[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

HALOGEN-METAL INTERCONVERSION AND METALATION IN THE NAPHTHALENE SERIES

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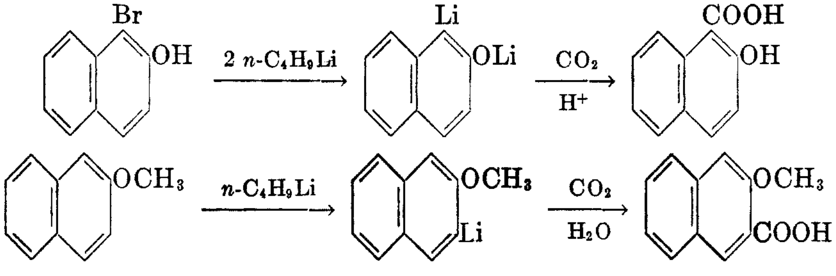
In connection with the synthesis of substituted naphthylsilanes, it was desirable to prepare some naphthyllithium compounds containing functional groups, such as hydroxyl or methoxyl. Suitable methods for the formation of such organolithium compounds are the halogen-metal interconversion reaction and metalation (1).

For the preparation of methoxynaphthyllithium compounds, both methods were employed, whereas the hydroxynaphthyllithium compounds were prepared exclusively by the halogen-metal interconversion reaction with n-butyllithium.



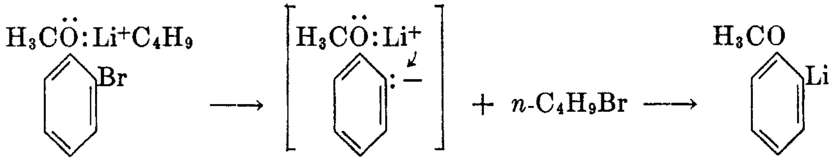
Previous work in this laboratory has shown that the reactivity of bromine towards n-butyllithium depends upon the position of bromine relative to other substituents in the ring (2). Therefore, 1-bromo-2-naphthol and 6-bromo-2-naphthol were selected to determine the optimum conditions for the halogen-metal interconversion reaction. n-Butyllithium was allowed to react with each of these compounds in ether at room temperature for different periods of time. The yields of the interconversion products were determined by the isolation of the acids obtained after carbonation of the organolithium compounds. Stirring the reaction mixtures for 30 to 45 minutes at room temperature gave the best yields and the same conditions were employed with the other compounds. In all cases, it was found by the identification of the corresponding acids that the halogen-metal interconversion reactions involve no rearrangements, nor was there any evidence for simultaneous metalation.

The dibromohydroxy compounds, however, showed a notable difference in their behavior with n-butyllithium. In the case of 2,4-dibromo-1-naphthol, even by using three equivalents of n-butyllithium, only the bromine in the *ortho*-position to the hydroxyl group reacted, since the acid obtained after carbonation of the lithium compound was 4-bromo-1-hydroxy-2-naphthoic acid. Similarly, 1,3-dibromo-2-naphthol reacted with n-butyllithium to give 1-bromo-2-hydroxy-3-naphthyllithium. 2,4-Dibromophenol, also, gave similar results, even though the reaction was carried out at ether-reflux temperature for three hours. It has been observed previously that in the halogen-metal interconversion reaction with bromophenols, bromine in the *para*-position is much less reactive than bromine in the *ortho*-position (3). For example, *o*-bromophenol reacts with *n*-butyllithium in about 40 minutes to give a 67% yield of the organolithium compound, while *p*-bromophenol requires an ether-reflux temperature for about two hours and the yield is only 41%. We have found that *m*-bromophenol under similar conditions gives a very low yield (15%). A comparison of the relative reactivities of *p*-bromophenol and 2,4-dibromophenol and also of 4-bromo-1-naphthol and 2,4-dibromo-1-naphthol with *n*-butyllithium reveals that the interconversion of the second halogen in the 4-position in the dibromo compounds is much more difficult than that of bromine in the monobromo compounds. Similar results were obtained in the case of 2,4-dibromoanisole which, after a halogen-metal interconversion reaction, yielded 5-bromo-2-methoxybenzoic acid.

