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NOVEL ELECTRON TRANSFER MECHANISM IN LITHIUM ALANATE REDUCTION OF BENZYLIC HALIDES[1]

P.R. Singh,[2] J.M. Khurana and Alok Nigam[3]
Department of Chemistry,
Indian Institute of Technology, Kanpur-208016, India

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

Metal hydrides[4] 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] S_N1 and S_N2 processes are reported[6] to occur in the metal hydride reductions of alkyl and aryl halides. In some lithium alanate reductions of organic halides, intervention of carbanions,[7] radicals[8] and four-centred transition state[9] have been considered. Electron transfer mechanisms have been recently demonstated in the $LiAlH_4$ reductions of o-bromophenyl allyl ether[10] 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-chloromethylanthrancene 1a, diphenylchloromethane 1b and 9-bromofluorene 1c. On adding equimolar amounts of $LiAlH_4$ contained in THF[12] 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 suggestion[13] 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-methylanthracene, 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 $LiAlD_4$ + LiD, wherein 1-deutero-1-phenylethane and undeuterated 2,3-diphenylbutane[15] 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

$$\underset{\underline{1}}{\text{Ar-CH(R)-X}} + AlH_4^- \longrightarrow \underset{\underline{2}}{\text{Ar-CH(R)-X}^{\dot{-}}} + \tfrac{1}{2}H_2 + AlH_3 \qquad (1)$$

$$\underset{\underline{2}}{\text{Ar-CH(R)-X}^{\dot{-}}} \longrightarrow \underset{\underline{3}}{\text{Ar-}\dot{C}\text{H-R}} + X^- \qquad (2)$$

$$2\ \underset{\underline{3}}{\text{Ar-}\dot{C}\text{H-R}} \longrightarrow \underset{\underline{4}}{\text{Ar-CH(R)-CH(R)Ar}} \qquad (3)$$

$$\underset{\underline{3}}{\text{Ar-}\dot{C}\text{H-R}} + AlH_4^- \longrightarrow \underset{\underline{5}}{\text{Ar-CH}_2\text{-R}} + AlH_3^{\dot{-}} \qquad (4)$$

$$\text{Ar-CH(R)-X} + AlH_3^{\dot{-}} \longrightarrow \underline{2} + AlH_3 \qquad (5)$$

The benzylic radicals $\underline{3}$ produced by the dissociation of the radical-anion $\underline{2}$ (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 $\underline{5}$ 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 precedented.[10,11] Besides producing monomeric reduction product $\underline{5}$, step 4 generates the radical-anion, $AlH_3^{\dot{-}}$ which competes with AlH_4^- in donating an electron to $\underline{1}$. 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 $\underline{1}$ in runs 2, 5 and 8 where only half the molar quantity of $LiAlH_4$ was used and similarly, more than 25% of $\underline{1}$ 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 $\underline{1c}$ 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 $\underline{4}$ (40%), monomeric reduction product $\underline{5}$ (11%) and starting compound $\underline{1c}$ (40%) were obtained.

These results are consistent with the well known ability of sodium naphthalene ($Na^+C_{10}H_8^{\dot{-}}$) to act as an electron donor.[19] Eqn. 6, therefore, represents the initiating process in place of step 1.

$$\text{Ar-CH(R)-X} + C_{10}H_8^{\dot{-}} \longrightarrow \text{Ar-CH(R)-X}^{\dot{-}} + C_{10}H_8 \qquad (6)$$

The halide ion, X^- produced from $\underline{2}$ (step 2) combines[20] with AlH_3 present in the medium giving AlH_3X^-. The latter anion then acts as a source of hydrogen atoms (eqn. 7)

$$\underset{\underline{3}}{\text{Ar-}\dot{C}\text{H-R}} + AlH_3X^- \longrightarrow \underset{\underline{5}}{\text{Ar-CH}_2\text{-R}} + AlH_2X^{\dot{-}} \qquad (7)$$

Species AlH_3X^- and $AlH_2X^{\dot{-}}$ can also donate electrons as inferior alternatives to AlH_4^- and $AlH_3^{\dot{-}}$, respectively. It is logical that species of the type

Table : Reaction[a] of 1, Ar-CH(R)-X with $LiAlH_4$

Halide, 0.01 mol	Run	$LiAlH_4$ mol	Reaction time, min	% Products			
				$[\text{Ar-CH(R)}]_2$	$\text{Ar-CH}_2\text{-R}$	Starting halide	H_2[b]
1a	1	0.01	35	64	23	-	63
1a	2	0.005	35	42	16	32	70
1a	3	0.0025	35	35	11	44	75
1b	4	0.01	35	42	25	-	58
1b	5	0.005	35	36	13	27	63
1b	6	0.0025	35	26	9	37	72
1c	7	0.01	35	72	20	-	58
1c	8	0.005	35	51	14	30	80
1c	9	0.0025	35	42	8	40	100

[a] Reaction 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.

[b] Volume of H_2 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 $LiAlH_4$.

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 D_2O 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 $LiAlH_4$ 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 signals[16] 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 AlH_4^- or the hydride anion[11] (made available from the dissociation of AlH_4^-) to the lowest ABMO of 1 producing radical-anion 2, hydrogen and AlH_3 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, $AlHX_2^{\dot{-}}$ and $AlX_3^{\dot{-}}$, 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 : $AlH_4^- > AlH_3X^- > AlH_2X_2^- > AlHX_3^- > AlX_4^-$

$AlH_3^{\dot{-}} > AlH_2X^{\dot{-}} > AlHX_2^{\dot{-}} > AlX_3^{\dot{-}}$

As hydrogen donor : $AlH_4^- > AlH_3X^- > AlH_2X_2^- > AlHX_3^-$

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 observation[21] 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.

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