818. *Acid-catalysed Rearrangements of Alkyl Aryl Ethers. Part I. Rearrangement of Butyl Phenyl Ethers with Aluminium Chloride.*

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Rearrangements of n- and s-butyl phenyl ethers in presence of aluminium chloride have been studied and the products shown to be identical. The products have been compared with those obtained by alkylation of phenol with n- and s-butyl chloride in similar conditions, and conclusions are drawn concerning the mechanism of the rearrangements. A number of n- and s-butyl derivatives of phenol have been synthesised as reference compounds.

THE rearrangement of alkyl aryl ethers to alkylphenols in presence of aluminium chloride was first noticed in 1892 by Hartmann and Gattermann,[1] who obtained in this way from isobutyl phenyl ether a product which they described as *p*-isobutylphenol; since then very little work has been published on reactions of this kind, with the notable exception of a series of papers by Smith in 1933—1934.

Smith found [2] that the rearrangement product isolated by Hartmann and Gattermann was, not *p*-isobutylphenol, but *p*-t-butylphenol, and they obtained the same compound by treating t-butyl phenyl ether with aluminium chloride. Smith therefore concluded that the reaction was intermolecular, involving removal of the butyl residue (presumably as isobutene or a butyl chloride) followed by Friedel–Crafts alkylation of the phenol simultaneously formed. This idea seemed to be confirmed by similar reactions in which alkyl groups migrated to foreign nuclei. Smith was able to isolate [3] 2,4-di-isopropylphenol in 10% yield, together with a mixture (50%) of *o*- and *p*-isopropylphenol, after rearrangement of isopropyl phenyl ether; and when the same ether was treated with aluminium chloride in presence of diphenyl ether, intermolecular migration of the alkyl group occurred.[4]

However, Smith also claimed [5] that rearrangement of n-butyl phenyl ether with aluminium chloride gave a mixture of *o*- and *p*-n-butylphenol. This would be difficult

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[1] Hartmann and Gattermann, *Ber.*, 1892, **25**, 3531.
[2] Smith, *J. Amer. Chem. Soc.*, 1933, **55**, 3718.
[3] *Idem, ibid.*, p. 849.
[4] *Idem, ibid.*, 1934, **56**, 717.
[5] *Idem, ibid.*, p. 1419.

to explain in terms of an intermolecular mechanism; for any alkylation of the Friedel–Crafts type should involve intermediate alkyl cations, and the n-butyl ion would immediately rearrange. It is, of course, known that such alkylations with n-alkyl chlorides invariably give rearranged products.

It is true that the analytical techniques available in Smith's time were scarcely adequate for dealing with the complex mixtures formed in reactions of this type; but his claim that the analogous rearrangement of s-butyl phenyl ether gave a mixture of s-butylphenols certainly seemed to indicate a difference between the rearrangement products in the two cases.

We therefore decided to re-examine the rearrangements of n- and s-butyl phenyl ether, using modern analytical techniques, and to compare the products with those formed by Friedel–Crafts alkylation of phenol in comparable conditions.

Preparation of Reference Compounds.—Since we intended to carry out our analyses by infrared spectroscopy, we had first to synthesise pure samples of all the possible rearrangement products.

The isomeric n-butylphenols were prepared (cf. Klages [6]) by addition of n-propylmagnesium iodide to the appropriate methoxybenzaldehyde, dehydration to the butenylanisole, reduction to n-butylanisole, and demethylation.

The three s-butylphenols were prepared in an analogous manner by Grignard reactions between the appropriate methoxyphenylmagnesium bromide and ethyl methyl ketone, followed again by dehydration, reduction, and demethylation; and 2,4-di-s-butylphenol was obtained likewise from 2-methoxy-5-s-butylphenylmagnesium bromide.

2,6-Di-s-butylphenol, which had not previously been described, was obtained by *ortho*-Claisen rearrangement of the but-2-enyl ether [7] of *o*-s-butylphenol, followed by reduction.

