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STERIC EFFECTS IN THE METALATION OF SOME AROMATIC SUBSTRATES WITH ALKYLLITHIUM REAGENTS

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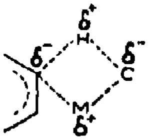
INTRODUCTION

A current idea on the mechanism of the metalation reaction indicates that the process is "protophilic"[1] in character proceeding via a 4-member ring transition state without appreciable disruption of the aromatic π orbitals.



Others[2] have put forth similar ideas. This concept has seemed applicable to metalation by alkyllithium reagents in such reactions as substitution of alkylbenzenes, biphenyl[3] and the *meta*- and *para*-positions of trifluoromethylbenzene[3]. However, an older and widely accepted concept[4] invokes a cyclic transition state formed from a coordination complex of RLi with donor functional groups on the ring. The major value of this latter idea has been the correlation it allows of the extensive data on substitution of the ring at positions *ortho* to donor groups or adjacent to donor heteroatoms in heterocyclic ring systems. Another role of the complex between RLi and donor atoms is to increase, by an inductive effect, the polarity of the ring C–H bonds and thereby aid in removal of H^+ from nearby positions by the carbanion or incipient carbanion of the metalating agent[5]. In any event, it seems clear that the cyclic transition state from the donor–RLi complex is not the only route of metalation by RLi.

The earlier ideas on the metalation mechanism require that the position of substitution by the metal atom be determined in the slow step. While a lithium atom should have a low steric requirement, the proposed close association with the relatively bulky alkyl anion or incipient anion should yield steric inhibition of substitution at positions adjacent to large groups. Also large alkyl anions from RLi should intensify the inhibition. Thus one should expect alteration in substitution position as a function of the steric requirements of the system. Also, one should observe in competition experiments between substrate molecules containing substituents of differing size, or between RLi reagents of differing size, a faster rate of reaction in the systems of lower steric requirements.

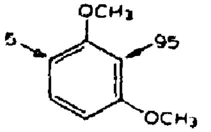
Among the large amounts of data now available on the reaction of metalation of aromatic and heterocyclic substrates with alkyllithium reagents are some observations which suggest a low steric requirement for the reaction. This was indicated in the product composition data from the metalation of anisole, phenetole, and 1,3-dimethoxybenzene given in the preceding paper[3]. Other recent observations which support this view are the report by Gronowitz[6] that 3-tert-butoxythiophene is metalated in the 2-position, and the report by Finnegan and Altschuld[7] that phenyl tert-butyl ether is metalated in the *ortho*-position by n-butyllithium.

It has been the objective of the present work to examine some sterically hindered metalation reactions, with careful analysis of product composition, in order to determine alterations in rate of attack at different ring positions caused by steric factors.

RESULTS AND DISCUSSION

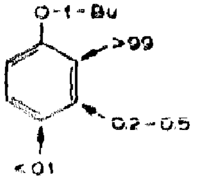
Since anisole metalates completely (>99.9%) in the *ortho*-position with n-BuLi[3], two runs were made with tert-BuLi as the metalating agent. One run in ether (41% conversion of anisole) and the other in cyclohexane (55% conversion), both at the boiling point of the solvent for 10 hours, showed no detectable metalation at other than the *ortho*-position.

1,3-Dimethoxybenzene with tert-BuLi in ether gave 45–60% of carboxylic acid mixture, analysis of which indicated ring metalation in the position and relative amounts shown. Since the reliability of the analyses are about ±1%, the results are essentially the same as found[3] for n-BuLi metalation of 1,3-dimethoxybenzene.



Prior to the report of the work by Finnegan[7], we carried out the metalation of phenyl tert-butyl ether with n-BuLi in cyclohexane at the reflux temperature for 12 hours. The carboxylic acid mixture represented 76% conversion of the ether. No substitution in the *meta*- and *para*-positions could be detected, and it was established that a level of 0.1% of these isomers in the carboxylic acid mixture could easily have been detected. Thus phenyl tert-butyl ether metalates *ortho* with seemingly as high a degree of selectivity as does anisole[3]. It was of interest that the tert-butoxy group undergoes, during the metalation reaction, about 2% of cleavage of the ring carbon-to-oxygen bond yielding phenyllithium and virtually none of the "normal" alkyl carbon-to-oxygen bond cleavage.

Turning to a more sterically hindered case, we carried out the metalation of phenyl tert-butyl ether with tert-butyllithium (cyclohexane reflux for 12 hours).



