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REARRANGEMENTS OF ORGANOMETALLIC COMPOUNDS

X*. THE MECHANISM OF 1,2-ARYL MIGRATION IN THE WITTIG REARRANGEMENT OF α-METALLATED BENZYL ARYL ETHERS

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Summary

The mechanism of 1,2-aryl shifts in the Wittig rearrangement of α-metallated benzyl aryl ethers has been investigated by a detailed examination of the behavior of the following ethers· benzyl phenyl ether, benzyl *para*-tert-butyl- and *meta*-tert-butyl-phenyl ethers, benzyl 2-bromo-4-tert-butylphenyl ether and dibenzo[*b,d*]pyran The failure to trap any aldehyde intermediate, the ease of rearrangement for the pyran, the lack of evidence for an aryne intermediate with the benzyl butyl ethers and other circumstantial evidence have led to the proposal of an intramolecular pathway in which radical pairs are generated and then collapse to the isomeric carbinolate

Introduction

Despite copious and definitive studies on some aspects of the Wittig rearrangement of α-metallated ethers, nothing definite is established concerning the mechanism of 1,2-aryl migration in α-metallated benzyl aryl ethers [1]. As with 1,2-aryl migrations in the β-arylethyl carbanionic [2,3] and the α-metallated benzyldiphenylamine [4] systems, such aryl migrations (eqn. 1) pose the following mechanistic questions. (*i*) whether the rearrangement is intramolecular or intermolecular, (*ii*) whether the intramolecular process occurs via a bridged intermediate (II) or via fragments trapped in a solvent cage (III); and (*iii*) whether the reaction involves ion-pair or radical species

Although 1,2-aryl migrations from carbon to carbon [2,3] and from nitrogen to carbon [4] have been shown to be intramolecular, this point

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*For part IX see ref 22
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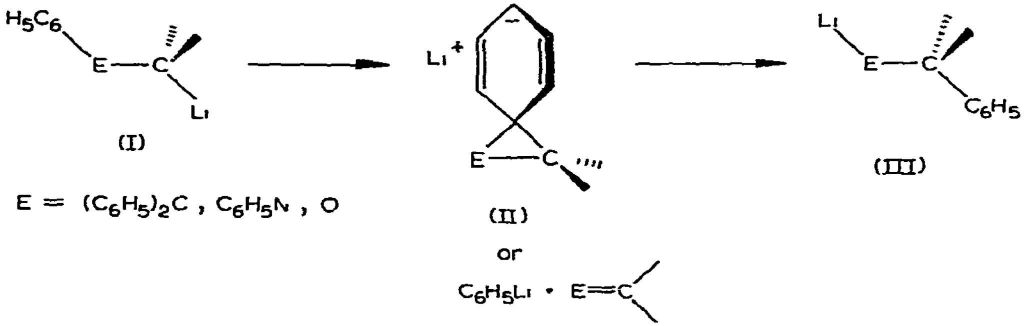
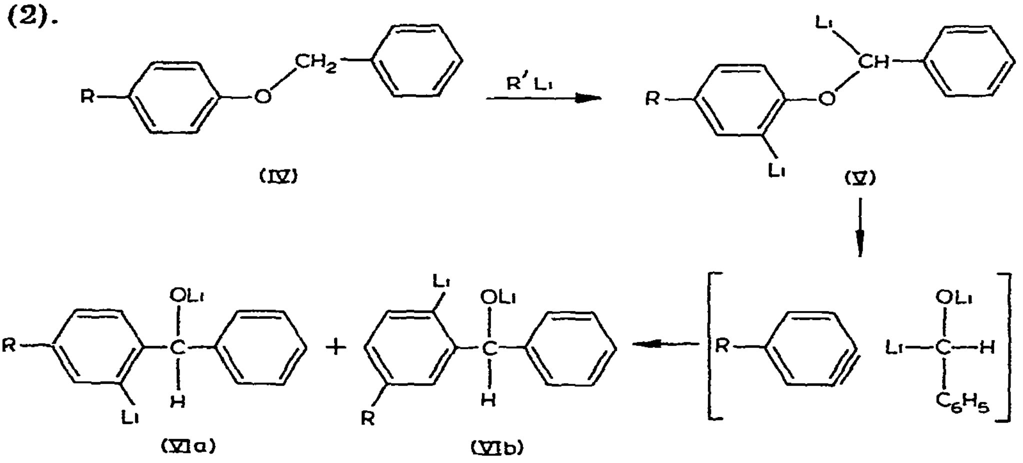
remained to be determined for such migrations from oxygen to carbon (Wittig rearrangement). Furthermore, attempted rearrangements with model systems support the necessity of a bridged aryl intermediate for successful migration in the cases where E in (II) is N [4] or C*. Finally, the question as to the ionic or radical character of such aryl migrations is not as cleanly settled [3] as initial publications in this field [2] have concluded. Indeed, 1,2-alkyl migrations in the Wittig ether rearrangement, originally thought to proceed via an ionic $S_N i$ substitution, have now been shown to involve radical pairs [1].



(1)

In addition to the foregoing general mechanistic questions for all the 1,2-aryl shifts summarized in eqn (1), aryl benzyl ethers present another possible route to the rearranged product, namely the aryne route shown in eqn. (2).



