1077. *Aromatic Reactivity. Part XXVI.*[1] *Relative Reactivities of Some Aryl-lithium Compounds in Couplings with Ethyldimethylsilane and its Chloro- and Ethoxy-derivatives.*

By C. Eaborn and D. R. M. Walton.

A competition method has been used to measure the relative reactivities of some aryl-lithium compounds, $X\cdot C_6H_4\cdot Li$ (where X = *p*-Me, *m*-Me, H, or *m*-CF_3), towards ethyldimethylsilane and its chloro- and ethoxy-derivatives in ether. Towards the chloride, all appear to be equally reactive, but towards the ethoxide and the parent the order is *p*-tolyl > Ph, *m*-tolyl > *m*-trifluoromethylphenyl. That electron-release in the substituent X facilitates, and electron-withdrawal hinders, reaction is consistent with regarding cleavage of the aryl–lithium bond as an electrophilic aromatic substitution.

Contrary to a possible implication of earlier experiments, *p*-dimethylaminophenyl-lithium is little, if any, less reactive than phenyl-lithium. The reactivity of *o*-tolyl-lithium could not be measured because of unexpected side reactions.

Previous papers in this series have shown that cleavage of $X\cdot C_6H_4-MR_3$ bonds, where M = Si, Ge, Sn, or Pb, by electrophilic reagents is facilitated by electron-release from the substituent X.[2] Similar substituent effects operate in the more familiar electrophilic aromatic substitutions, such as nitration and halogenation, and in electrophilic cleavages of aryl–mercury [3] and aryl–boron bonds.[4] It was of interest to see if cleavage of the much more reactive, more ionic $X\cdot C_6H_4-Li$ bonds by electrophilic reagents was similarly assisted by electron release in X.

In principle, any electrophilic reagent would serve, but those which react extremely readily with the aryl-lithium compounds (water, alcohols, and halogens, for example) are probably not sufficiently selective to reveal detectable differences between, say, phenyl- and *p*-tolyl-lithium, and so we used initially trialkylsilyl chlorides, and later trialkylsilyl ethoxides and trialkylsilanes. Such compounds are known to react cleanly with organolithium reagents in ether to give good yields of coupling products.[5]

For the comparisons, two aryl-lithiums were first prepared separately in ether from lithium and the aryl chlorides $X\cdot C_6H_4Cl$ and $Y\cdot C_6H_4Cl$, and the concentrations were measured by acid-titration (cf. ref. 6). A mixture of the two reagents in known molar ratio was then treated with a deficiency of the organosilicon compound, $EtMe_2SiZ$,* the relative yields of the products $EtMe_2Si\cdot C_6H_4\cdot X$ and $EtMe_2Si\cdot C_6H_4\cdot Y$ were determined by gas–liquid chromatography, and the relative reactivity k_X/k_Y of the two aryl-lithium was then calculated (see ref. 7). The results are shown in Table 1, and some comments and additional information are given below.

(1) The silyl chloride was too reactive to discriminate significantly between the aryl-lithiums. As expected, the selectivity increased as the reactivity of the silicon compounds was lowered by change from the chloride to the ethoxide, to the silane.

(2) The observed ratios $k_{p\text{-Me}}/k_{m\text{-CF}_3}$ agree within ±3% with those calculated from the

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* At first we intended to use chlorotrimethylsilane, but chromatographic separation of the products from unchanged aryl chlorides was unsatisfactory.

[1] Part XXV, Bott and Eaborn, *J.*, 1963, 2139.

[2] See, *e.g.*, Eaborn, *J.*, 1956, 4858; Deans and Eaborn, *J.*, 1959, 2299; Eaborn and Webster, *J.*, 1957, 4449; Eaborn and Pande, *J.*, 1961, 3715, 5082; Bott, Eaborn, and Waters, *J.*, 1963, 681.

