

Friedel–Crafts Reactions of Alkenones with Benzene

By **Martin F. Ansell*** and **S. Aleem Mahmud**, Queen Mary College, University of London, Mile End Road, London E1 4NS

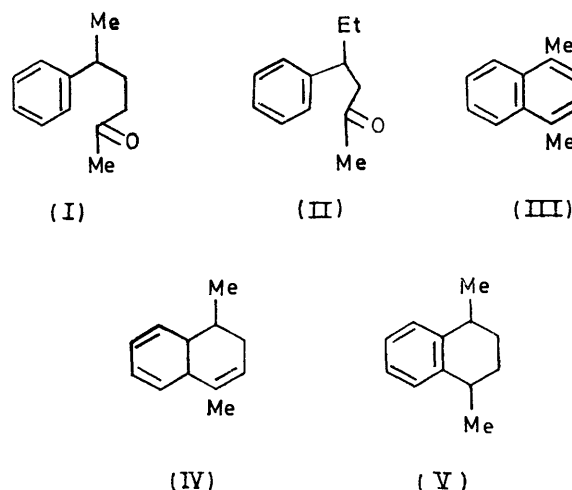
The Friedel–Crafts reactions of benzene with hex-3-en-2-one, hex-4-en-2-one, hex-5-en-2-one, hept-3-en-2-one, hept-4-en-2-one, oct-3-en-2-one, oct-4-en-2-one, oct-5-en-2-one, oct-6-en-2-one, oct-7-en-2-one, and 5-methylhex-5-en-2-one are reported. Hex-4-en-2-one and hex-5-en-2-one both yielded 5-phenylhexan-2-one as the sole monophenylation product. Each of the other ketones gave a mixture of phenylated alkanones, the composition of which depended on the position of the double bond relative to the carbonyl group in the starting ketone.

It has been shown¹ that in the Friedel–Crafts reaction of alkenoic acids, the nature of the product is dependent on the relative positions of the double bond and the carboxy-group. We now report an investigation into the Friedel–Crafts reactions of alkenones. Previous work in this field appears to have been confined to a study of the reactions of $\alpha\beta$ -unsaturated ketones and alkenones containing a terminal double bond.

The reaction of hex-5-en-2-one with benzene in the presence of aluminium chloride has been reported² to yield 5-phenylhexan-2-one (I) and that with anisole³ under similar conditions to give 5-*p*-methoxyphenylhexan-2-one. The exclusive formation of the 5-arylhexan-2-one has also been reported in the Friedel–Crafts reaction of hex-5-en-2-one with cumene,³ *p*-cymene,³ xylene,^{4a} tetralin,^{4b} and naphthalene.⁵

We have investigated a series of aluminium-chloride-catalysed reactions between alkenones and benzene. In each case the phenylalkanones produced were separated by g.l.c. and their structures deduced from their spectroscopic properties, and in some cases by comparison with authentic samples. In most of the reactions the yield of mono-phenylated material was low. The accompanying lower boiling material, which may have contained chloro-ketones, and higher boiling products were not investigated. Our results on the phenylation of hex-5-en-2-one are shown in Table 1. We agree with earlier workers that arylation occurs exclusively at the 5-position. The cyclic products (III)–(V) not mentioned by previous workers, clearly arise from 5-phenylhexan-2-one; this initially cyclises to 1,2-dihydro-1,4-dimethylnaphthalene (IV), which we have shown disproportionates to 1,4-dimethylnaphthalene (III) and 1,4-dimethyltetrahydronaphthalene (V). Such reactions have been previously observed with 5-phenylpentan-2-one,⁶ and in the formation³ of 1,2-dihydro-6-methoxy-1,4-dimethylnaphthalene from anisole, hex-5-en-2-one, and aluminium chloride. Exclusive arylation at the penultimate position of the chain in such reactions of terminally unsaturated alkenones does not always occur (see later).

In the Friedel–Crafts reaction of but-3-en-2-one^{7,8} with arenes, arylation occurs at the terminal position to yield a 4-arylbutan-2-one. This is to be expected, as formation of an intermediate with a positive charge at



C-3 adjacent to the carbonyl group will not be favoured. The report⁸ that phenylation of pent-3-en-2-one occurs at C-4 may be rationalised on the basis that the species with a secondary carbonium ion centre most remote from the carbonyl group is the preferred intermediate. In the case of the longer chain $\alpha\beta$ -unsaturated ketones, hex-3-en-2-one and hept-3-en-2-one, it is reported⁹ that reaction with benzene and aluminium chloride leads to 5-phenylhexan-2-one and 6-phenylheptan-2-one, respectively: no other products were reported. We have found that hex-3-en-2-one gives a mixture of 4- and 5-phenylhexan-2-one, in which the 4-phenyl isomer may predominate, together with cyclic non-ketonic products (see Table 1), and hept-3-en-2-one gives a mixture of 4-, 5-, and 6-phenylheptan-2-ones (see Table 2). Only small amounts of cyclic products were obtained in this reaction presumably because 5-phenylheptan-2-one is not a major product (see Table 2).

* J. Colonge and R. Domerrch, *Bull. Soc. chim. France*, 1952, 1000.

² H. P. Quillet and J. Dreux, *Compt. rend.*, 1964, 258, 1259; J. P. Quillet, A. Duperrier, and J. Dreux, *Bull. Soc. chim. France*, 1967, 255.

³ S. M. Mukherji, O. P. Vig, N. K. Maheswary, and S. S. Sandhu, *J. Indian Chem. Soc.*, 1957, 34, 1.

⁴ (a) O. P. Vig and S. S. Sandhu, *Science and Culture*, 1953, 19, 311; (b) O. P. Vig, S. V. Kessar, V. P. Kubba, and S. M. Mukherji, *J. Indian Chem. Soc.*, 1955, 32, 697.

⁵ J. Colonge and L. Pichat, *Bull. Soc. chim. France*, 1949, 177, 421.

⁶ C. D. Nenitzescu and I. G. Gavata, *Annalen*, 1935, 519, 260.

¹ M. F. Ansell and G. F. Whitfield, *J. Chem. Soc. (C)*, 1971, 1098.

² J. Colonge and L. Pichat, *Compt. rend.*, 1948, 226, 673; *Bull. Soc. chim. France*, 1949, 853.

³ S. M. Mukherji, O. P. Vig, N. K. Maheswary, and S. S. Sandhu, *J. Indian Chem. Soc.*, 1957, 34, 1.

⁴ (a) O. P. Vig and S. S. Sandhu, *Science and Culture*, 1953, 19, 311; (b) O. P. Vig, S. V. Kessar, V. P. Kubba, and S. M. Mukherji, *J. Indian Chem. Soc.*, 1955, 32, 697.

The results obtained from a study of the Friedel-Crafts reactions between benzene and the octen-2-ones are shown in Table 3.

