254. *Syntheses of Some Monoalkylbenzenes.*

By E. R. Lynch and E. B. McCall.

Syntheses of twelve monoalkylbenzenes, mostly containing branched C_{11} and C_{12} chains, are described. Ziegler's method was used to prepare 2-methyl-2-phenylalkanes *via* αα-dimethylbenzylpotassium. Phillips and Rabjohn's route gave alkylbenzenes containing a quaternary carbon atom *via* tri-β-substituted propionitriles. By hydrogenation of the alkylbenzenes three new alkylcyclohexanes were obtained.

Recently there has been interest in the microbiological degradation of the monoalkylbenzenesulphonates used in commercial detergents.[1] The alkylbenzene precursors are complex mixtures of hydrocarbons with an average side-chain length of about twelve carbon atoms and are largely manufactured by alkylation of benzene with an olefin mixture known as " propylene tetramer." Pure hydrocarbons of this type were required to determine the effect of side-chain branching on the ease of microbiological degradation of the sodium sulphonates and to facilitate vapour-phase chromatographic and infrared analyses[2] of the commercial product. Not many such hydrocarbons have previously been synthesised (for reviews see Francis[3] and Petrow[4]). In the present work syntheses involving alkylation of benzene were avoided, except for 2-methyl-2-phenyldecane which was also made by another method.

Five known alkylbenzenes have been prepared again: 1-phenyldodecane, from dodecanoylbenzene by the Huang-Minlon variation[5] of the Wolff–Kishner reduction; 2-phenyl-decane and -dodecane, by treating acetophenone with the appropriate alkylmagnesium bromides, dehydrating the resulting alcohols, and hydrogenating the olefins (cf. Gilman and Meals[6]); and 2-methyl-2-phenyl-pentane and -decane, by treating αα-dimethylbenzylpotassium with the appropriate alkyl bromides. Ziegler[7] used the last method for 2-methyl-2-phenyldecane, preparing the αα-dimethylbenzylpotassium in ether solution; Ziegler and Dislich[8] later prepared αα-dimethylbenzylpotassium conveniently in iso-octane suspension, which, although mixed with an equivalent quantity of sodium methoxide, is suitable for reaction with alkyl bromides. Similarly hexyl and 3,5,5-trimethylhexyl bromide gave respectively 2-methyl-2- and 2,2,4,7-tetramethyl-7-phenyloctane, which are new compounds.

Acetophenone and 3,5,5-trimethylhexylmagnesium bromide gave the tertiary alcohol, dehydrated by hot 90% formic acid to the olefin. That the olefin had the required skeleton was shown by ozonolysis and identification of acetophenone and 2,2,4-trimethylhexanal as the 2,4-dinitrophenylhydrazones. Hydrogenation of the olefin gave 2,2,4-trimethyl-7-phenyloctane containing an impurity (8%), shown in the gas chromatogram. The impurity had the same retention time as that of 2,2,4,9,11,11-hexamethyldodecane which was prepared from 3,5,5-trimethylhexylmagnesium bromide and silver bromide.[9] In a second synthesis of 2,2,4-trimethyl-7-phenyloctane, acetic anhydride and 3,5,5-trimethylhexylmagnesium bromide gave 5,7,7-trimethyloctan-2-one which on treatment with phenylmagnesium bromide, dehydration, and hydrogenation afforded the alkylbenzene, judged to be pure by gas chromatography.

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[1] Hammerton, *J. Appl. Chem.*, 1955, **5**, 517; *Proc. Soc. Water Treatment and Examination*, 1956, **5**, 145.

[2] Hawkes and Neale, unpublished work.

[3] Francis, *Chem. Rev.*, 1948, **42**, 107.

[4] Petrow, *Erdöl u. Kohle*, 1958, **11**, 855.

[5] Huang-Minlon, *J. Amer. Chem. Soc.*, 1946, **68**, 2487.

[6] Gilman and Meals, *J. Org. Chem.*, 1943, **8**, 126.

[7] Ziegler, *Annalen*, 1940, **542**, 90.

[8] Ziegler and Dislich, *Chem. Ber.*, 1957, **90**, 1113.

[9] Gutman and Hickinbottom, *J.*, 1951, 2064.

A general preparative scheme for synthesising alkanes containing a quaternary carbon atom, described by Phillips and Rabjohn,[10] is based on the 1,4-addition of Grignard reagents to αβ-unsaturated cyano-esters, a reaction discovered by Kohler [11] and extended by others.[12] The addition products are hydrolysed and decarboxylated to tri-β-substituted propionitriles. By this method there were prepared: 2-benzyl-2-methylpropyl cyanide, from benzylmagnesium chloride and ethyl 2-cyano-3-methylbut-2-enoate; 2-methyl-2-phenylpentyl cyanide, from phenylmagnesium bromide and ethyl 2-cyano-3-methylhex-2-enoate; and neopentyl cyanide, from methylmagnesium iodide and ethyl 2-cyano-3-methylbut-2-enoate. Treatment of these nitriles with hexyl-, pentyl-, and 5-phenylpentylmagnesium bromide gave the ketimines which were hydrolysed to the ketones. These long-chain ketones failed to give semicarbazones or 2,4-dinitrophenylhydrazones and, in the one case tried the Huang-Minlon variation of the Wolff–Kishner reduction gave a low yield of the alkylbenzene. Reduction of the ketones with lithium aluminium hydride to the secondary alcohols, then dehydration to the olefins, and hydrogenation over palladium–carbon gave the alkylbenzenes. The 2,2-dimethyl-9-phenylnonane obtained was contaminated with a large amount of alkylcyclohexane when too high a hydrogenation temperature was used. A pure sample of this alkylbenzene was obtained by another synthetic route: Gutman and Hickinbottom's preparation [13] of 6,6-dimethylheptanoic acid was repeated, and its acid chloride with diphenethylcadmium afforded 2,2-dimethyl-9-phenylnonan-7-one which was reduced to the alkylbenzene by the Huang-Minlon method. A second synthetic route was also used to prepare 2,2-dimethyl-1-phenyldecane. In this sodioisobutyrophenonew as alkylated with octyl bromide, to yield 2,2-dimethyldecanoylbenzene [14] which was reduced to the alkylbenzene by heating the semicarbazone with fused potassium hydroxide (cf. Cook and Linstead [15]). Unlike dodecanoylbenzene this ketone could not be reduced by the Huang-Minlon method. Although 4-methyl-4-phenylundecane has been reported [16] no physical properties are recorded, so that comparison with that product, made by the aluminium chloride-catalysed alkylation of benzene with the olefin obtained by dehydration of 4-methylundecan-4-ol, is impossible.

