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# REGIOSPECIFIC SYNTHESIS OF AROMATIC COMPOUNDS VIA ORGANOMETALLIC INTERMEDIATES

## I. *para*-SUBSTITUTED BENZENES

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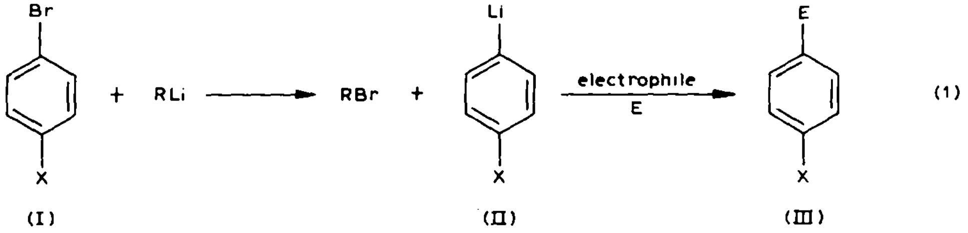
## Summary

*Para*-substituted benzene compounds, *p*-$XC_6H_4X'$ ($X = CF_3C(O)$ and $X' = CH_3$, $CO_2H$, $C(O)CF_3$, $C(O)CH_3$, $C(O)H$ and SH) have been prepared via sequential metal–halogen exchange reactions between *p*-$BrC_6H_4Br$ and n-$C_4H_9Li$ and the appropriate electrophiles. Low reaction temperature is critical to stabilization of the various intermediates. The $CF_3$ group has a pronounced effect on providing stability to the lithium hemiketal intermediates.

## Introduction

The metal–halogen exchange reaction [1] provides a convenient synthesis of aromatic organolithium compounds which subsequently may be used as intermediates in the synthesis of numerous compounds containing functional or nonfunctional substituents.



(1)

By this general procedure various functional groups (E in III) e.g. CHO, C(O)R, $CO_2H$, OH, $NH_2$, X etc. may be introduced into an aromatic structure. Certain

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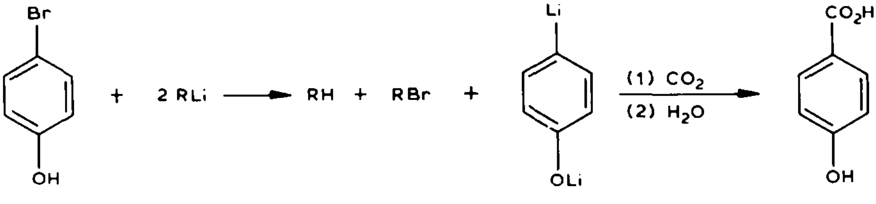
disubstituted aromatic compounds e.g. VI have been synthesized by this procedure [1,2] where one of the functional groups (X in I) is present prior to the metal–halogen exchange step.

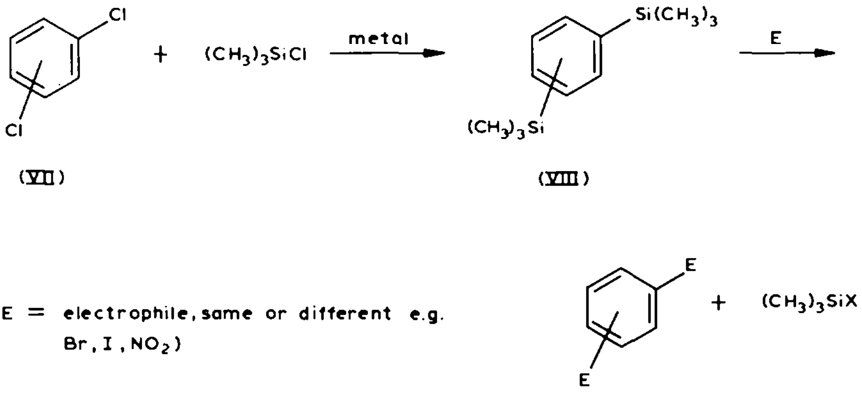


(IV) (V) (VI) (2)

Recently [3] we have shown that by sequential metal–halogen exchange reactions more than one functional group may be introduced to yield various substituted benzene compounds. Prior to our report, *ortho*-disubstituted thiophene [4] and benzothiophene [5] compounds with two different functional groups have been synthesized by the sequential metal–halogen exchange reaction followed by derivatization with appropriate electrophilic compounds.

