After three days the reaction was complete and the alcohol removed under reduced pressure in an atmosphere of nitrogen, leaving a brownish, highly viscous residue of 24.9 g. This contained some diol which was estimated by catalytic hydrogenation and found to be 20.5%. On the basis of the cyclopentadiene used, the yield of the diol was 20.7% and that of the tetrol 60.9%.

To remove the diol, the mixture was extracted a number of times with anhydrous ethyl acetate in which the tetrol is insoluble. Finally, the tetrol was precipitated a number of times from ethyl alcohol by the addition of ethyl acetate. This procedure yielded an amorphous, slightly colored and extremely hygroscopic solid which could not be crystallized. It had no definite m. p., turning brown at 190° and black at 200°. It is very soluble in water and alcohol but insoluble in ether, ethyl acetate and hydrocarbon solvents. Attempts to distil it at a very high vacuum caused decomposition and the product formed was no longer soluble in water.

The tetrabenzoate was prepared by shaking a mixture of tetrol (0.5 g.) in water (5 cc.) with benzoyl chloride (3 cc.) and 10 cc. of 10% sodium hydroxide solution. The oil which separated was extracted with ether, the ethereal solution washed with dilute sodium hydroxide, dried with anhydrous magnesium sulfate and the ether removed. A viscous liquid was obtained which failed to crystallize.

Anal. Calcd. for $C_{33}H_{28}O_8$: C, 72.0; H, 4.72. Found: C, 71.95; H, 5.20.

Saponification equivalent calculated for the tetrabenzoate, 138.8; found, 133.4. Attempts to prepare crystalline derivatives of the tetrol were not successful.

Summary

1. The hydroxylation of cyclopentadiene led to the production of cyclopentene-2-diol-1,4 and cyclopentanetetrol-1,2,3,4.

2. It has been shown that in the hydroxylation of a conjugated system, like that of cyclopentadiene, the hydroxyl groups add on to 1,4-positions of the conjugated system, and the addition results in the production of the *cis* isomer.

3. The hydrogenation of cyclopentene-2-diol-1,4 led to the production of a hitherto unknown cyclopentanediol-1,4.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

Some Factors Affecting Halogen–Metal Interconversions

BY HENRY GILMAN AND FRED W. MOORE

This report describes the examination of some factors affecting the halogen–metal interconversion reaction between α-bromonaphthalene and some organolithium compounds.

$$\alpha\text{-}C_{10}H_7Br + RLi \longrightarrow \alpha\text{-}C_{10}H_7Li + RBr$$

Although we have found that α-naphthyllithium can be obtained in a 97% yield by this reaction, the procedure is not recommended for the preparation of this organolithium compound which is available in a 96% yield by the more direct synthesis.[1] It is probable, however, that some of the optimal conditions determined for the conversion of α-bromonaphthalene to α-naphthyllithium can be extended to other RX compounds which either do not react at all or react in an unsatisfactory manner with lithium or other metals.

Solvents.—The most effective solvent was di-*n*-butyl ether, and the order of decreasing effectiveness of the other solvents examined was: diethyl ether, dimethylaniline, benzene, cyclohexane and petroleum ether (b. p. 28–38°). Although reaction proceeds slowest in petroleum ether, this solvent is one of choice for some halogen–metal interconversions like those of β-bromostyrene and some poly-halogen compounds.[5a]

Time.—The reaction in diethyl ether proceeds with great speed, and optimal yields in this solvent at room temperature are obtained in less than one-half minute. Thereafter, the yield decreases with time, probably because of the secondary coupling reaction which is discussed later. Under corresponding conditions the maximum yield in di-*n*-butyl ether is obtained in five minutes, and in dimethylaniline in ten minutes.

Temperature.—Cooling to −80° by a solid carbon dioxide–acetone mixture not only slowed down the interconversion reaction but also gave a distinctly lower maximum yield than that observed at room or reflux temperature. It will be recalled that marked cooling is essential in halogen–metal interconversions with some compounds having other functional groups: for example, *o*-bromonitrobenzene, bromo- and iodobenzoic acids, and bromopyridines and bromoquinolines.[2]

Catalytic Effect of Some Finely Divided Metals.—It was shown earlier that copper bronze

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[1] Gilman, Zoellner and Selby, THIS JOURNAL, **55**, 1252 (1933).

[2] Gilman and Spatz, *ibid.*, **62**, 446 (1940), and unpublished studies.

improved the metalation or hydrogen–metal interconversion reaction between triphenylcarbinol and *n*-butyllithium.[3] Finely divided copper increases the rate of interconversion in the reaction between α-bromonaphthalene and *n*-butyllithium in benzene, but is essentially without effect in a benzene–petroleum ether medium. Raney nickel is without effect on this reaction in a benzene–petroleum ether mixture at short time intervals, and reduces the yield (perhaps by accelerating the coupling reaction) in the longer-timed reactions.

