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

Philip A. Spanninger[1a] and J. L. von Rosenberg*

Contribution from the Departments of Chemistry and Geology, Clemson University, Clemson, South Carolina 29631. *Received June 3, 1971*

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

(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).

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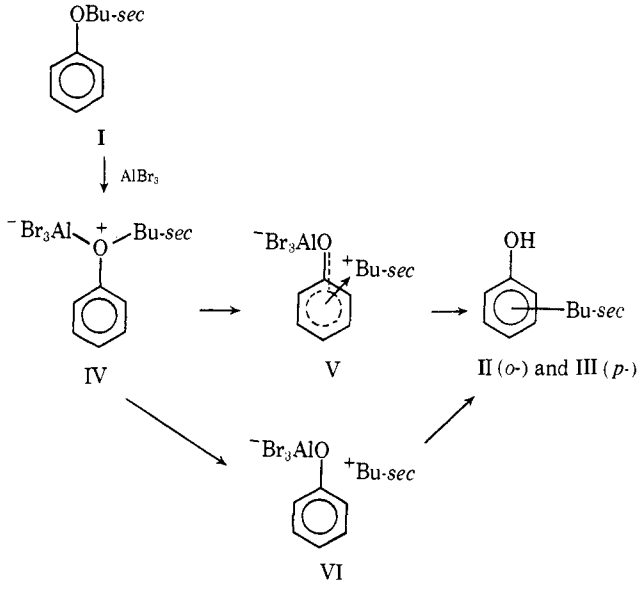
Table I. Per Cent Phenolic Components in Base Extract

sec-Bu ether in (solvent)	Phenol	*sec*-Bu- *o*-	*sec*-Bu- *p*-[a]	2,6-Di-	2,4-Di-	*m*-*sec*-Bu-[a]	o/p
C_6H_5Cl							
Normal addn	46.2	35.7	12.6	2.0	3.2	None[b]	2.8
Inverse addn	52.1	43.1	3.1	0.7	None	0.9[b]	13.8
$C_6H_5NO_2$	47.5	27.3	16.5	1.5	7.1	None	1.7
C_6H_6	78.7	16.0	3.9	0.6	0.8	None	4.1
$C_6H_5CH_3$	79.3	17.0	2.6	1.0	0.1	None	6.6

[a] Since *m*- and *p*-butylphenols could not be separated by glpc, the meta isomer was estimated by the ir spectrum of the 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. [b] In this case the meta isomer was determined by ir analysis of the isolated glpc peak corresponding to para isomer + meta isomer.

in chlorobenzene was used as a catalyst system for the rearrangement of *sec*-butyl phenyl ether (I), an unusually high ortho/para (o/p) ratio (8–11) of butylphenols (II/III) was observed. Since it was reasoned that intermolecular reaction would favor the para isomer, this catalyst system was suggested to cause an almost exclusive intramolecular mode of rearrangement. The proposed mechanism for this process involved a π-complex intermediate (V), whose presence in the reaction sequence demanded *complete* retention of configuration of the migrating *sec*-butyl group to *both* the ortho and para positions.



We decided to determine the validity of the π-complex mechanism by an investigation of the rearrangement of both optically active and racemic *sec*-butyl phenyl ethers in various solvent systems.

Discussion

The rearrangement of I with $AlBr_3$ in chlorobenzene was carried out as closely as possible to that as described by Dewar.[4c] The conditions used by these investigators were addition of the $AlBr_3$–chlorobenzene solution to I in chlorobenzene and the reaction run at (a) 70–80° for 10 min, (b) 5–10° for 1 hr, and (c) 5–10° for 24 hr. The three different conditions were claimed to have produced nearly the same results. Our rearrangement was performed at 0–5° for both 1 hr and zero time after addition of $AlBr_3$. By monitoring a rearrangement with gas–liquid phase chromatography (glpc), it was determined that the rearrangement was essentially complete immediately following addition of $AlBr_3$.

Optically Active I in Chlorobenzene. As stated previously the involvement of a π-complex intermediate would require complete retention of configuration of the migrating alkyl groups in both the ortho and para positions. Although previous workers had presented evidence that the ortho products obtained from optically active ethers showed retention of configuration,[3b,d] no such determination had been performed for the para isomers. This question was examined by performing the rearrangement of optically active I with $AlBr_3$ in the manner as just described. Unexpectedly, the rearrangement gave results contrary to those anticipated. Phenolic products (Table I)[5] isolated from the rearrangement of (+)-(*S*)-I gave (−)-(*R*)-II and (−)-(*R*)-III with 14.1 and 52.0% net *inversion* of configuration, respectively! In addition to the phenolic products, a relatively large amount of *racemic* butylated solvent was found (*ca.* 50% of available C_4H_9). The o/p ratio (2.8 ± 0.2 determined by glpc) was also lower than that previously reported[4c] (determined by infrared).

Clearly, these results are not consistent with the π-complex mechanism as originally envisaged by Dewar. A reasonable explanation of the net inversion must be that the reaction proceeds predominantly *via* a displacement by I on the $AlBr_3$ complexed ether (IV) (known as an *n* complex) or the ion pair VI. Evidence that this is indeed the case was revealed by the presence of both *sec*-butyl *o*- and *p*-*sec*-butylphenyl ethers upon analysis of aliquots from a monitored rearrangement. The compounds apparently form during the addition of $AlBr_3$ to I and then further react to butylphenols as addition is completed.