Product distribution was as shown. Since no *meta*-metalation was observed with n-BuLi, the small amount observed with tert-BuLi may represent a slight steric inhibition of *ortho*-metalation.

The above results point up the insensitivity of the metalation reaction to steric inhibition in systems which allow for competition between the available ring positions in the substrate (intramolecular competition). It then became of interest to study intermolecular competition. Even though both anisole and phenyl tert-butyl ether metalate virtually exclusively in the *ortho*-position, a competition between those substrates for insufficient alkyllithium might reveal differences in rate of attack which would be a function of the size of the ring substituent. It is well recognized that competition experiments will not yield quantitative data on relative rates, but do yield a qualitative indication of which substrate reacts faster providing both substrates react by the same mechanism and neither is consumed in significant amount by a side reaction. These conditions are likely met in the metalation reaction. In an experiment involving equimolar amounts of anisole, phenyl tert-butyl ether, and n-butyllithium in cyclohexane, it was evident that anisole was consumed faster. These results seem to indicate the operation of a steric factor; however, a similar experiment with tert-butyllithium showed no discrimination above experimental error. In the latter case the determination was made both at 3 hours and 12 hours of reaction, which we knew from other data represented two sharply different degrees of consumption of substrate molecules.

In another type of competition experiment, we allowed equimolar amounts of n-butyllithium and tert-butyllithium to compete for an insufficient amount of substrate phenyl tert-butyl ether in cyclohexane. In several such experiments at different reaction times, it was clearly evident that the tert-butyllithium reacted significantly *faster* than n-butyllithium.

The results of the orientation studies and the competition experiments do not seem to be in accord with the rate determining protophilic attack mechanism outlined above, because of the steric insensitivity which the reaction seems to show. The concept of a rate-determining removal of ring hydrogen has been supported, for metalation by alkyllithium reagents, by the hydrogen isotope effect observed only for the metalation of thiophene by n-butyllithium[8], and it seemed desirable to check for the presence of a hydrogen isotope effect in the metalation of anisole. Anisole-2-*d* was metalated with n-butyllithium in cyclohexane at reflux temperature (ca. 75°), the resulting *o*-lithioanisole carbonated and the carboxylic acid analyzed for deuterium. The reaction had occurred with an isotope effect (k_H/k_D) of the range of 6.0–8.2, which is in general agreement with the earlier[8] thiophene results. Since the magnitude of an isotope effect has been observed to depend on steric factors[9], we repeated the determination with tert-butyllithium and the value found was 6.0–7.5, not significantly different from the one above. These results support the generality of a rate-determining cleavage of the ring carbon-to-hydrogen bond during alkyllithium metalations.

The incompatibility of orientation results in sterically hindered systems and the isotope effect data seem to indicate that the orientation of the lithium atom is determined in a step of low steric requirement which *precedes* rather than occurs simultaneously with the step of cleavage of the ring carbon-to-hydrogen bond. In order to accommodate these and other accumulated data on the metalation reaction,

