815. *Alkylation of the Aromatic Nucleus. Part I. The Introduction of* sec.*-Alkyl and* cyclo*Hexyl Groups by Reaction with Esters of Toluene-*p*-sulphonic Acid.*

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The *cyclo*hexyl group has been introduced smoothly into the aromatic nucleus of toluene, *m*- and *p*-xylene, mesitylene, naphthalene, phenol, and anisole by heating the aromatic compound with *cyclo*hexyl toluene-*p*-sulphonate. *iso*Propyl and *sec.*-butyl sulphonates react similarly.

FÖLDI [1] reported that benzyl benzenesulphonate decomposed in hot benzene to diphenylmethane and benzenesulphonic acid; a similar substitution took place with toluene, phenol, anisole, or methyl salicylate. This behaviour of the benzyl sulphonate has since been confirmed and has been the subject of kinetic studies.[2,3]

It is shown in this paper that the reaction has a wider application and that it can be used for the introduction of *sec.*-alkyl and *cyclo*hexyl groups into the nucleus of aromatic hydrocarbons, phenols, and phenol ethers.[4] Since completion of this work,[5] alkylation of benzene by means of alkyl benzenesulphonates has been described by Nenitzescu, Ioan, and Teodorescu,[6] who added benzenesulphonic acid to assist the reaction. The experimental conditions we use for bringing about this reaction are simpler: the sulphonic ester, dissolved in a moderate excess of the appropriate aromatic compound, is heated at about

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[1] Földi, *Ber.*, 1928, **61**, 1609.
[2] Ogata, Yonetani, and Oda, *Bull. Inst. Phys. Chem. Res. Tokyo*, 1943, **22**, 583.
[3] Nenitzescu, Auram, and Sliam, *Bull. Soc. chim. France*, 1955, 1266.
[4] Hickinbottom, Rogers, and Rule, *Chem. and Ind.*, 1955, 539.
[5] Cf. Rogers, Ph.D. Thesis, London, 1956.
[6] Nenitzescu, Ioan, and Teodorescu, *Chem. Ber.*, 1957, **90**, 585.

120°; when reaction is complete, the free sulphonic acid is neutralised by aqueous alkali, and the neutral layer distilled. Our results are summarised in Table 1.

*cyclo*Hexyl toluene-*p*-sulphonate also reacts with chloro-, bromo-, and iodo-benzene but the yield of substitution product is only about 10%: the main reaction is thermal decomposition to sulphonic acid and polymers of *cyclo*hexene. No substitution occurs with nitrobenzene, methyl benzoate, or benzonitrile; decomposition of the ester is the only observed reaction. The precise identification of the isomers formed in each alkylation and an estimate of their relative abundance are essential to our investigation of the nature of this alkylation. From a comparison of the infrared spectrum of the product of the reaction with that of each of the possible isomers, accurate estimates have been made of the direction of substitution in each case, and it is evident from Table 1 that the reaction has the general characteristics of an electrophilic substitution.

TABLE 1.

Aromatic compound	Toluene-*p*-sulphonic ester	Products & yield (%)
Toluene	*cyclo*Hexyl	*cyclo*Hexyltoluenes, 57 (*o*-, 32%; *m*-, 21%; *p*-, 47%
m-Xylene	*cyclo*Hexyl	*cyclo*Hexyl-*m*-xylenes, 63 (4-*cyclo*hexyl, 93%; 5-, 7%; 2-, trace); di*cyclo*hexyl-*m*-xylenes
	Bu^s	4-*sec*.-Butyl-*m*-xylene, 46
p-Xylene	*cyclo*Hexyl	2-*cyclo*Hexyl-*p*-xylene, 67; 2 : 5-di*cyclo*hexyl-*p*-xylene
	Bu^s	2-*sec*.-Butyl-*p*-xylene, 45
Mesitylene	*cyclo*Hexyl	2-*cyclo*Hexylmesitylene, 74
	Bu^s	2-*sec*.-Butylmesitylene, 55
Naphthalene	Bu^s	*sec*.-Butylnaphthalenes, 41 (α-, 88%; β, 12%)
	Pr^i	1-*iso*Propylnaphthalene, 29
Phenol	*cyclo*Hexyl	*cyclo*Hexylphenols, 55 (*o*-, 48%; *p*-, 52%)
Anisole	*cyclo*Hexyl	*cyclo*Hexylanisoles, 61 (*o*-, 51·5%; *p*-, 48·5%)
	Bu^s	*sec*.-Butylanisoles, 40 (*o*-, 61%; *p*-, 39%)
	Pr^i	*iso*Propylanisoles, 40 (*o*-, 57%; *m*-, 6%; *p*-, 37%)