In the synthesis of 10-methyl-1-phenylundecane 7-phenylheptanoyl chloride and di-isopentylcadmium gave 10-methyl-1-phenylundecan-5-one which failed to give a semicarbazone or a 2,4-dinitrophenylhydrazone. The ketone was converted into the hydrocarbon *via* the secondary alcohol and olefin as outlined above.

Where ketonic derivatives could not be obtained the presence of the carbonyl group in the above ketones was shown by the infrared spectrum. Where two different syntheses of an alkylbenzene were carried out identity of the two products was established by means of infrared spectra and crystalline derivatives. These derivatives, prepared for all the alkylbenzenes described here, are the 2,4-dinitrophenylhydrazones of the acetylated alkylbenzenes (cf. Pines and Shaw [17]).

In connection with the infrared spectroscopic investigations 2,2,4-trimethyl-7-phenyloctane, 2,2-dimethyl-1-phenyldecane, and 4-methyl-4-phenylundecane were hydrogenated over Raney nickel to the alkylcyclohexanes. These were needed to determine which absorption bands were associated with the aromatic ring where unusual features were noticed in the infrared spectra of the alkylbenzenes.[2]

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[10] Phillips, Thesis, University of Missouri, 1957. University Microfilm No. 22,753, Ann Arbor, Michigan, U.S.A.

[11] Kohler and Reimer, *Amer. Chem. J.*, 1905, **33**, 333.

[12] Prout, Huang, Hartman, and Korpics, *J. Amer. Chem. Soc.*, 1954, **76**, 1911; Alexander, McCollum, and Paul, *ibid.*, 1950, **72**, 4791; Prout, *ibid.*, 1952, **74**, 5915; Hook and Robinson, *J.*, 1944, 152.

[13] Gutman and Hickinbottom, *J.*, 1951, 3344.

[14] Apolit, *Ann. Chim.* (*France*), 1924, **2**, 83.

[15] Cook and Linstead, *J.*, 1934, 949.

[16] Kooijman, Huijser, and Tjepkema, " Congrès Mondial de la Detergence," Paris, 1954, p. 130.

[17] Pines and Shaw, *J. Org. Chem.*, 1955, **20**, 373.

EXPERIMENTAL

Boiling points for the hydrocarbons were determined at atmospheric pressure in an apparatus of *ca.* 2 ml. capacity as described by Willard and Crabtree.[18]

Most of the liquid starting materials were fractionally distilled through a column (115 × 2 cm.) packed with $\frac{1}{8}''$ glass rings. All other fractional distillations referred to were carried out with a spinning-band column which had an efficiency of thirty-five theoretical plates at atmospheric pressure under total reflux. Each alkylbenzene was distilled through this column and, unless otherwise stated, no impurities were detected by gas chromatography in the fractions for which the physical constants are given. Gas chromatograms were run mainly with a stationary phase of 20% silicone oil supported on 60/90 mesh kieselguhr (May and Baker, " Embacel ") with a column length of 16 feet at 220°, a nitrogen flow rate of 20 ml./min., a sample size of *ca.* 0·5 mg., and a gas-density balance detector. Some gas chromatograms were also run at 150° with an ionisation detector.

1-*Phenyldodecane.*—Dodecanoyl chloride with benzene and aluminium chloride gave dodecanoylbenzene in 60% yield, having b. p. 148—152°/0·6 mm., m. p. 42—44°; recrystallised from methanol, it had m. p. 43—45°. Gilman and Meals [6] record m. p. 42·5°.

Dodecanoylbenzene (30 g.), 100% hydrazine hydrate (12·7 ml.), and diethylene glycol (130 ml.) were stirred at 80° under reflux during 1 hr. Powdered potassium hydroxide (17 g.) was added, and the temperature was raised to 200°, water and the excess of hydrazine hydrate being allowed to distil. After being stirred at 200° during a further 3 hr. the mixture was cooled and added to water, and the oil was isolated by means of ether. Distillation from a Claisen flask gave 1-phenyldodecane (20·1 g.), b. p. 140°/0·6 mm., n_D^{20} 1·4821. The nitrogenous residue from the distillation was heated on the steam-bath with 50% sulphuric acid during 1 hr. to give dodecanoylbenzene (5·8 g.), m. p. 40—42°. Fractionally distilled, 1-phenyldodecane had n_D^{20} 1·4820 (Found: C, 87·6; H, 12·3. Calc. for $C_{18}H_{30}$: C, 87·7; H, 12·3%). Francis [3] gives n_D^{20} 1·4838 as an average value. Schmidt [19] records n_D^{20} 1·4822.

2-*Phenylalkanes.*—(a) 2,2,4-*Trimethyl*-7-*phenyloctane* via *acetophenone.* 3,5,5-Trimethylhexyl bromide (b. p. 70·5°/11 mm., n_D^{25} 1·4510) was prepared as described by Turner and Turner [20] (cf. Gutman and Hickinbottom [9]). To the Grignard solution prepared from 3,5,5-trimethylhexyl bromide (156 g.), magnesium (18 g.), and ether (750 ml.) there was added acetophenone (75 g.) in ether (90 ml.), dropwise. The mixture was heated under reflux during 2 hr., cooled, and poured into ice and hydrochloric acid. The solution obtained by combination of the organic phase with the ethereal extract of the aqueous phase was washed with water and dried ($MgSO_4$). Removal of the ether gave an oil which was heated under reflux with 90% formic acid (175 ml.) during 18 hr. After dilution of this mixture with water the oil was isolated by means of ether, and distillation from sodium (nitrogen leak) gave the olefin (95 g.), b. p. 102—107°/0·7 mm., n_D^{25} 1·4945—1·5039. Hydrogenation in ethanol over 5% palladium–carbon at ordinary pressure gave 2,2,4-*trimethyl*-7-*phenyloctane*, b. p. 81—82°/0·3 mm., 272°/752 mm., n_D^{25} 1·4763 (Found: C, 87·6; H, 12·2. $C_{17}H_{28}$ requires C, 87·9; H, 12·1%). The gas chromatogram showed the alkylbenzene to contain 8% of an impurity which was not separated on fractional distillation through the spinning-band column. The impurity had the same retention time as 2,2,4,9,11,11-hexamethyldodecane, prepared (in 32% yield) from 3,5,5-trimethylhexylmagnesium bromide and silver bromide,[9] b. p. 153°/19 mm., 272°/752 mm., $n_D^{20.4}$ 1·4360 (Found: C, 85·1; H, 14·8. Calc. for $C_{18}H_{38}$: C, 85·0; H, 15·0%).

