TABLE I

No. substituents	1	2	3	4	5	6
All alike	1	3	3	3	1	1
All different	1	3	10	30	60	60
Two alike	..	3	6	16	30	30
Three alike	..	..	3	6	10	10
Two pairs	..	..	..	11	16	16
Four alike	..	..	..	3	3	3
Two alike and three alike	..	..	..	..	6	6
Five alike	..	..	..	..	1	1
Three alike and three alike	..	..	..	..	..	3
Two alike and four alike	..	..	..	..	..	3
Three pairs	..	..	..	..	..	11

importance of aromatic hydrocarbons, the exact numbers of these isomers are now computed up to a content of 24 carbon atoms.

The numbers of isomeric derivatives of benzene are shown in Table I (this applies to any substituents, *e. g.*, Cl, NO_2).

Using this table and the numbers of isomeric alkyl groups[5] (shown also in the top line in each column of Table II) the numbers of isomeric alkylbenzenes are calculated by itemizing the types and by summation as in Table II. Thus,

TABLE II

C_{10}		C_{12}		C_{13}		C_{14}	
Bu	4	Hex	17	Hept	39	Oct	89
MePr	6	MeAm	24	MeHex	51	MeHept	117
Et_2	3	EtBu	12	EtAm	24	EtHex[a]	51
Me_2Et	6	Me_2Bu	24	Me_2Am	48	Me_2Hex[a]	102
Me_4	3	Pr_2	9	PrBu	24	PrAm	48
	—	MeEtPr	20	MeEtBu	40	MeEtAm	80
	22	Me_3Pr	12	Me_3Bu	24	Me_3Am	48
		Et_3	3	$MePr_2$	22	Bu_2	30
		Me_2Et_2	11	Et_2Pr	12	MePrBu	80
		Me_4Et[a]	3	Me_2EtPr[a]	32	Et_2Bu[a]	24
C_{11}		Me_6	1	Me_4Pr[a]	6	Me_2EtBu	64
			—	$MeEt_3$[a]	6	Me_4Bu[a]	12
Am	8		136	Me_2Et_2	6	$EtPr_2$	22
MeBu	12			Me_3Et	1	Me_2Pr_2[a]	38
EtPr	6				—	$MeEt_2Pr$	32
Me_2Pr	12				335	Me_3EtPr[a]	20
$MeEt_2$	6					Me_3Pr[a]	2
Me_3Et	6					Et_4	3
Me_5	1					Me_2Et_3[a]	6
	—					Me_4Et_2[a]	3
	51						—
							871

[a] Not yet represented by known hydrocarbons.

for example, there are 80 methylpropylbutylbenzenes, obtained by multiplying 4 (kinds of butyl group), 2 (kinds of propyl group), and 10 from Table I. Types containing two or more alkyl groups of like carbon content above ethyl may be subdivided according to whether these groups are alike or unlike. Thus, for tributylbenzenes, there are 3 × 4 isomers with the three substituents alike, 6 × 4 × 3 isomers with two of them alike, and 10 × 4 isomers with all three different, a total of 124.

Table II has been extended similarly for alkylbenzenes containing 15 to 24 carbon atoms. The numbers increase a little more rapidly than in the case of the paraffin isomers[1,2] so that the ratio for the two series increases steadily as shown in Table III and should exceed 1.0 at C_{28}. Again there is an alternation in ratio of successive numbers, considerable at first, but quickly subsiding as shown in Fig. 2. Extrapolation would be still more precise using the ratio to number of alkyl groups,[2,5] which approaches 0.04718 asymptotically. This would give for C_{30} 4529 × 10^6.