The high proportion of *meta*-substitution in toluene appears at first sight to offer a serious objection to the unqualified acceptance of this view; indeed it suggests a free-radical substitution rather than an electrophilic one. There are, however, a number of observations on the formation of a high proportion of *meta*-isomer in the alkylation of toluene by olefins, alcohols, or alkyl halides under the influence of condensing agents such as hydrogen fluoride, sulphuric acid, boron trifluoride, or halides of aluminium, iron, or gallium;[7] while the isomerising action of the condensing agent makes many of these observations of little worth for our argument, there are some to which this objection cannot be applied. Among these are the *iso*propylation of toluene by propene and aluminium chloride in a mixture of benzene and nitrobenzene or by use of boron trifluoride, and the alkylation of toluene with alkyl bromides and gallium bromide. In these substitutions about 27% of *meta*-isomer is obtained in *iso*propylation; a somewhat lower proportion (20%) for ethylation and a higher (32%) for the introduction of the *tert*.-butyl group.[7] It is fairly generally accepted that these alkylations are electrophilic and take place either by way of a kinetically free carbonium ion or by a heterolytic displacement. The similarity between the distribution of isomers in these alkylations and in the reaction between toluene and *cyclo*hexyl toluene-*p*-sulphonate is sufficiently striking to suggest a common type of substitution for all of them.

If this argument is valid, there are two probable routes for the alkylation by esters of sulphonic acids: (*a*) thermal breakdown to olefin and sulphonic acid which, acting together, can alkylate the aromatic nucleus:

$$\mathrm{C_6H_{11}{\cdot}O{\cdot}SO_2{\cdot}C_6H_4Me} \longrightarrow \mathrm{C_6H_{10}} + \mathrm{HO{\cdot}SO_2{\cdot}C_6H_4Me} \xrightarrow{\mathrm{ArH}} \mathrm{C_6H_{11}{\cdot}Ar} + \mathrm{HO{\cdot}SO_2{\cdot}C_6H_4Me}$$

or (*b*) by proton catalysis with the formation of a kinetically free carbonium ion (scheme i)

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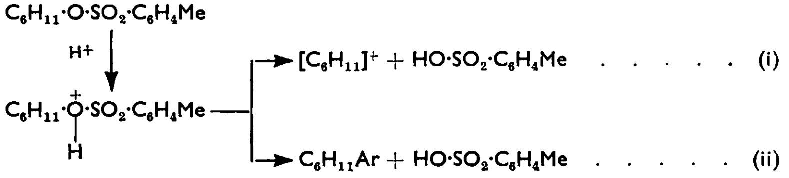
[7] Condon, *J. Amer. Chem. Soc.*, 1949, **71**, 3544; Schlatter, *ibid.*, 1953, **75**, 361; Brown and Nelson, *ibid.*, p. 6292; Brown and Smart, *ibid.*, 1956, **78**, 6255.

or a heterolytic bimolecular reaction between the ester and the aromatic hydrocarbon (cf. Nenitzescu *et al.*[3]):



A review of the experimental evidence excludes direct ionisation of the sulphonic ester as a serious factor in determining the course of the reaction.

There are several reasons for not accepting scheme (*a*) as representing the main course of the alkylation. The most cogent is that the benzyl esters react in the same way as *cyclo*hexyl and alkyl esters and the characteristics of the reactions are the same. It is clear that benzyl cannot effect substitution by mechanism (*a*) and it is a reasonable assumption that alkyl and *cyclo*hexyl also react by the same mechanism.

It has been established by Nenitzescu *et al.*[3] that the reaction of benzyl esters with the aromatic nucleus is autocatalytic and proton-catalysed. Our observations, although qualitative, agree that these conclusions apply to the alkyl esters and no alkylation occurs when proton-catalysis is excluded by using a weak base such as dimethylformamide as solvent. The retarding effect of diethyl ether [2] on the benzylation of benzene is no doubt attributable to the basic properties of the ether.

Formation of olefins during alkylations with *sec.*-butyl, *iso*propyl, and *iso*butyl esters of sulphonic acids has been established. This is best explained by deriving them from the carbonium ion, although it is not impossible that some may be obtained by thermal decomposition, especially during the earlier stages of the reaction.

