination–dehydrobromination sequence. Mass spectral analysis indicated the composition of (14) to be 92% $^2H_2$ and 8% $^2H_1$ and n.m.r. showed the anisylic location of the deuterium in (14) with the disappearance of the triplet at τ 7·47. Examination of the mass spectrum * of the product (17), obtained after treatment with boron trifluoride–ether, revealed that the probable location of the transferred deuterium corresponded to that required by a 1,5-hydride shift. The major peaks in the spectrum were found at *m/e* 134, 109, 108 (base peak), and 107, and may all be accommodated by postulating an initial homolysis of the substituted carbon–carbon bond (Scheme 4). Part of the intensity of the *m/e* 108 peak is therefore a result of its compound nature. The fragmentation (b) includes, in effect, a reversal of the formation of ketone (10) from the αβ-unsaturated ketone (4). To show the intramolecularity of the hydride shift, a mixture of di- and non-deuteriated αβ-unsaturated ketones (14) and (4) was treated with boron trifluoride–ether. Analysis of the resultant mixture by mass spectrometry showed that, at most, 6% of the reaction was proceeding by intermolecular hydride transfer.

Our attempts to effect the rearrangement after modifying the present system have not met with success. Treatment of 7-(*p*-methoxyphenyl)hept-3-en-2-one (18) with perchloric acid, toluene-*p*-sulphonic acid, trifluoroacetic acid, and hydrobromic acid–acetic acid gave either unchanged starting material or mixtures of high molecular weight compounds. No homogeneous product was isolated from attempts to rearrange 7,7-bis-(*p*-methoxyphenyl)hept-3-en-2-one (19), synthesised from (20) by a route similar to that outlined in Scheme (1). Similarly,



SCHEME 4

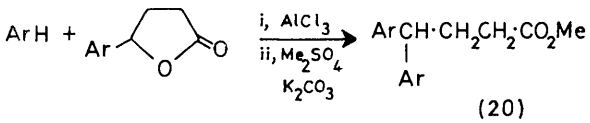
the αβ-unsaturated ester (21) on treatment with hydrobromic acid–acetic acid gave the unrearranged phenolic acid (22) with no detectable rearrangement products.

Assuming that a final ring closure of the dipolar species analogous to (13) (Scheme 3) would proceed readily, a 1,4-hydride shift seems less favourable than a 1,5-shift in the system in hand. This conclusion is in agreement with recent n.m.r. studies which indicate that 1,4-

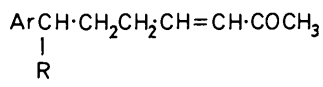
* The mass spectra of phenyl substituted αβ-unsaturated ketones analogous to (2) and (18) have been discussed in detail by Djerassi in ref. 8

[8] R. J. Liedtke, A. F. Gerrard, J. Diekman, and C. Djerassi, *J. Org. Chem.*, 1972, **37**, 776.

hydride shifts have higher energies of activation than 1,5- (or 1,3-) shifts.[9]

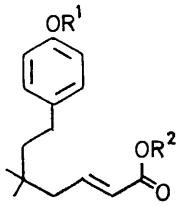


(20)



(18) R=H
(19) R=Ar

Ar=*p*-$MeOC_6H_4$



(21) R^1=Me, R^2=Et
(22) R^1=R^2=H

EXPERIMENTAL

M.p.s were determined with a Kofler hot-stage apparatus. The i.r. spectra of crystalline compounds were determined as Nujol mulls and of other compounds as thin films. N.m.r. spectra were measured with a Varian A60A or T60 and mass spectra with A.E.I. MS902 or MS9 spectrometers. The alumina used was Spence type 'H' and Kieselgel refers to Kieselgel G (Merck). For the *para*-substituted aromatic ring, the AA'BB' signals in the n.m.r. spectra are denoted by the position of the four main peaks.

Synthesis of the αβ-Unsaturated Ketone (2).—4-(*p*-Anisoyl)-3,3-dimethylbutyric acid (5) was prepared by the method previously reported.[10]

Wolff–Kishner reduction of acid (5). The keto-acid (5) (10 g) was heated under reflux for 0·5 h with hydrazine hydrate (7·2 g; 95%), potassium hydroxide (7 g), and ethylene glycol (50 ml). The mixture was then distilled till the vapour temperature reached 195°, then heated under reflux for 4 h. After cooling, the solution was poured into water, acidified, and extracted with ethyl acetate. The organic layer was washed with water, evaporated, the residual oil dissolved in ethanol (100 ml), and the ethanolic solution heated under reflux while dimethyl sulphate (10·1 ml) and sodium hydroxide (56·5 ml; 10% solution) were added simultaneously. After heating under reflux for 4 h the solvent was distilled off up to a temperature of 96°, the residual solution cooled, and extracted with ether. From this ether extract the diazepinone (6) was isolated (see below). The aqueous layer after ether extraction was acidified and further extracted with ether, and the ether layer dried and evaporated to give 5-(p-*methoxyphenyl*)-3,3-*dimethylpentanoic acid* (8·3 g, 88% from the keto-acid) as needles (from ethyl acetate–light petroleum), m.p. 80—81° (Found: C, 71·05; H, 8·6. $C_{14}H_{20}O_3$ requires C, 71·15; H, 8·55%), $\nu_{max.}$ 2680s,br and 1690s cm^{-1}; τ ($CDCl_3$) 8·90 (s, Me_2C), 8·65—8·15 (m, 4-H_2), 7·70 (s, 2-H_2), 7·65—7·20 (m, 5-H_2), 6·20 (s, OCH_3), 3·30, 3·15, 3·00, and 2·85 (4 × ArH), and 1·54 (s, CO_2H).