The butylated chlorobenzenes were *racemic* and apparently formed in the normal fashion by reaction of the racemized butyl cation and chlorobenzene. The complete lack of activity was conclusively demonstrated by removing the halogen from the aromatic ring and comparing the product to 2-phenylbutane, for which the configuration and optical purity are known.[7] Metalation of *o*-, *m*-, and *p*-*sec*-butylchlorobenzenes and subsequent hydrolysis with water produced racemic 2-phenylbutane. Furthermore, to assure that no racemization had occurred during metalation, the reaction was quenched with D_2O. Deuterium incorporation was found by nuclear magnetic resonance (nmr) spectroscopy to be only in the aromatic portion of the molecule.

(5) Details concerning the analysis of the racemic products may be found in the accompanying paper[6] in the Experimental Section.

(6) P. A. Spanninger and J. L. von Rosenberg, *J. Amer. Chem. Soc.*, **94**, 1970 (1972).

(7) F. Hawthorne and D. J. Cram, *ibid.*, **74**, 5860 (1952).

It is of interest that the net inversion of (−)-(*R*)-III exceeded that of (−)-(*R*)-II, while II was formed in greater amounts. This result can be rationalized if the displacement mechanism were masking an intramolecular reaction. While intramolecular collapse of the ion pair (VI) should form the ortho isomer predominantly, the para position would be activated toward a displacement mechanism over the ortho on the basis of both steric and electronic considerations. It appeared, therefore, that the excess I present during the reaction allowed the displacement mechanism to be the predominant, but not the only route to the butylphenols.

For these reasons, a rearrangement identical with the preceding was performed, except I was *added to* the $AlBr_3$–chlorobenzene. Such a mode of inverse addition would eliminate excess I, and the displacement reaction, and reveal the intramolecular pathway. This was indeed found to be the case. Thus rearrangement of *dl*-I gave a different composition of phenols (Table I) from that obtained previously and the o/p ratio increased to 13.8. Furthermore, when the rearrangement of (−)-(*R*)-I was performed by inverse addition, the isolated (−)-(*R*)-II corresponded to 54.2% net *retention* of configuration, while III was found to be *racemic!* The intramolecular route, therefore, differs from the proposed π-complex pathway since the latter demands complete retention of configuration in *both* ortho and para isomers.

Analysis (ir) of the glpc fraction corresponding to III showed it to contain 20–25% *m-sec*-butylphenol, *i.e.*, *ca.* 0.9% of the phenolic products. Thus, the para and meta isomers, in view of their racemic nature, must arise by intermolecular carbonium ion butylation of either phenol or unreacted I.

Concurrent isomerization of III (by ring protonation) to the meta isomer was ruled out on the basis of control experiments on III. Under conditions of the inverse addition rearrangement, III showed no significant production of meta isomer,[8] although butyl groups migrate to solvent to the extent of 26%. The meta isomer probably arises by butylation of a protonated phenol, which is meta directing.

To show that II isolated from the rearrangement mixture was actually the amount formed directly, further control experiments were carried out. When the ortho isomer II was treated under conditions of both normal and inverse addition experiments, it showed *no* propensity to rearrange to any other butylphenol. Loss of butyl groups to the extent of 22% to solvent (chlorobenzene) was, however, noted in the case of inverse addition. Since this was also similarly the case with III, both are directly formed and no positional isomerization occurs during rearrangement. In addition, (−)-(*R*)-II demonstrated *no* loss of enantiomeric purity under conditions of inverse addition. The value of 54.2% net retention (being less than 100%), therefore, could not be due to racemization under conditions of rearrangement by inverse addition. This must also be the case for the values of net inversion in II and III found in the rearrangement of (+)-(*S*)-I by the normal mode of addition, since these conditions are milder and even less likely to cause racemization in the reaction mixture.

It is perhaps significant that trace quantities of *sec*-butyl *o-sec*-butylphenyl ether were found in the reaction mixture from the inverse addition experiment. This indicates that, to a certain extent, butyl cations react with I, which would give rise to a small amount of racemization in the resulting butylphenols. While this may account for the production of the small quantities of III which are totally racemic, it certainly cannot explain the extent of racemization in II.

Furthermore, as noted, rearrangement of optically active I under conditions of normal addition produced butylphenols with net inversion of configuration. For this result to be consistent with the π-complex mechanism, I would be required to remove the migrating butyl group *via* π transfer. Such a process would give rise to net inversion in the butylphenols formed after cleavage of the butylated I. This is inconsistent, however, with the other data established. If such a π transfer were indeed occurring, the butylchlorobenzenes should also be formed with inversion of configuration. This was not the case. Additionally, the great extent to which butylchlorobenzenes were formed strongly shows that the solvent is not suppressing ionization. This is further substantiated by the data which will be discussed in the solvent study.

The lack of complete enantiomeric purity in II in the inverse addition rearrangement is perhaps consistent with a π-complex mechanism. For although Dewar does not comment on this point in defining the nature of a π complex,[4d] it is possible that a hydride shift could occur during intramolecular migration and be responsible for the extent of racemization observed. However, III from this rearrangement was racemic and if a π-complex mechanism were operative, some retention of configuration would be expected.[9]

Now if the major process whereby the ortho product is formed involves intramolecular collapse of an ion pair, lack of complete enantiomeric purity in II may be explained by means of a hydride shift in the *sec*-butyl cation.