EXPERIMENTAL

Introduction of cyclo*Hexyl into the Benzene Nucleus.*—(a) *Formation of* cyclo*hexylmesitylene.* Freshly distilled mesitylene (144 g., 1·2 moles) and *cyclo*hexyl toluene-*p*-sulphonate (102 g., 0·4 mole) were heated with stirring under reflux at 120°. Reaction set in after about ½ hr. and there was a slight evolution of heat and darkening. Heating was continued for 5 hr. On cooling, toluene-*p*-sulphonic acid separated as brownish crystals (benzylthiuronium salt, m. p. 182°); no sulphinic acid was detected. The acid was neutralised by an excess of aqueous alkali, and the hydrocarbon layer separated with the help of ether, dried, and distilled, to give mesitylene and *cyclo*hexylmesitylene, b. p. 160—164°/23 mm., n_D^{20} 1·5301 (59·5 g.). Reaction at 130° gave about 50% of *cyclo*hexylmesitylene and some di*cyclo*hexylmesitylene.

*cyclo*Hexylmesitylene, redistilled over sodium, boils at 156°/19 mm. and has n_D^{20} 1·5302 (Found: C, 88·9; H, 11·1. Calc. for $C_{15}H_{22}$: C, 89·0; H, 11·0%) (Bodroux [8] gives n_D^{9} 1·535). In concentrated sulphuric and fuming nitric acid at 30—40° it gives a pale yellow *dinitro-compound*, m. p. 170·5° (Found: C, 61·6; H, 6·9; N, 9·6. $C_{15}H_{20}O_4N_2$ requires C, 61·6; H, 7·1; N, 9·8%).

*Di*cyclo*hexylmesitylene*, b. p. 130°/0·1 mm., forms needles, m. p. 103—104°, from light petroleum [Found: C, 88·3; H, 11·4%; *M*, 270 (Rast). $C_{21}H_{32}$ requires C, 88·7; H, 11·3%; *M*, 284].

(b) *Formation of* cyclo*hexyltoluenes.* *cyclo*Hexyl toluene-*p*-sulphonate (127 g.) and toluene (280 g.), heated at 120° for 5 hr., gave *cyclo*hexyltoluenes, b. p. 120—129°/20 mm., n_D^{20} 1·5256 (42·2 g.), and di*cyclo*hexyltoluenes, b. p. 154—158°/1 mm., n_D^{20} 1·5366 (15·1 g.). Each fraction was distilled over sodium for analysis: *cyclo*hexyltoluene (Found: C, 89·7; H, 10·3. Calc. for $C_{13}H_{18}$: C, 89·6; H, 10·4%); di*cyclo*hexyltoluene (Found: C, 89·2; H, 10·9. Calc. for $C_{19}H_{28}$: C, 89·0; H, 11·0%).

For estimation of the ratio of the isomers, *o*-, *m*-, and *p*-*cyclo*hexyltoluene were prepared by

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[8] Bodroux, *Ann. Chim.* (*France*), 1929, **11**, 511.

hydrogenation of the corresponding *cyclo*hexenyltoluenes at 3—4 atm. over Raney nickel W4 in alcohol.

The *cyclo*hexenyltoluenes were prepared by dehydration of the tertiary alcohol from the reaction of *cyclo*hexanone with the appropriate tolylmagnesium bromide. Dehydration of the alcohols was accomplished cleanly and conveniently by refluxing them for several hours with acetic anhydride. Table 2 summarises the constants of the isomeric 1-*cyclo*hexenyltoluenes and of the *cyclo*hexyltoluenes.

TABLE 2.

	*cyclo*Hexenyltoluenes				*cyclo*Hexyltoluenes			
			Found (%)				Found (%)	
	B. p.	n_D (temp.)	C	H	B. p.	n_D (temp.)	C	H
ortho ...	108—109°/8 mm.	1·5453 (20°)	90·5	9·2	111°/10 mm.	1·5321 (18°)	89·7	10·2
meta ...	134°/13 mm.	1·5635 (17°)	90·7	9·4	122°/13 mm.	1·5239 (20°)	89·9	10·6
para ...	126°/9 mm.	1·5653 (16·5°)	90·3	9·4	114°/9 mm.	1·5243 (17°)	89·5	10·5

Infrared spectra gave the isomer ratios of Table 1 with an accuracy of ±1%.

(c) *Formation of* cyclo*hexyl*-m-*xyene.* *m*-Xylene (200 g.) and *cyclo*hex toluene-*p*-sulphonate (101·6 g.), heated at 120° for 5 hr., gave *cyclo*hexyl-*m*-xylenes, b. p. 131—137°/16 mm., n_D^{20} 1·5262—1·5261 (47·0 g.). Redistillation gave a pure sample, b. p. 136°/18 mm., n_D^{20} 1·5262 (Found: C, 89·5; H, 10·4. Calc. for $C_{14}H_{20}$: C, 89·3; H, 10·7%). A comparison of the infrared spectrum with those from pure specimens of 4- and 5-*cyclo*hexyl-*m*-xylenes showed that the product consisted of 4-*cyclo*hexyl-*m*-xylene with about 7% of the 5-isomer; there were indications of the presence of the 2-isomer, but in very small amount.