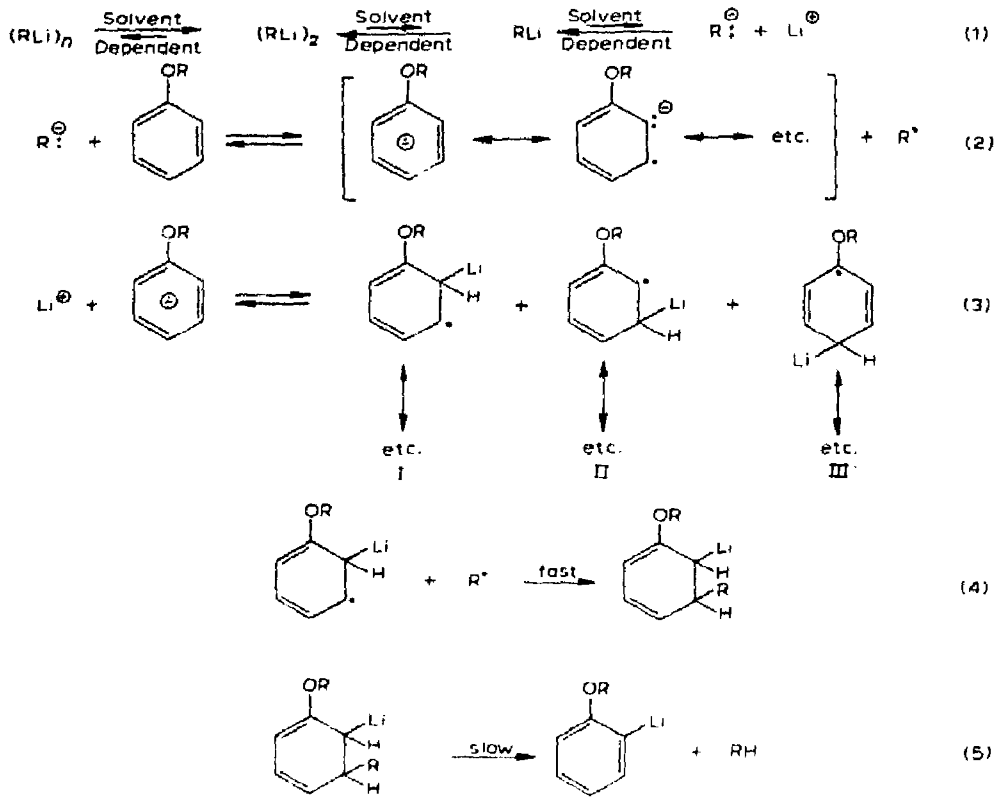


CHART I

we propose a multistep mechanism shown schematically in Chart I involving intermediate radical anions. It is believed that this mechanistic proposal requires additional experimental testing well beyond the results presented in the present paper; however, there are a number of previously uncorrelated observations reported in the literature which bear strongly on the proposed mechanism. These are presented and the mechanism is rationalized in more detail as follows.

Step (1) involves the dissociation of the alkyllithium polymer to the rather stable dimeric form[10] and dissociation to low equilibrium concentrations of monomer and ions or ion pairs. Formation of low equilibrium concentrations of ions is supported by conductivity studies on solutions of n-butyllithium and ethyllithium in hexane, benzene and tetrahydrofuran[11]. An alternative ionization path could involve the dimer, $(RLi)_2 \rightleftharpoons (R_2Li)^- + Li^+$.

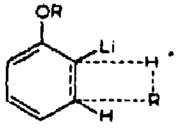
Step (2) involves the donation of a single electron from the carbanion to the aromatic substrate yielding an alkyl radical and an aryl radical anion. It should be noted that this single electron donation step does not require close approach by the alkyl anion to a bulky substituent present on the ring. Single electron transfers from strongly basic anions to aromatic, olefinic and acetylenic π systems to produce radical anions have been commonly observed in recent years[12]. Of importance here is an observation by Brown and Jones[13] of an ESR spectrum consistent with the radical anion of pyrene obtained from the action of n-butyllithium on pyrene. Pyrene metalates readily with n-butyllithium[14]. Another pertinent observation[15] is that it has been found "that various aromatic hydrocarbons (*e.g.*, anthracene and tetracene) yielded free radicals upon reaction with butyllithium, and that EPR spectra of these radicals were the same as those observed for the corresponding negative ions."

The greater reactivity of tert-butyllithium compared with n-butyllithium may be rationalized in terms of step (2). The tert-butyl anion is less stable than n-butyl while the tert-butyl radical is more stable than n-butyl. Therefore, the equilibrium (2) probably lies further to the right when R is tert-butyl giving a higher steady state concentration of radical anions on which the subsequent processes feed.

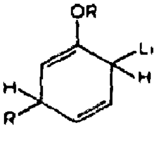
Step (3) involves reversible capture of the lithium cation by the radical anion and distribution among the product isomers shown. There seems to be at least two significant factors in the establishment of a much greater concentration of the *o*-isomer (I) than the other two, (II) and (III). One is the additional stability afforded by the opportunity for chelation of the lithium atom from adjacent heteroatoms (oxygen in this case)[16]. The other is that the inductive effect of electron attraction of ring substituents, long known to correlate very well the *ortho* orientation of entering lithium atoms, would operate to concentrate the negative charge of the radical anion of step (2) in the position adjacent to the –OR group. This would tend to produce larger equilibrium concentrations of (I) at the expense of (II) and (III). In this connection should be noted the results of calculations by Zimmerman[17] of total electron density at various positions in the radical anion of anisole. The results show the *ortho*-position to have the highest total electron density and also the highest electron pair density with the *meta*-positions intermediate and the *para*-position least. While not specifically shown in Chart 1, it is felt that the oxygen atom of the –OR group is complexed with alkyllithium reagent, and the resulting positive charge on the donor oxygen gives to this group a stronger inductive effect of electron attraction than is found in uncomplexed radical anions.

