57. *Alkylation of the Aromatic Nucleus. Part VIII.* Benzylation and Cyclohexylmethylation.*

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When benzyl arenesulphonates decompose in hot aromatic solvents, the benzyl group is introduced into the *ortho*- and the *para*-position of toluene, phenol, anisole, or fluorobenzene. No *meta*-substitution has been detected except with chloro- (2%), bromo-, and iodo-benzene (~9%). By contrast, cyclohexylmethyl toluene-*p*-sulphonate decomposes in toluene to give a product containing ~30% of *meta*-substituted toluene: isomerisation of cyclohexylmethyl group to 1-methylcyclohexyl also occurs. The 2- and 4-methylcyclohexyl esters with toluene give ~15% of *meta*-substituted toluene, and both groups isomerise to 1-methylcyclohexyl.

Földi[1] first reported that the benzyl group could be introduced into aromatic systems by thermal decomposition of benzyl benzenesulphonate in an excess of an aromatic solvent. We have studied benzylation in greater detail, to establish quantitatively the proportion of isomers formed, and to compare these results with those obtained with cyclohexylmethyl and 2- and 4-methylcyclohexyl groups.

The results are summarised in Table 1.

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* Part VII, *J.*, 1962, 870.

[1] Földi, *Ber.*, 1928, **61**, 1609.

TABLE 1.

Isomer distribution (%)

Subst.	PhMe			PhOH			PhOMe			PhF			PhCl			PhBr			PhI		
	o-	*m-*	*p-*	*o-*	*m-*	*p-*	*o-*	*m-*	*p-*	*o-*	*m-*	*p-*	*o-*	*m-*	*p-*	*o-*	*m-*	*p-*	*o-*	*m-*	*p-*
$Ph{\cdot}CH_2$	48	0	52	54	0	46	48	0	52[3]	19	0	81[5]	32	2	60*	36	2	64[6]	34	7	58[7]
$Cl{\cdot}C_6H_4{\cdot}CH_2$	45	2*[1]	53	58	0	42	42	0	58[4]	28	0	72	31	3	66	32	6	62	31	9	60*
$NO_2{\cdot}C_6H_4{\cdot}CH_2$	53	0	47*				59	0	41				51	0	49						
$C_6H_{11}{\cdot}CH_2$	17	31*[2]	52	50	0	50															
$2\text{-}Me{\cdot}C_6H_{10}$	18	16*[2]	66	55	0	45															
$4\text{-}Me{\cdot}C_6H_{10}$	20	14	66*				nd	0	nd												

Estimations are based on gas–liquid chromatography except where marked * which indicates infrared spectroscopy.

[1] Gas–liquid chromatography indicated *o-* 48% and *p-* 52%. [2] Gas–liquid chromatography indicated 5 components. [3–7] Infrared spectroscopy gave: (3) *o-* 50%, *p-* 50%; (4) *o-* 45%, *p-* 55%; (5) *o-* 21%, *p-* 79%; (6) *o-* 36%, *m-* 3%, *p-* 61%; (7) *o-* 36%, *m-* 6%, *p-* 58%. nd = Not determined.

The contrast between the isomer distribution in the benzylation of toluene with that from the introduction of the cyclohexylmethyl group is striking and informative. Although the accuracy of the estimation of the isomer proportions is not as high in the latter case there is no doubt about the relative magnitude of the *meta*-substitution. The only possible conclusion is that the substituting group has a marked influence on the proportion of *o*-, *m*-, and *p*-isomers. This is seen also to a less extent in the methylcyclohexylation of toluene and in the comparison of the products from benzylation and *p*-nitrobenzylation of chlorobenzene. Brown[2] postulated that the reactivity of the entering group has an important effect on the isomer distribution, but a discussion of the implications of this view is deferred to a later paper.

When a cyclohexylmethyl arenesulphonate reacts with an aromatic compound, extensive isomerisation occurs, to give a 1-methylcyclohexyl derivative. With benzene and a suitable sulphonic ester, 90% of the product consists of 1-methyl-1-phenylcyclohexane: its identity was established by infrared comparison with an authentic specimen, and by comparison of 1-*p*-acetylphenyl-1-methylcyclohexane 2,4-dinitrophenylhydrazone with an authentic specimen. Further, after reaction with phenol, 1-*p*-hydroxyphenyl-1-methylcyclohexane was isolated; the absence of both the two unrearranged products was established by noting that they produced new peaks in the gas–liquid chromatogram when added to the reaction product.

It is only in the reaction with mesitylene that there is evidence that the cyclohexylmethyl group reacts without rearrangement: 2,4,6-trimethylbenzylcyclohexane is formed in about 3% yield; it was identified by dehydrogenation to benzylmesitylene. The bulk of the product from this alkylation was a black tar containing about 35% of saturated and olefinic hydrocarbons, probably resulting from the failure of the rearranged methylcyclohexylcarbonium ion to react with mesitylene.