2,4,6-Tri-s-butylphenol was prepared in an analogous way from *p*-s-butylphenol, by two successive rearrangements.

The infrared spectra of all these compounds have been published in the D.M.S. records.

Rearrangements and Alkylations.—Smith [2–5] gave no indication of the temperature at which his rearrangements were carried out, apart from a statement that the heat evolved on adding aluminium chloride to the ether was absorbed in an external cooling bath. In the rearrangements and alkylations reported in this paper the aluminium chloride was added in small portions with cooling to the ether, or to the mixture of phenol or anisole with butyl chloride, during 30 minutes, with external cooling so that the temperature remained in the range 15—25°. The reactions were carried out both with equimolecular amounts of aluminium chloride, and with half-molar amounts. The products were analysed by means of infrared spectra measured for carbon tetrachloride solutions (2% w/w) on a Grubb–Parsons G.S. 2A double-beam grating spectrometer over the range 900—1120 $cm.^{-1}$.

Results.—The products from the alkylation of phenol, or rearrangement of butyl phenyl ether, all consisted of mixtures of all three s-butylphenols, a mixture of di-s-butylphenols, and phenol. No n-butylphenols were detected in the products from n-butyl chloride and phenol, or from n-butyl phenyl ether. Smith's claim [5] that n-butylphenols are formed in the latter reaction must therefore be rejected. Rearrangement cannot follow migration since *o*-n-butylphenol was unaffected by aluminium chloride in the conditions of the reaction.

The formation of *m*-alkylphenols by rearrangement of alkyl aryl ethers has not previously been reported. We were unable to isolate *m*-s-butylphenol from our products, but its presence in small amounts (*ca.* 2%) was definitely indicated in all cases by the spectra. Fractional distillation of the crude rearrangement product gave a fraction in which the concentration of *m*-s-butylphenol was about 15%, and there its presence was established unambiguously by the spectrum (see the Figure).

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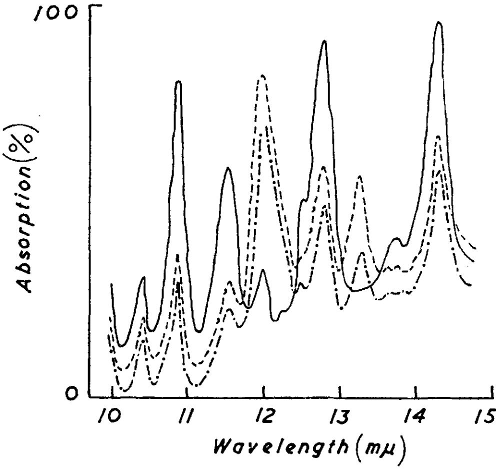
[6] Klages, *Ber.*, 1904, **37**, 3987.

[7] Claisen and Tietze, *Ber.*, 1926, **59**, 2344.

The mixture of dialkylphenols consisted of two isomers. One was 2,4-di-s-butylphenol. The other, which was not the 2,6-isomer, was not definitely identified. Since, however, the same compound was formed by rearrangement of s-butyl *p*-s-butylphenyl ether, it was probably 3,4-di-s-butylphenol, whose formation would not be surprising. Secondary alkyl cations are known [8] to show low selectivity, and so alkylation of *p*-s-butylphenol by s-butyl cations could well give comparable amounts of 2,4- and 3,4-di-s-butylphenol. The infrared spectrum of the unknown compound was found by difference, the spectrum of its mixture with 2,4-di-s-butylphenol being balanced against that of a solution of 2,4-di-s-butylphenyl itself.

The only other product we detected was 2,4,6-tri-s-butylphenol, which was formed in small amounts in the rearrangement of phenyl s-butyl ether.



Infrared spectral evidence for the presence of m-*s-butylphenol in the rearrangement product from phenyl s-butyl ether:* m-*s-butylphenol* (——); *an authentic mixture of s-butylphenols containing* 15% *of the* m-*isomer* (– – – –); *one fraction from the rearrangement product* (— · — · —).

