O-Halogen-acylsalicylic acids were prepared from the corresponding halogen-acyl chlorides and salicylic acid in a mixture of chloroform and pyridine at 0°: O-chloroacetylsalicylic acid,[7] m. p. 134–135° (needles, from 50% acetic acid).

Anal. Calcd. for $C_9H_7O_4Cl$: C, 50.5; H, 3.3. Found: C, 50.6; H, 3.6.

O-Dichloroacetylsalicylic acid, m. p. 126–127° (from benzene).

Anal. Calcd. for $C_9H_6O_4Cl_2$: C, 43.4; H, 2.4. Found: C, 43.1; H, 2.6.

(7) Barnett and Cook [*J. Chem. Soc.*, 797 (1922)], could not isolate this compound in a crystalline form. In our working conditions, the chloroacetylsalicylic acid crystallized directly from the chloroform solution.

O-Trichloroacetylsalicylic acid, m. p. 138–139° (from benzene).

Anal. Calcd. for $C_{10}H_5O_4Cl_3$: C, 40.6; H, 1.7. Found: C, 40.9; H, 1.8.

Summary

Introduction of chlorine into the acyl radical of acetylurea increases its toxicity, the dichloroacetyl compound being less toxic than the mono- and trichloro- compounds. In the parallel series of acylanilides and O-acylsalicylic acids, however, the dichloro- compound does not show this peculiar behavior.

Reversible Metal–Metal Interconversions Involving Lithium and Magnesium[1]

BY HENRY GILMAN AND R. G. JONES

Earlier investigations have shown that metal–metal interconversions take place with organolithium and with organomagnesium compounds. The other organometallic compounds involved in these exchanges have been those of mercury,[2] bismuth[3a] and lead.[3b] A typical reaction is: $2C_2H_5Li + (CH_3)_2Hg \longrightarrow 2CH_3Li + (C_2H_5)_2Hg$. We are now presenting evidence for the reversibility of some of these interconversions.

Mercury–Lithium.—A mixture of phenyllithium and di-*p*-tolylmercury in ether undergoes the following transformation:

$$2C_6H_5Li + (p\text{-}CH_3C_6H_4)_2Hg \rightleftharpoons (C_6H_5)_2Hg + 2p\text{-}CH_3C_6H_4Li \quad [I]$$
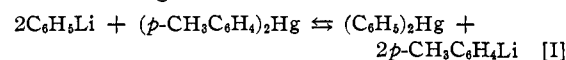
The procedure was to carbonate the mixture after a measured time interval, and then isolate the two mercurials. Both diphenylmercury and di-*p*-tolylmercury were obtained by starting with either phenyllithium and di-*p*-tolylmercury or *p*-tolyllithium and diphenylmercury.

Reactions of *n*-butyllithium with diphenylmercury and di-*p*-tolylmercury proceeded very rapidly in ether at room temperature with no appreciable heat effects. However, with these combinations the equilibria appear to be displaced largely in one direction, for no unchanged diphenylmercury or di-*p*-tolylmercury was recovered, and high yields of benzoic and *p*-toluic acids, respectively, were obtained.

$$(C_6H_5)_2Hg + 2n\text{-}C_4H_9Li \rightleftharpoons 2C_6H_5Li + (n\text{-}C_4H_9)_2Hg$$
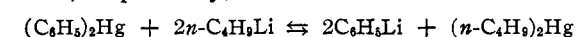
The di-*n*-butylmercury formed in these reactions underwent a further change, for some *n*-butylmercuric bromide was isolated. The bromine necessary for this product undoubtedly came from lithium bromide which was formed incidental to the preparation of *n*-butyllithium from *n*-butyl bromide and lithium. On the basis of other studies, it appears that *n*-butylmercuric bromide owes its formation to the following reaction:

$$(n\text{-}C_4H_9)_2Hg + LiBr \rightleftharpoons n\text{-}C_4H_9HgBr + n\text{-}C_4H_9Li$$
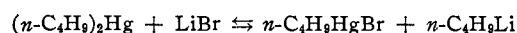
Mercury–Magnesium.—Interconversions between organomercury compounds and Grignard reagents take place readily in ether solution, but at a much slower rate than related reactions between R_2Hg and $R'Li$ compounds. The rates of interconversion may be correlated with the relative reactivities of organometallic compounds for no exchange was noted between *n*-butylmagnesium bromide and tetraphenyllead even on extended refluxing.[3b]

A reaction similar to [I] also takes place with Grignard reagents, for both benzoic and *p*-toluic acids were obtained subsequent to carbonation of a mixture of either diphenylmercury and *p*-

(1) Paper XXXVI in the series: "Relative reactivities of organometallic compounds." The preceding paper is in THIS JOURNAL, **63**, 839 (1941).