It is notewothy that 2-methylcyclohexyl toluene-*p*-sulphonate and benzene give a product which is the same as that from the cyclohexylmethyl ester; 90% of it is 1-methyl-1-phenylcyclohexane. Phenol similarly gives 1-*p*-hydroxyphenyl-1-methylcyclohexane among other substances. A similar result is obtained on using 4-methylcyclohexyl toluene-*p*-sulphonate. The significance of these rearrangements is discussed in later papers.

EXPERIMENTAL

A Grubb–Parsons double-beam grating spectrometer was used for infrared spectroscopy; quantitative analyses were carried out by the base-line technique[3] with the tabulated bands (μ). For the estimations by gas–liquid chromatography, a Pye argon unit equipped with an ionisation detector was used. The reproducibility was better than 1%, and when some of the results

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[2] Brown and Smoot, *J. Amer. Chem. Soc.*, 1956, **78**, 6255.
[3] Heigl, Bell, and White, *Ind. Eng. Chem., Analyt. Edn.*, 1947, **19**, 293.

were checked independently on other instruments of comparable sensitivity the agreement was good.

CH_2Ph deriv. of	*ortho-*	*meta-*	*para-*	*p*-$C_6H_4Cl{\cdot}CH_2$ deriv. of	*ortho-*	*meta-*	*para-*
Toluene	13·5	12·9	12·7	Toluene	13·5	12·9	11·85
Anisole	13·35	12·85	12·0	Anisole	13·35	12·8	11·9
Phenol	13·35	13·1	11·95	Phenol	13·35	12·9	11·9
Fluorobenzene	13·3	13·1	11·9	Fluorobenzene	13·3	12·8	11·9
Chlorobenzene	13·4	13·0	11·9, 12·7	Chlorobenzene	13·35	13·0	12·7
Bromobenzene	13·4	13·0	11·9, 12·7	Bromobenzene	13·35	13·0	11·8, 12·8
Iodobenzene	13·45	13·0	12·75	Iodobenzene	13·4	13·0	12·8

For the estimation of the isomeric methylcyclohexyltoluene the following bands were used: *ortho-*, 13·35 and 13·85; *meta-*, 12·85 and 14·3; and *para-*, 12·35.

The following general procedure was used for alkylation by thermal decomposition of sulphonates. The ester (~0·15 mole) and the aromatic compound (1·5 moles) were heated together at 125° for 5 hr. Aromatic compounds boiling below 125° were heated with the ester until darkening of the solution set in, and then for 4 hr. more to complete the reaction. The product was diluted with ether and washed successively with water, sodium hydrogen carbonate solution, and water till free from sulphonic acid. The solvent and excess of aromatic compound were removed and the residue was distilled.

Benzylation.—Benzyl toluene-*p*-sulphonate, recrystallised from light petroleum (b. p. 40—60°), had m. p. 58° (lit.,[4] 58°). The impure ester decomposes on storage, but a pure sample may be kept at room temperature over silica gel for at least 2 months. It decomposes at 128°. The results of benzylation are summarised in Table 2.

TABLE 2.

Products of benzylation.

	Yield (%)	B. p./mm.	n_D^{20}	Found (%) C	Found (%) H	Found (%) Hal	Formula	Calc. (%) C	Calc. (%) H	Calc. (%) Hal
PhMe *	79	142—145°/15	1·5713	†						
PhOH	73	176—182°/12	—	‡						
PhOMe	79	168—172°/15	1·5705							
PhF §	58	125—127°/12	1·5551	83·4	6·0	10·3	$C_{13}H_{11}F$	83·8	6·0	10·2
PhCl ¶	58	155—158°/13	1·5859	77·0	5·7	17·0	$C_{13}H_{11}Cl$	77·0	5·5	17·5
PhBr ¶	57	163—167°/14	1·6038	62·8	4·6	32·8	$C_{12}H_{11}Br$	63·1	4·5	32·4
PhI ¶	52	176—183°/12	1·6325	53·2	3·8	43·3	$C_{13}H_{11}I$	53·1	3·8	43·2

* Also present in the product were dibenzyltoluenes (9%), b. p. 237—238°/15 mm., n_D^{20} 1·5999. The purity of the main fraction, determined mass spectrographically, was $\nless$99·5%. † Földi [1] identified the *para*-isomer in this mixture by means of its nitro-derivative. ‡ The product became semisolid and *p*-hydroxydiphenylmethane (m. p. and mixed m. p. 83°) was isolated, after crystallisation from light petroleum (b. p. 40—60°); Földi [1] separated the *ortho-* and the *para*-isomer by crystallisation of the sodium salts. § Reaction mixture heated for 16 hr. ¶ Reaction mixture heated for 10 hr.