It would thus appear that if the sequential metal–halogen exchange reaction and derivatization at each step were to be developed more fully, a convenient and synthetically useful procedure would be made available for the preparation of di- or poly-substituted aromatic compounds. Since the metal–halogen exchange reaction and subsequent derivatization with electrophiles does not change the orientation of substitution, regiospecific synthesis may be made possible. The starting halides would provide a template for the orientation of the desired substituted aromatic product.

Another approach to regiospecific synthesis of aromatic compounds has been reported [6,7] which, in principle is similar to ours. Certain disubstituted benzene compounds have been synthesized regiospecifically as shown in eq. 3.



(VII) (VIII) (3)

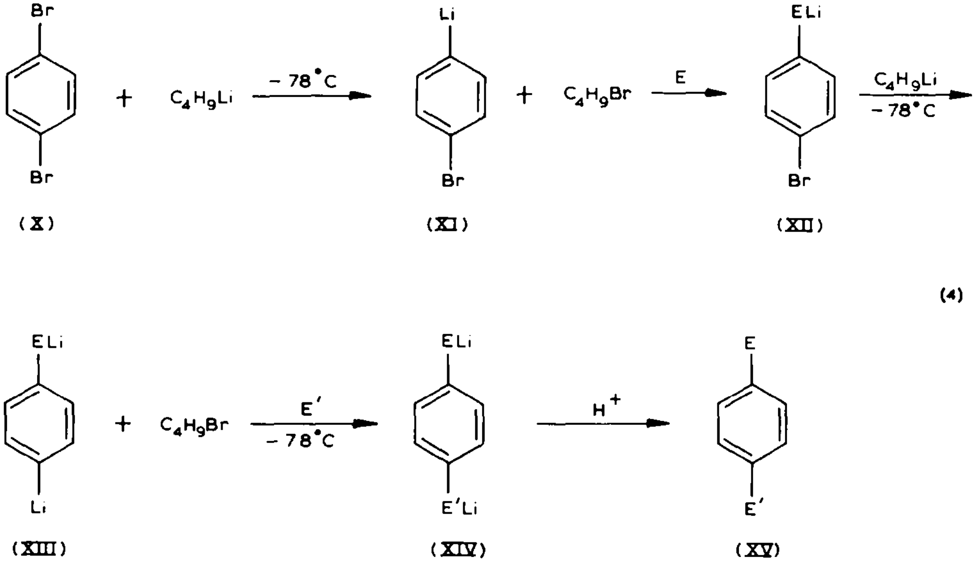
(E = electrophile, same or different e.g. Br, I, NO₂)

(IX)

By the proper selection of the starting dichlorobenzenes, various *ortho*, *meta* or *para* oriented disubstituted benzenes were synthesized. This process requires the cleavage of a carbon–silicon bond by an electrophile to yield the substituted products. As such the limitation of this method is to electrophiles capable of C–Si bond cleavage.

## Results and discussion

For our initial studies on regiospecific synthesis of aromatic compounds we have selected the *para* oriented benzene structure using *para*-dibromobenzene as the halo-aromatic starting compound. Metal–halogen exchange reactions proceed better with iodo- or bromo-aromatics than with chloro- or fluoro-aromatic compounds [1]. The general reactions of sequential metal–halogen exchange are shown in eq. 4.

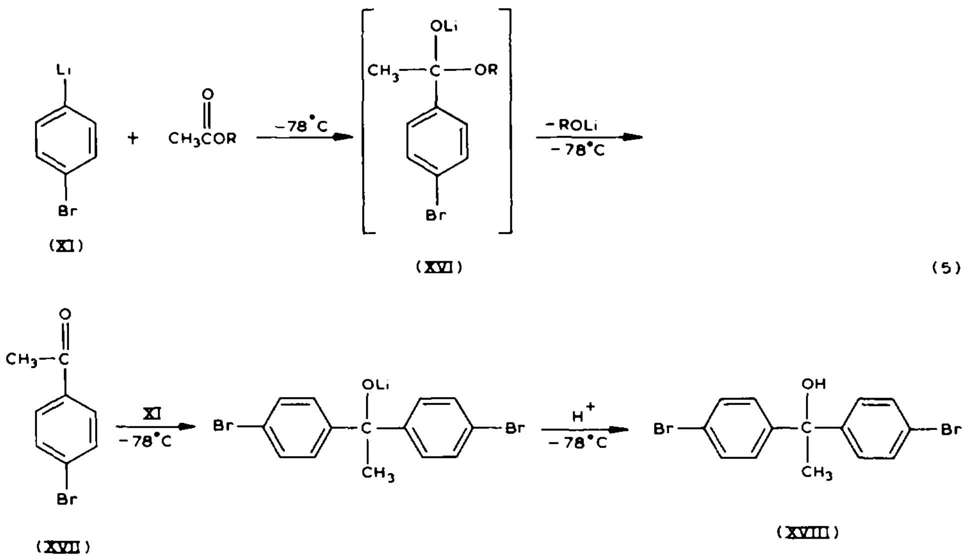


(4)

(E and E′ = electrophiles yielding a functional group e.g. $CO_2H$, SH, OH, CHO, $CO_2R$, C(O)R etc.)