The results in Tables 1—3, summarised in Table 4, make possible some generalisations as to the course of

under the reaction conditions we have used, that with straight chain $\alpha\beta$ -unsaturated ketones phenylation will occur at all positions from β to $\omega - 1$ (with methyl ketones $\beta = 4$). Similarly if the double bond is in the $\beta\gamma$ -position phenylation will occur at all positions from

TABLE 1
Reactions of hexen-2-ones with benzene-aluminium chloride and related reactions

Ketone or related compounds	Conditions *	Recovered hexenone	Ketonic products			Cyclic products			
			% Yield	% Composition (I) (II)		% Yield ^b	% Composition (III) (IV) (V)		
Hex-3-en-2-one	A	54	10 ^a	38	62	1.2	44	37	19
Hex-3-en-2-one	B	7	6 ^a	3	97	1.5 ^c	27	25	36
Hex-4-en-2-one	A		41	100		16.5	26	34	40
Hex-5-en-2-one	A		50	100		19	33	33	33
5-Phenylhexan-2-one	A		51	100		7.5	46	23	31
5-Phenylhexan-2-one	B		14	100		6	54	8	38
1,2-Dihydro-1,4-dimethylnaphthalene	A					30	15	8	77

* A, 3 h at 10—20°; B, 7 h at 35—40°.

^a Based on unrecovered ketone. ^b Based on C₁₂H₁₄. ^c 12% Product present, probably 1-ethyl-3-methylindene.

the Friedel-Crafts reactions of alkenones with benzene. Phenylation will never occur at the α -position (β -position

γ to $\omega - 1$ (with methyl ketones $\gamma = 5$), but if the double bond is initially in the $\gamma\delta$ -position (with methyl ketones the 5,6-position) or more remote from the carbonyl group, phenylation will not occur closer than the δ -position (position 6 with methyl ketones) except in the

TABLE 2

Reactions of hepten-2-ones with benzene-aluminium chloride

Hepten-2-one	Conditions *	Product phenylheptanone			
		% Yield	% Composition 4-Ph 5-Ph 6-Ph		
(i) Δ^3	A	26.1 ^a	13	11	71
(ii) Δ^3	B	20.0 ^a	72		26
(iii) Δ^4	A	75.0		11	89
(iv) Product from (iii)	B	75.0 ^b			100
(v) Δ^4	B	71.2 ^c		4	94

* See Table 1.

^a Based on unrecovered ketone. ^b 4-Ethyl-1,2-dihydro-1-methylnaphthalene obtained (ca. 5%). ^c 4-Ethyl-1,2-dihydro-1-methylnaphthalene obtained (ca. 2%).

TABLE 3

Reactions of octen-2-ones with benzene-aluminium chloride

Octen-2-one	Conditions *	Product phenyloctan-2-one				
		% Yield	% Composition 4-Ph 5-Ph 6-Ph 7-Ph			
Δ^3	A	12.5	18	7	12	62
Δ^3	B	27.3	56		13	31
Δ^4	A	46.4		8	25	67
Δ^4	B	46.2 ^a		8	17	72
Δ^5	A	31.0		1	35	64
Δ^5	B	56.7			34	66
Δ^6	A	36.1		3	14	84
Δ^6	B	56.7		2	28	70
Δ^7	A	31.2 ^b			6	94
Δ^7	B	51.6			29	71

* See Table 1.

^a 3% (?) Cyclic product present. ^b High-boiling product [C₈H₆ + 2 × C₈H₁₄O] from mass spectrum] also obtained.

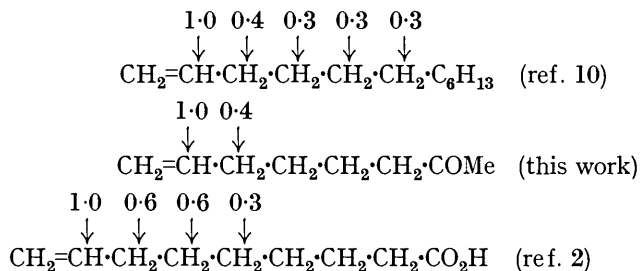
with a methyl ketone) as this would necessitate producing a carbonium ion centre adjacent to the electron attracting carbonyl group. Similarly, phenylation does not occur at the terminal position (except with but-3-en-2-one), as this would require the formation of a primary carbonium ion. It appears to be a general conclusion,

TABLE 4
Position of phenylation of alken-2-ones

Ketone	Unsaturation	Phenyl position in isomer obtained			
Hexenone	Δ^3	4	5		
	Δ^4		5		
	Δ^5		5		
Heptenone	Δ^3	4	5		
	Δ^4		5	6	
	Δ^5		5	6	7
Octenone	Δ^3	4	5	6	7
	Δ^4		5	6	7
	Δ^5		a	6	7
	Δ^6		a	6	7
	Δ^6			6	7

^a Trace of 5.

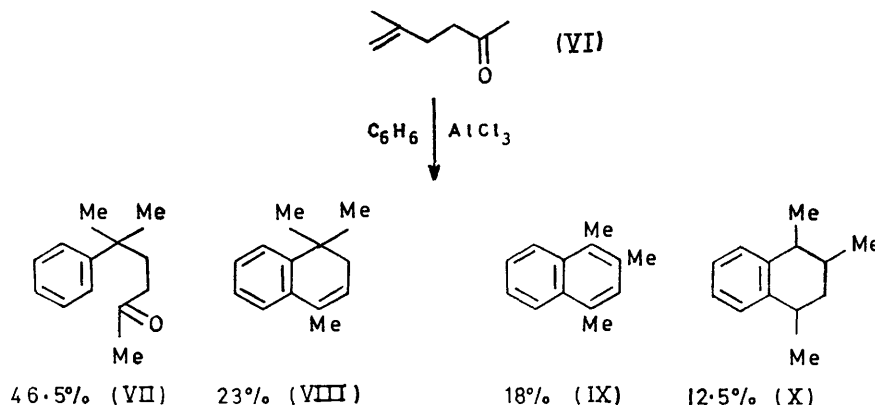
special case of hex-5-en-2-one where the δ -position is the terminal position. These results closely parallel those obtained with unsaturated acids and may be rationalised in the same way¹ in terms of steric and electronic effects. The effect of a carbonyl function on the Friedel-Crafts reaction of a terminally unsaturated compound is clearly shown in the Scheme where the arrows show the position of phenylation and the numbers indicate the ratios of the yields of products.



SCHEME

¹⁰ R. D. Swisher, E. F. Koelble, and S. K. Liu, *J. Org. Chem.*, 1961, **26**, 4066.

In the foregoing reactions, the observed disproportionation of the dihydronaphthalene by-products probably occurs by an ionic mechanism. Such a mechanism has been suggested,⁶ and is supported by our investigation of the reaction of 5-methylhex-5-en-2-one (VI) with benzene in the presence of aluminium chloride. The sole ketonic product was, as expected, 5-methyl-5-phenylhexan-2-one (VII), which was accompanied by 1,2-dihydro-1,1,4-trimethylnaphthalene (VIII) and 1,2,4-trimethylnaphthalene (IX) and its 1,2,3,4-tetrahydro-derivative (X).



