anol (5 drops) in the usual manner for 3 days. The crude product (252 mg), which was a colorless solid, was combined with the crude product (60 mg) from a similar reaction of **16** (52 mg, 0.12 mmol), and subjected to preparative thin layer chromatography on four silica plates (20 × 20 × 0.125 cm) with 13 elutions with 5–12% of ether in petroleum ether. Two compounds were isolated, the minor one being **16** (19 mg, 7%). The major product (205 mg) was a crystalline solid, which was recrystallized from methanol to give **17** as small prisms (192 mg, 74%), mp 165–166°, unchanged on further crystallization from methanol.

Anal. Calcd for $C_{32}H_{24}O_2$: C, 87.24; H, 5.49. Found: C, 86.90; H, 5.50.

Equilibration of 16 and 17 with Sodium Methoxide. Samples of compounds **16** (43 mg) and **17** (34 mg) were separately treated in ether with sodium hydride and methanol in the usual manner for 4 days. The crude products were chromatographed on silica columns as before to remove the paraffin from the sodium hydride dispersion. The mixtures of **16** and **17** eluted with 20–50% ether in petroleum ether were analyzed by pmr spectroscopy. In $CDCl_3$ solution the methylene proton signals of **16** and **17** were too close-lying ($\Delta\nu$ = 2.5 Hz at 60 MHz) to permit quantitative analysis; however, in C_6D_6 solution their separation was increased ($\Delta\nu$ = 7 Hz at 60 MHz) and they could be used for such analysis. The product ratio, **16**:**17**, from **16** was 23:77, while that from **17** was 15:85.

2,2,4-Triphenyl-1-(*p*-tolyl)-1,4-butanedione (18). The lactone **9** (802 mg, 2.57 mmol) in ether (30 ml) was treated with 0.765 *N* *p*-tolyllithium in ether–hexane [prepared from *p*-bromotoluene and *n*-butyllithium (Foote); 4.2 ml, 3.21 mmol] in the usual manner. The crude product was crystallized from methanol to give **18** as needles (652 mg, 63%), mp 160–162°; a second crop (109 mg), mp 158–160°, raised the yield to 73%. Several recrystallizations from methanol gave an analytical sample, mp 163.5–164°.

Anal. Calcd for $C_{29}H_{24}O_2$: C, 86.11; H, 5.98. Found: C, 85.80; H, 5.98.

4-Hydroxy-2,2-diphenyl-4-(*p*-tolyl)-3-butenoic Acid Lactone (20). 2-Diazo-4′-methylacetophenone was prepared from *p*-toluoyl chloride and diazomethane in ether in the usual manner; the crude product was crystallized from hexane to give fine yellow needles (78%), mp 46–49°; a second crystallization from hexane gave the product (67%): mp 48–51° (lit.[13] mp 49–51°); $\lambda_{max}^{CCl_4}$ 4.82, 6.17, 7.43 μ; δ^{CCl_4} 2.40 (s, 3 H), 5.85 (s, 1 H), 7.15 (d, J = 8.5 Hz, 2 H), 7.60 (d, J = 8.5 Hz, 2 H).

The lactone **20** was prepared from 2-diazo-4′-methylacetophenone (1.40 g, 8.75 mmol) and diphenylketene[10] (1.90 g, 9.19 mmol) in ether (20 ml) by the procedure used for the preparation of lactone **9**[1] except that the reaction solution was stirred for 18 hr at room temperature and the residue after removal of the ether was heated for 1 hr on the steam bath. The crude product was combined with that from a similar reaction of the diazo ketone (189.5 mg, 1.18 mmol) with diphenylketene (255 mg, 1.31 mmol) and chromatographed on silica (400 g) packed in petroleum ether. The product was introduced onto the column in hot petroleum ether, and when the column had cooled elution was continued with petroleum ether containing increasing proportions of ether. The crude lactone **20** (2.46 g, 76%) was eluted with 8% ether in petroleum ether; two recrystallizations from methanol gave large needles (1.53 g), mp 152–153°. Two further recrystallizations from methanol followed by one from heptane gave an analytical sample: mp 152–152.5°; $\lambda_{max}^{CCl_4}$ 5.58, 6.07 (m); δ^{CDCl_3} 2.36 (s, 3 H), 6.27 (s, 1 H), 7.33 (m, 12 H), 7.58 (d, J = 8 Hz, 2 H); *m/e* 326 (7%).