Kind of Organolithium Compound.—The most effective organolithium compound of those so far examined is *n*-propyllithium. The order of decreasing effectiveness of the others is: ethyllithium, *n*-butyllithium, phenyllithium and methyllithium. It is interesting to note that under conditions where *n*-propyllithium gives a 95% interconversion, and ethyllithium gives a 90% interconversion, only a trace of interconversion product is obtained with methyllithium. Methyllithium is recommended as a reagent of choice for the metalation of some bromo compounds where halogen–metal interconversion is not desired.

Coupling Reaction.—The Wurtz–Fittig coupling reaction very probably involves, to some extent, the intermediate formation of organoalkali compounds.[4]

$$\mathrm{RX + 2M \longrightarrow RM + MX}$$
$$\mathrm{RM + RX \longrightarrow R{-}R + MX}$$

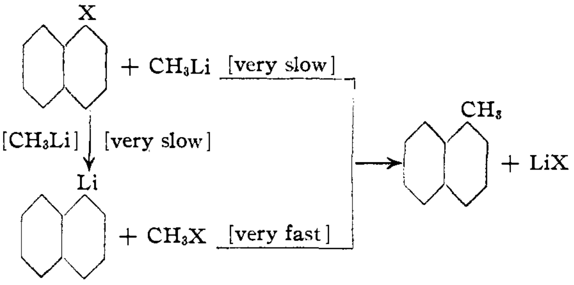
The halogen–metal interconversion reaction appears to be involved, to some extent, in coupling reactions where the more reactive metals are used. For example, in the reaction between *p*-bromotoluene and *n*-butyllithium, the first reaction appears to be

$$p\text{-}\mathrm{CH_3C_6H_4Br} + n\text{-}\mathrm{C_4H_9Li} \longrightarrow p\text{-}\mathrm{CH_3C_6H_4Li} + n\text{-}\mathrm{C_4H_9Br}$$

and the second reaction is a coupling of the products:

$$p\text{-}\mathrm{CH_3C_6H_4Li} + n\text{-}\mathrm{C_4H_9Br} \longrightarrow p\text{-}\mathrm{CH_3C_6H_4C_4H_9}\text{-}n + \mathrm{LiBr}$$

The coupling reaction is favored when the RX compound is an alkyl bromide or iodide. This is strikingly illustrated in the results now reported with the α-naphthyl and methyl combinations. As previously stated, there is practically no halogen–metal interconversion with α-bromonaphthalene and methyllithium. However, α-naphthyllithium reacts promptly with methyl iodide to give α-methylnaphthalene in high yields, and α-methylnaphthalene is formed very slowly from α-bromonaphthalene and methyllithium. The sequence of reactions might be illustrated as follows:



It is, however, quite clear that halogen–metal interconversions probably play a very subordinate role in many coupling reactions. First, there is no present evidence of any significant halogen–metal interconversion in reactions between alkyl halides and RLi compounds, and this would exclude coupling reactions leading to alkyl-alkyl products. Second, there is no convincing evidence that aryl fluorides or aryl chlorides undergo halogen–metal interconversions with RLi compounds. For example, α-chloronaphthalene and *n*-butyllithium apparently do not react to give α-naphthyllithium and *n*-butyl chloride. Third, no halogen–metal interconversion has been observed with an organolithium compound like phenylethynyllithium [$\mathrm{C_6H_5C{\equiv}CLi}$]. Fourth, the relatively slow rate of halogen–metal interconversion exhibited by the less reactive organomagnesium and organoaluminum compounds makes it appear unlikely that any possibly intermediately formed organocopper and organonickel compounds participate appreciably in interconversion reactions when copper and nickel are used in producing coupling.

In those reactions where interconversions may take a part it is probable that environmental conditions are significant. For example, *p*-bromotoluene and *n*-butyllithium when heated in petroleum ether (b. p. 35–50°) for twenty hours give an 86% yield of *p*-toluic acid, subsequent to carbonation.[5a] However, when the same reactants were allowed to stand in the same medium at room temperature for thirty days, the yield of *p*-*n*-

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(3) Gilman, Brown, Webb and Spatz, THIS JOURNAL, **62**, 977 (1940). See, also, Gilman, St. John, St. John and Lichtenwalter, *Rec. trav. chim.*, **55**, 577 (1936).

(4) See p. 452 in Gilman, "Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1938.