The formation of compounds (IX) and (X) appears to involve rearrangement of 1,2-dihydro-1,1,4-trimethylnaphthalene to 1,2-dihydro-1,2,4-trimethylnaphthalene, followed by disproportionation. Similar rearrangements have been reported.^{11,12}

Synthesis of Ketones.—The synthesis of *trans*-hex-3-en-2-one by the base-catalysed condensation of propionaldehyde and acetone has been reported.¹³ In our hands this led to a complex mixture of products from which pure hex-3-en-2-one could not be isolated. As an alternative the oxidation of *cis*-hex-3-en-2-ol¹⁴ was investigated. The use of manganese dioxide,¹⁵ silver carbonate on Celite,¹⁶ or nickel peroxide¹⁷ gave, in low yield, what appeared to be *trans*-hex-3-en-2-one, together with the starting alcohol. Oxidation with Jones reagent (chromic acid in aqueous acetone)¹⁸ or with chromium trioxide in a two-phase system¹⁹ gave a mixture containing the required hex-3-en-2-one (*ca.* 75%) together with hex-4-en-2-one and hex-5-en-2-one. The partial reduction of hex-3-en-2-one could not be controlled to give exclusively the unsaturated ketone. The

¹¹ N. Deno, H. Peterson, and G. Saines, *Chem. Rev.*, 1960, **60**, 7.

¹² M. C. Kloetzel, *J. Amer. Chem. Soc.*, 1940, **62**, 1708.

¹³ V. Grignard and M. Fluchaire, *Ann. Chim. (France)*, 1928, **9**, 5; E. R. Alexander and G. R. Coraer, *J. Amer. Chem. Soc.*, 1951, **73**, 2721; E. D. Bergman and C. Resnik, *J. Org. Chem.*, 1952, **17**, 1291.

¹⁴ R. S. Airs, M. P. Balfe, and J. Kenyon, *J. Chem. Soc.*, 1942, 18.

¹⁵ J. Attenburrow, A. F. B. Cameron, J. H. Chapman, R. M. Evans, B. A. Hems, A. B. A. Jansen, and T. Walker, *J. Chem. Soc.*, 1952, 1094.

¹⁶ M. Fertizon and M. Gulfier, *Compt. rend.*, 1968, **266**, 900.

¹⁷ K. Nakagawa, R. Konaka, and J. Sugita, *Ann. Reports Shionogi Research Lab.*, 1969, No. 19.

¹⁸ K. Bowden, I. M. Heilbron, E. R. H. Jones, and B. C. L. Weedon, *J. Chem. Soc.*, 1946, 39.

synthesis of *trans*-hex-3-en-2-one was eventually conveniently effected by the reaction of pent-2-enoic acid with methyl-lithium following a procedure developed by Tegner.²⁰ *trans*-Hex-4-en-2-one was similarly obtained. It had been previously prepared,²¹ in admixture with *trans*-hex-3-en-2-one, by dehydration of hex-4-ene-2,3-diol. Hex-5-en-2-one was prepared by the published method.²²

Hept-4-enone was prepared from hex-3-enoic acid and methyl-lithium. It had been previously obtained²³

from hex-3-enoyl chloride and methyl iodide in the presence of a zinc-copper couple, although the authors reported that no satisfactory (analytical) figures could be obtained for the ketone itself. 5-Methylhex-5-en-2-one was prepared by the reported^{22,24} method.

The oct-3-, 4-, 5-, and 6-en-2-ones were conveniently prepared by the action of methyl-lithium on the appropriate heptenoic acids. Oct-3-en-2-one²⁵ and oct-5-en-2-one²⁶ had been previously synthesised by unambiguous routes, oct-4-en-2-one was reported²⁷ to be formed in 2.3% yield by the action of acetic anhydride on hex-1-ene in the presence of zinc chloride, but oct-6-en-2-one had not been reported previously. Oct-7-en-2-one was synthesised by the published method.²⁸

Of the phenylhexan-2-ones needed as reference compounds, the 3- and the 4-phenyl isomers were prepared by the methods of refs. 29 and 30, respectively. The 5-phenyl isomer had been previously obtained from the Friedel-Crafts reaction of benzene and hex-5-en-2-one

¹⁹ A. E. Vanstane and J. S. Whitehurst, *J. Chem. Soc.*, 1966, 1972.

²⁰ C. Tegner, *Acta Chem. Scand.*, 1952, **6**, 782.

²¹ C. Prevost, *Bull. Soc. chim. France*, 1944, **11**, 218.

²² M. S. Schechter, N. Green, and F. B. LaForge, *J. Amer. Chem. Soc.*, 1949, **71**, 3165.

²³ E. N. Escott and R. P. Linstead, *J. Chem. Soc.*, 1930, 905.

²⁴ J. Colonge, G. Descotes, and R. Mugnier, *Bull. Soc. chim. France*, 1965, 2733.

²⁵ M. H. Durand, *Bull. Soc. chim. France*, 1961, 2393.

²⁶ L. Crombie and S. H. Harper, *J. Chem. Soc.*, 1952, 869.

²⁷ A. P. Meshcheryabov, L. V. Petrova, and A. D. Petrov, *Izvest. Akad. Nauk S.S.S.R., Otdel. khim. Nauk*, 1960, 98 (*Chem. Abs.*, 1960, **54**, 20,868f).

²⁸ F. Rouessac, P. L. Perchec, and J.-M. Conia, *Bull. Soc. chim. France*, 1967, 818.

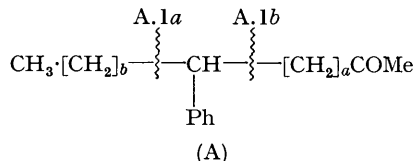
²⁹ A. E. M. Schultz, J. B. Bicking, S. Mickey, and F. S. Crossley, *J. Amer. Chem. Soc.*, 1953, **75**, 1072.

³⁰ H. O. House, D. D. Traficante, and R. A. Evans, *J. Org. Chem.*, 1963, **28**, 348.

(see before). We have prepared it from 4-phenylpentanoic acid³¹ and methyl-lithium. A new synthesis of 6-phenylhexan-2-one from 1-bromo-3-phenylpropane and ethyl acetoacetate is reported.

EXPERIMENTAL

N.m.r. spectra were determined at 60 MHz for solutions in deuteriochloroform. Mass spectra were determined on an A.E.I. MS 902 instrument. The cleavage modes of branched-chain compounds are defined in structure (A) where A.1a signifies cleavage at the position shown with detection of the fragment $(\text{PhCH}[\text{CH}_2]_a\text{COMe})^+$ and A.1b cleavage signifies cleavage with detection of the fragment $(\text{CH}_3[\text{CH}_2]_b\text{CHPh})^+$. G.l.c. analyses and separations were



effected with the following columns: A, 4 ft \times 0.25 in 30% polyethylene glycol adipate on firebrick; B, 10 ft \times 0.25 in diethylene glycol succinate on firebrick; C, 50 m \times 0.25 mm *m*-bis-(*m*-phenoxyphenoxy)benzene, capillary column; D, 4 ft \times 0.25 in 10% polyethylene glycol adipate on firebrick; E, 10 ft \times 0.75 in 20% Carbowax on 60–80 mesh Chromosorb; F, 2 m \times 0.125 in 20% diethylene glycol succinate on 80–100 mesh Chromosorb W HMSS; G, 2 m \times 0.125 in 5% diethylene glycol succinate on 80–100 mesh Chromosorb W HMSS.