(2) Schlenk and Holtz, *Ber.*, **50**, 262 (1917). Hein, Petzchner, Wagler and Segitz, *Z. anorg. allgem. Chem.*, **141**, 161 (1925). Ziegler and Schäfer, *Ann.*, **479**, 150 (1930).

(3) (a) Gilman, Yablunky and Svigoon, THIS JOURNAL, **61**, 1170 (1939). (b) Gilman and Moore, *ibid.*, **62**, 3206 (1940). References to other metal–metal interconversions are contained in the series of comprehensive studies by Calingaert and co-workers; the most recent account is to be found in *ibid.*, **62**, 1542 (1940).

Table I

Mercury–Lithium and Mercury–Magnesium Interconversions

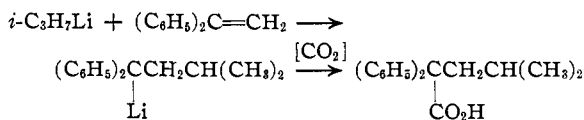| R₂Hg	Mole	R'M	Mole	Reaction Time	Temp.	Acid	Products Yield, %	Mercurial	Yield, %
$(C_6H_5)_2Hg$	0.015	$n\text{-}C_4H_9Li$	0.04	3 min.	25°	C_6H_5COOH	84	a	
$(p\text{-}CH_3C_6H_4)_2Hg$	.015	$n\text{-}C_4H_9Li$	.04	3 min.	25°	$p\text{-}CH_3C_6H_4COOH$	76.5	b	
$(p\text{-}CH_3C_6H_4)_2Hg$	.013	C_6H_5Li	.028	10 min.	25°			$(p\text{-}CH_3C_6H_4)_2Hg$	89
								$(C_6H_5)_2Hg$	20 mg.
$(C_6H_5)_2Hg$	.013	$p\text{-}CH_3C_6H_4Li$	.025	15 min.	25°			$(p\text{-}CH_3C_6H_4)_2Hg$	83
$(C_6H_5)_2Hg$	.012	C_2H_5MgBr	.052	8.5 hr.	35°	C_6H_5COOH	94.5	c	
$(p\text{-}CH_3C_6H_4)_2Hg$	.017	C_2H_5MgBr	.052	10 hr.	35°	$p\text{-}CH_3C_6H_4COOH$	92[d]	$(C_2H_5)_2Hg$	74
$(p\text{-}CH_3C_6H_4)_2Hg$	.013	C_6H_5MgBr	.052	10 hr.	35°	$p\text{-}CH_3C_6H_4COOH$ C_6H_5COOH	16[d] 71[d]	$(p\text{-}CH_3C_6H_4)_2Hg$	59.6
$(C_6H_5)_2Hg$	.013	$p\text{-}CH_3C_6H_4MgBr$	.052	20 hr.	25°	C_6H_5COOH $p\text{-}CH_3C_6H_4COOH$	44[d] 42[d]	$(p\text{-}CH_3C_6H_4)_2Hg$	81.5

[a] The $(n\text{-}C_4H_9)_2Hg$ was not isolated, but an 18% yield of $n\text{-}C_4H_9HgBr$ was obtained. This latter product did not result from cleavage of the $(n\text{-}C_4H_9)_2Hg$ in working up the reaction mixture. It was probably formed by the following reaction in anhydrous ether solution: $(n\text{-}C_4H_9)_2Hg + LiBr \longrightarrow n\text{-}C_4H_9HgBr + n\text{-}C_4H_9Li$. [b] A 19% yield of $n\text{-}C_4H_9$-HgBr was obtained. The $(n\text{-}C_4H_9)_2Hg$ was not isolated. [c] The $(C_2H_5)_2Hg$ was not isolated, but a 65% yield of C_2H_5-HgBr was obtained based upon the reaction: $(C_2H_5)_2Hg + C_2H_5MgBr \longrightarrow (C_2H_5)_2Mg + C_2H_5HgBr$ [d] The yields of acids are based upon the quantity of RMgX used.

tolylmagnesium bromide or di-p-tolylmercury and phenylmagnesium bromide.

