Cleavage of a hot chloroform solution by passing in hydrogen chloride for fifty minutes gave a 37.5% yield of diphenyllead dichloride, identified by converting (by reaction with phenylmagnesium bromide) to tetraphenyllead in a 94% yield; a 60.7% yield of triphenyllead chloride (mixed m. p.); and a 46.3% yield of anisole. The anisole was characterized by boiling point, and by conversion to 2,4-dinitroanisole which was shown to be identical with an authentic specimen.[8]

The preparation of triphenyl-*p*-methoxyphenyllead was the only reaction in this study in which *p*-methoxyphenyllithium was used. Only recently[9] has it been shown that the *p*-methoxyphenyllithium prepared in this manner is not pure. The unequivocal establishment of the identity of anisole as a cleavage product shows that triphenyl-*p*-methoxyphenyllead was prepared.

Reaction of Tri-*p*-methoxyphenyllead and Hydrogen Chloride.—Hydrogen chloride was passed into a solution of 10.56 g. (0.01 mole) of tri-*p*-methoxyphenyllead in 200 cc. of warm chloroform for one and one-quarter hours. A gas analysis showed that no hydrogen was evolved. The precipitate, which started to form soon after hydrogen chloride was admitted, weighed 7.1 g. and contained lead chloride. To remove the lead chloride, the precipitate was shaken with ammonium acetate which incidentally converted the di-*p*-methoxyphenyllead dichloride to the corresponding di-*p*-methoxyphenyllead diacetate, in a 42.7% yield.

Anal. Calcd. for $C_{18}H_{20}O_5Pb$: Pb, 38.43. Found: Pb, 38.21.

In another experiment, hydrogen chloride was passed for only twenty-five minutes into a solution of 5.28 g. (0.005 mole) of tri-*p*-methoxyphenyllead in 200 cc. of chloroform warmed to 50°. From the precipitate there was isolated 1.3 g. of lead chloride and 0.5 g. or 9.28% of di-*p*-methoxyphenyllead diacetate. The chloroform filtrate gave a 51.42% yield of tri-*p*-methoxyphenyllead chloride. Earlier studies have been reported on the action of triaryllead compounds with aqueous hydrochloric and hydrobromic acids,[10] and with hydrogen chloride.[11] Aqueous halogen acids appear more suitable than the halogen hydrides for converting R_3Pb compounds to R_3PbX compounds.

Summary

Tri-*p*-methoxyphenyl-2-furyllead and di-*p*-methoxyphenyl-di-2-furyllead have been cleaved by hydrogen chloride. Furan is removed more readily than anisole. On the basis of these experiments, the 2-furyl radical appears to be cleaved more rapidly than any nuclear radical so far examined in the cleavage of unsymmetrical organometallic compounds by hydrogen chloride.

(8) Meldola, Woolcott and Wray, *J. Chem. Soc.*, **69**, 1330 (1896).

(9) Gilman and Jacoby, *J. Org. Chem.*, **3**, 108 (1938); Wittig, Pockels and Dröge, *Ber.*, **71**, 1903 (1938); Gilman, Langham and Jacoby, THIS JOURNAL, **61**, 106 (1939).

(10) Austin, *ibid.*, **53**, 1548, 3514 (1931).

(11) Gilman and Bailie, *ibid.*, **61**, 731 (1939).

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

Relative Reactivities of Organometallic Compounds. XXIII.* Allylic Rearrangements

BY HENRY GILMAN AND JOSEPH F. NELSON

Introduction

Tiffeneau and Delange[1] observed that the product of the reaction between benzylmagnesium chloride and formaldehyde was *o*-tolylcarbinol and not the expected β-phenylethyl alcohol. Subsequently it was shown that rearrangements occurred with other Grignard reagents having an allylic system, such as α-naphthylmethyl-, benzohydryl-, triphenylmethyl- and cinnamyl-magnesium halides.[2] Rearrangement also takes place with organoalkali compounds.[3] It is now known

that the allylic rearrangements of benzylmagnesium halide types occur with a variety of reagents other than formaldehyde.[4]

In extension of studies concerned with preferential reactions of polyfunctional compounds, it was necessary to learn whether allylic rearrangements result with organometallic compounds of lesser reactivity than the Grignard reagents. The present paper reports the reactions of benzylmetallic compounds of zinc, cadmium, mercury and aluminum with formaldehyde, acetyl chloride and carbon dioxide. In addition to the so-called normal products, there were isolated ortho, para, and mixtures of ortho and para rearrangement products. On the basis of these experiments, it seems reasonable to conclude that, in general,[3] organometallic compounds having an

(*) Paper XXII, Gilman and Towne, THIS JOURNAL, **61**, 739 (1939).