4-*Chlorobenzylation.*—4-Chlorobenzyl toluene-*p*-sulphonate, prepared in 84% yield in the same way as the benzyl ester, had m. p. 54° [from light petroleum (b. p. 40—60°)] (Found: C, 56·8; H, 4·4; Cl, 12·1; S, 11·1. Calc. for $C_{14}H_{13}ClO_3S$: C, 56·6; H, 4·4; Cl, 12·0; S, 10·8%) (Fang *et al.*[5] gave m. p. 53—53·5°). The ester is stable at room temperature for several months; it decomposes at 148—150°.

In the 4-chlorobenzylation of all the benzene derivatives examined, only mono-substitution was observed. The yields and physical properties of the products are listed in Table 3.

4-*Nitrobenzylation.*—4-Nitrobenzyl bromobenzene-*p*-sulphonate acid separates from chloroform–ethanol as faint yellow plates, m. p. 145—146° (Found: C, 41·95; H, 2·5; N, 3·6; 21·0; S, 8·4. $C_{13}H_{10}BrNO_5S$ requires C, 41·9; H, 2·7; N, 3·8; Br, 20·5; S, 8·6%). It was prepared in 58% yield by the reaction of 4-nitrobenzyl alcohol and the sulphonyl chloride in ether in presence of potassium hydroxide. It decomposes at 208—210°. It reacted as follows.

(*a*) *With toluene.* After 18 hours' heating, the ester (0·10 mole) gave a slightly yellow oil, b. p. 152—157°/0·3 mm. (Found: C, 73·9; H, 5·7; N, 6·35. Calc. for $C_{14}H_{13}NO_2$: C, 74·0;

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[4] Medwedew and Alexejewa, *Ber.*, 1932, **65**, 131.

[5] Fang, Kochi, and Hammond, *J. Amer. Chem. Soc.*, 1958, **80**, 563.

H, 5·8; N, 6·2%), which became semisolid on cooling. From it, 4-methyl-4′-nitrodiphenylmethane, m. p. and mixed m. p. 76°, was isolated by crystallisation from alcohol.

A more satisfactory separation was achieved by chromatography [Al_2O_3; light petroleum (b. p. 40—60°)]. 2-Methyl-4′-nitrodiphenylmethane was obtained as a yellow oil (5·1 g. from 10 g.). It was identified by hydrogenation to the amine and deamination (diazo-reaction with hypophosphorous acid) to 2-methyldiphenylmethane, b. p. 145—147°/18 mm., n_D^{20} 1·5756, whose infrared spectrum was superimposable on that of authentic 2-methyldiphenylmethane. The more firmly absorbed fractions were removed by benzene to give a solid (4·5 g. from 10 g.), m. p. 73°. The identification was completed by hydrogenation to the amine and deamination to 4-methyldiphenylmethane, identified by its infrared spectrum.

(*b*) *With anisole.* The ester (0·10 mole) and an excess of anisole, heated under reflux for 10 hr., gave a product (76%; b. p. 162—169°/0·2 mm.) which solidified (Found: C, 68·6; H, 5·5; N, 6·0. $C_{14}H_{13}NO_3$ requires C, 69·1; H, 5·4; N, 5·8%). From it, 4-*methoxy*-4′-*nitrodiphenylmethane* was isolated, having m. p. 61° (from methanol) (Found: C, 68·8; H, 5·5; N, 5·7%); it was identified by oxidation by chromic acid in acetic acid to 4-methoxy-4′-nitrobenzophenone, m. p. 124° (2,4-dinitrophenylhydrazone, red needles, m. p. 263°) (Burton and Praill [6] give m. p. 121° for the ketone and m. p. 265° for the 2,4-dinitrophenylhydrazone).

TABLE 3.

Products of 4-chlorobenzylation.

	Yield			Found (%)				Calc. (%)		
	(%)	B. p./mm.	n_D^{20}	C	H	Cl	Formula	C	H	Cl
PhMe	69	173—178°/13	1·5769	77·9	6·2	16·0	$C_{14}H_{13}Cl$	77·6	6·0	16·4
PhOH *	59	208—213°/13		71·2	4·8	16·6	$C_{13}H_{11}ClO$	71·3	5·0	16·3
PhOMe *	65	181—185°/11		71·9	5·7	15·7	$C_{14}H_{13}ClO$	72·2	5·6	15·3
PhF	63	155—156°/10	1·5666	70·6	4·7	16·2 ¶	$C_{13}H_{10}ClF$	70·7	4·6	16·1
PhCl *†	59	180—182°/13		65·8	4·2	30·0	$C_{13}H_{10}Cl_2$	65·8	4·3	29·9
PhBr ‡	55	186—189°/11		55·4	3·8	12·8	$C_{13}H_{10}BrCl$	55·4	3·6	12·6
PhI *§	54	195—200°/5	1·6487	47·6	3·2	10·6	$C_{13}H_{10}ClI$	47·4	3·1	10·8

* Semisolid when cold. † 4,4′-Dichlorodiphenylmethane, m. p. and mixed m. p. 55—56°, was isolated by crystallisation from light petroleum. ‡ 4-Bromo-4′-chlorodiphenylmethane, m. p. and mixed m. p. 52°, was isolated by crystallisation from light petroleum. § 4-Chloro-4′-iododiphenylmethane, m. p. and mixed m. p. 46°, was isolated by crystallisation from light petroleum. ¶ Found: F, 8·4. Calc.: F, 8·6%.