Anal. Calcd for $C_{23}H_{18}O_2$: C, 84.64; H, 5.56. Found: C, 84.51; H, 5.65.

1,2,2-Triphenyl-4-(*p*-tolyl)-1,4-butanedione (19). The lactone **20** (503 mg, 1.54 mmol) in ether (35 ml) was treated with 1.15 *N* phenyllithium in ether–hexane (1.5 ml, mmol) in the usual manner. The crude product (580 mg), which was a colorless crystalline solid, was combined with that from a similar reaction of **20** (93 mg, 0.29 mmol) and recrystallized from methanol to give **19** as fine flakes, contaminated with a small amount of **20** as needles. The latter were removed by hand-picking to give **19** (474.5 mg, 64%), mp 153–155°. Several recrystallizations from methanol gave an analytical sample, mp 155–155.5°.

Anal. Calcd for $C_{29}H_{24}O_2$: C, 86.11; H, 5.98. Found: C, 85.97; H, 5.95.

Equilibration of 18 and 19 with Sodium Methoxide. Samples of compounds **18** (55 mg) and **19** (53 mg) were separately treated in ether with sodium hydride and methanol in the usual manner for 1 week. The mixtures of **18** and **19** thus obtained were analyzed by pmr spectroscopy. In $CDCl_3$ solution the methyl proton signals of **18** and **19** at δ 2.21 and 2.32, respectively, were utilized for this analysis. The product ratio, **18**:**19**, from **18** was 38:62, while that from **19** was 39:61. The mixtures could not be resolved by thin layer chromatography.

Acknowledgment. We gratefully acknowledge the support of this work by the National Research Council of Canada.

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[13] A. R. Daniewski and T. Urbański, *Rocz. Chem.*, **42**, 289 (1968).

Mechanism of the Rearrangement of Alkyl Phenyl Ethers. Aluminum Chloride Catalyzed Rearrangement of *n*-Butyl and *sec*-Butyl Phenyl Ethers

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Abstract: The neat rearrangement of *n*-butyl phenyl ether (I) using $AlCl_3$ at 0–5° gave rise to ring *n*-butylated and *sec*-butylated I and the corresponding phenols. Similarly, rearrangement of *sec*-butyl phenyl ether (II) with half-molar amounts of catalyst was found to give higher ortho/para ratios than those with equimolar amounts. These results are mechanistically interpreted.

In the course of a study of the rearrangement of optically active butyl phenyl ethers[2] catalyzed by $AlBr_3$ in solvents, an investigation of the neat rearrangement of *n*-butyl and *sec*-butyl phenyl ethers (I and II, respectively) with $AlCl_3$ seemed appropriate. Rearrangements of the latter sort have been reported to be largely intermolecular.[3] However, much earlier, Smith[4] had reported that the rearrangement of I with $AlCl_3$ gave a

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[2] P. A. Spanninger and J. L. von Rosenberg, *Chem. Commun.*, 795 (1970); also see following paper: *J. Amer. Chem. Soc.*, **94**, 1973 (1972).

[3] M. J. S. Dewar and N. A. Puttnam, *J. Chem. Soc.*, 4080 (1959).

[4] R. A. Smith, *J. Amer. Chem. Soc.*, **56**, 1419 (1934).

Table I. Per Cent Phenolic Component in Base Extract

Ether: catalyst, BuOPh	PhOH	*o*-*sec*-Bu	*p*-*sec*-Bu[a]	*o*-*n*-Bu	*p*-*n*-Bu	2,6-Di	2,4-Di	*m*-*sec*-Bu[a]	Unidentified Unknown	2,4,6 (?)[c]	*sec*-Bu o/p
1:0.5 (*n*-Bu)	90.3	4.1	0.6	3.5	1.6	None	None	None	None	None	6.8[b]
1:1 (*n*-Bu)	21.1	13.7	28.2	Trace	Trace	0.3	9.5	12.5	14.7	14.7	0.5
1:1 (*sec*-Bu)	22.1	9.7	32.9			0.1	6.8	12.5	16.0	14.4	0.3
1:0.5 (*sec*-Bu)	29.8	19.2	17.0			4.4	15.5	9.0	5.2	2.6	1.1

