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Relative Reactivities of Organometallic Compounds. XXII.* Hydrogen Chloride Cleavage Rates of *p*-Methoxyphenyl-2-furyllead Compounds

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Introduction

Where comparisons can be made, there is a general agreement between the rates of cleavage by hydrogen chloride of unsymmetrical organolead compounds[1a] and the rates of cleavage of other unsymmetrical organometallic compounds like those of mercury.[2] The *p*-methoxyphenyl radical heads the series of radicals (the cyanogen radical excluded) definitely placed in the order of decreasing rates of cleavage of mercurials by hydrogen chloride.

It appeared of interest, in connection with other studies, to compare the *p*-methoxyphenyl radical with the 2-furyl radical. This was done by means of appropriate unsymmetrical organolead compounds. The starting compound was tetra-*p*-methoxyphenyllead which was prepared with difficulty by the Grignard procedure. The chief product of reaction between *p*-methoxyphenylmagnesium bromide and lead chloride was the trivalent radical, tri-*p*-methoxyphenyllead, which on subsequent pyrolysis gave satisfactory yields (75%) of the tetra compound. The corresponding R_3PbCl and R_2PbCl_2 compounds were prepared in the customary manner from the R_4Pb compound and hydrogen chloride. These chlorides were then treated with 2-furylmagnesium iodide to yield the desired *p*-methoxyphenyl-2-furyl compounds.

$$(p\text{-}CH_3OC_6H_4)_3PbCl + 2\text{-}C_4H_3OMgI \longrightarrow (p\text{-}CH_3OC_6H_4)_3Pb(C_4H_3O\text{-}2)$$

$$(p\text{-}CH_3OC_6H_4)_2PbCl_2 + 2\text{-}C_4H_3OMgI \longrightarrow (p\text{-}CH_3OC_6H_4)_2Pb(C_4H_3O\text{-}2)_2$$

When the *p*-methoxyphenyl-2-furyl compounds were cleaved by hydrogen chloride, the furyl radical was first removed.

$$(p\text{-}CH_3OC_6H_4)_2Pb(C_4H_3O\text{-}2)_2 + 2HCl \longrightarrow (p\text{-}CH_3OC_6H_4)_2PbCl_2 + 2C_4H_4O$$

On the basis of these experiments, if the general correlation of cleavage rates of unsymmetrical organolead and organomercury compounds holds, it may be concluded that the 2-furyl radical cleaves more readily than any other nucleus so far examined.

No comparison has been reported of the rates of cleavage of the 2-thienyl radical and the *p*-methoxyphenyl radical, although it is known that the 2-furyl radical cleaves more readily than the analogous 2-thienyl radical.[1c] As might have been expected, the *p*-methoxyphenyl radical was found to cleave more readily than the phenyl radical.

$$(C_6H_5)_3PbC_6H_4OCH_3\text{-}p + HCl \longrightarrow (C_6H_5)_3PbCl + C_6H_5OCH_3$$

Experimental Part

The general procedures for the preparation and analysis of symmetrical and unsymmetrical organolead compounds have been described in earlier reports.[1]

p-Methoxyphenylmagnesium Bromide and Lead Chloride.—In one of several preparations, 1 mole of *p*-anisylmagnesium bromide in 550 cc. of ether and 700 cc. of toluene was treated with 120 g. (0.432 mole) of finely divided, dry lead chloride. The products isolated were tetra-*p*-methoxyphenyllead, tri-*p*-methoxyphenyllead, tri-*p*-methoxyphenyllead bromide and bi-*p*-methoxyphenyl. The total yield of tetra-*p*-methoxyphenyllead was 21.6 g. or 15.8%, and this includes the tetra-*p*-methoxyphenyllead isolated as such as well as the tetra compound obtained by treating the tri-*p*-methoxyphenyllead bromide with additional *p*-methoxyphenylmagnesium bromide. Because the separation was laborious and the yields low, it seemed preferable first to prepare tri-*p*-methoxyphenyllead and then pyrolyze it to the tetra compound.

To 0.5 mole of *p*-methoxyphenylmagnesium bromide in 280 cc. of ether was added over a four-hour period, 53.14 g. (0.191 mole) of lead chloride in 0.5-g. portions. The reaction mixture was stirred for three hours, no external heat being applied. The products isolated after hydrolysis were 44 g. or 65.4% of tri-*p*-methoxyphenyllead and 2.2 g. or 3.6% of tetra-*p*-methoxyphenyllead. The tri compound melted with decomposition at 198–200° after crystallization from chloroform.