Our initial studies have shown that all combinations of functional groups (E and E′) cannot be introduced conveniently by this sequential metal–halogen exchange procedure because of certain limitations which will be discussed in this report as well as others to follow. We have identified some important requirements necessary for introducing two different E substituents in the *para* position. The first requirement necessitates that the intermediate XII and XIII (eq. 4) are thermally stable at the reaction temperature and do not either contain or produce a functional group capable of reacting with an organolithium intermediate. As an example, the reaction between XI and an aliphatic hydrocarbon ester, e.g. $CH_3C(O)OCH_3$, does not yield a ketone (XVII) in good yield. The instability of the intermediate XVI at the reaction temperature yields a ketone XVII capable of further reaction with the organolithium XI to yield the tertiary alcohol XVIII [8] as the principal product (see eq. 5).

The rate of decomposition of the intermediate XVI at −78°C and the rates of reaction between XI and $CH_3CO_2R$ versus XVII govern the ratio of the final products. In this particular example, the intermediate XVI is extremely unstable at −78°C forming the ketone XVII which then competes preferentially with $CH_3CO_2R$ for the organolithium XI. The intermediate XIII must also be thermally stable such that it does not decompose to yield a product containing a functional group capable



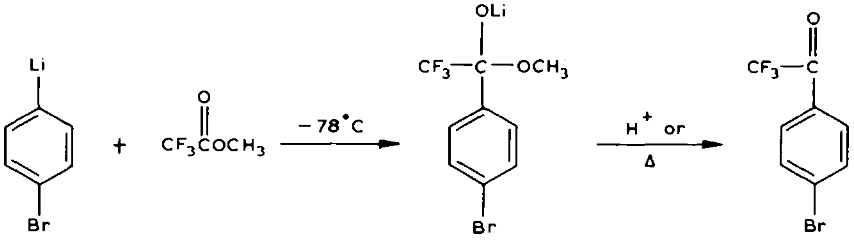
(5)

of reacting with an organolithium compound, e.g. $C_4H_9Li$ or XIII. The second requirement is concerned with the order of introducing the functional groups by the electrophilic agent. An example of this is the introduction of a carboxyl group by carbonation of the organolithium reagent. This is generally accomplished by the addition of an excess of gaseous carbon dioxide or by the inverse method of adding the organolithium to an excess of solid carbon dioxide in a solvent e.g. diethyl ether. Under these conditions the excess carbon dioxide cannot be conveniently removed from the reaction mixture and thus will react with the second equivalent of n-$C_4H_9Li$ (eq. 4, step XII-XIII) preferentially to a metal–halogen exchange of the second bromine. To avoid this situation the carboxyl group should be introduced as the last functional group (eq. 4 as E′). Another reason why the carboxyl group should be introduced lastly is to avoid the n-$C_4H_9Li$ from reaction with the carbonyl group to form ketones and subsequently tertiary alcohols.

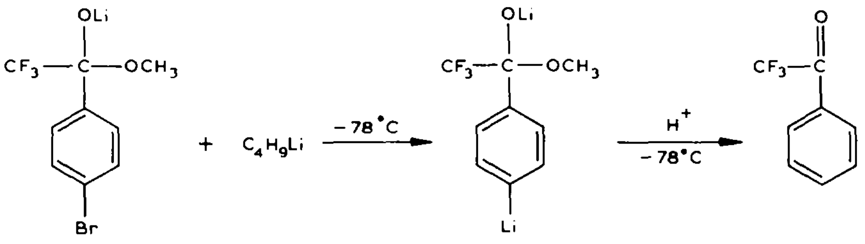
Numerous combinations of functional groups (E and E′) similar or dissimilar can be introduced by this sequential metal–halogen exchange reaction. In this present study we have selected as the first (E) functional group, $CF_3C(O)$ for reasons which will follow. The second group (E′) was varied to include $CF_3C(O)$, $CH_3C(O)$, SH, CHO, and $CO_2H$ and the non-functional group $CH_3$. The variety of substituents which can be introduced, indicate the versatility of this sequential metal–halogen exchange reaction.