[a] Since *m*- and *p*-butylphenols were not separable by glpc, the meta isomer was estimated by the infrared (ir) spectrum of the phenolic mixture and subtracted from the amount of para isomer obtained by glpc. Per cent meta isomer is an average of the range detected by ir measured against standard spectra. [b] For *n*-Bu the o/p ratio = 2.2; the total o/p ratio (*sec*-Bu + *n*-Bu) = 3.5. [c] Inferred to be 2,4,6-tri-*sec*-butylphenol from glpc.

mixture of *o*- and *p*-*n*-butylphenols. This finding would be difficult to explain in terms of an ionic intermolecular mechanism, since any alkylation of the Friedel–Crafts type should involve intermediate *n*-butyl cations which would be expected to isomerize to *sec*-butyl cations before substitution. Indeed, the analogous rearrangement of *sec*-butyl phenyl ether as reported by Dewar[3] gave a mixture of alkylphenols similar to those obtained from the reaction of I, and, in contrast to the report of Smith, no *n*-butylphenols were detected.

It has been suggested that the homogeneity of the reaction mixture plays an important role in $AlCl_3$-induced rearrangements of alkyl phenyl ethers.[3] Thus, decreasing the ether:catalyst molar ratio from 1:1 to 1:0.5 to produce a homogeneous mixture resulted in a corresponding increase in the ratio of *o*-butylphenol to *p*-butylphenol (o/p ratio).[5]

It was reasoned, therefore, that a large part of the intermolecular reaction occurred on the catalyst surface, while the homogeneous reaction followed to a greater extent the intramolecular pathway.

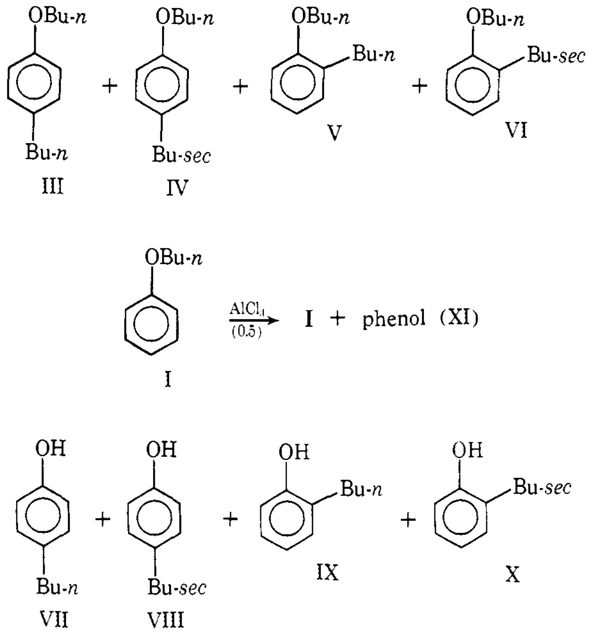
We decided to investigate this rearrangement in the light of our previously described work[2] using the superior analytical technique of gas–liquid partition chromatography (glpc) to quantitatively analyze all components.

Results

The temperature of the reaction mixture during addition of the catalyst was maintained at 0–5°, instead of 15–25° (in order to be consistent with other studies in solvent systems).[2] Furthermore shorter reaction times than those used in the earlier studies were employed.[3] Thus, I and II were allowed to react with $AlCl_3$ using 1:1 and 1:0.5 molar ratios of ether to catalyst to give the relative amounts of phenolic products shown in Table I.

It can be seen that *n*-butylphenols were indeed formed to a significant extent in the 1:0.5 (I:$AlCl_3$) rearrangement (Scheme I). The noticeably large amount of phenol indicates that apparently significant quantities of butene were eliminated. Analysis of the neutral residue of this reaction revealed not only *sec*-butylated, but *n*-butylated *n*-butyl ethers (VI:V:IV:III ≡ 2.16:3.14:1.00:4.86). It follows, therefore, that *n*-butylphenols would be formed from cleavage of III and V. Although this is in contrast to what was reported earlier[3] for this reaction at 15–25°, at no previous time was the neutral residue analyzed for products III–VI. However, only trace amounts of both neutral products and *n*-butylphenols were detected in the rearrangement of I using equimolar amounts of catalyst. Clearly, this latter reaction resembled more closely the rearrangement of II than that of I with half-molar amounts of catalyst employed.