In step (4) is postulated the rapid combination of R$\cdot$ with the aromatic radical. It is believed that the sequence of steps (2), (3) and (4) may occur rapidly with reactants, intermediates and products not migrating from the solvent cage in which the RLi ion pair and aromatic substrate undergo initial reaction.

Step (5) is a rate-determining loss of RH from the adduct formed in (4). The transition state (IV) for this last process is similar to one postulated by Finnegan and Kutta[18] for the thermal loss of lithium hydride from n-butyllithium. The product in step (4) also allows for the formation of alkylation products known to occur among products from reactions of alkyllithium (particularly tert-butyllithium) and aromatic compounds. Loss of lithium hydride from the adduct would yield alkylation product. The adduct from (4) could also be of another form (V) resulting from attachment of R$\cdot$ at the position *para* to lithium. Support for the intermediacy of the adduct from step (4) is given by the observations by Dixon, Fishman and Dudinyak[19] of the reaction of tert-butyllithium with naphthalene at 60° in hydrocarbon solvent. These workers isolated from hydrolyzed reaction mixture 1,4-dihydro-1-tert-butylnaphthalene.



(IV)



(V)

1,2-dihydro-1-tert-butylnaphthalene and 1,2-dihydro-2-tert-butylnaphthalene as well as 1- and 2-tert-butylnaphthalenes.

It is apparent that the product mixture from metalation of anisole and related types should be examined for alkylation products. This is currently under investigation in our laboratories.

The proposed mechanism seems to be in agreement with the salient experimental facts on the metalation reaction, and in particular, allows for the apparent requirement that orientation-determining and rate-determining steps are different. However, we should give attention to the "anomalous" orientation in the metalation of biphenyl described in the preceding paper[3].

The distribution of metalation in biphenyl was 8 % *ortho*, 58 % *meta* and 34 % *para*. The phenyl group is a weak electron-attracting group (Hammett sigma value for a *meta*-phenyl is 0.06) and on this basis should give predominantly *ortho*-metalation. Unlike the alkoxy group, phenyl would not complex strongly to alkyllithium by electron donation and thereby increase its inductive effect in a metalation system. Consequently, the intermediates corresponding to (I), (II) and (III) in Chart 1 are present in more nearly equal amounts in the biphenyl case than in the phenyl alkyl ether case. Thus a steric effect discriminating against *ortho*-attack may be more apparent in the biphenyl case. The 58 % *meta*-metalation compared with the 34 % *para*-metalation represents, on a per-position basis, a small but perhaps significant greater rate of metalation at the *para*-position than at the *meta*. This may be attributed to the greater stabilization of the radical intermediate from *ortho*- and *para*-attack (*i.e.*, I and II where –OR is replaced by phenyl) compared with the intermediate from *meta*-attack.

One important aspect of alkyllithium metalations should be considered in terms of the proposed mechanism, and this is the striking acceleration in rate of metalation in the presence of tertiary amines, particularly those having the proper geometry for chelation[20-22]. We believe that the catalytic effect of the amine is on the equilibria represented in (1) Chart 1, and more specifically, on the concentration of alkyl anion or incipient anion. Amine coordination with the lithium cation provides energy for the dissociation and increases the concentration of ionic species (ions or ion pairs), and this latter view has been expressed by others[11,21]. Such effects could produce a many fold increase in the otherwise low concentration of ionic species without providing gross effects on the dielectric properties of amine-alkyllithium solutions in hydrocarbon solvents.

EXPERIMENTAL

General features

Solution of n-butyllithium in hexane were obtained from Foote Mineral Co. and the tert-butyllithium from Lithium Corporation of America. Deuterium analyses were by Dr. Josef Nemeth of Urbana, Illinois and are by the "falling drop" method.

The procedures for conducting the metalation experiments, the reaction work-up, conversion to methyl esters of the carboxylic acids, and VPC analysis of the esters were performed as described in the preceding paper[3]. Studies on anisole and resorcinol dimethyl ether in this paper involved identification of the same products and in the same manner as reported earlier[3].

Metalation of phenyl tert-butyl ether

Three metalations were run, two using tert-BuLi and one with n-BuLi. In all runs equimolar (0.1 mole each) amounts of RLi and phenyl tert-butyl ether (shown to be pure by VPC analysis) were used in 100 ml of cyclohexane at the reflux temperature and a reaction time of 12 h. The yields of the crude carboxylic acid mixture were 91 and 82% in two runs with tert-BuLi and 76% in one run with n-BuLi.