In a separate experiment, a sample of the crude acid (280 mg) obtained after evaporation of the ethyl acetate extract above, was esterified with boiling ethanol (10 ml) containing dry hydrogen chloride gas overnight. The bulk of the ethanol was removed, chloroform was added, and the organic layer was washed with sodium hydrogen carbonate solution and water, dried, and evaporated. T.l.c. examination of the residual oil showed the presence of two products R_F 0·8 and 0·3 in benzene–ethyl acetate (10 : 1). Chromatography of the mixture over Kieselgel using benzene–ethyl acetate (15 : 1) gave *ethyl* 5-(p-*methoxyphenyl*)-3,3-*dimethylpentanoate* (145 mg) as a mobile liquid, b.p. (bulb–tube; bath temp.) 140—144° at 1 mmHg (Found: C, 72·4; H, 9·35. $C_{16}H_{24}O_3$ requires C, 72·7; H, 9·15%), $\nu_{max.}$ 1730s cm^{-1}; τ (CCl_4) 8·96 (s, Me_2C), 8·77 (t, *J* 7 Hz, CH_3CH_2), 8·67—8·27 (m, 4-H_2), 7·81 (s, 2-H_2), 7·67—7·31 (m, 5-H_2), 6·28 (s, OCH_3), 5·92 (q, *J* 7 Hz, CH_3CH_2), and 3·38, 3·24, 3·06, and 2·92 (4 × ArH). Further elution with benzene–ethyl acetate (5 : 1) gave the slower running spot on t.l.c. (120 mg). Distillation afforded *ethyl* 5-(p-*hydroxyphenyl*)-3,3-*dimethylpentanoate* as an oil, b.p. (bulb–tube; bath temp.) 150—155° at 1 mmHg (Found: C, 71·65; H, 8·65. $C_{15}H_{22}O_3$ requires C, 71·95; H, 8·85%), $\nu_{max.}$ 3465m, 1726s, and 1710s cm^{-1}; τ ($CDCl_3$) 8·93 (s, Me_2C), 8·73 (t, *J* 7 Hz, CH_3CH_2), 8·63—8·22 (m, 4-H_2), 7·71 (s, 2-H_2), 7·62—7·26 (m, 5-H_2), 5·84 (q, *J* 7 Hz, CH_3CH_2), and 3·32, 3·18, 3·02, and 2·88 (4 × ArH).

Reduction of the foregoing ester (100 mg) with excess of lithium aluminium hydride in ether (20 ml) gave 5-(p-*hydroxyphenyl*)-3,3-*dimethylpentan*-1-*ol* (74 mg, 84%) as blades (from ethyl acetate), m.p. 120·5—121° (Found: C, 75·05; H, 9·35. $C_{13}H_{20}O_2$ requires C, 74·95; H, 9·70%).

5-(p-*Methoxyphenyl*)-3,3-*dimethylpentan*-1-*ol*. The acid (5) (2·6 g) was esterified by heating under reflux with ethanol containing hydrogen chloride overnight. The crude ester was reduced with excess of lithium aluminium hydride in ether for 2 h at room temperature. After destroying excess of hydride with ethyl acetate and then water, removal of solvent gave the *alcohol*, b.p. (bulb–tube; bath temp.) 145—150° at 1 mmHg, as an oil (2·2 g, 84%) (Found: C, 75·25; H, 9·7. $C_{14}H_{22}O_2$ requires C, 75·65; H, 9·95%), $\nu_{max.}$ 3440br cm^{-1}; τ ($CDCl_3$) 9·02 (s, Me_2C), 8·72—8·26 (m, 2-H_2 and 4-H_2), 8·43 (t, *J* 7·5 Hz, OH), 7·69—7·32 (m, 5-H_2), 6·30 (t, *J* 7·5 Hz, 1-H_2), 6·24 (s, OCH_3), and 3·30, 3·15, 2·98, and 2·84 (4 × ArH).

5-(p-*Methoxyphenyl*)-3,3-*dimethylpentanal*. Chromium trioxide (12·75 g) was added in portions to a mixture of freshly dried pyridine (21 ml; distilled from calcium hydride) and dichloromethane (140 ml) with stirring.[11] After 20 min, the foregoing alcohol (1·5 g) dissolved in dichloromethane (20 ml) was added, the mixture stirred for 1 min at room temperature then the dichloromethane was decanted from the precipitated chromium salts which were further washed with dichloromethane by decantation. The combined organic solutions were washed successively with sodium hydroxide (2N), dilute hydrochloric acid (2N), sodium carbonate, and sodium chloride solution. Removal of the solvent gave the aldehyde as a pale yellow oil (1·2 g, 79%) which was used directly in the following steps; $\nu_{max.}$ 2740w and 1720s cm^{-1}; τ (CCl_4) 8·95 (s, Me_2C), 8·8—8·2 (m, 4-H_2), 7·80 (d, *J* 3 Hz, 2-H_2), 7·70—7·30 (m, 5-H_2), 6·35 (s, OCH_3), 3·40, 3·25, 3·10, and 2·95 (4 × ArH), and 0·50br (1H, t, CHO).

[9] M. Saunders and J. J. Stofko, *J. Amer. Chem. Soc.*, 1973, **95**, 252.
[10] R. S. Atkinson, *J. Chem. Soc.* (*C*), 1971, 784.
[11] R. Ratcliffe and R. Rodehorst, *J. Org. Chem.*, 1970, **35**, 4000.