TABLE III

Carbon atoms	Numbers of isomeric: Alkylbenzenes	Paraffins	Ratio
7	1	9	0.1111
8	4	18	.2222
9	8	35	.2286
10	22	75	.2933
11	51	159	.3208
12	136	355	.3831
13	335	802	.4177
14	871	1,858	.4688
15	2,217	4,347	.5100
16	5,749	10,359	.5550
17	14,837	24,894	.5960
18	38,636	60,523	.6384
19	100,622	148,284	.6786
20	263,381	366,319	.7190
21	690,709	910,726	.7584
22	1,817,544	2,278,658	.7976
23	4,793,449	5,731,580	.8363
24	12,675,741	14,490,245	.8748

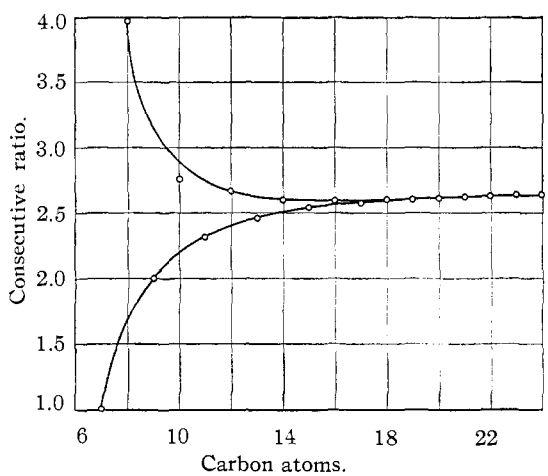

Fig. 2.—Alternations in consecutive ratios in number of isomeric alkylbenzenes.

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Halogen–Metal Interconversions with Halides Containing Functional Groups

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In connection with studies concerned with physiological action, it was necessary to have

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TABLE I

REACTIONS OF RX COMPOUNDS WITH n-C_4H_9Li

RX	RX in ether, mole	cc.	n-C_4H_9Li mole	ether, cc.	Temp. of n-C_4H_9Li sol., °C.	Time of addition, min.	Stirring period, min.	Product	Yield, g.	Yield, %
o-BrC_6H_4OH	0.041	25	0.082	250	Room	Rapidly	40	o-HOC_6H_4COOH[a]	3.77	67
p-BrC_6H_4OH	.05	50	.1	200	Room		[b]	p-HOC_6H_4COOH		35[c]
p-IC_6H_4OH	.0437	50	.0875	190	Room	4[d]	3	p-HOC_6H_4COOH		50[e]
o-BrC_6H_4COOH	.05	100	.1	200	−75	2	10 at −75°	o-$C_6H_4(COOH)_2$	2.9	35[f]
o-IC_6H_4COOH	.05	125	.1	150	−75	4	6 at −75°	o-$C_6H_4(COOH)_2$	1	12[g]
p-IC_6H_4COOH	.05[h]		*ca.* .1	200	−75		4 at −75°	p-$C_6H_4(COOH)_2$		62[i,j]
p-$IC_6H_4SO_2N(C_2H_5)_2$	.02	60	*ca.* .02	100	−75[l]	2[k]	1	p-$HOOCC_6H_4SO_2N(C_2H_5)_2$[m]	3.7	78

[a] Identified by mixed melting point. [b] Refluxed without stirring for two hours. [c] When p-bromophenol was allowed to react with n-butyllithium for one and one-half hours, the yield of p-hydroxybenzoic acid was 41% (studies by R. W. Leeper). [d] The mode of addition was reversed in this experiment, the n-butyllithium being added to the RX compound. This is the preferred order of addition. [e] When p-iodophenol was allowed to react with n-butyllithium for twenty minutes, the yield of acid was 48% (studies by R. K. Abbott). [f] Also obtained here was 9 g. of an oil containing neutral components which was not investigated further. [g] Weight of neutral oil obtained was 11 g. [h] Powdered p-iodobenzoic acid was added in one portion to the n-butyllithium solution. [i] Weight of neutral oil obtained was 9 g. [j] In addition to the terephthalic acid formed (identified as the dimethyl ester by mixed melting point) there was recovered 7% of p-iodobenzoic acid. The separation was accomplished by extraction with acetone. Recovery of starting material indicates that an insufficient quantity of n-butyllithium was used. The experiment was carried out before the precise method for determining the titer of alkyllithium compounds was completed (see Gilman and Haubein, THIS JOURNAL, **66**, 1515 (1944)). Also the yield would probably have been improved by the reverse method of addition. [k] A bright yellow precipitate formed immediately. [l] When the interconversion was carried out at room temperature, a tar was obtained. [m] Melting point 192–194° (with turbidity). Recrystallization from ethanol or acetic acid did not raise the melting point. *Anal.* Calcd. for $C_{11}H_{15}O_4NS$: N, 5.44; neut. equiv., 257. Found: N, 5.38 and 5.41; neut. equiv., 253.