From the residues of the distillation of the *cyclo*hexyl-*m*-xylenes from the alkylation, 4 : 6-di-cyclo*hexyl*-m-*xylene* was obtained crystalline; it formed colourless needles, m. p. 108—108·5°, from alcohol (Found : C, 88·8; H, 11·3. $C_{20}H_{30}$ requires C, 88·8; H, 11·2%).

4-cyclo*Hexyl*-m-*xylene* was prepared in 12% yield by reaction of 2 : 4-dimethylphenylmagnesium bromide with *cyclo*hexyl toluene-*p*-sulphonate (*cyclo*hexene and *p*-xylene were also formed), and had b. p. 145—146°/20 mm., n_D^{20} 1·5263 (Found: C, 89·3; H, 10·8%).

5-*cyclo*Hexyl-*m*-xylene had b. p. 126°/8 mm., n_D^{18} 1·5243 (Found: C, 89·3; H, 10·5%), and gave a trinitro-compound, m. p. 117—118° (Battegay and Keppeler [9] give b. p. 142—143°/17 mm., trinitro-compound, m. p. 117—118°). This hydrocarbon was prepared by hydrogenation (Raney nickel W4; alcohol; 3—4 atm.) of 5-*cyclo*hex-1′-enyl-*m*-xylene, b. p. 139°/12 mm., n_D^{18} 1·5530 (Found: C, 90·4; H, 9·7. Calc. for $C_{14}H_{18}$: C, 90·3; H, 9·7%) (Hey and Jackson [10] give b. p. 157—158°/20 mm.).

For comparison, the product of the reaction of *cyclo*hexene with *m*-xylene and aluminium chloride was examined; it had b. p. 128°/11 mm., n_D^{20} 1·5238 (Found: C, 89·3; H, 10·6%). From its infrared spectrum it was estimated to consist of 94% of 5-*cyclo*hexyl-*m*-xylene with 4% of the 4-isomer. That it consisted mainly of 5-*cyclo*hexyl-*m*-xylene was confirmed by the preparation of the trinitro-compound, m. p. and mixed m. p. 117—118°.

(d) *Formation of* 2-cyclo*hexyl*-p-*xylene.* *p*-Xylene (250 g.) and *cyclo*hexyl toluene-*p*-sulphonate (127 g.), heated together for 5 hr., gave 2-*cyclo*hexyl-*p*-xylene (63·2 g.), b. p. 135°/12 mm., n_D^{20} 1·5270 (Found: C, 89·5; H, 10·8%). Bodroux [8] gives b. p. 261°, n_D^{18} 1·529.

2 : 5-Di*cyclo*hexyl-*p*-xylene (9·6 g.) was left after the mono*cyclo*hexyl compound had been distilled off. It crystallised from alcohol, and had m. p. 156—157° (Found: C, 88·5; H, 11·0%). When it was refluxed with palladised charcoal for 36 hr. 2 : 5-dimethyl-*p*-terphenyl, m. p. 180—182°, was formed (Deuschel [11] gives m. p. 182—184°).

(e) *Formation of* o- *and* p-cyclo*hexylphenols.* Phenol (235 g.) and *cyclo*hexyl toluene-*p*-sulphonate (127 g.) were heated at 120° for 5 hr. The product was treated with aqueous sodium hydrogen carbonate solution, and the phenols were taken up in ether and distilled to remove excess of phenol. The residue, consisting essentially of *cyclo*hexylphenols, was separated into *o*- and *p*-isomers by taking advantage of the sparing solubility of the sodium salt of the *para*-isomer in an excess of 10% aqueous sodium hydroxide. The yield of crude *p*-*cyclo*hexylphenol liberated from the sodium salt was 25 g. (m. p. 123—127°); purified by

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[9] Battegay and Keppeler, *Bull. Soc. chim. France*, 1924, **35**, 989.

[10] Hey and Jackson, *J.*, 1934, 645.

[11] Deuschel, *Helv. Chim. Acta*, 1951, **34**, 2403.

recrystallisation from toluene and light petroleum (b. p. <40°) it had m. p. 131° (Bodroux [8] gives m. p. 131°) [benzoate, m. p. 117—118° (Lefebvre and Levas [12] give m. p. 118—119°)].