(2)

The ready *ortho*-metallation of various aryl ethers [6] makes the presence of intermediates such as (V) highly likely under the rearrangement conditions. Furthermore, there is a precedent for the elimination of ROM from (V) in the benzyne-derived products reported for the reaction of diphenyl ether with phenylsodium [7]

Therefore, to answer these mechanistic questions, various aryl benzyl ethers were subjected to rearrangement: (*a*) benzyl phenyl ether itself (IV, R = H), in order to look for products ascribable to fragmentation (II, E = O): (*b*)

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* Unpublished studies [5] have shown that, under conditions where 2,2-diphenylpropyllithium rearranges to 1,2-diphenyl-2-propyllithium [6], 2 2-(2,2′-biphenylene)propyllithium does not rearrange Presumably in the latter case the fluorene system is too rigid to permit attainment of a bridged aryl group necessary for rearrangement

dibenzo [*b*,*d*] pyran, to see if a bridging intermediate (II, E = O) were involved in the rearrangement; (*c*) both benzyl *para*-tert-butylphenyl ether (IV, R = t-C_4H_9) and its *meta* isomer, to test whether an aryne process (eqn 2) were important; and (*d*) benzyl 2-bromo-4-tert-butylphenyl ether, as a precursor for generating the corresponding α,2-dilithio benzyl 4-tert-butylphenyl ether and thus again testing for fragmentation.

Results and discussion

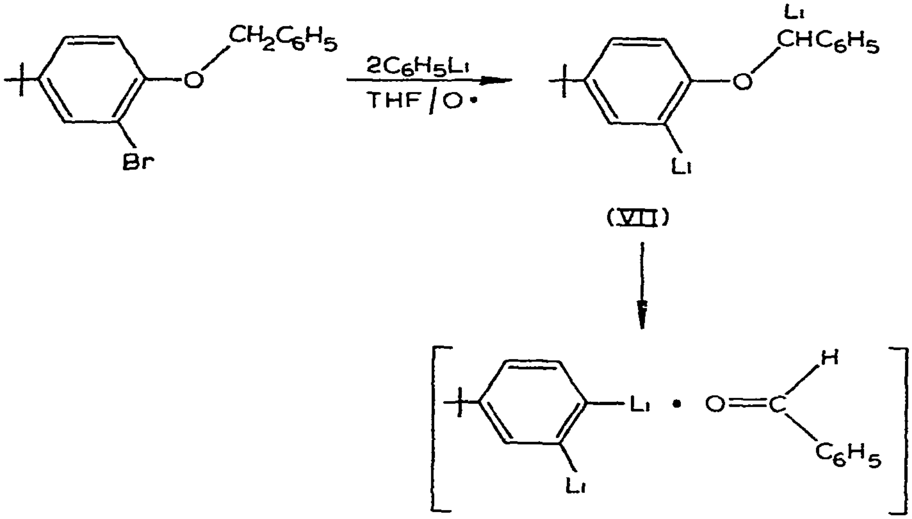
The reported rearrangement of benzyl phenyl ether [8], achieved by treatment with n-butyllithium in tetrahydrofuran, in our hands proceeded in >95% yield to yield diphenylcarbinol upon hydrolysis The reaction was also effected by means of methyllithium in a 1/1 v/v mixture of tetrahydrofuran and 1,2-dimethoxyethane, again in high yield (*ca* 80%) In both cases, the crude product was carefully examined for the presence of the carbinol expected if any intermediate benzaldehyde were captured by the lithium alkyl. However, NMR spectral analysis was unable to detect any n-butyl(phenyl)carbinol or methyl(phenyl)carbinol, respectively, even in mother liquors remaining after the majority of the diphenylcarbinol had been removed. Hence, if any fragmentation as depicted in (II) (E = O) did occur, less than 1%, at most, was able to react with extramolecular lithium alkyl

Dibenzo[*b*,*d*] pyran underwent prompt rearrangement to lithium 9-fluorenoxide when treated with n-butyllithium in THF. In fact, the rearrangement even proceeded readily in diethyl ether. Such behavior contrasts with that of benzyl phenyl ether, which undergoes almost exclusively α-elimination when treated with n-butyllithium in diethyl ether to yield lithium phenoxide and products attributable to phenylcarbenoid intermediates [9]. Again, a thorough search was made for any sign of *ortho*-biphenylyl(n-butyl)carbinol, a product expected to arise if any intermediate *ortho*-phenylbenzaldehyde were intercepted. By comparison with authentic samples, it was established that neither *ortho*-biphenylyl(n-butyl)carbinol nor 9-n-butyl-9-fluorenol were formed in significant amounts. However, some butyl-substituted fluorenol was detected, possibly due to an aromatic butylation of the 9-fluorenoxide similar to that observed with other polynuclear aromatic systems [10].

In individual reactions it was established that the rearrangement of benzyl *para*-tert-butylphenyl ether by n-butyllithium in THF gave only *para*-tert-butyldiphenylcarbinol and the *meta* ether only *meta*-tert-butyldiphenylcarbinol. Hence, the aryne mechanism considered in eqn. (2) cannot obtain, for the mechanism requires that each tert-butylphenyl ether give rise to a mixture of *meta*- and *para*-tert-butylphenyl carbinols.

As a further check on whether the rearrangement of an aryl benzyl ether involved any intermediate benzaldehyde, (II, E = O), benzyl *meta*-tert-butylphenyl and benzyl *para*-tert-butylphenyl ethers were individually rearranged by means of phenyllithium in THF. In both cases, the crude products could be readily analyzed by GLC and the proportion of the corresponding tert-butyldiphenylcarbinol shown to be ca. 95%. In neither case was any diphenylcarbinol detected (<0 5%), the product expected if any benzaldehyde were trapped by phenyllithium.