In the first tert-BuLi run, it was observed upon work-up that essentially complete cleavage of the tert-butyl-to-oxygen bond in the phenyl tert-butyl ether had occurred. This could have occurred either during the metalation or during the subsequent work-up procedure which had involved treatment with excess hydrochloric acid. It was definitely shown to be the latter by withdrawal of a sample from the second metalation reaction just prior to carbonation, hydrolysis of the sample and VPC analysis for phenol and phenyl tert-butyl ether. Only about 1% of phenol was present to about 99% of the ether. It was found that boiling the reaction mixture with excess aqueous HCl following the carbonation and hydrolysis steps allowed complete cleavage of the tert-Bu group.

Another complication was that the diazomethane methylation procedure partially methylated the phenolic hydroxyl group. Therefore, the reaction product was examined by VPC for six components, the *o*-, *m*- and *p*-methoxy- and hydroxybenzoates. Two columns were needed on the Perkin–Elmer, 154-D instrument, an SE-30 silicone and a polyester (succinic acid/diethylene glycol) "P" type column for sorting out all peaks. No methyl *p*-methoxybenzoate was found in the mixture and only a trace, representing less than 0.1%, of methyl *p*-hydroxybenzoate was found.

The analytical results were given in the discussion section, and are calculated on the usual[3] basis of total nuclear metalation given a value of 100. We found methyl benzoate in the methyl ester mixture from the metalations. This must have arisen from phenyllithium formed by an unexpected cleavage by the RLi of the oxygen-to-phenyl bond* of the phenyl tert-butyl ether. The cleavage occurred to the extent of 2% of the mixed carboxylic acid product when n-BuLi was the metalating agent and 6% when tert-BuLi was used.

Competitive metalation of anisole and phenyl tert-butyl ether with n-butyllithium

A three-neck flask was fitted with a stirrer and a rubber septum through which samples could be introduced to and removed from the flask with a hypodermic syringe. Anisole (5.41 g or 0.050 mole) and phenyl tert-butyl ether[24] (7.50 g or 0.050 mole) were placed in the flask containing 100 ml of cyclohexane. A sample was withdrawn for VPC analysis for determination of the curve peak areas represented by the equimolar amounts of reactants. The Perkin–Elmer 154-D with the silicone SE-30 column was used at a column temperature of 150°. n-BuLi (0.05 mole) was introduced by hypodermic syringe and the mixture stirred at room temperature for 13 h. The mixture was carbonated and hydrolyzed in the usual manner, and the ether layer analyzed by VPC for the mole ratio of anisole to phenyl tert-butyl ether. This ratio initially 1.00 was 0.68 at the end of the reaction indicating a faster consumption of anisole.

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* A similar but much larger (about 50%) cleavage of the sulfur-to-phenyl bond was observed in the metalation of thiophenetole[23]. So far as we know this type of cleavage by RLi compounds has not been observed by others.

Competitive metalation of anisole and phenyl tert-butyl ether with tert-butyllithium

The procedure used was similar in all respects to the one immediately above, except that the reaction mixture was sampled after 3 h of reaction and after 12 h. The mole ratio of the remaining anisole to phenyl tert-butyl ether was essentially unchanged from the initial ratio at both reaction times.

Competitive metalation of phenyl tert-butyl ether by n-butyllithium and tert-butyllithium

The apparatus used in the other competitive experiments was also used here. Approximately equimolar (0.05 mole) amounts of the two RLi compounds were placed in the flask and 100 ml of cyclohexane added. About 25 ml of solvent was distilled from the mixture in order to remove butane or isobutane which may have been present from an earlier contact of the RLi solutions with moisture. A sample of the reaction mixture was then withdrawn and added slowly to excess anhydrous ethanol at −70° to prevent escape of butane and isobutane. The resulting mixture was analyzed by VPC and showed an initial mole ratio of n-butane to isobutane of 1.04.

To the reaction mixture was added 7.50 g (0.05 mole) of phenyl tert-butyl ether and samples were withdrawn at reaction times of 3 h and 7 h (room temperature). The samples were quenched with cold ethanol as before and analyzed by VPC. The butane/isobutane mole ratio from the remaining RLi reagents increased from the initial 1.04 value to 2.8 at 3 h and 16.3 at 7 h. This shows an appreciably faster consumption of tert-BuLi compared with n-BuLi by the phenyl tert-butyl ether.

Determination of the hydrogen–deuterium isotope effect in the metalation of anisole

A. Preparation of anisole-2-d. A commercial sample of *o*-bromoanisole was chromatographed in the Perkin–Elmer 154-D, silicone SE-30 column at 190°. Approximately 1.5% of anisole was the only impurity found and two distillations through an 8 inch Vigreux column and collection at 96° at 3 mm removed the anisole peak in the VPC curve.