The *ortho*-isomer (22·9 g.), b. p. 136—138°/11 mm., m. p. 50—52°, liberated from the aqueous alkaline solution was recrystallised from light petroleum (b. p. <40°) and had m. p. 55—56° (Bodroux [8] gives m. p. 56—57°) [dinitro-derivative, m. p. 106° (Baroni and Kleinau [13] give m. p. 106°)].

(f) *Formation of* cyclo*hexylanisoles.* Heating anisole (216 g.) with *cyclo*hexyl toluene-*p*-sulphonate (127 g.) for 5 hr. gave a mixture of *cyclo*hexylanisoles, b. p. 140—146°/17 mm., n_D^{20} 1·5328 (Found: C, 82·0; H, 9·6. Calc. for $C_{13}H_{18}O$: C, 82·1; H, 9·5%). Comparison of the infrared spectra gave the isomeric ratios of Table 1.

Chilling the reaction product caused *p-cyclo*hexylanisole to separate, having m. p. 57—57·5° after recrystallisation from aqueous alcohol (Bodroux [8] gives m. p. 57—58°). This gave *p-cyclo*hexylphenol, m. p. and mixed m. p. 131°, when heated with hydrobromic-acetic acid.

Direct isolation of pure *o-cyclo*hexylanisole could not be conveniently accomplished by distillation: the reaction product, freed as far as possible from the *para*-isomer, was heated with hydrobromic acid in acetic acid. *o-cyclo*Hexylphenol, isolated as described above, had m. p. and mixed m. p. 50—52°.

Treatment of the *o-cyclo*hexylphenol in alkaline solution with dimethyl sulphate gave *o-cyclo*hexylanisole, b. p. 127°/10 mm., m. p. 27—28°, n_D^{20} 1·5352 (supercooled) (Bodroux [8] gives b. p. 267—268·5°, n_D^{18} 1·5365).

*m-cyclo*Hexylanisole, b. p. 135°/9 mm., n_D^{18} 1·5325 (Musser and Adkins [14] give b. p. 105—106°/1 mm., n_D^{25} 1·5175) (Found: C, 82·1; H, 9·4%), was obtained by hydrogenation (Raney nickel W4, alcohol, 3—4 atm.) of 3-*cyclo*hex-1′-enylanisole, b. p. 149—150°/10 mm., $n_D^{16\cdot5}$ 1·5702 (Found: C, 83·2; H, 8·5. Calc. for $C_{13}H_{16}O$: C, 82·9; H, 8·6%). The latter compound was obtained by refluxing the product of the reaction of *cyclo*hexanone and *m*-methoxyphenylmagnesium bromide with acetic anhydride.

(g) *Formation of chlorophenyl*cyclo*hexane.* From chlorobenzene (280 g.) and *cyclo*hexyl toluene-*p*-sulphonate (127 g.), heated at 120° for 5 hr., there were obtained a fraction (A), b. p. 125—145°/25 mm., n_D^{20} 1·5350 (8·0 g.), and a dark residue of polymers of *cyclo*hexene (30 g.). A pure compound was not obtained from (A) but it was shown that it consisted essentially of *p*-chlorophenyl*cyclo*hexane (Found: Cl, 18·6. Calc. for $C_{12}H_{15}Cl$: Cl, 18·3%) by oxidation to *p*-chlorobenzoic acid, m. p. and mixed m. p. 240—241°, with dichromate and diluted sulphuric acid.

(h) *Formation of bromophenyl*cyclo*hexane.* Bromobenzene (250 g.) and *cyclo*hexyl toluene-*p*-sulphonate (101·6 g.), heated at 120° for 5 hr., gave a product which was mainly polymerised *cyclo*hexene (30 g.). There was a fraction (10 g.), b. p. 158—170°/20 mm., n_D^{20} 1·5555—1·5550, which contained a high proportion of *p*-bromophenyl*cyclo*hexane (Found: Br, 26·5. Calc. for $C_{12}H_{15}Br$: Br, 33·4%). No pure compound was isolated from this fraction but the presence of *p*-bromophenyl*cyclo*hexane was shown by converting it, through its Grignard compound, into *p-cyclo*hexylbenzoic acid, m. p. and mixed m. p. 198° (Mayes and Turner [15] give m. p. 199°).

A portion of the fraction oxidised by dichromate and dilute sulphuric acid gave *p*-bromobenzoic acid, m. p. and mixed m. p. 250—252°.