In our initial studies we have selected $CF_3C(O)$ as the first substituent group because a stable intermediate, XIX was formed. Unlike its $CH_3$ analog (see eq. 5 using $CH_3C(O)OCH_3$), this lithium salt of a trifluoromethyl hemiketal is very stable towards thermal elimination of $CH_3OLi$. It can be isolated and characterized conveniently at room temperature. It is, however, sensitive to water as would be expected. On heating at higher temperatures or hydrolysis, XIX is converted to XX (eq. 6).

The unusual stability of XIX must be related to the electronic effect of the $CF_3$ group which stabilizes the anion [9]. Since XIX was found to be thermally stable, no



(XI) (XIX) (XX) (6)



(XIX) (XXI) (XXII) (7)

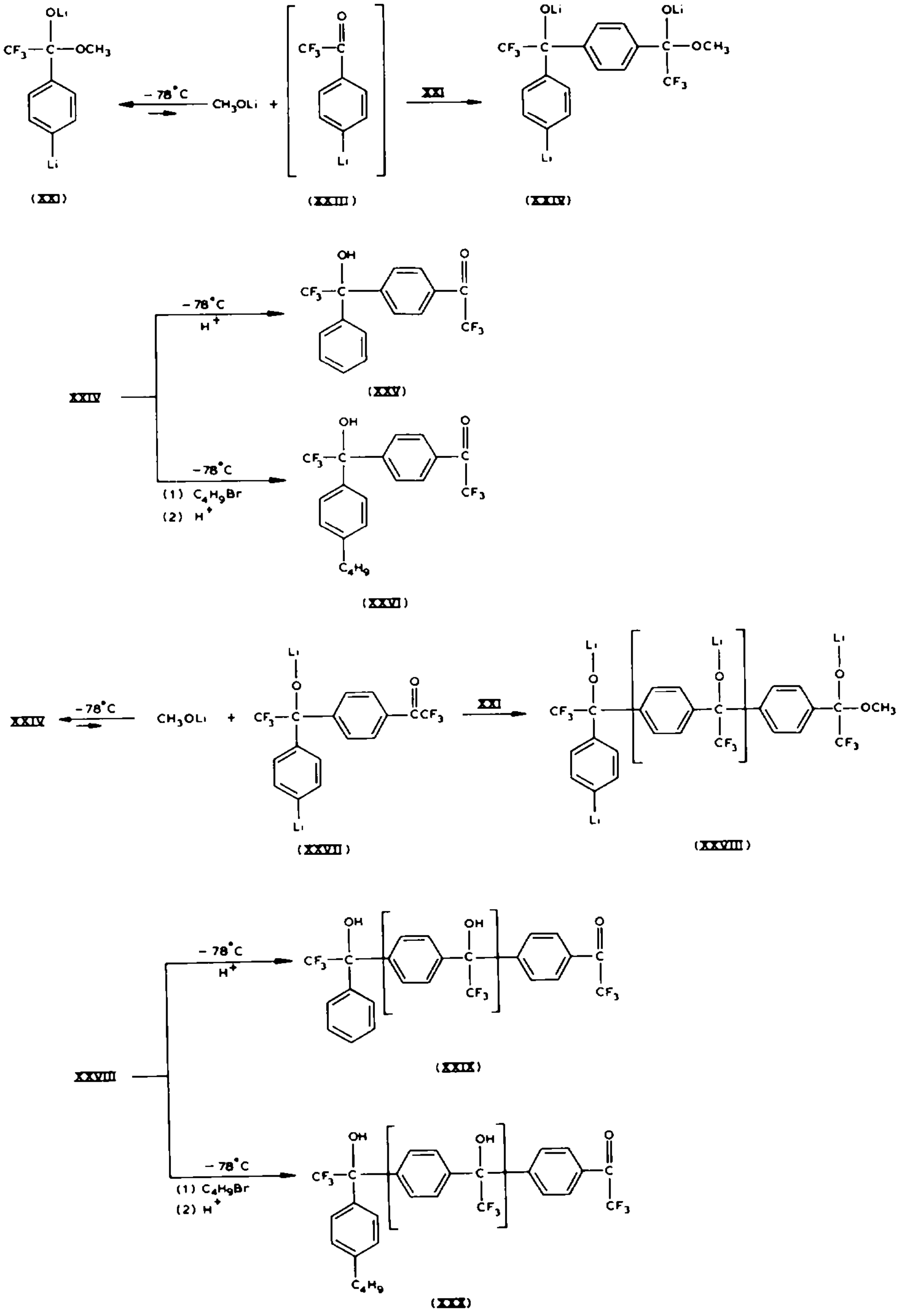
major problem with this functional group was encountered in the second metal–halogen exchange reaction as shown in eq. 7.