some organolithium compounds in which were contained a functional group, like hydroxyl or carboxyl. One of the better ways for the synthesis of such types is the halogen-metal interconversion reaction[1a]: RX + R'Li → RLi + R'X. Some of the yields by this reaction are quite satisfactory. For example, the RLi compound from o-bromophenol is formed to an extent of at least 67%, because carbonation after interconversion gives a 67% yield of salicylic acid. By a corresponding procedure it was shown that the yields of RLi compounds from p-iodobenzoic acid and p-iodo-N,N-diethylbenzenesulfonamide were 62 and 72%, respectively.

In those cases where the functional group has an active hydrogen it is preferable to add the n-butyllithium to the RX compound so that the primary product is not consumed in a secondary halogen–metal interconversion with RX. This is illustrated by the sequence of reactions

$$o\text{-}BrC_6H_4OH + n\text{-}C_4H_9Li \longrightarrow o\text{-}BrC_6H_4OLi + n\text{-}C_4H_{10} \quad (I)$$

$$o\text{-}BrC_6H_4OLi + n\text{-}C_4H_9Li \longrightarrow o\text{-}LiC_6H_4OLi + n\text{-}C_4H_9Br \quad (II)$$

$$o\text{-}LiC_6H_4OLi + o\text{-}BrC_6H_4OH \longrightarrow C_6H_5OLi + o\text{-}BrC_6H_4OLi \quad (III)$$

Reaction (I) generally proceeds at a much more rapid rate than reaction (II). When (II) is under way, there are contained in the mixture two RLi compounds which can participate in the interconversion reaction: o-LiC_6H_4OLi and n-C_4H_9Li. The extent to which the o-LiC_6H_4OLi contributes to the interconversion results essentially in the destruction of a corresponding amount of the substituted RX compound [Reaction (III)]. Accordingly the addition of n-butyllithium to the RX compound ensures a maximum initial replacement of the active hydrogen.

(1a) For general references, see pp. 538–539 of Gilman, "Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1943.

Experimental

General Procedure.—The solution of the RX compound in ether was added, in the first experiments, over a short period of time to an ether solution of butyllithium. After stirring the mixture, it was carbonated by pouring over solid carbon dioxide. The product was obtained by acidification of the sodium hydroxide extract. From p-iodophenol and from o- and p-bromophenol, the hydroxybenzoic acids obtained as products were separated from the phenols by saturating the alkaline extract with carbon dioxide and extracting with ether. Details are given in the accompanying table.

p-Iodo-N,N-diethylbenzenesulfonamide.—p-Iodobenzenesulfonyl chloride was prepared from iodobenzene in accordance with the directions of Baxter and Chattaway.[2] Then, to a solution of 8 g. (0.026 mole) of the sulfonyl chloride in 100 cc. of ether was added 3.8 g. (0.052 mole) of diethylamine. After one hour, the diethylamine hydrochloride was removed by filtration and the ether solution washed with dilute hydrochloric acid followed by dilute potassium hydroxide. The yield of p-iodo-N,N-diethylbenzenesulfonamide, melting at 57–58.5° after crystallization from ethanol, was 7 g. (80%).

Anal. Calcd. for $C_{10}H_{14}O_2NIS$: N, 4.13. Found: N, 4.05.

(2) Baxter and Chattaway, *J. Chem. Soc.*, **107**, 1814 (1915).

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4,7-Phenanthroline

BY L. HASKELBERG

4,7-Phenanthroline has been prepared from p-phenylenediamine,[1] 6-nitroquinoline,[2] and 6-ami-

(1) Smith, THIS JOURNAL, **52**, 397 (1930); see Wibaut and coworkers, *Rec. trav. chim.*, **56**, 1219 (1937).

(2) Kuczynski and Sucharda, *C. A.*, **31**, 3921 (1937).