

NOVEL ELECTRON TRANSFER MECHANISM IN LITHIUM ALANATE REDUCTION
OF BENZYLIC HALIDES¹

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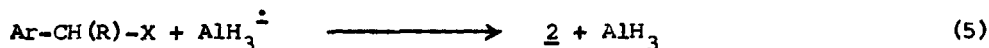
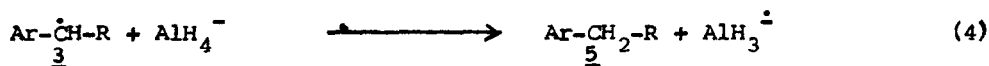
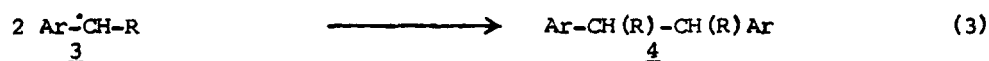
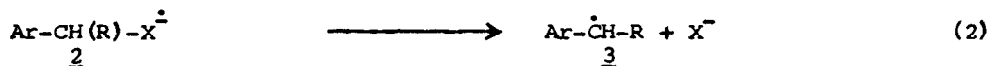
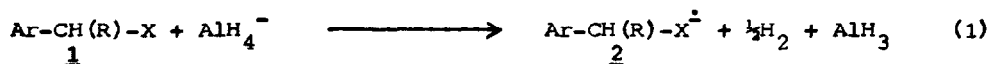
Summary: Occurrence of a new electron transfer mechanism in the LiAlH_4 reduction of 9-chloromethylantracene, diphenylchloromethane and 9-bromofluorene is demonstrated. Alanate anion serves as a source of electrons and hydrogen atoms.

Metal hydrides⁴ are generally believed to react as nucleophilic hydride species. Reduction of the carbonyl group with lithium alanate (LiAlH_4), for example, involves a direct transfer of hydride ion.⁵ $\text{S}_{\text{N}}1$ and $\text{S}_{\text{N}}2$ processes are reported⁶ to occur in the metal hydride reductions of alkyl and aryl halides. In some lithium alanate reductions of organic halides, intervention of carbanions,⁷ radicals⁸ and four-centred transition state⁹ have been considered. Electron transfer mechanisms have been recently demonstrated in the LiAlH_4 reductions of o-bromophenyl allyl ether¹⁰ and Z-2-chlorostilbene.¹¹

We now report the occurrence of a new electron transfer mechanism in LiAlH_4 reductions of three benzylic halides viz., 9-chloromethylantracene 1a, diphenylchloromethane 1b and 9-bromofluorene 1c. On adding equimolar amounts of LiAlH_4 contained in THF¹² to the solutions of these halides in the same solvent at ice-bath temperature under dry nitrogen with magnetic stirring, green, yellow and red colors, respectively, appeared immediately but faded away slowly. Hydrogen gas was evolved within the first 3 min. The reaction mixture in each case was worked up after all the starting halide 1 was consumed (tlc). The results of these and related experiments are summarized in the Table.

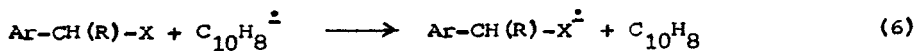
An earlier suggestion¹³ favoring the formation of dimers 4 via metallation of 5 followed by nucleophilic attack of the resultant carbanion on 1 is untenable as our treatment of authentic samples of 9-methylantracene, diphenylmethane and fluorene, respectively, with LiAlH_4 under the original conditions and subsequent work up in the presence of D_2O resulted in the quantitative recovery of undeuterated hydrocarbons (nmr). The same conclusion is also derived from the results of 1-chloro-1-phenylethane,¹⁴ using $\text{LiAlD}_4 + \text{LiD}$, wherein 1-deutero-1-phenylethane and undeuterated 2,3-diphenylbutane¹⁵ were obtained. We consider the approach of a hydride ion to the negative halogen end of the C-X dipole in 1 improbable. This view makes the formation of a carbanion via abstraction of a halonium ion from 1 and hence, dimer 4 by this route unlikely. The possibility

Scheme

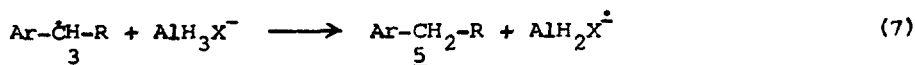


The benzylic radicals 3 produced by the dissociation of the radical-anion 2 (step 2) are known to prefer dimerization via step 3 rather than hydrogen abstraction from THF solvent.¹⁷ A look at the quantity of hydrogen gas evolved in accordance with step 1 on one hand and formation of substantial amounts of 5 on the other, makes the existence of hydrogen atom abstracting process represented by step 4 obvious. Abstraction of a hydrogen atom by radical species from AlH_4^- is preceded.^{10,11} Besides producing monomeric reduction product 5, step 4 generates the radical-anion, $\text{AlH}_3^{\cdot-}$ which competes with AlH_4^- in donating an electron to 1. Combination of steps 1 to 5 accounts for the involvement of only one out of four hydrogens present in AlH_4^- in the reduction process. But the consumption of significantly more than 50% of 1 in runs 2, 5 and 8 where only half the molar quantity of LiAlH_4 was used and similarly, more than 25% of 1 in runs 3, 6 and 9 with only one-fourth molar quantity of the reducing agent indicate utilization of the hydrogens of AlH_3 in these cases. An investigation of this process using equimolar quantity of AlH_3 prepared *in situ*¹⁸ with 1c under otherwise unchanged reaction conditions showed no reaction. On repeating the above reaction by replacing one-fourth of AlH_3 with equal number of moles of sodium naphthalene,¹⁹ dimer 4 (40%), monomeric reduction product 5 (11%) and starting compound 1c (40%) were obtained.

