[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

Relative Reactivities of Organometallic Radicals[1]

BY HENRY GILMAN AND FRED W. MOORE

On general grounds one might predict that an organometallic radical like triphenyllead would be more reactive than tetraphenyllead which has the metal in a normal, higher valence state. The several organometallic radicals which have been described[2] have either not been examined with respect to their possible reactions with a typical functional group, such as the carbonyl, or are not sufficiently reactive to combine with such a group. These organometallic radicals have properties which are remindful of those of triphenylmethyl. For example, they show a marked tendency to assume a normal valence by addition of oxygen, iodine, sodium and nitrogen oxides.[2,3] Such addition reactions, however, do not afford a basis of comparison with RM compounds having the metal in a normal valence state. There was needed, therefore, a reaction which could be used to determine the relative firmness of attachment of R groups to M in compounds like R_3M and R_4M, where R_3M is the compound with abnormal valence.[4]

Metal–Metal Interconversion of Triphenyllead and of Tetraphenyllead with *n*-Butyllithium.—Tetraphenyllead reacts at a fairly rapid rate with *n*-butyllithium in ether as follows:

$$(C_6H_5)_4Pb + 4n\text{-}C_4H_9Li \rightleftarrows (n\text{-}C_4H_9)_4Pb + 4C_6H_5Li$$

The tetra-*n*-butyllead can be isolated, and the phenyllithium is readily estimated, after carbonation, as benzoic acid.

Under corresponding conditions triphenyllead reacts more rapidly in a similar manner

$$(C_6H_5)_3Pb + 3n\text{-}C_4H_9Li \rightleftarrows (n\text{-}C_4H_9)_3Pb + 3C_6H_5Li$$

the rates being measured by the quantities of benzoic acid isolated after a short time reaction.

Interconversion Rates with Triphenyllead and Tri-*p*-tolyllead.—Tri-*p*-tolyllead undergoes a more rapid metal–metal interconversion with *n*-butyllithium than does triphenyllead. This result is in agreement with earlier findings on the rates of cleavage of R_4Pb compounds, and several other RM types, by such reactants as halogens, halogen acids and some salts.[5] Also in line with these findings is the fact that tetra-*p*-tolyllead undergoes a more rapid interconversion than does tetraphenyllead.

There is, however, no exact correlation between the order of cleavage of radicals by halogen acids and either the rates of metal–metal interconversion or the order of cleavage by other reactants. For example, the *p*-chlorophenyl radical is cleaved from phenyl-*p*-chlorophenylmercury less rapidly than the phenyl radical by hydrogen chloride,[6] but in a metal–metal interconversion with *n*-butyllithium the *p*-chlorophenyl radical is cleaved more rapidly than the phenyl radical in compounds like diphenyl-di-*p*-chlorophenyllead and triphenyl-*p*-chlorophenyllead. This is also true with some compounds of tin and of bismuth. Also, the order of cleavage of radicals from unsymmetrical organolead compounds by sodium in liquid ammonia is not the same as that observed when hydrogen chloride is the cleaving agent. Furthermore, although tetra-*p*-tolyllead is cleaved more rapidly by *n*-butyllithium than is tetraphenyllead, tri-*p*-tolylbismuth is cleaved less rapidly than triphenylbismuth by this same agent. It is apparent, therefore, that any order of cleavage of radicals is dependent not only on the cleaving agent but also on the central atom holding the R groups.

Preferential Interconversion with Diphenyl-di-*p*-tolyllead.—It has been known for some time that unsymmetrical organolead compounds are less stable and more reactive than symmetrical compounds. This broad generalization seems applicable to all unsymmetrical organometallic compounds; for example, triphenylbismuth undergoes metal–metal interconversion much more slowly than diphenyl-α-naphthylbismuth. One might expect, therefore, that diphenyl-di-*p*-tolyllead would undergo a more rapid metal–

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[1] This is paper XXXIV in the series entitled: "Relative Reactivities of Organometallic Compounds." The preceding paper, XXXIII, is in THIS JOURNAL, **62**, 2357 (1940).