Perhaps an estimate of the extent of hydride transfer occurring during the reaction can be made from a consideration of data produced upon rearrangement of 2-octyl phenyl ether.[3f] For example, reaction of the ether with $AlBr_3$ in chlorobenzene gave 56% *o*-2-octylphenol in addition to a mixture of *o*-3- and 4-octylphenols. The latter two products could of course arise by means of hydride shifts in the 2- and 3-octyl ions. The data certainly indicate that racemization of the ion pair by hydride shifts is possibly an important process in the rearrangement of I. Nevertheless, additional work on an appropriately deuterium-labeled butyl system is necessary to answer the question. Some racemization could also occur *via* an intermolecular followed by an intramolecular process as described in the accompanying paper.

Studies in Other Solvent Systems. The relatively large amount of butylated solvent found in the rearrangement of I conducted in chlorobenzene prompted

(8) Concurrent isomerization of small amounts of *sec*-butyl *o*- and/or *p-sec*-butylphenyl ethers, which are present to a very minor extent under these conditions, has not been ruled out.

(9) Our data reasonably exclude an "allowed" concerted sigmatropic [1,3] shift with inversion of configuration as an explanation for the inversion noted at the ortho position under the normal mode of addition. If such a mechanism were operative it should also be operative in the inverse mode of addition.

us to study the effects of various other solvents on the reaction.

Chlorobenzene was originally chosen[4c] as a solvent because of its apparent capability to favor the intramolecular rearrangement.[3d,10] This ability was rationalized by the fact that chlorobenzene was relatively nonpolar and therefore should suppress ionization (in comparison to the sulfuric acid–acetic acid solvent system).[4b] If this were the case, a π-complex mechanism would be favored simply because it is not ionic. However, despite the fact of the relatively nonpolar solvent, ionization must indeed take place to a very large extent, as evidenced from the large amount of butylated chlorobenzene formed in both methods of rearrangement: normal and inverse additions, *i.e.*, addition of catalyst to ether or ether to catalyst, respectively. The solvents chosen for study differed in both dielectric constant and their ability to be alkylated in the Friedel–Crafts reaction. These solvents (dielectric constant at 25°) were nitrobenzene (34.82), chlorobenzene (5.62), benzene (2.27), and toluene (2.38).

When the rearrangement of I was performed in nitrobenzene, no butylation of solvent occurred. Formation of 2-butyl ions would be facilitated, however, due to the high dielectric constant of the media. The o/p ratio of the butylphenols is much lower (1.7) than when using chlorobenzene and larger amounts of disubstitution occurs (Table I) as would be expected from the presence of solvent-separated butyl cations. Since solvent does not irreversibly remove the carbonium ions, the possibility of their reaction in an intermolecular fashion with other species present is greatly enhanced.

Benzene, having the lowest dielectric constant, is butylated to the extent of *ca.* 73% and an o/p ratio of 4.1 is realized. (Note also the corresponding increase in phenol as shown in Table I.) In toluene as solvent, although a higher o/p ratio is observed (6.6), butylation is less (45%) than with benzene and varies with the time the $AlBr_3$–toluene catalyst system has been prepared. Apparently the catalyst system itself is complicating matters by undergoing transformations, such as disproportionation, to form other products as evidence by glpc analysis of higher boiling fractions.

It is clear that as the ease of alkylation of solvent increases the o/p ratio of butylphenols also increases. There are two points to be made here. First, *if* both II and III were formed by an intermolecular carbonium ion mechanism, the o/p ratio probably would not change significantly by variation of solvents. However, if III is formed completely and II only partly by an intermolecular mechanism, then a variation in o/p ratios as found would be expected. In the more reactive solvent the intermolecular reaction of butyl ions to yield alkylated solvent will compete with alkylated phenol formation. Thus, that portion of ortho product formed in an intramolecular reaction will appear enhanced. Second, it must be recalled that normal addition of $AlBr_3$–chlorobenzene to optically active I gave rise to net inversion in the butylphenols II and III. Solvent must therefore be capable of acting in a manner other than simply trapping the migrating butyl cations. The significance of this possibility was demonstrated by carrying out the rearrangement of optically active I in benzene solvent. The isolated 2-phenylbutane had a rotation corresponding to 13.9% net inversion! As will be remembered this is in contrast to the results of the reaction performed in chlorobenzene which produced racemic butylchlorobenzenes. Apparently the more nucleophilic benzene is competing favorably with I in the displacement mechanism and thus decreases the amount of III (and probably II) arising by this pathway. The net result, then, of both increasing the ability of solvent to irreversibly remove carbonium ions and compete in the displacement reaction with I is to increase the o/p ratios. Furthermore, as the o/p ratio increases, the pathways to II should become dominated by the intramolecular mechanism.

Butylation of Solvents. In order to test the ability of the aromatic solvents to be butylated, separate experiments were carried out by treating 2-butanol with the solvent under conditions of rearrangement by "normal" addition of $AlBr_3$–solvent. The percentages of 2-arylbutanes obtained were as follows: nitrobenzene (...); chlorobenzene (<2.2); benzene (7.2); toluene (58.0).