(5) (a) Gilman, Langham and Moore, THIS JOURNAL, **62**, Aug. (1940); (b) Marvel, Hager and Coffman, *ibid.*, **49**, 2323 (1927); (c) Gilman and Jones, *ibid.*, **62**, 1243 (1940).

butyltoluene was 75%.[5b] Different solvents may also influence the course of reactions by means of coördination compounds.[5c]

Inasmuch as lead has more than a formal resemblance to carbon in some organolead compounds, a possible halogen–metal interconversion reaction was examined with triphenyllead halides and phenyllithium. No interconversion was noted; instead a practically quantitative yield of tetraphenyllead was obtained. A more significant experiment would be the reaction between an RLi compound and a possible organolead compound in which the halogen was attached to lead in a so-called aromatic cycle.

Experimental Part

General directions for the preparation of organolithium compounds are described in a forthcoming paper (Ref. 5a). The extent of interconversion was determined in each case by adding the reaction mixture to solid carbon dioxide[6a] and then weighing the α-naphthoic acid.

Solvents.—Approximately 0.25 molar solutions of *n*-butyllithium were prepared in diethyl ether and in petroleum ether (b. p. 28–38°, "unsaturate free"), respectively. Solutions of the organolithium compound were prepared in the other solvents by taking the requisite quantity of a 1.0 molar solution of *n*-butyllithium in the low boiling petroleum ether, removing practically all of this solvent under reduced pressure, and then adding the necessary quantity of the desired solvent. The volume of residual petroleum ether did not exceed 1% of the final volume of organometallic solution. It is recommended that not all of the petroleum ether be removed because solution of the dry RLi compound in other solvents is then made extremely difficult. The reactions were carried out at room temperature (25 ± 2°). Aliquots were removed with a pipet and carbonated at regular intervals, and yields are based on α-bromonaphthalene.

Table I

Yields (%) of α-Naphthoic Acid in Various Solvents

Time, min.	$(C_2H_5)_2O$	(n-$C_4H_9)_2O$	$C_6H_5N(CH_3)_2$	C_6H_6	C_5H_{12}	Pet. ether
<0.5	84	88	23	..	..	..
1.0	78	88	38	..	..	..
5.0	73	91	69	..	..	..
10.0	68	86	74	3	3	..
30	..	83	70	8	..	10
60	..	60	..	17	15	16
120	..	..	..	29	24	30
240	..	..	..	45	41	..
360	..	..	..	44	53	..

Di-*n*-butyl ether has been used in the preparation of Grignard reagents.[6b] It enjoys a number of advantages over diethyl ether: (1) it makes easier the separation of some products that distill near the boiling point of diethyl ether; (2) it is a sort of "self-purifying" solvent in the sense that simple purification by distillation removes water and also decomposes any peroxides; and (3) it is more readily recovered than diethyl ether. A word of caution is in order with the possible use of dioxane as a solvent: impure or deteriorated dioxane reacts violently with organolithium compounds.

It is unlikely that dimethylaniline is metalated to any significant extent in the short time required to effect a halogen–metal interconversion.

Temperature.—The several experiments concerned with the effect of temperature were made concurrently, using a 0.15 *M* ether solution of *n*-butyllithium and an equivalent quantity of α-bromonaphthalene.

Table II

Effect of Temperature on % Yields of α-Naphthoic Acid

Time, min.	Room temp. (*ca.* 25°)	Reflux temp. (*ca.* 35°)	−80°
15	..	78	20
30	72	75	26
60	69	73	34
90	63	70	33
120	56	46	31

Concentration.—The *n*-butyllithium solutions were prepared by dilution of a stock solution (0.65 molar) in benzene and the temperature was 25 ± 2°. Again, equivalent quantities of reactants were used.

Table III

Effect of Molar Concentration on % Yields of α-Naphthoic Acid

Time, min.	0.50	0.25	0.10	0.05
10	2	3	..	..
30	8	8	5	..
60	19	17	8	5
90	29	24	15	7
120	41	29	20	14
180	54	40	31	27
240	57	45	46	39
360	55	44	50	..

Effect of Some Finely Divided Metals.—Solutions of *n*-butyllithium (0.25 molar) were prepared in benzene and in benzene–petroleum ether (4:1). To each solution (other than the controls) was added either finely divided copper or Raney nickel.

Table IV

Effect of Finely Divided Metals on % Yields of α-Naphthoic Acid

Time, min.	Benzene (control)	Benzene (0.5 g. copper)	Benzene–pet. ether (control)	Benzene–pet. ether		Benzene–pet. ether (0.5 g. Raney nickel)
				(0.5 g. copper)	(2.0 g. copper)	
10	3	7	6	8	7	6
20	..	..	8	12	11	8
30	8	23	11	15	14	10
60	17	36	20	24	22	17
90	..	..	29	30	29	24
120	29	52	37	37	34	27

Kind of Organolithium Compound.—An equivalent of α-bromonaphthalene was added to a 0.25 molar solution of

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(6) (a) Gilman and Van Ess, This Journal, **55**, 1258 (1933); (b) Gilman and McCracken, *Rec. trav. chim.*, **46**, 463 (1927).

each of the organolithium compounds prepared in diethyl ether. These reactions were carried out at room temperature.

