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ELECTRON TRANSFER MECHANISM IN LITHIUM ALUMINIUM HYDRIDE REDUCTION OF ORGANOMERCURIC HALIDES

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Summary: A new electron transfer free radical mechanism has been proposed for the reduction of a few organomercuric halides with $LiAlH_4$. Symmetrization of arylmercuric halides in these reactions has been observed for the first time.

Occurrence of new electron transfer mechanisms[1-3] involving radical intermediates in the uncatalyzed $LiAlH_4$ reduction of Z-2-chlorostilbene and certain benzylic halides has been recently demonstrated in our laboratory. Though radicals have been assumed[4] to intervene in the reduction of alkylmercuric halides with $LiAlH_4$, the mode of formation of these intermediates is not understood.[5] We now report the occurrence of an electron transfer mechanism in $LiAlH_4$ reductions of benzylmercuric chloride $C_6H_5CH_2$-HgCl 1a, and arylmercuric chlorides p-R-C_6H_4-HgCl (1b, 1c, 1d, where R = H, CH_3, NO_2, respectively).

On the addition of $LiAlH_4$ contained in THF[6] solvent to a solution of the organomercuric chloride 1, in the same solvent at 30°C under dry nitrogen with magnetic stirring, the reaction commenced with the evolution of hydrogen gas and simultaneous separation of metallic mercury. The reaction mixtures in different runs, on work up,[7] gave the results summarized in the Table. An earlier suggestion[8] favouring the formation of an intermediate organoaluminium compound in the reactions with 1b, which accounts for the formation after work up of benzene, is untenable since the amount of benzene in the reaction mixture, estimated in run 6 before and after work up, was found to remain essentially the same. Furthermore, such a process would not explain the formation of diorganomercurials 5 and dimeric products 6, obtained in these reactions. The absence of highly nucleophilic phenyl lithium in the $LiAlH_4$ reduction of 1b has been demonstrated by Traylor[9] who found that in the presence of carbon dioxide no benzoic acid was formed. It is evident from the product distribution listed in the Table that symmetrization of the organomercurial predominates over demercuration, but this trend is reversed in the presence of cumene (run 5). These arguments coupled with an earlier observation[4] establish that radicals are effective intermediates in the reactions of 1a, 1b, 1c and 1d with $LiAlH_4$.

The conceivable production of radicals[10] via the nucleophilic attack of

Table: Reactions[a] of organomercuric halides 1 with $LiAlH_4$

Run	Organomercuric halide, 1 0.005 mol	$LiAlH_4$ mol	Reaction time, min	% yield of products[b]				H_2[c] ml
				R-Hg-R 5	R-R 6	R-H 7	Starting material 1	
1	1a	0.005	30	53	11	25	-	53
2	1a	0.0025	30	55	13	14	12	49
3	1a	0.00125	30	50	10	8	26	30
4	1a	0.00125	300	52	14	10	17	33
5[d]	1a	0.00125	30	8	2	39	48	36
6	1b	0.005	30	58	2	32[e]	-	54
7	1b	0.0025	30	60	2	26	11	48
8	1b	0.00125	30	55	3	16	25	31
9	1b	0.00125	300	57	3	18	17	33
10[f]	1b	0.005	30	37	2	23	28	57
11	1c	0.005	30	41	2	20	26	40
12	1c	0.0025	30	38	2	16	31	35
13	1c	0.00125	30	33	2	10	40	21
14[g]	1d	0.0025	30	45	3	21	5	51
15[g]	1d	0.00125	30	42	3	10	19	37

a. Reactions conducted in THF (60 ml) at 30°C under dry nitrogen.

b. Percentage yields based on R-Hg-Cl, 1. An unestimated amount of metallic mercury was also obtained.

c. Volume of H_2 was determined at atmospheric pressure by comparison with control experiment in the absence of 1 using same batch of reactants and solvent under identical conditions.

d. In presence of cumene (0.1 mol).

e. Yield remained essentially unaltered on estimation before and after work up of the reaction mixture.

f. In presence of naphthalene (0.005 mol). Naphthalene was recovered back unchanged after the reaction.

g. Unestimated amounts of azobenzene and azoxybenzene were also obtained. Additional coloured product mixture could not be analyzed.

hydride on the electrophilic mercury of 1, resulting in the intermediate organomercuric hydride R-Hg-H, followed by homolysis of the carbon-mercury bond is untenable in view of the observed retardation of the reaction in the presence of naphthalene[11] in run 10. Furthermore, the formation of R-Hg-H itself is unlikely in view of the endothermicity of the overall reaction reflecting unfavourable energetics. Thus, homolysis of the Hg-H bond in hypothetical R-Hg-H as a means of hydrogen evolution is also considered unlikely. Electron transfer from $LiAlH_4$ to 1 on the other hand, is quite feasible as the 2-nitropropanate anion which is known to be inferior to $LiAlH_4$ as electron donor towards 9-chloromethylanthracene[3,12] readily transfers an electron to alkylmercuric chlorides.[13]

In view of the foregoing arguments, we conclude that the reactions under consideration are triggered off by a fast electron transfer[3] from $\mathrm{AlH_4^-}$ to the lowest ABMO of $\underline{1}$ producing radical anion $\underline{2}$, hydrogen and $\mathrm{AlH_3}$, as shown in step 1 of the scheme.