Anal. Calcd. for $C_{21}H_{21}O_3Pb$: Pb, 39.23. Found: Pb, 39.27, 39.42.

When a solution of tri-*p*-methoxyphenyllead in benzene was heated, decomposition soon took place as evidenced by the black color and the deposition of a lead mirror on the walls of the flask. Heating was continued for eleven hours, and the yield of tetra-*p*-methoxyphenyllead melting at 145–146° after crystallization from alcohol

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(*) Paper XXI, Gilman and Bailie, THIS JOURNAL, **61**, 731 (1939).

[1] (a) Gilman, Towne and Jones, THIS JOURNAL, **55**, 4689 (1933); (b) Gilman, Bywater and Parker, *ibid.*, **57**, 885 (1935); (c) Gilman and Towne, *Rec. trav. chim.*, **51**, 1054 (1932). This article contains a bibliography of earlier work on the hydrogen chloride cleavage of organolead compounds.

[2] See pp. 747–748 of Krause and von Grosse, "Die Chemie der metall-organischen Verbindungen," Borntraeger, Berlin, 1937, for the series of radicals obtained by Kharasch and co-workers, two recent references are: Kharasch, Pines and Levine, *J. Org. Chem.*, **3**, 347 (1938), and Whitmore and Bernstein, THIS JOURNAL, **60**, 2626 (1938).

was 77.7%. From two other pyrolysis experiments heated for ten and seven hours, respectively, the yields were 68.3 and 75.3%.

Tri-*p*-methoxyphenyllead Chloride.—Hydrogen chloride was passed into a hot chloroform solution of 6.35 g. (0.01 mole) of tetra-*p*-methoxyphenyllead. Precipitation of some di-*p*-methoxyphenyllead dichloride set in at the end of one and one-quarter hours, but the passage of hydrogen chloride was continued for an additional twenty minutes. The products isolated were 8.1% of di-*p*-methoxyphenyllead dichloride, and 90.4% of tri-*p*-methoxyphenyllead chloride. When crystallized from chloroform, the tri-*p*-methoxyphenyllead chloride melted with decomposition at 152–153°.

Anal. Calcd. for $C_{21}H_{21}O_3ClPb$: Cl, 6.29. Found: Cl, 6.16.

Di-*p*-methoxyphenyllead Dichloride.—Hydrogen chloride was passed for five minutes into a solution of 5.5 g. (0.0087 mole) of tetra-*p*-methoxyphenyllead in 100 cc. of benzene heated to just below boiling. The white precipitate was filtered, and hydrogen chloride was passed into the hot filtrate for five minutes. The precipitates were combined and washed with ether, to yield 98.6% of di-*p*-methoxyphenyllead dichloride.

Anal. Calcd. for $C_{14}H_{14}O_2Cl_2Pb$: Cl, 14.41. Found: Cl, 14.37.

Several runs were made, and although the yields were uniformly satisfactory it is clear that when the passage of hydrogen chloride is extended too long the yield drops.

Tri-*p*-methoxyphenyl-2-furyllead.—From a reaction between 7.25 g. (0.013 mole) of tri-*p*-methoxyphenyllead chloride and 0.0385 mole (by titration) of 2-furylmagnesium iodide[3] was isolated 5.2 g. or 68% tri-*p*-methoxyphenyl-2-furyllead melting at 76–77°. The compound is very soluble in ether, alcohol, acetone and petroleum ether (b. p. 60–68°). When crystallized from 80% alcohol there was obtained 4.4 g. of feathery needles melting at 83°.

Anal. Calcd. for $C_{25}H_{24}O_4Pb$: Pb, 34.81. Found: Pb, 34.38, 34.61.

The yield of pure compound in a second run was 84%, crystallization being effected from 60% alcohol.

Di-*p*-methoxyphenyl-di-2-furyllead.—To an ether suspension of 9.84 g. (0.02 mole) of di-*p*-methoxyphenyllead dichloride was added a slight excess of 2-furylmagnesium iodide, using the color test[4] for organometallic compounds as an indicator. The yield of pure di-*p*-methoxyphenyl-di-2-furyllead was 55.9%, and the feathery needles melted at 72–73° after crystallization from pentane. The crystals turn pink when exposed to the light.