Scheme I



The rearrangement of both I and II using equimolar amounts of $AlCl_3$ is further complicated by the very viscous nature of the heterogeneous media. The resulting formation of HCl gas as the normal by-product of Friedel–Crafts reactions in the media additionally catalyzes the rearrangement. The gas becomes entrapped in the mass and is only permitted to escape through vigorous stirring. These factors make exact mechanistic analysis of the equimolar reaction difficult, if not impossible.

Discussion

The results obtained from the half-molar $AlCl_3$ catalyzed rearrangement of I are in accord with those

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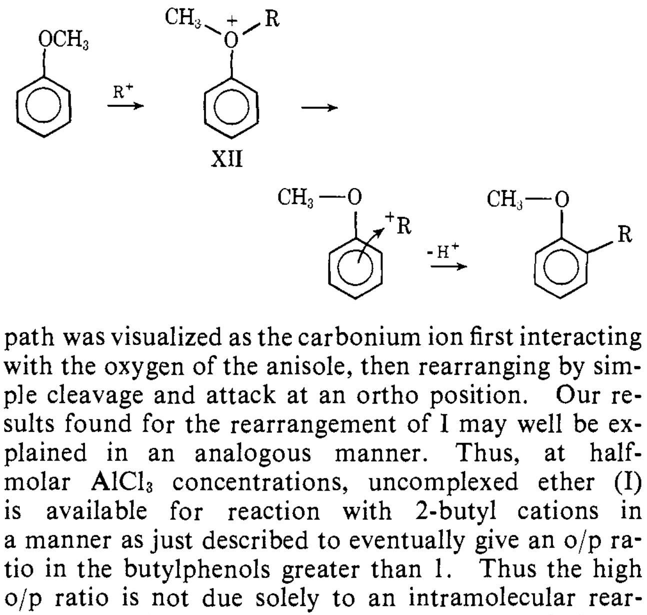
(5) Data indicated[3,6] the o/p ratio to be a good measure of the intra- *vs.* intermolecularity of a rearrangement. Since the para isomer was apparently more favored by intermolecular alkylation,[3] a low o/p ratio was observed. Intramolecular migration during rearrangement, on the other hand, should give a higher o/p ratio, since the ortho position would be favored simply due to its close proximity to the migrating group.

(6) D. V. Banthorpe, J. A. Thomas, and D. L. H. Williams, *J. Chem. Soc.*, 6135 (1965), and references therein.

found using optically active *sec*-butyl phenyl ether[2] in chlorobenzene with $AlBr_3$. In the latter, when the catalyst was *added to* the ether, net inversion of the *sec*-butylphenols resulted. In a similar fashion, *n*-butyl *o*- and *p*-*n*-butylphenyl ether (V and III) would be formed by an intermolecular displacement mechanism as previously described,[2] with para substitution predominating. It is interesting to note that while III was the major butylated ether, *n*-butyl *o*-*sec*-butylphenyl ether (VI) was formed to a considerably larger extent than the corresponding *n*-butyl *p*-*sec*-butylphenyl ether (IV) (VI/IV = 2.16). Initially this result seemed somewhat curious because the *sec*-butyl group probably arose *via* a carbonium ion isomerization of the cleaved *n*-butyl group which attacked unreacted ether in an intermolecular fashion. Previously, the assumption had been made that a low o/p ratio (less than 1) showed intermolecular character (*i.e.*, ionization of butyl groups) because the para position of *phenol* would be preferentially alkylated under normal Friedel–Crafts conditions.[3] Correspondingly the higher o/p ratios were said to indicate a greater intramolecular character. The application of this argument to this rearrangement must be strongly questioned in the light of recent work,[7] which reported relatively high o/p ratios (1.91) for the alkylation of anisole. As shown in Scheme II, the reaction path was visualized as the carbonium ion first interacting with the oxygen of the anisole, then rearranging by simple cleavage and attack at an ortho position. Our results found for the rearrangement of I may well be explained in an analogous manner. Thus, at half-molar $AlCl_3$ concentrations, uncomplexed ether (I) is available for reaction with 2-butyl cations in a manner as just described to eventually give an o/p ratio in the butylphenols greater than 1. Thus the high o/p ratio is not due solely to an intramolecular rearrangement, but to an intermolecular process followed by an intramolecular one. This effect was revealed because I was so unreactive. This reaction pathway was also probably operative during the rearrangement of II with half-molar amounts of $AlCl_3$, since the o/p ratio is higher relative to equimolar quantities of catalyst. However, the extreme reactivity of II prohibited the detection of this process.