[2] Chap. IV of Gilman, "Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1938, pp. 478–481.

[3] Mr. R. K. Abbott has established the addition of nitrogen oxides to triphenyllead.

[4] The recent study by Gilman and Jones, THIS JOURNAL, **62**, 2357 (1940), on the more rapid addition of phenylthallium over triphenylthallium with some functional groups is the first reported case of a distinctly reactive organometallic radical.

[5] See Gilman and Bailie, *ibid.*, **61**, 731 (1939), for a recent study of organolead compounds together with pertinent references to earlier literature.

[6] Kharasch and Flenner, *ibid.*, **54**, 674 (1932).

metal interconversion than either tetraphenyllead or tetra-*p*-tolyllead. Also, on the basis of the results obtained with these two latter compounds, the *p*-tolyl radical should be cleaved more rapidly than the phenyl radical. Such was found to be the case, and under appropriate experimental conditions the *p*-tolyl radical is cleaved predominantly over phenyl as indicated by the isolation of almost pure *p*-toluic acid subsequent to carbonation and hydrolysis.

$$(C_6H_5)_2Pb(C_6H_4CH_3\text{-}p)_2 + 2n\text{-}C_4H_9Li \longrightarrow p\text{-}CH_3C_6H_4Li \xrightarrow[\text{[HOH]}]{\text{[CO}_2\text{]}} p\text{-}CH_3C_6H_4CO_2H$$

Miscellany.—Earlier reports from this Laboratory have shown that, in general, the rates of interconversion reactions like hydrogen–metal (metalation), halogen–metal, and metal–metal, follow the order of relative reactivities of RM compounds with typical functional groups. In agreement with such a generalization, we have observed that the metal–metal interconversion with tetraphenyllead and *n*-butyllithium proceeds rapidly. The corresponding reaction with tetraphenyllead and *n*-butylmagnesium bromide gives no interconversion in the same length of time.

Unsuccessful attempts were made to metalate tetraphenyllead incidental to the preparation of organolead compounds having water-solubilizing groups and groups which lend themselves to resolution studies of racemic RM compounds. The rate of metal–metal interconversion is more rapid than the rate of hydrogen–metal interconversion (or metalation). It may be possible by a proper choice of solvents to effect such metalations by slowing down the metal–metal interconversion reaction.

Experimental Part

Tetraphenyllead and *n*-Butyllithium.—A solution made up of 0.05 mole of *n*-butyllithium in 100 cc. of ether and 0.004 mole of tetraphenyllead in 200 cc. of benzene was refluxed at 60°. At the end of the time intervals shown in Table I, carbonation was effected by pouring upon solid carbon dioxide and the products were isolated by customary procedures.

TABLE I

REACTION BETWEEN TETRAPHENYLLEAD AND *n*-BUTYLLITHIUM

Time, hours	Yield $(n\text{-}C_4H_9)_4Pb$, %	Yield $C_6H_5CO_2H$, %
0.5	40	37
1	75	75
3	72	70
6	69	65
12	70	60
24	68	55
48	69	26

The one-half and one hour experiments were checked. The yields of benzoic acid can be influenced by two factors. First, in long-time experiments, *n*-butyllithium can metalate benzene. For example, a 15% yield of benzoic acid was obtained after carbonating a mixture of 0.05 mole of *n*-butyllithium in 100 cc. of ether and 50 cc. of benzene which was refluxed for twenty-four hours. Second, *n*-butyllithium gradually cleaves ether, but at a more rapid rate than does phenyllithium.[7]

From a separate reaction in which 0.05 mole of *n*-butyllithium and 0.003 mole of tetraphenyllead in 100 cc. of ether were refluxed for seven hours and then carbonated was obtained 0.88 g. or 70% of tetra-*n*-butyllead (identified by b. p., refractive index and density).