(i) *Formation of iodophenyl*cyclo*hexane.* Iodobenzene (250 g.) and *cyclo*hexyl toluene-*p*-sulphonate (63 g.), heated at 120° for 5 hr., gave a fraction, b. p. 112—114°/0·8 mm., n_D^{20} 1·5770 (11·2 g.), which contained a high proportion of *p*-iodophenyl*cyclo*hexane (Found: I, 40·6. Calc. for $C_{12}H_{15}I$: I, 44·4%). It was oxidised to *p*-iodobenzoic acid, m. p. and mixed m. p. 267—270°: by the Grignard reaction *p-cyclo*hexylbenzoic acid, m. p. and mixed m. p. 196°, was obtained.

Introduction of sec.-*Butyl into the Aromatic Nucleus.*—*sec.*-Butyl toluene-*p*-sulphonate was obtained as a reddish oil from the reaction of *sec.*-butyl alcohol with toluene-*p*-sulphonyl chloride in pyridine under the conditions described elsewhere for the *cyclo*hexyl ester.[16] It distilled, in small quantities, without decomposition, but in the quantities required, distillation at 10^{-2} mm.

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[12] Lefebvre and Levas, *Compt. rend.*, 1945, **220**, 782.
[13] Baroni and Kleinau, *Monatsh.*, 1936, **68**, 251.
[14] Musser and Adkins, *J. Amer. Chem. Soc.*, 1938, **60**, 664.
[15] Mayes and Turner, *J.*, 1929, 50.
[16] Hickinbottom and Rogers, *J.*, 1957, following note.

gave rise to considerable decomposition; for the experiments described below it was freed from excess of solvent and unchanged alcohol by drawing a stream of air through it at 0·1 mm., and then had n_{D}^{20} 1·5028 (Kenyon *et al.*[17] give n_{D}^{13} 1·5080).

The reaction between this ester and the aromatic compound was carried out essentially as described for *cyclo*hexylmesitylene. In all these alkylations an unsaturated gas, b. p. ~ 0°, was evolved and condensed in a cold trap. It was not further characterised, but from its method of formation and its approximate b. p. it was assumed to be but-2-ene.

Reactions of sec.*-Butyl Toluene-*p*-sulphonate.*—(a) *With mesitylene.* The sulphonic ester (45·6 g.) and mesitylene (120 g.) at 125°, in 5 hr., gave sec.*-butylmesitylene*, b. p. 102—103°/10 mm., n_{D}^{20} 1·5078 (19·8 g.) (Found: C, 88·7; H, 11·3. $C_{13}H_{20}$ requires C, 88·6; H, 11·4%).

(b) *With* p*-xylene.* From *p*-xylene (265 g.) and *sec.*-butyl toluene-*p*-sulphonate (114 g.) at 125° in 5 hr., sec.*-butyl-*p*-xylene* was obtained (36·7 g.), having b. p. 81—81·5°/8 mm., n_{D}^{20} 1·4996 (Found: C, 88·9; H, 11·1. $C_{12}H_{18}$ requires C, 88·8; H, 11·2%).

(c) *With* m*-xylene.* The yield of *sec.*-butyl-*m*-xylene, b. p. 215—217·5°, n_{D}^{20} 1·4980—1·4983, from *sec.*-butyl toluene-*p*-sulphonate (114 g.) and *m*-xylene (265 g.) at 122° (6 hr.) was 37·3 g. Redistillation gave hydrocarbon of constant refractive index, n_{D}^{20} 1·4982, and b. p. 96°/16 mm. (Found: C, 88·7; H, 11·1. Calc. for $C_{12}H_{18}$: C, 88·8; H, 11·2%).

For comparison, 4-*sec.*-butyl-*m*-xylene was prepared from 2 : 4-dimethylphenylmagnesium bromide and *sec.*-butyl toluene-*p*-sulphonate in 21% yield. It boiled at 96°/16 mm. and had n_{D}^{22} 1·4980 (Found: C, 88·9; H, 11·4%). Infrared spectra showed that the hydrocarbons are substantially identical. Nightingale and Smith[18] record b. p. 84°/8 mm., n_{D}^{25} 1·4939.

(d) *With naphthalene.* Naphthalene (128 g.) and *sec.*-butyl toluene-*p*-sulphonate (45·6 g. at 120° in 5 hr. gave 14·1 g. of *sec.*-butylnaphthalene, b. p. 140—146°/15 mm., n_{D}^{20} 1·5836 (Found: C, 91·3; H, 8·7. Calc. for $C_{14}H_{16}$: C, 91·2; H, 8·8%). The infrared spectra indicated the isomer ratio of Table 1 with an accuracy of ±2%.