However, even at $-78°C$, the intermediate XXI shows a minor amount of thermal decomposition to yield a series of additional products. Analysis of the by-products were consistent with the structures XXV, XXVI, XXIX, and XXX whose formation as shown in Scheme 1 seems reasonable. Apparently in compound XXI the substitution of Li or Br (as in XIX) destabilizes the intermediate to some extent at $-78°C$ to form the transient ketone XXIII which must react immediately with the organolithium compound XXI to form XXIV. The intermediate XXIV behaves similarly to XXI repeating the process to yield XXVIII.

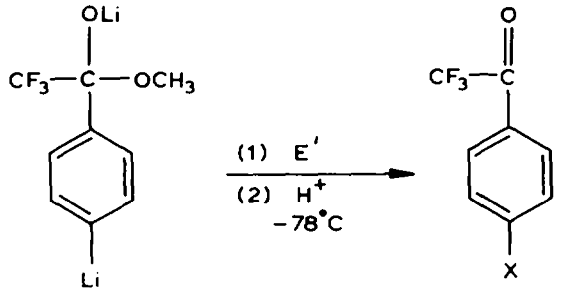
If XXI is allowed to warm up to room temperature and is subsequently hydrolyzed, compounds XXV, XXVI, XXIX, and XXX were found to be the principal products. Compound XXII, the hydrolysis product of XXI, was not present indicating complete decomposition of XXI. In the absence of another nucleophile, the organolithium intermediates XXIV and XXVIII will react (especially in the presence of tetrahydrofuran) with the exchange product n-$C_4H_9Br$. The rate of reaction at $-78°C$ is very slow and as expected increases as the reaction temperature is allowed to warm up to room temperature. In this manner the butylated products XXVI and XXX are formed. At $-78°C$, $CH_3I$ unlike n-$C_4H_9Br$ reacts more rapidly with the organolithium reagent XXI to yield the methylated product XXXI (see Experimental section).

In addition to the above isolable products (by distillation and/or GLC separation) there was a residual amount of very high boiling viscous material. We suspect this residue to consist of higher molecular weight polymeric materials formed by the continued process as shown in Scheme 1.

Most of our studies on synthesis and reactions of XXI were performed at $-78°C$ and as such the yield of the desired difunctional products were somewhat lower


OLi
CF3—C—OCH3
Li
− 78°C
CH3OLi +
CF3—C
O
Li
XXI
OLi
CF3—C
C—OCH3
CF3
Li
(XXI)
(XXIII)
(XXIV)
XXIV
− 78°C
H+
OH
CF3—C
O
C
CF3
(XXV)
−78°C
(1) C4H9Br
(2) H+
C4H9
(XXVI)
XXIV
−78°C
CH3OLi +
CF3—C
Li
O
CCF3
Li
XXI
(XXVII)
(XXVIII)
XXVIII
− 78°C
H+
(XXIX)
− 78°C
(1) C4H9Br
(2) H+
(XXX)

SCHEME 1



| $E'$ | X | (isolated yield) |
|---|---|---|
| $H_2O$ | H | (93% by GLC) |
| $CH_3I$ | $CH_3$ | (78%) |
| $CO_2$ | $CO_2H$ | (86%) |
| $CF_3CO_2CH_3$ | $C(O)CF_3$ | (86%) |
| $CH_3C(O)N(CH_3)_2$ | $C(O)CH_3$ | (72%) |
| $HC(O)N(CH_3)_2$ | HC(O) | (65%) |
| S | SH | (81%) |

SCHEME 2

because of the partial instability of XXI at this temperature. We subsequently prepared and reacted XXI at temperatures between −100 to −110°C and found that XXI was stable and reactive at this temperature and provided higher yields of the difunctional compounds.

The reactions between XXI and various substrates are shown in Scheme 2 and indicate their versatility of the sequential metal–halogen exchange reaction.

In order to utilize the sequential metal–halogen exchange reactions as described above for the synthesis of other di- or poly-substituted aromatics, the optimum experimental conditions must be determined for each of the substituents. The most important factor, thermal stability of the various intermediates, as indicated in eq. 4, may vary and must be determined in order to provide the desired products in substantial yields. Studies presently underway are directed at examining a variety of E and E′ (eq. 4) substituents in the various isomeric configurations.