Scheme II



Such an intramolecular rearrangement from an *n* complex (XII) has recently been questioned.[8] The results suggest that the high ortho product is "not a necessary or sufficient criterion" for an intermediate *n* complex and perhaps the *n* electrons exert a levelling effect on electrophilic reactivity.

Although we cannot rule out, at this point, any effect of heterogeneous media on the amount of para isomer formed by an intermolecular process, we can say that the higher o/p ratio in homogeneous reactions without solvent may be due not only to an intramolecular process (ion pair)[2] but also to an intermolecular carbonium ion reaction on the unreacted ether followed by, perhaps, an intramolecular one. Furthermore, depending on the reactivity of the ether, the temperature of the reaction and, probably, the rate of addition of catalyst, a displacement mechanism by unreacted ether plays an important role.

Experimental Section

Gas–liquid partition chromatographic (glpc) analyses were carried out on a F & M Model 810 vapor-phase chromatograph equipped with a flame ionization detector, using helium as a carrier gas, and a 3-m, 10% Carbowax 20M on Chromosorb G-AW, 60–80 mesh column; the method of quantitative analysis of rearrangement mixtures follows that as described by Schupp.[9]

In the case of *m*-*sec*-butylphenol and *p*-*sec*-butylphenol, no separation was able to be achieved. Thus, infrared analysis (ir) was used since characteristic absorptions of the *m*-*sec*-butylphenol occur at ~785 cm^{-1} (12.7 μ) and ~915 cm^{-1} (10.9 μ).[3] By ir analysis, the lower limit of detectability of meta isomer in the phenolic mixture was determined to be at least 1.4–2.0%. When the peak in the glpc corresponding to the *p*- + *m*-*sec*-butylphenols was isolated by preparative glpc, the lower limit of detectability of meta isomer in the original mixture was 0.25–0.30%.

Nuclear magnetic resonance (nmr) spectra were obtained from a Varian A-60 instrument using tetramethylsilane (TMS) as an internal standard.

Materials. Ethers were prepared by the method of Niederl and Natelson:[10] *n*-butyl phenyl ether, bp 206°, $n^{20}\mathrm{D}$ 1.4978 (lit.[3] bp 207°, $n^{17}\mathrm{D}$ 1.4984); *sec*-butyl phenyl ether, bp 191°, $n^{23}\mathrm{D}$ 1.4942 (lit.[3] bp 195°, $n^{18}\mathrm{D}$ 1.4962). Preparation of authentic butylphenols generally followed those described by Dewar:[3] *m*-*sec*-butylphenol, bp 74–75° (0.10 mm) (244°), $n^{26}\mathrm{D}$ 1.5216 (lit.[11] $n^{20}\mathrm{D}$ 1.5192 and 247°);[12] *p*-*n*-butylphenol, bp 74–76° (0.3 mm), $n^{23}\mathrm{D}$ 1.5191 (lit.[3] bp 245° (760 mm), $n^{15}\mathrm{D}$ 1.5202); *o*-*n*-butylphenol, bp 63–64° (0.30 mm), $n^{24}\mathrm{D}$ 1.5201 (lit.[3] bp 226°, $n^{20}\mathrm{D}$ 1.5202); 2,4-di-*sec*-butylphenol, bp 73° (0.10 mm), $n^{25}\mathrm{D}$ 1.5057 (lit.[3] bp 259° (760 mm), $n^{20}\mathrm{D}$ 1.5063); *o*- and *p*-*sec*-butylphenols were purchased from Aldrich Chemical Co. or K & K Laboratories, Inc., as was 2,6-di-*sec*-butylphenol.

Rearrangements. The method by which rearrangements were carried out generally followed that as described by Dewar[3] with the major exceptions that the temperature was initially maintained at 5° rather than 15–25° and the reaction time was 24 hr rather than 48 or 72 hr.