From the present results, and from the extensive investigations of the halogen-metal interconversion reactions carried out in this laboratory (1), and by Wittig and co-workers (4), the following broad generalizations may be made: (a) The reactivity of halogen increases as the electronegativity of the element decreases, *i.e.* the reactivity series I > Br > Cl > F is obtained. (b) The reactivity of halogen depends upon its position in the ring with respect to other activating groups, *i.e.* *o* > *p* > *m*. (c) Alkyllithium compounds, except methyllithium, are more reactive than aryllithium compounds. (d) In the polyhalogen-compounds, the interconversion reaction with one *ortho*-halogen atom is much more rapid than the interconversion with further halogen atoms.[1]

Since the reactivity of the halogens depends upon the relative electronegativity of the element, it may be inferred that the reaction involves the removal of halogen, in the positive condition, in a neucleophilic attack by the anion of the organolithium compound.[2] The second of the above generalizations suggests that the inductive forces also have some effect. The order of reactivity of a halogen atom (*o* > *p* > *m*) is such as would be predicted from the inductive effect of the other group in the ring. In the case of *meta* compounds, especially *m*-bromophenol and *m*-bromoanisole, it seems that the other reactions compete with the halogen-metal interconversion reactions (4c).

The general high reactivity of the halogens in the *ortho*-position may be attributed to the coordination of a lithium cation, from an organolithium compound, with a pair of electrons on the substituent group. The possible coordination step in the *ortho*-position facilitates the reaction in two ways (5). Since ethyl ether is



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[1] Unpublished studies by B. Hofferth indicate that in certain cases attempts to interconvert a second *ortho*-halogen atom may lead to replacement of the halogen by hydrogen. This reaction is still under investigation.

[2] For a different viewpoint see reference (4c).

characterized by having a low dielectric constant, it is anticipated that RLi compounds will exist for the most part as tightly bound ion pairs with a number of highly polarized solvent molecules being rather closely associated with each of the ions of these pairs.[3] The displacement of one or more of these solvent molecules by the bromo compound will have several important effects. First, a closer approach of the R^- portion of the pair to the halogen will be facilitated because of the departure of one or more bulky solvent molecules. Second, it is likely that the bond $>\overset{\delta-}{\mathrm{O}}\text{-----}\overset{+}{\mathrm{Li}}$ will be stronger if the oxygen is attached to the relatively highly polarizable aromatic system than it is when the oxygen is part of the saturated system. This will have the effect of loosening the attraction between Li^+ and R^- making the latter more available for attack on halogen. A third factor which is of importance in determining the relative reactivity of *ortho-* and *para-*compounds is the inhibition, in the complex described, of the usual resonance interaction of the unshared pairs of oxygen with the ring. This effect normally increases the negative charge on the *ortho-* and *para-*carbon atoms and should therefore tend to impede nucleophilic attack on halogen located at these positions. The effects due to the coordination are well evidenced in the case of 2,4,6-tribromoanisole, in which the bromine atoms in the 2- and 6-positions are more reactive than one in the 4-position (2).

The interconversion of a second halogen atom would produce a divalent aryl anion. The difficulty encountered in the second interconversion may be attributed to resistance to this accumulation of negative charge on the aryl ring. In addition, if the second halogen atom is in the *meta-* or *para-*position with respect to oxygen, it will not be in proximity to the coordinated butyllithium ion pair. The mechanism of reactions taking place at a second *ortho* halogen atom is still under investigation.[1]

Regarding the third generalization, the carbanion from the alkyllithium compounds is more reactive because it is not stabilized by the intramolecular effects due to polarizability and resonance which cause, to some extent, the stabilization of the carbanion from the aryllithium compounds.