The trend is exactly that which would be expected by normal electrophilic aromatic substitution. The interesting result, particularly in the cases of chlorobenzene and benzene, is the comparatively larger amounts of butylation which occur during the rearrangement of I (50.1 and 72.9%, respectively). It seems therefore that $Ar–O–AlBr_3^-$ (or $Ar–O–AlBr_2$) is a better leaving group than $H–O–AlBr_3^-$ (or $H–O–AlBr_2$) under these conditions, therefore increasing the ease of cleavage.

A test for a displacement mechanism was also carried out using (+)-(*S*)-2-butanol with benzene under rearrangement conditions. Thus, (−)-(*R*)-2-phenylbutane was produced with 26.7% net inversion.

The results shown here with butylation of benzene indicate that the conditions of rearrangement are particularly amenable to a displacement reaction. The reason greater net inversion is not observed in the 2-phenylbutane isolated from the rearrangement, in comparison to direct butylation with (+)-2-butanol, may be due to the larger amount of solvent separated *sec*-butyl ions (*i.e.*, racemic) captured by benzene in the former system, thereby lowering the optical purity of the 2-phenylbutane.

Experimental Section

Most methods and materials were previously discussed.[6] All rotations were taken on a Rudolph & Sons, Inc. Model 70 polarimeter. All elemental analyses were done by Galbraith Laboratories, Inc., Knoxville, Tenn.

(+)-(*S*)- and (−)-(*R*)-*sec*-Butyl Phenyl Ether (I). 2-Butanol was resolved in the usual fashion[11] *via* the half phthalate ester. The active alcohols were separately carried to the corresponding 2-bromobutanes using PBr_3 giving (−)-(*R*)-2-bromobutane, $[\alpha]^{24}D$ −20.09 ± 0.02° (neat), 51.0% optical purity, and (+)-(*S*)-2-bromobutane, $[\alpha]^{25}D$ +11.80 + 0.02° (neat), 30% optical purity.[12] Formation of the butyl phenyl ethers from the bromides followed that as generally described by Hughes and Ingold[13] for the alcoholysis of bromides. Thus, (+)-(*S*)-*sec*-butyl phenyl ether from the (−)-(*R*)-bromide had $\alpha^{25}D$ +27.27 ± 0.02° (neat, *l* 1), bp 46–48° (1.1 mm), $n^{23}D$ 1.4942, assumed[14] optical purity of 51.0% as based

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(11) J. W. Kantor and C. R. Hauser, *ibid.*, **75**, 1744 (1953).

(12) P. S. Skell, R. G. Allen, and G. K. Helmkemp, *ibid.*, 82, 410 (1960).

(13) E. D. Hughes and C. K. Ingold, *J. Chem. Soc.*, 1196 (1937).

(14) Little racemization occurs in ether formation. These conditions[13] are claimed to proceed with >98% bimolecular reaction. Any

on bromide, and the (−)-(*R*) ether had α_D −15.41 ± 0.02° (neat, *l* 1), $n^{24}D$ 1.4913, assumed optical purity of 30.0%.

sec-Butyl *p*- and *o*-*sec*-butylphenyl ethers were prepared similarly as I from the *p*- and *o*-*sec*-butylphenols: *sec*-butyl *p*-*sec*-butylphenyl ether, bp 72° (0.25 mm, $n^{25}D$ 1.4880 (lit.[4a] bp 238° (760 mm), $n^{19}D$ 1.4925); *sec*-butyl *o*-*sec*-butylphenyl ether, bp 59–60° (0.20 mm), $n^{24.5}D$ 1.4890.

Anal. Calcd for $C_{14}H_{22}O$: C, 81.74; H, 10.68. Found: C, 81.60; H, 10.81.

Determination of Optical Purity and Configuration of *p*-*sec*-Butylphenol. (+)-(*S*)-2-Butanol *p*-toluenesulfonate was prepared by the method of Cram[15] at −14° using (+)-(*S*)-2-butanol, $[\alpha]D$ +2.62 ± 0.10° (19.4% optical purity).[11] The resulting sulfonate with *p*-anisylmagnesium bromide gave (−)-(*R*)-*sec*-butylanisole, after purification by preparative glpc, $[\alpha]^{26}D$ −4.42 ± 0.01° (*c* 15.38, benzene), α_D −4.16 ± 0.01° (neat, *l* 1, $n^{25}D$ 1.5000, 19.4% optical purity as based on (+)-(*S*)-2-butanol (lit.[4a] for *dl*-*p*-*sec*-butylanisole, bp 219°, $n^{16}D$ 1.5031). Thus, maximum rotation should be $[\alpha]D$ −22.78° (benzene) and α_D −21.44° (neat, *l* 1).

(−)-*p*-*sec*-Butylphenol, isolated from the rearrangement of (+)-(*S*)-I, $[\alpha]D$ −6.98 ± 0.01° (*c* 6.73, benzene), was treated with NaOH and dimethyl sulfate to give the corresponding anisole, $[\alpha]D$ −6.03 ± 0.01° (*c* 11.94, benzene), 26.5% optical purity as based on the preceding experiment.