8-(p-*Methoxyphenyl*)-6,6-*dimethyloct*-3-*en*-2-*one* (2). Acetonyltriphenylphosphonium chloride (2·4 g) and sodium carbonate (0·8 g) were dissolved in a mixture of water (7 ml) and tetrahydrofuran (15 ml) and stirred at room temperature for 0·5 h. The foregoing aldehyde (1·2 g) dissolved in tetrahydrofuran (8 ml) was quickly added and the mixture heated under reflux overnight, under nitrogen. After cooling, the mixture was poured into water and extracted with ether, and the extracts were washed with sodium chloride solution, dried, and evaporated. Trituration of the residual brown oil with light petroleum (× 4) and removal of the light petroleum yielded an oil (1·3 g) which was purified by chromatography over Kieselgel eluting with benzene–ethyl acetate (3 : 1). Distillation gave the *αβ-unsaturated ketone* (2) as an oil (0·95 g, 67%), b.p. (bulb–tube; bath temp.) 173—175° at 0·2 mmHg (Found: C, 78·2; H, 9·25. $C_{17}H_{24}O_2$ requires C, 78·4; H, 9·3%), $\nu_{max.}$ 1670s and 1625 cm^{-1}; τ (CCl_4) 9·05 (s, Me_2C), 8·75—8·3 (m, 7-H_2), 7·80 (s, MeCO), 8·0—7·2 (m, 5-H_2 and 8-H_2), 6·25 (s, OCH_3), 5·95 (d, *J* 16 Hz, 3-H), and 3·30, 3·15, 3·00, and 2·85 (5H, 4 × ArH superimposed on 4-H).

Ethyl 7-(p-*Methoxyphenyl*)-5,5-*dimethylhept*-2-*enoate* (21). —Triethylphosphonoacetate (3·86 g) in dry tetrahydrofuran (50 ml) was added dropwise to a stirred suspension of sodium hydride (0·20 g) in dry tetrahydrofuran (25 ml) and stirring was continued for 16 h at room temperature. The aldehyde prepared above (2·2 g) in dry tetrahydrofuran (50 ml) was then added dropwise and the mixture stirred for 0·75 h before pouring into water and extracting with ether. The ether layer was washed with water, dried, and evaporated to yield a yellow oil (2·8 g). Chromatography over Kieselgel, eluting with benzene, followed by distillation gave the *αβ-unsaturated ester* (21) (2·0 g, 69%) as an oil, b.p. (bulb–tube; bath temp.) 170—180° at 0·1 mmHg (Found: C, 74·2; H, 8·75. $C_{18}H_{26}O_3$ requires C, 74·45; H, 9·05%); $\nu_{max.}$ 1720s and 1650m cm^{-1}; τ (CCl_4) 9·00 (s, Me_2C), 8·91—8·2 (m, 6-H_2), 8·75 (t, *J* 7 Hz, CH_3CH_2), 7·9 (d, *J* 8 Hz, 4-H_2), 7·7—7·3 (m, 7-H_2), 6·25 (s, OCH_3), 5·9 (q, *J* 7 Hz, CH_3CH_2), 4·3 (d, *J* 16 Hz, 2-H), and 3·45, 3·30, 3·15, and 3·00 (5H, 4 × ArH superimposed on 3-H).

Isolation of 2,4,5,6-*Tetrahydro*-7-(p-*methoxyphenyl*)-2,5,5-*trimethyl*-1,2-*diazepin*-3-*one* (6).—Wolff–Kishner reduction to the keto-acid (5) followed by re-methylation with dimethyl sulphate and sodium hydroxide was carried out as described above. The ether extracts obtained from the basic solution were dried and evaporated to yield a colourless oil which was purified by chromatography over silica. Elution with ethyl acetate and crystallisation from ethyl acetate–light petroleum gave the N-*methyldiazepinone* (6) as cubes, m.p. 77—78° [8% from the keto-acid (5)] (Found: C, 69·05; H, 7·8; N, 10·55. $C_{15}H_{20}N_2O_2$ requires: C, 69·2; H, 7·75; N, 10·75%), $\nu_{max.}$ 1645s and 1610m cm^{-1}; τ ($CDCl_3$) 8·90 (s, Me_2C), 7·90 (s, 4-H_2), 7·40 (s, 6-H_2), 6·75 (s, NCH_3), 6·20 (s, OCH_3), and 3·25, 3·10, 2·35, and 2·20 (4 × ArH).

The parent diazepinone (7) was obtained by the following procedure: the acid (5) (1 g) was dissolved in ethanol (100 ml), hydrazine hydrate (1·3 ml; 95%) was added, and the mixture heated under reflux for 2 h. Potassium carbonate (3 g) was then added followed by dimethyl sulphate (1·2 g), and the mixture was heated under reflux for a further 3 h then stirred overnight. The mixture was poured into water extracted with ether, and the extracts were dried and evaporated to yield 2,4,5,6-*tetrahydro*-7-(p-*methoxyphenyl*)-5,5-*dimethyl*-1,2-*diazepin*-3-*one* (7) as a white solid (500 mg, 51%) which crystallised as needles (from ethanol), m.p. 180—181° (Found: C, 68·1; H, 7·45; N, 11·3. $C_{14}H_{18}N_2O_2$ requires C, 68·25; H, 7·35; N, 11·3%), $\nu_{max.}$ 3180w, 3060w, and 1645s cm^{-1}; τ ($CDCl_3$) 8·80 (s, Me_2C), 7·70 (s, 4-H_2), 7·20 (s, 6-H_2), 6·05 (s, OCH_3), 2·55 (s, NH), and 3·00, 2·85, 2·10, and 1·95 (4 × ArH). The diazepinone (7) was converted into its *N*-methyl derivative (6) on treatment with dimethyl sulphate–potassium hydroxide.

