[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

The Labilities or Electronegativities of Some Unsaturated Alkyl Radicals as Determined by Hydrogen Chloride Scission of Organolead Compounds

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Introduction

The scission of phenylfuryl-, phenylthienyl- and furylthienyl-lead compounds by hydrogen chloride has been advanced in support of the super-aromaticity of furan.[1] In order to test the validity of such evidence it appeared desirable to establish the relative labilities of some other unsaturated radicals, particularly of the aliphatic series.

On the basis of a significant amount of experimental data, it appeared altogether reasonable to expect that in accordance with the following general reaction

$$(\text{Aryl})_3\text{Pb}(\text{Alkyl}) + \text{HCl} \longrightarrow (\text{Aryl})_2\text{Pb}(\text{Cl})(\text{Alkyl}) + \text{Aryl H} \qquad (\text{I})$$

a mixed organolead compound containing aryl and alkyl groups would be cleaved by hydrogen chloride to give an aromatic but not an aliphatic hydrocarbon. However, Austin[2a] has shown that when an alcoholic solution of triphenylallyllead is heated with hydrobromic acid, triphenyllead bromide is formed in practically quantitative yields

$$(C_6H_5)_3PbC_3H_5 + HBr \longrightarrow (C_6H_5)_3PbBr \qquad (\text{II})$$

This splitting reaction is at variance with what might have been expected on the assumption that the allyl radical is a weakly electronegative group.[2b]

Inasmuch as cleavage of R_4Pb compounds by hydrogen chloride in chloroform or benzene proceeds quite smoothly, and inasmuch as these conditions were used in the aromaticity studies, we treated a chloroform solution of triphenylallyllead with hydrogen chloride. The yield of phenyllead halides (triphenyllead chloride and diphenyllead dichloride) was about 95%, and propene was identified. The formation of propene as a cleavage product is significant, for it shows that the allyl group as such was cleaved and that at least a part of the allyl groups did not undergo addition of hydrogen chloride at the olefinic linkage prior to cleavage. Even if hydrogen chloride added first to the olefinic linkage, the splitting would still have been anomalous, according to some interpretations, in the sense that an aliphatic radical, in this case a chloropropyl group, would have been cleaved prior to an aryl or phenyl group.

Comparison of Cleavage of Organolead with Other Organometallic Compounds.—The unexpected splitting products of triphenylallyllead suggested that cleavage of organolead compounds might possibly be unlike

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[1] Gilman and Towne, *Rec. trav. chim.*, **51**, 1054 (1932). This article contains references to earlier studies on the cleavage of organolead compounds by hydrogen chloride.

[2] (a) Austin, THIS JOURNAL, **53**, 3514 (1931); (b) "Annual Survey of American Chemistry," 1931, Vol. VI, p. 210.

that of other organometallic compounds, particularly the unsymmetrical organomercurials which have been so satisfactorily studied by Kharasch and co-workers.[3] In order to supplement early work, the splitting of a miscellany of mixed R_4Pb compounds by hydrogen chloride was investigated. The results indicate that the decreasing order of lability of the radicals, with hydrogen chloride as the cleavage agent, is as follows: $\alpha\text{-}C_{10}H_7\text{–} > C_6H_5\text{–} > C_6H_5CH_2\text{–}$. This order, together with that established for the α-furyl and α-thienyl radicals as well as for many alkyl radicals, indicates that the radicals conform rather closely with the order established by the hydrogen chloride cleavage of other organometallic compounds.

It should be stated that orienting cleavage experiments with diphenyldibiphenyllead and triphenylbiphenyllead gave both diphenyl and benzene as splitting products with the former in slight excess. Orienting experiments with diphenyl-di-*p*-dimethylaminophenyllead, $(C_6H_5)_2Pb[C_6H_4N(CH_3)_2]_2$, and with triphenyl-*p*-dimethylaminophenyllead, were more conclusive and showed definitely that the *p*-dimethylaminophenyl radical is cleaved more rapidly than the phenyl radical. This is as one would have predicted, both on the basis of so-called relative electronegativities and relative aromaticities.

