664. *Chemical Constitution and Sex-hormonal Activity: The Synthesis of of Some* 1-cyclo*Pentyl- and* 1-cyclo*Hexyl*-1 : 2-*diarylethylenes.*

By D. H. Hey and O. C. Musgrave.

A number of 1-*cyclo*pentyl- and 1-*cyclo*hexyl-1 : 2-diarylethylenes (I; R = C_5H_9, C_6H_{11}; X = H, OMe, OEt; Y = H, OMe, OEt) have been prepared for examination for œstrogenic and androgenic properties. The ethylenes were prepared by the dehydration of the hydroxy-compounds (IV) and (VII) which resulted (*a*) from the reduction of the corresponding ωω-di-substituted acetophenones (III; R = C_5H_9, C_6H_{11}; Y = H, OMe, OEt) and (*b*) from the reaction of benzyl- or *p*-methoxybenzyl-magnesium chloride with a *cyclo*pentyl or *cyclo*hexyl aryl ketone (V; R = C_5H_9, C_6H_{11}; X = H, OMe, OEt). None of the ethylenes tested showed any significant activity on œstrogenic and anti-œstrogenic assay.

Since the initial observation of Robson and Schönberg (*Nature*, 1937, **140**, 196) concerning the notably prolonged duration of œstrus induced by triphenylethylene, the œstrogenic properties of this substance and of its substitution derivatives have received considerable attention (Solmssen, *Chem. Reviews*, 1945, **37**, 481; Buu-Hoï *et al.*, *Compt. rend.*, 1944, **219**, 589; Buu-Hoï and Lecocq, *J.*, 1947, 641; Buu-Hoï and Royer, *J.*, 1948, 1078; Carter and Hey, *J.*, 1948, 150; Tadros *et al.*, this vol., p. 439, 442; etc.). These investigations have resembled to some extent those which took place in the stilbene series of synthetic œstrogens, especially with regard to the effect of variation in the nuclear substituents, but, in contrast to the considerable number of stilbene derivatives prepared containing hydrogenated rings (Solmssen, *loc. cit.*; Ungnade and Ludutsky, *J. Org. Chem.*, 1945, **10**, 307; *J. Amer. Chem. Soc.*, 1947, **69**, 2629; Wilds and McCormack, *ibid.*, 1948, **70**, 884; Ungnade and Tucker, *ibid.*, 1949, **71**, 1381), little information is available concerning triphenylethylene derivatives containing hydroaromatic in place of aromatic nuclei. The perhydrogenation of stilbene derivatives (of which diethylstilbœstrol has received the most attention) gives products which possess much weaker œstrogenic properties than those of the parent substance (Solmssen, *loc. cit.*). The appreciable androgenic activity reported for one of these compounds, namely, 3-(*cyclo*hexan-4-onyl)-4-(*cyclo*hex-2-en-4-onyl)-hexane, by Schoeller *et al.* (U.S.P. 2,392,864), supports the postulation that the lowering of œstrogenic activity on hydrogenation (and consequent increase in molecular dimensions) may be accompanied by a corresponding increase in androgenic activity, and is apparently in agreement with Schueler's hypothesis (*Science*, 1946, **103**, 221) that sex-hormonal activity is essentially a function of molecular size. The only "reduced" triphenylethylenes previously reported are 1-*cyclo*hexyl-1 : 2-di-(*p*-hydroxyphenyl)ethylene and its dimethyl ether (Dodds *et al.*, *Proc. Roy. Soc.*, 1944, *B*, **132**, 83) and 1-*cyclo*hexyl-1 : 2-diphenylethylene. The preparations of the latter compound and of its phenyl derivative, 1-*cyclo*hexyl-1 : 2 : 2-triphenylethylene, were described by Buu-Hoï and Royer (*Bull. Soc. chim.*, 1946, **13**, 117) and by Buu-Hoï *et al.* (*loc. cit.*) respectively during a search for compounds with "anti-œstrogenic" properties.

In order to obtain further knowledge of the effect on the œstrogenic activity of triphenylethylene and its derivatives by the hydrogenation of one of the aryl nuclei, a series of 1-*cyclo*hexyl-1 : 2-diarylethylenes has now been prepared. The substituents which most enhance the œstrogenic activity of triphenylethylene itself are (if non-nuclear halogenation be excepted) *p*-alkoxy-groups. In particular, the highest activities have been observed with compounds in which two benzene nuclei attached to different carbon atoms of the ethylenic bond are thus substituted (Carter and Hey, *loc. cit.*). In the new series of ethylenes now prepared, the aromatic nuclei are therefore either unsubstituted or carry one or two *p*-alkoxy-groups. In order to assess the importance of the size of the hydroaromatic ring, a similar series of compounds has also been prepared in which the *cyclo*hexyl group is replaced by the *cyclo*pentyl group.

Of the various methods available for the preparation of 2 : 2-diphenylethylene derivatives those in which the olefinic bond is formed by dehydration of the corresponding hydroxy-

p-X·C_6H_4·CR:CH·C_6H_4Y-p (I.) $\qquad$ p-X·C_6H_4·CO·CH_2·C_6H_5 (II.)

C_6H_5·CHR·CO·C_6H_4Y-p (III.) ⟶ C_6H_5·CHR·CH(OH)·C_6H_4Y-p (IV.)

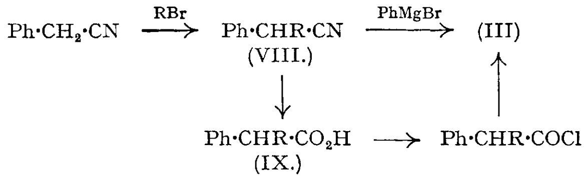
p-X·C_6H_4·COR (V.) + p-Y·C_6H_4·CH_2·MgCl (VI.) ⟶ p-X·C_6H_4·CR(OH)·CH_2·C_6H_4Y-p (VII.)

compounds appeared the most attractive, and of the possible synthetic routes available for the preparation of these compounds the following were investigated in detail: (A) The reaction of *cyclo*pentylmagnesium bromide with deoxybenzoin or a *p*-substituted deoxybenzoin (II; X = H, OMe, OEt). (B) The reduction of an ωω-disubstituted acetophenone (III; R = C_5H_9, C_6H_{11}; Y = H, OMe, OEt). (C) The interaction of benzyl- or a substituted benzyl-magnesium chloride (VI; Y = H, OMe) with a *cyclo*alkyl aryl ketone (V; R = C_5H_9, C_6H_{11}; X = H, OMe, OEt).

Method A.—This method is similar to that used by Dodds *et al.* (*loc. cit.*), who investigated the reaction between deoxyanisoin and *cyclo*hexylmagnesium chloride. Buu-Hoï and Royer (*loc. cit.*) reported the preparation of 1-*cyclo*hexyl-1 : 2-diphenylethylene by a similar reaction between *cyclo*hexylmagnesium chloride and deoxybenzoin. The deoxybenzoins (II; X = H, OMe, OEt) required in this method were obtained by Friedel–Crafts condensations with phenylacetyl chloride and benzene, anisole, or phenetole, anhydrous aluminium chloride being used as catalyst. *cyclo*Pentyl bromide was obtained from *cyclo*pentanone by reduction to *cyclo*pentanol and subsequent treatment with phosphorus tribromide according to the method of Adams (*J. Amer. Chem. Soc.*, 1926, **48**, 1084). The reduction of *cyclo*pentanone to *cyclo*pentanol by hydrogenation proved to be very sensitive to change of solvent and to the condition of the platinum oxide catalyst, which was easily poisoned, and an alternative method of effecting the reduction was sought. Although Edwards and Reid (*ibid.*, 1930, **52**, 3235) obtained *cyclo*pentanol by the addition of excess of sodium to a moist ethereal solution of *cyclo*pentanone, a repetition of their method failed to give any appreciable yield of *cyclo*pentanol, 2-*cyclo*pentylidene*cyclo*pentanone (identified as the semicarbazone) being isolated from the product. The addition of sodium to an alcoholic solution of the ketone and the use of Raney nickel–aluminium alloy and alkali, as described by Papa, Schwenk, and Whitman (*J. Org. Chem.*, 1942, **7**, 587), also gave this product (cf. Wallach, *Ber.*, 1896, **29**, 2963; Godchot and Taboury, *Bull. Soc. chim.*, 1913, **13**, 16). Mozingo, Spencer, and Folkers (*J. Amer. Chem. Soc.*, 1944, **66**, 1859) have, however, reported the reduction of *cyclo*pentanone to *cyclo*pentanol by the use of Raney nickel in aqueous alcohol, and this catalyst has now been found to be suitable for the large-scale preparation of *cyclo*pentanol by hydrogenation in dry methanol at 100° and a pressure of 125 atmospheres.