TABLE V

EFFECT OF KIND OF RLi COMPOUND ON % YIELDS OF α-NAPHTHOIC ACID

Time, min.	CH_3Li	C_2H_5Li	*n*-C_3H_7Li	*n*-C_4H_9Li	C_6H_5Li
<0.5	Trace	90	95	84	..
1	Trace	85	96	78	Trace
5	1	87	97	73	1
10	2	86	94	68	5
20	3	81	92	..	..
30	1.5	79	91	65	38

β-Bromonaphthalene and *n*-Butyllithium.—An equivalent of β-bromonaphthalene was added to a 0.25 molar solution of *n*-butyllithium in diethyl ether at room temperature. The time and yields are as follows: 0.5 min., 55%; 1 min., 55%; 2.5 min., 55%; 5 min., 58%; and 10 min., 61%. The lower yields of β-naphthyllithium when contrasted with the yields of α-naphthyllithium under corresponding conditions are remindful of related yields by the direct formation of these RLi compounds from the respective bromides and lithium.[1]

α-Naphthyllithium and Methyl Iodide.—A solution of 0.072 mole of α-naphthyllithium in 200 cc. of ether was cooled in an ice-bath, and 10.5 g. (0.074 mole) of methyl iodide was added dropwise as rapidly as possible without causing excessive refluxing. The reaction was vigorous and complete; a negative color test[7] on 10 cc. of the resultant solution was obtained directly after the addition of the methyl iodide. The yield of α-methylnaphthalene was 8.1 g. or 80%.

α-Chloronaphthalene and Alkyllithiums.—From reactions of α-chloronaphthalene with *n*-butyllithium and methyllithium, respectively, there was isolated a small quantity of an as yet unidentified acidic material which apparently contains no α-naphthoic acid.

Triphenyllead Chloride and Bromide with Phenyllithium.—A slight excess of phenyllithium in ether was added to 2.37 g. (0.005 mole) of triphenyllead chloride, and the mixture was stirred for one hour. Then a large excess (0.03 mole) of ethyl bromide was added, and the stirring continued for another hour. The purpose of the ethyl bromide was to convert any $(C_6H_5)_3PbLi$ to $(C_6H_5)_3PbC_2H_5$. However, no triphenylethyllead was isolated, and the only product obtained was a 98% yield of tetraphenyllead.

Inasmuch as halogen–metal interconversions have so far been observed only with bromides and iodides, the experiment was repeated by adding 0.01 mole of triphenyllead bromide in benzene to a slight excess of phenyllithium in ether. Again, ethyl bromide gave no triphenylethyllead, and the yield of tetraphenyllead was 98%. The reaction is very rapid, as evidenced by the isolation of tetraphenyllead when an aliquot of the reaction mixture was removed at once (<fifteen seconds). Austin[8] earlier used organolithium compounds to form organolead compounds.

Combined Effects of Di-*n*-butyl Ether and Copper.—In order to determine whether there was an advantage to the use of both di-*n*-butyl ether and copper in accelerating the rate of halogen–metal interconversion, some orienting studies were carried out with α-bromonaphthalene and methyllithium. The results which follow show an improvement in yield beyond experimental error. Whether the increase in this particular case is due to either di-*n*-butyl ether or copper or both is not known. The accompanying comparable results in diethyl ether indicate that beginning with one hour the rate of coupling is accelerated with the consequent reduction in yield of halogen–metal interconversion product.

TABLE VI

COMBINED EFFECTS OF DI-*n*-BUTYL ETHER AND COPPER

Time, min.	Yield (%) of α-Naphthoic Acid Using Methyllithium Diethyl ether	Di-*n*-butyl ether + copper
5	1	1
10	2	2.5
20	3	2.8
30	2	2.8
60	1	4.1
120	0	4.5
180	0	4.1

Acknowledgment.—The authors are grateful to H. A. Pacevitz for suggestions and assistance.

Summary

An examination has been made of some factors affecting the halogen–metal interconversion reaction between α-bromonaphthalene and RLi compounds. Yields as high as 97% interconversion have been obtained.

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(7) Gilman and Schulze, THIS JOURNAL, **47**, 2002 (1925).

(8) Austin, *ibid.*, **54**, 3726 (1932).