Table 1 records the products formed by rearrangement of n- and s-butyl phenyl ether under various conditions; Table 2 records the products formed in comparable alkylations of phenol.

TABLE 1. *Rearrangements in the presence of aluminium chloride at* 15—20° (*yields in moles* % *and* ortho/para *ratios*.

Ether	$AlCl_3$ (mol.)	Time (hr.)	PhOH	s-Butylphenols *o-*	*m-*	*p-*	Di-s-butyl phenols	*o-* : *p-* Ratio
Bu^n	1·0	36	30·4	11·2	2·0	34·5	16·6	0·325
	1·0	48	27·3	14·4	1·8	44·1	10·5	0·328
	0·5	70	13·5	11·3	0·7	14·5	Trace	0·780
	0·5	72	11·2	14·6	0·8	19·2	Trace	0·760
Bu^s	1·0	24	23·4	12·5	2·0	51·5	7·1	0·243
	0·5	24	28·5	14·5	2·0	44·0	8·5	0·330
	0·5	24	33·7	14·0	1·7	39·1	9·4	0·358
	1·0	24	24·0	12·7	2·4	48·9	9·3	0·260

TABLE 2. *Alkylation of phenol with n- and s-butyl chloride in presence of aluminium chloride* (*mol.*) *at* 15—20% (*yields in moles* % *and* ortho/para *ratios*).

Alkylating agent	Time (hr.)	PhOH	s-Butylphenols *o-*	*m-*	*p-*	Di-s-butyl-phenols	*o-* : *p-* Ratio
Bu^nCl	60	23·0	8·7	1·9	43·4	13·2	0·200
Bu^sCl	36	25·9	8·7	2·0	42·3	13·3	0·206
	28	29·3	7·6	2·0	38·8	16·3	0·196
	24	25·2	9·3	2·0	46·5	10·4	0·200

In this work we also examined the alkylation of anisole by n- and s-butyl chloride; the results are shown in Table 3. Each monoalkyl fraction was shown to contain all three

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[8] Brown and Nelson, *J. Amer. Chem. Soc.*, 1953, **75**, 6292.

isomeric s-butylanisoles, but no n-butylanisoles. No attempt was made to analyse the products quantitatively.

TABLE 3. *Products (moles %) from alkylation of anisole with n- and s-butyl chloride at* 15—20°.

Reagent	Time (hr.)	PhOH	PhOMe	Mono-s-butyl-anisoles	Di-s-butyl-anisoles
Bu^nCl	60	3·3	58·7	12·4	1·8
Bu^sCl	48	4·9	18·5	40·4	13·6

Discussion.—If the rearrangements are intermolecular, one would expect (*a*) that n-butyl would rearrange to s-butyl during migration; (*b*) that rearrangement of n-butyl and s-butyl phenyl ethers would give identical products; (*c*) that rearrangement of either butyl ether would give the same products as alkylation of phenol under similar conditions, with either n- or s-butyl chloride.

The first of these conditions certainly seems to be met; we could not detect n-butylphenols in the rearrangement products of n-butyl phenyl ether.

The rearrangement products of n-butyl and s-butyl phenyl ethers under comparable conditions were similar but not identical (see Table 1); rearrangement of the n-butyl ether gave a larger proportion of *o*-butylphenol. The difference was more marked with half-molar proportions of catalyst.

Comparison of Tables 1 and 2 shows that the products from the rearrangements and and alkylations, though similar, were again not identical. The proportion of *o*-butylphenol in the alkylation products was much less than in the rearrangement products.

That these differences were real is indicated by the constancy of the *ortho*/*para* ratios in the various alkylation products; all the alkylation products gave very similar analyses. It therefore seems unlikely that the rearrangements involve only a simple intermolecular process, as proposed by Smith.[2] The mechanism of these reactions will be considered in detail in a later paper of this series (cf. ref. 9); there it will be shown that two distinct reactions are probably involved, one a heterogeneous intermolecular reaction on the surface of the solid catalyst, the other a homogeneous intramolecular rearrangement catalysed by the aluminium chloride dissolved in the ether.