## Experimental section

*General procedures.* All melting and boiling points are uncorrected. Infrared spectra were recorded on a Perkin–Elmer Model 600 computing infrared spectrophotometer. Mass spectra were obtained on a du Pont Model 21-490 mass spectrometer using a chemical ionization mode. Gas chromatographic analysis (GLC) were performed on a Perkin–Elmer Sigma 1 using 6′ stainless steel columns (1/4″ d.) packed with 10% SE-30 on Chromosorb W. All reactions were carried out in oven-dried glassware under an atmosphere of dry nitrogen. Diethyl ether was distilled from $LiAlH_4$ prior to use. Tetrahydrofuran was dried over sodium wire and was distilled from sodium-benzophenone ketyl. Dimethyl formamide and dimethyl acetamide were dried over $P_2O_5$ followed by distillation from CaO prior to use.

### *Preparation and stability of compound XXI*

Into a diethyl ether (150 ml) and tetrahydrofuran (150 ml) solution of *p*-dibromobenzene (16 g, 67.8 mmol) was slowly added n-$C_4H_9Li$ (42.4 ml of a 1.60 *M* hexane solution, 67.8 mmol) at −78°C over 16 min. The solution turned a cloudy, pale yellow color and the reaction temperature rose to −75°C. Methyl trifluoroacetate (8.85 g, 67.8 mmol) was slowly added at −78°C during 10 min. A colorless solution was obtained and the reaction temperature rose to a maximum of −70°C. After 30 min, n-$C_4H_9Li$ (42.4 ml of a 1.60 *M* hexane solution, 67.8 mmol) was slowly added to the above solution at −78°C over 10 min. A white cloudy mixture resulted and the reaction temperature rose to a maximum of −73°C. After 10 min, the reaction mixture at −78°C was hydrolyzed with precooled (−78°C) concentrated HCl (15 ml) dissolved in ethanol (10 ml). The reaction mixture was then poured into 2 *N* HCl (400 ml), phase separated and dried ($MgSO_4$). A GLC analysis indicated one major product, (93% GLC area) $CF_3C(O)C_6H_5$ (XXII); with a b.p. 151°C, MS, *m/e* 174 ($M^+$); IR (neat liquid) 1724 $cm^{-1}$ (C=O). The minor products were XXV (3% GLC area) and XXVI (1% GLC area), see below.

The above experiment was repeated except that the compound XXI was allowed to warm up from −78 to 0°C. After an additional 1 h, the reaction mixture was hydrolyzed with 2 *N* HCl (400 ml) at 0°C and then allowed to warm up to room temperature. The diethyl ether layer was analyzed by GLC. Analysis indicated the following compounds expressed in GLC area percent: XXV (17%), XXVI (20%), XXIX (18%) and XXX (17%) (See Scheme 1). Compound XXV: Found: C, 54.92; H, 3.01. $C_{16}H_{10}F_6O_2$ calcd.: C, 55.17; H, 2.89%. IR (neat liquid) 1723 (C=O), 3535 $cm^{-1}$ (broad, OH). MS, 348 ($M^+$). $^{19}F$ NMR ($CDCl_3$ solvent, $\delta$ in ppm from $CFCl_3$) −72.2 (singlet, 1, $CF_3$) and −74.7 (singlet, 1, $CF_3$). $^1H$ NMR ($\delta$ in ppm from TMS) 8.02, 7.70 (AB pattern, 4H, *p*-disubstituted aromatic) 7.39 multiplet 5H, $C_6H_5$), 3.23 (singlet, 1H, OH). Compound XXVI: Found: C, 59.65; H, 4.58. $C_{20}H_{18}F_6O_2$ calcd.: C, 59.41; H, 4.49%. IR (neat liquid) 1718 (C=O), 3521 $cm^{-1}$ (broad, OH). MS, 404 ($M^+$). Compound XXIX: IR (neat liquid) 1722 (C=O), 3520 $cm^{-1}$ (broad, OH). MS, 522 ($M^+$). Compound XXX: Found: C, 58.48; H, 4.37. $C_{28}H_{23}F_9O_3$ calcd.: C, 58.13; H, 4.09%. IR (neat liquid) 1720 (C=O), 3510, 3300 $cm^{-1}$ (broad, OH). MS, 561 $(M - OH)^+$, 509 $(M - CF_3)^+$.

### *Preparation of para-substituted trifluoroacetophenones (p-$XC_6H_4C(O)CF_3$)*

Unless otherwise noted the lithium organometallic intermediate, XXI was prepared at −78°C using the procedure stated above for the synthesis of $C_6H_5C(O)CF_3$.