The Grignard reactions between the deoxybenzoins (II) and *cyclo*pentylmagnesium bromide (present in excess) did not take the expected course, and, in place of normal addition, reduction of the carbonyl groups to the secondary alcohols occurred. Thus, from deoxybenzoin, phenylbenzylcarbinol was obtained in good yield. The reaction with *p*-methoxyphenyl benzyl ketone (II; X = OMe) afforded 4-methoxystilbene, the carbinol initially formed having undergone dehydration during purification. In the reaction with *p*-ethoxyphenyl benzyl ketone (II; X = OEt) most of the ketone was recovered unchanged from the reaction mixture, probably as a result of its low solubility in ether, but from the fractional crystallisation of the product a small quantity of impure *p*-ethoxyphenylbenzylcarbinol was obtained. The Grignard reaction between 1-methyl*cyclo*pentylmagnesium chloride and deoxybenzoin was also found to lead to the reduction of the carbonyl group of the latter compound, and from the product of this reaction stilbene was isolated (formed by the dehydration of phenylbenzylcarbinol during purification), together with unchanged deoxybenzoin. Since it was not possible to isolate the normal addition compounds from any of the above reactions, the method was not further investigated. Kharasch and Weinhouse (*J. Org. Chem.*, 1936—1937, **1**, 209) have also noted the reduction of ketones by *cyclo*pentylmagnesium bromide, which would seem to resemble the *cyclo*hexylmagnesium halides in this property.

Method B.—For the preparation of ωω-disubstituted acetophenones without alkoxyl substituents (III; R = C_5H_9, C_6H_{11}; Y = H), the direct *cyclo*alkylation of deoxybenzoin was attempted, but no reaction was found to take place with *cyclo*hexyl bromide on use of sodium ethoxide (cf. Dodds *et al.*, *Proc. Roy. Soc.*, 1939, *B*, **127**, 140) or sodamide (cf. Haller and Bauer, *Compt. rend.*, 1909, **148**, 129) as condensing agents, and this approach was not pursued. On the other hand, the method of Vasiliu and Radvan (*Bul. Soc. Chim. Romania*, 1938, **20**, *A*, 243; *Chem. Abstracts*, 1940, **34**, 4058) was found to be satisfactory for the preparation of both ω-*cyclo*pentyl- and ω-*cyclo*hexyl-ω-phenylacetophenone. The *cyclo*alkylation of phenylacetonitrile with sodamide and either *cyclo*pentyl or *cyclo*hexyl bromide gave the *cyclo*alkylphenylacetonitriles (VIII; R = C_5H_9, C_6H_{11}) but the conversion of the latter into the corresponding phenyl ketones (III; Y = H) by reaction with phenylmagnesium bromide took place in only moderate yield (*ca.* 40%) in spite of the use of four molecular proportions of the Grignard reagent as suggested by Shriner and Turner (*J. Amer. Chem. Soc.*, 1930, **52**, 1267). The use of an even greater excess of the Grignard reagent led to a considerable diminution in the yield of ketone. The preparation of the two ωω-disubstituted acetophenones from *cyclo*pentyl- and *cyclo*hexylphenylacetic acid (IX), obtained by prolonged hydrolysis of *cyclo*pentyl- and *cyclo*hexyl-phenylacetonitrile with 66% sulphuric acid, was also investigated. The Friedel–Crafts reaction

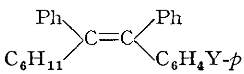


between *cyclo*pentylphenylacetyl chloride and benzene in the presence of anhydrous aluminium chloride led to the formation of only a trace of ω-cyclo*pentyl*-ω-*phenylacetophenone*. A variety of by-products was obtained, in accordance with the usual results of such condensations using substituted acetyl chlorides (Thomas, "Anhydrous Aluminium Chloride in Organic Chemistry," 1941, p. 245).

The alkoxy-substituted acetophenones (III; R = C_5H_9, C_6H_{11}; Y = OMe, OEt) were prepared by the general method used by Wilds and Biggerstaff (*J. Amer. Chem. Soc.*, 1945, **67**, 789; cf. also Hill and Short, *J.*, 1935, 1125) for the preparation of α-ethyldeoxyanisoin. The Friedel–Crafts condensations with *cyclo*pentyl- and *cyclo*hexyl-phenylacetyl chloride and anisole and phenetole using stannic chloride as catalyst gave excellent yields of the corresponding p-*alkoxyphenyl ketones*.

The ωω-disubstituted acetophenones thus prepared were characterised as their 2 : 4-*dinitrophenylhydrazones* with the exception of the *p*-alkoxy-ω-*cyclo*hexyl-ω-phenylacetophenones, which could not be induced to react with 2 : 4-dinitrophenylhydrazine even in the presence of anhydrous zinc chloride. However, the reaction of the latter compounds with phenylmagnesium bromide and subsequent dehydration afforded the 1-cyclo*hexyl*-1 : 2 : 2-*triarylethylenes* (X; Y = OMe, OEt), which were suitable for purposes of characterisation.

Both ω-*cyclo*pentyl- and ω-*cyclo*hexyl-ω-phenylacetophenone were reduced in good yield by the Meerwein–Ponndorf method, and the resulting secondary *alcohols* (IV; R = C_5H_9, C_6H_{11}; Y = H) were characterised as their 3 : 5-*dinitrobenzoates*. The dehydration of these carbinols to the corresponding *ethylenes* (I; R = C_5H_9, C_6H_{11}; X = Y = H) was effected without difficulty by boiling them under reflux in glacial acetic acid containing a trace of concentrated sulphuric acid. The reduction of ω-*cyclo*pentyl-ω-phenylacetophenone to the secondary alcohol was also effected with *iso*propylmagnesium bromide. The reduction of the *p*-alkoxy-ketones (III; R = C_5H_9, C_6H_{11}; Y = OMe, OEt) proved more difficult and the action of a variety of reducing agents was examined. The reaction of (III; R = C_5H_9; Y = OMe, OEt) with moist ether and sodium, with sodium amalgam and alcohol, with aluminium *iso*propoxide in toluene, or with *iso*propylmagnesium bromide in ether gave either unchanged material or unidentified oily products, and the use of *iso*propylmagnesium bromide in benzene solution led to the production of viscous,



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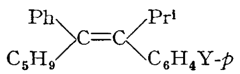
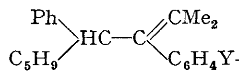


(XI.)