(1) *n*-Butyl Phenyl Ether (Ether to Halide Ratio, 1:0.5). *n*-Butyl phenyl ether, 60.0 g (0.40 mol), was cooled with stirring, and 26.7 g (0.20 mol) of anhydrous $AlCl_3$ was added so that the temperature remained at 5° (10 min).

After the mixture was stirred for 1 hr, the cooling bath was removed and stirring continued for 6 hr as the mixture warmed to room temperature and became viscous; then it was allowed to stand overnight, during which time it assumed a deep red color. No undissolved $AlCl_3$ remained.

The cooled mixture was carefully hydrolyzed with 500 ml of ice-water. After extraction with ether, the organic phase was washed twice with 100-ml portions of Claisen's alkali.[13] The base extract was neutralized with concentrated HCl to a Congo Red end point and worked up in the usual manner to give 4.60 g of phenolic

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(7) P. Kovaic and J. J. Miller, *J. Org. Chem.*, 30, 1581 (1965).

(8) D. A. Simpson, S. G. Smith, and P. Beak, *J. Amer. Chem. Soc.*, **92**, 1071 (1970).

(9) O. E. Schupp, "Techniques of Organic Chemistry," Vol. XIII, "Gas Chromatography," Interscience, New York, N. Y., 1968, p 367.

(10) J. B. Niederl and S. Natelson, *J. Amer. Chem. Soc.*, 53, 1928 (1931).

(11) J. Macak and J. Kubes, *Collect. Czech. Chem. Commun.*, 25, 301 (1960).

(12) "Handbook of Chemistry and Physics," 43rd ed, Chemical Rubber Publishing Co., Cleveland, Ohio, 1961, p 1153.

(13) L. F. Fieser and M. Fieser, "Reagents for Organic Synthesis," Vol. I, Wiley, New York, N. Y., 1967, p 15,321.

products, which glpc showed to be phenol, *o-sec*-butylphenol, *o-n*-butylphenol, and *p-sec*-butylphenol. See Table I for quantitative data.

Distillation of the dried neutral residue gave *n*-butyl phenyl ether (I), bp 71° (3.5 mm), 35.0 g (0.233 mol), 58.3% recovery. The residue remaining in the flask was distilled and further separated by preparative glpc to give four components (i–iv). No *sec*-butyl phenyl ether (II) was detected in the reaction mixture by glpc. Samples of I and II could cleanly be separated under test conditions.

Analysis of the components i–iv showed them to be (i) *n*-butyl *o-sec*-butylphenyl ether, 70 mg, ir 749 cm^{-1}, nmr ($CDCl_3$) δ 7.02 (m, 4), 3.95 (t, 2), 3.15 (sex., 1), 1.20 (d, 3), 1.65 and 1.92 (m, 12); (ii) *n*-butyl *o-n*-butylphenyl ether, 70 mg, ir 752 cm^{-1}, nmr ($CDCl_3$) 6.94 (m, 4), 3.96 (t, 2), 2.65 (t, 2), 1.55 and 0.95 (m, 14); (iii) *n*-butyl *p-sec*-butylphenyl ether, <50 mg, ir 833, 810 cm^{-1}, nmr ($CDCl_3$) 6.95 (A_2B_2, 4), 3.95 (t), 2.50 and 1.20 (m); aromatic:-O-CH_2- plus ring methine:alkyl, 4:3:15; (iv) *n*-butyl *p-n*-butylphenyl ether, 150 mg, ir 830, 806 cm^{-1}, nmr 7.05 (A_2B_2, 4), 4.00 (t, 2), 2.11 (t, 2), 1.65 and 1.05 (m, 14).

Anal. Calcd for $C_{14}H_{22}O$: C, 81.55; H, 10.68. Found: C, 81.82; H, 10.82. The relative peak area ratio of the i–iv components in the original residue was i:ii:iii:iv, 2.16:3.14:1.00:4.86, and their purities after isolation by glpc were 99, 98, 98, and 98%, respectively.

(2) ***n*-Butyl Phenyl Ether (Ether to Halide Ratio, 1:1).** Thus, as described above, 30.0 g (0.20 mol) of *n*-butyl phenyl ether and 26.7 g (0.20 mol) of anhydrous $AlCl_3$ were allowed to react to give 19.7 g of base-soluble products and a trace of neutral products. This reaction was heterogeneous. Glpc analysis showed the neutral products to be unreacted ether and four minor components identical with the four isomeric butylated ethers identified above. The base extract was composed of phenol, *o-sec*-butylphenol, *o-n*-butylphenol, *p-sec*-butylphenol, *p-n*-butylphenol, *m-sec*-butylphenol, 2,4- and 2,6-di-*sec*-butylphenols, and an unidentified component. See Table I for quantitative data.