Cleavage of Unsaturated Radicals Other than Allyl.—Having shown that R_4Pb compounds might be used generally to determine the relative labilities of radicals, it was of interest to learn whether the allyl radical was peculiar in the sense that it alone among unsaturated alkyl radicals was cleaved prior to an aromatic radical. First, the cleavage of triphenyl-β-styryllead was effected in chloroform by hydrogen chloride. The yield of phenyllead chlorides was 96% and styrene was identified.

$$(C_6H_5)_3PbCH{=}CHC_6H_5 + HCl \longrightarrow (C_6H_5)_3PbCl + C_6H_5CH{=}CH_2 \qquad \text{(III)}$$

Here, also, an unsaturated radical is removed prior to an aryl group. Second, the scission of triphenyl-3-butenyllead under corresponding conditions gave diphenyl-3-butenyllead chloride and benzene

$$(C_6H_5)_3PbCH_2CH_2CH{=}CH_2 + HCl \longrightarrow (C_6H_5)_2Pb(Cl)(CH_2CH_2CH{=}CH_2) + C_6H_6 \qquad \text{(IV)}$$

From this reaction it follows that the 3-butenyl radical, unlike the allyl and β-styryl radicals, is less labile than the phenyl radical. The order of decreasing labilities on the basis of hydrogen chloride cleavage of mixed organolead compounds is

$$[CH_2{=}CHCH_2\text{—} \text{ and } C_6H_5CH{=}CH\text{—}] > C_6H_5\text{—} > C_2H_5\text{—} > CH_2{=}CHCH_2CH_2\text{—}$$

The ethyl radical was shown to be more labile than the 3-butenyl radical by the formation of ethane and ethyl-3-butenyllead dichloride from the cleavage of triethyl-3-butenyllead. Other studies indicate that the

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(3) Kharasch and Flenner, This Journal, **54**, 674 (1932). Other references to the extensive studies by Kharasch and co-workers are contained in this most recent paper. In addition a critical survey is presented of the splitting of other organometallic compounds.

phenylacetenyl radical ($C_6H_5C\equiv C-$) is more labile and the 4-pentenyl radical ($CH_2=CHCH_2CH_2CH_2-$) is less labile than the phenyl radical.

If one might generalize from these restricted observations with unsaturated alkyl radicals, it appears that unsaturated radicals vary significantly in their relative labilities, depending on the position of the unsaturated linkage with respect to the carbon–metal bond and on the nature of substituents in the unsaturated radical. It seems probable that different types of unsaturated radicals might form a series related to that of aryl and saturated alkyl groups. The preferential cleavage of $C_6H_5C\equiv C-$ and $C_6H_5CH=CH-$ indicates that α,β-unsaturation with lead may be a significant factor in the greater labilities of some unsaturated radicals. If this be the case, it raises a question on the structure of triphenylallyllead. We may have in this compound a $CH_3CH=CH-$ and not a $CH_2=CH\text{-}CH_2-$ linkage. This remains to be determined.

The results with the allyl and β-styryl radicals appear to be at variance with some conclusions on relative aromaticities drawn from a series of relative labilities as measured by rates of hydrogen chloride cleavage.[1] However, the allyl and styryl radicals do have some physical and chemical characteristics which might warrant a formal if not a compelling analogy with aromatic types. Admittedly, that particular evidence for the superaromaticity of furan based on organometallic cleavage is apparently impaired by the present findings.

Experimental Part

The point of departure for most of the syntheses was tetraphenyllead,[4a] and directions for its preparation have been improved so that the yield has reached 80%. Triphenyllead chloride and diphenyllead dichloride were prepared by standard procedures;[4b] and the method of analysis for lead was that described earlier.[4c] Details of the cleavage of $R^1_2PbR^2_2$ and $R^1_3PbR^2$ types have already been given,[1] and the same general procedure was followed in the experiments to be described.