Synthesis of 8-(p-*Hydroxyphenyl*)-6,6-*dimethyloct*-3-*en*-2-*one* (3).—5-(*p*-Methoxyphenyl)-3,3-dimethylpentan-1-ol (8·85 g) in ice-cold pyridine (50 ml) was treated with toluene-*p*-sulphonyl chloride (8·9 g) and the mixture stirred at 0° for 5 h. The oil obtained on pouring the mixture into ice–water solidified on standing. Crystallisation from ethanol gave 5-(p-*methoxyphenyl*)-6,6-*dimethyloctyl tosylate* as blades (9·2 g, 61%), m.p. 39—41° (Found: C, 66·95; H, 7·35. $C_{21}H_{28}O_4S$ requires C, 67·0; H, 7·5%), τ ($CDCl_3$) 9·07 (s, Me_2C), 8·79—8·44 (m, 4-H_2), 8·35 (t, *J* 7·5 Hz, 2-H_2), 7·76—7·38 (m, 5-H_2), 7·57 (s, CH_3Ar), 6·22 (s, OCH_3), 5·88 (t, *J* 7·5 Hz, CH_2OTs), 3·29, 3·14, 3·03, and 2·89 (C_6H_4OMe), and 2·75, 2·62, 2·27, and 2·13 (MeC_6H_4).

Ethyl 2-*Acetyl*-7-(p-*methoxyphenyl*)-5,5-*dimethylheptanoate*. Ethanol (50 ml) containing sodium (0·61 g) was treated with ethyl acetoacetate (3·46 g) and then in portions with the foregoing tosylate (9·1 g) and the mixture heated under reflux for 6 h with vigorous magnetic stirring. The cooled mixture was acidified with acetic acid, the bulk of the alcohol removed under reduced pressure, and the residue extracted with ethyl acetate and water. After washing the organic layer with sodium hydrogen carbonate and water and then evaporating, the oil obtained was chromatographed over Kieselgel (250 g) eluting with benzene–ethyl acetate (20 : 1). I.r. examination of the first fraction eluted (3 g) suggested this was the *O*-alkylated product. Further elution gave the *β-keto-ester* (3·1 g, 38%) as a mobile oil, b.p. (bulb–tube; bath temp.) 180—185° at 0·1 mmHg (Found: C, 71·95; H, 9·2. $C_{20}H_{30}O_4$ requires C, 71·8; H, 9·05%), $\nu_{max.}$ 1743s and 1716s cm^{-1}; τ (CCl_4) 9·05 (s, Me_2C), 8·73 (t, *J* 7·5 Hz, CH_3CH_2), 8·96—7·97 (m, 3-H_2, 4-H_2, and 6-H_2), 7·87 (s, CH_3CO), 7·74—7·35 (m, 7-H_2), 6·85 (t, *J* 7 Hz, 2-H), 6·28 (s, OCH_3), 5·85 (q, *J* 7·5 Hz, CH_3CH_2), and 3·42, 3·27, 3·08, and 2·94 (4 × ArH).

8-(p-*Methoxyphenyl*)-6,6-*dimethyloctan*-2-*one*. The foregoing β-keto-ester (2 g) was heated under reflux with glacial acetic acid (26 ml), concentrated hydrochloric acid (2·3 ml), and water (2 ml) for 3·5 h. After removal of the bulk of the acetic acid under reduced pressure, the residue was neutralised with sodium carbonate and extracted with chloroform. The chloroform extract was washed with water, dried, and evaporated, and distillation of the residue gave the *ketone* (1·15 g, 73%) as an oil, b.p. (bulb–tube; bath temp.) 170—174° at 2 mmHg (Found: C, 77·6; H, 10·2. $C_{17}H_{26}O_2$ requires C, 77·8; H, 10·0%), $\nu_{max.}$ 1711s cm^{-1}; τ (CCl_4) 9·07 (s, Me_2C), 8·95—8·3 (m, 4-H_2, 5-H_2, and 7-H_2), 7·97 (s, CH_3CO), 7·89—7·36 (m, 3-H_2 and 8-H_2), 6·28 (s, OCH_3), and 3·43, 3·27, 3·08, and 2·94 (4 × ArH).

8-(p-*Hydroxyphenyl*)-6,6-*dimethyloctan*-2-*one*. The foregoing ketone (500 mg), glacial acetic acid (5·5 ml), and hydrobromic acid (1·2 ml; 48%) were heated under reflux for 1 h. The bulk of the solvent was removed under reduced pressure, the residue dissolved in chloroform, and the chloroform layer washed with sodium hydrogen carbonate and water, dried, and evaporated. Distillation gave the *phenolic ketone* (380 mg, 80%) as a glass, b.p. (bulb–tube; bath temp.) 175—180° at 1 mmHg (Found: C, 77·0; H,

9·5. $C_{16}H_{24}O_2$ requires C, 77·35; H, 9·75%), $\nu_{max.}$ 3445m and 1702s cm^{-1}; τ (CCl_4) 9·07 (s, Me_2C), 8·85—8·36 (m, 4-H_2, 5-H_2, and 7-H_2), 7·88 (s, CH_3CO), 7·79—7·38 (m, 3-H_2 and 8-H_2), 4·14br (s, OH), and 3·47, 3·32, 3·17, and 3·02 (4 × ArH).