[3] Dessy and Kim, *J. Amer. Chem. Soc.*, 1960, **82**, 686; 1961, **83**, 1167; Dessy and Lee, *ibid.*, p. 689.

[4] Kuivila and Hendrickson, *J. Amer. Chem. Soc.*, 1952, **74**, 5068; Kuivila and Benjamin, *ibid.*, 1955, **77**, 4834.

[5] Eaborn, "Organosilicon Compounds," Butterworths Scientific Publns., London, 1960, pp. 19—25.

[6] Kamiensky and Esmay, *J. Org. Chem.*, 1960, **25**, 115.

[7] Ingold and Shaw, *J.*, 1927, 2918.

TABLE 1.

Relative rates of reaction of $X{\cdot}C_6H_4{\cdot}Li$ and $Y{\cdot}C_6H_4{\cdot}Li$ compounds with $EtMe_2SiZ$ compounds.

		k_X/k_Y for Z =		
X	Y	Cl	OEt	H
p-Me	H	1·00	1·09	1·25
m-Me	H	1·00	—	1·00
p-Me	*m*-CF_3	1·00	1·16	1·47
m-Me	*m*-CF_3	1·00	1·08	1·21

ratios $k_{p\text{-Me}}/k_{m\text{-Me}}$ and $k_{m\text{-Me}}/k_{m\text{-CF}_3}$. This confirms the reliability of the experiments, and indicates that interaction, if any, between the aryl-lithiums does not cause complications.

The reactivity of *m*-trifluoromethylphenyl- relative to phenyl-lithium can safely be taken to be the same as that relative to *m*-tolyl-lithium.

(3) The electron-releasing *p*-methyl substituent raises the reactivity while the electron-withdrawing *m*-trifluoromethyl substituent lowers it (the effect of a *m*-methyl group was too small to be detected); the reactivity clearly does not increase with the degree of ionic character of the aryl–lithium bond, which would be greatest for the *m*-trifluoromethyl compound. The results are consistent with regarding the cleavage of the aryl–lithium bond as an electrophilic aromatic substitution, analogous to some cleavages of aryl–silicon and related bonds, although, even with such a small spread of reactivity, deactivation by a *m*-trifluoromethyl would be expected to be markedly greater than activation by a *p*-methyl group.

Attempts at detailed interpretation of the results would be pointless in view of the possible effects of substituents on association between aryl-lithium molecules and between aryl-lithium and lithium chloride or solvent molecules, and the unknown influence of such association on reactivity.

(4) The results are in accord with the recent observation [8] that electron-release from X facilitates, and electron-withdrawal by X hinders, reaction of $X{\cdot}C_6H_4{\cdot}MgBr$ compounds with hex-1-yne.

Reactivity of p-*Dimethylaminophenyl-lithium*.—Having found that electron-releasing substituents increase the reactivity of the aryl-lithium compound, we were puzzled by Gilman, Plunkett, and Dunn's observation that three equivalents of *p*-tolyl- or phenyl-lithium in ether reacted almost instantaneously with silicon tetrachloride at 0°, but that 48 hours' refluxing was required with *p*-dimethylaminophenyl-lithium.[9] Our vapour-phase chromatographic analysis could not be applied to dimethylamino-compounds, so we used fractional distillation to separate the products of a competition between equimolar amounts of phenyl- and *p*-dimethylaminophenyl-lithium in ether for a deficiency of chlorotrimethylsilane. We isolated trimethylphenyl- and *p*-dimethylaminophenyltrimethylsilane in a ratio of 1·14 : 1; the total yield, based on chlorotrimethylsilane taken, was only 84%, and, since most of the loss was probably of the highest-boiling product (*p*-dimethylaminophenyltrimethylsilane), there is no difference between the reactivity of the two aryl-lithiums within the experimental error.