Aluminum Bromide–Solvent Solution. All solutions were prepared by dissolving a known weight of anhydrous $AlBr_3$ in dry reagent solvent, filtering, and storing under a dry nitrogen atmosphere. The concentration of the solution was determined by taking an aliquot and injecting it into a flask containing ice–water, then titrating the released HBr with standard NaOH using phenolphthalein as indicator.

Rearrangements of *dl*-*sec*-Butyl Phenyl Ether. (a) Chlorobenzene as Solvent. Into a dried flask was placed 22.5 g (0.15 mol) of *dl*-*sec*-butyl phenyl ether in 25.6 ml (28.1 g, 0.25 mol; molar ratio of ether to solvent is 0.6) of chlorobenzene. To the cold, vigorously stirred solution was added, dropwise, 165.5 ml (0.24 g/ml or 40.1 g, 0.15 mol) of $AlBr_3$–chlorobenzene solution so that the temperature was maintained at 0–5°. After the addition of $AlBr_3$ (30 min), the reaction mixture was stirred at 5° for an additional hour, then hydrolyzed by careful dropwise addition of 500 ml of cold water such that the temperature did not rise above 20°. The aqueous layer was extracted with ether and the combined ether extracts were extracted twice with 75 ml of freshly prepared Claisen's alkali. The basic solution was neutralized with HCl to a Congo Red end point, extracted with ether, and worked up in the normal fashion to give 13.7 g of phenolic products.

(1) Base-Soluble Products. The phenolic mixture was found by glpc to contain phenol, *o*-*sec*-butylphenol, *p*-*sec*-butylphenol, 2,6-di-*sec*-butylphenol, and 2,4-di-*sec*-butylphenol. No *m*-*sec*-butylphenol was detectable. In this particular reaction, the phenolic products were isolated by preparative glpc using a 9-ft 30% Carbowax 20M on Chromosorb G-AW column. All spectra of the separated phenols were consistent with the structures previously assigned on the basis of coinjection with authentic samples. Furthermore, the ir spectrum of the para isomer showed no evidence of contamination by meta isomer; *i.e.*, if the meta isomer was present, it must be less than 0.20%.

(2) Neutral Products. Distillation of the residue reserved after extraction with base gave (a) a clear oil, bp 55–60° (1.5 mm), 11.60 g, $n^{29}D$ 1.5090, and (b) oil, bp 70–72° (0.60 mm), 700 mg.

Analysis of (a) by preparative glpc on a Carbowax column gave (i) *o*-*sec*-butylchlorobenzene ($n^{26}D$ 1.5113), (ii) *m*-*sec*-butylchlorobenzene, and (iii) *p*-*sec*-butylchlorobenzene ($n^{26}D$ 1.5090) (lit.[16] for *p*-*sec*-butylchlorobenzene, $n^{20}D$ 1.5095). Satisfactory elemental, ir, and nmr analyses were obtained for all three compounds. The components were in a ratio of 4.40 (i):1.00 (ii):3.89 (iii) and totaled 11.60 g (46.0%).

Analysis of (b) by glpc showed three higher retention components, in the ratio of 2.66:1.00:1.49. These were suspected to be isomeric di-*sec*-butylchlorobenzenes. *Anal.* Calcd for $C_{14}H_{21}Cl$: C, 74.83; H, 9.35. Found: C, 75.02; H, 9.32. The nmr ($CDCl_3$) indicated two *sec*-butyl groups at different positions on the ring (*i.e.*, not symmetrically substituted) with an integration of 3:2:4:6:6. On this basis, fraction (b), 700 mg (3.10 mmol), accounts for 4.1% of available butyl groups (or 2.06% yield).

(b) Nitrobenzene as Solvent. The rearrangement was carried out as described for chlorobenzene as solvent. Thus, 37.5 g (0.25 mol) of *dl*-I in 50 g of nitrobenzene and 322.7 ml (0.21 g/ml or 66.8 g, 0.25 mol) of $AlBr_3$–nitrobenzene solution were reacted.

The reaction gave 28.9 g of base-soluble material, which glpc showed to contain phenol, *o*-*sec*-butylphenol, *p*-*sec*-butylphenol, and 2,6- and 2,4-di-*sec*-butylphenols.

In the neutral residue no butylated solvent was found.

(c) Benzene as Solvent. Thus, as above, 37.5 g (0.25 mol) of *dl*-I in 35.6 ml (31.2 g) of benzene and 319.5 ml (0.21 g/ml or 66.8 g, 0.25 mol) of $AlBr_3$–benzene solution were allowed to react.

The reaction gave 13.3 g of base-soluble products shown to be phenol, *o*-*sec*-butylphenol, *p*-*sec*-butylphenol, and 2,6- and 2,4-di-*sec*-butylphenols.

The neutral residue was distilled to give 2-phenylbutane, bp 35° (3 mm) [175° (760 mm)], 24.4 g (0.18 mol), $n^{25}D$ 1.4885, 72.9% yield (lit.[17] for *dl*-2-phenylbutane: bp 173.5°, $n^{20}D$ 1.4898). Neither *tert*-butylbenzene nor isobutylbenzene could be detected by glpc or nmr analysis.

(d) Toluene as Solvent. As above, 37.5 g (0.25 mol) of *dl*-I dissolved in 44.2 ml of toluene and 267 ml (0.14 g/ml or 66.8 g, 0.25 mol) of $AlBr_3$–toluene solution were allowed to react.