8-(p-*Hydroxyphenyl*)-6,6-*dimethyloct*-3-*en*-2-*one* (3). The phenolic ketone above (1·14 g) was heated under reflux for 0·5 h with copper(II) bromide (2·05 g) in chloroform (6 ml) and ethyl acetate (6 ml) with magnetic stirring. After stirring for a further 0·5 h at room temperature, the white copper(I) bromide was separated, washed well with chloroform, and the chloroform layer was washed with sodium hydrogen carbonate, water, dried, and evaporated. The residual oil was heated under reflux with lithium bromide (2·4 g) and lithium carbonate (2·4 g) in dimethylformamide (6 ml) with vigorous magnetic stirring for 1·5 h. Benzene was added to the cooled mixture and the bulk of the dimethylformamide and inorganic salts were removed by washing (×3) with water. Drying of the benzene solution and evaporation yielded an oil which was chromatographed over Kieselgel using benzene–ethyl acetate (5 : 1). The αβ-unsaturated ketone (3) (350 mg, 31%) was obtained as a viscous oil, b.p. 175—182° at 1 mmHg, $\nu_{max.}$ 3410m, 1660s, and 1620s cm^{-1}; τ (CCl_4–$CHCl_3$, 10 : 1) 9·03 (s, Me_2C), 8·80—8·38 (m, 7-H_2), 8·0—7·4 (m, 5-H_2 and 8-H_2), 7·80 (s, CH_3CO), 3·98 (d, *J* 16 Hz, 3-H), 3·6br (s, OH), and 3·5—3·0 (4 × ArH superimposed on m, 4-H); τ (after treatment with 1 drop CF_3CO_2H) 7·85 (d, *J* 7·5, 5-H_2) visible, OH removed; *m/e* 246, 161, 125, and 107 (11, 16, 12, and 100%), *m** 105·4 (246 ⟶ 161). The 3,5-*dinitrobenzoate* was prepared, using 3,5-dinitrobenzoyl chloride in pyridine, as plates, m.p. 80—84° (from ethanol) (Found: M^+, 440·158301. $C_{23}H_{24}N_2O_7$ requires *M*, 440·158358).

Synthesis of 8-(p-*Hydroxyphenyl*)*oct*-3-*en*-2-*one* (4).—5-(*p*-Methoxyphenyl)pentan-1-ol was prepared from 4-(*p*-anisoyl)butyric acid by Wolff–Kishner reduction [12] [with re-methylation of the phenol as described for (5)], followed by esterification and lithium aluminium hydride reduction. It was converted into the title αβ-unsaturated ketone by a sequence of reactions analogous to those described for the preparation of (3). The crude oily tosylate was used directly to alkylate ethyl acetoacetate; *ethyl* 2-*acetyl*-7-(p-*methoxyphenyl*)*heptanoate* was obtained (51%) as a mobile oil, b.p. (bulb–tube; bath temp.) 170—177° at 1 mmHg (Found: C, 70·35; H, 8·75. $C_{18}H_{26}O_4$ requires C, 70·55; H, 8·55%), $\nu_{max.}$ 1736s and 1712s cm^{-1}; τ (CCl_4) 8·74 (t, *J* 7 Hz, CH_3CH$_2$), 8·87—8·02 (m, 3-H_2, 4-H_2, 5-H_2, and 6-H_2), 7·88 (s, CH_3CO), 7·50 (t, *J* 6·5 Hz, 7-H_2), 6·79 (t, *J* 7 Hz, 2-H), 6·26 (s, OCH_3), 5·87 (q, *J* 7 Hz, CH_3CH_2), and 3·41, 3·26, 3·09, and 2·95 (4 × ArH).

Hydrolysis of the above β-keto-ester gave 8-(p-*methoxyphenyl*)*octan*-2-*one* (76%) as an oil, b.p. (bulb–tube; bath temp.) 160—165° at 1 mmHg (Found: C, 77·15; H, 9·6. $C_{15}H_{22}O_2$ requires C, 76·9; H, 9·45%), $\nu_{max.}$ 1711s cm^{-1}; τ (CCl_4) 8·9—8·21 (m, $[CH_2]_4$), 7·98 (s, CH_3CO), 7·71 and 7·50 (2 overlapping t, *J* 7 and 6·5 Hz, 3-H_2 and 8-H_2, respectively), 6·28 (s, OCH_3), and 3·40, 3·25, 3·09, and 2·95 (4 × ArH).

Further hydrolysis of the aromatic methyl ether was effected by heating the ketone above (1 g) with glacial acetic acid (11 ml) and hydrobromic acid (2·5 ml; 48%) under reflux. Approximately half the solvent was evaporated off under reduced pressure and the residue diluted with water. The solid obtained was separated and crystallised from chloroform–light petroleum to give 8-(p-*hydroxyphenyl*)-*octan*-2-*one* (15) (0·75 g, 79%) as prisms, m.p. 67—68° (Found: C, 76·05; H, 8·85. $C_{14}H_{20}O_2$ requires C, 76·3; H, 9·15%), $\nu_{max.}$ 3480s and 1707s cm^{-1}; τ ($CDCl_3$) 8·95—8·22 (m, $[CH_2]_4$), 7·85 (s, CH_3CO), 7·59 (t, *J* Hz, 3-H_2) overlapping 7·49 (t, *J* 6·5 Hz, 8-H_2), 4·69br (s, OH), and 3·34, 3·18, 3·05, and 2·92 (4 × ArH); *m/e* 220, 120, 107, and 43 (24, 33, 100, and 20%), *m** 65·5 (220 ⟶ 120)

[8,8-$^2H_2$]-8-(p-*Hydroxyphenyl*)*octan*-2-*one* (16).—The foregoing phenol (1 g) in ethyl acetate (20 ml) was shaken with palladium–charcoal (200 mg; 10%) for 3 h in an atmosphere of deuterium, the deuterium being renewed three times. After separation of the catalyst, the ethyl acetate was removed and the residue crystallised from chloroform–light petroleum. The n.m.r. spectrum shows the disappearance of the triplet at τ 7·49; *m/e* 222, 121, 109, and 43 (22, 27, 100, and 28%).