In the literature, there are some results contradictory to the above generalizations. These may be due to various reasons. First, the halogen-metal interconversion reaction is often very prompt and also reversible (6), and is sometimes accompanied by other side reactions such as metalation and coupling (4c); therefore proper conditions are to be chosen for each compound according to its reactivity to get the appropriate yields. Second, the yields of the halogen-metal interconversion reactions are based on the yields of the acids obtained after carbonation of the organolithium compounds. During carbonation, generally some ketones and carbinols are formed, and these reduce considerably the yields of the acids. Furthermore, a slight solubility in water of some of the organic acids prevents their complete recovery. The yields of the acids recorded in the literature, therefore, do not represent the true yields of the organometallic compounds.

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[3] Clusters of ions in higher states of aggregation may also be of importance, but their existence will not materially change the argument.

Next, the metalation of some naphthylmethyl ethers with *n*-butyllithium was examined. 1-Methoxynaphthalene was metalated mainly in the 2-position, since the only acid isolated after the carbonation of the metalated product was 1-methoxy-2-naphthoic acid. Similarly, the metalation of 2-methoxynaphthalene gave 2-methoxy-3-naphthyllithium. The metalation in the 3-position instead of in the 1-position has been observed also in 2-naphthol and 2-ethoxynaphthalene (3). 2,7-Dimethoxynaphthalene gave only a monometalation product, the lithium atom entering the 3-position, when the compound was refluxed in ether for 26 hours with about one equivalent of *n*-butyllithium. But, when the reaction was repeated with four equivalents of *n*-butyllithium for 48 hours, di-metalation took place in about 30% yield. The demethylation of the methoxy acids gave the corresponding hydroxy acids. 2,7-Dihydroxy-3-naphthoic acid has been reported (7), but the diacid is referred to only in the patent literature (8). For identification purposes, therefore, attempts were made to brominate the diacid. Even by the use of various methods of bromination, the only compound obtained was the monobromo derivative. The 2,7-dimethoxynaphthalene-3,6-dicarboxylic acid also gave on bromination only the monobromo compound. However, the coupling of 2,7-dihydroxynaphthalene-3,6-dicarboxylic acid with diazonium salts yields *bis*-azo dyes. Since in 2,7-dihydroxynaphthalene, 1- and 8- are very probably the only positions where coupling can take place, it is evident that during the metalation these two positions are not involved. By analogy with 2-methoxynaphthalene and from the various examples of the *ortho*-metalation of other ethers, therefore, it can be inferred that the metalation of 2,7-dimethoxynaphthalene has taken place in the 3- and 6-positions. 2,7-Dihydroxynaphthalene was not metalated, even though 2-naphthol has been metalated (7%) by *n*-butyllithium (3).

Two contrary viewpoints have been suggested for the mechanism of metalation. In the first, the metalation is pictured as a process of attraction of the metal cation for electrons. Due to the availability of the electrons on the substituent groups, first the coordination complex is formed and then the migration of the metal to the *ortho*-position of high electron density takes place, with the simultaneous removal of a proton. In other words, the mechanism is supposed to involve mainly an electrophilic attack by a metallic cation (9).

In the second, it is suggested that the proton in the *ortho*-position, which is made acidic by the initial coordination, is removed by the nucleophilic attack by the carbanion from the metalating agent; or the primary process in the mechanism is a nucleophilic attack on a proton (5).

According to the first viewpoint, the metalation of 2-methoxynaphthalene should take place in the 1-position, which is invariably attacked by the other electrophilic reagents (10, 11). Furthermore it, being *ortho* to the methoxyl group, should be favored by the initial coordination for the electrophilic attack by the lithium cation. Therefore it seems inappropriate to describe the reaction as involving, primarily, an electrophilic attack by the cation.

An explanation for the generally observed low metalation yields with phenols may now be given. The powerful field effect of the phenoxide ion formed initially by the action of an organometallic compound on the active hydrogen, makes the *ortho*-hydrogen less acidic, and reduces its chances of removal by a nucleophilic attack.

