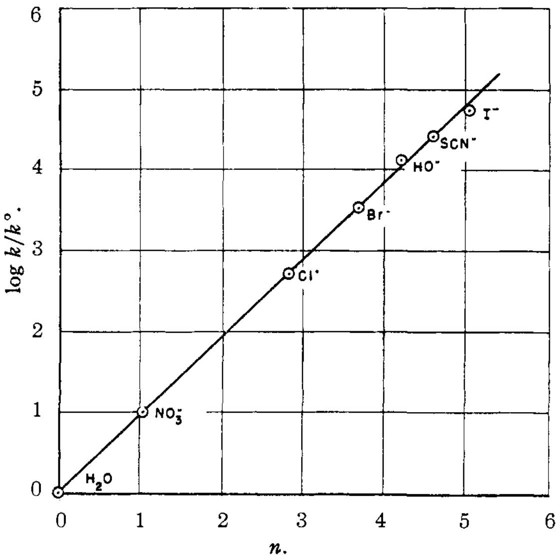


Fig. 4.—Rate correlation curve for glycidol.

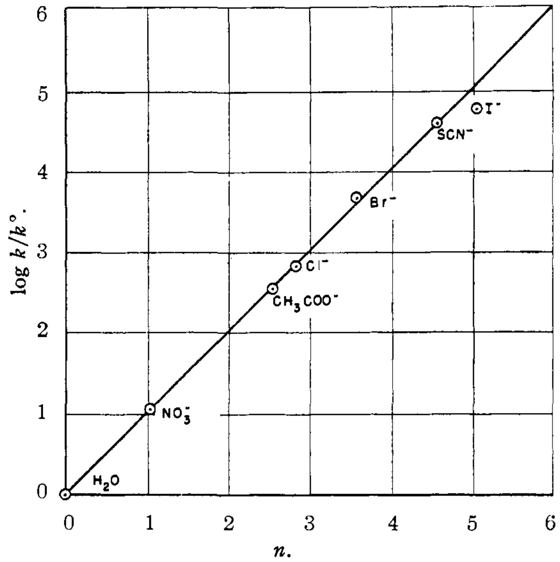


Fig. 5.—Rate correlation curve for epichlorohydrin.

proximately true, but at low concentrations equation 10 is far from valid. By retaining the quadratic term it can be shown that at higher oxide concentrations of E the ratio of n/N_0 to g/W_0 will be lower than r approximately by the fractional amount $E(r - 1)/(rN_0 + W_0)$. Therefore, under conditions of synthesis as described previously,[5] equation 10 can be expected to hold reasonably well in solutions as high as 5 and 6 molar.

PASADENA, CALIF.

[CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY OF IOWA STATE COLLEGE AND HARVARD UNIVERSITY]

Some Halogen-Metal Interconversion Reactions with Methylphenyl Halides[1]

BY SANDERS D. ROSENBERG[2]

RECEIVED MARCH 26, 1954

A series of halogen-metal interconversion reactions have been run between phenyllithium and some methylphenyl halides. From the results of these, and several other interconversions reported, a series of relative electronegativities has been worked out; phenyl > *o*-tolyl > 2,4-dimethylphenyl > 2,6-dimethylphenyl, mesityl > butyl. Interconversion of *p*-bromobenzyl bromide with *n*-butyllithium yielded 1-amyl-4-bromobenzene and *p*-bromo-α-(*p*-bromomethylphenyl)-toluene.

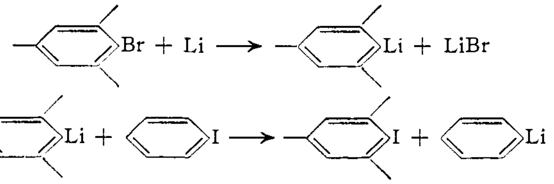
It has been postulated that the position of equilibrium in a halogen-metal interconversion reaction largely depends upon the relative electronegativities of the groups R and R'. When R and R' have

$$RX + R'Li \rightleftarrows RLi + R'X$$

approximately the same electronegativity, the equilibrium mixture contains about equal amounts of the four compounds involved.[3] This idea has been supported by the halogen-metal interconversion of iodobenzene with *p*-tolyllithium followed by carbonation to yield benzoic acid (47%) and interconversion of *p*-iodotoluene with phenyllithium to give *p*-toluic acid (34%).[4] A study was undertaken to measure the changes in the position of equilibrium as more methyl groups were substituted on the benzene ring.

o-Iodotoluene was subjected to halogen-metal interconversion with phenyllithium to yield, on carbonation, *o*-toluic acid (15%). Phenyllithium and 2,4-dimethyliodobenzene gave 2,4-dimethylbenzoic acid (8%). Reactions between phenyllithium and 2,6-dimethyliodobenzene, bromomesitylene and iodomesitylene, respectively, gave no halogen-metal interconversions.