For ozonolysis the above olefin was fractionally distilled (b. p. 93°/0·5 mm., n_D^{25} 1·5065), then ozonised in acetic acid; the ozonide solution was added to water containing zinc dust and steam-distilled. A 2,4-dinitrophenylhydrazone mixture obtained from the distillate was chromatographed on a bentonite–kieselguhr (4 : 1) column in benzene. By elution with benzene and subsequent recrystallisation from ethanol there were obtained yellow crystals, m. p. 96° undepressed on admixture with the 2,4-dinitrophenylhydrazone (m. p. 96°) of 3,5,5-trimethylhexanal (Found: C, 56·2; H, 6·7; N, 17·2. Calc. for $C_{15}H_{22}O_4N_4$: C, 55·9; H, 6·9; N, 17·4%). Lieberman [21] records m. p. 92—93° for this hydrazone. Further elution of the chromatogram

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[18] Willard and Crabtree, *Ind. Eng. Chem., Analyt.*, 1936, **8**, 79.

[19] Schmidt, *Ber.*, 1939, **72**, 1893.

[20] Turner and Turner, *J.*, 1951, 2544.

[21] Lieberman, *J. Amer. Chem. Soc.*, 1955, **77**, 1116.

with chloroform afforded orange crystals, m. p. 247° alone or mixed with acetophenone 2,4-dinitrophenylhydrazone, m. p. 250°.

(b) 2,2,4-*Trimethyl*-7-*phenyloctane* via 5,7,7-*trimethyloctan*-2-*one*. The general directions of Newman and Booth [22] were followed for preparing methyl ketones from a Grignard reagent and acetic anhydride. The Grignard solution from 3,5,5-trimethylhexyl bromide (96 g.), magnesium (11·1 g.), and ether (*ca.* 250 ml.), cooled to *ca.* $-60°$ under nitrogen, was added dropwise to a solution of acetic anhydride (81 ml.) in ether (80 ml.) at $<-60°$, with stirring during 1½ hr. After being stirred overnight at $<-60°$ the mixture was allowed to reach room temperature and then added to ice and hydrochloric acid. The solution obtained by combination of the organic phase with an ethereal extract of the aqueous phase was washed with water, the ether was distilled off, and the residual oil was boiled with water to hydrolyse unchanged acetic anhydride. The oil was isolated by means of ether and fractionally distilled, to give 5,7,7-trimethyloctan-2-one (32·8 g.), b. p. 108°/20 mm., n_D^{25} 1·4263 [semicarbazone, m. p. 147—147·5° (from ethanol)]. Gutman and Hickinbottom [9] record b. p. 103°/28 mm., n_D^{20} 1·4309 (semicarbazone, m. p. 147·5—148·5°).

5,7,7-Trimethyloctan-2-one (29·5 g.) was added to the Grignard solution prepared from bromobenzene (50 g.), magnesium (7·5 g.), and ether (320 ml.). After being heated under reflux during 5 hr. the mixture was poured into ice and hydrochloric acid, the organic phase was washed with water, and the ether removed. The residual oil was boiled with 90% formic acid (80 ml.) during 16 hr., then diluted with water, and the layers were separated. The aqueous phase was neutralised with sodium hydroxide and extracted with ether; the ether solution obtained by combining the extract with the organic phase was washed with water and dried ($MgSO_4$). Removal of the ether gave the olefin (29·9 g.), n_D^{25} 1·5063, which was hydrogenated in ethanol over 5% palladium–carbon at atmospheric pressure. Fractional distillation yielded 2,2,4-trimethyl-7-phenyloctane, b. p. *ca.* 79°/0·4 mm., 276°/755 mm., n_D^{25} 1·4800.

(c) 2-*Phenyldecane*. By the procedure in (a) acetophenone and octyl bromide yielded 2-phenyldecane, b. p. 94°/0·5 mm., 278°/754 mm., n_D^{25} 1·4800 (Found: C, 87·6; H, 11·9. Calc. for $C_{16}H_{26}$: C, 88·0; H, 12·0%). Francis [3] gave n_D^{20} 1·4864.

(d) 2-*Phenyldodecane*. As in (c), but by use of decyl bromide, there was obtained 2-phenyldodecane (overall yield 44% after fractional distillation), b. p. *ca.* 104°/0·5 mm., 310°/772 mm., n_D^{25} 1·4792 (Found: C, 87·9; H, 12·1%). Francis [3] gave n_D^{20} 1·4822.

2-*Methyl*-2-*phenylalkanes*.—(a) 2,2,4,7-*Tetramethyl*-7-*phenyloctane*. By treating a stirred suspension of potassium (14 g.) in iso-octane (130 ml.) at 70° under nitrogen with 2-methoxy-2-phenylpropane [8] (29 g.) there was obtained a violet suspension containing αα-dimethylbenzylpotassium and potassium methoxide (Ziegler and Dislich [8]). To the stirred mixture, cooled by water, there was added 3,5,5-trimethylhexyl bromide [20] (45·4 g.) in iso-octane (30 ml.) at a rate such that the temperature did not rise above 35°. After a further 2 hours' stirring at room temperature the violet colour disappeared. Water was added dropwise to dissolve the potassium salts, and the organic phase was washed with water and dried ($CaCl_2$). Removal of the solvent gave the crude alkylbenzene (48 g.) which on fractional distillation yielded 2,2,4,7-*tetramethyl*-7-*phenyloctane* (23·4 g.), b. p. 77°/0·2 mm., 280°/756 mm., n_D^{25} 1·4821 (Found: C, 87·7; H, 12·3. $C_{18}H_{30}$ requires C, 87·8; H, 12·2%).