Gilman, Plunkett, and Dunn's results [9] are not necessarily in error. One possibility is that *p*-dimethylaminophenyl- and phenyl-lithium react equally readily with silicon tetrachloride, but that the products *p*-$Me_2N{\cdot}C_6H_4{\cdot}SiCl_3$ and (*p*-$Me_2N{\cdot}C_6H_4)_2SiCl_2$ are much less reactive than the corresponding $PhSiCl_3$ and $PhSiCl_2$ compounds (though we think this unlikely), so that three equivalents of *p*-dimethylaminophenyl-lithium are used up only slowly. A second possibility is that a solution of *p*-dimethylaminophenyl-lithium is considerably less reactive than one of phenyl-lithium because of co-ordination between the amino-group and the lithium atom. In a mixture of the solutions, the phenyl-lithium

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[8] Dessy and Salinger, *J. Org. Chem.*, 1961, **26**, 4206.

[9] Gilman, Plunkett, and Dunn, *J. Amer. Chem. Soc.*, 1951, **73**, 1686.

might be affected to the same extent, so that it does not differ much in reactivity from the *p*-dimethylaminophenyl-lithium even though it is markedly less reactive than when on its own.

Attempted Study of p-*Methoxyphenyl-lithium.*—We wished to include *p*-methoxyphenyl-lithium in this study, but we encountered complications. The organolithium reagent from *p*-chloroanisole was brought into competition with *p*-tolyl-lithium for a deficiency of chlorotrimethylsilane, but even when the initial concentration of the reagent from *p*-chloroanisole, as measured by the usual acid-titration, was five times as great as that of the *p*-tolyl-lithium, only a small proportion of *p*-methoxyphenyltrimethylsilane was produced. In agreement with this, *p*-methoxyphenyltrimethylsilane was obtained in only 15% yield from a preparative-scale reaction between chlorotrimethylsilane and the organo-lithium reagent from *p*-chloroanisole in ether. It is likely that most of the organolithium reagent from *p*-chloroanisole was 5-chloro-2-methoxyphenyl-lithium, not *p*-methoxyphenyl-lithium (see ref. 10). In agreement with these suggestions, when *p*-chloroanisole was treated with phenyl-lithium in ether and chlorotrimethylsilane was added, 4-chloro-2-trimethylsilylanisole was obtained in 60% yield.

Experiments with o-*Tolyl-lithium.*—It is known that *o*-tolyl-lithium is markedly less reactive towards some sterically hindered organosilicon compounds than is, say, *p*-tolyl-lithium.[11] In an attempt to measure the relative reactivities of *o*-tolyl- and phenyl-lithium towards a relatively unhindered silicon chloride, the organolithium reagents were brought into competition for a deficiency of ethyldimethylsilyl chloride in ether, but after the excess of aryl-lithium compounds had been destroyed by hydrolysis the usual chromatographic analysis revealed the presence of two unexpected products. Their retention times corresponded to those of benzylethyldimethylsilane and ethyldimethyl-*m*- or *p*-tolylsilane (the last two compounds have the same retention time). The materials giving the additional peaks were not present in the products of hydrolysis of *o*-tolyl- and phenyl-lithium, either separately or in admixture, and so were probably organosilicon compounds; they will be assumed to be benzylethyldimethyl- and ethyldimethyl-*p*-(or *m*)-tolyl-silane in the discussion below.