(1) Tiffeneau and Delange, *Compt. rend.*, **137**, 573 (1903).

(2) See Gilman and Harris, THIS JOURNAL, **53**, 3541 (1931), for pertinent references as well as an account of the rearrangements of cinnamylmagnesium chloride.

(3) Gilman and Breuer, *ibid.*, **56**, 1127 (1934). A noteworthy exception is the reaction between triphenylmethylsodium and formaldehyde as reported by Schlenk and Ochs, *Ber.*, **49**, 610 (1916). See, also, Morton and Fallwell. THIS JOURNAL, **60**, 1429 (1938), for the formation of β-phenylethyl alcohol from benzylsodium and trioxymethylene.

(4) Austin and Johnson, *ibid.*, **54**, 647 (1932); Gilman and Kirby, *ibid.*, **54**, 345 (1932). These articles review the earlier literature and amplify discussion of reaction mechanisms.

allylic system will show the rearrangements of corresponding Grignard reagents.

The extent of rearrangement varies with the nature of the RM compound. Although no rigorously quantitative separations were effected with the limited reaction products obtained from the experiments now reported, it does appear that rearrangement varies broadly with relative reactivities: the less reactive organometallic compounds undergoing rearrangement to a lesser extent. For example, it may be predicted that the products of reaction of benzylmanganese compounds and formaldehyde will contain β-phenylethyl alcohol as well as o-tolylcarbinol.

The reaction of dibenzylzinc and formaldehyde gave some benzaldehyde. This product was unexpected, particularly because the reaction was carried out in an inert atmosphere. Some benzylmetallic compounds like tribenzylbismuth are known to give benzaldehyde when exposed to the air.[5]

The different behavior of dibenzylzinc in ether and in benzene or toluene, suggested a reaction in benzene between an essentially ether-free benzylmagnesium chloride and formaldehyde. Here, as in ether solution, the only product isolated was o-tolylcarbinol.

TABLE I
REACTIONS OF BENZYL-METALLIC COMPOUNDS

RM compound	Reactant	Products
$(C_6H_5CH_2)_2Zn^a$	HCHO	$C_6H_5CH_2CH_2OH$ (10%) C_6H_5CHO (trace)
$C_6H_5CH_2ZnCl^b$	HCHO	$C_6H_5CH_2CH_2OH$ $C_6H_5CH_2OH$
$(C_6H_5CH_2)_2Zn^c$	CH_3COCl	Ketones (9%)
$(C_6H_5CH_2)_2Zn^d$	CO_2	$p\text{-}CH_3C_6H_4CO_2H$ (0.6%)
$(C_6H_5CH_2)_2Cd^e$	HCHO	$C_6H_5CH_2CH_2OH$ (8%)
$(C_6H_5CH_2)_2Cd^f$	CH_3COCl	$C_6H_5CH_2COCH_3$ (18%)
$(C_6H_5CH_2)_2Hg^g$	CH_3COCl	
$C_6H_5CH_2HgCl^h$	CH_3COCl	
$(C_6H_5CH_2)_3Al^i$	HCHO	$C_6H_5CH_2CH_2OH$ and $o\text{-}CH_3C_6H_4CH_2OH$ (7.7%)
$C_6H_5CH_2MgCl^j$	HCHO	$o\text{-}CH_3C_6H_4CH_2OH$ (21.3%)

[a] This 0.15 mole reaction, which was checked, was carried out in benzene. The weight of benzaldehyde semi-

(5) Challenger and Ridgway, J. Chem. Soc., 121, 104 (1922), and unpublished observations by H. L. Yablunky. For the formation of benzaldehyde from tribenzylarsine, see Michaelis and Paetow, Ann., 233, 62 (1886); and for the formation of benzaldehyde from tribenzylamine, see Limpricht, ibid., 144, 307 (1867). Tsukervanik and Smirnov, J. Gen. Chem. (U. S. S. R.), 7, 1527 (1937) [C. A., 31, 8518 (1937)], reported recently that tribenzylantimony oxidizes readily in the air to give tribenzylantimony oxide. It would not be surprising to find some benzaldehyde from an oxidation of tribenzylantimony under these or related conditions.