(b) 2-*Methyl*-2-*phenyloctane*. By a procedure as in (a), 2-*methyl*-2-*phenyloctane*, b. p. *ca.* 102°/3 mm., 254°/748 mm., n_D^{25} 1·4868, was obtained by using hexyl bromide (Found: C, 88·2; H, 11·8. $C_{15}H_{24}$ requires C, 88·2; H, 11·8%).

(c) 2-*Methyl*-2-*phenylpentane*. As in (b), but by use of propyl bromide, there was obtained 2-methyl-2-phenylpentane, b. p. 82·5°/11 mm., *ca.* 204°/760 mm., n_D^{25} 1·4912. Hughes [23] records b. p. 206—208° and 196—197°, n_D^{20} 1·4935 and 1·4943. Pines, Huntsman, and Ipatieff [24] record b. p. 126·8—127°/66 mm., n_D^{20} 1·4929.

(d) 2-*Methyl*-2-*phenyldecane*.—This hydrocarbon was prepared by two methods:

(i) *Via* αα-dimethylbenzylpotassium. By the procedure in (a), 2-methyl-2-phenyldecane, b. p. 102·5°/0·9 mm., 286°/754 mm., n_D^{25} 1·4848, was obtained from octyl bromide (50% yield based on 2-methoxy-2-phenylpropane) (Found: C, 87·6; H, 12·4%). Ziegler [7] records b. p. 160°/20 mm., n_D^{20} 1·48594. Weinmayr [25] records b. p. 140—145°/1 mm., n_D^{20} 1·4875.

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[22] Newman and Booth, *J. Amer. Chem. Soc.*, 1945, **67**, 154.
[23] Hughes, *J.*, 1958, 3704.
[24] Pines, Huntsman, and Ipatieff, *J. Amer. Chem. Soc.*, 1953, **75**, 2314.
[25] Weinmayr, U.S.P. 2,467,170 (*Chem. Abs.*, 1949, **43**, 6232).

(ii) *Via* 2-chloro-2-methyldecane. 2-Methyldecan-2-ol (from acetone and octylmagnesium bromide) was treated in ether with hydrogen chloride, washed with water, and dried ($MgSO_4$). The ether was distilled off and the chloride with benzene and ferric chloride gave 2-methyl-2-phenyldecane, b. p. 123°/3·5 mm., n_D^{25} 1·4848. Although fractionally distilled this preparation contained 1% of a low-boiling impurity.

Preparation of Tri-β-substituted Propionitriles.—αβ-Unsaturated cyano-esters were prepared as described by Cope *et al.*[26] by condensing ethyl cyanoacetate with the appropriate ketone. Methyl propyl ketone (b. p. 101·8°, n_D^{25} 1·3885) gave ethyl 2-cyano-3-methylhex-2-enoate, b. p. 116°/8 mm., n_D^{25} 1·4650; acetone gave ethyl 2-cyano-3-methylbut-2-enoate, b. p. 119—120°/18 mm., m. p. 26—27°. These were treated with Grignard reagents as described below and the addition products were hydrolysed and decarboxylated to the tri-β-substituted nitriles.

(a) 2-*Methyl*-2-*phenylpentyl cyanide*. To the Grignard solution prepared from bromobenzene (173 g.), magnesium (26 g.), and ether (*ca.* 1 l.) containing cuprous iodide (Hook *et al.*[12]) (1 g.), there was added, dropwise, ethyl 2-cyano-3-methylhex-2-enoate (180 g.) in ether. The mixture was stirred and heated under reflux overnight, cooled, and added to ice and hydrochloric acid. The ethereal phase was washed with dilute sodium hydrogen sulphite solution to remove unchanged unsaturated cyano-ester, washed with water, and dried ($MgSO_4$). Distillation gave an oil, b. p. 125°/0·25 mm., $n_D^{25·2}$ 1·5018 (60% yield on unsaturated cyano-ester), which was hydrolysed by heating it in ethanol (180 ml.) and water (1400 ml.) with potassium hydroxide (240 g.) during 7 hr. The ethanol was distilled off and the residual aqueous solution was acidified with hydrochloric acid. The liberated oil was taken up in ether, washed with water, and dried (Na_2SO_4). Removal of the ether gave a viscous oil, decarboxylated by copper powder (0·5 g.) at 120—125° (bath) during 30 min. and then at 130° (bath) until carbon dioxide was no longer evolved. Distillation gave an oil, 2-*methyl*-2-*phenylpentyl cyanide* (104 g.), b. p. (mainly) 98°/0·25 mm., n_D^{22} 1·5109 (Found: C, 83·5; H, 9·2; N, 7·1. $C_{13}H_{17}N$ requires C, 83·4; H, 9·1; N, 7·5%), and residual 3-*methyl*-3-*phenylhexanamide* (36 g.) which, recrystallised from light petroleum (b. p. 60—80°), had m. p. 61·5—62° (Found: C, 76·3; H, 9·3; N, 6·7. $C_{13}H_{19}ON$ requires C, 76·1; H, 9·3; N, 6·8%). The amide was the major product on decarboxylation if the hydrolysis was conducted by heating the tri-β-substituted cyano-ester (29 g.) with potassium hydroxide (30 g.) in water (30 ml.) and ethanol (70 ml.) under reflux for 18 hr.

(b) 2-*Benzyl*-2-*methylpropyl cyanide*. Ethyl 2-cyano-3-methylbut-2-enoate was treated with benzylmagnesium chloride as described by Prout *et al.*,[12] to give ethyl β-benzyl-α-cyano-β-methylbutyrate, b. p. *ca.* 150°/1·5 mm., n_D^{20} 1·5041—1·5045. When hydrolysis and simultaneous decarboxylation of this cyano-ester was carried out in ethylene glycol by the method of Prout *et al.*[12] only a 35% yield of 2-benzyl-2-methylpropyl cyanide was obtained. Separate hydrolysis and decarboxylation as described below gave an 82% yield of nitrile.