(XII.)

high-boiling oils (after acetic–sulphuric acid dehydration) having the empirical formulæ of the dehydrated normal addition products (XI or XII; Y = OMe, OEt). The compounds were unsaturated and gave strongly coloured solutions in concentrated sulphuric acid. The successful reduction of the ketones (III; R = C_5H_9 or C_6H_{11}, Y = OMe or OEt) was finally effected by the use of lithium aluminium hydride and the products were dehydrated, without the isolation of the intermediate secondary alcohols, to the *ethylenes* (I; R = C_5H_9, C_6H_{11}; X = H; Y = OMe, OEt) by boiling under reflux in acetic acid containing concentrated sulphuric acid. It is possible, however, that partial or even complete dehydration occurred concurrently with reduction.

Method C.—The cyclo*alkyl aryl ketones* (V; R = C_5H_9, C_6H_{11}; X = H, OMe, OEt) were prepared by Friedel–Crafts reactions from *cyclo*pentane- and *cyclo*hexane-carboxyl chloride, and benzene, anisole, or phenetole. *cyclo*Pentanecarboxylic acid was obtained from the action of carbon dioxide on *cyclo*pentylmagnesium bromide. *cyclo*Pentyl and *cyclo*hexyl phenyl ketone (V; R = C_5H_9, C_6H_{11}; X = H) were prepared from the acid chlorides and benzene, anhydrous aluminium chloride being used as catalyst. The former ketone had been previously prepared by Dr. D. V. N. Hardy (private communication) and the latter by Meyer and Scharvin (*Ber.*, 1897, **30**, 1940) but in both cases experimental detail was lacking. For the preparation of the *cyclo*pentyl and *cyclo*hexyl *p*-alkoxyphenyl ketones (V; R = C_5H_9, C_6H_{11}; X = OMe, OEt) anhydrous stannic chloride was used as catalyst. *cyclo*Hexyl *p*-methoxyphenyl ketone had previously been described by Hughes and Lions (*J. Proc. Roy. Soc., N.S.W.*, 1938, **71**, 494), who used anhydrous aluminium chloride.

The reaction of benzylmagnesium chloride with the various ketones mentioned above led to normal addition to the carbonyl group. The tertiary alcohols (VII; R = C_5H_9, C_6H_{11}; X = H, OMe, OEt; Y = H) were not isolated, but were dehydrated to the corresponding *ethylenes* (I; R = C_5H_9, C_6H_{11}; X = H, OMe, OEt; Y = H) by boiling under reflux in glacial acetic acid containing sulphuric acid. In most cases, a single fractional distillation afforded pure samples of the ethylenes, but 1-*cyclo*pentyl- and 1-*cyclo*hexyl-1 : 2-diphenylethylene were separated from dibenzyl only with difficulty.

The extension of this method to ethylenes possessing *p*-alkoxyl groups on both aryl nuclei was made possible by the recent observation of Campen, Meisner, and Parmerter (*J. Amer. Chem. Soc.*, 1948, **70**, 2296) that *p*-alkoxybenzylmagnesium halides can be prepared by a modification of the usual Grignard procedure. The tertiary alcohols (VII; R = C_5H_9, C_6H_{11}; X = H, OMe, OEt; Y = OMe) resulting from the reaction between *p*-methoxybenzylmagnesium chloride and the ketones previously mentioned were not isolated but were converted directly into the *ethylenes* (I; R = C_5H_9, C_6H_{11}; X = H, OMe, OEt; Y = OMe) by dehydration as before. Some 4 : 4′-dimethoxydibenzyl was formed as a by-product.

All the ethylenes prepared by methods (B) and (C) absorb bromine, react with ozone, and give coloured solutions in concentrated sulphuric acid, the depth of colour depending on the nature of the substituents in the aryl nuclei. Confirmation of the structures assigned to the above compounds is provided by the fact that specimens of 1-*cyclo*hexyl-1 : 2-diphenylethylene, prepared by both methods, showed the same refractive indices and ultra-violet absorption spectra, and 1-*cyclo*hexyl-1-phenyl-2-(*p*-methoxyphenyl)ethylene, also obtained by both methods, showed no depression in melting point on admixture of the two specimens. In addition, the oxidative decomposition of the ozonide of 1-*cyclo*hexyl-1-phenyl-2-(*p*-ethoxyphenyl)ethylene (prepared by method B) gave *cyclo*hexyl phenyl ketone and *p*-ethoxybenzoic acid, and in similar manner 1-*cyclo*hexyl-1 : 2-diphenylethylene (prepared by method C) afforded *cyclo*hexyl phenyl ketone and benzaldehyde after reductive decomposition of the ozonide.

The ethylenes described above should all exist in geometrically isomeric forms, in which the aryl nuclei have the *cis*- or *trans*-configuration about the central double bond. No positive evidence of the existence of two forms was found during the preparative work, presumably because of the preferential formation of the more stable isomeride during the dehydration reaction, and, since the ethylenes differ from each other only in the nature of the aryl groups or by the substitution of the *cyclo*pentyl group for *cyclo*hexyl, it is considered that all are of the same geometrically isomeric type. Comparison of the compounds (which are liquids or low-melting solids) with *cis*-stilbene (a liquid) and *trans*-stilbene (m. p. 124°) suggests that they possess the *cis*-stilbene configuration. This view is supported by the ultra-violet absorption spectrum of 1-*cyclo*hexyl-1 : 2-diphenylethylene, the maximum absorption of which in ethanol resembles that of *cis*-stilbene (band II) rather than that of the *trans*-isomer (Table I).

TABLE I.

		$\varepsilon_{max.}$	$\lambda_{max.}$, A.
1-*cyclo*Hexyl-1 : 2-diphenylethylene		12,840	2570
cis-Stilbene †	I	34,000	2000
		23,000	2220
	II	13,500	2800
trans-Stilbene †	I	23,000	2000
		15,000	2260
	II	27,000	2950

† Values taken from Braude, *Ann. Reports*, 1945, **42**, 125.

The compounds marked with an asterisk in the Experimental section were tested for œstrogenic activity, the vaginal smear method of assay being used, but none of the compounds showed significant activity. The 1-*cyclo*hexyl-1 : 2 : 2-triphenylethylene derivatives (X; Y = OMe, OEt) show some slight degree of œstrogenic activity, but are much less active than triphenylethylene itself. A representative of each group was also tested for anti-œstrogenic activity, but all were inactive. The tests were carried out at the British Schering Research Institute by Miss Audrey Hudson, to whom our thanks are due. From these results it is apparent that the saturation of one of the aryl nuclei in triphenylethylene derivatives destroys the œstrogenic activity of the parent substances. This inactivity can hardly be due to the size of the hydroaromatic ring formed, but may be a consequence of the probable *cis*-configuration of the resulting diphenylethylenes.

Experimental

Method A.—cyclo*Pentyl bromide.* A solution of *cyclo*pentanone (Thorpe and Kon, *Org. Synth.*, Coll. Vol. 1, 1944, p. 192) (379 g.) in dry methanol (400 c.c.) was hydrogenated at 125 atm. and 100° with stirring in the presence of Raney nickel (Mozingo, *Org. Synth.*, 1941, **21**, 15) (20—30 g.). After 16 hours the mixture was filtered and fractional distillation gave *cyclo*pentanol (309 g.), b. p. 138°. Treatment of the *cyclo*pentanol (207 g.) with phosphorus tribromide (231 g.) according to Adams (*loc. cit.*) gave *cyclo*pentyl bromide (304 g.), the reaction temperature being kept below 0° during the addition of the phosphorus tribromide.