α-*sec.*-Butylnaphthalene, prepared from α-naphthylmagnesium bromide and *sec.*-butyl toluene-*p*-sulphonate in 20% yield, had b. p. 148°/18 mm., n_{D}^{20} 1·5853 (Found: C, 91·2; H, 8·6%), and gave a picrate, m. p. 76°, and 1 : 3 : 5-trinitrobenzene adduct, greenish-yellow (from alcohol), m. p. 68—71°. The constants recorded for α-*sec.*-butylnaphthalene do not agree with our values: Diuguid[19] gives b. p. 180—189°/20—30 mm., n_{D}^{20} 1·5780; Tzukervanik and Terenteva[20] give b. p. 105—107°/2 mm., n_{D}^{20} 1·5693 (picrate, m. p. 76°).

β-*sec.*-Butylnaphthalene, b. p. 142°/13 mm., n_{D}^{20} 1·5793 (Found: C, 91·2; H, 8·8%) (Bergmann and Weizmann[21] give b. p. 147—148°/33 mm., n_{D}^{20} 1·5814) [picrate, m. p. 60—64° (Brown and Hammick[22] give m. p. 64—68°); 1 : 3 : 5-trinitrobenzene adduct, greenish-yellow, m. p. 81—85° (Brown and Hammick[22] give m. p. 80—83°)], was obtained by hydrogenation of β-sec.*-butenylnaphthalene*, b. p. 157—158°/13 mm., n_{D}^{19} 1·6304 (Found: C, 92·2; H, 7·8. $C_{14}H_{14}$ requires C, 92·3; H, 7·7%) with Raney nickel W4 in alcohol at 3—4 atm. at room temperature.

β-*sec.*-Butenylnaphthalene was obtained by dehydration with boiling aqueous-alcoholic hydrochloric acid of 2-β-naphthylbutan-2-ol from methyl β-naphthyl ketone.

(e) *With anisole.* Anisole (108 g.) and *sec.*-butyl toluene-*p*-sulphonate (45·6 g.) at 120° (5 hr.) gave *sec.*-butylanisoles, b. p. 86—93°/8 mm., n_{D}^{20} 1·5050—1·5030 (13·0 g.) (Found: C, 80·3; H, 9·8. Calc. for $C_{11}H_{16}O$: C, 80·4; H, 9·8%). Infrared spectra showed the isomer ratios of Table 1 with an accuracy of ±3%.

o-sec.*-Butylanisole*, b. p. 83—84°/9 mm., n_{D}^{17} 1·5070 (Found: C, 80·5; H, 9·8%) was prepared in 11% yield from 2-methoxyphenylmagnesium bromide and *sec.*-butyl toluene-*p*-sulphonate. Its infrared spectrum indicated that it contained 3% of *meta-* and 5% of *para*-isomer.

p-sec.-Butylanisole, b. p. 91·5°/9 mm., n_{D}^{17} 1·5038 (Found: C, 80·2; H, 10·0%) (Klages[23] gives b. p. 106—108°/16 mm., n_{D}^{20} 1·5062) was obtained in 23% yield from *p*-methoxyphenylmagnesium bromide and *sec.*-butyl toluene-*p*-sulphonate. From its infrared spectrum this sample was estimated to contain 10% of *meta-* and 5% of *ortho*-isomer.

m-sec.*-Butylanisole*, b. p. 100°/14 mm., $n_{\mathrm{D}}^{18\cdot5}$ 1·5027 (Found: C, 80·4; H, 9·8%), was obtained by the hydrogenation (Raney nickel W4; alcohol; 3—4 atm.) of m-sec.*-butenylanisole*, b. p.

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110—112°/13 mm., $n_{\rm D}^{18\cdot5}$ 1·542 (Found: C, 81·5; H, 8·8. $C_{11}H_{14}O$ requires C, 81·4; H, 8·7%), itself prepared from *m*-methoxyphenylmagnesium bromide and ethyl methyl ketone.

Introduction of iso*Propyl into the Aromatic Nucleus.*—*iso*Propyl toluene-*p*-sulphonate was obtained (from *iso*propyl alcohol) as a reddish oil as described for the preparation of *cyclo*hexyl toluene-*p*-sulphonate.[16] Small amounts could be distilled in a high vacuum without decomposition, but for larger quantities this was impracticable. The ester used in the work described below was freed from excess of *iso*propyl alcohol by drawing air through it at 0·1 mm. to give $n_{\rm D}^{20}$ 1·5050 (Drahowzal and Klamann [24] give $n_{\rm D}^{20}$ 1·5065).