The following facts emerged: (i) No additional peaks were given by the products of reaction of *o*-tolyl- and phenyl-lithium separately with the silicon chloride. (ii) The additional peaks were undetectable when the reactant ratios *o*-tolyl-Li : PhLi : $Me_2EtSiCl$ were 1·0 : 1·0 : 0·4, but in this case the peak for ethyldimethyl-*o*-tolylsilane was very small. (iii) The heights of the additional peaks increased as the ratio of *o*-tolyl- to phenyl-lithium was increased. (It should be noted that the ratio of unchanged *o*-chlorotoluene to phenyl-lithium would also be increased.) For initial reactant ratios of $o\text{-}Me{\cdot}C_6H_4Li : PhLi : Me_2EtSiCl$ of 7·0 : 1·0 : 0·5, the ratios of $o\text{-}Me{\cdot}C_6H_4{\cdot}SiEtMe_2 : p\text{-}Me{\cdot}C_6H_4{\cdot}SiEtMe_2 : Ph{\cdot}CH_2SiEtMe_2$ were *ca.* 1 : 1 : 0·5. (iv) When *o*-tolyl- and phenyl-lithium were initially present in 2 : 1 mole ratio, the additional peaks were of a good size when the ratio of PhLi : $Me_2EtSiCl$ was 1·0 : 0·5, very small when this ratio was 1·0 : 0·75, and undetectable when it was 1·0 : 1·0. (v) For reactant ratios of $o\text{-}Me{\cdot}C_6H_4{\cdot}Li : PhLi : Me_2EtSiCl$ of 2·0 : 1·0 : 0·5, refluxing the mixture of organo-lithium compounds for 8 hours before addition of the silicon chloride caused no change in the product composition.

Intramolecular rearrangement of *o*-tolyl- to *p*(or *m*)-tolyl- and benzyl-lithium is ruled out by observation (i) above. A possible explanation of the results is that phenyl-lithium metallates some *o*-tolyl-lithium to give α, 2-, and 2,4(or less probably, 2,5)-dilithiotoluene. These species, having lithium atoms at unhindered positions,* would

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* The aryl–lithium bond *para* to the methyl group in 2,4-dilithiotoluene would, if the observations noted under (3) above can be generalized, be considerably activated by strong electron-release from the other aryl–lithium bond.

[10] Wittig, Pockels, and Dröge, *Ber.*, 1938, **71**, 1903.

[11] Ref. 5, pp. 22—25.

compete effectively with phenyl-lithium for the silicon chloride, to give the compounds 4(or 5)-Me_2EtSi-2-$Li{\cdot}C_6H_4Me$ and 2-$Li{\cdot}C_6H_4{\cdot}CH_2{\cdot}SiEtMe_2$, and hydrolysis would give the compounds 4(or 5)-$Me_2EtSi{\cdot}C_6H_4Me$ and $Ph{\cdot}CH_2{\cdot}SiEtMe_2$. If enough silicon chloride were present, it could react with the compounds 4(or 5)-Me_2EtSi-2-$Li{\cdot}C_6H_4Me$ and 2-$Li{\cdot}C_6H_4{\cdot}CH_2{\cdot}SiEtMe_2$ to give α, 2-, and 2,4(or 2,5)-bis(ethyldimethylsilyl)toluene, which would be high-boiling and have too long a retention time to be disclosed in the chromatographic analysis. A weakness of this explanation is that dilithiation of aromatic hydrocarbons is not normally thought to occur under such mild conditions.

A variation on the above explanation involves production of *p*(or *m*)-tolyl-lithium by reaction sequence (1) and (2) (and of benzyl-lithium analogously). We consider this less likely, since the amounts of ethyldimethyl-*p*(or *m*)-tolyl- and benzylethyldimethyl-silane formed would not depend on the initial PhLi : $Me_2EtSiCl$ ratio.

$$\text{2-Li}{\cdot}C_6H_4{\cdot}Me + PhLi \longrightarrow \text{2,4-Li}_2{\cdot}C_6H_3{\cdot}Me + PhH \qquad (1)$$

$$\text{2,4-Li}_2{\cdot}C_6H_3{\cdot}Me + PhH \longrightarrow \text{4-Li}{\cdot}C_6H_4{\cdot}Me + PhLi \qquad (2)$$

It is possible that the extra products arise from interaction between phenyl-lithium and the excess of *o*-chlorotoluene, and when a mixture of phenyl-lithium and *o*-chlorotoluene was treated with ethyldimethylsilyl chloride a small peak corresponding to ethyldimethyl-*o*-tolylsilane and very small peaks corresponding to benzyl- and *p*(or *m*)-tolyl-silane were obtained. An explanation of the formation of ethyldimethyl-*m*-tolylsilane can be devised involving initial interaction of phenyl-lithium and *o*-chlorotoluene to give 3-methylbenzyne, to which ethyldimethylsilyl-lithium adds, but we do not elaborate on this suggestion since there is no parallel explanation for the formation of benzylethyldimethylsilane.