One point should be emphasised in this connexion; since in no case was a n-butylphenol detected after rearrangement of n-butyl phenyl ether, either the n-butyl group must isomerise during migration, or the n-butyl ether must isomerise to s-butyl ether before rearrangement. In an experiment where the rearrangement of n-butyl phenyl ether was interrupted before completion, no trace of s-butyl phenyl ether could be detected in the unchanged ether recovered. Therefore, either the n-butyl ether is not isomerised before rearrangement, or the s-butyl ether formed from it rearranges as fast as it is formed. The latter is not impossible: rearrangement of s-butyl phenyl ether is certainly very much faster than that of the n-isomer.

EXPERIMENTAL

Microanalyses were carried out by the Microanalytical Laboratory, Imperial College, South Kensington, London, S.W.7, and by Alfred Bernhardt, Max-Planck-Institut, Mülheim Germany.

Alkyl phenyl ethers, prepared from phenol, the alkyl bromide, and potassium hydroxide according to the method of Niederl and Natelson[10] were: phenyl s-butyl ether, b. p. 195°, n_D^{18} 1·4962; n-butyl phenyl ether, b. p. 207°, n_D^{17} 1·4984; s-butyl *p*-s-butylphenyl ether, b. p. 238°, n_D^{19} 1·4925; and n-butyl *p*-s-butylphenyl ether, b. p. 236°, n_D^{17} 1·4927.

Aryloxyacetic acids were prepared by refluxing the phenol (1 g.) in water (30 ml.) with potassium hydroxide (4 g.) and chloroacetic acid (1·5 g.) for 1 hr. and were recrystallised from water or light petroleum (b. p. 60—80°).

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[9] Dewar and Puttnam, *Proc. Chem. Soc.*, 1959, 58.

[10] Niederl and Natelson, *J. Amer. Chem. Soc.*, 1931, **53**, 1928.

Phenylurethanes were prepared according to Steinkopf and Hopner's procedure [11] and recrystallised from light petroleum (b. p. 60—80°).

o-*n-Butylphenol*.—*o*-Anisaldehyde (54·5 g.) in dry ether (200 ml.) was added to a Grignard reagent prepared from magnesium (10·7 g.) and n-propyl iodide (304 g.) in dry ether (250 ml.). Next day the complex was hydrolysed, the ether layer evaporated, and the residue boiled under reflux for 18 hr. with acetic anhydride (500 ml.), then poured into water. The organic layer was collected and distilled; 1-*o*-methoxyphenylbut-1-ene was collected at 92—94°/1·5 mm. Hydrogenation over 5% palladised charcoal in ethanol at room temperature and 15 atm. gave *o*-n-butylanisole, b. p. 217°, n_D^{16} 1·5047 (Found: C, 80·6; H, 10·0. Calc. for $C_{11}H_{16}O$: C, 80·5; H, 9·8%). Demethylation with acetic acid and hydriodic acid gave *o*-n-butylphenol, b. p. 226°, n_D^{20} 1·5205 (aryloxyacetic acid, m. p. 101—102°; phenylurethane, m. p. 72°).

p-*n-Butylphenol*.—This was prepared in the same way as the *o*-isomer; 1-*p*-methoxyphenylbut-1-ene had b. p. 246°, n_D^{19} 1·5334; *p*-n-butylanisole had b. p. 88°/2 mm., n_D^{17} 1·5021; *p*-n-butylphenol had b. p. 245°, n_D^{15} 1·5202 (Found: C, 80·3; H, 9·6%) (aryloxyacetic acid, m. p. 83·5—84·5°; phenylurethane, m. p. 113—114°).