(*c*) *With chlorobenzene.* The ester (0·10 mole) and chlorobenzene (1·0 mole) were heated together under reflux for 12 hr. A slightly yellow oil, b. p. 159—166°/0·2 mm. (73%) (Found: C, 62·8; H, 4·3; N, 5·7; Cl, 14·4. Calc. for $C_{13}H_{10}ClNO_2$: C, 63·0; H, 4·1; Cl, 14·3; N, 5·65%), was obtained, which solidified and on crystallisation from light petroleum (b. p. 40—60°) gave 4-chloro-4′-nitrodiphenylmethane, m. p. 103—104°. This was oxidised as above to 4-chloro-4′-nitrobenzophenone, m. p. 102° [2,4-*dinitrophenylhydrazone*, deep orange plates (from chloroform–ethanol), m. p. 256—258° (Found: N, 16·2. $C_{19}H_{12}ClN_5O_6$ requires N, 15·9%)]. Montagne [7] reports 4-chloro-4′-nitrodiphenylmethane, m. p. 104°, and 4-chloro-4′-nitro-benzophenone, m. p. 100°.

Alkylations by Cyclohexylmethyl Sulphonates.—Cyclohexylmethanol, b. p. 84—85°/14 mm., n_D^{20} 1·4647, was obtained in 81% yield by reduction of cyclohexanecarboxylic acid with lithium aluminium hydride (Gilman and Catlin [8] give b. p. 91°/18 mm., n_D^{20} 1·4644).

Cyclohexylmethyl toluene-p-*sulphonate*, needles, m. p. 33—34° [from light petroleum (b. p. <40°)] (Found: C, 62·8; H, 7·2; S, 11·8. $C_{14}H_{20}O_3S$ requires C, 62·7; H, 7·5; S, 11·9%), was prepared in 79% yield by the addition of potassium hydroxide to 1 mol. each of the alcohol and the sulphonyl chloride in ether. The ester decomposes at 205—208°.

Cyclohexylmethyl p-*bromobenzenesulphonate.* The alcohol (0·20 mole) was added in four equal portions during 40 min. to *p*-bromobenzenesulphonyl chloride (0·20 mole) in pyridine (150 c.c.). After 12 hr. at room temperature, the mixture was poured into 20% hydrochloric acid and ice. The ester was taken up in ether, washed with dilute hydrochloric acid and sodium hydrogen carbonate solution, and dried. It crystallised from light petroleum (b. p.

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[6] Burton and Praill, *J.*, 1951, 529.
[7] Montagne, *Ber.*, 1916, **49**, 2243.
[8] Gilman and Catlin, *Org. Synth.*, Coll. Vol. I, 2nd edn., p. 188.

40—60°) as plates, m. p. 43—44° (73%) (Felkin and Le Ny [9] give m. p. 42·5—43°). The ester decomposes violently at 180°.

Cyclohexylmethyl 2,5-*dichlorobenzenesulphonate*, needles, m. p. 90—91° (Found: C, 48·5; H, 5·2; Cl, 21·7; S, 10·0. $C_{13}H_{16}Cl_2O_3S$ requires C, 48·3; H, 5·0; Cl, 22·0; S, 9·9%), was prepared similarly to the bromobenzene-*p*-sulphonate. It decomposes violently at 165°; it was recovered unchanged after 16 hr. in boiling benzene.

Cyclohexylmethyl m-*nitrobenzenesulphonate*, similarly prepared (49%) in pyridine, crystallises from light petroleum as plates, m. p. 51° (Found: C, 52·3; H, 5·45; N, 4·8; S, 10·9. $C_{13}H_{17}NO_5S$ requires C, 52·2; H, 5·7; N, 4·7; S, 10·7%). It decomposes at 145°.

Reactions of these esters were effected as follows.

(*a*) Cyclohexylmethyl *m*-nitrobenzenesulphonate (0·15 mole) and benzene (2 moles) were heated together under reflux for 60 hr. The product (23%), b. p. 128—130°/22 mm., n_D^{20} 1·5238 (Found: C, 89·3; H, 10·8. Calc. for $C_{13}H_{18}$: C, 89·6; H, 10·4%), was shown by its gas–liquid chromatogram to contain 90% of one component with two others in about equal amount. The infrared spectrum and gas–liquid chromatogram were essentially the same as those of 1-methyl-1-phenylcyclohexane prepared [10] from 1-methylcyclohexanol, benzene, and aluminium chloride. The hydrocarbons from both sources reacted with acetyl chloride and aluminium chloride in carbon disulphide to give the same ketone, characterised by its 2,4-dinitrophenylhydrazone, orange needles, m. p. 181—182° (lit.,[11] 181°) (Found: N, 14·4. Calc. for $C_{21}H_{24}N_4O_4$: N, 14·1%).