(a) *Formation of* iso*propylnaphthalene.* Naphthalene (256 g.) and *iso*propyl toluene-*p*-sulphonate (85·6 g.) at 125° in 4 hr. gave propene and *iso*propylnaphthalene (19·5 g.), b. p. 134—134·5°/15 mm., $n_{\rm D}^{21\cdot5}$ 1·5918 (Found: C, 91·8; H, 8·4. Calc. for $C_{13}H_{14}$: C, 91·7; H, 8·3%) (picrate, m. p. 80—82°; 1 : 3 : 5-trinitrobenzene adduct, greenish-yellow, m. p. 95—98°).

α-*iso*Propylnaphthalene, obtained in 30% yield by the reaction of α-naphthylmagnesium bromide with *iso*propyl toluene-*p*-sulphonate, had b. p. 138·5—39·5°/18 mm., $n_{\rm D}^{21\cdot5}$ 1·5924 (Found: C, 91·7; H, 9·4%) [picrate, m. p. and mixed m. p. 81—83°; 1 : 3 : 5-*trinitrobenzene adduct* (from alcohol), m. p. and mixed m. p. 98—100·5° (Found: C, 59·1; H, 4·6; N, 10·9. $C_{13}H_{14},C_6H_3O_6N_3$ requires C, 59·5; H, 4·5; N, 11·0%)]. Kutz *et al.*[25] give b. p. 267·9°, $n_{\rm D}^{20}$ 1·5950 for α-*iso*propylnaphthalene; b. p. 268·2°, $n_{\rm D}^{20}$ 1·5860 for the β-isomer. Cook [26] gives m. p. 83·5—86° for the picrate of the α-isomer.

The infrared spectrum of α-*iso*propylnaphthalene was identical with that of *iso*propylnaphthalene from the alkylation of naphthalene.

(b) *Formation of* iso*propylanisoles.* Anisole (270 g.) and *iso*propyl toluene-*p*-sulphonate (107 g.) at 123° in 5 hr. gave propene (8 c.c.) and *iso*propylanisoles, b. p. 73—80°/15 mm., $n_{\rm D}^{20}$ 1·5077—1·5063 (30·1 g.) (Found: C, 79·9; H, 9·4. Calc. for $C_{10}H_{14}O$: C, 80·0; H, 9·4%) Infrared spectra indicated the isomer ratios of Table 1 with an accuracy of ±3%.

o-*iso*Propylanisole, b. p. 80°/13 mm., $n_{\rm D}^{20}$ 1·5085 (Found: C, 80·2; H, 9·5%) (Tambovtseva and Tzukervanik [27] give b. p. 212—214°, $n_{\rm D}^{20}$ 1·5070), was obtained in 20% yield from *o*-methoxyphenylmagnesium bromide and *iso*propyl toluene-*p*-sulphonate. From its infrared spectrum it contained 5% of *meta*- and 5% of *para*-isomer.

p-*iso*Propylanisole, b. p. 86°/13 mm., $n_{\rm D}^{19}$ 1·5062 (Found: C, 80·2; H, 9·3%) (Tambovtseva and Tzukervanik [27] give b. p. 198—200°, $n_{\rm D}^{20}$ 1·5056), was prepared similarly from *p*-methoxyphenylmagnesium bromide and contained 10% of *meta*- and 27% of the *ortho*-isomer.

m-*iso*Propylanisole, b. p. 87°/13 mm., $n_{\rm D}^{19}$ 1·5042 (Found: C, 79·9; H, 9·6%), was prepared by hydrogenation (Raney nickel W4; alcohol; 3—4 atm.) of 2-*m*-methoxyphenylpropene, b. p. 86—87°/13 mm., $n_{\rm D}^{19}$ 1·5445 (Found: C, 81·0; H, 8·4. Calc. for $C_{10}H_{12}O$: C, 81·0; H, 8·2%). Carpenter *et al.*[28] give *m*-*iso*propylanisole, b. p. 59°/3 mm., $n_{\rm D}^{25}$ 1·5042. Bergmann and Weizmann [29] give b. p. 110°/22 mm., $n_{\rm D}^{20}$ 1·5399 for *m*-*iso*propenylanisole.

The authors thank the Hydrocarbons Research Group of the Institute of Petroleum for support and the Department of Scientific and Industrial Research for a high-pressure hydrogenator. Measurements of infrared absorption and calculations of the proportions of isomers present in the alkylation products were made at the Coal Research Establishment of the National Coal Board and we are grateful to Dr. R. R. Gordon and the Director of this Establishment for putting their results at our disposal.

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