Triphenylallyllead.—The yield of triphenylallyllead[2a] from triphenyllead chloride and allylmagnesium bromide was 82.4%. Five cleavage experiments were carried out with hydrogen chloride, using chloroform as the solvent. The runs varied from 0.01 to 0.02 mole; the temperature from 26 to 50°; and the time of reaction from forty-five minutes to two hours. Triphenyllead chloride was identified by the method of mixed melting points. Diphenyllead dichloride was converted, by means of phenylmagnesium bromide, to tetraphenyllead. The yield of phenyllead halides (composed of the soluble triphenyllead chloride and the insoluble diphenyllead dichloride) averaged about 95%. In a typical cleavage the yield of diphenyllead dichloride was 17.4%, and the yield of triphenyllead chloride was 77.6%. Cleavage was generally carried slightly beyond the R_3PbCl stage and to the R_2PbCl_2 stage in order to avoid contamination with R_4Pb compound. The propene was characterized by conversion to 1,2-dibromopropane.

Triphenyl-3-butenyllead.—3-Buten-1-ol ($CH_2=CHCH_2CH_2OH$) was prepared by the addition of gaseous formaldehyde to a magnesium-free ethereal solution of allylmagnesium bromide. The formaldehyde was added until the absence of the color test showed the Grignard reagent to be used up. The yield of crude 3-buten-1-ol, based on allylmagnesium bromide, was 59%; and rectification by distillation gave a 43% yield.

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[4] (a) THIS JOURNAL, **49**, 2315 (1927); (b) *ibid.*, **51**, 3112 (1929); (c) *ibid.*, **50**, 1714 (1928).

3-Butenyl bromide ($CH_2=CHCH_2CH_2Br$) was prepared in accordance with the directions of Juvala[5] from the alcohol, phosphorus tribromide and pyridine.

3-Butenylmagnesium bromide was prepared in practically a quantitative yield under standard conditions,[6] the yield being determined by titration. This Grignard reagent was prepared previously by a less direct method, from 1,2,4-tribromobutane and magnesium in ether.[7] In order to characterize our RMgBr compound, it was carbonated to give allylacetic acid ($CH_2=CHCH_2CH_2COOH$), and this in turn was characterized by the preparation of 3,4-dibromovaleric acid[8] by means of bromine in carbon tetrachloride.

Triphenyl-3-butenyllead was prepared by adding the Grignard reagent to a suspension of triphenyllead chloride in ether. The yield of crude product, based on triphenyllead chloride, was 96%. Purification was effected from petroleum ether (b. p. 30–80°) to give a white solid melting at 84–86°.

Anal. Calcd. for $C_{22}H_{22}Pb$: Pb, 42.01. Found: Pb, 41.78 and 41.87.

The triphenyl-3-butenyllead in chloroform was treated with dry hydrogen chloride in the customary manner, the solution being kept at 40–45°. After thirty minutes a flocculent white precipitate formed. From the chloroform there was isolated diphenyl-3-butenyllead chloride [see Reaction (IV)] which melted with decomposition at 134–135° when recrystallized from alcohol.

Anal. Calcd. for $C_{16}H_{17}ClPb$: Cl, 7.85. Found: Cl, 7.72 and 7.79.

The diphenyl-3-butenyllead chloride was characterized by treatment with phenylmagnesium bromide, which converted it to the known triphenyl-3-butenyllead (mixed melting point determination). There was no evidence of any significant cleavage to give butene. However, benzene was identified as a product of cleavage, the yield of *m*-dinitrobenzene (mixed m. p.) being 42%. Another scission product appears to be phenyl-3-butenyllead dichloride formed in about one-half the quantity of diphenyl-3-butenyllead chloride. The instability of this R_2PbCl_2 compound is remindful of di-2-thienyllead dichloride.[1]

Triethyl-3-butenyllead, $(C_2H_5)_3PbCH_2CH_2CH=CH_2$.—The triethyl-3-butenyllead was prepared from triethyllead chloride and 3-butenylmagnesium bromide. The yield of crude material was 81%, and this on fractionation gave a 63% yield of product distilling at 78° (3 mm.); d_4^{20} 1.5616; n_D^{20} 1.5230.

Anal. Calcd. for $C_{10}H_{22}Pb$: Pb, 59.34. Found: Pb, 59.10.

Cleavage with hydrogen chloride was effected separately in ether, in chloroform and in benzene solutions. The same products were obtained from each medium. The yield of ethyl-3-butenyllead dichloride, from benzene, was 82%.

Anal. Calcd. for $C_6H_{12}Cl_2Pb$: Cl, 19.58. Found: Cl, 19.70.