(*b*) Cyclohexylmethyl toluene-*p*-sulphonate (0·20 mole) and phenol (2·0 moles) were heated together at 135°. An exothermic reaction set in and the mixture became deep red. Heating was continued for 3 hr. The product, b. p. 157—170°/15 mm., partially solidified (73% yield) (Found: C, 82·0; H, 9·3. Calc. for $C_{13}H_{18}O$: C, 82·1; H, 9·5%). Crystallisation from light petroleum (b. p. 40—60°) gave 1-*p*-hydroxyphenyl-1-methylcyclohexane, m. p. 110—111° (Found: C, 82·2; H, 9·3. Calc. for $C_{13}H_{18}O$: C, 82·1; H, 9·5%) (benzoate, m. p. 80—81°). The identity was established by comparison (infrared and mixed m. p.) with a specimen prepared by the method of Siderova [10] who gives the phenol, m. p. 108° (benzoate, m. p. 80—81°), and as the methyl ether, m. p. 40° (lit.,[12] 40—41°).

According to its gas–liquid chromatogram the reaction mixture is a mixture of six components, presumably isomeric methylcyclohexylphenols; the absence of cyclohexyl-*o*- and -*p*-hydroxyphenylmethane (the expected products of the alkylation if no isomerisation had occurred) was shown by adding both to the reaction mixture and examining this mixture by gas–liquid chromatography: it gave two new peaks.

(*c*) Cyclohexylmethyl toluene-*p*-sulphonate (0·13 mole) was unchanged after 18 hr. in boiling toluene (1·4 moles). On addition of anhydrous toluene-*p*-sulphonic acid (0·10 mole) reaction was complete after a further 9 days' boiling. The product (57%) distilled at 146—149°/26 mm. and had n_D^{20} 1·5251 (Found: C, 89·2; H, 10·4. Calc. for $C_{14}H_{20}$: C, 89·3; H, 10·7%). Its gas–liquid chromatogram indicated five components. The proportions of *o*-, *m*- and *p*-substitution were determined from the infrared spectrum with cyclohexyltolylmethanes and 2′-methylcyclohexyltoluenes as reference compounds.

(*d*) Cyclohexylmethyl *p*-bromobenzenesulphonate (0·14 mole) and *p*-xylene (1·4 moles) were heated together under reflux for 16 hr. The product, b. p. 143—149°/17 mm., n_D^{20} 1·5248 (57%) (Found: C, 88·9; H, 11·1. Calc. for $C_{15}H_{22}$: C, 89·0; H, 11·0%), was identical with that from the reaction of *p*-xylene with 1-methylcyclohexanol or 1-chloro-1-methylcyclohexane and aluminium chloride. The gas–liquid chromatograms were almost identical and showed the presence of four major components. The infrared spectra were also almost identical. Attempts to isolate a derivative of one of the components by acylation in carbon disulphide with aluminium chloride and then conversion into a 2,4-dinitrophenylhydrazone gave a mixture, m. p. 155—160°, which could not be resolved by crystallisation or chromatography. The corresponding derivative from 1-methyl-1-*p*-xylylcyclohexane has m. p. 172—174°; that from the 2-methyl isomer has m. p. 193—194·5°.

(*e*) Cyclohexylmethyl toluene-*p*-sulphonate (0·12 mole) and mesitylene were heated together under reflux for 8 hr. Two main fractions were obtained: (i) b. p. 78—80°/0·5 mm., n_D^{20}

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[9] Felkin and Le Ny, *Bull. Soc. chim. France*, 1957, 1169.

[10] Siderova, *J. Gen. Chem.* (*U.S.S.R.*), 1951, **21**, 869.

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

[12] Buu-Hoï, Lebihon, and Binon, *J. Org. Chem.*, 1951, **16**, 185.

1·4975 (13 g.); and (ii) b. p. 110—116°/0·4 mm., n_D^{20} 1·5200 (0·8 g.). A black intractable tar (15 g.) remained.

Fraction (i) was unsaturated and from its infrared spectrum was not aromatic [Found: C, 87·6; H, 12·3. Calc. for $(C_7H_{12})_x$: C, 87·4; H, 12·6%]. The gas–liquid chromatogram showed the presence of at least five components. Fraction (ii), from its gas–liquid chromatogram, was essentially one compound (85% pure), and its infrared spectrum is similar to that of mesitylcyclohexane (Found: C, 89·2; H, 10·6. Calc. for $C_{16}H_{24}$: C, 88·8; H, 11·2%). It was dehydrogenated (0·4 g.) by selenium (0·1 g.) at 260—270° for 3 days. After filtration through talc and alumina with the help of light petroleum (b. p. 40—60°) and chilling the solution to −30°, crystals, m. p. 33—38°, were deposited; the m. p. was not depressed on admixture with benzylmesitylene. When this alkylation was repeated the yield of crude trimethylbenzylcyclohexane was less than 1%.