A solution of 130 g (0.70 mole) of the purified *o*-bromoanisole in 100 ml of ether was treated (20 min) with 0.70 mole of n-BuLi during which time external cooling was used to control the rate of reflux of the reaction mixture. Then 14 g (0.70 mole) of 99.5% D_2O was added slowly and the mixture stirred and heated to reflux, after which additional D_2O was added until no more heat was evolved. This required an additional 50 g of D_2O. The ether layer was separated, dried and distilled through a 9 inch Vigreux and the fraction boiling at 140–160° was redistilled to yield 32.9 g boiling between 151–156°. Successive one ml portions of this material were chromatographed in the Wilkins "Autoprep" with the DEGA preparative column at 150°. The anisole-2-*d* fractions were collected and a 1 µl sample was analyzed in the Perkin–Elmer 154-D silicone SE-30 analytical columns. No trace of impurity could be detected. A sample was retained for deuterium analysis (anisole A).

B. Metalation of anisole-2-d by n-butyllithium. Anisole-2-*d* (6.53 g, 0.0599 mole) in 100 ml cyclohexane was treated with 0.0478 mole of n-BuLi. The mixture was heated under reflux for 12 h and then carbonated with powdered solid carbon dioxide and hydrolyzed with 50 ml water. The ether layer was separated and extracted with

2% aqueous NaOH solution, and the combined aqueous layers acidified (HCl) to a pH of about 2. The precipitated acid was collected and dried, after which it was sublimed at 90° and 0.3 mm and the product melted at 102–102.5° (anisic acid A). A sample of this acid was dissolved in aqueous NaOH and reprecipitated with HCl, dried and sublimed as before (anisic acid B). This latter operation was designed to determine if there was any appreciable hydrogen–deuterium exchange during the brief contract with HCl in the work-up procedure.

The ether layer above was dried, the ether evaporated and the residue chromatographed through the "Autoprep" as before for recovery of unreacted anisole-2-*d* (anisole B).

The four samples were analyzed for deuterium with the results given in Table I.

TABLE I

DEUTERIUM ANALYSIS RESULTS FROM METALATION OF ANISOLE-2-*d*

Sample	*Monodeuteration (mole %)*	*Monodeuteration (average mole %)*
Anisole A	98.40	98.40
	98.40	
Anisole B	98.80	98.60
	98.40	
Anisic acid A	86.00	85.80
	85.60	
Anisic acid B	86.00	86.20
	86.40	

C. Determination of the isotope effect in the metalation of anisol-2-d with n-butyllithium. First it should be stated that there was no loss of deuterium in the acidification stage of the metalation work-up, since the two samples of anisic acid show the same deuterium content within experimental error. Anisole B would be expected to be enriched in deuterium relative to the starting anisole A; however, the isotopic content of anisole A was so high the enrichment is not discernible above experimental error. It is difficult to synthesize monodeuterated compounds via the organolithium or Grignard reagent routes[5] much above 98% labelling, nevertheless the 1.6% isotopic impurity of anisole A makes it difficult to determine accurately the isotope effect, unless the fraction of consumption of anisole A is not also determined accurately. We have used a device of calculation of a "minimal value" of the isotope effect by neglect of the 1.6% isotopic impurity and assumption of 100% labelling, and also calculation of a "maximal value" depending on the assumption that all of the 1.6% of unlabelled anisole comes through to unlabelled anisic acid. The true value of the isotope effect will lie between the minimal and maximal values. Calculation of these values gives 6.0 for the minimal and 8.2 for the maximal value.

D. Determination of the isotope effect in the metalation of anisol-2-d with tert-butyllithium. The procedure described above was repeated using tert-BuLi in place of n-BuLi. The minimal value of the isotope effect was determined to be 6.0 and the maximal value at 7.5 in fair agreement with the results with n-BuLi.

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SUMMARY

Metalation experiments have been designed involving anisole, resorcinol dimethyl ether, and phenyl tert-butyl ether with n-butyl- and tert-butyllithium to probe for steric effects in the reaction. The process is strikingly free of steric response, which suggests a multistep mechanism in which the orientation-determining step and the rate-determining removal of ring hydrogen are in separate steps. Metalation of anisole-2-*d* occurs with an isotope effect of magnitude comparable to thiophene metalation. A new mechanism involving radical anions and free radicals is proposed for the reaction.

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