It will be noticed that the halogen-metal interconversion and the metalation reactions involve a similar kind of mechanism. The former reaction, however, is much more prompt than the latter, because of the higher polarizability of halogens than that of hydrogen, and therefore it is more suitable for synthetic work. Furthermore, the halogen-metal interconversion reaction facilitates the substitution of metal in the desired position in the ring.

EXPERIMENTAL

HALOGEN-METAL INTERCONVERSION REACTIONS

General procedure. The solution of *n*-butyllithium (12) in ether was added, over a short period of time (about 5–10 minutes), to the RX compound in ether. After stirring the mixture at room temperature, it was carbonated by being poured jet-wies into a slurry of Dry Ice in ether. After completion of the reaction, the mixture was hydrolyzed with water. The naphthoic acids were separated from the naphthols by acidifying the hydrolysate with dilute hydrochloric acid and then extracting the ether layer with sodium bicarbonate. From the ether layer were obtained neutral oils which were contaminated with the naphthols. These oils were not investigated. The naphthoic acids were obtained by acidifying the aqueous portions. In most cases, the yields of the crude acids, after carbonation, exceeded 60%. The yields of the pure acids, however, are considerably reduced, as it is difficult to recover completely the acids from their aqueous solutions. In addition, 2-hydroxy-1-naphthoic acid (13) and 1-hydroxy-4-naphthoic acid (14) decarboxylate, even in boiling water.

METALATION REACTIONS

General procedure. The appropriate amounts of *n*-butyllithium in ether were added to the naphthalene derivatives dissolved in ether, and the mixtures were refluxed with stirring for several hours in nitrogen atmospheres. The reaction products were carbonated by pouring slowly into slurries of Dry Ice in ether. After about two to three-hours time, the carbonated products were hydrolyzed. The aqueous portions, being basic due to lithium hydroxide formed during hydrolysis, contained most of the organic acids. In order to recover the remaining portions of the organic acids, the ethereal layers were extracted with 20% sodium hydroxide solution. The extracts were added to the aqueous layers and the combined basic solutions were acidified with dilute hydrochloric acid. The organic acids which separated were freed from any phenolic impurities by solution in sodium bicarbonate solutions and reprecipitation. The acids, being highly contaminated with valeric acid, were purified by repeated crystallizations from appropriate solvents. Tables I and II give the details of the experiments.

The following are typical metalation experiments:

2,7-Dimethoxy-3-naphthoic acid. To a solution of 4.7 g. (0.025 mole) of 2,7-dimethoxynaphthalene in 100 ml. of ether was added 0.03 mole of *n*-butyllithium in 30 ml. of ether and the mixture was refluxed with stirring for 26 hours. The product was carbonated and then hydrolyzed. The organic acid, isolated by the usual procedure by the sodium carbonate extraction, weighed 3.8 g. (70.3%) and melted over the range of 155–170°, being highly contaminated with valeric acid. The crude acid was purified by crystallizing once from glacial acetic acid and twice from benzene. The yield of pure 2,7-dimethoxy-3-naphthoic acid was 2.5 g. (43%) m.p. 185.5°.

Anal. Calc'd for $C_{13}H_{12}O_4$: C, 67.2; H, 5.2; Neut. equiv., 232.
Found: C, 66.88, 66.90; H, 5.5, 5.2; Neut. equiv., 230.

2,7-Dihydroxy-3-naphthoic acid. To 15 ml. of hydriodic acid (*d.* 1.5) was added 1 g. of