General Procedure for Friedel-Crafts Reactions.—*Conditions (a)*. The ketone (0.033 mol) was added dropwise to a stirred suspension of powdered aluminium chloride (7 g, 0.05 mol) in dry benzene (13 ml). The temperature was maintained at 10–20° throughout the addition and while the mixture was stirred for a further 3 h. The mixture was then cooled and a mixture of ice and 6M-hydrochloric acid (25 ml) was added. The benzene phase was separated and the aqueous phase extracted with benzene (2 \times 25 ml). The combined benzene extracts were washed with saturated sodium hydrogen carbonate solution (10 ml) and water (10 ml) and dried (MgSO_4). The bulk of the solvent was evaporated off and the residue was distilled.

Conditions (b). As conditions (a) except that the reaction temperature was 35–40° and the reaction time 7 h.

Friedel-Crafts Reaction of Hex-5-en-2-one.—*Conditions (a)*. Distillation gave a product (4.0 g), b.p. 70–76° at 0.2 mmHg, which contained (g.l.c., column C at 125°) *cis*- and *trans*-1,2,3,4-tetrahydro-1,4-naphthalene (8%), 1,2-dihydro-1,4-dimethylnaphthalene (8%), 5-phenylhexan-2-one (75%), and 1,4-dimethylnaphthalene (8%) (retention times 21.5, 29.0, 54.5, and 71.5 min, respectively). The components were separated by preparative scale g.l.c. (B at 160°).

cis- and *trans*-1,2,3,4-Tetrahydro-1,4-dimethylnaphthalene showed M^+ 160 (Calc. for $\text{C}_{12}\text{H}_{16}$: M , 160); ν_{max} . 3020, 2060, and 3100 (=CH stretch in aromatic homocycle), 2935, 2960, and 2865 (C–Me stretch), 1490 and 1605 (C=C in aromatic homocycle), 1380 (CH_3 sym. def.), and 750 cm^{-1} (1,2-disubst. benzene); δ (CDCl_3) 1.27 (3H, d, J 7 Hz, 1- and 4-Me, *cis* or *trans*), 1.24 (3H, d, J 7 Hz, 1- and 4-Me, *trans* or *cis*), 1.45–2.1 (4H, m, 2- and 3- H_2), 2.6–3.15 (2H, m, 1- and 4-H), and 7.15 (4H, s, aromatic). From the integration at δ 1.27 and 1.24 the *cis*–*trans* ratio was 1 : 1.

1,2-Dihydro-1,4-dimethylnaphthalene showed M^+ 158 (Calc. for $\text{C}_{12}\text{H}_{14}$: 158); δ 1.22 (3H, d, J 7 Hz, 1-Me), 2.05 (3H, d, J 1 Hz, 4-Me), 2.15–2.5 (2H, m, 2- H_2), 2.6–3.1 (1H, m, 1-H), 5.6–5.9 (1H, m, 3-H), and 7.2 (4H, s, aromatic), and was identical with an authentic sample.¹²

The components of the mixture of 5-phenylhexan-2-one and 1,4-dimethylnaphthalene [ν_{max} . 1715 cm^{-1} (C=O)] were identified by comparison of the n.m.r. spectra of the two authentic compounds with that of the mixture: (a) assigned to 5-phenylhexan-2-one δ 1.25 (3H, d, J 7 Hz, 5-Me), 1.65–1.95 (1H, m, 5-H), 2.01 (3H, s, 1- H_3), 2.15–3.0 (4H, m, 3- and 4- H_2), 7.2br (5H, s, aromatic); (b) assigned to 1,4-dimethylnaphthalene δ 2.65 (s, 1- and 4-Me), 7.3–7.5 (m), and 7.9–8.2 (m). From the integrations at δ 2.1 and 2.65 the ratio of 1,4-dimethylnaphthalene to 5-phenylhexan-2-one was between 6 : 1 and 10 : 1.

Friedel-Crafts Reaction of trans-Hex-4-en-2-one.—*Conditions (a)*. Distillation gave a product (3.0 g), b.p. 68–74° at 0.2 mmHg, which was analysed by g.l.c. (C at 125°) and the components were identified from their retention times (see Table 1).

Friedel-Crafts Reaction of trans-Hex-3-en-2-one.—*Conditions (a)*. Distillation gave a fraction (1.7 g), b.p. 30–34° at 5.5 mmHg, containing [from g.l.c. (A at 125°) with peak enhancement experiments] hex-5-en-2-one (7%), *trans*-hex-4-en-2-one (7%), and *trans*-hex-3-en-2-one (86%); and a fraction (0.3 g), b.p. 78–80° at 0.15 mmHg, containing (g.l.c., C at 125°) 1,2-dihydro-1,4-dimethylnaphthalene (ca. 2%), 4-phenylhexan-2-one (58%), 5-phenylhexan-2-one (38%), and 1,2-dimethylnaphthalene (2%). The 4-phenylhexan-2-one was isolated by preparative scale g.l.c. (B at 170°) and was identical with an authentic sample (see later). The other components were identified by peak enhancement experiments.

Conditions (b). Distillation gave a fraction (0.2 g), b.p. 38–40° at 13 mmHg, containing [identified as for conditions (a)] hex-5-en-2-one (ca. 1%), *trans*-hex-4-en-2-one (ca. 2%), and *trans*-hex-3-en-2-one (97%); and a fraction (0.4 g), b.p. 72–74° at 0.2 mmHg, containing [from g.l.c. (C at 125°)] 1,4-dimethyltetrahydronaphthalene (11%), 1,2-dihydro-1,4-dimethylnaphthalene (4%), 4-phenylhexan-3-one (75%), 5-phenylhexan-2-one (identified by peak enhancement experiments), together with 1-ethyl-3-methylindene (ca. 2%) and 1,4-dimethylnaphthalene (6%). A mixture of the last two components, separated by preparative scale g.l.c. (B at 170°), exhibited the following n.m.r. spectrum: (a) attributed to 1,4-dimethylnaphthalene δ 2.63 (6H, s), 7.18br (6H, s), 7.35–7.55 (2H, m), and 7.99 (dd, J 6 and 3 Hz) (see later); (b) attributed to 1-ethyl-3-methylindene δ 0.75 (t, J 7 Hz, 1- CH_3CH_2), 1.22 (appears as broad d, 1- CH_3CH_2), 1.98 (3-Me), and 2.4–2.75 (m, 1-H).

Reaction of the 4-, 5-, and 6-Phenylhexan-2-ones with Benzene and Aluminium Chloride.—*Conditions (a) and (b)*. With 4- and 6-phenylhexan-2-one only unchanged ketone was recovered. With 5-phenylhexan-2-one a mixture of unchanged ketone and cyclic products (identified by g.l.c. peak enhancement experiments) was obtained (see Table 1).

Reaction of 1,2-Dihydro-1,4-dimethylnaphthalene with Benzene and Aluminium Chloride.—A mixture of the hydrocarbon (1.3 g) and aluminium chloride (1.4 g) in benzene (3 ml) was treated under conditions (a). Distillation gave a product (0.5 g) which was analysed by g.l.c. (C at 125°); see Table 1.

Friedel-Crafts Reaction of 5-Methylhex-5-en-2-one.—*Con-*

³¹ R. V. Christian, jun., *J. Amer. Chem. Soc.*, 1952, **74**, 1591.

ditions (a). Distillation gave material (1.8 g), b.p. 86—92° at 0.2 mmHg, which [g.l.c. (C at 125°)] contained 1,2,4-trimethylnaphthalene (13%), 1,2-dihydro-1,1,4-trimethylnaphthalene (23%), 5-methyl-5-phenylhexan-2-one (46%), and 1,2,4-trimethylnaphthalene (18%), retention times 21.5, 30.0, 80.0, and 145.0 min, respectively. Each component was isolated by preparative scale g.l.c. (B at 130°).