o-*s-Butylphenol*.—This was prepared in an analogous manner to the n-butylphenols, starting with the Grignard reagent from *o*-bromoanisole and ethyl methyl ketone; 2-*o*-methoxyphenylbut-2-ene had b. p. 219°, n_D^{17} 1·5316 (Found: C, 81·6; H, 8·9. Calc. for $C_{11}H_{14}O$: C, 81·5; H, 8·7%); *o*-s-butylanisole had b. p. 51°/0·4 mm., n_D^{17} 1·5052; *o*-s-butylphenol had m. p. 18°, b. p. 223°, n_D^{20} 1·5225 (aryloxyacetic acid, m. p. 112°; phenylurethane, m. p. 85°).

p-s-Butylphenol was prepared likewise; 2-*p*-methoxyphenylbut-2-ene had b. p. 233°, n_D^{17} 1·5478; *p*-s-butylanisole had b. p. 219°, n_D^{16} 1·5031; *p*-s-butylphenol had m. p. 58·5—9·5° (phenylurethane, m. p. 103—105°; aryloxyacetic acid, m. p. 60°).

2,4-*Di-s-butylphenol*.—Bromination of *p*-s-butylphenol in carbon tetrachloride at room temperature gave 2-bromo-4-s-butylphenol, b. p. 83·5°/0·4 mm., n_D^{18} 1·5499, which with methyl sulphate gave 2-bromo-4-s-butylanisole, b. p. 101°/0·6 mm., n_D^{18} 1·5428. This was converted as above *via* 2,4-di-s-butylanisole, b. p. 66·7°/0·1 mm., n_D^{23} 1·4940, into 2,4-di-s-butylphenol, b. p. 259°, n_D^{20} 1·5063 (Found: C, 81·8; H, 10·8. Calc. for $C_{14}H_{22}O$: C, 81·5; H, 10·8%). No solid aryloxyacetic acid or phenylurethane could be obtained.

2,6-*Di-s-butylphenol*.—A solution of but-2-enyl *o*-s-butylphenyl ether [8] (6·6 g.) in diethylaniline (50 ml.) was boiled under reflux for 5 hr. When cold, the solution was poured into hydrochloric acid and extracted with light petroleum (b. p. 40—60°). The hydrocarbon layer was extracted with Claisen solution [potassium hydroxide (350 g.) in water (250 ml.), made up to 1 l. with methanol]; acidification and distillation gave 2-1′-methylallyl-6-s-butylphenol, b. p. 80°/0·3 mm., n_D^{16} 1·5200 (phenylurethane, m. p. 120—121°); reduction with hydrogen (3 atm.) over 10% palladised charcoal in ethanol gave 2,6-*di-s-butylphenol*, b. p. 255°, n_D^{19} 1·5080 (Found: C, 81·3; H, 10·5. $C_{14}H_{22}O$ requires C, 81·5; H, 10·8%). The phenylurethane had m. p. 124—125°.

2-1′-*Methylallyl*-4-*s-butylphenol*.—But-2-enyl bromide (20·3 g.) was added slowly to a solution of *p*-s-butylphenol (22·5 g.) in acetone (50 ml.) containing anhydrous potassium carbonate (20·7 g.). The mixture was stirred at room temperature for 12 hr., and then boiled under reflux for 3 hr. Water and light petroleum (b. p. 40—60°) were added, and the organic layer separated, washed with Claisen solution, dried ($MgSO_4$), and distilled, giving but-2-enyl *p*-s-butylphenyl ether, b. p. 92°/0·5 mm., n_D^{15} 1·5096. Rearrangement of the ether as before gave 2-1′-methylallyl-4-s-butylphenol, b. p. 94°/0·5 mm., n_D^{22} 1·5176 (phenylurethane, m. p. 82°).