Bromination–dehydrobromination of the phenolic ketone gave 8-(p-*hydroxyphenyl*)*oct*-3-*en*-2-*one* (4) (40%) as an oil, b.p. (bulb–tube; bath temp.) 167—172° at 1 mmHg, $\nu_{max.}$ 3400m,br and 1666s cm^{-1}; τ ($CDCl_3$) 8·65—8·15 (m, 6-H_2 and 7-H_2), 8·03—8·63 (m, 5-H_2), 7·77 (s, CH_3CO), 7·47 (t, *J* 6·5 Hz, 8-H_2), 4·33 (s, OH), 3·97 (dt, *J* 16 and 1·2 Hz, 3-H), and 3·34, 3·19, 3·06, and 2·92 (4 × ArH superimposed on 4-H), *m/e* 218, 160, 133, 120, and 107 (23, 13, 23, 13, and 100%), *m** 117·4 (218 ⟶ 160) and 52·5 (218 ⟶ 109). A crystalline p-*nitrobenzoate* was obtained with *p*-nitrobenzoyl chloride and pyridine and crystallised from methanol as pale yellow prisms, m.p. 96—97·5° (Found: M^+, 367·139969. $C_{21}H_{21}NO_5$ requires *M*, 367·141962).

Likewise [8,8-^{2}H]-8-(*p*-hydroxyphenyl)oct-3-en-2-one (14) was obtained from the dideuteriated phenol (16). The n.m.r. spectrum of the pure product showed the absence of the triplet at τ 7·47; *m/e* 220, 109, and 43 (37, 100, and 23%). A crystalline *dideuteriated* p-*nitrobenzoate* was obtained (Found: M^+, 369·154298. $C_{21}H_{19}D_2NO_5$ requires *M*, 369·154517).

Rearrangement of the αβ-*Unsaturated Ketone* (3) *with Boron Trifluoride–Ether.*—The αβ-unsaturated ketone (3) (110 mg) was heated under reflux with benzene (9 ml) and boron trifluoride–ether (9 ml) for 1·25 h. After cooling, the mixture was added cautiously to sodium hydrogen carbonate solution and the benzene layer was washed with water, dried, and evaporated. Chromatography of the residue over silica in benzene–ethyl acetate (5 : 1) gave 2-(p-*hydroxyphenyl*)-4,4-*dimethylcyclohexyl methyl ketone* (9) (70 mg, 63%) as needles (from chloroform–light petroleum), m.p. 130—131° (Found: C, 77·9; H, 8·9. $C_{16}H_{22}O_2$ requires C, 78·0; H, 9·0%), $\nu_{max.}$ 3310m and 1687s cm^{-1}; τ ($CDCl_3$) 9·2 and 8·96 (2s, Me_2C), 8·9—8·1 (m, 3-H_2, 5-H_2, and 6-H_2), 8·05 (s, CH_3CO), 7·6—7·0 (m, 1-H and 2-H), and 3·35, 3·20, 3·03, and 2·88 (4 × ArH); *m/e* 246, 161, 107, and 43 (83, 100, 92, and 72%), *m** 105·4 (246 ⟶ 161).

Rearrangement of 8-(p-*Methoxyphenyl*)-6,6-*dimethyloct*-3-*en*-2-*one with Perchloric Acid.*—The αβ-unsaturated ketone (2) (135 mg) was dissolved in perchloric acid (5 ml; 70%) and stirred at room temperature for 2 h. Cautious addition of the red reaction mixture to sodium carbonate solution and extraction with benzene followed by washing of the benzene solution, drying, and evaporating gave a brown oil (65 mg). Chromatography over Kieselgel, eluting with benzene, and distillation yielded 2-(p-*methoxyphenyl*)-4,4-*dimethylcyclohexyl methyl ketone* (12) (58 mg, 43%), b.p. (bulb–tube, bath temp.) 200—210° at 3 mmHg (Found: C, 78·5; H, 9·15.

[12] D. Papa, E. Schwenk, and H. Hankin, *J. Amer. Chem. Soc.*, 1947, **69**, 3018.

$C_{17}H_{24}O_2$ requires C, 78·4; H, 9·3%), $\nu_{max.}$ 1710s cm^{-1}; τ (CCl_4) 9·05 and 8·94 (2s, Me_2C), 8·9—8·0 (m, 3-H_2, 5-H_2, and 6-H_2), 8·15 (s, CH_3CO), 7·4—6·8 (m, 1-H and 2-H), 6·20 (s, OCH_3), and 3·30, 3·15, 2·95, and 2·80 (4 × ArH). The foregoing methyl ether was identical with a sample prepared by methylation of the phenol (9) with dimethyl sulphate and potassium carbonate in acetone.

2-(p-*Hydroxyphenyl*)*cyclohexyl Methyl Ketone* (10).—The αβ-unsaturated ketone (4) (53 mg) was heated under reflux for 2 h with boron trifluoride–ether (2·5 ml) in benzene (2·5 ml). After cooling the reaction mixture was added cautiously to sodium hydrogen carbonate solution, more benzene was added, and the benzene layer was washed with water, dried, and evaporated. A yellow oil remained which solidified on standing. Recrystallisation (from benzene) gave the *ketone* (10) (30 mg) as flat white needles. A further quantity (11 mg, total 41 mg, 77%) of product was obtained after filtering the residues through alumina in ethyl acetate–ethanol (1 : 1). An analytical sample was prepared by sublimation (142° at 1 mmHg) as white rods, m.p. 158·5—159·5° (Found: C, 77·0; H, 8·15. $C_{14}H_{18}O_2$ requires C, 77·05; H, 8·3%), $\nu_{max.}$ 3340s and 1688s cm^{-1}; τ ($CDCl_3$) 8·85—7·91 (m, $[CH_2]_4$), 8·14 (s, CH_3CO), 7·49—7·13 (m, 1-H and 2-H), 3·55br (s, OH), and 3·44, 3·29, 3·08, and 2·94 (4 × ArH); *m/e* 218, 160, 133, and 107 (61, 24, 50, and 100%), *m** 117·4 (218 ⟶ 160) and 52·6 (218 ⟶ 107).