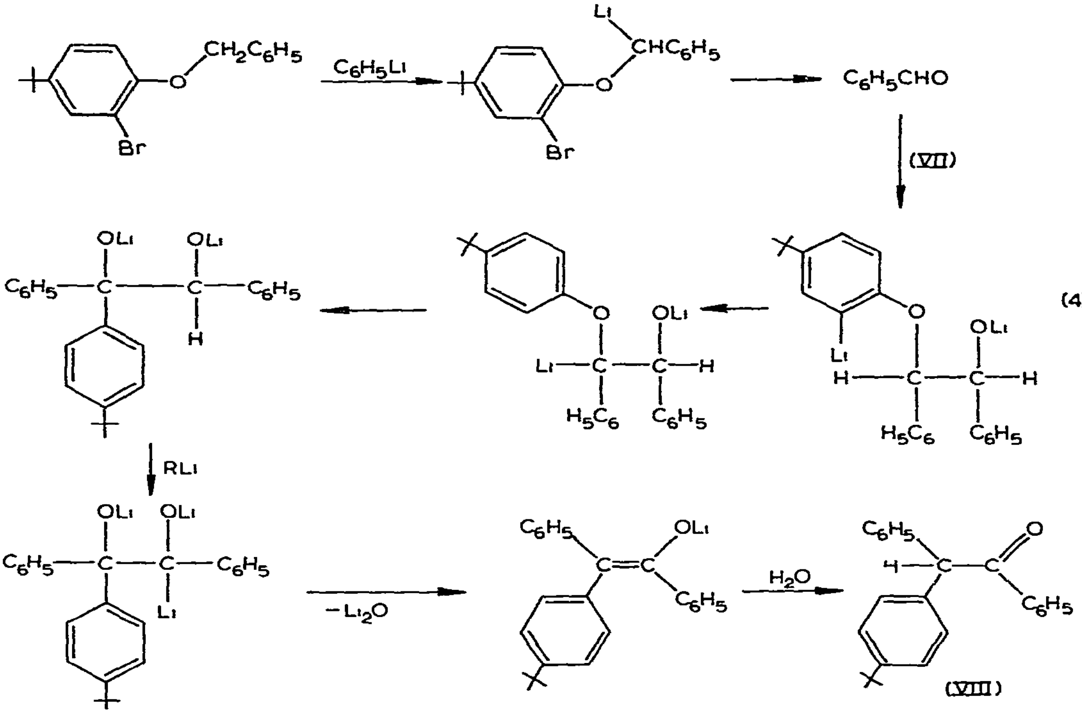
Finally, benzyl 2-bromo-4-tert-butylphenyl ether was treated with two equivalents of phenyllithium in THF at 0°, in order to generate the dilithio derivative (VII) (eqn.3). If any dissociation into organolithium reagent and aldehyde were then to ensue, the rearranged products would again be a mixture of *meta*-and *para*-tert-butyldiphenylcarbinols (VIa and VIb).



(3)

However, when the reaction was carried out, no *meta*- or *para*-tert-butyldiphenylcarbinol was formed. In fact, a normal Wittig rearrangement failed to occur Yet there is no doubt that substantial amounts of (VII) were formed in the early stages of the reaction, as evidenced by the deep red color and by the significant amounts of benzyl *para*-tert-butylphenyl ether detected upon hydrolysis. Apparently the high anionic character of (VII) inhibits the Wittig rearrangement and thus permits the α-elimination leading to *para*-tert-butylphenol (30%) and possibly a polyphenylmethylene product [9] to be significant. The high proportion of biphenyl can be ascribed to a benzyne pathway arising from the bromobenzene and phenyllithium [11]. In addition, a 5% yield of *para*-tert-butylbenzhydryl phenyl ketone (VIII) was obtained. The origin of this product can be rationalized by the following sequence (eqn 4): (*a*) α-metallation of the starting bromo ether and β-elimination to yield benzaldehyde and a labile 2-bromo-4-tert-butylphenyllithium; (*b*) capture of the aldehyde by (VII) at the more reactive benzylic—lithium bond; (*c*) α-metallation by α,β′-transmetallation and a Wittig rearrangement, and (*d*) the metallative elimination of Li_2O [12] to yield the enolate precursor to (VIII). Clearly ketone (VIII) could not have survived as such in the organolithium reaction mixture.

One other observation bears on the mechanism of these 1,2-aryl shifts. An attempt was made to observe NMR signals due to chemically induced dynamic nuclear polarization [13] just after mixing either benzyl phenyl ether or dibenzo[*b,d*]pyran with n-butyllithium. Although no signal enhancement was observed, during the first 60 seconds after mixing, the NMR signals in the region, 4.0 - 8.0 ppm, were obliterated. As the rearrangement went to completion, the signals due to the resulting lithium carbinolate again became fairly

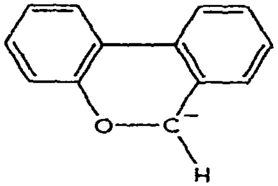


(4)

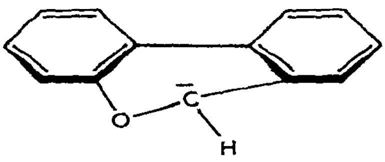
sharp. Even though the presence of short-lived free radicals was not revealed by a CIDNP signal, the obliteration of the NMR signal does support the presence of relatively long-lived paramagnetic reagents in the reaction mixture. However, these experimental findings are suggestive, rather than decisive, evidence that this rearrangement proceeds via a radical mechanism.