1,2,4-Trimethyltetrahydronaphthalene showed no C=O i.r. absorption; δ 1.2—1.45 (9H, m, 1-, 2-, and 4-Me), 1.55—2.1 (3H, m, 2-H and 3-H₂), 2.4—2.6 (2H, m, 1- and 4-H), and 7.15 (4H, s, aromatic). 1,2-Dihydro-1,1,4-trimethylnaphthalene showed no C=O i.r. absorption; δ 1.22 (6H, s, 1-Me), 1.92—2.65 (5H, m, 2-H₂ and 4-Me), 5.6—5.9 (1H, m, 3-H), and 7.18 (4H, s, aromatic). 5-Methyl-5-phenylhexan-2-one showed ν_{\max} 1710 cm⁻¹ (C=O); δ 1.31 (6H, s, 5-Me₂), 1.6—2.4 (4H, m, 3- and 4-H₂), 2.0 (3H, s, 3H, 2-Me), and 7.26 (5H, s, aromatic). 1,2,4-Trimethylnaphthalene showed no C=O i.r. absorption; δ 2.42, 2.54, and 2.6 (each 3H, s, 1-, 2-, and 4-Me), 7.12 (1H, s, 3-H), and 7.36—7.54 and 7.84—8.06 (each 2H, m, 5-, 6-, 7-, and 8-H). This compound was also obtained by dehydrogenating 1,2-dihydro-1,1,4-trimethylnaphthalene with *o*-chloranil.

Friedel-Crafts Reaction of trans-Hept-3-en-2-one.—Conditions (a). Distillation gave *trans*-hept-3-en-2-one (2.5 g; 65% recovery, 94% pure), b.p. 86—100° at 5 mmHg, and a mixture (0.5 g) containing [g.l.c. (C at 140°)] an unknown (6%), 4-phenylheptan-2-one (13%), 5-phenylheptan-2-one (11%), and 6-phenylheptan-2-one (70%), retention times 29.5, 34.0, 38.0, and 52.5 min, respectively. These compounds were identified by peak enhancement experiments with authentic samples (see later).

Conditions (b). Distillation gave *trans*-hept-3-en-2-one (1.9 g; 51% recovered, 94% purity), b.p. 50—52° at 2.5 mmHg, and a mixture (0.6 g), b.p. 100—104° at 15 mmHg, containing [g.l.c. (C at 125°)] an unknown (*ca.* 2%), 4-phenylheptan-2-one (72%), and 6-phenylheptan-2-one (26%), retention times 22.5, 59.0, and 93.0 min, respectively, separated by preparative scale g.l.c. (B at 190°).

4-Phenylheptan-2-one showed ν_{\max} 1720 cm⁻¹; δ 0.83 (3H, t, *J* 5 Hz, 6-Me), 1.02—1.9 (4H, m, 5- and 6-H₂), 1.98 (3H, s, 2-Me), 2.59—2.8 (2H, m, 3-H₂), 2.85—3.3 (1H, m, 4-H), and 7.2 (5H, s, aromatic); *m/e* 190 (34%, M⁺), 147 (56% M — C₃H₇, A.1a cleavage), 132 (90% M — C₃H₆, McLafferty rearrangement of molecular ion), 117 (16% M — C₄H₉O), 91 (65%, tropylium ion), and 43 (100%, acetyl ion), *m** 103.7 (132 → 117, loss of Me).

6-Phenylheptan-2-one showed ν_{\max} 1718 cm⁻¹ (C=O); δ (CDCl₃) 1.23 (3H, d, *J* 7 Hz, 6-Me), 1.35—1.85 (4H, m, 4- and 5-H₂), 2.05 (3H, s, 2-Me), 2.15—2.5 (2H, m, 3-H₂), 2.55—2.85 (1H, m, 6-H), and 7.2 (5H, s, aromatic); *m/e* 190 (29%, M⁺), 132 (12%, M — C₃H₆O, McLafferty rearrangement of molecular ion), 117 (20%, M — C₄H₉O), 105 (100%, M — C₅H₉O, A.1b cleavage), 91 (18%, tropylium ion), 85 (27.5%, C₅H₉O), and 43 (50%, acetyl ion), *m** 103.7 (132 → 117, loss of Me).

Friedel-Crafts Reaction of trans-Hept-4-en-2-one.—Conditions (a). Distillation gave a product (4.6 g), b.p. 108—112° at 2.5 mmHg. G.l.c. analysis (C at 140°) showed the presence of 5-phenylheptan-2-one (10%) and 6-phenylheptan-2-one (90%), retention times 37.5 and 52.0 min, respectively. The latter was identified by peak enhancement experiments and the former from its physical constants: ν_{\max} 1720 cm⁻¹ (C=O); δ 0.76 (3H, t, *J* 6.5 Hz, 6-Me), 1.0—1.9 (4H, m, 4- and 6-H₂), 2.01 (3H, s, 2-Me),

2.03—2.5 (3H, m, 3-H₂ and 5-H), and 7.1—7.3 (5H, m, aromatic); *m/e* 190 (23%, M⁺), 175 (10%, M — CH₃), 132 (100%, M — C₃H₆O, McLafferty rearrangement), 117 (28%, M — C₄H₉O), 105 (34%, M — C₅H₉O), 91 (53%, tropylium ion), and 43 (93%, acetyl ion), *m** 103.7 (132 → 117, loss of Me). The involvement of the benzylic hydrogen atom in the McLafferty rearrangement promotes the latter so that A.1 cleavage is not observed.

The mixture of 5- and 6-phenylheptan-2-one (0.2 g) and aluminium chloride (0.3 g) in benzene (2 ml) was treated under conditions (b). G.l.c. (C at 140°) of the distilled material (0.15 g; b.p. 90—100° at 0.2 mmHg) showed the presence of 1-ethyl-4-methyltetrahydronaphthalene (5%) (see next experiment), 6-phenylheptan-2-one (88%), and (?) 1-ethyl-4-methylnaphthalene (7%, retention time 56.0 min). The n.m.r. spectrum of a mixture of the last two components (isolated by g.l.c., B at 190°) showed, in addition to signals due to 6-phenylheptan-2-one, a small signal at δ 2.65 suggestive of the presence of 1-ethyl-4-methylnaphthalene (*cf.* 1,4-dimethylnaphthalene aromatic methyl signal at δ 2.65).

Conditions (b). Distillation gave a mixture (4.5 g), b.p. 100—103° at 0.5 mmHg, containing [g.l.c. (C at 140°)] 1-ethyl-4-methyltetrahydronaphthalene (*ca.* 2%, retention time 19.5 min) [δ (CDCl₃) 0.95 (3H, t, *J* 6.5 Hz, 1-MeCH₂), 1.1—1.4 (5H, 1-MeCH₂ and 4-Me), 1.45—2.2 (4H, m, 2- and 3-H₂), 2.2—2.3 (m, 1- and 4-H), and 6.95—7.3 (4H, m, aromatic)], together with 5-phenylheptan-2-one (*ca.* 4%) and 6-phenylheptan-2-one (94%), identified by peak enhancement experiments.