*Alkylations by 2-Methylcyclohexyl Toluene-*p*-sulphonate.*—The ester, prepared in pyridine, had m. p. 7—10° (*cis*- and *trans*-2-methylcyclohexyl toluene-*p*-sulphonates [13] each have m. p. 27°).

(*a*) The ester (0·45 mole) and benzene (7 moles), heated under reflux for 18 hr., gave a product, b. p. 47—50°/0·2 mm., n_D^{20} 1·5235 (21%) (Found: C, 89·4; H, 10·4. Calc. for $C_{13}H_{18}$: C, 89·6; H, 10·4%). The gas–liquid chromatogram showed that it consisted of three components, one of which constituted 90% of the product. The infrared spectrum is essentially that of 1-methyl-1-phenylcyclohexane. This was confirmed by the formation of 1-*p*-acetylphenyl-1-methylcyclohexane 2,4-dinitrophenylhydrazone, m. p. and mixed m. p. 180°.

(*b*) A fraction, b. p. 79—81°/0·3 mm., n_D^{20} 1·5228 (57%), was obtained when the ester (0·13 mole) and toluene (1·6 moles) were boiled together for 6 hr. According to vapour-phase chromatography, the product contained four components. An approximate estimate of the isomeric derivatives of toluene was based on the infrared spectrum.

(*c*) The ester (0·15 mole) and *p*-xylene (2·0 moles) were heated together under reflux for 8 hr., to give a fraction, b. p. 141—146°/15 mm., n_D^{20} 1·5250 (53%) (Found: C, 88·7; H, 11·1. Calc. for $C_{15}H_{22}$: C, 89·0; H, 11·0%), whose gas–liquid chromatogram was very similar to that of the product from cyclohexylmethyl *p*-bromobenzenesulphonate and *p*-xylene. No new peaks were obtained by chromatographing a mixture of the two products.

Acetylation of the product in carbon disulphide with aluminium chloride gave a mixture of ketones, the 2,4-dinitrophenylhydrazones of which could not be separated by column chromatography or crystallisation. After several crystallisations, the 2,4-dinitrophenylhydrazone was obtained as orange needles, m. p. 154—158°, not depressed by the same derivative from the product of the alkylation of *p*-xylene with cyclohexylmethyl *p*-bromobenzenesulphonate.

(*d*) 2-Methylcyclohexyl toluene-*p*-sulphonate (0·14 mole) and phenol (2·0 moles) were heated at 120° for 5 hr. The product, b. p. 156—157°/12 mm., became emisolid and from it 1-*p*-hydroxyphenyl-1-methylcyclohexane, m. p. and mixed m. p. 110°, was isolated by crystallisation from light petroleum (b. p. 40—60°); it gave a benzoate, m. p. and mixed m. p. 80°.

*Alkylations by 4-Methylcyclohexyl Toluene-*p*-sulphonate.*—*trans*-4-Methylcyclohexanol and toluene-*p*-sulphonyl chloride in pyridine gave the ester as needles, m. p. 71—72° (67%) (lit.,[14] m. p. 72—73°). The ester decomposes at 145°.

(*a*) The ester (0·13 mole) and toluene (1·6 moles), after 10 hours' refluxing, gave a product b. p. 138—141°/20 mm., n_D^{20} 1·5231 (60%).

(*b*) An excess of anisole and the ester (0·13 mole), heated together for 5 hr., gave a fraction b. p. 149—153°/12 mm., n_D^{20} 1·5269 (66%) (Found: C, 82·5; H, 9·7. Calc. for $C_{14}H_{20}O$: C, 82·3; H, 9·9%). The infrared spectrum indicated the presence only of *ortho*- and *para*-substituted products, although from gas–liquid chromatography four components were present. Demethylation with hydrogen bromide in acetic acid afforded 1-*p*-hydroxyphenyl-1-methylcyclohexane, m. p. and mixed m. p. 108—110°.

*Alkylations by Phenethyl Toluene-*p*-sulphonate.*—The ester was prepared in 83% yield by reaction of phenethyl alcohol with toluene-*p*-sulphonyl chloride in ether in presence of solid potassium hydroxide and had m. p. 40—41° [from light petroleum (b. p. 40—60°)] (lit.,[15] 39—40°). The ester decomposes at 235—240°. It was unchanged after being heated in toluene for 48 hr.; most of it was recovered unchanged when heating was continued for 5 days after

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[13] Vavon, Perlin, and Horeau, *Bull. Soc. chim. France*, 1932, **51**, 644.
[14] Kenyon, Gough, and Hunter, *J.*, 1926, 2052.
[15] Klamaan, *Monatsh.*, 1953, **84**, 54.

addition of 0·12 mole of anhydrous toluene-*p*-sulphonic acid to 0·16 mole of ester in 2·7 moles of toluene.