In light of the foregoing results we can now address ourselves to the mechanism of 1,2-aryl migration in the Wittig rearrangement First of all, the behavior of the aryl benzyl ethers and the failure to trap any aldehyde intermediate or any other reaction fragment are consistent with an intramolecular process. Secondly, the aryne mechanism proposed in eqn. (2) has been shown not to be involved under these reaction conditions Thirdly, the readiness with which dibenzo[*b*,*d*]pyran undergoes rearrangement to 9-fluorenol, both in tetrahydrofuran and in ethyl ether solution, is in our judgment a telling point against invoking a bridged pathway for this 1,2-shift [cf. (II), E = O].

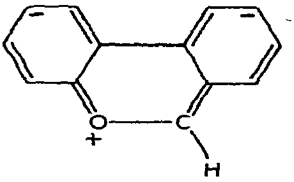
The basis for our interpretation of the dibenzo[*b*,*d*]pyran experiment lies in the following considerations First of all, the metallated ether itself (XII) could exist in solution as almost a completely planar anion (XIIa) or as a non-planar structure with an axial anion (XIIb). The known C—O—C bond angles in aryl ethers (118° - 123°) should permit structures such as these to exist without excessive angle strain. The π-overlap of both the benzylic anion and the oxygen's unshared electron pair with their respective aryl π-clouds should be maximized in (XIIa) but still be considerable in (XIIb) or (XIIc). This overlap in (XIIa) may contribute some anti-aromatic character to the central ring, and hence destabilization, but the total overlap in (XIIa) and (XIIb) should contribute to their overall electronic stabilization. Hence, from bond angle and electronic considerations, anion (XII) would not seem to be unduly strained.



(XIIa)

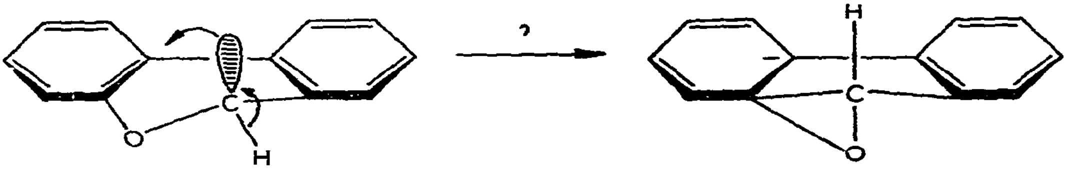


(XIIb)



(XIIc)

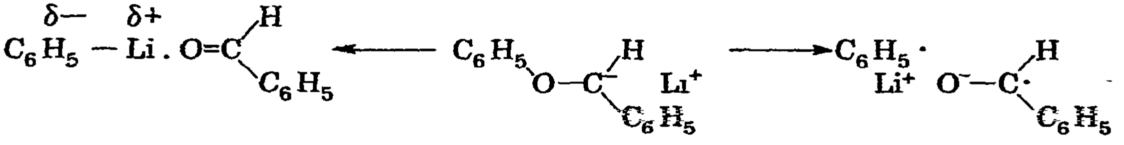
In contrast with the open-chained metallated ethers, however, the formation of a bridged intermediate or transition state from (XII) would entail almost complete loss of the benzylic anionic overlap shown in (XIIc). The resulting bridged structure (XIId), a cyclopentene oxide anion, could only be formed from (XIIb) by strained torsion about the benzylic carbon—aryl bond, necessary to have the anion's orbital interact with C_1 of the aryloxy group in a σ-bonding fashion. Thus, although the attainment of structure (XIId) would require a larger investment of energy than that expected for open-chained ethers [e g. (II), E = O], it is observed that dibenzo[*b*,*d*]pyran actually undergoes the Wittig rearrangement more readily, namely in ethyl ether solution.



(XIIb) (XIId)

Finally, a strong argument can be made against the operation of a nucleophilic S_Ni mechanism, either with dibenzo[*b*,*d*]pyran or with any other benzylic aryl ether. In effect, such a mechanism requires a carbanion to attack the π-cloud of an electron-rich aryloxy group under relatively mild conditions. The intermolecular counterpart of such a reaction, the alkylation of aryl ethers by direct displacement of an alkoxyl group, is to our knowledge unknown.

These considerations compel us to postulate some type of fragmentation process, wherein the α-metallated benzyl aryl ether breaks into a pair of reactants held together in a solvent cage until they recombine to form the lithium carbinolate. Two different fragmentation schemes can be entertained, either an ionic, (XIII), or a radical anionic process, (XIV). The failure to detect any alkyl(phenyl)carbinol, derivable from the lithium alkyl used, under a wide variety of experimental conditions, seems to argue against a pathway involving

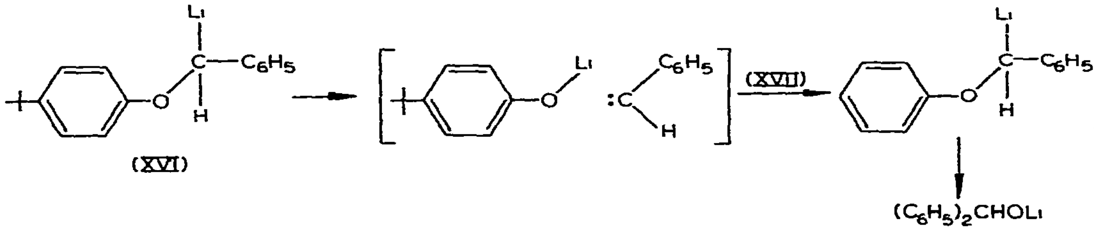


(XIII) (XV) (XIV)

(XIII). A large excess of n-butyllithium, very much more reactive than the phenyllithium in (XIII), did not intercept any benzaldehyde. In the reported rearrangement of dibenzyl ether [14], a five-fold excess of the less reactive methyllithium was able to trap up to 25% of the benzaldehyde intermediate, even though the external organolithium reagent was competing with the much more reactive, internal benzyllithium.