The reaction gave 10.7 g of base-soluble material shown to be a mixture of phenol *o*-*sec*-butylphenol, *p*-*sec*-butylphenol, and 2,6- and 2,4-di-*sec*-butylphenols.

The neutral residue on distillation gave a clear oil, bp 48° (3 mm), 14.2 g, $n^{24}D$ 1.4923 (lit.[18,19] for *o*-*sec*-butyltoluene, bp 125° (100 mm), $n^{24}D$ 1.4976–82; *m*-*sec*-butyltoluene, bp 189.5°, $n^{20}D$ 1.4919; *p*-*sec*-butyltoluene, bp 192–193°, $n^{20}D$ 1.4900). On analysis by glpc, a three-component mixture in the ratio of 0.66:1.00:0.75 was revealed. *Anal.* Calcd for $C_{11}H_{16}$: C, 89.18; H, 10.81. Found: C, 89.11; H, 10.98. The nmr spectrum (neat) showed one butyl group per ring present, but in different environments (*i.e.*, different isomers were present). Thus, the isomeric mono-2-butyltoluenes corresponded to 94 mmol (37.6%). Small amounts of unidentified higher boiling material were also observed.

(e) Monitored Rearrangement in Chlorobenzene. An identical rearrangement, as described above for the chlorobenzene experiment, was carried out and 5-ml aliquots were taken as follows: (a) after one-half of the $AlBr_3$ solution was added, ~20 min, (b) after all of the $AlBr_3$ solution was added, ~30 min, (c) after 15 min running, (d) after 40 min running, (e) after 50 min running, (f) after 60 min running.

Analysis of aliquot (a) revealed the presence of unreacted I, of *sec*-butyl *o*- and *p*-*sec*-butylphenyl ethers and easily detectable amounts of 2,4- and 2,6-dibutylphenols. Small amounts of three dibutylchlorobenzenes were detected in each of the aliquots. Furthermore, aliquot (b) indicated only a trace of unreacted I and *sec*-butyl *o*-*sec*-butylphenyl ether, but none of the corresponding para isomer. Neither of the butylated ethers was present in later aliquots. The concentration of dibutylphenols increased from aliquot (a) to (b) but remained nearly constant thereafter. Little change was noted in the chromatograms from aliquot (c) to (f).

(f) Inverse Addition of $AlBr_3$–Chlorobenzene Rearrangement. The rearrangement was run as described for rearrangement in chlorobenzene except instead of the halide solution being *added to* I ("normal addition"), the solution of I was added to the cold stirring $AlBr_3$–chlorobenzene solution ("inverse addition"). Thus, 5 g (33 mmol) of *dl*-I dissolved in 6.3 ml of chlorobenzene was added to a cold, stirred 40.1-ml (0.22 g/ml of solution or 8.82 g, 33 mmol) $AlBr_3$–chlorobenzene solution.

The reaction gave 2.95 g (17.5 mmol, 53%) of butylchlorobenzenes in the ratio ortho/meta/para of 1.10:1.00:0.25, o/p = 0.40. A trace amount of *sec*-butyl *o*-*sec*-butylphenyl ether but no para isomer was detected by glpc. The base-soluble products, 940 mg, were phenol, *o*-*sec*-butylphenol, *p*-*sec*-butylphenol, *m*-*sec*-butylphenol, and 2,6-di-*sec*-butylphenol.

(g) Rearrangements Using Optically Active I. (1) In Chlorobenzene. As described for *dl*-I in chlorobenzene by normal addition, 25 g (0.17 mol) of (+)-(*S*)-I, α_D +27.27 ± 0.02° (neat, *l* 1), 51% optical purity, dissolved in 10.2 ml of chlorobenzene was

racemization which may occur would only result in lowering the percentages cited for net inversion or retention of configuration. Thus, those percentages must be *at least* what is claimed and the overall result does not effect the mechanistic interpretations.

(15) D. J. Cram, *J. Amer. Chem. Soc.*, 71, 3881 (1949).

(16) G. F. Hennion and V. R. Pieronek, *ibid.*, 64, 2751 (1942).

(17) "The Merck Index," 6th ed, Merck and Co., Rahway, N. J., 1952, p 173.

(18) H. Pines and L. Schaap, *J. Amer. Chem. Soc.*, 80, 3076 (1958).

(19) M. J. Schlatter, *Amer. Chem. Soc., Div. Pet. Chem.*, Symposium 35-S,5-16 (1955); *Chem. Abstr.*, 51, 11264*i* (1957).

allowed to react by dropwise addition of 186 ml (0.24 g/ml of solution or 44.6 g, 0.17 mol) of $AlBr_3$–chlorobenzene solution.