(*a*) The ester (0·15 mole) and mesitylene were heated together under reflux for 48 hr. The product, b. p. 174—176°/12 mm., n_D^{20} 1·5586 (76%), solidified and crystallisation from methanol gave phenethylmesitylene as needles, m. p. and mixed m. p. 39° (Found: C, 90·9; H, 9·0. Calc. for $C_{17}H_{20}$: C, 91·0; H, 9·0%). The infrared spectrum of the total alkylation product was identical with that of the pure material. A specimen prepared as described by Fuson *et al.*[16] had m. p. 39°.

(*b*) Phenethyl toluene-*p*-sulphonate (0·15 mole) and phenol (2·1 mole) were heated together for 12 hr. The product, b. p. 183—189°/11 mm. (73%), solidified (Found: C, 85·0; H, 7·0. Calc. for $C_{14}H_{14}O$: C, 84·8; H, 7·1%). It was a mixture which was separated, not very satisfactorily, by treatment with 10% aqueous sodium hydroxide. The sodium salt of *p*-phenethylphenol separated, and from it the phenol was obtained, having m. p. and mixed m. p. 102° (Stoermer and Kippe [17] give m. p. 99°). From the alkali-soluble fractions *o*-phenethylphenol was isolated, as leaflets [from light petroleum (b. p. 80—100°)], m. p. and mixed m. p. 83—84° (Ruggli and Staub [18] give m. p. 85°) [*benzoate*, m. p. 33° (Found: C, 83·4; H, 6·0. $C_{21}H_{18}O_2$ requires C, 83·4; H, 6·0%)]. Separation was also achieved by fractional crystallisation of the benzoates; the benzoate of the *para*-isomer, crystallised from methanol, had m. p. 101·5—102° (lit.,[17] 99°); from the mother-liquors the *ortho*-isomer was obtained.

Preparation of Reference Compounds.—Reference samples, for infrared analysis and gas-liquid chromatography, required for benzylation and 4-chlorobenzylation have been described by Blackwell and Hickinbottom.[19] Others that were required are listed below, with brief indications of the methods of preparation.

α-*Cyclohexyl-2-methoxybenzyl alcohol*, b. p. 112—116°/0·2 mm., n_D^{20} 1·5406 (Found: C, 76·0; H, 9·4. $C_{14}H_{20}O_2$ requires C, 76·3; H, 9·2%), was obtained *o*-methoxybenzaldehyde and cyclohexylmagnesium bromide; it gave a 3,5-*dinitrobenzoate*, slightly yellow flat crystals, m. p. 133° (Found: C, 61·0; H, 5·7; N, 7·1. $C_{21}H_{22}N_2O_7$ requires C, 60·9; H, 5·4; N, 6·8%). It was reduced by lithium aluminium hydride and aluminium chloride [19] in ether to *cyclohexyl*-o-*methoxyphenylmethane*, b. p. 159—161°/24 mm., n_D^{20} 1·5282 (Found: C, 82·5; H, 9·9. $C_{14}H_{20}O$ requires C, 82·3; H, 9·9%), whence hydrogen bromide in acetic acid afforded o-*cyclohexylmethylphenol*, m. p. 66—67° [from light petroleum (b. p. 40—60°)] (Found: C, 82·0; H, 9·5. $C_{13}H_{18}O$ requires C, 82·1; H, 9·5%) {*phenylurethane*, m. p. 97—98° [from light petroleum (b. p. 60—80°)] (Found: 77·8; H, 7·5; N, 4·5. $C_{20}H_{23}NO_2$ requires C, 77·6; H, 7·5; N, 4·5%)}. A chloroform solution of the phenol with nitric acid (*d* 1·42) at room temperature gave a *dinitro-compound*, pale yellow needles [from light petroleum (b. p. 40°)] or bright orange needles (from water), m. p. 79° (Found: C, 55·7; H, 5·6; N, 9·6. $C_{13}H_{16}N_2O_5$ requires, C, 55·7; H, 5·8; N, 10·0%).

α-Cyclohexyl-4-methoxybenzyl alcohol, m. p. 89—90° (lit.,[20] 89°) was reduced to *cyclohexyl*-p-*methoxyphenylmethane*, b. p. 109°/0·4 mm., n_D^{20} 1·5241 (Found: C, 82·5; H, 10·0. $C_{14}H_{20}O$ requires C, 82·3; H, 9·9%), which gave p-*cyclohexylmethylphenol*, m. p. 84—85° (Found: C, 82·0; H, 9·6. $C_{13}H_{18}O$ requires C, 82·1; H, 9·5%) [*benzoate* (from acetone), needles m. p. 94—95° (Found: C, 81·5; H, 7·5. $C_{20}H_{22}O_2$ requires C, 81·6; H, 7·5%)].