TABLE I

REACTIONS OF RX COMPOUNDS WITH n-C_4H_9Li

RX	RX IN ETHER		n-C_4H_9Li IN ETHER		STIRRING PERIOD, Hour	PRODUCT	M.P. OF PURE ACID, °C.	YIELD OF PURE ACID[a]	
	Mole	Ml.	Mole	Ml.				grams	%
1,2-Br(OH)$C_{10}H_6$[b]	0.03	50	0.06	50	1	1,2-(COOH)(OH)$C_{10}H_6$[c]	156–157	2.41	42.7[d]
1,2-I(OH)$C_{10}H_6$	.0125	50	.025	25	1	1,2-(COOH)(OH)$C_{10}H_6$	156–157	0.35	15
6,2-Br(OH)$C_{10}H_6$[b]	.02	50	.04	65	$\frac{1}{2}$	6,2-(COOH)(OH)$C_{10}H_6$[e]	240–241	1.8	48[f]
1,4-Br(OH)$C_{10}H_6$[g]	.02	50	.04	40	1	1,4-(COOH)(OH)$C_{10}H_6$[h]	185–186	2.2	55.5
1,2,4-(OH)$Br_2C_{10}H_5$	.0133	75	.027	25	$\frac{3}{4}$	1,2,4-(OH)(COOH)Br$C_{10}H_5$[i]	243–244	1.2	30[j]
1,3,2-Br_2(OH)$C_{10}H_5$[k]	.015	50	.045	50	$\frac{1}{2}$[l]	1,2,3-Br(OH)(COOH)$C_{10}H_5$[m]	230–231	-	31[n]
1,2-Br(OCH_3)$C_{10}H_6$	.019	80	.019	80	$\frac{3}{4}$	1,2-(COOH)(OCH_3)$C_{10}H_6$[o]	175	2.7	70.4[p]
1,3-(OH)BrC_6H_4	.030	50	.060	40	2[q] (ether-reflux)	1,3-(OH)(COOH)C_6H_4[r]	199–200	0.6	15
1,2,4-(OH)$Br_2C_6H_3$	.03	75	.09	60	1[s]	1,2,4-(OH)(COOH)BrC_6H_3[t]	168–169	3.6	55.3
1,2,4-(OCH_3)$Br_2C_6H_3$	.0128	50	.026	28	1[u]	1,2,4(OCH_3)(COOH)BrC_6H_3[v]	119	1.25	42

[a] The yields of the crude acids were 10–15% higher. [b] Prepared by the procedure of Franzen and Stauble (15). [c] Crystallized from dilute ethanol and identified through the acetyl derivative, m.p. 130–131°; the reported (16) m.p. of 1-acetoxy-2-naphthoic acid is 130.5–131.5°. [d] The yields of the crude acid were 60% and 44.8% after 3 and 17 hours respectively. [e] Crystallized from water. The acetyl derivative melted at 220–221°; the m.p. reported (17) is 221–223°. [f] After reacting for 1, 3, and 17 hours, the yields of the crude acid were 65.2, 37.3, and 31.1%, respectively. [g] Prepared according to the method of Militzer (18). [h] Its acetyl derivative melted at 178–179°. Heller reports (14) the m.p. of 1-acetoxy-4-naphthoic acid is 178–179°. [i] Identified by mixed m.p. with 1-hydroxy-4-bromo-2-naphthoic acid, prepared by the bromination of 1-hydroxy-2-naphthoic acid (19). [j] The yield of the pure acid is low, because it is obtained after several crystallizations from ethanol. [k] Prepared according to the procedure of Fries and Schimmelschmidt (20). [l] n-Butyllithium was added to the naphthol at −20°, and the temperature was allowed to rise to room temperature during $\frac{1}{2}$ hour, since the reactions at room temperature yielded only a dark-brown colored side product. [m] Identified by mixed melting point with 1-bromo-2-hydroxy-3-naphthoic acid (21). [n] Represents the yield of the crude product. [o] *Anal.* Calc'd for $C_{12}H_{10}O_3$: Neut. equiv., 202. Found: Neut. equiv., 200, 201. [p] Reaction for only 10 minutes gave 65% yield of the pure acid. [q] The reaction at room temperature for $\frac{1}{2}$ hour gave no acid. [r] Identified through its acetyl derivative, m.p. 130°. [s] The reaction at ether-reflux temperature for $1\frac{1}{2}$ and 3 hours gave 27 and 45% yields. [t] Identified by mixed melting point with 5-bromosalicylic acid. [u] The reaction for two hours gave 43% yield of the acid. [v] Identified by demethylation and mixed m.p. with 5-bromosalicylic acid.