(i) **Base-Soluble Products.** The reaction gave 10.2 g of phenolic products. Phenol was removed by distillation to leave 3.5 g of butylphenols, $[\alpha]D$ $-3.87 \pm 0.02°$ (*c* 1.55, ethanol), which were separated by preparative glpc. The butylphenols gave the following results: (1) (−)-(*R*)-*sec*-butylphenol, 580 mg, $[\alpha]D$ $-1.33 \pm 0.03°$ (neat), 7.18% optical purity,[7] $[\alpha]D$ $-1.05 \pm 0.01°$ (*c* 13.36, benzene), corresponding to 14.1% *net* inversion (*i.e.*, correcting to 100% optically pure I), ~98% purity by glpc; (2) (−)-(*R*)-*p*-*sec*-butylphenol, 301 mg, mp 54–56°, $[\alpha]D$ $-6.49 \pm 0.02°$ (*c* 6.93, ethanol), $[\alpha]D$ $-6.98 \pm 0.01°$ (*c* 6.73, benzene), 26.5% optical purity (as based on (−)-(*R*)-*p*-*sec*-butylanisole), corresponding to 52.0% *net* inversion, ~99% purity by glpc (the ir spectrum showed no evidence of contamination by the meta isomer); (3) (−)-2,4-di-*sec*-butylphenol, 53.5 mg, $[\alpha]D$ $-8.59 \pm 0.01°$ (*c* 5.35, ethanol), contaminated with ~5% para isomer; (4) 2,6-di-*sec*-butylphenol, insufficient for analysis.

(ii) **Neutral Products.** The neutral residue was distilled to yield (1) bp 56° (~1.5 mm), 13.0 g (7.73 mmol), 46.2%, αD $+0.11 \pm 0.02°$ (neat, *l* 1), isomeric *sec*-butylchlorobenzenes, which were contaminated with unreacted (+)-(*S*)-I; and (2) bp 70° (0.6 mm), 500 mg, 2%, di-*sec*-butylchlorobenzenes, αD $0.00 \pm 0.01°$ (*c* 10.10, benzene). The monobutylchlorobenzenes were collected collectively by preparative scale glpc. Rotation of the purified butylchlorobenzenes, which were still contaminated by a trace of unreacted ether, was αD $+0.06 \pm 0.03°$ (neat, *l* 1).

The monobutylchlorobenzenes were degraded to 2-phenylbutane (for which the optical purity and configuration are known)[7,20] by metalation. Thus, 1.4 g (0.07 g-atom) of sodium metal in 25 ml of dry pentane and 5 g (0.03 mol) of isomeric *sec*-butylchlorobenzenes, isolated from the rearrangement of (*S*)-(+)-I above, were allowed to react in a N_2 atmosphere. The metalated hydrocarbon was hydrolyzed with cooling and the organic layer processed in the usual fashion to give 2-phenylbutane, bp 41° (3 mm), 175 g (13 mmol) (43%), which, after purification by glpc, had a rotation of αD $+0.02 \pm 0.03°$ (neat, *l* 1).

In a separate experiment, halide isolated from rearrangement of racemic I was treated as described above and hydrolyzed with cold D_2O. The 2-phenylbutane showed *no* deuterium in the methine position of the *sec*-butyl group.

(2) **In Benzene.** As for chlorobenzene, 2 g (13.3 mmol) of (+)-(*S*)-I, αD $+10.77 \pm 0.04°$ (neat, *l* 1), 22.4% optical purity, dissolved in 1.7 g (1.9 ml) of benzene and 15.4 ml (0.23 g/ml of solution or 3.55 g, 13.3 mmol) of $AlBr_3$–benzene solution were allowed to react. Insufficient phenolic extracts were available for polarimetric analysis; however, the glpc was the same as for the racemic ether rearranged in benzene.

The neutral residue was distilled to yield 2-phenylbutane. The 2-phenylbutane gave a rotation of αD $-0.76 \pm 0.05°$ (neat, *l* 1), 3.1% optical purity,[7,20] which corresponds to 13.9% *net* inversion.

(3) **In Chlorobenzene *via* Inverse Addition of Reagents.** Thus, 15.01 g (0.1 mol) of (−)-(*R*)-I, αD $-15.41 \pm 0.01°$ (neat, *l* 1), 30% optical purity, and 107.1 ml (0.25 g/ml of solution or 26.7 g, 0.1 mol) of $AlBr_3$–chlorobenzene solution were allowed to react by inverse addition.

(i) **Base-Soluble Products.** Phenol was removed and the butylphenols separated by glpc. The butylphenols gave the following results: (1) (−)-(*R*)-*o*-*sec*-butylphenol, 366.7 mg, $[\alpha]D$ $-2.38 \pm 0.02°$ (*c* 17.62, benzene), 16.27% optical purity, corresponding to 54.2% *net* retention, >99% purity determined by glpc; (2) *p*-*sec*-butylphenol, 30 mg, αD $-0.01 \pm 0.01°$ (*c* 2.79, benzene, *l* 1), >98% purity as determined by glpc (being contaminated with a trace of ortho isomer); (3) 2,6-di-*sec*-butylphenol, insufficient for analysis.

(ii) **Neutral Products.** Distillation of the neutral residue at bp ~60° (1.5 mm) gave 9.1 g of the three *sec*-butylchlorobenzenes (53.5%) along with barely detectable amounts of disubstituted butylchlorobenzenes.

Butylation of Solvents with 2-Butanol under Conditions of Rearrangement with $AlBr_3$. (a) Butylation of Chlorobenzene. The butylation was performed as described for the rearrangement of I with $AlBr_3$, except 2-butanol was substituted, under conditions of normal addition. Thus, 14.8 g (0.20 mol) of freshly distilled *dl*-2-butanol in 40 ml of chlorobenzene and 273 ml (0.20 g/ml of solution or 53.5 g, 0.20 mol) of $AlBr_3$–chlorobenzene were allowed to react.