SCHEME

$$\underset{\underline{1}}{\mathrm{R{-}Hg{-}Cl}} + \mathrm{AlH_4^-} \longrightarrow \underset{\underline{2}}{[\mathrm{R{-}Hg{-}Cl}]^{\overline{\cdot}}} + \tfrac{1}{2}\,\mathrm{H_2} + \mathrm{AlH_3} \qquad ..\ (1)$$

$$(a)\ \underline{2} \longrightarrow \underset{\underline{3}}{\mathrm{R{-}Hg^{\cdot}}} + \mathrm{Cl^-};\quad (b)\ \mathrm{AlH_3} + \mathrm{Cl^-} \longrightarrow \mathrm{AlH_3Cl^-} \qquad ..\ (2)$$

$$\underline{3} \longrightarrow \mathrm{R^{\cdot}} + \mathrm{Hg^0} \qquad ..\ (3)$$

$$\mathrm{R^{\cdot}} + \underset{\underline{1}}{\mathrm{R{-}Hg{-}Cl}} \rightleftharpoons \underset{\underline{4}}{[\mathrm{R_2HgCl}]^{\cdot}} \xrightarrow{\mathrm{e^-\ from\ AlH_4^-}} \underset{\underline{5}}{\mathrm{R{-}Hg{-}R}} + \mathrm{Cl^-} \qquad ..\ (4)$$

$$\mathrm{R^{\cdot}} + \mathrm{R^{\cdot}} \longrightarrow \underset{\underline{6}}{\mathrm{R{-}R}} \qquad ..\ (5)$$

$$\mathrm{R^{\cdot}} + \mathrm{AlH_4^-} \xrightarrow{\mathrm{slow}} \underset{\underline{7}}{\mathrm{R{-}H}} + \mathrm{AlH_3^{\overline{\cdot}}} \qquad ..\ (6)$$

$$\underline{1} + \mathrm{AlH_3^{\overline{\cdot}}} \longrightarrow \underline{2} + \mathrm{AlH_3} \qquad ..\ (7)$$

The fragmentation of $\underline{2}$ into the organomercury radical $\underline{3}$ and $\mathrm{Cl^-}$ favoured by the high electronegativity of Cl has been established by electrochemical[14] and polarographic[15] reduction studies on similar substrates. The unstable organomercury radical $\underline{3}$ is known[16] to undergo very fast fragmentation yielding alkyl or aryl radical $\mathrm{R^{\cdot}}$ and metallic mercury. This radical $\mathrm{R^{\cdot}}$ may then combine with $\underline{1}$ giving adduct $\underline{4}$ which on acceptance of an electron from $\mathrm{AlH_4^-}$ would fragment[16] into $\mathrm{Cl^-}$ and diorganomercurial $\underline{5}$, dimerize to yield $\underline{6}$ or abstract a hydrogen atom from $\mathrm{AlH_4^-}$ to yield $\underline{7}$ and $\mathrm{AlH_3^{\overline{\cdot}}}$. Abstraction of a hydrogen atom by an alkyl or aryl radical from $\mathrm{AlH_4^-}$ is precedented.[2,3] The $\mathrm{AlH_3^{\overline{\cdot}}}$ generated in step 6 effectively competes with $\mathrm{AlH_4^-}$ in electron donation to $\underline{1}$. Generation of and electron donation by $\mathrm{AlH_3^{\overline{\cdot}}}$ is evident from the volume of hydrogen gas evolved in accordance with step 1 and the amount of $\underline{1}$ consumed in these reactions. Abstraction of a hydrogen atom by the radical $\mathrm{R^{\cdot}}$ from cumene, a good hydrogen atom donor, results in enhanced yields of $\underline{7}$ in run 5 at the expense of products $\underline{5}$ and $\underline{6}$. The retardation of the reaction in the presence of naphthalene as observed in run 10 is rationalized in terms of the equilibrium shown in Eq. (8), existence of which has been demonstrated in a separate study.[17]

$$[\mathrm{R{-}Hg{-}Cl}]^{\overline{\cdot}} + \mathrm{C_{10}H_8} \rightleftharpoons \mathrm{R{-}Hg{-}Cl} + [\mathrm{C_{10}H_8}]^{\overline{\cdot}} \qquad ..\ (8)$$

The anion $\mathrm{AlH_3Cl^-}$, formed in step (2b) may also donate a hydrogen atom to radical $\mathrm{R^{\cdot}}$ yielding $\mathrm{AlH_2X^{\overline{\cdot}}}$. The ion $\mathrm{AlH_3Cl^-}$ and the radical anion $\mathrm{AlH_2X^{\overline{\cdot}}}$ can also donate electrons to $\underline{1}$, as inferior alternatives to $\mathrm{AlH_4^-}$ and $\mathrm{AlH_3^{\overline{\cdot}}}$, respectively. Similarly, ions $AlH_2X_2^-$, $AlHX_3^-$ and AlX_4^- and radical anions $AlHX_2^{\cdot-}$ and $AlX_3^{\cdot-}$ formed in the medium in succession may donate electrons to 1. The recovery of lesser amounts of unreacted organomercuric halides, on increasing the reaction time in runs 4 and 9, is in conformity with the expected[3] order of efficiency in reactivities of alanates and alane radical anions.

This mechanism is also consistent with the reported[4] reductive demercuration and cyclization of 5-hexenylmercuric chloride with $LiAlH_4$. Since both AlH_4^- and BH_4^- are known[2,18] to transfer hydrogen atoms to radicals, the near agreement in deuterium isotope effects obtained for the $LiAlH_4$ and $NaBH_4$ reductions of this mercurial may be accounted for, without invoking the hydrogen atom transfer from the hypothetical alkylmercuric hydride (R-Hg-H).

The diorganomercurials formed in these reactions may be reduced further by electron transfer, though more slowly than 1. Indeed, it has been observed by us that the reaction[19] of dibenzylmercury with $LiAlH_4$ yields toluene, bibenzyl, metallic mercury, and hydrogen gas and that only the first hydrogen in $LiAlH_4$ is involved in the reaction. Further work is in progress to establish the mechanism of these reductions conclusively.

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References and Notes

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