EXPERIMENTAL

Ethyldimethylsilyl Compounds.—Ethyldimethylsilyl chloride had b. p. 89·5°, and the ethoxide b. p. 106°, n_D^{20} 1·3888. *Ethyldimethylsilane*, b. p. 48·2°, was prepared in 92% yield by reduction of the chloride with lithium aluminium hydride in dioxan followed by fractional distillation (Found: available H, 1·13. $C_4H_{12}Si$ requires available H, 1·15%).

Trialkylarylsilanes.—The following trialkylarylsilanes were prepared by the Wurtz–Fittig reaction in the usual way (see ref. 12) from the aryl chloride, trialkylchlorosilane, and sodium in toluene: (*a*) $X{\cdot}C_6H_4{\cdot}SiMe_3$, where X = H, b. p. 167·5°, n_D^{20} 1·4904; *o*-Me, b. p. 197·5°, n_D^{20} 1·5030; or *p*-Me, b. p. 192·5°, n_D^{20} 1·4920. (*b*) $X{\cdot}C_6H_4{\cdot}SiEtMe_2$ *compounds* where X = H, b. p. 197·5°, n_D^{20} 1·4942; *o*-Me, b. p. 220°, n_D^{20} 1·5058 (Found: C, 74·2; H, 10·4. $C_{11}H_{18}Si$ requires C, 74·0; H, 10·2%); *m*-Me, b. p. 213—215°, n_D^{20} 1·4970 (Found: C, 74·0; H, 10·3%); or *p*-Me, b. p. 215·5°, n_D^{20} 1·4962 (Found: C, 73·9; H, 10·2%).

n-Butyl-lithium (0·12 mole) in ether was added with stirring to *m*-bromobenzotrifluoride (22·5 g., 0·10 mole) in ether (100 ml.) during 45 min. at −5°. Stirring was continued for 1 hr. at −5°, and then for 2 hr. at room temperature. To the deep green solution, ethyldimethylsilyl chloride (12·3 g., 0·10 mole) in ether (15 ml.) was added during 30 min., and the mixture was then refluxed for 2 hr. Treatment with saturated aqueous ammonium chloride, followed by the usual working-up and fractionation, gave *ethyldimethyl-*m*-trifluoromethylphenylsilane* (14·2 g., 61%), b. p. 193·5°, n_D^{20} 1·4478 (Found: C, 56·5; H, 7·0. $C_{11}H_{15}F_3Si$ requires C, 56·85; H, 6·5%. The presence of fluorine lowers the accuracy of the microanalysis).

Bis-(m*-trifluoromethylphenyl)mercury.*—To a filtered solution of the Grignard reagent from *m*-bromobenzotrifluoride (62 g., 0·28 mole) and magnesium (8·5 g.) in ether (200 ml.) were added benzene (200 ml.), and then, with vigorous stirring and under dry nitrogen, mercuric chloride (32·6 g.), in *ca.* 3-g. lots. The mixture was refluxed for 6 hr., then treated with saturated aqueous ammonium chloride. The organic layer was separated, washed, dried (Na_2SO_4), filtered, concentrated to about one-third of its volume, and allowed to cool. The solid separating was recrystallized twice from chloroform, to give *bis-*(m*-trifluoromethylphenyl) mercury*, m. p. 181·5—182° (Found: C, 34·3; H, 1·4. $C_{14}H_8F_6Hg$ requires C, 34·3; H, 1·6%).