2,4,6-*Tri-s-butylphenol*.—2-1′-Methylallyl-4-s-butylphenol was converted as above through but-2-enyl 2-1′-methylallyl-4-s-butylphenyl ether, b. p. 110°/0·3 mm., n_D^{20} 1·5106, into 2,6-di-1′-methylallyl-4-s-butylphenol, b. p. 104°/0·2 mm., n_D^{18} 1·5186. Hydrogenation gave 2,4,6-tri-s-butylphenol, b. p. 282°, n_D^{16} 1·4995 (Found: C, 82·1; H, 11·4. Calc. for $C_{18}H_{20}O$: C, 82·4; H, 11·5%). No solid phenylurethane was obtained.

Rearrangement of n-Butyl Phenyl Ether.—(a) n-Butyl phenyl ether (125 g., 0·832 mole) was placed in a flask, equipped with condenser, stirrer, thermometer pocket, and polythene aluminium chloride dropper,[12] and surrounded with an external cooling bath; anhydrous aluminium chloride (111·3 g., 0·834 mole) was then added slowly with stirring during 30 min. so that the temperature was maintained within the range 15—25°. The cooling bath was then removed and the mixture left at room temperature for 48 hr., during which the mixture became

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[11] Steinkopf and Hopner, *J. prakt. Chem.*, 1926, **113**, 137.

[12] Puttnam, Ph.D. Thesis, London, 1958.

dark red and very viscous and hydrogen chloride was slowly evolved. The mixture was hydrolysed with ice and hydrochloric acid, then the oil which separated was extracted with ether. This ethereal solution was washed with water until neutral, dried ($MgSO_4$), and evaporated. The residue (116 g.) was completely soluble in Claisen solution and was analysed by infrared spectroscopy. Partial separation of the products was effected by extraction with 15% potassium hydroxide solution. The alkali-soluble material (67 g.) was fractionated through a 15 cm. Dixon gauze column to give three fractions. The first fraction, b. p. 55—60°/0·5 mm., gave a phenylurethane, m. p. 126° undepressed by *ON*-diphenylurethane. The second fraction, b. p. 65—75°/0·5 mm. (Found: C, 79·6; H, 9·5. Calc. for $C_{10}H_{14}O$: C, 80·0; H, 9·4%), was shown by spectroscopy to be a mixture of *o*- (27%), *m*- (15%), and *p*-s-butylphenol (57%). The last fraction, b. p. 81—83°/0·5 mm., solidified and was shown by comparison with authentic samples to be *p*-s-butylphenol. The alkali-insoluble material (38·6 g.) was separated into three fractions. Fraction (i), b. p. 75—83°/0·5 mm., gave an aryloxyacetic acid, m. p. 111° (mixed with *o*-s-butylphenoxyacetic acid, m. p. 112°). Fraction (ii), b. p. 86—97°/0·5 mm., was shown by its spectrum to be a mixture of *o*-s-butylphenol, 2,4-di-s-butylphenol, and an unknown component. Fraction (iii), b. p. 98—102°/0·5 mm. (Found: C, 81·3; H, 10·9. Calc. for $C_{14}H_{22}O$: C, 81·5; H, 10·8%), was shown by its spectrum to be a 1 : 1 mixture of 2,4-di-s-butylphenol and the unknown component referred to above. A spectrum of this component was obtained by comparing a 2% solution of this fraction with a 1% solution of 2,4-di-s-butylphenol.

(b) The rearrangement was repeated with n-butyl phenyl ether (90 g., 0·6 mole) and anhydrous aluminium chloride (40 g., 0·3 mole). The products were separated as described above and extracted with Claisen solution, leaving an insoluble residue (49 g.) which was shown by its spectrum to be solely unchanged n-butyl phenyl ether. The material (33 g.) soluble in Claisen solution was analysed spectroscopically.