*(a) p-Methyltrifluoroacetophenone (XXXI).* Methyl iodide (16.6 g, 116 mmol) was added to compound XXI (106 mmol) at −78°C over a period of 10 min. After 30 min, the reaction mixture was hydrolyzed with a precooled solution (−78°C) of concentrated HCl (20 ml) dissolved in ethanol (10 ml). The reaction mixture was then poured into 2 *N* HCl (400 ml), phase separated and dried ($MgSO_4$). The solvent was removed under reduced pressure and the residue was distilled to yield the product XXXI, *p*-$CH_3C_6H_4C(O)CF_3$, 15.4 g (78%), b.p. 85°C/20 mmHg, MS, 188 ($M^+$), IR (neat liquid) 1710 $cm^{-1}$ (C=O). Found: C, 57.25; H, 3.82. $C_9H_7F_3O$ calcd.: C, 57.45; H, 3.75%.

*(b) p-Trifluoroacetylbenzoic acid (XXXII).* Compound XXI (148 mmol) was poured into a mixture of solid $CO_2$ and diethyl ether at −78°C. After 15 min stirring, the mixture was hydrolyzed with a precooled (−78°C) solution of concentrated HCl (30 ml) in ethanol (15 ml). The mixture was then poured into 2 *N* HCl (500 ml), phase separated and dried ($MgSO_4$). The solvent was evaporated and the residual crude solid was recrystallized from $CHCl_3$ to yield the product XXXII. 16.5 g (51%), m.p. 174–175°C, MS, 218 ($M^+$), IR (KBr pellet) 1721, 1687 $cm^{-1}$ (C=O). Found: C, 49.64; H, 2.03. $C_9H_5F_3O_3$ calcd.: C, 49.56; H, 2.31%.

The above experiment was repeated except the second metal–halogen exchange to yield the organolithium compound XXI was performed at −105°C. The reaction mixture (at −105°C) was poured into a mixture of solid $CO_2$ and diethyl ether and worked up as described above. The yield of the product XXXII was increased to 86%.

*(c) p-Di(trifluoroacetyl)benzene (XXXIII).* Methyl trifluoroacetate (10.0 g, 78.1 mmol) was added over a period of 10 min to compound XXI (63.6 mmol) at −78°C. The cloudy mixture turned into a pale yellow clear solution with a temperature rise of up to −66°C. After an additional 10 min, the solution was hydrolyzed with precooled (−78°C) concentrated HCl (10 ml) dissolved in ethanol (5 ml). The solution was then poured in 2 *N* HCl (300 ml), phase separated and dried ($MgSO_4$). After removing the solvent under reduced pressure, the residue was distilled to yield the product *p*-$CF_3C(O)C_6H_4C(O)CF_3$ (XXXIII), 10.3 g (60%), b.p. 75°C/2.6 mmHg, MS, 270 ($M^+$) IR (neat liquid) 1729 $cm^{-1}$ (C=O). Found: C, 44.49; H, 1.58. $C_{10}H_4F_6O_2$ calcd.: C, 44.46; H, 1.49%.

The above experiment was repeated except the second metal–halogen exchange reaction to yield the organolithium compound XXI was performed at −110°C. The isolated yield of XXXIII was increased to 86%.

*(d) p-Trifluoroacetylacetophenone (XXIV).* Freshly distilled *N,N*-dimethyl acetamide (6.3 g, 72.4 mmol) was added over a period of 2 min to compound XXI (63.6 mmol) at −78°C. The reaction temperature increased to −66°C. After an additional 1 h, the reaction mixture was hydrolyzed with precooled (−78°C) concentrated HCl (5 ml) dissolved in ethanol (8 ml). The solution was then poured in 2 *N* HCl (200 ml), phase separated and dried ($MgSO_4$). After removing the solvent under reduced pressure, the residue was distilled to yield the product *p*-$CF_3C(O)C_6H_4C(O)CH_3$ (XXXIV), 9.9 g (72%), b.p. 73°C/0.8 mmHg, m.p. 38°C, MS, 216 ($M^+$), IR (neat liquid) 1725 $cm^{-1}$, 1691 $cm^{-1}$ (C=O). Found: C, 55.36; H, 3.05. $C_{10}H_7F_3O_2$ calcd.: C, 55.56; H, 3.26%.