Treatment of [8,8-$^2H_2$]-8-(p-*Hydroxyphenyl*)*oct*-3-*en*-2-*one with Boron Trifluoride–Ether*.—The procedure above was repeated using the deuteriated αβ-unsaturated ketone (14). Mass spectral analysis showed the product was [2,6-$^2H_2$]-2-(*p*-hydroxyphenyl)cyclohexyl methyl ketone (17), *m/e* 220, 134, 109, 108, 107, and 43 (87, 56, 33, 100, 40, and 65%).

Repetition of the foregoing two experiments using a 3 : 2 mixture of non-deuteriated (4) and dideuteriated (14) αβ-unsaturated ketones gave a product containing at most a 6% excess of monodeuteriated product ketone (from analysis of the *m/e* 218, 219, and 220 peaks in the mass spectrum).

A sample of the phenolic ketone (10) was synthesised by the following procedure: the Grignard reagent from *p*-methoxyphenyl bromide (4·61 g) was prepared by heating under reflux for 0·5 h with magnesium (1 g) in ether (50 ml) under a nitrogen atmosphere. Dry tetrahydrofuran (90 ml) was added and *ca.* 70 ml of solution distilled off. Copper(I) chloride (200 mg) was added followed by 1-acetylcyclohexene (3·05 g) in dry tetrahydrofuran (25 ml) dropwise, with vigorous magnetic stirring of the solution at room temperature. After stirring for 20 min, a saturated solution of ammonium chloride was added and the solution extracted with ether. The ether layer was washed with sodium thiosulphate solution and water, dried, and evaporated. A yellow oil was obtained which was chromatographed over silica using benzene. A waxy white solid was first eluted followed by 2-(p-*methoxyphenyl*)*cyclohexyl methyl ketone* (11) (3 g, 52%), b.p. 140—145° at 0·2 mmHg (Found: C, 77·45; H, 8·45. $C_{15}H_{20}O_2$ requires C, 77·55; H, 8·7%), $\nu_{max.}$ 1706s cm^{-1}; τ (CCl_4) 8·65—7·92 (m, $[CH_2]_4$), 8·35 (s, CH_3CO), 7·41—6·96 (m, 1-H and 2-H), 6·28 (s, OCH_3), and 3·38, 3·23, 3·03, and 2·88 (4 × ArH). This methyl ether (130 mg) was heated under reflux with glacial acetic acid (2·2 ml) and hydrobromic acid (0·45 ml; 48%). Some acetic acid was evaporated off under reduced pressure, the residue was diluted with water, and a solid separated. Crystallisation from benzene gave a sample of the ketone (10) (80 mg, 65%) identical with that isolated previously.

Attempted Rearrangement of Ethyl 7-(p-*Methoxyphenyl*)-5,5-*dimethylhept*-2-*enoate* (21) *with Hydrobromic Acid–Acetic Acid*.—The ester (21) (202 mg) was heated under reflux with hydrobromic acid (2 ml; 48%) and glacial acetic acid (2 ml). After cooling, the mixture was added carefully to sodium hydrogen carbonate solution and extracted twice with dichloromethane. The basic aqueous solution was acidified with concentrated hydrochloric acid and re-extracted twice with dichloromethane. This extract was dried, evaporated, and the residue crystallised from ethyl acetate–light petroleum to give 7-(p-*hydroxyphenyl*)-5,5-*dimethylhept*-2-*enoic acid* (22) as plates, m.p. 130—132° (94 mg, 54%) (Found: C, 72·3; H, 7·95. $C_{15}H_{20}O_3$ requires C, 72·55; H, 8·1%), $\nu_{max.}$ 3170m,br, 1685s, and 1635m cm^{-1}; τ (CF_3CO_2H) 8·90 (s, Me_2C), 8·69—8·15 (m, 6-H_2), 7·85—7·1 (m, 4-H_2 and 7-H_2), 3·95 (d, *J* 15 Hz, 2-H), 3·15, 3·00, 2·90, and 2·75 (4 × ArH), and 2·57 (dt, *J* 15 and 7 Hz, 3-H).

Synthesis of Ethyl 6-(p-*Methoxyphenyl*)*hex*-2-*enoate and* 7-(p-*Methoxyphenyl*)*hept*-3-*en*-2-*one* (18).—4-(*p*-Methoxyphenyl)butan-1-ol, was prepared by the method of Baird and Winstein.[13] It was oxidised to the aldehyde which was converted into the title *ester* in 41% yield by the method described earlier. The analytical sample was distilled to give an oil, b.p. (bulb–tube; bath temp.) 175—180° at 1·5 mmHg (Found: C, 72·9; H, 8·35. $C_{15}H_{20}O_3$ requires C, 72·55; H, 8·1%), $\nu_{max.}$ 1720s and 1655m cm^{-1}; τ ($CDCl_3$) 8·70 (t, *J* 7 Hz, CH_3CH_2), 8·50—7·20 (m, $[CH_2]_3$), 6·20 (s, OCH_3), 5·80 (q, *J* 7 Hz, CH_3CH_2), 4·20 (d, *J* 16 Hz, 2-H), and 3·30, 3·10, 2·95, and 2·85 (4 × ArH superimposed on 3-H).