These results are consistent with the well known ability of sodium naphthalene ($\text{Na}^+\text{C}_{10}\text{H}_8^{\cdot-}$) to act as an electron donor.¹⁹ Eqn. 6, therefore, represents the initiating process in place of step 1.



The halide ion, X^- produced from 2 (step 2) combines²⁰ with AlH_3 present in the medium giving AlH_3X^- . The latter anion then acts as a source of hydrogen atoms (eqn. 7)



Species AlH_3X^- and $\text{AlH}_2\text{X}^{\cdot-}$ can also donate electrons as inferior alternatives to AlH_4^- and $\text{AlH}_3^{\cdot-}$, respectively. It is logical that species of the type

Table : Reaction^a of 1, Ar-CH(R)-X with LiAlH₄

Halide, 0.01 mol	Run	LiAlH ₄ mol	Reaction time, min	% Products			
				[Ar-CH(R)] ₂	Ar-CH ₂ -R	Starting halide	H ₂ ^b
<u>1a</u>	1	0.01	35	64	23	-	63
<u>1a</u>	2	0.005	35	42	16	32	70
<u>1a</u>	3	0.0025	35	35	11	44	75
<u>1b</u>	4	0.01	35	42	25	-	58
<u>1b</u>	5	0.005	35	36	13	27	63
<u>1b</u>	6	0.0025	35	26	9	37	72
<u>1c</u>	7	0.01	35	72	20	-	58
<u>1c</u>	8	0.005	35	51	14	30	80
<u>1c</u>	9	0.0025	35	42	8	40	100

^aReaction conducted in THF (50 ml) at ice-bath temperature; products isolated by a combination of fractional crystallization and chromatography over activated silica-gel column, and characterized by mp and nmr spectra; 1b also yielded fluorene 7% 5% and <5% in runs 4, 5 and 6, respectively, by cyclization of diphenylmethyl radicals.

^bVolume of H₂ determined at atmospheric pressure by comparison with control experiments in the absence of 1 using same batch of reactants and solvent under identical conditions and percentage calculated based on the availability of only one out of four hydrogens of LiAlH₄.

of abstraction of a proton from 1 by hydride, leading to the formation of α -halo carbanion with simultaneous evolution of hydrogen is ruled out on the basis of total absence of deuterium (nmr) in the unreacted starting halides recovered in runs 1, 4 and 7 on quenching each reaction with D₂O after 5 and 10 min. The possibility of formation of dimers 4 by the reduction of corresponding compounds of the type, Ar-C(R)=C(R)-Ar thought to arise via heterolytic reaction of 1 with LiAlH₄ received our attention, but in control experiments with authentic samples of tetraphenylethylene and 9,9'-bifluorenylidene under otherwise similar conditions no reduction was observed. Similarly, conceivable cleavage of the central C-C bond in 4 giving corresponding monomeric product 5 is also ruled out on the basis of control experiments with authentic samples of 9,9'-bianthrylethane, and 9,9'-bifluorenyl wherein the starting hydrocarbons were recovered unchanged. However, intermediacy of radicals is evident from the strong esr signals¹⁶ assignable to diphenylmethyl and 9-fluorenyl radicals recorded in runs 4 and 7, respectively.

In view of the foregoing observations, we conclude that the reactions under consideration are triggered off by fast transfer of an electron from either AlH₄⁻ or the hydride anion¹¹ (made available from the dissociation of AlH₄⁻) to the lowest ABMO of 1 producing radical-anion 2, hydrogen and AlH₃ simultaneously, as shown in step 1 of the Scheme:

AlH_2X_2^- , AlHX_3^- and AlX_4^- may also be similarly formed in the medium in succession. The first two of these would, to some extent, act as hydrogen atom donors producing radical-anions, $\text{AlHX}_2^{\cdot-}$ and $\text{AlX}_3^{\cdot-}$, respectively. The expected order of efficiency in reactivities of alanates and alane radical-anions likely, to occur in the title reactions is as follows:

As electron donor : $\text{AlH}_4^- > \text{AlH}_3\text{X}^- > \text{AlH}_2\text{X}_2^- > \text{AlHX}_3^- > \text{AlX}_4^-$
 $\text{AlH}_3^{\cdot-} > \text{AlH}_2\text{X}^{\cdot-} > \text{AlHX}_2^{\cdot-} > \text{AlX}_3^{\cdot-}$

As hydrogen donor : $\text{AlH}_4^- > \text{AlH}_3\text{X}^- > \text{AlH}_2\text{X}_2^- > \text{AlHX}_3^-$

This explains why in runs 3, 6 and 9, only 37-44% of the starting halide remains unreacted in 35 min. and provides a rationale for an earlier observation²¹ that first hydrogen in alanate reacts more efficiently than others. In conformity with this view, we found that the extension of the reaction time in runs 3, 6 and 9 to 240 min. indeed left lesser quantities of unreacted halides; 1a (36%), 1b (30%) and 1c (34%), respectively.

Acknowledgement: We thank the C.S.I.R., New Delhi for the award of Research Fellowships to J.M.K. and A.N.

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