A solution of the cyano-ester (120 g.) in ethanol (480 ml.) and 2N-sodium hydroxide (600 ml.) was heated under reflux during 2½ hr. The cyano-acid (110 g.) was obtained on working up as in (a) and was decarboxylated by copper powder at 140° (bath) for 30 min. and at 200° (bath) for 45 min. On distillation there was obtained 2-benzyl-2-methylpropyl cyanide (70 g.), b. p. 145—150°/17 mm., n_D^{24} 1·5088 (Prout *et al.*[12] give b. p. 148—149°/17 mm., n_D^{25} 1·5078), and residual β-*benzyl*-β-*methylbutyramide* which, recrystallised from light petroleum (b. p. 100—120°), had m. p. 118° (Found: C, 75·2; H, 8·6; N, 7·3. $C_{12}H_{17}ON$ requires C, 75·3; H, 9·0; N, 7·3%).

(c) *Neopentyl cyanide*. Ethyl 2-cyano-3-methylbut-2-enoate and methylmagnesium iodide gave ethyl α-cyano-ββ-dimethylbutyrate, b. p. 102—104°/14 mm., $n_D^{21·4}$ 1·4263, as described by Alexander *et al.*[12] Hydrolysis as under (b) gave the cyano-acid which was decarboxylated by heating it under reflux with a little copper powder during 26 hr. Distillation gave neopentyl cyanide (26%), b. p. 136—137°, m. p. 30·5°, and a residue containing the amide, m. p. 129·5—131° [from light petroleum (b. p. 60—80°)]. Homeyer *et al.*[27] record m. p. 132° for the amide, and b. p. 135—136·4°/737 mm., m. p. 32·5°, for the cyanide.

4-*Methyl*-4-*phenylundecane*.—To the stirred Grignard solution prepared from pentyl bromide (108 ml.), magnesium (21 g.), and ether (800 ml.) there was added 2-methyl-2-phenylpentyl cyanide (98 g.) in ether (100 ml.) during 1½ hr. at the b. p. The mixture was heated under reflux for a further 20 hr. then cooled and poured into ice and hydrochloric acid. The aqueous phase was extracted with ether and the extract combined with the ethereal phase; the ether was removed to leave the ketimine hydrochloride, an oil, which was hydrolysed under reflux in

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[26] Cope, Hofmann, Wyckoff, and Hardenburgh, *J. Amer. Chem. Soc.*, 1941, **63**, 3452.
[27] Homeyer, Whitmore, and Wallingford, *J. Amer. Chem. Soc.*, 1933, **55**, 4209.

2N-hydrochloric acid during 2 hr. The oil, isolated by means of light petroleum (b. p. 40—60°), was fractionally distilled to give 4-*methyl*-4-*phenylundecan*-6-*one* (100 g.), b. p. 102°/0·2 mm., n_D^{25} 1·4939. Attempts to prepare the oxime and semicarbazone failed.

The ketone (100 g.) in dry ether (150 ml.) was added during 1 hr. to a stirred solution of lithium aluminium hydride (16·5 g.) in dry ether (350 ml.). The heat evolved caused the mixture to boil. After a further 20 hours' heating, the excess of hydride was decomposed by ethyl acetate, followed by 2N-sulphuric acid, with cooling and stirring. The solution obtained by combining the ethereal phase with an ethereal extract of the aqueous phase was washed with water and dried ($MgSO_4$). Removal of the ether gave 4-methyl-4-phenylundecan-6-ol (97·7 g.), n_D^{25} 1·4969. Dehydration of this alcohol (45 g.) over powdered potassium hydrogen sulphate (10 g.) at 180—190° (bath)/15 mm. during 28 hr. (until liberated water no longer distilled into a cold trap) gave an oil which was separated by means of ether and distilled from sodium *in vacuo* to give the olefin (37·3 g.), b. p. 89—100°/0·2 mm., n_D^{25} 1·4961.

The olefin was hydrogenated over 5% palladium–carbon at 70—80°/80 atm. to 4-*methyl*-4-*phenylundecane*, b. p. 107·5°/0·7 mm., 301°/766 mm., n_D^{25} 1·4860 (Found: C, 87·7; H, 12·1. $C_{18}H_{30}$ requires C, 87·8; H, 12·2%). The gas chromatogram showed the presence of a little high-boiling impurity which was probably 4-cyclohexyl-4-methylundecane.

The hydrocarbon was also obtained in low yield by reduction of 4-methyl-4-phenylundecan-6-one as described for the reduction of dodecanoylbenzene. The ketone (15 g.) yielded the alkylbenzene (4 g.), b. p. 93—93·5°/0·3 mm., n_D^{25} 1·4862.

2,2-*Dimethyl*-1-*phenyldecane*.—(a) *Preparation* via 2-*benzyl*-2-*methylpropyl cyanide*. This cyanide (70 g.) in ether was added during 1 hr. to the Grignard solution prepared from hexyl bromide (80 g.), magnesium (12 g.), and ether. The mixture was heated under reflux during 20 hr. and worked up as for the similar reaction described under 4-methyl-4-phenylundecane. There was obtained 2,2-dimethyl-1-phenyldecan-4-one (62·5 g.), b. p. 110—112°/0·1 mm., which failed to yield a 2,4-dinitrophenylhydrazone.

The ketone (60 g.) was reduced to the secondary alcohol (57 g.) by lithium aluminium hydride (11 g.) in ether as described above. Dehydration was carried out at 190—200° (bath)/15 mm. over powdered potassium hydrogen sulphate (20 g.); during 7 hr. the theoretical quantity of water was collected in a cold trap. Working up as before gave the olefin (43·5 g.), b. p. 170—172°/17 mm., n_D^{25} 1·4922. Hydrogenation to the alkylbenzene was probably complete at 65—80°/100 atm. over 5% palladium–carbon but was continued at 90° during a further 1 hr. 2,2-Dimethyl-1-phenyldecane (35·4 g.) had b. p. 107°/0·5 mm., n_D^{25} 1·4844, and the infrared spectrum and derivative were identical with those of the hydrocarbon synthesised by route (b).