Conversely, interconversion of iodobenzene with 2,6-dimethylphenyllithium yielded benzoic acid (63%) and 2,6-dimethyliodobenzene (70%). Iodobenzene with mesityllithium gave benzoic acid (39%) and iodomesitylene (69%). The latter reaction offers a method for the preparation of iodomesitylene from bromomesitylene which gives a much better yield than the direct iodination of mesitylene.[5]



As it has been observed that the lithium atom tends to become attached to the more electronega-

---

[1] Part of this research was supported by the Rubber and Plastics Branch, Wright Air Development Center.

[2] Research Laboratory, Metal & Thermit Corp., Rahway, N. J.

[3] "Organic Reactions," Vol. VI, 1951, p. 339.

[4] H. Gilman and R. G. Jones, THIS JOURNAL, **63**, 1441 (1941).

[5] R. L. Datta and N. R. Chatterjee, *ibid.*, **39**, 438 (1917).

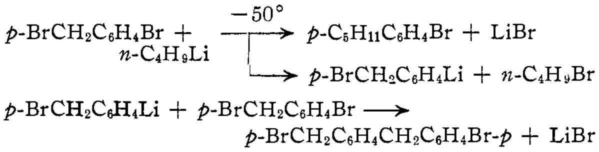
TABLE I

SOME HALOGEN–METAL INTERCONVERSION REACTIONS

Reactants		Products	
Halide	Lithium reagent	Acid, %	Halide, %
o-Iodotoluene	Phenyl-	*o*-Toluic, 15 Benzoic, 43	
2,4-Dimethyliodobenzene	Phenyl-	2,4-Dimethylbenzoic, 8.0 Benzoic, 43	
2,6-Dimethyliodobenzene	Phenyl	Benzoic, 53	2,6-Dimethyliodobenzene, 68
Iodobenzene	2,6-Dimethylphenyl	Benzoic, 63	2,6-Dimethyliodobenzene, 70
Bromomesitylene	Phenyl-	Benzoic, 38	Bromomesitylene, 83
Bromomesitylene	Butyl-	Mesitoic, 58	
Iodomesitylene	Butyl-	Mesitoic, 63	
Iodomesitylene	Phenyl-	Benzoic, 63	Iodomesitylene, 36
Iodobenzene	Mesityl-	Benzoic, 39	Iodomesitylene, 69
1-Iodonaphthalene	Phenyl-	1-Naphthoic, 43	

tive R group, it would seem that the phenyl group is more electronegative than *o*-tolyl, 2,4-dimethylphenyl, 2,6-dimethylphenyl and mesityl, in that order. Bromomesitylene and iodomesitylene were interconverted successfully with butyllithium, demonstrating that the mesityl group is more electronegative than butyl.

An attempt was made to interconvert *p*-bromobenzyl bromide with *n*-butyllithium at −50°. The course of the reaction was followed by the addition of trimethylchlorosilane. Instead of the hoped-for trimethyl-*p*-bromomethylphenylsilane, the products isolated were 1-amyl-4-bromobenzene (24%) and *p*-bromo-α-(*p*-bromomethylphenyl)-toluene (32%). This latter structure was selected as a result of an elemental analysis in relation to the other compounds that might have been formed.



$$p\text{-BrCH}_2\text{C}_6\text{H}_4\text{Br} + n\text{-C}_4\text{H}_9\text{Li} \xrightarrow{-50^\circ} p\text{-C}_5\text{H}_{11}\text{C}_6\text{H}_4\text{Br} + \text{LiBr}$$

$$\longrightarrow p\text{-BrCH}_2\text{C}_6\text{H}_4\text{Li} + n\text{-C}_4\text{H}_9\text{Br}$$

$$p\text{-BrCH}_2\text{C}_6\text{H}_4\text{Li} + p\text{-BrCH}_2\text{C}_6\text{H}_4\text{Br} \longrightarrow p\text{-BrCH}_2\text{C}_6\text{H}_4\text{CH}_2\text{C}_6\text{H}_4\text{Br-}p + \text{LiBr}$$

Apparently, the halogen–metal interconversion reaction is in competition with a simple nucleophilic substitution reaction. In addition, whatever *p*-bromomethylphenyllithium is formed reacts immediately with more *p*-bromobenzyl bromide.