Friedel-Crafts Reaction of trans-Oct-3-en-2-one.—Conditions (a). Distillation gave *trans*-oct-3-en-2-one (3.3 g, *ca.* 80% recovery), b.p. 50—52° at 2 mmHg (pure by g.l.c.), and a mixture (0.17 g), b.p. 94—104° at 1 mmHg, containing [g.l.c., C at 150°] 4-phenyloctan-2-one (18%), 5-phenyloctan-2-one (7%), 6-phenyloctan-2-one (12%), and 7-phenyloctan-2-one (62%), identified by peak enhancement experiments with authentic samples (see later).

Conditions (b). Distillation gave a mixture (2.9 g), b.p. 32—34° at 0.4 mmHg, containing [g.l.c. (A at 125°)] *trans*-oct-4-en-2-one (25%) and *trans*-oct-3-en-2-one (75%), and a fraction (0.9 g), b.p. 82—90° at 0.2 mmHg, containing [g.l.c., C at 150°] 4-phenyloctan-2-one (56%), 6-phenyloctan-2-one (13%), and 7-phenyloctan-2-one (31%), retention times 32.5, 41.5, and 53.5 min, respectively. The mixture was separated by preparative scale g.l.c. (E at 200°).

4-Phenyloctan-2-one showed ν_{\max} 1710 cm⁻¹ (C=O); δ (CDCl₃) 0.8 (3H, t, *J* 5.5 Hz, 7-Me), 1.1—1.8 (6H, m, 5-, 6-, and 7-H₂), 1.98 (3H, s, 2-Me), 2.6—2.8 (3H, m, 3-H₂ and 4-H), and 7.2 (5H, s, aromatic); *m/e* 204 (21%, M⁺), 147 (50%, M — C₄H₉, A.1a cleavage), 146 (70%, M — C₂H₅O, McLafferty rearrangement), 119 (20%), 117 (20%, M — C₅H₁₁O), 91 (50%, tropylium ion), and 43 (100%, acetyl).

6-Phenyloctan-2-one showed ν_{\max} 1720 cm⁻¹ (C=O); δ (CDCl₃) 0.75 (3H, t, *J* 7 Hz, 7-Me), 1.1—1.8 (6H, m, 4-, 5-, and 7-H₂), 2.05 (3H, s, 2-Me), 2.15—2.75 (3H, m, 3-H₂ and 5-H), and 7.0—7.3 (5H, m, aromatic); *m/e* 204 (75%, M⁺), 175 (28%, M — C₂H₅, A.1a cleavage), 146 (22%, M — C₃H₆O, McLafferty rearrangement), 131 (6%, M — C₄H₉O), 119 (49%), 117 (100%), 91 (80%, tropylium ion), 85 (45%), 71 (7%), and 43 (60%, acetyl ion), *m** 117.5 (146 → 131, loss of Me) and 69.7 (85 → 71, loss of CH₂).

7-Phenyloctan-2-one showed ν_{\max} 1720 cm⁻¹ (C=O); δ (CDCl₃) 1.21 (3H, d, *J* 7 Hz, 7-Me), 1.05—1.8 (6H, m,

4-, 5-, and 6-H₂), 2.06 (3H, s, 2-Me), and 2.15—2.8 (3H, m, 3-H₂ and 7-H); *m/e* 204 (14%, M⁺), 105 (100%, M - C₆H₁₁O, A.1b cleavage), 91 (25%, tropylium ion), 79 (15%, C₆H₇), 77 (19%, C₆H₅), and 43 (70%, acetyl ion).

Friedel-Crafts Reaction of trans-Oct-4-en-2-one.—*Conditions (a).* Distillation gave a product (3.3 g), b.p. 100—108° at 0.1 mmHg, containing (g.l.c., C at 150°) 5-phenyloctan-2-one (8%, retention time 34.0 min), 6-phenyloctan-2-one (25%), and 7-phenyloctan-2-one (67%). The last two compounds were identified by peak enhancement experiments and the 5-phenyloctan-2-one was isolated by preparative scale g.l.c. (E at 200°); ν_{\max} . 1720 cm⁻¹ (C=O); δ (CDCl₃) 0.83 (3H, t, *J* 6 Hz, 7-Me), 1.0—1.7 (6H, 4-, 6-, and 7-H₂), 2.0 (3H, s, 2-Me), and 2.1—2.8 (3H, 3-H₂ and 5-H); *m/e* 204 (33%, M⁺), 146 (54%, M - C₃H₆O, McLafferty rearrangement), 131 (28%, M - C₄H₈O), 118 (100%), 91 (66%, tropylium ion), 77 (7%, C₆H₅), and 43 (66%, acetyl ion), *m** 117.5 (146 → 131, loss of Me). The involvement of the benzylic proton in the McLafferty rearrangement promotes the latter so that A.1 cleavage is not observed.

Conditions (b). See Table 3.

Friedel-Crafts Reactions of trans-Oct-5- and 6-en-2-ones.—These reactions were effected under both conditions (a) and conditions (b). The products were identified by peak enhancement experiments and the results are given in Table 3.

Friedel-Crafts Reaction of Oct-7-en-2-one.—*Conditions (a).* Distillation gave a mixture (2.6 g), b.p. 104—108° at 0.2 mmHg, of 6-phenyloctan-2-one (6%) and 7-phenyloctan-2-one (94%), identified by peak enhancement experiments, and a mixture of bis-(2-oxo-octyl)benzenes (2.0 g), b.p. 230—240° at 0.1 mmHg; M⁺ 330 (C₂₂H₃₄O₂); ν_{\max} . 1720 cm⁻¹ (C=O); δ 1.2 (6H, d, *J* 7 Hz, 2 × CH·CH₃), 1.0—1.85 (12H, m, 2 × 3 × CH₂), 2.06 (6H, s, 2 × MeCO), 2.35 (4H, *J* 7 Hz, 2 × CH₂-CO), 2.5—2.85 (2H, m, 2 × CHAr), and 6.76—7.3 (4H, aromatic) (Found: C, 80.6; H, 10.4. Calc. for C₂₂H₃₄O₂: C, 80.0; H, 10.4).

Conditions (b). Distillation gave a mixture (3.7 g), b.p. 120—122°, shown by g.l.c. (C at 150°) peak enhancement experiments to contain 6-phenyloctan-2-one (29%) and 7-phenyloctan-2-one (71%).

Preparation of Alkenones.—*General Procedure for Reaction of Acids with Methyl-lithium* (based on the procedure of Tegner²⁰). A solution of methyl-lithium in ether (*ca.* 0.5—0.6M) was prepared and its concentration estimated. A volume containing 0.40 mol was added slowly to a stirred solution of the alkenoic acid (0.20 mol) in dry ether (100 ml). Both solutions were kept under nitrogen. A vigorous reaction ensued; the ether boiled and initially a precipitate formed which dissolved as more methyl-lithium was added. The mixture was then heated under reflux for 30 min and cooled, and water (100 ml) was slowly added. The ethereal layer was separated and the aqueous layer extracted with ether (3 × 100 ml). The combined extracts were washed with water (3 × 50 ml), dried (MgSO₄), and distilled to give the ketone. *trans*-Pent-2-enoic acid¹ gave *trans*-hex-3-en-2-one (34%), b.p. 86—88° at 103 mmHg, 97% pure by g.l.c. (A at 125°) (lit.,³² b.p.