1-*Methyl*cyclo*pentyl chloride.* 1-Methyl*cyclo*pentanol was prepared by the method of Zelinsky and Namjetkin (*Ber.*, 1902, **35**, 2683) from methyl iodide (102 g.), magnesium (18 g.), and *cyclo*pentanone (60 g.) in dry ether (400 c.c.). The product was decomposed by pouring into ice and ammonium chloride to prevent the dehydration of the carbinol (b. p. 78—82°/85 mm.; 40 g.). This could not be converted into the corresponding bromide by reaction with either phosphorus tribromide or phosphorus and bromine, but treatment with excess of dry hydrogen chloride in the cold (Meerwein and Mühlendyk, *Annalen*, 1914, **405**, 171) gave 1-methyl*cyclo*pentyl chloride (56% yield), b. p. 64—74°/152—162 mm.

Deoxybenzoins. Deoxybenzoin was prepared by a modification of the method due to Allen and Barker (*Org. Synth.*, Coll. Vol. 2, 1944, p. 156), the phenylacetyl chloride being obtained by the action of thionyl chloride instead of phosphorus trichloride. *p*-Methoxyphenyl benzyl ketone was prepared by the method of Ney (*Ber.*, 1888, **21**, 2450) by the addition of phenylacetyl chloride (50 g.) to a mixture of anhydrous aluminium chloride (60 g.), anisole (40 g.), and carbon disulphide (200 c.c.). Crystallisation of the product from benzene–light petroleum (b. p. 60—80°) gave *p*-methoxyphenyl benzyl ketone (42·5 g.) in colourless plates, m. p. 75—76·5°. *p*-Ethoxyphenyl benzyl ketone (Tiffeneau, Oryékhov, and Roger, *Bull. Soc. chim.*, 1931, **49**, 1757) was prepared in a similar manner from phenylacetyl chloride (58 g.), anhydrous aluminium chloride (65 g.), phenetole (55 g.), and carbon disulphide (100 c.c.). Crystallisation from methanol gave the ketone (57·2 g.) in needles, m. p. 104°.

Grignard reactions with the deoxybenzoins. (i) A solution of deoxybenzoin (19·6 g.) in dry ether (250 c.c.) was added to the Grignard reagent prepared from *cyclo*pentyl bromide (29·8 g.), magnesium (4·86 g.), and dry ether (250 c.c.). After boiling under reflux for 30 minutes the mixture was added to crushed ice (800 g.) and ammonium chloride (50 g.). Ether-extraction afforded phenylbenzylcarbinol (15 g.), m. p. 65·5—66·5°, which did not depress the m. p. of an authentic sample prepared from benzylmagnesium chloride and benzaldehyde (Hell, *Ber.*, 1904, **37**, 456) (Found: C, 84·6; H, 7·0. Calc. for $C_{14}H_{14}O$: C, 84·8; H, 7·1%).

(ii) A solution of *p*-methoxyphenyl benzyl ketone (22·6 g.) in dry ether (600 c.c.) was added to a solution of *cyclo*pentylmagnesium bromide (0·11 mol.) in dry ether (150 c.c.). After 30 minutes' boiling and working up of the product as described above, the ethereal extract afforded a solid (20·9 g.), which on crystallisation from aqueous ethanol afforded a small amount of unchanged ketone. Concentration of the alcoholic solution on the water-bath caused dehydration (shown by a sudden decrease in solubility), and crystallisation of the product from benzene–light petroleum (b. p. 60—80°) gave colourless crystals of 4-methoxystilbene (12 g.), m. p. 133·5—135·5° (Found: C, 86·0; H, 6·7. Calc. for $C_{15}H_{14}O$: C, 85·7; H, 6·7%), which did not depress the m. p. of an authentic sample prepared by the Meerwein–Ponndorf reduction of *p*-methoxyphenyl benzyl ketone followed by dehydration of the resulting *p*-methoxyphenylbenzylcarbinol by boiling it under reflux with glacial acetic acid containing a trace of concentrated sulphuric acid.

(iii) A suspension of *p*-ethoxyphenyl benzyl ketone (24 g.) in dry ether (600 c.c.) was added to a solution of *cyclo*pentylmagnesium bromide (0·1 mol.) in dry ether (150 c.c.). After boiling and working up as in the previous examples, the ether extract afforded a solid m. p. 60—90° (20 g.). Fractional crystallisation from light petroleum (b. p. 60—80°) gave unchanged *p*-ethoxyphenyl benzyl ketone (14 g.) and impure p-*ethoxyphenylbenzylcarbinol*, m. p. 65—69° (1 g.). The pure carbinol, obtained in 92% yield by the Meerwein–Ponndorf reduction of *p*-ethoxyphenyl benzyl ketone, crystallised from light petroleum (b. p. 60—80°) in colourless needles, m. p. 74—74·5°, with a pleasant camphor-like odour (Found: C, 79·0; H, 7·6. $C_{16}H_{18}O_2$ requires C, 79·3; H, 7·5%).

(iv) To the Grignard reagent prepared from 1-methyl*cyclo*pentyl chloride (17 g.), magnesium (3·6 g.), and dry ether (150 c.c.) was added a solution of deoxybenzoin (20 g.) in dry ether (150 c.c.). After boiling under reflux for 30 minutes the product was worked up as described above. The solid obtained from the ethereal extract was distilled under reduced pressure and crystallisation from light petroleum (b. p. 60—80°) of the fraction (9 g.), b. p. 120—160°/*ca.* 1 mm., gave stilbene in colourless plates, m. p. 119—121°. Crystallisation of the fraction (6 g.), b. p. 160—180°/*ca.* 1 mm., from ethanol afforded unchanged deoxybenzoin (m. p. 53°).

Method B.—1-cyclo*Pentyl*-1 : 2-*diphenylethylene* (I; $R = C_5H_9$; X = Y = H). *cyclo*Pentylphenylacetonitrile was prepared by a modification of the method of Vasiliu *et al.* (*Chem. Abstr.*, 1944, **38**, 5493). A solution of phenylacetonitrile (62·7 g.) in dry ether (250 c.c.) was added slowly with cooling to powdered sodamide (20·9 g.). After this had been boiled under reflux for 30 minutes and cooled, a solution of *cyclo*pentyl bromide (80 g.) in dry ether (100 c.c.) was added slowly. After further boiling under reflux the mixture was poured into ice-water (500 c.c.). Distillation of the ethereal extract under reduced pressure gave first unchanged *cyclo*pentyl bromide (10 g.) and phenylacetonitrile (4 g.), followed by *cyclo*pentylphenylacetonitrile (b. p. 120—128°/1—1·8 mm.; 72·5 g.), which solidified to a hard crystalline mass. A solution of the nitrile (20 g.) in dry ether (100 c.c.) was added during 15 minutes to the ice-cold Grignard reagent prepared from bromobenzene (68 g.), magnesium (10·5 g.), and dry ether (250 c.c.). The mixture was kept overnight and poured into a mixture of ice (500 g.) and concentrated hydrochloric acid (100 c.c.). The solid which separated was collected, combined with the aqueous layer, and boiled under reflux with concentrated hydrochloric acid to ensure decomposition of the ketimine hydrochloride. After filtration, crystallisation of the residue from light petroleum (b. p. 60—80°) gave ω-cyclo*pentyl-ω-phenylacetophenone* (10·8 g.) in colourless needles, m. p. 88·5—89·5° (Found : C, 86·3; H, 7·8. $C_{19}H_{20}O$ requires C, 86·3; H, 7·6%). The *dinitrophenylhydrazone* crystallised from light petroleum (b. p. 80—100°) in small orange cubes, m. p. 136·5—138° (Found : C, 67·7; H, 5·5. $C_{25}H_{24}O_4N_4$ requires C, 67·5; H, 5·45%).