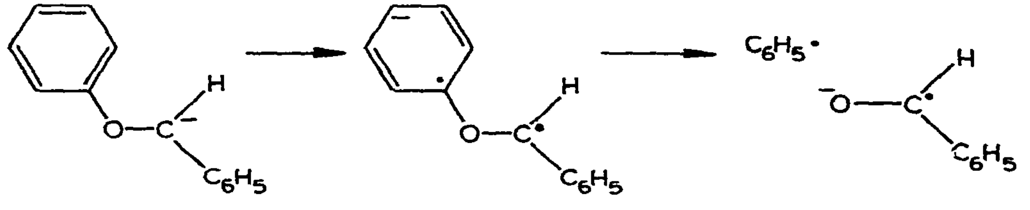
On the other hand, homolysis of the phenyl—oxygen bond in (XV) with the formation of (XIV) is in accord with the temporary obliteration of the NMR signals in the rearrangements of benzyl phenyl ether and dibenzo[*b*,*d*]-pyran, for the radical anion of the aromatic aldehyde would at once be a relatively long-lived paramagnetic intermediate, which would explain the NMR broadening, and a derivative resisting the attack of an external organolithium reagent on the C—O linkage

Finally, it remains to learn whether there is any connection between the foregoing view of 1,2-aryl shifts in the Wittig rearrangement and the concurrent α-eliminations leading to carbenoid reactions [9]. Both processes stem from the α-metallated ether, the difference being that the rearrangement requires the solvent-separated ionization of the carbon—lithium bond [12,15,16]. This is shown clearly with benzyl phenyl ether by the dominance of the Wittig rearrangement in THF (90% of benzhydrol) and that of α-elimination in diethyl ether (81% of phenol) [9]. In the present work the possibility of a reversible α-elimination was tested by generating (XVI) in the presence of lithium phenoxide, (XVII) (eqn.5). If any phenylcarbene were ever free, it should combine with (XVII) and, by rearrangement, eventually lead to diphenylcarbinol. Since none of this carbinol was detected, no reversible α-elimination is operative in THF solution (eqn.5).



(5)

That the rearrangement proceeds through the ionized form, (XV), suggests that intramolecular electron transfer from the benzylic ion to the aryloxy ring may be the pathway leading to fragment pair (XIV). If the ease of rearrangement is related to the ease of forming (XVI), then the failure of (VII) to rearrange is understandable in terms of the resistance an *ortho*-lithiophenoxy ring would offer to electron acceptance. Also the remarkable ease with which



(XV) (XVI) (XIV)

dibenzo[*b,d*]pyran rearranges, even in diethyl ether, can be ascribed to the superior electron affinity of the biphenylyl system [17]. This view of the Wittig rearrangement of aryl benzyl ethers bears a strong similarity to the radical anionic mechanism proposed for the alkali—metal cleavage of aryl ethers [18,19].

Experimental

General operations

Infrared spectra were recorded with a Perkin—Elmer spectrophotometer, model 137, proton NMR spectra with a Varian A—60 and mass spectra with a MAT—Varian CH—5. The GLC analyses were performed on an F & M 720, equipped with 2 ft columns packed with 10% silicone gum rubber on Chromosorb W and programmed to heat up at a rate of 3°/min between 150° and 290°. Melting points were taken in capillary tubes with a Thomas—Hoover oilbath apparatus and are uncorrected. All operations involved in the preparation, transfer and interconversion of organometallic reagents were conducted under an atmosphere of dry, oxygen-free nitrogen.

Starting materials

Benzyl phenyl ether. A mixture of 10.5 g (0.112 mol) of phenol, 12.6 g (0.10 mol) of benzyl chloride and 13.8 g (0.10 mol) of anhydrous potassium carbonate was heated and stirred under reflux in 20 ml of acetone for 12 h. The cooled reaction mixture was treated with 100 ml of 4 *N* sodium hydroxide solution and the organic layer extracted by 3 × 100 ml portions of ether. The ethereal layers were separated, dried and evaporated to yield the crude product. Distillation provided 17.0 g (92%) of colorless benzyl phenyl ether [8] b.p. 95 - 96°/0.15 mmHg, upon solidification, m.p. 37 - 38°. Its NMR spectrum ($CDCl_3$) showed the CH_2 peak at 5.05, multiplets (5H) at 6.8 - 7.5 and a phenyl singlet at 7.38 ppm.

Benzyl meta-tert-butylphenyl ether. This unreported substance was prepared analogously and in comparable yield, b.p. 78 - 79°/0.2 mmHg. NMR spectrum in $CDCl_3$: 1.25, s (9H), 4.90, s (2H); and 6.6 - 7.35, m (9H). Analysis found: C, 84.74, H, 8.45, $C_{17}H_{20}O$ calcd.: C, 84.96; H, 8.39%.

Benzyl para-tert-butylphenyl ether. This product, prepared analogously, melted at 59 - 60°. NMR spectrum in $CDCl_3$. 1.30, s (9H), 5.05, s (2H) and 6.85 - 7.4, m (9H). Analysis found. C, 84.83; H, 8.55, $C_{17}H_{20}O$ calcd.: C, 84.96, H, 8.39%.