Ethane was identified as the other product of cleavage, and no significant quantity of butene was contained in the ethane.

Triphenyl-β-styryllead.—Triphenyllead chloride was added to a filtered ether solution of β-styrylmagnesium bromide which was obtained in 77% yield. The yield of triphenyl-β-styryllead, melting at 107–109°, after crystallization from alcohol, was 28%. In addition, the usual amount of 1,4-diphenylbutadiene (from coupling during the Grignard reaction) was obtained, as well as a small quantity of tetraphenyllead.

Anal. Calcd. for $C_{26}H_{22}Pb$: Pb, 38.26. Found: Pb, 38.11 and 37.97.

Cleavage was effected in warm chloroform solution, the flask being swept out by a

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(5) Juvala, *Ber.*, **63**, 1989 (1930).

(6) THIS JOURNAL, **51**, 1576 (1929).

(7) V. Braun and Deutsch, *Ber.*, **44**, 3699 (1911).

(8) Messerschmidt, *Ann.*, **208**, 100 (1881).

stream of dry nitrogen prior to the admission of hydrogen chloride. The yield of diphenyllead dichloride was 16.2% and this was identified as tetraphenyllead subsequent to treatment with phenylmagnesium bromide. The yield of triphenyllead chloride (mixed m. p.) was 80.17%, making a total yield of phenyllead halides of 96.37%. Styrene was isolated and identified.

Triphenyl-α-naphthyllead.—This compound was prepared in a customary manner by adding α-naphthylmagnesium bromide to triphenyllead chloride. The yield was 66% of a compound which when recrystallized from alcohol melted at 131°.[9]

Anal. Calcd. for $C_{28}H_{22}Pb$: Pb, 36.66. Found: Pb, 36.57 and 36.70.

Scission of a chloroform solution gave a 62.5% yield of naphthalene.

Diphenyl-di-α-naphthyllead.—The yield of this compound from diphenyllead dichloride and α-naphthylmagnesium bromide was 81.2%, and after crystallization from alcohol it melted at 196–197°.[9] Hydrogen chloride cleavage in benzene gave 93% of diphenyllead dichloride and 88.2% of naphthalene.

Triphenylbenzyllead.—Slightly more than one equivalent of benzylmagnesium chloride was necessary to give a positive color test in the reaction with triphenyllead chloride. The yield of triphenylbenzyllead[10] melting at 91° after crystallization from alcohol was 89%.

Anal. Calcd. for $C_{25}H_{22}Pb$: Pb, 39.33. Found: Pb, 38.94 and 38.86.

Cleavage of a boiling chloroform solution gave some unaltered triphenylbenzyllead, lead chloride and diphenylbenzyllead chloride which sinters at 157°.

Anal. Calcd. for $C_{19}H_{17}ClPb$: Pb, 42.48. Found: Pb, 42.25 and 41.80.

Cleavage in petroleum ether (b. p. 50–60°) gave a 76% yield of pure diphenylbenzyllead chloride and an 86% yield of benzene as determined by the weight of *m*-dinitrobenzene.

Summary

1. In connection with relative aromaticities, a study has been made of the rates of cleavage of unsymmetrical organolead compounds by means of hydrogen chloride.

2. The relative order of labilities or so-called electronegativities of radicals is essentially that observed in the scission reactions of other organometallic compounds by hydrogen chloride: [α-C_4H_3S– and α-$C_{10}H_7$–] > C_6H_5– > [C_2H_5– and $C_6H_5CH_2$–].

3. Triphenylallyllead gives triphenyllead chloride and propene, indicating (contrary to expectations) that the allyl group is more labile than the phenyl group. Likewise, the β-styryl group is cleaved before phenyl. However, the phenyl radical is removed before the 3-butenyl radical. Accordingly, it appears that the unsaturated radicals can form a series the members of which are more or less labile than the phenyl radical depending on the position of the unsaturated linkage and the nature of substituents in the unsaturated alkyl group. Also, the results appear to be at variance with some concepts of relative aromaticities, particularly as they concern furan.

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[9] Krause and Schmitz, *Ber.*, **52**, 2150 (1919).

[10] Krause and Schlöttig, *ibid.*, **63**, 1384 (1930).