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:

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

AMES, IOWA RECEIVED JULY 31, 1940

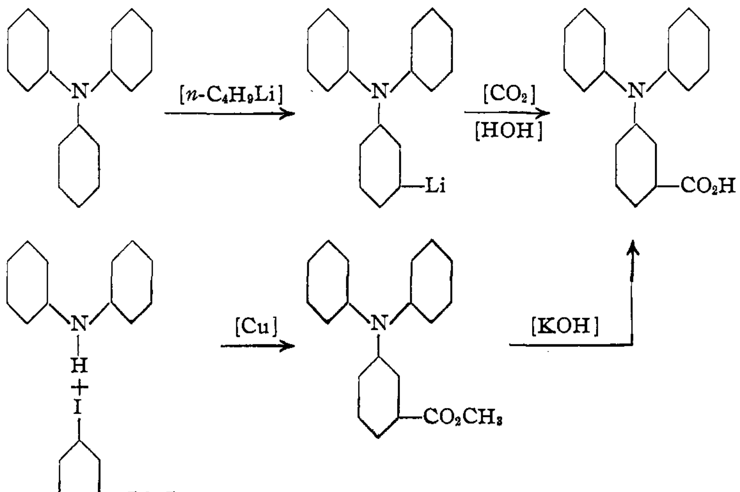
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

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).

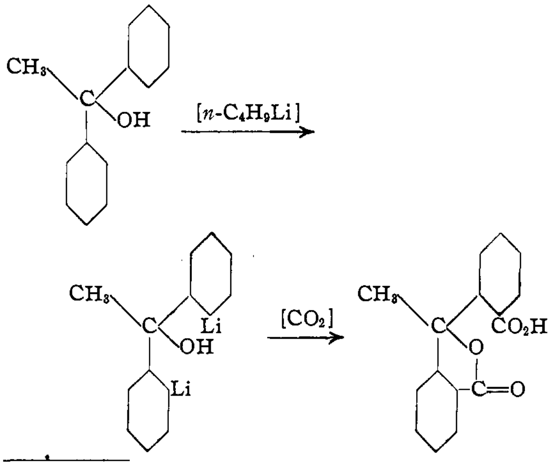
[2] Gilman and Kirby, *J. Org. Chem.*, **1**, 146 (1936).

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

condensing diphenylamine with *p*-iodobenzoic acid. However, we found that the methyl ester of *p*-iodobenzoic acid condensed readily with diphenylamine in essential accordance with the conditions used by Kawai[4] for the preparation of *p*-nitrotriphenylamine. In like manner, we prepared N-phenyl-*p*-aminobenzoic acid from methyl *p*-aminobenzoate and iodobenzene.

Metalation of Amino Compounds by the Grignard Reagent.—Houben and co-workers[5] have shown that when N-alkylanilines are treated with the Grignard reagent and then with carbon dioxide at high temperatures and high pressures carbonation takes place predominantly in the para position. Oddo[6] obtained an acid which melted at 152° after treating diphenylamine with a Grignard reagent and then carbonating the reaction mixture at an elevated temperature. His acid cannot be the ortho isomer, N-phenylanthranilic acid which melts at 185°, nor can it be the purported meta isomer which melts at 220° and was prepared by Claus and Nicolaysen[7] from aniline hydrochloride and *m*-aminobenzoic acid. It is undoubtedly the para acid which we prepared and found to melt at 156°.

Metalation of Diphenylmethylcarbinol.—Metalation of benzyl alcohol, benzohydrol and triphenylcarbinol[1] has been shown to involve hydrogens on carbon atoms ortho to the group holding oxygen. By analogy with the orientation of these compounds, it is highly probable that the lactone-acid obtained by metalation of diphenylmethylcarbinol, followed by carbonation, is the lactone of diphenylmethylcarbinol-2,2′-dicarboxylic acid.



Metalation of triphenylcarbinol with four equivalents of *n*-butyllithium has been found to increase markedly the yield of the lactone of triphenylcarbinol-2,2′-dicarboxylic acid.