Dibenzo[b,d]pyran [20]

Benzyl ortho-nitrophenyl ether. The *ortho*-nitrophenol (39.6 g, 0.285 mol) was added to a solution of 15.8 g of potassium hydroxide in 400 ml of a 1/3 (v/v) water—ethanol medium. After 3 h of stirring, 35.0 g (0.276 mol) of benzyl chloride were added and the mixture stirred at reflux for 48 h. The ethanol was then evaporated under reduced pressure and the residue treated with 100 ml of 3 *N* potassium hydroxide solution. The organic product was taken up in 300 ml of ether, the ether extracts dried over anhydrous calcium sulfate and the solvent evaporated. The product distilled at 140 - 142°/

0 5 mmHg, 38.6 g (61%). NMR spectrum ($CDCl_3$): 4.82, s (2H) and 6 45 - 7.5 ppm, m (9H).

ortho-Aminophenyl benzyl ether To a solution of 38 5 g of the aforementioned ether in 300 ml of benzene were added 44 g (0.79 g-atom) of iron powder, which had previously been activated by washing with concentrated hydrochloric acid and then drying. The stirred and heated suspension was then treated with 12 ml of water in small portions. After the vigorous reaction had subsided, the suspension was filtered. Addition of concentrated hydrochloric acid to the filtrate caused precipitation of the amine hydrochloride, (20.3 g) Recrystallization from 95% ethanol yielded 18.6 g, m.p. 203 - 204°.

Dibenzo[b,d]pyran To a suspension of 18.6 g (0.079 mol) of the abovementioned amine hydrochloride in 350 ml of 2 *N* sulfuric acid at 0° were added 5.6 g (0.081 mol) of sodium nitrite in 25 ml of water over a period of 15 min. After 30 min of stirring the solution was filtered and then treated with 4 g of copper bronze. The suspension was stirred for 16 h during which time an additional 4 g of copper bronze was added in portions The reaction mixture was filtered and the filtrate extracted with 3 × 100 ml portions of ethyl ether. The brown oil, which was obtained by the drying of the ethereal extracts with anhydrous calcium sulfate and evaporating the solvent, was chromatographed on neutral alumina (20 × 600 mm) with hexane to give 6 3 g of colorless product (44%), which upon distillation resulted in 5.3 g of dibenzo[*b*,*d*]pyran, b.p. 99 - 101°/0 5 mmHg. NMR spectrum ($CDCl_3$): 5 01, s (2H), 6.8 - 7 45, m (6H) and 7.5 - 7.8, m (2H). IR spectrum (neat) 3040 m, 2830 m, 1600 s, 1485 s, 1440 s, 1370 w, 1295 m, 1245 s, 1195 s, 1040 s, 1015 s, 815 s, 755 vs, 735 s and 725 s cm^{-1}

Benzyl 2-bromo-4-tert-butylphenyl ether

A solution of 24.0 g (0 10 mol) of benzyl tert-butyl ether and 8.2 g (0 10 mol) of anhydrous sodium acetate in 120 ml of glacial acetic acid was treated dropwise with 106 ml of *N* bromine (0.106 mol) in glacial acetic acid. After 15 h of stirring at 25° 200 ml of 5% solution of sodium thiosulfate was added and the organic layer taken up in ethyl ether. The ether layer was washed with aqueous sodium hydroxide solution and with water and then dried over anhydrous magnesium sulfate. After removal of solvent and distillation 30 g (75%) of the pale yellow product were obtained, b.p. 159 - 161°/ 0 10 mmHg NMR spectrum ($CDCl_3$): 1.18, s (9H), 4 92, s (2H), 6.75, d (1H), 7 05 - 7.45, m (6H) and 7 58, d(1H). MS(70eV). 320 (39, *P*), 318 (39, *P*), 239 (31, *P*—Br), 92 (67, C_7H_8) and 91 (100, C_7H_7). Analysis found: C, 64.15, H, 6.28; $C_{17}H_{19}BrO$ calcd : C, 63.96, H 6 00%

Rearrangement of benzyl phenyl ether

Typical rearrangement A stirred solution of 0.92 g (5.0 mmol) of benzyl phenyl ether in 25 ml of anhydrous tetrahydrofuran was treated with 6.0 ml of 2.1 *N* n-butyllithium (12.6 mmol) in hexane. The resulting red solution was stirred at room temperature for 48 h and then hydrolyzed. Usual work-up and drying with anhydrous calcium sulfate yielded 0.90 g of oil, whose NMR spectrum was identical with that of diphenylcarbinol (98%). Upon standing the oil solidified and was recrystallized from petroleum ether (b r. 30 - 60°), m.p. 64 - 66°

Attempted trapping of benzaldehyde intermediate. Methyllithium, prepared from methyl idiode and lithium metal in ethyl ether solution, was freed of solvent under reduced pressure and was then redissolved in anydrous tetrahydrofuran-1,2-dimethoxyethane (1/1 v/v) to give a 1.1 *N* solution. One gram of benzyl phenyl ether (5.5 mmol) was added to 10 ml of the methyllithium solution and the resulting red solution thereupon allowed to stir for 4 days at room temperature. Usual work-up gave 0.80 g of oil, whose NMR spectrum was essentially that of diphenylcarbinol with a small rounded absorption between 3.4 - 3.5 and a weak multiplet between 0.9 - 1.3 ppm. No absorption was detectable between 3.7 and 5.2, whereas the benzylic proton of methylphenylcarbinol, if present, should be displayed at 4.65 ppm.