The ketone was reduced by two methods : (*a*) A mixture of the ketone (6·7 g.) and a molar solution of aluminium *iso*propoxide in *iso*propanol (50 c.c.) was slowly distilled until acetone could no longer be detected in the distillate (*ca.* 9 hours), after which the excess of solvent was removed and the residue hydrolysed with hydrochloric acid. Ether extraction afforded 2-cyclo*pentyl-*1 : 2-*diphenylethan-*1-*ol* (5·55 g.), which distilled under reduced pressure as a colourless, viscous oil, b. p. 160°/5 × 10^{-3} mm., n_D^{25} 1·5732 (Found: C, 85·3; H, 8·3. $C_{19}H_{22}O$ requires C, 85·65; H, 8·3%). (*b*) A solution of ω-*cyclo*pentyl-ω-phenylacetophenone (4 g.) in dry ether (50 c.c.) and benzene (10 c.c.) was added slowly to the Grignard reagent prepared from *iso*propyl bromide (4·7 g.), magnesium (0·92 g.), and dry ether (125 c.c.). After being kept overnight, the reaction mixture was added to ice (500 g.) and ammonium chloride (50 g.). Distillation of the ethereal extract afforded the same product (3 g.), b. p. 150—153°/5 × 10^{-3} mm., as in method (*a*). Both samples of the carbinol gave the same 3 : 5-*dinitrobenzoate*, which crystallised from light petroleum (b. p. 80—100°) in small colourless needles, m. p. 142·5—143·5° (Found : C, 68·0; H, 5·3. $C_{26}H_{24}O_6N_2$ requires C, 67·8; H, 5·25%). The carbinol (4·7 g.) was heated under reflux for one hour with glacial acetic acid (40 c.c.) and concentrated sulphuric acid (0·2 c.c.) and then diluted with water. Fractional distillation of the ethereal extract gave 1-cyclo*pentyl-*1 : 2-*diphenylethylene* * (3·56 g.) as a colourless oil, b. p. 118—120°/9 × 10^{-2} mm. The analyses, refractive indices, and colour reactions of this compound and of the other diphenylethylenes described in this paper are recorded in Table II.

Action of cyclo*Pentylphenylacetyl Chloride on Benzene in the Presence of Aluminium Chloride.*—*cyclo*Pentylphenylacetyl chloride (0·1 mol.; prepared as described below) was added dropwise to a mixture of dry benzene (120 c.c.) and powdered anhydrous aluminium chloride (15 g.) at 0°. The mixture was stirred at room temperature overnight and poured on crushed ice (500 g.) and concentrated hydrochloric acid (100 c.c.). The benzene layer was separated, washed with water, dried ($CaCl_2$), and distilled. The following fractions were obtained : (i) a mobile liquid, b. p. 100—140°/0·4 mm. (2·5 g.), which gave an unidentified 2 : 4-dinitrophenylhydrazone, m. p. 235°; (ii) a viscous liquid, b. p. 160—200°/0·8—1·5 mm. (4·0 g.), which on storage deposited crystals of ω-*cyclo*pentyl-ω-phenylacetophenone (1 g.), m. p. 87—88°, both alone and on admixture with the specimen prepared above; and (iii) a glass, b. p. 220—260°/0·55 mm. (6·1 g.), which afforded an unidentified solid, m. p. 136—136·5° (1 g.), on crystallisation from benzene. There was a residue (7·3 g.) which could not be distilled.

1-cyclo*Hexyl-*1 : 2-*diphenylethylene* (I; R = C_6H_{11}; X = Y = H).—*cyclo*Hexylphenylacetonitrile was prepared by a modification of Hancock and Cope's procedure (*Org. Synth.*, 1945, **25**, 25), benzene being substituted for toluene as solvent, and powdered sodamide being used. A solution of the nitrile (10 g.) in dry ether (150 c.c.) was added to the Grignard reagent prepared from magnesium (2·43 g.), bromobenzene (15·7 g.), and dry ether (200 c.c.), cooled to −2°. After being kept overnight, the mixture was decomposed with ice and hydrochloric acid and the solid and the aqueous layer were combined and boiled under reflux for 30 minutes. Crystallisation of the resulting solid from light petroleum (b. p. 60—80°) gave ω-*cyclo*hexyl-ω-phenylacetophenone (5·1 g.) in colourless needles, m. p. 118—119° (Vasiliu and Radvan, *loc. cit.*, give m. p. 120—121°). The 2 : 4-*dinitrophenylhydrazone* separated from light petroleum (b. p. 80—100°) in orange cubes, m. p. 153·5—155° (Found : C, 68·65; H, 5·7. $C_{26}H_{26}O_4N_4$ requires C, 68·1; H, 5·7%). A mixture of ω-*cyclo*hexyl-ω-phenylacetophenone (15 g.) and a molar solution of aluminium *iso*propoxide in *iso*propanol (125 c.c.) was slow-distilled for 16 hours. Hydrolysis and ether-extraction as before gave 2-cyclo*hexyl-*1 : 2-*diphenylethan-*1-*ol* (11·25 g.), which crystallised from light petroleum (b. p. 40—60°) in colourless needles, m. p. 80·5—82° (Found: C, 85·4; H, 8·5. $C_{20}H_{24}O$ requires C, 85·65; H, 8·6%). The 3 : 5-*dinitrobenzoate* crystallised from light petroleum (b. p. 60—80°) in colourless needles, m. p. 163—164° (Found : C, 68·9; H, 5·5. $C_{27}H_{26}O_6N_2$ requires C, 68·3; H, 5·5%). The carbinol (10 g.) was boiled under reflux with glacial acetic acid (80 c.c.) and concentrated sulphuric acid (0·5 c.c.) for one hour. The product was poured into water, and fractionation of the residue obtained from the ethereal extract under reduced pressure afforded 1-*cyclo*hexyl-1 : 2-diphenylethylene * (7·32 g.) as an almost colourless oil, b. p. 141°/0·14 mm. Light absorption in ethanol: $\varepsilon_{max.}$ = 12,600; $\lambda_{max.}$ = 2610 A.

1-cyclo*Pentyl-*1-*phenyl-*2-(p-*alkoxyphenyl*)*ethylenes* (I; R = C_5H_9; X = H; Y = OMe, OEt).—*cyclo*Pentylphenylacetonitrile (35 g.) was heated under reflux with 66% sulphuric acid (300 c.c.) for 6 hours. The mixture was poured into water, and the solid collected. Purification of the acid through the sodium salt gave *cyclo*pentylphenylacetic acid (28·6 g.), which crystallised from light petroleum (b. p. 80—100°) in colourless cubes, m. p. 99—101° (Vasiliu *et al.*, *loc. cit.*, record m. p. 103°). To a solution of the acid (0·1 mol.) in dry benzene (50 c.c.) were added purified thionyl chloride (14 c.c.) and one drop of pyridine, and the solution was kept at 50° for 2 hours. The excess of thionyl chloride and the benzene were removed at 50° under reduced pressure. Benzene (2 × 20 c.c. portions) was added, and the distillation repeated. The residual acid chloride was dissolved in dry benzene (100 c.c.), anisole or phenetole (0·5 mol.) added, and the whole cooled in ice; a solution of anhydrous stannic chloride (40 c.c.) in benzene (40 c.c.) was then added dropwise. The mixture was stirred overnight at room temperature, after which it was poured on a mixture of ice (500 g.) and concentrated hydrochloric acid (200 c.c.) and extracted with ether. After removal of the ether the residue was distilled with steam to remove solvents and the excess of anisole or phenetole. Extraction of the residue with ether afforded the crude *p*-alkoxyphenyl ketone (cf. Hill and Short, *loc. cit.*; Wilds and Biggerstaff, *loc. cit.*). p-*Methoxy-ω-*cyclo*pentyl-ω-phenylacetophenone* (94% yield) crystallised from light petroleum (b. p. 60—80°) in colourless needles, m. p. 104—105·5° (Found : C, 80·9; H, 7·6. $C_{20}H_{22}O_2$ requires C, 81·6; H, 7·5%), and the 2 : 4-*dinitrophenylhydrazone* separated from light petroleum (b. p. 80—100°) in orange-red cubes, m. p. 150—151·5° (Found : C, 66·3; H, 5·5. $C_{26}H_{26}O_5N_4$ requires C, 65·8; H, 5·5%). p-*Ethoxy-ω-*cyclo*pentyl-ω-phenylacetophenone* (91% yield) crystallised from light petroleum (b. p. 60—80°) in colourless needles, m. p. 96—97° (Found: C, 81·3; H, 7·7. $C_{21}H_{24}O_2$ requires C, 81·7; H, 7·8%), and the 2 : 4-*dinitrophenylhydrazone* separated from light petroleum (b. p. 80—100°) in orange cubes, m. p. 148·5—149° (Found: C, 66·7; H, 5·8. $C_{27}H_{28}O_5N_4$ requires, C, 66·4; H, 5·8%).