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[12] Ref. 5, pp. 27—29; cf. Eaborn and Pande, *J.*, 1960, 3200.

Preparation of Aryl-lithium Solutions.—(i) Solutions of phenyl-lithium, *o*-, *m*-, and *p*-tolyl-lithium were made by adding, with vigorous stirring and under nitrogen, a mixture of the aryl chloride (0·2 mole) and an equal volume of ether to ether (800 ml.) and small, very thin slices of lithium (0·6 g.-atom), at such a rate as to maintain refluxing. The mixture was subsequently refluxed for 30 min., and then set aside at room temperature overnight. (Probably little reaction of the aryl-lithium with the ether or unchanged aryl-chloride occurs under these conditions.[13,14]) The next day the solution was filtered under nitrogen pressure through a sintered-glass disc into a burette. Moisture was rigorously excluded, and a nitrogen atmosphere maintained throughout.

(ii) *m*-Trifluoromethylphenyl-lithium could not be made in the above way because the aryl chloride did not react with lithium. For preparative purposes it was made from *m*-bromo-benzotrifluoride, and n-butyl-lithium in ether (see above) but, when a 1 : 1 mole ratio of these reactants was used, subsequent coupling with chlorotrimethylsilane gave n-butyltrimethylsilane as well as *m*-trifluoromethylphenyltrimethylsilane, showing that unchanged n-butyl-lithium had been present.

Lithium shot, about 0·5 mm. in diameter, was prepared under argon by vigorously stirring lithium (0·9 g.-atom) with high-boiling mineral oil (normally used for storage of sodium; it was treated with molten sodium before use) at 180° (see ref. 15). The mixture was allowed to cool, most of the oil was decanted through glass wool, and the shot was washed by decantation several times with ether and then flushed with ether into a glass-stoppered flask. The volume of ether was made up to 250 ml., bis-(*m*-trifluoromethylphenyl)mercury (46 g., 0·09 mole) was added, and the flask was shaken at room temperature for 38 hr. The dark brown solution was filtered through glass wool and then through a sintered-glass disc into a burette. All operations were conducted under argon.

Competitions.—The strengths of the two aryl-lithium solutions, which were contained under nitrogen in burettes as indicated above, were measured by running suitable small volumes into water and titrating the liberated hydroxide against aqueous acid, with phenolphthalein as indicator. The two aryl-lithium solutions were then mixed in such volumes as to give a mixture containing equimolar amounts (0·02—0·05 mole) of the aryl-lithiums, and the total volume of ether was adjusted so that the concentration of each was about 0·1M. The transfers were made under nitrogen as was the subsequent addition, at room temperature (*ca.* 18°) during 15 min. with vigorous stirring, of an 0·2M-solution of the organosilicon compound, Me_2EtSiZ, in ether. The mixture was stirred for an additional 15 min., then treated with an excess of saturated aqueous ammonium chloride (100 ml.) containing ice (50 g.). The ethereal layer was separated, washed, dried (Na_2SO_4), and concentrated to about 20 ml. by careful removal of ether through a column packed with glass helices. The relative amounts of the two trialkyl-arylsilanes were then determined by vapour-phase chromatography as described below. Tests on standard mixtures showed the procedure to be reliable.

The results are shown in Table 2.

TABLE 2.

Competition of $X{\cdot}C_6H_4{\cdot}Li$ and $Y{\cdot}C_6H_4{\cdot}Li$ for Me_2EtSiZ.