Lithium–Magnesium.—Ziegler and Dersch[4] established ingeniously the following interconversion

$$2C_6H_5Li + i\text{-}C_3H_7MgBr \longrightarrow i\text{-}C_3H_7Li + (C_6H_5)_2Mg + LiBr \quad [II]$$

The formation of isopropyllithium was shown by adding 1,1-diphenylethylene to a mixture of phenyllithium and isopropylmagnesium bromide, and then isolating 1,1-diphenyl-3-methylbutyric acid subsequent to carbonation.

$$i\text{-}C_3H_7Li + (C_6H_5)_2C{=}CH_2 \longrightarrow$$
$$(C_6H_5)_2CCH_2CH(CH_3)_2 \xrightarrow{[CO_2]} (C_6H_5)_2CCH_2CH(CH_3)_2$$
$$\overset{|}{Li} \qquad\qquad\qquad \overset{|}{CO_2H}$$

Under these conditions RMgX compounds do not add to an olefinic linkage; aryllithium compounds add slowly; and alkyllithium compounds add rapidly.

In order to demonstrate the reversibility of a reaction like [II]

$$(C_6H_5)_2Mg + 2n\text{-}C_4H_9Li \rightleftarrows (n\text{-}C_4H_9)_2Mg + 2C_6H_5Li$$
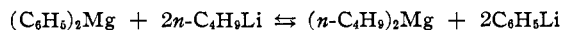
it is necessary to characterize the phenyllithium. This was done by adding p-methoxybenzonitrile to a mixture of n-butyllithium and diphenylmagnesium, and then hydrolyzing after a short time. The chief product isolated was p-methoxybenzophenone (54%). Under corresponding conditions diphenylmagnesium gave but an 18% yield of p-methoxybenzophenone. It was shown earlier that p-methoxybenzonitrile reacts unusually

(4) Ziegler and Dersch. *Ber.*, **64**, 448 (1931).

slowly with RMgX compounds,[5a] but very rapidly with RLi compounds.[5b]

Experimental Part

Mercury–Lithium and Mercury–Magnesium Interconversion Reactions.—The reactions were carried out under nitrogen in a volume of from 50 to 100 cc. of ether solution. The Grignard reagent or RLi compound was added quickly and with stirring to an ether suspension of the diarylmercury compound. After a measured interval of time the reaction mixture was carbonated by pouring it upon powdered solid carbon dioxide. All solid products were identified by the method of mixed melting points.[6] Mixtures of p-toluic and benzoic acids were separated for identification by fractional crystallization from water, but the yields of the two acids were estimated from the weights and neutralization equivalents of the mixtures.

Magnesium–Lithium Interchange.—Diphenylmagnesium was prepared by precipitating the halides from a solution of phenylmagnesium bromide with dioxane.[7] After centrifuging, the ether solution was siphoned off and titrated to determine the concentration of diphenylmagnesium. The preparation gave a negative test for halogen.

To 50 cc. of 0.35 molar diphenylmagnesium solution was added 25 cc. of 0.90 molar n-butyllithium solution. After standing for twenty minutes at room temperature, 2.66 g. (0.02 mole) of p-methoxybenzonitrile in 25 cc. of ether was added during one minute. Four minutes later the reaction mixture was hydrolyzed by pouring into ice water. The ether layer was separated and washed with 100 cc. of 2 N hydrochloric acid. After heating the total aqueous solution to boiling to remove dissolved ether, it was allowed to stand in a warm place for forty-eight hours. The partially crystalline oily product which separated from the water was collected in ether, the ether extract was dried, the ether removed and the residue recrystallized from petroleum ether (b. p. 60–68°) to give 2.30 g. (54%) of p-

(5) (a) Gilman and Lichtenwalter, *Rec. trav. chim.*, **55**, 561 (1936); (b) Gilman and Kirby, This Journal, **55**, 1265 (1933).

(6) The melting point of $n\text{-}C_4H_9HgCl$ (126–126.5°) is not lowered by the presence of $n\text{-}C_4H_9HgBr$ (m. p. 129–130°).

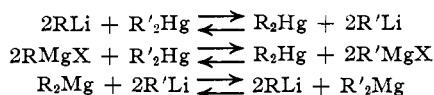(7) Noller and White, This Journal, **59**, 1354 (1937).

methoxybenzophenone. No unreacted p-methoxybenzo-nitrile was found. This experiment was repeated, and a 50% yield of p-methoxybenzophenone was obtained.