*(e) p-Trifluoroacetylbenzaldehyde (XXXV).* Freshly distilled *N,N*-dimethyl formamide (9.28 g, 127 mmol) was added over a period of 1–2 min to compound XXI (106 mmol) at −78°C. The reaction temperature increased to −65°C. After an additional 1 h, the reaction mixture was hydrolyzed with precooled (−78°C) concentrated HCl (20 ml) dissolved in ethanol (10 ml). The solution was then poured into 2 *N* HCl (500 ml), phase separated and dried ($MgSO_4$). The solvent was removed under reduced pressure. To the crude residue was added hexane (200 ml). The mixture was stirred and the resulting precipitate was filtered and washed with additional hexane (3 × 10 ml) to yield a monohydrate of compound XXXV 16.2 g (70%), m.p. 78°C (dec.), MS 220 (weak), 202 ($(M-H_2O)^+$), IR (Nujol mull) 1680 (C=O), 3100, 3360 $cm^{-1}$ (OH). Found: C, 48.91; H, 2.92. $C_9H_7F_3O_3$ calcd.: C, 49.10; H, 3.21%.

The monohydrate XXXV was refluxed in benzene (70 ml) using a Dean/Stark trap to remove the benzene/water azeotrope. A pale yellow benzene solution resulted which on further distillation yielded the non-hydrated compound XXXV 14.0 g (65%) b.p. 102°C/1 mmHg, MS 202 ($M^+$), IR (neat liquid) 1720 $cm^{-1}$ (C=O), 1707 $cm^{-1}$ (C=O). Found: C, 53.76; H, 2.56. $C_9H_5F_3O_2$ calcd.: C, 53.48; H, 2.49%.

*(f) p-Trifluoroacetylthiophenol (XXXVI).* Sulfur (3.60 g, 113 mmol) was added to the compound XXI (106 mmol) at −78°C causing a rise in temperature to −71°C. After 1 h of additional stirring the reaction mixture was hydrolyzed with a precooled (−78°C) concentrated HCl (20 ml) dissolved in ethanol (10 ml). The solution was then poured into 2 *N* HCl, phase separated and dried ($MgSO_4$). Distillation of the diethyl ether layer yielded the product XXXVI 6.1 g (28%), b.p. 98°C/3 mmHg, MS, 206 ($M^+$), IR (neat liquid) 1710 (C=O), 2580 $cm^{-1}$ (SH). Found: C, 46.99; H, 2.24; S, 15.50. $C_8H_5F_3SO$ calcd.: C, 46.60; H, 2.44; S, 15.55%.

To the pot residue from the above distillation was added hexane (40 ml). The solid product in the hexane was filtered and recrystallized from hexane to yield 3.0 g (14%) 4,4'-bis(trifluoroacetyl)-diphenyldisulfide, m.p. 80°C, MS 410 ($M^+$), IR (thin film) 1710 $cm^{-1}$ (C=O). Found: C, 46.71; H, 1.61, S, 15.55. $C_{16}H_8F_6O_2S_2$ calcd.: C, 46.83; H, 1.97; S, 15.62%.

When the above experiment was repeated, except the second metal-halogen exchange reaction to yield the organolithium compound XXI was performed at −115°C, the yield of compound XXXVI was increased to 81%.

### *Reaction of 4-bromophenyllithium with methyl acetate*

To a diethyl ether (200 ml), tetrahydrofuran (200 ml) solution of *p*-dibromobenzene (25 g, 106 mmol) was slowly added n-butyllithium (48.2 ml of a 2.2 *M* hexane solution, 106 mmol) at −78°C over 20 min. After an additional 45 min at −78°C, methyl acetate (9.41 g, 127 mmol) was added over 25 min. The reaction temperature increased to −70°C. After an additional 1 h, the mixture was poured into 2 *N* HCl (300 ml) at 0°C, phase separated and dried ($MgSO_4$). The solvent was removed under reduced pressure. The remaining solid was separated by filtration, washed with hexane (3 × 20 ml) and recrystallized from hexane to yield 1,1-bis(*p*-bromophenyl)-ethanol (XVIII), 12.6 g (67%), m.p. 85°C, MS 354, 356, 358 ($M^+$), IR (Nujol mull) 3600–3400 $cm^{-1}$ (OH), $^1H$ NMR (DMSO-$d_6$) $\delta$ from TMS (internal) 7.4 ppm (multiplet, $C_6H_4$), 5.9 ppm (singlet, OH), 1.8 ppm (singlet, $CH_3$). Found: C, 47.18; H, 3.38; Br, 44.83. $C_{14}H_{12}Br_2O$ calcd.: C, 47.19; H, 3.37; Br, 44.94%.

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