Anal. Calcd. for $C_{22}H_{20}O_4Pb$: Pb, 37.32. Found: Pb, 36.94.

Cleavage of Tri-*p*-methoxyphenyl-2-furyllead.—In an apparatus provided for the collection of furan, 6.75 g. (0.0114 mole) of tri-*p*-methoxyphenyl-2-furyllead in 175 cc. of warm chloroform was treated in the usual way with hydrogen chloride. At the end of one hour and forty minutes a precipitate of di-*p*-methoxyphenyllead dichloride started to form. The products isolated were 57.35% of di-*p*-methoxyphenyllead dichloride and 43% of tri-*p*-methoxyphenyllead chloride. The former compound was characterized by conversion to tetra-*p*-methoxyphenyllead, by means of *p*-methoxyphenylmagnesium bromide, and the latter compound in the same manner as well as by a mixed m. p. determination.

Furan was characterized by the color test obtained with vanillin and concd. hydrochloric acid.[5] With furan, the pink color quickly turns to a murky purple and finally to a brownish-green. The reddish-pink color with anisole is permanent. Blank runs with authentic specimens of furan and anisole, as well as mixtures of these compounds, showed the color test to be reliable. With larger quantities of furan, a derivative can be prepared as was done in the cleavage experiments with di-*p*-methoxyphenyl-di-2-furyllead.

Cleavage of Di-*p*-methoxyphenyl-di-2-furyllead.—Into a solution of 5.56 g. (0.01 mole) of di-*p*-methoxyphenyl-di-2-furyllead in dry benzene was passed hydrogen chloride for one hour. The heavy precipitate of di-*p*-methoxyphenyllead dichloride was filtered, and the filtrate treated with hydrogen chloride for one-half hour. The total yield of di-*p*-methoxyphenyllead dichloride was 87.4%. Identification was established by conversion to tetra-*p*-methoxyphenyllead. Incidentally, the precipitate of di-*p*-methoxyphenyllead dichloride was shown by the vanillin color test[5] to be free of 2-furyl components, and to contain the *p*-methoxyphenyl radical.

The benzene filtrates, obtained after hydrogen chloride cleavage, gave a positive furan color test. The furan was characterized by an appropriate derivative prepared from maleic anhydride.[6] The furan-maleic anhydride compound, 3,6-endoxytetrahydrophthalic anhydride, melted at 119° and showed no depression in a mixed melting point determination with an authentic specimen.

Preliminary blank tests were carried out to make certain that if furan were liberated in the hydrogen chloride cleavages, it would survive, under our experimental conditions, the action of hydrogen chloride. In one of these experiments, 2.83 g. (0.042 mole) of furan in 50 cc. of chloroform was treated with hydrogen chloride for one and one-half hours. Then, after bubbling nitrogen through the solution for a few minutes, the chloroform solution was washed with cold 5% sodium hydroxide, and finally with water. The solution was then dried over calcium chloride, and treatment in the usual manner with maleic anhydride gave a 24.4% yield of the furan-maleic anhydride compound melting at 118–119°. It is known that some negatively substituted furans are extremely resistant to the action of acids.[7]

Triphenyl-*p*-methoxyphenyllead.—From a reaction between 0.04 mole of triphenyllead chloride and the organolithium compounds prepared from 0.08 mole of *p*-methoxyphenyl bromide, there was obtained 11.2 g. of triphenyl-*p*-methoxyphenyllead which melted at 152° after several recrystallizations from alcohol.

Anal. Calcd. for $C_{25}H_{22}OPb$: Pb, 38.0. Found: Pb, 38.22, 38.35.

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[3] Gilman, Mallory and Wright, THIS JOURNAL, **54**, 733 (1932).

[4] Gilman and Schulze, *ibid.*, **47**, 2002 (1925).

[5] This test can also be used for furyl-lead and *p*-methoxyphenyllead compounds. See Asahina, *Acta phytochim.* (*Japan*), **2**, 1 (1924) [*C. A.*, **21**, 2897 (1927)].

[6] Diels and Alder, *Ber.*, **62**, 554 (1929).

[7] Gilman and Young, *Rec. trav. chim.*, **51**, 761 (1932).

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 $C_{18}H_{20}O_6Pb$: 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.

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[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).

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Relative Reactivities of Organometallic Compounds. XXIII.* Allylic Rearrangements

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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

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(*) 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.