37° at 13 mmHg). *trans*-Pent-3-enoic acid gave *trans*-hex-4-en-2-one (25%), 100% pure by g.l.c. (A at 125°; retention time 6.5 min), b.p. 74—76° at 75 mmHg; ν_{\max} . 1725 (sat. C=O) and 970 cm⁻¹ (*trans*-CH=CH); δ 1.5—1.9 (3H, m, 5-Me), 2.13 (3H, s, 2-Me), 3.0—3.2 (2H, m, 3-H₂), and 5.4—5.7 (2H, m, 4- and 5-H) (Found: C, 73.2, H, 10.2. C₆H₁₀O requires C, 73.5; H, 10.2%). *trans*-Hex-2-enoic acid³³ gave *trans*-hept-3-en-3-one (45%), b.p. 74—76° at 31 mmHg, 95% pure by g.l.c. (A at 125°, retention time 14.5 min) (lit.,³⁴ b.p. 51—52° at 11 mmHg). *trans*-Hex-3-enoic acid³⁵ gave *trans*-hept-4-en-2-one (36%), 100% pure by g.l.c. (A at 125°, retention time 9.5 min), b.p. 54° at 17 mmHg; ν_{\max} . 1720 (sat. C=O) and 967 cm⁻¹ (*trans*-CH=CH); δ 1.0 (3H, t, *J* 7 Hz, 6-Me), 1.73—2.2 (2H, m, 6-H₂), 2.15 (3H, s, 2-Me), 3.1 (2H, dm, *J* 5.1 Hz, 3-H₂), and 5.45—5.7 (2H, m, 4- and 5-H) (Found: C, 74.7; H, 10.8%; M⁺, 112. C₇H₁₂O requires C, 74.95; H, 10.8%; M, 112). *trans*-Hept-2-enoic acid³⁶ gave *trans*-oct-3-en-2-one (43%), b.p. 70—72° at 10 mmHg, 100% pure by g.l.c. (A at 125°, retention time 24.5 min) (lit.,³⁷ b.p. 53—55° at 15 mmHg). *cis*-Hept-2-enoic acid³⁸ gave a mixture (2.0 g), b.p. 80—85° at 33 mmHg, shown (by g.l.c., A at 125°) to contain *cis*-oct-3-en-2-one (63%, retention time 12.5 min) and *trans*-oct-3-en-2-one (37%, retention time 17.0 min). The latter was identified by peak enhancement experiments with an authentic sample. The former, isolated by preparative scale g.l.c. (D at 100°), showed ν_{\max} . 1620 (conj. C=C) and 1685 cm⁻¹ (conj. C=O) (no absorption at 960—990 cm⁻¹, *trans*-CH=CH); δ 0.9 (3H, t, *J* 6 Hz, 7-Me), 1.15—1.7 (4H, m, 6- and 7-H₂), 2.2 (3H, s, 2-Me), 2.3—2.8 (2H, m, 5-H₂), and 6.05—6.15 (2H, m, 3- and 4-H); λ_{\max} . 225 nm (ϵ 9540), M⁺ 126 (C₈H₁₄O). *trans*-Hept-3-enoic acid³⁹ gave *trans*-oct-4-en-2-one (27%), 95% pure by g.l.c. (A at 125°, retention time 12.5 min), b.p. 86—88° at 40 mmHg; ν_{\max} . 1710 (sat. C=O) and 970 cm⁻¹ (*trans*-CH=CH); δ 0.9 (3H, t, *J* 6 Hz, 7-Me), 1.1—1.7 (4H, m, 6- and 7-H₂), 2.03 (3H, s, 2-Me), 2.9—3.1 (2H, m, 3-H₂), and 5.35—5.6 (2H, 4- and 5-H) (Found: C, 76.0; H, 11.0%; M⁺, 126. Calc. for C₈H₁₄O: C, 76.1; H, 11.1%; M, 126). *trans*-Hept-4-enoic acid³⁸ gave *trans*-oct-5-en-2-one (71.2%), *ca.* 99% purity by g.l.c. (A at 125°, retention time 18.0 min), b.p. 86—87° at 36 mmHg (lit.,⁴⁰ b.p. 169—173°); ν_{\max} . 1725 (sat. C=O) and 970 cm⁻¹ (*trans*-CH=CH); δ 0.93 (3H, t, *J* 7 Hz, 7-Me), 1.7—2.2 (2H, m, 3-H₂), 2.11 (3H, s, 2-Me), 2.2—2.65 (4H, m, 4- and 7-H₂), and 5.3—5.6 (2H, m, 5- and 6-H) (Found: C, 76.4; H, 11.1%; M⁺, 126. Calc. for C₈H₁₄O: C, 76.2; H, 11.1%; M, 126). *trans*-Hept-5-enoic acid³⁶ gave *trans*-oct-6-en-2-one (58%), *ca.* 100% pure from g.l.c. (A at 125°), b.p. 81—83° at 30 mmHg; ν_{\max} . 1725 (C=O) and 970 cm⁻¹ (*trans*-CH=CH); δ 1.42—2.15 (7H, m, 7-Me, 4- and 5-H₂), 2.13 (3H, s, 2-Me), 2.41 (2H, t, *J* 6.5 Hz, 3-H₂), and 5.3—5.5 (2H, m, 5- and 6-H) (Found: C, 76.1; H, 11.3%; M⁺, 126. C₈H₁₄O requires C, 76.2; H, 11.1%; M, 126). 4-Phenylpentanoic acid gave 5-phenylhexan-2-one (51%), *ca.* 97% pure by g.l.c. (C at 125°). Preparative scale g.l.c. (B at 120°) gave material showing ν_{\max} . 1720 cm⁻¹ (sat. C=O); δ (CCl₄) 1.23 (3H, d, *J* 7 Hz, 5-CH₃), 1.4—1.9 (2H, m, 4-H₂), 1.93 (3H, s, 2-CH₃), 2.05—2.35 (2H, m,

³⁶ M. F. Ansell, J. C. Emmett, and R. V. Coombe, *J. Chem. Soc. (C)*, 1968, 217.

³⁷ G. Strutz, *Bull. Soc. chim. France*, 1967, 2477.

³⁸ C. Rappe and R. Adestrom, *Acta Chem. Scand.*, 1965, **19**, 383.

³⁹ J. B. Knight and J. H. Diamond, *J. Org. Chem.*, 1959, **24**, 400.

⁴⁰ L. Crombie and S. Harper, *J. Chem. Soc.*, 1952, 869.

³² G. Sturtz, *Bull. Soc. chim. France*, 1967, 2477.

³³ C. Niemann and C. P. Redemann, *J. Amer. Chem. Soc.*, 1946, **68**, 1932.

³⁴ V. Theus, W. Surber, L. Colombi, and H. Schinz, *Helv. Chim. Acta*, 1955, **38**, 239.

³⁵ R. P. Linstead, E. G. Noble, and E. J. Boorman, *J. Chem. Soc.*, 1933, 557.