Experimental

Organolithium Compounds.—*n*-Butyllithium was prepared as outlined by Gilman and co-workers.[6] The method of Gilman and Jones[7] was used to synthesize phenyllithium and 2,6-dimethylphenyllithium. Mesityllithium was prepared by refluxing, with good stirring, a mixture of 19.9 g. (0.10 mole) of bromomesitylene, 1.7 g. (0.2 g. atom plus 20%) of finely sliced lithium wire and 200 ml. of ether for 48 hours. The yield, as ascertained by acid titration, was 90%.

Methylphenyl Halides.—With the exception of iodomesitylene, all of the halides used were purchased from Eastman Kodak Co. (white label). Iodomesitylene was prepared by the iodination of mesitylene in the presence of nitric acid.[5]

Reaction of *o*-Iodotoluene with Phenyllithium.—In a 250-ml. flask were placed 10.9 g. (0.05 mole) of *o*-iodotoluene in 50 ml. of ether and 0.05 mole of phenyllithium in 46 ml. of ether. The solution was stirred for one hour and carbonated by pouring onto a Dry Ice–ether slurry. Work-up of the carbonation mix led to the isolation of 3.6 g. of mixed acid melting at 95–107°. This mixed acid had a neutral equivalent of 125.3. Assuming the mixed acid to contain only *o*-toluic and benzoic acids, its composition must be 28% *o*-toluic and 72% benzoic acid. On this basis the yield of *o*-toluic acid is 1.0 g. (14.7%) and of benzoic acid is 2.6 g. (42.6%). Infrared studies on authentic specimen and the mixed acid showed these percentages to be approximately correct.[8]

This same general method was used in the other reactions summarized in Table I. Only in the reaction of 2,4-dimethyliodobenzene and phenyllithium was another mixed acid isolated. As above, infrared studies were used to corroborate the figures obtained by neutral equivalent measurements. In five of the reactions listed in Table I, the ether layer of the carbonation mixture was worked-up in order to recover the halide present.

Reaction of *p*-Bromobenzyl Bromide with *n*-Butyllithium.—To 25.0 g. (0.10 mole) of *p*-bromobenzyl bromide[9] suspended in 150 ml. of ether at −50° was added 0.10 mole of *n*-butyllithium in 142 ml. of ether, dropwise and with good stirring. Upon completion of addition, 10.9 g. (0.1 mole) of trimethylchlorosilane in 100 ml. of ether was added in a thin stream. The cooling bath was removed and the reaction mixture stirred for three hours. The ethereal solution was filtered under nitrogen, the ether removed by distillation from a steam-bath and the residual oil fractionally distilled under reduced pressure.

Fraction 1 distilled at 68–71° (0.15 mm.), weighed 5.5 g. (24.2%), n^{21}_{D} 1.5228. 1-Amyl-4-bromobenzene[10] distils at 109–110° (4.0 mm.), n^{20}_{D} 1.5237.

Fraction 2 distilled at 152–156° (0.3 mm.), m.p. 85–105°. The solid was crystallized from 12 ml. of a 50% methanol–benzene solution to yield 5.5 g. of material melting at 112–113°.

Anal. Calcd. for $C_{14}H_{12}Br_2$: C, 49.43; H, 3.56. Found: C, 49.83; H, 3.72.

The yield of *p*-bromo-α-(*p*-bromomethylphenyl)-toluene was 32.4%.

CAMBRIDGE, MASSACHUSETTS

---

[6] H. Gilman, J. A. Beel, C. G. Brannen, M. W. Bullock, G. E. Dunn and L. S. Miller, THIS JOURNAL, **71**, 1499 (1949).

[7] "Organic Reactions," Vol. VI, 1951, p. 353.

[8] The author is indebted to Dr. V. A. Fassel and M. Margoshes of the Ames Laboratory, Iowa State College, for the infrared studies reported herein.

[9] J. R. Sampey and E. M. Hicks, THIS JOURNAL, **62**, 3252 (1940).

[10] J. W. Copenhaver, M. F. Roy and C. S. Marvel, *ibid.*, **57**, 1311 (1935).