On distillation, 6 g (94 mmol), 47%, of 2-butanol was recovered along with three monobutylchlorobenzenes in the ratio of (ortho/meta/para) 5.75:1.00:4.53 (o/p = 1.27), <2.2% butylated solvent.

(b) Butylation of Benzene. (1) With *dl*-2-Butanol. As above, 18.5 g (0.25 mol) of *dl*-2-butanol in 35.6 ml of benzene and 315 ml (0.21 g/ml of solution or 66.7 g, 0.25 mol) of $AlBr_3$–benzene were allowed to react. Distillation gave 2-phenylbutane, 2.41 g (18 mmol), bp 35° (~3 mm), $n^{26}D$ 1.4911, 7.2%.

(2) With (+)-(*S*)-2-Butanol. As above, 3.8 g (51.8 mmol) of (+)-(*S*)-2-butanol, $[\alpha]D$ $+7.72 \pm 0.01°$, 57% optical purity, dissolved in 6.7 g (7.7 ml) of benzene and 62.2 ml (0.22 g/ml of solution or 13.9 g, 51.8 mmol) of $AlBr_3$–benzene were allowed to react to give 13.5 mg of pure (glpc) (−)-(*R*)-2-phenylbutane which was dissolved in 1 ml of pure *dl*-2-phenylbutane. The hydrocarbon gave a rotation of αD $-3.70 \pm 0.01°$ (neat, *l* 1), 15.2% optical purity,[20] corresponding to 26.7% net inversion of configuration.

(3) Butylation of Toluene. As before, 11.1 g (0.15 mol) of *dl*-2-butanol in 23 g (36.5 ml) of toluene and 281 ml (0.14 g/ml of solution or 40 g, 0.15 mol) of $AlBr_3$–toluene were allowed to react to produce 13 g (58%) of the three isomeric *sec*-butyltoluenes, bp 53–56° (3 mm), $n^{24}D$ 1.4925. A complicated mixture (2.5 g) of high retention material was also detected.

Stability of *dl*-*o*-*sec*-Butylphenol to Conditions of Rearrangement by Normal Addition. As described previously, 110 ml (0.24 g/ml of solution or 26.7 g, 0.10 mol) of $AlBr_3$–chlorobenzene was added slowly to 15 g (0.10 mol) of *dl*-*o*-*sec*-butylphenol dissolved in 25 g (22.6 ml) of chlorobenzene at 0–5°. After 1 hr, the mixture was quenched. Analysis (glpc) detected traces of phenol and isomeric 2-butylchlorobenzenes, as well as the unchanged *o*-butylphenol. There was no evidence of meta isomer contamination in the ir spectrum.

Stability of *sec*-Butylphenols to Conditions of Rearrangement by Inverse Addition. (1) *dl*-*o*-*sec*-Butylphenol. As for the rearrangement, 3 g (20 mmol) of *dl*-*o*-*sec*-butylphenol in 3.1 ml of chlorobenzene was added slowly to 22.3 ml (0.24 g/ml of solution or 5.34 g, 20 mmol) of $AlBr_3$–chlorobenzene at 0–5°.

The base-soluble portion, 2.32 g, consisted of phenol (a), *o*-*sec*-butylphenol (b), and *p*-*sec*-butylphenol (c) in the ratio of (a:b:c) 6.48:32.43:1.00. The neutral residue was distilled and 700 mg (4.2 mmol), 21%, of *sec*-butylchlorobenzenes (ortho/meta/para) 0.16:1.00:0.41; o/p = 0.39) was collected.

(2) (−)-(*R*)-*o*-*sec*-Butylphenol. In the same manner as above, 270.6 mg (2.47 mmol) of (−)-*o*-*sec*-butylphenol, $[\alpha]D$ $-1.33 \pm 0.05°$ (neat), dissolved in 0.63 ml of chlorobenzene was treated with 2.77 ml (0.24 g/ml of solution or 660 mg, 247 mmol) of $AlBr_3$–chlorobenzene. The isolated (glpc) (−)-*o*-*sec*-butylphenol, 59.5 mg, had a rotation of $[\alpha]D$ $-1.35 \pm 0.01°$ (*c* 5.95, benzene) and was >99% pure by glpc. No para isomer was detectable. The isolated *sec*-butylchlorobenzenes, 26.8 mg, were racemic, αD $0.00 \pm 0.01°$ (*c* 2.68, benzene, *l* 1).

(3). *dl*-*p*-*sec*-Butylphenol. As for the ortho isomer, 3 g (20 mmol) of *dl*-*p*-*sec*-butylphenol dissolved in 3.1 ml of chlorobenzene and 22.3 ml (0.238 g/mol of solution or ~5.34 g, 20 mmol) of $AlBr_3$–chlorobenzene were allowed to react (39 min).

The base-soluble portion, 2.30 g, showed phenol (a), *o*-butylphenol (b), and *p*-butylphenol (c) in the ratio of (a:b:c) 6.00:1.00:19.56. No meta isomer was formed in the reaction. The isolated *sec*-butylchlorobenzenes, 890 mg (5.3 mmol), 26.4%, were in the ratio of (ortho/meta/para) 0.14:1.00:0.43; o/p = 3.33.

(20) D. J. Cram, *J. Amer. Chem. Soc.*, **74**, 2137 (1952).