Reactants and amounts (mmole)			$\frac{X{\cdot}C_6H_4{\cdot}SiEtMe_2}{Y{\cdot}C_6H_4{\cdot}SiEtMe_2}$	Reactants and amounts (mmole)			$\frac{X{\cdot}C_6H_4{\cdot}SiEtMe_2}{Y{\cdot}C_6H_4{\cdot}SiEtMe_2}$
X	Y	Z		X	Y	Z	
p-Me (50)	H (50)	Cl (20)	1·00	*p*-Me (20)	*m*-CF_3 (20)	Cl (10)	1·00
		OEt (20)	1·08			OEt (10)	1·14
		H (20)	1·22			H (10)	1·39
m-Me (50)	H (50)	Cl (20)	1·00	*m*-Me (20)	*m*-CF_3 (20)	Cl (10)	1·00
		H (20)	1·00			OEt (10)	1·07
						H (10)	1·18

The rate ratios k_X/k_Y differ slightly from the product ratios, R, ($X{\cdot}C_6H_4{\cdot}Z/Y{\cdot}C_6H_4{\cdot}Z$), being given [7] by

$$k_X/k_Y = \log\left(1 - \frac{Z_0}{X_0}\cdot\frac{1}{1+R}\right)\Big/ \log\left(1 - \frac{Z_0}{Y_0}\cdot\frac{R}{1+R}\right),$$

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[13] Coates, " Organometallic Compounds," Methuen and Co. Ltd., London, 2nd edn., 1960, p. 7.

[14] Huisgen and Sauer, *Chem. Ber.*, 1959, **92**, 192.

[15] Ref. 13, p. 4.

where X_0, Y_0, and Z_0 are the initial molar amounts of the compounds $X{\cdot}C_6H_4{\cdot}Li$, $Y{\cdot}C_6H_4{\cdot}Li$, and $EtMe_2SiZ$.

Vapour-phase Chromatography.—The column was a glass U-tube 60 cm. long and 0·4 cm. in diameter, packed with "Embacel" kieselguhr (May and Baker, Ltd.) (60—80 mesh) containing 5 wt.-% of dinonyl phthalate and maintained at 115°. The detector, of the argon-ionization type, was kept at 98°, and argon was used as carrier gas, at a flow rate of 36—44 ml./min., maintained constant to within ±0·2 ml./min. for any given separation. Samples (0·05—0·10 µl.) of the reaction products in ether (see above) were introduced in small capillary tubes which could be dropped into the flash-heater (220°) without interruption of the argon flow.

Retention times were compared with those determined separately for the expected products and the unchanged starting materials. For each pair of products, calibrations were carried out with standard mixtures, because the molar ratios of the two trialkylarylsilanes were not proportional to relative peak heights or peak areas; the amount was linearly related to the relative peak heights. The ratios of the peak heights were determined on six samples of each product mixture, and the average value was used in derivation of the molar ratio.

Experiments with o-*Tolyl-lithium.*—Mixtures of *o*-tolyl- and phenyl-lithium in ether were made and brought into reaction with a deficiency of ethyldimethylsilyl chloride as described above for other pairs of aryl-lithiums. Quantitative determination of the relative amounts of the expected products was impossible, because, in all the experiments, for a large-enough peak from the ethyldimethyl-*o*-tolylsilane the peak from the phenyl compound was too high to be on the scale. Additional peaks were observed; they corresponded exactly in position with those for benzylethyldimethylsilane and ethyldimethyl-*p*(or *m*)-tolylsilane, and will be assumed below to arise from these compounds.

From ethyldimethylsilyl chloride (MCl) (0·020 mole) with *o*-tolyl- (0·050 mole) and phenyl-lithium (0·050 mole) were obtained a large peak for the compound PhM and a very small one for the compound *o*-$Me{\cdot}C_6H_4{\cdot}M$. From *o*-tolyl-lithium (0·258 mole), phenyl-lithium (0·037 mole), and the compound MCl (0·018 mole), the peak for the product PhM was at least 4 times as high as that for the product *o*-$Me{\cdot}C_6H_4{\cdot}M$, and the heights of the peaks for the compounds *o*-$Me{\cdot}C_6H_4{\cdot}M$, *p*(or *m*)-$Me{\cdot}C_6H_4{\cdot}M$, and $Ph{\cdot}CH_2M$ corresponded to molar ratios of approximately 1·0 : 1·0 : 0·5.