The anomalous formation of benzaldehyde from dibenzylzinc and formaldehyde suggested an oxidation experiment. When 0.15 mole of dibenzylzinc was oxidized by air and then oxygen, no benzaldehyde was isolated and the yield of benzyl alcohol was 54%.

carbazone was 0.2 g. Oxidation of 2 g. of the alcohol gave 0.4 g. of benzoic acid and 0.01 g. of phthalic acid. The benzaldehyde obtained when reaction was effected in toluene was characterized as the phenylhydrazone. No terephthalic acid was isolated. When the reaction was carried out in ether, the yield of β-phenylethyl alcohol was 3%. [b] The combined yield of β-phenylethyl alcohol and benzyl alcohol was 10%. The α-naphthylurethans were separated by fractional crystallization and identified by the method of mixed m. p. [c] This reaction was carried out in petroleum ether (b. p. 28–38°), and yielded 3 g. of a mixture of ketones. The mixture of semicarbazones melted over the range 165–186°. Oxidation of 1 g. of the mixture of ketones gave 0.15 g. of benzoic acid, 0.01 g. of phthalic acid and 0.1 g. of terephthalic acid. [d] The p-toluic acid was apparently free of the other possible isomeric rearrangement product, o-toluic acid. [e] This reaction was carried out in ether, and oxidation of 2 g. of the alcohol gave 0.5 g. of benzoic acid and a trace of phthalic acid. No search was made for terephthalic acid. [f] This reaction was also carried out in ether, and oxidation of 1 g. of the mixture of ketones gave 0.21 g. of benzoic acid, 0.04 g. of phthalic acid and 0.05 g. of terephthalic acid. Undoubtedly, the benzyl methyl ketone reported earlier [Gilman and Nelson, Rec. trav. chim., 55, 518 (1936)] contained some other ketones formed by rearrangement. [g] The reactants, with no solvent, were refluxed for fourteen days. The products isolated were a 97% recovery of dibenzylmercury and 0.6 g. of a yellow oil. This oil yielded no semicarbazone, but on oxidation gave traces of benzoic, phthalic and terephthalic acids. [h] After refluxing the reactants for fifty-six hours with no solvent, much tar was formed together with a small amount of an unidentified oil which gave a semicarbazone melting at 208–210°. Oxidation of the residue from semicarbazone formation yielded traces of phthalic and terephthalic acids. The authors are grateful to H. L. Yablunky for assistance in some of the oxidations. When reaction was carried out by refluxing for sixty-eight hours in a mixture of ether and petroleum ether, 87% of the benzylmercuric chloride was recovered. [i] This reaction was carried out in ether, and oxidation of one g. of the mixture of alcohols yielded 0.05 g. of benzoic acid and 0.3 g. of phthalic acid. No search was made for terephthalic acid. [j] The formaldehyde and ether-free Grignard reagent were refluxed in benzene. The α-naphthylurethan of o-tolylcarbinol melted at 142–143°. This apparently is a new compound, and a mixed m. p. determination with a specimen prepared from authentic o-tolylcarbinol showed no depression. Oxidation of 1 g. of the carbinol obtained from the benzylmagnesium chloride experiment gave 0.9 g. of phthalic acid.

Experimental Part

The reactions were carried out by customary procedures. When formaldehyde and acetyl chloride were used, a part of the mixture of alcohols or ketones, respectively, was oxidized. The products of oxidation were then examined for benzoic, phthalic, and terephthalic acids. Terephthalic acid was always identified as its dimethyl ester. The method of mixed melting points was used for

the final characterization of products or their derivatives. The α-naphthylurethan derivatives were used for β-phenylethyl alcohol and o-tolylcarbinol. In Table I the chief products in the mixtures are listed in the third column.

Summary

Allylic rearrangement products have been ob-tained by reaction of benzyl-metallic compounds of zinc, cadmium, mercury and aluminum with formaldehyde, acetyl chloride and carbon dioxide. Such rearrangements now appear to be general with benzyl-metallic types, and the extent of rearrangement generally decreases with the decreasing reactivity of organometallic compounds.