Solvents have a marked influence on the rate of metal–metal interconversion reactions, as illustrated by these two experiments. After heating a solution of 0.05 mole of *n*-butyllithium and 0.004 mole of tetraphenyllead in 150 cc. of benzene (with no ether present) for twenty-four hours at 60°, and then carbonating, only a trace of benzoic acid was isolated after removal of the *n*-valeric acid. From a corresponding experiment in which petroleum ether (b. p., 60–68°) was used as the medium, no benzoic acid was isolated.

Tetraphenyllead and Other RM Compounds.—First, it was shown that there was no appreciable reaction between sodium and tetraphenyllead in benzene: the recovery of tetraphenyllead was 80% after carbonation, and no acidic material was isolated. Then, benzylsodium, prepared[8] from 0.035 mole of chlorobenzene and 0.07 g. atom of sodium in 50 cc. of toluene, was refluxed with 0.004 mole of tetraphenyllead at 107° for twenty-four hours. Carbonation yielded phenylacetic acid, no benzoic acid, about 50% of tetraphenyllead, and an as yet unresolved tarry residue. In a second experiment carried out at room temperature, essentially the same results were obtained with an 80% recovery of tetraphenyllead. The absence of metal–metal interconversion with benzylsodium is undoubtedly due to the medium used.

A mixture of 0.05 mole of phenylsodium and 0.004 mole of tetraphenyllead in 300 cc. of benzene was stirred at 60° for twenty-four hours. Carbonation yielded only benzoic acid, and 80% of the tetraphenyllead was recovered.

A solution of 0.04 mole of phenyllithium in 100 cc. of ether and 0.004 mole of tetraphenyllead in 250 cc. of benzene was refluxed for twenty-four hours. Carbonation yielded only benzoic acid, and the recovery of tetraphenyllead was practically quantitative. Similar results were obtained in another experiment where refluxing was carried out for forty-eight hours.

After refluxing a solution of 0.05 mole of *n*-butylmagnesium bromide in 100 cc. of ether and 0.004 mole of tetraphenyllead in 200 cc. of benzene at 60° for forty-eight hours, carbonation yielded no solid acid, and the recovery of tetraphenyllead was 95%.

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[7] *s*-Butyllithium and *t*-butyllithium cleave ether rapidly.

[8] Gilman, Pacevitz and Baine, THIS JOURNAL, **62**, 1514 (1940).

Rates of Cleavage of R_3Pb and R_4Pb Compounds by *n*-Butyllithium.—To 75 cc. of ether containing one mole of *n*-butyllithium for each mole of R radical attached to lead was added separately 0.002 mole of each of the organolead compounds listed in Table II. The solution was refluxed for ten minutes and then carbonated. No attempt was made to isolate or characterize any of the organolead compounds formed in these or in the following reactions.

TABLE II

CLEAVAGE OF R_3Pb AND R_4Pb BY *n*-BUTYLLITHIUM

Organolead compound	Acid	Acid, % isolated	
$(C_6H_5)_4Pb$	None	0	0
$(C_6H_5)_3Pb$	$C_6H_5CO_2H$	13	14
$(p\text{-}CH_3C_6H_4)_4Pb$	$p\text{-}CH_3C_6H_4CO_2H$	25	28
$(p\text{-}CH_3C_6H_4)_3Pb$	$p\text{-}CH_3C_6H_4CO_2H$	59	62

Diphenyl-di-*p*-tolyllead and *n*-Butyllithium.—To 0.02 mole of *n*-butyllithium in 100 cc. of ether was added 0.01 mole of diphenyl-di-*p*-tolyllead and the mixture was refluxed for ten minutes. Carbonation yielded 30 and 31 per cent. of *p*-toluic acid (melting point and mixed melting point, 176–178°) in two duplicate experiments. A small quantity of benzoic acid was obtained.