Experimental Part

Metalation of Triphenylamine.—A mixture of 12.25 g. (0.05 mole) of triphenylamine, 0.1 mole of *n*-butyllithium and 0.5 g. of copper bronze was stirred and refluxed for forty-eight hours, and then carbonated by pouring on crushed, solid carbon dioxide. The yield of acidic material was 2.16 g., and from this was isolated 1.02 g. or 7% of N,N-diphenyl-*m*-aminobenzoic acid as yellow crystals which melted at 186° after crystallization from glacial acetic acid. The experiment was checked with similar results.

Anal. Calcd. for $C_{19}H_{15}O_2N$: N, 4.84. Found: N, 4.93 and 5.10.

Decarboxylation of the N,N-diphenyl-*m*-aminobenzoic acid by heating with soda-lime gave a 94% yield of triphenylamine (mixed melting point).

Mr. H. A. Pacevitz attempted the following orienting metalation of triphenylamine with phenylsodium. A benzene solution of 10.3 g. (0.042 mole) of triphenylamine was added to a benzene suspension of phenylsodium prepared from 10.62 g. (0.03 mole) of diphenylmercury and 10 g. (0.435 g. atom) of sodium. The mixture was stirred and refluxed for twenty-four hours and then carbonated with solid carbon dioxide. The products isolated were a 29% yield of benzoic acid, some as yet unresolved oily tar, and 9.3 g. or 87% of the initial triphenylamine.

Methyl N,N-Diphenyl-*m*-aminobenzoate.—A mixture of 13 g. (0.05 mole) of methyl *m*-iodobenzoate, 9 g. (0.051 mole) of diphenylamine, 8.5 g. of powdered anhydrous potassium carbonate, 2 cc. of xylene and 2 g. of copper bronze was stirred and heated between 190–220° for eleven hours. The cold mixture was extracted with dry ether, and the ether then removed by distillation. Inasmuch as the residue resisted crystallization it was distilled at 205° (3 mm.). The yield of pale yellow viscous liquid was 10.1 g. or 70.5%.

Anal. Calcd. for $C_{20}H_{17}O_2N$: OCH_3, 10.23. Found: OCH_3, 10.08.

A mixture of 2 g. of the methyl N,N-diphenyl-*m*-aminobenzoate and 20 cc. of a 10% potassium hydroxide solution was refluxed vigorously for thirty minutes. Acidification of the resulting solution gave a quantitative yield of N,N-diphenyl-*m*-aminobenzoic acid which after one crystallization from acetic acid melted at 186° and was shown to be identical, by the method of mixed melting points, with the acid obtained by metalation of triphenylamine with *n*-butyllithium.

Methyl N,N-Diphenyl-*p*-aminobenzoate.—A suspension of 13 g. (0.05 mole) of methyl *p*-iodobenzoate, 9 g. (0.051 mole) of diphenylamine, 8.5 g. of powdered anhydrous potassium carbonate, 2 cc. of xylene and 2 g. of copper bronze was stirred and heated at 200° for fifteen hours. The oil obtained by extraction with ether and sub-

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[4] Kawai, *J. Chem. Soc. Japan*, **49**, 235 (1928) [*C. A.*, **24**, 80 (1930)].

[5] Houben and co-workers, *Ber.*, **37**, 3978 (1904); **42**, 3729, 4488, 4815 (1909); **46**, 3833 (1913).

[6] Oddo, *Gazz. chim. ital.*, **41**, I, 255 (1911) [*C. A.*, **5**, 2638 (1911)].

[7] Claus and Nicolaysen, *Ber.*, **18**, 2711 (1885).

sequent removal of the ether was crystallized from cyclohexane to give 10 g. or a 66.5% yield of ester which melted at 89°.

Anal. Calcd. for $C_{20}H_{17}O_2N$: N, 4.62. Found: N, 4.78.

A 3-g. sample of the methyl N,N-diphenyl-*p*-aminobenzoate was hydrolyzed (in accordance with the conditions described above with the *m*-ester), and gave a quantitative yield of **N,N-diphenyl-*p*-aminobenzoic acid** which melted at 202° after crystallization from acetic acid.

Anal. Calcd. for $C_{19}H_{15}O_2N$: N, 4.84. Found: N, 4.85 and 4.82.