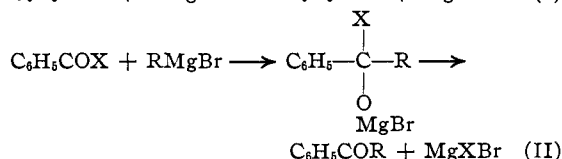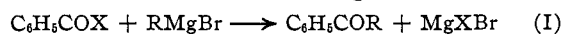# Relative Reactivities of Organometallic Compounds. XXIV.* Reaction Rates of Benzoyl Halides with Di-*p*-tolylmercury

BY HENRY GILMAN AND JOSEPH F. NELSON

Introduction

There is no direct evidence concerning the mechanism of reaction between acid derivatives and organometallic compounds. For example, the ketones formed by interaction of benzyl halides and Grignard reagents may have resulted from either or both of the following transformations

$$C_6H_5COX + RMgBr \longrightarrow C_6H_5COR + MgXBr \quad (I)$$

$$C_6H_5COX + RMgBr \longrightarrow C_6H_5-\overset{\overset{\displaystyle X}{|}}{\underset{\underset{\displaystyle MgBr}{|}}{C}}-R \longrightarrow$$

$$C_6H_5COR + MgXBr \quad (II)$$

That is, reaction may have occurred by direct metathesis (I) or by preliminary addition to the carbonyl group (II).

Indirect evidence for Reaction II has been supplied by Entemann and Johnson.[1] These authors have formulated a very useful series of relative reactivities of functional groups. The series, obtained by competitive reactions of a pair of compounds with an insufficient quantity of phenylmagnesium bromide to react with both, is as follows: —CHO > —COCH₃ > —NCO > —COF > —COC₆H₅, —COCl, —COBr > —COOC₂H₅ > —C≡N. If Reaction I were correct one would expect the acid fluoride to be the least reactive of the three benzoyl halides examined. However, because the acid fluoride was actually found to be the most reactive, it was concluded that reaction occurs through addition to the carbonyl group (II).

This conclusion, we now find, cannot be applied

to some less reactive organometallic compounds like the mercurials. In general, organomercury compounds are unreactive toward most functional groups. They react exceedingly slowly with the carbonyl group in Michler's ketone to give a color test[2]; slowly with ketenes to give methyl ketones[3]; with sulfonyl iodides to give sulfones[4]; and with acyl halides, under relatively forced conditions, to give ketones.[5] For the purposes of the present study, the following reaction was examined

$$2C_6H_5COX + (p\text{-}CH_3C_6H_4)_2Hg \longrightarrow$$
$$2C_6H_5COC_6H_4CH_3\text{-}p + HgX_2$$
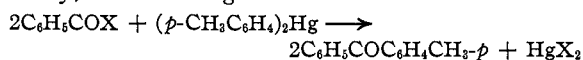
The wide range in reactivity of the benzoyl halides made it desirable to compare the halides in pairs using, for example, relatively moderate conditions when comparing benzoyl iodide with benzoyl bromide and more drastic conditions when comparing benzoyl bromide with benzoyl chloride. Decisive results were obtained when relative reactivities were measured by the yields of pure phenyl *p*-tolyl ketone and the yields of recovered acid halide (determined as benzoic acid). The order of relative reactivities is

$$C_6H_5COI > C_6H_5COBr > C_6H_5COCl > C_6H_5COF$$
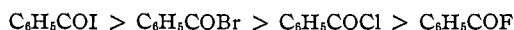
This order appears to hold for other mercurials as well as other acid halides like those of acetic acid. Although there is no assurance that the order established with mercurials will be the same with other organometallic compounds of relatively low reactivity, one may predict that no signifi-

(*) Paper XXIII, Gilman and Nelson, THIS JOURNAL, **61**, 741 (1939).

(1) Entemann and Johnson, THIS JOURNAL, **55**, 2900 (1933).

(2) Gilman and Schulze, *ibid.*, **47**, 2002 (1925).

(3) Gilman, Woolley and Wright. *ibid.*, **55**, 2609 (1933).

(4) Whitmore and Thurman, *ibid.*, **45**, 1068 (1923).

(5) Otto, *Ber.*, **3**, 197 (1870); Calvery, THIS JOURNAL, **48**, 1009 (1926). The reaction with acid halides goes easier with mercurials of thiophene [Steinkopf and Bauermeister *Ann.*, **403**, 59 (1914)], and with mercurials of furan [Gilman and Wright, THIS JOURNAL, **55**, 3302 (1933)].