Rearrangement of s-Butyl Phenyl Ether.—(*a*) s-Butyl phenyl ether (100 g., 0·67 mole) was treated as above with anhydrous aluminium chloride (88·9 g., 0·67 mole) at 17—21°. The mixture was left at room temperature for 24 hr. and the products were separated as above. The rearranged material (97·2 g.), which was completely soluble in Claisen solution, was analysed spectroscopically. The products were partly separated by extraction with 20% potassium hydroxide solution. The alkali-soluble material (75·9 g.) was fractionated. The first fraction gave a urethane, m. p. 126° undepressed by *ON*-diphenylurethane. The second fraction, b. p. 82—86°/1·5 mm., was found by its spectrum to be a mixture of *o*- (38%), *m*- (12%) and *p*-s-butylphenol (50%). The third fraction was shown by comparison with an authentic specimen to be *p*-s-butylphenol. The last fraction, b. p. 102—106°/1·0 mm., was a mixture of *p*-s-butylphenol, 2,4-di-s-butylphenol, and the unknown component. The alkali-insoluble material (18·3 g.) was also fractionated. Fraction (i), b. p. 82—88°/1·0 mm., gave an aryloxyacetic acid, m. p. 112° undepressed by *o*-s-butylphenoxyacetic acid. Fraction (ii), b. p. 96—101°/1·0 mm., was found by its spectrum to be a 3 : 2 mixture of 2,4-di-s-butylphenol and the unknown di-s-butylphenol. Fraction (iii) was similarly shown to be a mixture of these two components, together with 2,4,6-tri-s-butylphenol (10%).

(*b*) s-Butyl phenyl ether (52·5 g., 0·35 mole) was treated with anhydrous aluminium chloride (23·3 g., 0·175 mole) at 15—18°. After 24 hr. at room temperature the mixture was hydrolysed and the organic layer separated as above. Removal of the ether gave rearranged material (49·8 g.) which was completely soluble in Claisen solution and was analysed spectroscopically.

Alkylations of Phenol. (*a*) Aluminium chloride (133·4 g.) was added slowly to a stirred mixture of phenol (94·1 g.) and n-butyl chloride (92·6 g.), at 15—20°. After 60 hr. at room temperature, the product was worked up as above, giving a mixture of alkylphenols (154·3 g.) which was analysed spectroscopically.

(*b*) A similar reaction with s-butyl chloride gave a mixture of alkylphenols (151·2 g.) which was similarly analysed.

Rearrangement of s-Butyl p-*s-Butylphenyl Ether.*—Rearrangement of s-butyl *p*-s-butylphenyl ether (10·5 g., 0·05 mole) with aluminium chloride (6·8 g., 0·05 mole) gave a product which was separated into two fractions by treatment with 10% aqueous potassium hydroxide. The soluble fraction (3·7 g.) gave a phenylurethane which did not depress the m. p. of *N*-phenyl-*O*-s-butylphenylurethane. The insoluble part was fractionated; one fraction, b. p. 259°, n_D^{22} 1·5070, was shown by its spectrum to be a mixture of 2,4-di-s-butylphenol and the unknown di-s-butylphenol. Another fraction, b. p. 278°, n_D^{22} 1·5058, was a mixture of these two compounds with 2,4,6-tri-s-butylphenol.

Effect of Aluminium Chloride on o-*n-Butylphenol.*—Aluminium chloride (0·9 g.) was added to *o*-n-butylphenol (1 g.). After 48 hr. at room temperature, the mixture was hydrolysed and extracted with ether, and the ether extract was distilled. The spectrum of the product was identical with that of *o*-n-butylphenol.

Alkylations of Anisole. These reactions were carried out with molar proportions of aluminium chloride as before. The products were treated with Claisen solution; the soluble part in each case was phenol. The insoluble part was fractionally distilled. The first fraction consisted of anisole. The second (b. p. 218°) was shown by its spectrum to be a mixture of *o*- and *p*-s-butylanisole, with a trace of the *m*-isomer. The third fraction apparently consisted of dibutylanisoles (Found: C, 81·8; H, 11·1. Calc. for $C_{15}H_{24}O$; C, 81·8; H, 11·0%); the last of trialkylanisoles (Found: C, 82·3; H, 11·4. Calc. for $C_{19}H_{32}O$: C, 82·6; H, 11·6%).

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