(b) *Preparation* via 2,2-*dimethyldecanoylbenzene*. Sodamide (23·8 g., 92% purity) was stirred in dry boiling toluene (450 ml.) whilst isobutyrophenone (83·5 g.; b. p. 108°/15 mm., n_D^{25} 1·5156) was added dropwise. The mixture was stirred and heated under reflux during 2½ hr., and whilst it still boiled octyl bromide (109 g.) was added during 2½ hr. Heating and stirring were continued for a further 8½ hr. Water was added to the cooled mixture, and the organic phase was washed with water. Distillation gave 2,2-dimethyldecanoylbenzene (117 g.), b. p. 125—127°/0·25 mm., n_D^{25} 1·4928. The oxime had m. p. 116·5—117° (from ethanol) (Found: C, 78·4; H, 10·3; N, 5·2. Calc. for $C_{18}H_{29}ON$: C, 78·5; H, 10·6; N, 5·1%). Apolit [14] gives b. p. 195—197°/16 mm., and oxime, m. p. 116—117°.

The ketone (101 g.), semicarbazide hydrochloride (40 g.), and fused sodium acetate (32 g.) were boiled in ethanol (800 ml.) under reflux during 2 hr. Sodium chloride was filtered off and the filtrate was evaporated to a small volume on the steam-bath, dissolved in ether, washed with water, and dried (Na_2SO_4). Removal of the ether yielded an oily solid, m. p. 43—48°, which was recrystallised twice from ethereal solution at −50° giving the semicarbazone (60 g.), m. p. 57—58·5°. By further recrystallisation in the same way a sample having m. p. 57·5—59° was obtained for analysis but no satisfactory value for carbon was obtained (Found: C, 70·1; H, 9·9; N, 12·9. Calc. for $C_{19}H_{31}ON_3$: C, 71·9; H, 9·8; N, 13·2%). Apolit [14] records m. p. 49—50° for the semicarbazone.

The semicarbazone (49 g.) and powdered potassium hydroxide (49 g.) were ground together, melted, and stirred whilst the temperature was raised to 200°. During 15 min. at 200—210° (bath) ammonia was evolved and stirring was continued at 210—220° (bath) for a further 45 min. until gas evolution ceased. Whilst the mixture was still warm, water was added and, when cool, the oil was taken up in ether, and the ethereal solution was washed with water and dried ($CaCl_2$). Evaporation gave the oil (34·4 g.) which, together with the product (32 g.) of a similar experiment, was distilled leaving a nitrogenous residue. Fractional distillation of the distillate gave 2,2-*dimethyl*-1-*phenyldecane* (41·2 g.), b. p. 93°/0·2 mm., 311°/756 mm., n_D^{25} 1·4847 (Found: C, 87·7; H, 12·1. $C_{18}H_{30}$ requires C, 87·8; H, 12·2%). The infrared spectrum was identical with that for the hydrocarbon prepared as under (a) above and showed no carbonyl absorption.

5-*Phenylpentyl Bromide*.—Glutaric anhydride and benzene gave γ-benzoylbutyric acid,[28] which by the Huang-Minlon modification [5] of the Wolff–Kishner reduction gave δ-phenylvaleric acid, m. p. 57°, in 88% yield. The acid chloride (67·7 g.), b. p. 151°/18 mm. (obtained by means of thionyl chloride), in dry ether (100 ml.) was added dropwise to a stirred solution of lithium aluminium hydride (8·3 g.) in dry ether (250 ml.) during 1 hr. and after several hours' heating under reflux the excess of hydride was decomposed by ethyl acetate, and 2N-sulphuric acid was added with cooling. The ethereal phase and the ethereal washings of the aqueous phase were combined and washed with water and dried ($MgSO_4$). Distillation gave 5-phenylpentyl alcohol (53·8 g.), b. p. 85°/0·2 mm., n_D^{25} 1·5140, having the typical lemon-like odour.

5-Phenylpentyl bromide (63·2 g.), b. p. 78—79°/0·3 mm., n_D^{25} 1·5313, was obtained from the alcohol (53·8 g.) by reaction with 48% hydrobromic acid (100 ml.) and concentrated sulphuric acid (20 ml.) during 4 hr. at 115°.

8,8-*Dimethyl*-1-*phenylnonane*.—*Preparation* via *neopentyl cyanide*. Neopentyl cyanide (20·5 g.) in ether (50 ml.) was added in 15 min. to a stirred Grignard solution prepared from 5-phenylpentyl bromide (56 g.), magnesium (6 g.), and ether (250 ml.). The mixture was heated under reflux during 40 hr., then worked up as described for the ketonic intermediate under 4-methyl-4-phenylundecane. There was obtained 8,8-dimethyl-1-phenylnonan-4-one (28·1 g.), b. p. 108—112°/0·25 mm., n_D^{25} 1·4881, and a fore-fraction containing 1-phenylpentane. The ketone (28·1 g.) was reduced to the secondary alcohol by lithium aluminium hydride as described for the similar reaction in the synthesis of 4-methyl-4-phenylundecane, and the alcohol (25·8 g.) was dehydrated over powdered potassium hydrogen sulphate (9 g.) at 160—170° (bath)/15 mm., until, after 27 hr., the theoretical amount of water had distilled into a cold trap. The olefin (21·3 g.), b. p. 84—86°/0·2 mm., n_D^{25} 1·4880, was isolated by means of ether. Hydrogenation as described for the olefinic precursor of 4-methyl-4-phenylundecane (except that the temperature inadvertently rose to 184°) gave a product, b. p. 104—113°/0·4 mm., n_D^{25} 1·4548—1·4530, containing a large proportion of alkylcyclohexane. The material was heated over 5% palladium–carbon at 295—300° (bath) during 24 hr. to yield a partly dehydrogenated product. This was fractionally distilled and the fraction of highest refractive index (n_D^{25} 1·4694) was acetylated and the 2,4-dinitrophenylhydrazone of the acetyl compound was prepared; the m. p. (155—155·5°) was undepressed on admixture with the similar derivative made from 8,8-dimethyl-1-phenylnonane prepared in the other synthesis.