In another attempt, 1.0 g (5.5 mmol) of the ether in 30 ml of a 1/1 THF—DME mixture was treated with 84 mmol of n-butyllithium in hexane at 0°. Usual work-up after 72 h at room temperature yielded 1.1 g of oil, whose NMR spectrum again was essentially that of diphenylcarbinol, having no absorptions discernible between 3.8 - 5.0 ppm where n-butylphenylcarbinol should reveal itself. There were some absorptions between 0.9 - 3.0 ppm, hence the diphenylcarbinol was largely removed by crystallization and the residue recovered from the mother liquors reexamined. Again, no benzylic signals expected for the carbinol were observed, only signals ascribable to residual solvent or decomposition products of the solvents were detected.

Attempted detection of a CIDNP signal Into an NMR tube previously purged with nitrogen were introduced 0.10 g of benzyl phenyl ether (0.55 mmol) and 0.5 g of anhydrous THF. The tube was closed with a rubber septum and an NMR spectrum of the solution then recorded. Thereafter, 0.5 ml of 2.1 *N* n-butyllithium (1.05 mmol) in hexane was added to the NMR tube by means of a syringe. The benzylic region was rapidly scanned ca. 20 s after mixing. Although no CIDNP signal, either as an enhancement or as a negative signal, was observed, all spectral signals in this region were obliterated. Another set of scans after 60 s now showed the small sharp singlet at 5.4 ppm, ascribable to lithium diphenylcarbinolate. With time this signal grew, but the signal due to starting ether never did reappear, even in low intensity or as a shifted signal due to $C_6H_5O{-}C^{-}H{-}C_6H_5$.

The same disappearance of the ether signal was observed when the reaction and NMR scans were conducted in TMEDA solution.

Work-up of the foregoing reactions and NMR analysis of the hydrolysates showed that only diphenylcarbinol was formed in each case.

Rearrangement of dibenzo[b,d]pyran

Typical rearrangement A solution of 0.91 g (5.0 mmol) of dibenzo[*b,d*]-pyran in 20 ml of THF at 0° was treated with 6 ml of n-butyllithium in hexane. The green reaction mixture was stirred at room temperature for 48 h. Usual hydrolytic work-up gave 0.80 g of product, whose NMR spectrum showed the absorptions expected for 9-fluorenol, as well as signals in the 3.3 - 3.6 and 0.8 - 1.7 ppm regions. Crystallization from chloroform afforded 0.55 g (61%) of pure 9-fluorenol, m.p. 152 - 154°, as confirmed by mixture m.p. and both IR and NMR (2.02, 5.5 and 7.25 - 7.75 ppm) comparisons.

Repetition of this reaction in diethyl ether solution over a 5-day period gave a crude product whose NMR spectrum was identical with that of the THF reaction. After the bulk of the 9-fluorenol was removed by recrystallization, the mother liquor was combined with that of the THF run and the chloroform removed. The residue was chromatographed on a 20 × 500 mm silica gel column by use of n-hexane and chloroform as successive eluants. By means of TLC on alumina with a 3/1 petroleum ether/ethyl ether developer the chromatographic fractions were monitored. In addition to 9-fluorenol, early fractions contained substance(s) having an aromatic/alipathic proton ratio of 9/22 (at 7.0 - 7.7 and 0.8 - 1.7 ppm, respectively). A later fraction, showing only one spot by TLC, had the following spectral characteristics. NMR: 0.7 - 1.7, m (7H); 2.4 - 2.9, m (2H), 6.6 - 7.8, m (10H). IR: 3450 (br) and 3550 (sh) cm^{-1}. MS· 238(3); 237(5), 220(7), 196(11); 191(11); 182(75) and 181(100). These data are consistent with butyl group incorporation in the 9-fluorenol. However, comparison with the NMR spectra of authentic *ortho*-biphenylyl(n-butyl)-carbinol, 9-n-butyl-9-fluorenol, *ortho*-1-pentenylbiphenyl and 9-1-butylenefluorene [21] showed that neither of the above chromatographic fractions contained these compounds as principal components.

Attempted detection of a CIDNP signal As with benzyl phenyl ether, 259 mg of the cyclic ether in 0.7 ml of THF was treated with 1 0 ml of 2.1 *N* n-butyllithium. Within 20 s of mixing an NMR spectral scan showed the complete disappearance of NMR signals between 3.7 and 8.0 ppm. After 60 s the benzylic peak of the cyclic ether at 5 0 ppm showed faintly, as did the phenyl multiplet. After 5 min both signals began to emerge, but both were still broadened After a further 20 min both peaks were distinct again but still broad

Rearrangements of the benzyl meta- and para-tert-butylphenyl ethers by means of n-butyllithium

In separate experiments, 2 4 g (0.01 mol) of the ether in 50 ml of THF was treated at 0° with 10 ml of 2 1 *N* n-butyllithium in hexane. After a 48 h reaction period at room temperature the usual work-up gave the diarylcarbinol· (*a*) *para* Isomer, 2.4 g, m.r. 60 - 69°, whose NMR spectrum was essentially that of pure *para*-tert-butyldiphenylcarbinol, m p. 80 - 82° from hexane. NMR spectrum: 1.28, s (9H), 5.8, s (1H) and 7.2 - 7.4, m (9H). IR spectrum· 3350 (br) and 3560 (sh) cm^{-1}. Analysis found: C, 85 07; H, 8.58; $C_{17}H_{20}O$ calcd.: C, 84.96, H, 8.39%. (*b*) *meta* Isomer, 2.3 g of oil, NMR spectrum. 1.28, s (9H), 5 7, s (1H) and 7.1 - 7.4, m (9H), IR spectrum: 3350 (br) and 3560 (sh) cm^{-1}. Crystallization of this oil from hexane gave a colorless solid, m.p. 65 - 66° Analysis found· C, 84.90, H, 8 20. $C_{17}H_{20}O$ calcd.· C, 84.96; H, 8.39%.