Hydrolysis of the foregoing ester with sodium hydroxide solution (2N) containing ethanol for 1 h gave 6-(p-*methoxyphenyl*)*hex*-2-*enoic acid* (72%) as microcrystals, m.p. 83—85° (from ethyl acetate–light petroleum) (Found: C, 70·95; H, 7·15. $C_{13}H_{16}O_3$ requires C, 70·9; H, 7·3%), $\nu_{max.}$ 2660w,br, 1690s, and 1645m cm^{-1}; τ ($CDCl_3$) 8·85—7·20 (m, $[CH_2]_3$), 6·25 (s, OCH_3), 4·10 (d, *J* 15 Hz, 2-H), 3·20, 3·05, 2·90, and 2·73 (4 × ArH superimposed on 3-H), and −1·3br (s, CO_2H).

Reaction of the same aldehyde above with acetonyltriphenylphosphonium chloride using the method of Djerassi [8] gave 7-(p-*methoxyphenyl*)*hept*-3-*en*-2-*one* (54%) after chromatography over Kieselgel. Distillation gave an oil, b.p. (bulb–tube; bath temp.) 160—170° at 0·7 mmHg (Found: C, 77·55; H, 8·1. $C_{14}H_{18}O_2$ requires C, 77·05; H, 8·3%), $\nu_{max.}$ 1680s and 1630m cm^{-1}; τ (CCl_4) 8·50—7·10 (m, $[CH_2]_3$), 7·90 (s, CH_3CO), 6·25 (s, OCH_3), 4·05 (d, *J* 15 Hz, 3-H), and 3·55—2·90 including peaks at 3·35, 3·20, 3·05, and 2·90 (4 × ArH superimposed on 4-H).

Synthesis of 7,7-*Bis*-(p-*methoxyphenyl*)*hept*-3-*en*-2-*one* (19).—Powdered aluminium chloride (15·0 g) was dissolved in dry nitrobenzene (200 ml) with stirring at room temperature. The solution was cooled to 0°, anisole (14 g) was added, and then the mixture was treated with 4-(*p*-methoxyphenyl)-butyrolactone (9·1 g) [14] in small portions keeping the temperature below 5°. After addition, the flask was stoppered and kept in a refrigerator (3 °C) for 13 days. The resulting red solution was poured onto a 1 : 1 mixture of ice and concentrated hydrochloric acid and then steam distilled until all nitrobenzene was removed. Extraction of the residual solution with ethyl acetate (×3), drying of the ethyl acetate, and evaporating gave a brown oil (13·6 g).

[13] R. Baird and S. Winstein, *J. Amer. Chem. Soc.*, 1962, **84**, 78.
[14] M. Julia, S. Julia, and B. Bémont, *Bull. Soc. chim. France*, 1960, 304.

The n.m.r. spectrum revealed that this was a mixture of the expected acid and its demethylated product(s), and methylation of the crude material was carried out by dissolving in acetone (200 ml) and heating under reflux with dimethyl sulphate (6·6 g) and potassium carbonate (7·3 g). Most of the acetone was removed, water added, and the solution extracted with ether. The ether extract was washed with sodium hydroxide solution (2N), sodium chloride solution, dried, and evaporated. A dark brown oil (4·6 g) was obtained which was purified by chromatography over silica (180 g) using benzene–ethyl acetate (2 : 1) and then distillation to give *methyl* 4,4-*bis*-(p-*methoxyphenyl*)*butyrate* (20) (3·2 g, 22%) as a glass, b.p. (bulb–tube; bath temp.) 190—200° at 0·06 mmHg (Found: C, 72·95; H, 6·9. $C_{19}H_{22}O_4$ requires C, 72·6; H, 7·05%), $\nu_{max.}$ 1735s cm^{-1}; τ ($CDCl_3$) 7·70 and 7·65 (2 narrow m, $[CH_2]_2$), 6·35 (s, CO_2CH_3) and 6·20 (s, 2 × OCH_3 superimposed on 4-H), and 3·25, 3·10, 2·90, and 2·75 (8 × ArH),

4,4-Bis-(*p*-methoxyphenyl)butan-1-ol was obtained by reduction of the ester (20) with excess of lithium aluminium hydride in ether. The product was purified by chromatography over silica using ethyl acetate–benzene (2 : 1) giving the alcohol (79%), $\nu_{max.}$ 3380m,br cm^{-1}; τ ($CDCl_3$) 8·7—7·7 (m, $[CH_2]_2$ and OH), 6·45 (t, *J* 6 Hz, CH_2OH), 6·30 (2 × OCH_3, superimposed on 4-H), and 3·30, 3·15, 2·95, and 2·80 (8 × aromatic H).

The foregoing alcohol (0·5 g) was oxidised with chromium trioxide (1·43 g) in dichloromethane (40 ml) and pyridine (2·3 ml) as described earlier except that the solution was stirred for 15 min at room temperature before the mixture was decanted and worked up. The crude aldehyde was homologated with acetonyltriphenylphosphonium chloride (0·5 g) and sodium carbonate (0·17 g) in water (1·5 ml) and tetrahydrofuran (5 ml) as described earlier. Chromatography over Kieselgel eluting with benzene–ethyl acetate (3 : 1) and distillation gave 7,7-*bis*-(p-*methoxyphenyl*)*hept*-3-*en*-2-*one* (19) (240 mg, 42%) as a glass, b.p. (bulb–tube; bath temp.) 240—250° at 0·5 mmHg (Found: C, 77·75; H, 7·35. $C_{21}H_{24}O_3$ requires C, 77·75; H, 7·35%), $\nu_{max.}$ 1670s and 1625m cm^{-1}; τ ($CDCl_3$) 7·90 (s on a narrow m, CH_3CO and $[CH_2]_2$), 6·30 (s, 2 × OCH_3, superimposed on 7-H), 4·05 (d, *J* 16 Hz, 3-H), and 3·35, 3·20, 3·00, and 2·85 (8 × ArH superimposed on 4-H).

We thank the S.R.C. for a grant (to R. H. G.).

[3/1976 *Received*, 26*th September*, 1973]