In another experiment using 0.002 mole of diphenyl-di-*p*-tolyllead and 0.002 mole of *n*-butyllithium in 75 cc. of ether a mixture of acids, 21% benzoic and 79% *p*-toluic, was obtained.

Summary

Some factors affecting the following metal–metal interconversion reaction have been examined.

$$(C_6H_5)_4Pb + 4n\text{-}C_4H_9Li \rightleftarrows (n\text{-}C_4H_9)_4Pb + 4C_6H_5Li$$

The order of increasing rate of cleavage of some R_3Pb and R_4Pb compounds by *n*-butyllithium is: $(C_6H_5)_4Pb$, $(C_6H_5)_3Pb$, $(p\text{-}CH_3C_6H_4)_4Pb$, $(p\text{-}CH_3C_6H_4)_3Pb$. The *p*-tolyl radical can be almost exclusively cleaved in a reaction between diphenyl-di-*p*-tolyllead and *n*-butyllithium:

$$(C_6H_5)_2Pb(C_6H_4CH_3\text{-}p)_2 + 2n\text{-}C_4H_9Li \longrightarrow p\text{-}CH_3C_6H_4Li.$$

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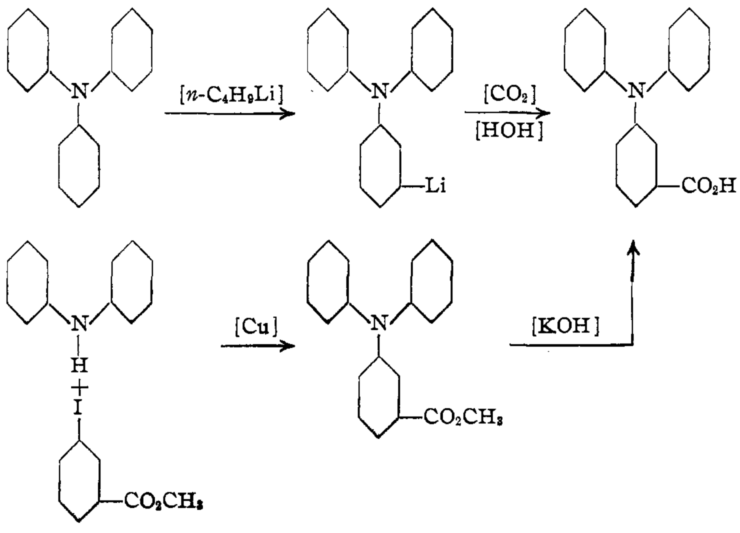
Anomalous Metalation of Triphenylamine

BY HENRY GILMAN AND GEORGE E. BROWN

In nuclear metalations by organolithium compounds, the hydrogen replaced by lithium is almost invariably attached to a carbon which is ortho to the group containing the hetero element. No exceptions have been reported when the hetero element is nitrogen, and the compounds which have been examined are aniline, N-*n*-butylaniline, diphenylamine,[1] together with carbazole and N-ethylcarbazole.[2]

We are now reporting a case of anomalous metalation of a compound containing nitrogen. Metalation of triphenylamine, followed by carbonation and hydrolysis, did not give the expected ortho-carboxytriphenylamine; instead the metacarboxytriphenylamine was formed. The sequence of reactions together with a synthesis of an authentic specimen are diagrammed.



N,N-Diphenyl-*p*-aminobenzoic Acid.—After having shown that the acid obtained by metalation of triphenylamine was not the expected ortho acid, we considered that the compound was probably the para isomer or N,N-diphenyl-*p*-aminobenzoic acid. Goldberg[3] was unable to prepare the para acid by the procedure used for the synthesis of the ortho isomer, N,N-diphenylanthranilic acid. We also were unsuccessful in

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[1] Gilman, Brown, Webb and Spatz, THIS JOURNAL, **62**, 977 (1940).

[2] Gilman and Kirby, *J. Org. Chem.*, **1**, 146 (1936).

[3] Goldberg, *Ber.*, **40**, 4541 (1907).