A solution of the ωω-disubstituted *p*-alkoxyacetophenone (0·12 mol.) in a mixture of dry ether (30 c.c.) and dry benzene (10 c.c.) was added to a boiling solution of lithium aluminium hydride (0·5 g.) in dry ether (50 c.c.). After the addition of water and acidification, the ethereal layer was distilled. The residue was boiled under reflux with glacial acetic acid (70 c.c.) containing concentrated sulphuric acid (0·1 c.c.) for one hour and then poured into water. The ethereal extract on evaporation afforded the crude ethylene. 1-cyclo*Pentyl-1-phenyl-2-*(p-*methoxyphenyl*)*ethylene* * (36% yield) separated from methanol in colourless needles, m. p. 78—79°. 1-cyclo*Pentyl-1-phenyl-2-*(p-*ethoxyphenyl*)*ethylene* * (53% yield) distilled as a colourless oil, b. p. 100—102°/2 × 10^{-3} mm.

1-cyclo*Hexyl-1-phenyl-2-*(p-*alkoxyphenyl*)*ethylenes* (I; R = C_6H_{11}; X = H; Y = OMe, OEt).—*cyclo*Hexylphenylacetonitrile (40 g.) was boiled under reflux with 66% sulphuric acid (350 c.c.) for 6 hours. After dilution, the solid was collected and washed with water. Crystallisation from light petroleum (b. p. 80—100°) gave *cyclo*hexylphenylacetic acid (41 g.) in colourless cubes, m. p. 148—149° (Venus-Danilova and Bol'shukin, *J. Gen. Chem. U.S.S.R.*, 1937, **7**, 2830; *Chem. Abstracts*, 1938, **32**, 2925, record m. p. 150—151°). The acid was converted into the *p*-alkoxyphenyl ketones as previously described for the *cyclo*pentyl analogues. p-*Methoxy-ω-*cyclo*hexyl-ω-phenylacetophenone* (75% yield) crystallised from light petroleum (b. p. 60—80°) in small colourless needles, m. p. 95—96·5° (Found: C, 81·9; H, 7·8. $C_{21}H_{24}O_2$ requires C, 81·8; H, 7·8%). A solution of the ketone (5·1 g.) in a mixture of dry benzene (20 c.c.) and dry ether (40 c.c.) was added to a solution of phenylmagnesium bromide (0·033 mol.) in dry ether (50 c.c.). Most of the ether was distilled off and replaced by an equal volume of benzene, and the mixture was boiled under reflux for 4 hours. After decomposition with ice (100 g.) and hydrochloric acid (100 c.c.), ether was added and the ether–benzene extract distilled. The residue was boiled under reflux for 1 hour with glacial acetic acid (50 c.c.) containing concentrated sulphuric acid (0·1 c.c.) and then poured into water. Ether-extraction afforded 1-cyclo*hexyl-1 : 2-diphenyl-2-*(p-*methoxyphenyl*)-*ethylene* * (2·84 g.), which crystallised from light petroleum (b. p. 80—100°) in colourless cubes, m. p. 127—127·5° (Found: C, 87·9; H, 7·8. $C_{27}H_{28}O$ requires C, 88·0; H, 7·7%). p-*Ethoxy-ω-*cyclo*hexyl-ω-phenylacetophenone* (72% yield) separated from light petroleum (b. p. 80—100°) in colourless needles m. p. 89—90° (Found: C, 82·2; H, 8·0. $C_{22}H_{26}O_2$ requires C, 81·9; H, 8·1%). By the reaction of the ketone (5·4 g.) with phenylmagnesium bromide exactly as described above, 1-cyclo*hexyl-1 : 2-diphenyl-2-*(p-*ethoxyphenyl*)*ethylene* * (1·8 g.) was obtained, which crystallised from light petroleum (b. p. 60—80°) in colourless prisms, m. p. 127·5—129·5° (Found: C, 87·5; H, 8·1. $C_{28}H_{30}O$ requires C, 87·9; H, 7·9%).

The reduction and dehydration of the two ketones were carried out in a manner similar to that previously described for the *cyclo*pentyl analogues. 1-cyclo*Hexyl-1-phenyl-2-*(p-*methoxyphenyl*)-*ethylene* * (53% yield) was obtained in colourless needles, m. p. 79°, on crystallisation from light petroleum (b. p. 40—60°). 1-cyclo*Hexyl-1-phenyl-2-*(p-*ethoxyphenyl*)*ethylene* * (65% yield) crystallised from ethanol in colourless needles, m. p. 57—58°.

Grignard Reactions between p-*Alkoxy-ω-*cyclo*pentyl-ω-phenylacetophenones and* iso*Propylmagnesium Bromide*.—To a solution of *iso*propylmagnesium bromide (0·2 mol.) in dry ether (200 c.c.) was added a solution of *p*-methoxy-ω-*cyclo*pentyl-ω-phenylacetophenone (15 g.) in a mixture of dry benzene (80 c.c.) and ether (80 c.c.). Approximately 200 c.c. of the mixed solvents were removed by distillation and replaced by an equal volume of benzene, and the process repeated to remove as much ether as possible. The mixture was then boiled under reflux for 6 hours, set aside overnight, and poured on a mixture of crushed ice (500 g.) and ammonium chloride (50 g.). The benzene layer afforded on evaporation a viscous oil which was dehydrated by being heated under reflux with glacial acetic acid (150 c.c.) and sulphuric acid (1 c.c.). After dilution, ether-extraction afforded a *compound* * as a colourless viscous oil (6·82 g.), b. p. 148—151°/2 × 10^{-4} mm., n_D^{18} 1·5768 (Found: C, 86·5; H, 8·9. $C_{23}H_{28}O$ requires C, 86·2; H, 8·8%). On similar treatment, *p*-ethoxy-ω-*cyclo*pentyl-ω-phenylacetophenone (14·9 g.) gave (after boiling under reflux for 40 hours with the Grignard reagent) a *compound* * as a colourless oil (6·94 g.), b. p. 123—129°/6 × 10^{-4} mm., n_D^{18} 1·5619 (Found: C, 86·3; H, 9·2. $C_{24}H_{30}O$ requires C, 86·2; H, 9·0%). Both compounds gave blood-red solutions in concentrated sulphuric acid.