6,6-*Dimethylheptanoic Acid*.—4,4-Dimethylpent-1-ene, b. p. 71·6°, n_D^{25} 1·3893, was obtained in 56% yield from allyl bromide and t-butylmagnesium chloride by the method of Whitmore and Homeyer [29] who record b. p. 72·35°/760 mm. and n_D^{20} 1·3911 for the olefin.

The olefin was treated with hydrogen bromide in the presence of t-butyl peroxide below 25°, to give 4,4-dimethylpentyl bromide, b. p. 63—63·8°/25 mm., n_D^{20} 1·4485 (Gutman and Hickinbottom [13] record b. p. 56—57°/19 mm., n_D^{20} 1·4485).

The bromide (133 g.) with malonic ester yielded diethyl 4,4-dimethylpentylmalonate (140 g.), b. p. 136—140°/9 mm., n_D^{25} 1·4252, which on alkaline hydrolysis gave 4,4-dimethylpentylmalonic acid, m. p. 98—102°, and decarboxylation of this at 160° (bath) gave 6,6-dimethylheptanoic acid (75·5 g.), b. p. 126—129°/11 mm., n_D^{20} 1·4296. Gutman and Hickinbottom [13] record $n_D^{20.1}$ 1·4298. The 4-phenylphenacyl ester had m. p. 89·5—90° (lit.,[13] m. p. 89°); the *anilide* had m. p. 70·5° (Found: C, 77·1; H, 9·7; N, 6·1. $C_{15}H_{23}ON$ requires C, 77·2; H, 9·9; N, 6·0%).

The acid chloride, b. p. 79—80°/10 mm., was prepared by means of thionyl chloride.

8,8-*Dimethyl*-1-*phenylnonane*.—6,6-Dimethylheptanoyl chloride (79·5 g.) treated in benzene with diphenethylcadmium, prepared by treating the Grignard solution from phenethyl bromide (185 g.), magnesium (24 g.), and ether (*ca.* 600 ml.) with anhydrous cadmium chloride (95 g.) and replacing the ether by benzene (Cason [30]). Working up in the usual manner gave the crude

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[28] Somerville and Allen, *Org. Synth.*, 1943, Coll. Vol. II, p. 82 (note 9).
[29] Whitmore and Homeyer, *J. Amer. Chem. Soc.*, 1933, **55**, 4555.
[30] Cason, *Chem. Rev.*, 1947, **40**, 15.

ketone (118 g.) and fractional distillation gave 8,8-dimethyl-1-phenylnonan-3-one, b. p. 130°/1·5 mm., n_D^{25} 1·4878, which yielded a *semicarbazone*, m. p. 86·5—87·5° (Found: C, 70·8; H, 9·5; N, 13·7. $C_{18}H_{29}ON_3$ requires C, 71·2; H, 9·64; N, 13·8%).

The ketone (44·6 g.) was stirred with 100% hydrazine hydrate (19·1 ml.) in diethylene glycol (195 ml.) at 80° during 1 hr. under a reflux condenser. Powdered potassium hydroxide (25·5 g.) was then added and the temperature was raised to 200°, water and the excess of hydrazine hydrate being allowed to distil off. After a further 3 hours' stirring at 200° the two-phase mixture was cooled, then diluted with water, and the oil was isolated by means of ether. Fractional distillation gave 8,8-*dimethyl*-1-*phenylnonane* (26 g.), b. p. 111°/1·5 mm., 293°/754 mm., n_D^{25} 1·4773 (Found: C, 88·1; H, 12·0%).

7-*Phenylheptanoic Acid*.—4-Cyclohex-1-enylmorpholine, b. p. 128—130°/18 mm., n_D^{25} 1·5100 (prepared as described by Hünig *et al.*[31]) was treated with benzoyl chloride and triethylamine in chloroform to yield 4-(2-benzoylcyclohex-1-enyl)morpholine which, hydrolysed by 20% hydrochloric acid (cf. ref. 31), gave 2-benzoylcyclohexanone, b. p. 184—200°/17 mm., m. p. 81—84°. A sample had m. p. 86—86·5° after recrystallisation from light petroleum.

2-Benzoylcyclohexanone (43·7 g.) was hydrolysed by boiling 2N sodium hydroxide (200 ml.) during 1 hr. The cyclohexanone formed was removed by extraction with ether, and the aqueous solution, freed from ether, was poured into ice and hydrochloric acid to yield a white precipitate (39·2 g.), m. p. 63—64°. Recrystallisation twice from light petroleum (b. p. 80—100°) gave 6-benzoylhexanoic acid (21·6 g.), m. p. 82—83° (lit.,[32] m. p. 84—85°); a little benzoic acid separated from the mother-liquors.

6-Benzoylhexanoic acid (66 g.) was reduced as described by Huang-Minlon [5] to 7-phenylheptanoic acid (58·2 g.), b. p. 145—150°/0·7 mm. The amide had m. p. 89° (from ethanol) (von Braun [33] gives m. p. 89°). The acid chloride, b. p. 131—132°/0·9 mm., was obtained by reaction of the acid with thionyl chloride.

10-*Methyl*-1-*phenylundecan*-5-*one*.—7-Phenylheptanoyl chloride (50·2 g.) reacted in benzene with di-isopentylcadmium, prepared by treating the Grignard solution from isopentyl bromide (75 g.), magnesium (12 g.), and ether (400 ml.) with anhydrous cadmium chloride (50 g.) and replacing the ether by benzene, to give the ketone (41 g.), b. p. 133—136°/0·3 mm., n_D^{25} 1·4885. This failed to give a 2,4-dinitrophenylhydrazone or a semicarbazone.