TABLE II

Metalation of Naphthylmethyl Ethers

COMPOUND METALATED	IN ETHER		n-C_4H_9Li IN ETHER		HOURS[d]	PRODUCT	M.P., °C.	YIELD OF ACID,	
	Mole	Ml.	Mole	Ml.				GRAMS	%
$1\text{-}(OCH_3)C_{10}H_7$	0.075	50	0.075	40	24	$1,2\text{-}(OCH_3)(COOH)C_{10}H_6$[a]	125–126	—	20–25
$2\text{-}(OCH_3)C_{10}H_7$	.10	100	.10	90	18	$2,3\text{-}(OCH_3)(COOH)C_{10}H_6$[b]	131–132	10.2	50
$2,7\text{-}(OCH_3)_2C_{10}H_6$	.025	100	.030	30	26	$2,7,3\text{-}(OCH_3)_2(COOH)C_{10}H_5$	185.5	2.5	43
$2,7\text{-}(OCH_3)_2C_{10}H_6$	.10	100	.40	330	48[c]	$2,7,3,6\text{-}(OCH_3)_2(COOH)_2C_{10}H_4$	271–272	7	25

[a] Identified by mixed melting point with 1-methoxy-2-naphthoic acid, prepared by refluxing a mixture of 1-hydroxy-2-naphthoic acid with methyl sulfate (3 parts), anhydrous potassium carbonate (5 parts), and acetone, and by hydrolyzing the resulting ester with 10% potassium hydroxide. [b] Demethylation of the acid with HI (*d*, 1.5) at steam-bath temperature for six hours, gave 93–97% of 2-hydroxy-3-naphthoic acid, which was identified by mixed m.p. 220–221°. [c] When the reaction was carried out for 66 hrs., the yield of the acid was 35%. [d] That mixture was stirred at ether-reflux temperature.

2,7-dimethoxy-3-naphthoic acid and the mixture was refluxed for three hours. The product was poured into 200 ml. of water. The hydroxy acid, (0.75 g., m.p. 250–254°), was extracted with benzene. The residue was crystallized from dilute ethanol; m.p. 254–256°. The reported (7) melting point for 2,7-dihydroxy-3-naphthoic acid is 254–256°.

Anal. Calc'd for $C_{11}H_8O_4$: C, 64.71; H, 3.92.
Found: C, 64.86, 65.2; H, 3.99, 4.01.

Metalation of 2,7-dimethoxynaphthalene. To 2,7-dimethoxynaphthalene (18.8 g., 0.10 mole) in 100 ml. of ether was added *n*-butyllithium (0.4 mole) in 330 ml. of ether and the mixture was refluxed for 48 hours. The product was carbonated and hydrolyzed with dilute hydrochloric acid. The ether layer was extracted with sodium carbonate solution. The dicarboxylic acid obtained by acidifying carbonate extracts was purified by extraction with ethanol. The ethanol-insoluble acid weighed 9 g. (28.2%), m.p. 268–270°. The pure 2,7-dimethoxynaphthalene-3,6-dicarboxylic acid melted at 271–272°, when it was crystallized from glacial acetic acid.

Anal. Calc'd for $C_{14}H_{12}O_6$: C, 60.9; H, 4.3; Neut. equiv., 138.
Found: C, 60.92, 60.70; H, 4.34, 4.23; Neut. equiv., 137.

From the ethanolic mother liquor a small amount of substance (0.3 g.) of m.p. 198–200° was obtained; it was not identified.

2,7-Dihydroxynaphthalene-3,6-dicarboxylic acid. 2,7-Dimethoxynaphthalene-3,6-dicarboxylic acid (6 g., 0.021 mole) was added to 50 ml. of hydriodic acid (*d.* 1.5) and the mixture was heated on a steam-bath for six hours. The yellowish product was collected; 4.4 g. (81.6%), m.p. 350–360° (dec.). It was crystallized from glacial acetic acid. The pure acid melted on rapid heating at 365–368° (dec.). The reported m.p. is above 300° (8). It gives an olive-green color with ethanolic ferric chloride and is soluble in ethanol and alkali.