In order to determine the extent of reaction of diphenyl-magnesium with p-methoxybenzonitrile under conditions comparable with the above reaction, the following experiment was carried out. A solution of 0.67 g. (0.005 mole) of p-methoxybenzonitrile in a little ether was added to 50 cc. of 0.0085 molar diphenylmagnesium. After five minutes the mixture was hydrolyzed and worked up, as described above, to give 0.19 g. (18%) of p-methoxybenzo-phenone. From the ether layer was recovered 0.45 g. (67%) of unchanged p-methoxybenzonitrile. From a

check experiment the yield of p-methoxybenzophenone was 19%.

Summary

It has been shown that some metal–metal interconversions involving the following organometallic combinations are reversible

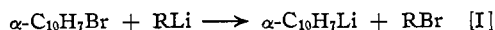$$2RLi + R'_2Hg \rightleftarrows R_2Hg + 2R'Li$$
$$2RMgX + R'_2Hg \rightleftarrows R_2Hg + 2R'MgX$$
$$R_2Mg + 2R'Li \rightleftarrows 2RLi + R'_2Mg$$

AMES, IOWA   RECEIVED JANUARY 27, 1941


Reversible Halogen–Metal Interconversion Reactions[1]

BY HENRY GILMAN AND R. G. JONES

A study has been reported on some factors affecting the following typical halogen-metal interconversion reaction.[2]

$$\alpha\text{-}C_{10}H_7Br + RLi \longrightarrow \alpha\text{-}C_{10}H_7Li + RBr \quad [I]$$

It seemed of interest to examine the possible reversibility of halogen–metal interconversion reactions. For this purpose, the following combinations were selected: phenyllithium–p-tolyl iodide and phenyl iodide–p-tolyllithium. We are now reporting that this reaction is, in fact, reversible.

$$C_6H_5Li + p\text{-}CH_3C_6H_4I \rightleftarrows p\text{-}CH_3C_6H_4Li + C_6H_5I$$
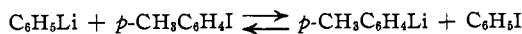
An X–M reaction, more typical from the viewpoint of synthesis, was next investigated: namely, that of an aryl halide with an alkyllithium compound. No experimental evidence was obtained for the reversibility of the following reaction.

$$C_6H_5I + n\text{-}C_4H_9Li \longrightarrow C_6H_5Li + n\text{-}C_4H_9I \quad [II]$$
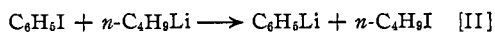
Under our experimental conditions, there was isolated a 71% yield of benzoic acid subsequent to carbonation,[3] but no n-valeric acid. The absence of any evidence for the formation of n-butyl-lithium by a reversal of reaction [II] was not entirely unexpected, for in a related reaction [I] between α-bromonaphthalene and n-propyl-lithium, the yield of α-naphthoic acid (subsequent

to carbonation) was 97%.[2] We are of the opinion that despite the lack of present experimental support there is a reversible reaction between aryl halides and alkyllithium compounds, but that the equilibrium with such combinations is displaced far to the right. It was surprising to observe that incidental to reaction [II] there was no significant coupling of the phenyllithium and n-butyl iodide to give n-butylbenzene. An earlier study[2] showed that α-naphthyllithium reacted rapidly with methyl iodide to give an 80% yield of α-methylnaphthalene.

Next, a third possible combination was examined: namely, an *alkyl* iodide and an *alkyl*lithium compound. The combinations selected were ethyl iodide–n-butyllithium and ethyllithium–n-butyl iodide. The reactions were carried out at a low temperature and were shown to be reversible: $C_2H_5I + n\text{-}C_4H_9Li \rightleftarrows C_2H_5Li + n\text{-}C_4H_9I$.

Possible Applications.—Preceding papers in this series have shown that the X–M interconversion reaction with aryl halides and alkyllithium compounds is a procedure of choice for the synthesis of some aryllithium compounds which are either difficultly accessible or which can be obtained by no other method. This applies particularly to aryl halides which contain functional groups, like azomethylene and carbonyl, that normally react very promptly with RLi compounds.

The demonstration of reversibility suggests that the reaction may be useful not only for comparing the relative reactivities of RM and RX

(1) Paper XXXVII in the series "Relative reactivities of organometallic compounds." The preceding paper is Gilman and Jones, THIS JOURNAL, **63**, 1439 (1941).

(2) Gilman and Moore, *ibid.*, **62**, 1843 (1940). The most recent reference on X-M interconversions is Langham, Brewster and Gilman, *ibid.*, **63**, 545 (1941).

(3) In some earlier orienting experiments by Gilman, Langham and Moore, *ibid.*, **62**, 2327 (1940), there was obtained a 51% yield of benzoic acid.