Although the tert-butyl signals of the two isomeric products coincide, their benzylic signals do not. Admixture of authentic samples of the *para* and *meta* carbinol isomers in a 90/10 proportion still shows the minor component as a clear shoulder peak at 5.7 ppm. Accordingly, we conclude, from examining the NMR spectrum of the crude product from each ether rearrangement, that none of the other carbinol (max. <5%) is simultaneously formed. Thus, for example, the *para*-tert-butyl ether gave only the *para*-tert-butylcarbinol

Rearrangements of the benzyl meta- and para-tert-butylphenyl ether by means of phenyllithium and the search for diphenylcarbinol

In individual runs, 12.0 g (0.050 mol) of the benzyl tert-butylphenyl ether in 200 ml of anhydrous THF was treated with 50 ml of 2 *N*-phenyllithium (from Alpha Chemicals, solution in a 70/30 mixture of benzene and ethyl ether) at 0°. The initial yellow color soon gave way to a dark purple color as the ice bath was removed and the solution allowed to stand at 25° for 24 h. Usual hydrolytic work-up and separation gave ca. 13 g of neutral product, which by GLC in each case was shown to be ca 95% of the corresponding tert-butylphenylcarbinol. The remaining 5% was a mixture of biphenyl and the corresponding tert-butylphenol. Significantly, neither these crude oils nor the residual oils obtained after crystallizing out the pure tert-butyl-diphenylcarbinols showed any trace of diphenylcarbinol itself. This demonstrated that no detectable capture of any intermediate benzaldehyde by phenyllithium had occurred.

Acidification of the original, basic aqueous layer from the hydrolytic work-up yielded ca. 0.3 g of an oil consisting of phenol and the tert-butylphenol.

Rearrangement of benzyl para-tert-butyl ether by means of phenyllithium in the presence of lithium phenoxide· attempted trapping of phenylcarbene

The lithium phenoxide was prepared by adding 80 ml of 1.4 *N* n-butyllithium to 9.4 g (0.10 mol) of phenol After a 20 min stirring period 12 0 g (0.10 mol) of benzyl *para*-tert-butyl ether was introduced, followed by an additional 80 ml of 1.4 *N* n-butyllithium. The dark purple solution was stirred for 30 h and then worked up in the usual manner, except that the organic layer was repeatedly extracted with 4*N* sodium hydroxide solution The neutral organic layer yielded 11.9 g of crude oil which by GLC analysis was predominantly *para*-tert-butyldiphenylcarbinol No trace of diphenylcarbinol was discernible

Attempted rearrangement of benzyl 2-bromo-4-tert-butylphenyl ether

A solution of 14.8 g (0.046 mol) of the benzyl ether in 200 ml of anhydrous THF cooled to 15° was treated with 50 ml of 2 *N* phenyllithium in benzene—ethyl ether. The solution turned successively yellow, green and then greenish brown during the 12 h at —10°. Hydrolysis* and GLC analysis of an aliquot showed the presence of *para*-tert-butylphenol, biphenyl, benzyl *para*-tert-butylphenyl ether, starting ether, and compound (A) in an 8 / 6 / 3 / 1 / 2 ratio. However, there was no sign of *para*-tert-butyldiphenylcarbinol or diphenylcarbinol. (The foregoing two components would have been easily seen under the GLC conditions used)

The original reaction mixture was allowed to stand for 5 h at room temperature and then worked up in the usual way. By GLC analysis bromobenzene (5%), *para*-tert-butylphenol (30%), biphenyl (20%), benzyl *para*-tert-butylphenyl ether (2%), starting ether (1%), compound (A) (5%), polymer (30%) and several unknowns (7%).

The total crude oil (12 g) was subjected to distillation. The fraction

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* Hydrolysis was carried out with 2 *N* aqueous sodium hydroxide solution Separate acidification of the aqueous layer yielded only *para*-tert-butylphenol, which was added to the organic layer for GLC analysis Thus, compound (A) was not exposed to acid and hence it is unlikely that this ketone arose from a pinacol rearrangement of a glycol precursor

boiling at 160 - 165° (0.1 mmHg) was chromatographed on silica gel and eluted, in turn, with petroleum ether, petroleum ether with 5% benzene and petroleum ether with 10% benzene. Earlier fractions gave 500 mg of compound (A), which after recrystallization from 95% ethanol melted at 108.5 - 110°.

Analysis found: C, 87.40; H, 7.24. $C_{24}H_{24}O$ calcd : C, 87.76, H, 7.36%. NMR spectrum in $CDCl_3$: 1.17, s (t-C_4H_9), 6.58, s (1H) and 6.9 - 7.7, m (14H) IR spectrum in $CHCl_3$. >3100, clear, 1640 s (C=O), 1600 s. MS. 328 (40,*P*), 223(27,*P*—C_6H_5CO), 179(45) and 178(100)

These data are in best accord with compound (A) being *para*-tert-butylbenzhydryl phenyl ketone, the *P*—105 peak, signaling the loss of the benzoyl fragment, is especially decisive

Later fractions from the chromatography yielded only pale yellow, waxy solids whose NMR spectra showed only two broad peaks, one in the tert-butyl and one in the aromatic regions.

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