Method C.—*cyclo*Pentanecarboxylic acid was prepared in 59% yield by the action of carbon dioxide on *cyclo*pentylmagnesium bromide according to the general method of Gilman and Kirby (*Org. Synth.*, Coll. Vol. 1, 1944, p. 361), excess of solid carbon dioxide being added after gas absorption had ceased. *cyclo*Pentane- and *cyclo*hexane-carboxyl chloride were prepared by the treatment of the acid (0·1 mol.) with a solution of thionyl chloride (14 c.c.) in dry benzene (40 c.c.) and one drop of pyridine at 50° for 2 hours. The benzene and excess of thionyl chloride were removed by distillation under reduced pressure at 60° and benzene (2 × 20 c.c. portions) was added and removed in the same way. The residual acid chloride (90% yield) was not further purified.

Phenyl ketones. A solution of the acid chloride (0·1 mol.) in dry benzene (100 c.c.) was added to powdered anhydrous aluminium chloride (18 g.). The mixture was heated on the water-bath for 1 hour, then poured into ice (300 g.) and concentrated hydrochloric acid (200 c.c.), whence the ketone was obtained by ether extraction. cyclo*Pentyl phenyl ketone* (60% yield) was obtained as a colourless mobile oil, b. p. 136—140°/16 mm., 64°/12 × 10^{-3} mm., n_D^{25} 1·5404 (Found: C, 81·9; H, 7·8. $C_{12}H_{14}O$ requires C, 82·7; H, 8·1%). The 2 : 4-*dinitrophenylhydrazone* separated from ethanol in yellow plates, m. p. 142—143° (Found: C, 60·8; H, 5·1. $C_{18}H_{18}O_4N_4$ requires C, 61·0; H, 5·1%), and the *semicarbazone* crystallised from light petroleum (b. p. 60—80°)–benzene in thick, colourless needles, m. p. 107·5—109·5° (Found: C, 67·3; H, 7·3. $C_{13}H_{17}ON_3$ requires C, 67·5; H, 7·4%). The *oxime* separated from light petroleum (b. p. 60—80°) in colourless needles, m. p. 106—108° (Found: C, 75·8; H, 8·0. $C_{12}H_{15}ON$ requires C, 76·1; H, 7·9%). *cyclo*Hexyl phenyl ketone (64% yield) was obtained in colourless needles, m. p. 55—56°, on crystallisation (charcoal) from light petroleum (b. p. 40—60°) (cf. Meyer and Scharvin, *loc. cit.*). The dinitrophenylhydrazone crystallised from ethyl acetate in yellow needles, m. p. 196·5—197·5°, whereas Hughes and Lions (*loc. cit.*) reported m. p. 192° (Found: C, 62·2; H, 5·7. Calc. for $C_{19}H_{20}O_4N_4$: C, 61·9; H, 5·5%).

p-*Alkoxyphenyl ketones.* The acid chlorides (0·1 mol.) were converted into the corresponding *p*-alkoxyphenyl ketones by reactions with anisole or phenetole and stannic chloride, by means of the procedure described in Method B. cyclo*Pentyl* p-*methoxyphenyl ketone* (95% yield) was obtained as a colourless oil, b. p. 105·5—106°/0·2 mm., n_D^{25} 1·5546, which, on cooling, became a colourless crystalline solid, m. p. 15—16° (Found: C, 76·2; H, 7·7. $C_{13}H_{16}O_2$ requires C, 76·45; H, 7·9%). The 2 : 4-*dinitrophenylhydrazone* separated from light petroleum (b. p. 80—100°) in orange needles, m. p. 98—99° (Found: C, 59·55; H, 5·2. $C_{19}H_{20}O_5N_4$ requires C, 59·4; H, 5·2%). cyclo*Pentyl* p-*ethoxyphenyl ketone* (64% yield) crystallised from light petroleum (b. p. 40—60°) (charcoal) in flat colourless needles, m. p. 40° (Found: C, 76·8; H, 8·1. $C_{14}H_{18}O_2$ requires C, 77·0; H, 8·3%). The 2 : 4-*dinitrophenylhydrazone* separated from light petroleum (b. p. 80—100°) in orange needles, m. p. 99—99·5° (Found: C, 60·5; H, 5·7. $C_{20}H_{22}O_5N_4$ requires C, 60·3; H, 5·6%). *cyclo*Hexyl *p*-methoxyphenyl ketone (77% yield) crystallised from light petroleum (b. p. 40—60°) in colourless needles, m. p. 65—65·5° (Found: C, 76·3; H, 8·2. Calc. for $C_{14}H_{18}O_2$: C, 77·0; H, 8·3%). The 2 : 4-dinitrophenylhydrazone separated from alcohol in fine orange needles, m. p. 121—122° (cf. Hughes and Lions, *loc. cit.*). cyclo*Hexyl* p-*ethoxyphenyl ketone* (75% yield) crystallised from light petroleum (b. p. 40—60°) in colourless needles, m. p. 57·5—58° (Found: C, 77·4; H, 8·75. $C_{15}H_{20}O_2$ requires C, 77·6; H, 8·7%). The 2 : 4-*dinitrophenylhydrazone* crystallised from light petroleum (b. p. 80—100°) in red plates, m. p. 128·5—129·5° (Found: C, 61·8; H, 5·9. $C_{21}H_{24}O_5N_4$ requires C, 61·2; H, 5·9%).

Grignard Reactions with Benzylmagnesium Chloride.—A solution of the *cyclo*alkyl aryl ketone (0·05 mol.) in dry ether (100 c.c.) was added to the Grignard reagent prepared from benzyl chloride (12·65 g.), magnesium (2·43 g.), and dry ether (100 c.c.). The mixture was boiled under reflux for one hour, kept overnight, and poured into ice (200 g.) and either concentrated hydrochloric acid (200 c.c.) or ammonium chloride (100 g.). The product isolated by ether-extraction was heated under reflux for one hour with glacial acetic acid (100 c.c.) containing concentrated sulphuric acid (0·1 c.c.) and poured into water. Ether-extraction, followed by evaporation of the solvent and subsequent fractional distillation under reduced pressure to remove benzyl acetate and dibenzyl, gave the ethylene. The following were obtained in this way as colourless viscous oils: 1-*cyclo*pentyl-1 : 2-diphenylethylene (I; R = C_5H_9; X = Y = H) (54% yield; b. p. 101°/4 × 10^{-2} mm.), which was freed from dibenzyl only by repeated distillation; 1-cyclo*pentyl-2-phenyl-*1-(p-*methoxyphenyl*)*ethylene* * (I; R = C_5H_9; X = OMe; Y = H) (72% yield; b. p. 104°/1·3 × 10^{-4} mm.); 1-cyclo*pentyl-2-phenyl-*1-(p-*ethoxyphenyl*)*ethylene* * (R = C_5H_9; X = OEt; Y = H) (75% yield; b. p. 114°/7 × 10^{-4} mm.); 1-*cyclo*hexyl-1 : 2-diphenylethylene (I; R = C_6H_{11}; X = Y = H) (50% yield; b. p. 88°/3·3 × 10^{-4} mm.) which, like the *cyclo*pentyl analogue, was separated from dibenzyl with difficulty (light absorption in ethanol: $\varepsilon_{max.}$ = 12,840, $\lambda_{max.}$ = 2570 A.; inflection at ε = 10,200, λ = 2680 A.); 1-cyclo*hexyl-2-phenyl-*1-(p-*methoxyphenyl*)*ethylene* * (I; R = C_6H_{11}; X = OMe; Y = H) (74% yield; b. p. 108°/4·7 × 10^{-5} mm.); and 1-cyclo*hexyl-2-phenyl-*1-(p-*ethoxyphenyl*)*ethylene* * (I; R = C_6H_{11}; X = OEt; Y = H) (63% yield; b. p. 118—122°/1·3 × 10^{-4} mm.).