10-*Methyl*-1-*phenylundecane*.—The foregoing ketone, undecan-5-one (40 g.), was reduced to the secondary alcohol (39 g.), n_D^{25} 1·4928, by lithium aluminium hydride in ether (cf. preparation of 4-methyl-4-phenylundecane), and this was heated over potassium hydrogen sulphate (14 g.) at 180—200° (bath)/16 mm. Dehydration was stopped after 12 hr. because the mixture had become dark and tar was formed. The oil was separated from the solid by using light petroleum (b. p. 40—60°) and distilled, giving the olefin (28·5 g.), b. p. 125—129°/1 mm., n_D^{25} 1·4900. The olefin, hydrogenated at 1 atm. over 5% platinum–carbon, gave 10-methyl-1-phenylundecane, b. p. 114°/0·3 mm., n_D^{25} 1·4795 (Found: C, 87·7; H, 12·5%).

Hydrogenation of Alkylbenzenes.—(a) 7-*Cyclohexyl*-2,2,4-*trimethyloctane*. 2,2,4-Trimethyl-7-phenyloctane (containing 8% of 2,2,4,9,11,11-hexamethyldodecane) was hydrogenated in hexane over Raney nickel at 70—90°/90 atm. to 7-*cyclohexyl*-2,2,4-*trimethyloctane*, b. p. *ca.* 86·5°/0·4 mm., n_D^{25} 1·4542 (Found: C, 85·8; H, 14·4. $C_{17}H_{34}$ requires C, 85·6; H, 14·4%). Gas chromatography showed the hydrocarbon to contain 2% of a low-boiling impurity, probably a hexamethyldodecane which had not been completely separated by fractional distillation.

(b) 1-*Cyclohexyl*-2,2-*dimethyldecane*. 2,2-Dimethyl-1-phenyldecane was hydrogenated at 95—112°/90 atm. during *ca.* 1 hr. to give 1-*cyclohexyl*-2,2-*dimethyldecane*, b. p. 111°/0·55 mm., n_D^{25} 1·4561 (Found: C, 85·6; H, 14·4. $C_{18}H_{36}$ requires C, 85·6; H, 14·4%). Gas chromatography showed the hydrocarbon to be at least 99% pure.

(c) 4-*Cyclohexyl*-4-*methylundecane*. 4-Methyl-4-phenylundecane was only partly hydrogenated under the conditions used in (a). Further hydrogenation at 100—110°/133 atm. gave 4-cyclohexyl-4-methylundecane, b. p. 116—116·5°/0·6 mm., n_D^{25} 1·4630 (Found: C, 85·9; H, 14·3%). Gas chromatography showed the hydrocarbon to be at least 99% pure.

Infrared data on the alkylcyclohexanes are to be published along with those for the alkylbenzenes.[2]

Derivatives of Alkylbenzenes.—The alkylbenzene was acetylated on a small scale, giving an

[31] Hünig, Benzing, and Lücke, *Chem. Ber.*, 1957, **90**, 2838.

[32] Hauser, Swamer, and Ringler, *J. Amer. Chem. Soc.*, 1948, **70**, 4024.

[33] von Braun, *Ber.*, 1911, **44**, 2878.

2,4-*Dinitrophenylhydrazones of alkylacetophenones.*

Parent alkylbenzene	M. p. of deriv.	Found (%) C	Found (%) H	Found (%) N	Formula	Required (%) C	Required (%) H	Required (%) N
2-Methyl-2-phenylpentane [a]	162°	—	—	—	—	—	—	—
2-Methyl-2-phenyloctane [b]	114·5—115·5	64·5	6·9	13·5	$C_{23}H_{30}N_4O_4$	64·8	7·1	13·1
2-Phenyldecane	108	64·6	7·2	13·4	$C_{24}H_{32}N_4O_4$	65·4	7·3	12·7
2-Methyl-2-phenyldecane	98·5—99	65·4	7·6	12·3	$C_{25}H_{34}N_4O_4$	66·0	7·5	12·3
8,8-Dimethyl-1-phenylnonane [c]	155—155·5	65·7	7·3	12·1	,,	,,	,,	,,
2,2,4-Trimethyl-7-phenyloctane	117 [d]	66·5	7·6	12·5	,,	,,	,,	,,
1-Phenyldodecane [f]	128—128·5	66·5	7·9	11·8	$C_{26}H_{36}N_4O_4$	66·6	7·7	11·9
2,2-Dimethyl-1-phenyldecane [g]	117—117·5	67·0	7·8	12·3	,,	,,	,,	,,
2-Methyl-11-phenylundecane [b, g]	107·5—108	66·6	7·5	12·0	,,	,,	,,	,,
2-Phenyldodecane [b, h]	108	66·2	7·7	11·6	,,	,,	,,	,,
4-Methyl-4-phenylundecane [a, g]	109	66·4	7·7	11·6	,,	,,	,,	,,
2,2,4,7-Tetramethyl-7-phenyloctane [a]	112—113 [d]	66·1	7·4	*e*	,,	,,	,,	,,

[a] Prisms; lit.,[17] m. p. 162—163°. [b] Plates. [c] Needles. [d] Mixed m. p. 112—113°. [e] Variable. [f] Orange-red. [g] Red. [h] Orange-yellow.

alkylacetophenone which was converted into the 2,4-dinitrophenylhydrazone by the method of Pines and Shaw [17] but with ethylene dichloride in place of carbon disulphide. The 2,4-dinitrophenylhydrazone was chromatographed in benzene on a 20 × 1 cm. column of 4 : 1 bentonite–kieselguhr before being recrystallised to constant m. p. from ethanol. All the *derivatives* (see Table), except that of 2-methyl-2-phenylpentane, are new. They are orange except as stated. Satisfactory analytical values, particularly for nitrogen, were difficult to obtain in some cases.

Where the derivatives had close m. p.s, mixed m. p.s of any two compounds showed a depression of at least 15° (except as noted in footnote *d*).

The authors are indebted to Mr. J. C. Hawkes, Mr. R. A. Lidgett, and Dr. A. J. Neale for gas-chromatographic and infrared determinations. The Directors of Monsanto Chemicals Limited are thanked for allowing this work to be published.

NICKELL LABORATORIES, MONSANTO CHEMICALS LIMITED,
RUABON, WREXHAM, N. WALES.

[*Received, September 8th,* 1959.]