Methyl N-Phenyl-*p*-aminobenzoate.—A mixture of 75 g. (0.3 mole) of iodobenzene, 7.5 g. (0.05 mole) of methyl *p*-aminobenzoate, 13.8 g. of anhydrous potassium carbonate, 0.5 g. of potassium iodide, 1 g. of copper bronze, and 40 cc. of nitrobenzene was heated at 200° for six hours. After removal of the nitrobenzene and the excess of iodobenzene by steam distillation, the oil obtained from the ether extract of the residue was crystallized from methanol to give 3 g. or 27% of the ester melting at 115°.

Anal. Calcd. for $C_{14}H_{13}O_2N$: N, 6.17. Found: N, 6.20.

One gram of the ester was hydrolyzed (under conditions previously described with the diphenylamino esters) to give a quantitative yield of **N-phenyl-*p*-aminobenzoic acid** which melted at 156° after crystallization from acetic acid or ethanol.

Anal. Calcd. for $C_{13}H_{11}O_2N$: N, 6.57. Found: N, 6.64.

Metalation of Diphenylmethylcarbinol.—An ether solution of 19.8 g. (0.1 mole) of diphenylmethylcarbinol and three equivalents of *n*-butyllithium was refluxed with stirring for forty-eight hours and then carbonated by solid carbon dioxide. From the acidic product was isolated 8.62 g. of oily crystals melting between 160–200°. Two crystallizations from ethanol gave 4.7 g. or 17.3% of the **lactone of diphenylmethylcarbinol-2,2′-dicarboxylic acid** melting at 211–212°.

Anal. Calcd. for $C_{16}H_{12}O_4$: C, 71.6; H, 4.47. Found: C, 71.4 and 71.7; H, 4.39 and 4.37.

Metalation of Triphenylcarbinol.—Metalation of triphenylcarbinol, in essential accordance with earlier directions[1] but with 4 molecular equivalents of *n*-butyllithium, gave a 57.7% yield of the lactone of triphenylcarbinol-2,2′-dicarboxylic acid, in addition to a 32% recovery of triphenylcarbinol.

Summary

Metalation of triphenylamine by *n*-butyllithium involves the meta position, and not the ortho position as was the case with an earlier series of representative nitrogen compounds. N,N-Diphenyl-*m*-aminobenzoic acid prepared for identification of the reaction product is readily synthesized from diphenylamine and methyl *m*-iodobenzoate (followed by hydrolysis), whereas the use of the corresponding *m*-iodobenzoic acid is unsatisfactory.

Metalation of diphenylmethylcarbinol, followed by carbonation, gives the lactone of diphenylmethylcarbinol-2,2′-dicarboxylic acid.

Ames, Iowa Received July 31, 1940

[Contribution from the Laboratories of the Shell Development Company]

The Catalyzed Cleavage of Diacetone Alcohol and Other Ketols and Unsaturated Ketones[1]

By S. H. McAllister, Wm. A. Bailey, Jr., and C. M. Bouton

In the course of an investigation of the chemical properties of ketols, a series of experiments was made on the catalytic vapor phase reactions of diacetone alcohol. It was found that a solid phosphoric acid type catalyst caused the cleavage of the diacetone alcohol to acetic acid and isobutylene, and since no previous work had been reported on this cleavage at the time the subject was being studied, the reaction was subjected to a rather thorough investigation which was extended to include analogous reactions of other ketols and unsaturated ketones.

Experimental

General Procedure.—The experimental work was carried out in a gas-fired catalytic furnace using a $32 \times {}^3/_4''$ stainless steel catalyst tube. The catalyst in the form of 6–8 mesh particles occupied the center 42 cc. of the tube, the rest being packed with glass balls. Fresh catalyst was used for each experiment. The temperature gradient through the tube was measured by means of a sliding thermocouple; the reaction temperature was arbitrarily taken as the average temperature over the catalyst bed. Typical temperature profiles are shown in Fig. 1.

The ketol or unsaturated ketone was fed by means of nitrogen pressure directly to the furnace. The products were cooled to room temperature to remove the normally liquid material, the gases were scrubbed with water to remove acids, acetone, or ketene which might be carried over, and the isobutylene or propylene was collected in carbon dioxide-cooled receivers. Permanent gases were metered, but no significant amounts were obtained.

The silica–phosphoric acid catalyst used in the earlier experiments was Universal Oil Products Company commercial olefin polymerization catalyst. It contained 60.4% total phosphorus as phosphorus pentoxide and 25%

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(1) Presented at the Baltimore meeting of the American Chemical Society, April, 1939.