Grignard Reactions with p-*Methoxybenzylmagnesium Chloride.*—*p*-Methoxybenzyl alcohol, prepared from anisaldehyde by the method of Davidson and Bogert (*J. Amer. Chem. Soc.*, 1935, **57**, 905), was converted into *p*-methoxybenzyl chloride as described by Shriner and Hull (*J. Org. Chem.*, 1945, **10**, 228). A solution of the halide (7·9 g.) in dry ether (80 c.c.) was added during 3—6 hours to a stirred mixture of magnesium turnings (3·05 g.) and magnesium powder (3·05 g.) in dry boiling ether (80 c.c.) under nitrogen (cf. Campen, Meisner, and Parmerter, *loc. cit.*). The reagent was filtered through glass-wool under nitrogen and a solution of the *cyclo*alkyl aryl ketone (0·025 mol.) in dry ether (70 c.c.) was added. After boiling under reflux for 30 minutes, the mixture was kept overnight and poured on ice (50 g.) and concentrated hydrochloric acid (50 c.c.). The product from the ether-extract was heated under reflux for 30 minutes with glacial acetic acid (40 c.c.) containing concentrated sulphuric acid (0·05 c.c.) and poured into water. Fractional distillation of the ethereal extract under reduced pressure gave 4 : 4′-dimethoxydibenzyl, followed by the ethylene, which was purified only with difficulty either by crystallisation or by redistillation. The following ethylenes were obtained in this manner: 1-cyclo*pentyl-*1 : 2-*di-*(p-*methoxyphenyl*)*ethylene* (I; R = C_5H_9; X = Y = OMe) (66% yield; b. p. 165°/1·5 × 10^{-3} mm.); 1-cyclo*pentyl-*2-(p-*methoxyphenyl*)-1-(p-*ethoxyphenyl*)*ethylene* (I; R = C_5H_9; X = OEt; Y = OMe) (35% yield; b. p. 164°/4·7 × 10^{-3} mm.); 1-*cyclo*hexyl-1-phenyl-2-(*p*-methoxyphenyl)ethylene (I; R = C_6H_{11}; X = H; Y = OMe) (35% yield; m. p. 78°, which did not depress the m. p. of the same compound prepared by method B); 1-*cyclo*hexyl-1 : 2-di-(*p*-methoxyphenyl)ethylene (I; R = C_6H_{11}; X = Y = OMe) (42% yield; b. p. 168—174°/5 × 10^{-2} mm.); and 1-cyclo*hexyl-*2-(p-*methoxyphenyl*)-1-(p-*ethoxyphenyl*)-*ethylene* (I; R = C_6H_{11}; X = OEt; Y = OMe) (53% yield; b. p. 168°/3 × 10^{-2} mm.), colourless needles, m. p. 78—78·5°, from light petroleum (b. p. 60—80°). The liquid ethylenes were obtained as colourless, highly viscous oils.

Ozonolysis Experiments.—(*a*) A stream of ozonised oxygen (3%) was passed into a cold solution of 1-*cyclo*hexyl-1 : 2-diphenylethylene (2 g.) in light petroleum (b. p. 40—60°; 30 c.c.) until reaction was complete. Raney nickel sludge (5 g.) was added and the mixture was warmed on the water-bath for ten minutes and filtered (cf. Cook and Whitmore, *J. Amer. Chem. Soc.*, 1941, **63**, 3540). After removal of the solvent by distillation, the residual oil was dissolved in ether and shaken successively with aqueous sodium carbonate and aqueous sodium hydrogen sulphite. The product obtained from the ethereal extract gave *cyclo*hexyl phenyl ketone as the 2 : 4-dinitrophenylhydrazone (1 g.), which after crystallisation from ethyl acetate melted at 196·5—197·5°, alone or on admixture with an authentic specimen. The hydrogen sulphite extract, after acidification and extraction with ether, afforded an oil which gave benzaldehyde as the dinitrophenylhydrazone (0·1 g.); this after crystallisation from ethyl acetate melted at 235·5—236·5°, both alone and on admixture with an authentic specimen. (*b*) Ozonised oxygen (3%) was passed into a solution of 1-*cyclo*hexyl-1-phenyl-2-(*p*-ethoxyphenyl)ethylene (1 g.) in glacial acetic acid (30 c.c.) at room temperature until reaction was complete. The solution was heated under reflux with 6% aqueous hydrogen peroxide (20 c.c.) for one hour. After removal of the solvents under reduced pressure the residue was dissolved in ether and shaken with aqueous sodium carbonate. The product from the ethereal extract gave *cyclo*hexyl phenyl ketone isolated as the 2 : 4-dinitrophenylhydrazone (0·52 g.), m. p. and mixed m. p. 196·5—197·5°. Acidification of the sodium carbonate solution and ether-extraction afforded *p*-ethoxybenzoic acid (0·07 g.), m. p. 192—193° after crystallisation from benzene, which after further crystallisation did not depress the m. p. (195°) of an authentic specimen (Cohen and Dudley, *J.*, 1910, **97**, 1741).

TABLE II.

Ethylenes, *p*-$C_6H_4X\cdot CR{:}CH\cdot C_6H_4Y$-*p*.

R.	X.	Y.	Formula.	Method of prepn.	Analysis, %. Found. C.	Found. H.	Required. C.	Required. H.	n_D^{18}.	Colour with conc. H_2SO_4.
C_5H_9	H	H	$C_{19}H_{20}$	B C	91·8 91·9	7·9 8·1	91·9	8·1	1·5880 1·5864	Dark olive-green
C_5H_9	H	OMe	$C_{20}H_{22}O$	B	86·5	8·0	86·3	8·0	—	Red-brown
C_5H_9	H	OEt	$C_{21}H_{24}O$	B	85·7	8·4	86·2	8·3	1·5879	Red
C_5H_9	OMe	H	$C_{20}H_{22}O$	C	86·3	8·0	86·3	8·0	1·5838	Red-brown
C_5H_9	OEt	H	$C_{21}H_{24}O$	C	86·4	8·6	86·2	8·3	1·5774	Blood-red
C_5H_9	OMe	OMe	$C_{21}H_{24}O_2$	C	81·4	8·0	81·75	7·8	1·5855	Blood-red
C_5H_9	OEt	OMe	$C_{22}H_{26}O_2$	C	82·1	8·2	81·9	8·1	1·5781	Blood-red
C_6H_{11}	H	H	$C_{20}H_{22}$ ‡	B C	91·4 91·1	8·5 8·4	91·6	8·45	1·5918 1·5924	Pale olive-green
C_6H_{11}	H	OMe	$C_{21}H_{24}O$	B (& C)	86·0	8·4	86·2	8·3	—	Orange
C_6H_{11}	H	OEt	$C_{22}H_{26}O$	B	86·4	8·4	86·2	8·55	—	Yellow
C_6H_{11}	OMe	H	$C_{21}H_{24}O$	C	86·2	8·4	86·2	8·3	1·5876	Yellow-orange
C_6H_{11}	OEt	H	$C_{22}H_{26}O$	C	85·8	8·6	86·2	8·55	1·5768	Dark red
C_6H_{11}	OMe	OMe	$C_{22}H_{26}O_2$ †	C	82·3	8·2	81·9	8·1	1·5915	Blood-red
C_6H_{11}	OEt	OMe	$C_{23}H_{28}O_2$	C	82·2	8·4	82·1	8·4	1·5841	Blood-red

‡ Previously prepared by Buu-Hoï and Royer (*loc. cit.*).
† Previously prepared by Dodds *et al.* (*loc. cit.*).

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