(3) ***dl-sec*-Butyl Phenyl Ether (Ether to Halide Ratio, 1:1).** Thus, as above, 30.0 g (0.20 mol) of *dl-sec*-butyl phenyl ether and 26.7 g (0.20 mol) of anhydrous $AlCl_3$ were allowed to react. This reaction was heterogeneous and noticeably more exothermic, and hydrogen chloride gas evolution was quite apparent during the stirring at room temperature.

The reaction gave 15.40 g of base-soluble products. Neither neutral products nor unreacted ether was detected from this reaction. The base extract was composed of phenol, *o-sec*-butylphenol, *p-sec*-butylphenol, *m-sec*-butylphenol, 2,4- and 2,6-di-*sec*-butylphenols, and three unidentified components. See Table I for quantitative data.

(4) ***dl-sec*-Butyl Phenyl Ether (Ether to Halide Ratio, 1:0.5).** Thus, as above, 30.0 g (0.20 mol) of *dl-sec*-butyl phenyl ether and 13.4 g (0.10 mol) of anhydrous $AlCl_3$ were allowed to react. This homogeneous reaction was very similar to the 1:1 molar ratio of ether of $AlCl_3$, since it also evolved hydrogen chloride gas during the reaction.

The reaction gave 16.0 g of base-soluble material and trace amounts (glpc) of unidentifiable neutral products. The base extract consisted of phenol, *o-sec*-butylphenol, *p-sec*-butylphenol, *m-sec*-butylphenol, 2,4- and 2,6-di-*sec*-butylphenol, and two unidentified components. See Table I for quantitative data.

Mechanism of the Rearrangement of Alkyl Phenyl Ethers. Aluminum Bromide Catalyzed Rearrangement of *sec*-Butyl Phenyl Ether

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Abstract: Treatment of optically active *sec*-butyl phenyl ether (I) at 0–5° with $AlBr_3$ in chlorobenzene gave *o*- and *p-sec*-butylphenols (II and III) with net inversion of configuration (14.1 and 52.0%, respectively). Further analysis of the rearrangement indicated that inversion was caused by displacement of an active *sec*-butyl group by unreacted I from an *n* complex or ion pair to form butylated I, which cleaved to give phenols with inverted configurations. This process was masking an intramolecular pathway to rearrangement. The duality of mechanisms was demonstrated when the addition of reagents was reversed, *i.e.*, I added to $AlBr_3$ in chlorobenzene; thus, II was formed with net retention (54.2%), while III was racemic. The intramolecular rearrangement was suggested to be controlled, not by a π-complex intermediate as previously described in the literature, but by collapse of an intimate ion pair to II. Furthermore, variation of aromatic solvents for the rearrangement indicated a large participation by irreversible removal of *sec*-butyl ions. As the ease of alkylation of the solvent increased, so the ortho/para ratio of butylphenols (II/III) increased. In addition, benzene as solvent was found to enter into a displacement mechanism with the active I such that 2-phenylbutane was formed with 13.9% net inversion, while butylation of benzene with active 2-butanol under conditions of rearrangement produced 2-phenylbutane with 26.7% net inversion. A general mechanism for the rearrangement is presented.

The acid-catalyzed rearrangement of alkyl aryl ethers to alkylphenols was first reported in 1892.[2] Since that time, there has been considerable evidence that the rearrangement proceeded *via* both intermolecular and intramolecular pathways.[3]

Dewar[4] concluded that the extent of intramolecular migration was dependent on the catalyst and homogeneity of the reaction media. Thus when $AlBr_3$ dissolved

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(1) (a) Department of Chemistry, The University of Texas at Austin, Austin, Texas 78712. (b) A preliminary account of a portion of this work has already been reported: P. A. Spanninger and J. L. von Rosenberg, *Chem. Commun.*, 795 (1970).

(2) C. Hartmann and L. Gatterman, *Ber.*, **25**, 2531 (1892).

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