From *o*-tolyl- (0·040 mole) and phenyl-lithium (0·020 mole), in addition to those for the products *o*-$Me{\cdot}C_6H_4{\cdot}M$ and PhM, peaks for the compounds $Ph{\cdot}CH_2{\cdot}M$ and *p*(or *m*)-$Me{\cdot}C_6H_4{\cdot}M$ were clear when 0·010 mole of the chloride MCl was taken, very small when 0·015 mole was taken, and undetectable when 0·020 mole was taken. The result from 0·010 mole of chloride was unchanged when the mixture of aryl-lithiums was refluxed for 8 hr. before addition of the chloride.

To *o*-chlorotoluene (0·050 mole) in ether (100 ml.) was added phenyl-lithium (0·050 mole) in ether (100 ml.), and after 10 min. the silicon chloride, MCl (0·025 mole), was added. The usual working-up and chromatography gave peaks corresponding to the products PhM (large), *o*-$Me{\cdot}C_6H_4{\cdot}M$ (small), *p*(or *m*)-$Me{\cdot}C_6H_4{\cdot}M$ (very small), and $Ph{\cdot}CH_2{\cdot}M$ (very small).

Experiments with p-*Dimethylaminophenyl-lithium.*—Solutions of phenyl- and *p*-dimethylaminophenyl-lithium were prepared separately from the appropriate aryl bromide (1·0 mole) and lithium shot (3·5 g.-atom) in ether (600 ml.) under nitrogen. Unchanged lithium was removed by centrifugation, and the concentrations of the aryl-lithiums were determined in the usual way. Hydrolyses of small samples, followed by vapour-phase chromatography, showed that unchanged aryl bromides were absent.

Appropriate volumes of the solutions were mixed to give a solution of phenyl- (0·60 mole) and *p*-dimethylaminophenyl-lithium (0·60 mole) in ether (900 ml.) under nitrogen. To the mixture maintained at 25°, chlorotrimethylsilane (54 g., 0·50 mole) in ether (60 ml.) was added during 2 hr., and the mixture was stirred at 25° for an additional 12 hr. The mixture was poured into ice–water, and the ethereal layer was separated, washed, dried (Na_2SO_4), and fractionated to give trimethylphenylsilane (36·6 g., 0·244 mole), b. p. 167—169°, n_D^{25} 1·4878, dimethylaniline (43·6 g., 0·362 mole), b. p. 192—194°, n_D^{25} 1·5577, *p*-dimethylaminophenyltrimethylsilane (36·9 g., 0·191 mole), b. p. 116°/10 mm., n_D^{25} 1·5320, biphenyl (3·2 g.), m. p. 70·0°, and a water-insoluble residue (15 g.). The yield of aryltrimethylsilanes based on chlorotrimethylsilane taken was 87%, while the combined yield (0·55 mole) of products from *p*-dimethylaminophenyl-lithium was 92%.

In another experiment, the mixture from reaction between phenyl-lithium (0·56 mole), *p*-dimethylaminophenyl-lithium (0·56 mole), and chlorotrimethylsilane (54 g., 0·50 mole) was added to a vigorously stirred slurry of solid carbon dioxide and ether. The mixture was set aside for 18 hr., water (1 l.) was added, and the mixture was refluxed until the lithium salts had dissolved. Working-up as above gave phenyltrimethylsilane (33·6 g., 0·224 mole), dimethylaniline (11·0 g., 0·091 mole), and *p*-dimethylaminophenyltrimethylsilane (37·8 g., 0·196 mole). The yield of aryltrimethylsilanes was 84% based on chlorotrimethylsilane taken.

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DEPARTMENT OF CHEMISTRY, THE UNIVERSITY, LEICESTER. [*Received, April* 27*th*, 1963.]