3-H₂), 2.66 (1H, q, *J* 7 Hz, 5-H), and 7.13 (5H, s, aromatic). The minor product (*ca.* 3%) was also isolated and shown to be 2-methyl-5-phenylhexan-2-ol (from 5-phenylhexan-2-one and methyl-lithium); ν_{\max} , 3500 cm⁻¹ (OH); δ 1.15 (6H, s, 2-Me₂), 1.25 (3H, d, *J* 7 Hz, 5-CH₃), 1.35–2.5 (5H, m, 3- and 4-H₂, and 2-OH), 2.45–2.9 (1H, m, 5-H), and 7.21 (5H, s, aromatic).

6-Phenylhexan-2-one.—Ethyl acetoacetate (12.2 g) was added to a solution of sodium ethoxide [from sodium (2.15 g) in ethanol (62.5 ml)]. 1-Bromo-3-phenylpropane (20.7 g) was then added dropwise during 1 h to the boiling solution. Heating and stirring were continued for 10 h, the bulk of the ethanol was distilled off, the residue was cooled, and sufficient water was added to dissolve the precipitated sodium bromide. The mixture was acidified with glacial acetic acid and extracted with ether (3 × 100 ml). The extracts were washed with saturated sodium chloride solution, dried (MgSO₄), and distilled to give *ethyl 2-oxo-6-phenylhexane-3-carboxylate* [9 g; 34% *ca.* 94% pure by g.l.c. (D at 125°)], b.p. 132–140° at 0.25 mmHg; ν_{\max} , 1730 cm⁻¹ (sat. C=O); δ 1.18 (3H, t, *J* 7 Hz, CH₃ of CO₂Et), 1.4–1.9 (4H, m, 4- and 5-H₂), 2.04 (3H, s, 2-CH₃), 2.55 (2H, t, *J* 7 Hz, 6-H₂), 3.21 (1H, t, *J* 7 Hz, 3-H), 4.07 (2H, q, *J* 7 Hz, CH₂ of 3-CO₂Et), and 7.1 (5H, aromatic) (Found: C, 72.6; H, 8.35. C₁₅H₂₀O₃ requires C, 75.6; H, 8.1%).

The foregoing ester (5 g), glacial acetic acid (25 ml), and concentrated hydrochloric acid (10 ml) were heated on a steam-bath for 5 h. The mixture was then cooled, diluted with a four-fold excess of water, and extracted with ether. The extract was washed with 5% sodium hydroxide solution (100 ml), dried (MgSO₄), and distilled to give 6-phenylhexan-2-one [2 g, 57%; *ca.* 94% pure (by g.l.c., C at 125°)], b.p. 92–94° at 0.1 mmHg; ν_{\max} , 1710 cm⁻¹ (sat. C=O); δ 1.45–1.85 (4H, m, 4- and 5-H₂), 2.04 (3H, s, 2-Me), 2.2–2.8 (4H, m, 3- and 6-H₂), and 7.16 (5H, s, aromatic) (lit.,⁴¹ b.p. 133–135° at 13 mmHg).

Other Ketones.—Published methods were used to prepare hex-5-en-2-one,²² 5-methylhex-5-en-2-one,^{22,24} oct-7-en-2-one,²⁸ and 4-phenylhexan-2-ones.³⁰ In each case the ketone was obtained essentially pure before use.

cis-Hex-3-en-2-one by Oxidation of cis-Hex-3-en-2-ol.—(a) A solution of *cis*-hex-3-en-2-ol (2.5 g) in light petroleum (b.p. 40–60°; 130 ml) was stirred with manganese dioxide³⁵ (22.5 g) at room temperature for 2 h. The catalyst was filtered off and washed with petroleum (3 × 10 ml). The filtrate was distilled (fractionating column) to give, after removal of the solvent, a fraction (0.1 g), b.p. 120–122°, ν_{\max} , 1685 cm⁻¹ (conj. C=O), containing 35% unchanged *cis*-hex-3-en-2-ol and *ca.* 60% hex-3-en-2-one (g.l.c., D at 75°).

(b) A mixture of *cis*-hex-3-en-2-ol (2 g), silver carbonate on Celite¹⁶ (22.5 g), and benzene (150 ml) was boiled under a Dean–Stark separator for 3 h. The catalyst was then filtered off and washed with benzene (20 ml). Distillation of the dried (MgSO₄) combined benzene solutions gave a fraction (0.1 g), b.p. 121–124°, ν_{\max} , 1680 cm⁻¹ (conj. C=O) containing (g.l.c., D at 75°) unchanged hex-3-en-2-ol (60%) and hex-3-en-2-one (30%) (together with 10% unknown) (identified from i.r. spectra and retention times).

(c) A mixture of chromium trioxide (9.2 g), water (28 ml), and concentrated sulphuric acid (8 ml) was added dropwise to a well stirred solution of *cis*-hex-3-en-2-ol (8 g) in acetone (4 ml). The mixture was water-cooled and stirred for 30 min after the addition, then diluted with water (40 ml), and extracted with ether (3 × 10 ml). Distillation of the dried (MgSO₄) extract gave a fraction (2 g), b.p. 136–142° [ν_{\max} , 1670 (conj. C=O), 1700sh and 1710 (sat. C=O), and 980 cm⁻¹ (*trans*-C=C)] containing [from g.l.c. analysis (D at 75°)] hex-5-en-2-one (5%), hex-4-en-2-one (15%), and hex-3-en-2-one (7%), together with three unidentified components (10%). Identification was performed by peak enhancement experiments.

(d) A solution of chromium trioxide (3.45 g) in concentrated sulphuric acid (3.0 ml) and water (10.5 ml) was added dropwise to a well stirred and cooled (water-bath) solution of *cis*-hex-3-en-2-ol (3.0 g) in ether (40 ml). The mixture was then stirred for 8 h, and the ether layer was separated and washed with saturated sodium hydrogen carbonate solution (5 ml) and water (10 ml). Distillation of the dried (MgSO₄) extract gave a product containing starting material [ν_{\max} , 3500 (OH) and 1675 cm⁻¹ (conj. C=O)] which was re-oxidised as above. Distillation gave a product (0.3 g), b.p. 120–122° [ν_{\max} , 1675 (conj. C=O), 1700w (sat. C=O), and 980 cm⁻¹ (*trans*-C=C)]. G.l.c. analysis showed the presence of hex-5-en-2-one (5%), hex-4-en-2-one (20%), and hex-3-en-2-one (75%).

Dehydrogenation of 1,2-Dihydro-1,4-dimethylnaphthalene.—A mixture of the dihydro-compound (0.05 g) and *o*-chloranil (0.15 g) in benzene (2 ml) was boiled for 2 h. The product was chromatographed on neutral alumina, with 1:1 benzene–light petroleum (b.p. 40–60°) as eluant. The bulk of the solvent was removed to leave a product which was essentially pure (g.l.c., C at 125°) 1,4-dimethylnaphthalene. Preparative scale g.l.c. (B at 180°) gave material showing δ 2.65 (6H, s, 1- and 4-Me), 7.18 (2H, s, 2- and 3-H), and 7.49 (dd, *J* 6 Hz and 3 Hz) and 7.99 (dd, *J* 6 and 3 Hz) (4H, 5-, 6-, 7-, and 8-H).

[3/458 Received, 1st March, 1973]

⁴¹ J. Colonge and J. C. Brunil, *Compt. rend.*, 1962, **255**, 161.