Cyclohexyl o-*tolyl ketone*, b. p. 112—114°/0·2 mm., n_D^{20} 1·5338 (Found: C, 83·1; H, 9·0. $C_{14}H_{18}O$ requires C, 83·1; H, 9·0%), was obtained (72%) by reaction of cyclohexanecarbonyl chloride [21] with di-*o*-tolylcadmium in benzene and gave a 2,4-*dinitrophenylhydrazone*, pale yellow prisms, m. p. 103—104° (Found: N, 14·7. $C_{20}H_{22}N_4O_4$ requires N, 14·7%). Reduction of the ketone with lithium aluminium hydride and aluminium chloride in ether [19] gave *cyclohexyl*-o-*tolylmethane*, b. p. 135°/14 mm., n_D^{20} 1·5237 (86%) (Found: C, 89·4; H, 10·7. $C_{14}H_{20}$ requires C, 89·3; H, 10·7%).

Cyclohexyl-m-*tolylmethane*, b. p. 134—135°/14 mm., n_D^{20} 1·5206 (85%) (Found: C, 89·0; H, 10·8%), was similarly prepared from *cyclohexyl* m-*tolyl ketone*, b. p. 141—144°/20 mm., n_D^{20} 1·5386 (Found: C, 83·1; H, 9·0%) [2,4-*dinitrophenylhydrazone*, yellow needles (from ethanol), m. p. 129—130° (Found: N, 14·8. $C_{20}H_{22}N_4O_4$ requires N, 14·7%)].

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[16] Fuson, Denton, and Best, *J. Org. Chem.*, 1943, **8**, 64.
[17] Stoermer and Kippe, *Ber.*, 1903, **36**, 4009.
[18] Ruggli and Staub, *Helv. Chim. Acta*, 1937, **20**, 37.
[19] Blackwell and Hickinbottom, *J.*, 1961, 1405.
[20] Elphimoff-Felkin and Tschoubar, *Compt. rend.*, 1951, **233**, 799.
[21] Lumsden, *J.*, 1905, **87**, 90.

Cyclohexyl-p-*tolylmethane*, b. p. 135°/15 mm., n_D^{20} 1·5108 (87%) (Found: C, 89·0; H, 10·8%), was obtained from cyclohexyl *p*-tolyl ketone, m. p. 68—89° (2,4-dinitrophenylhydrazone, m. p. 166·5°).

For 2-methylcyclohexyl derivatives the general method consisted in reaction of an arylmagnesium bromide with 2-methylcyclohexanone and dehydration of the resulting alcohol by boiling 15% aqueous oxalic acid for several hours. The olefin formed was hydrogenated in ethanol over palladium–charcoal at 3 atm. Thus were obtained:

o-, b. p. 123—125°/11 mm., n_D^{20} 1·5306 (Found: C, 90·4; H, 9·7. $C_{14}H_{18}$ requires C, 90·3; H, 9·7%), m-, b. p. 139—141°/16 mm., n_D^{20} 1·5442 (Found: C, 90·5; H, 9·6%), and p-2-*methylcyclohexenyltoluene*, b. p. 139—141°/13 mm., n_D^{20} 1·5450 (Found: C, 90·3; H, 9·5%).

o-(Hydrogenation at 50°), b. p. 127—128°/15 mm., n_D^{20} 1·5296 (Found: C, 89·5; H, 10·4. $C_{14}H_{20}$ requires C, 89·3; H, 10·7%), m-, b. p. 132—133°/14 mm., n_D^{20} 1·5248 (Found: C, 89·5; H, 10·6%), and p-2-*methylcyclohexyltoluene*, b. p. 135°/14 mm., n_D^{20} 1·5259 (Found: C, 89·5; H, 10·6%).

2-*Methyl*-1-p-*xylylcyclohexanol*, b. p. 105—108°/0·2 mm., n_D^{20} 1·5343 (Found: C, 82·2; H, 10·2. $C_{15}H_{22}O$ requires C, 82·5; H, 10·2%).

2-2′-*Methylcyclohexenyl*-p-*xylene*, b. p. 86—90°/0·2 mm., n_D^{20} 1·5316 (Found: C, 89·5; H, 10·4. $C_{15}H_{20}$ requires C, 89·9; H, 10·1%).

1-*Methyl*-2-p-*xylylcyclohexane*, b. p. 82—86°/0·2 mm., n_D^{20} 1·5251 (Found: C, 89·1; H, 11·1. $C_{15}H_{22}$ requires C, 89·0; H, 11·0%). With nitric and sulphuric acids at 60° this gives a *dinitro-compound*, slightly yellow plates, m. p. 139—140° (Found: C, 61·5; H, 6·8; N, 9·6. $C_{15}H_{20}N_2O_4$ requires C, 61·6; H, 6·9; N, 9·6%). Treatment in carbon disulphide with acetyl chloride and aluminium chloride gave a ketone characterised by its 2,4-*dinitrophenylhydrazone*, red needles, m. p. 193—195° (Found: C, 64·8; H, 6·6; N, 13·1. $C_{23}H_{28}N_4O_4$ requires C, 65·1; H, 6·65; N, 13·2%).

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