Anal. Calc'd for $C_{12}H_8O_6$: C, 58.07; H, 3.23.
Found: C, 58.14, 58.07; H, 3.43, 3.60.

Bromination of 2,7-dihydroxynaphthalene-3,6-dicarboxylic acid. To a suspension of 2,7-dihydroxynaphthalene-3,6-dicarboxylic acid (1.9 g., 0.007 mole) in 40 ml. of glacial acetic acid was added dropwise a solution of 2.4 g. (0.015 mole) of bromine in 10 ml. of acetic acid and the mixture was stirred at room temperature for six hours. The yellow product weighed 2 g., m.p. 335–340° (dec.); yield, 1.65 g. (72%).

Anal. Calc'd for $C_{12}H_7BrO_6$: Br, 24.44. Found: Br, 24.30, 24.37.

When the above bromination was repeated at steam-bath temperature, the same monobromo product was obtained. Similarly, the bromination of 2,7-dihydroxynaphthalene-3,6-dicarboxylic acid in carbon tetrachloride, using iron powder as a catalyst, gave the same monobromo derivative.

Bromination of 2,7-dimethoxynaphthalene-3,6-dicarboxylic acid. To a mixture of 1 g. of the acid and 0.4 g. of anhydrous aluminum chloride in 25 ml. of glacial acetic acid was added dropwise 0.4 ml. of bromine dissolved in 20 ml. of glacial acetic acid. During the addition of bromine, the reaction mixture was kept cooled by ice-water. After the addition, the mixture was heated on a steam-bath for 4½ hours. The product was poured into dilute hydrochloric acid. The yellowish precipitate, which weighed 1.2 g. (93%), m.p. 275–280°, was crystallized from glacial acetic acid. Pure 1-bromo-2,7-dimethoxynaphthalene-3,6-dicarboxylic acid, 0.6 g. (46.5%) melted at 281–282°.

Anal. Calc'd for $C_{14}H_{11}BrO_6$: Br, 22.54. Found: Br, 21.65.

Azo dye from 2,7-dihydroxynaphthalene-3,6-dicarboxylic acid and p-sulfonylamidobenzenediazonium chloride. To a solution of 0.9 g. (0.004 mole) of 2,7-dihydroxynaphthalenedicarboxylic acid dissolved in 300 ml. of ethanol and 20 ml. of 10% sodium hydroxide was added a filtered diazonium chloride solution prepared from 1.9 g. (0.01 mole) of sulfanilamide. The dark-brown colored mixture was stirred for two hours, keeping the temperature of the mixture below 10°. The dye was washed with dilute ethanol and water. It was insoluble in most of the organic solvents. Therefore, it was dissolved in concentrated sulfuric acid, filtered, and reprecipitated by water. The purified dye, 0.6 g., fused above 400° and gave an intense brown-red color with concentrated sulfuric acid.

Anal. Calc'd for $C_{24}H_{18}N_6O_{10}S_2$: S, 10.42. Found: S, 9.62.

The *azo dye* prepared from *p*-nitrobenzenediazonium chloride could not be purified.

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SUMMARY

1. The halogen-metal interconversion reactions with *n*-butyllithium have been carried out with several bromo compounds.

2. In the case of dibromo-hydroxy and -methoxy compounds, it has been observed that the interconversion takes place, even by using appropriate equivalents of *n*-butyllithium, only with the *ortho*-bromine atoms.

3. A mechanism for the halogen-metal interconversion reaction has been proposed.

4. Three naphthylmethyl ethers have been metalated with *n*-butyllithium and the results have been found to agree with the predictions derived from the supposed mechanism involving a nucleophilic attack on hydrogen.

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