Tetrahedron Letters Vol. 21, pp 4753 - 4756
©Pergamon Press Ltd. 1980. Printed in Great Britain

0040-4039/80/1201-4753$02.00/0

REDUCTION OF *Z*-2-CHLOROSTILBENE WITH LITHIUM ALUMINUM HYDRIDE: EVIDENCE FOR AN ELECTRON TRANSFER RADICAL MECHANISM[1]

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

Summary: *Z*-2-Chlorostilbene undergoes uncatalyzed LiAlH$_4$ reduction giving phenanthrene and *Z*-stilbene. An electron transfer radical mechanism is proposed. LiAlH$_4$ induced isomerization of *Z*-stilbene produces *E*-stilbene.

Aryl bromides and iodides undergo uncatalyzed LiAlH$_4$ reduction conveniently;[3,4] but aryl chlorides at best, give poor yields (26-50%) of the reduction products.[4,5] The only successful reduction of a chloroaromatic viz. 1-chloronaphthalene reported in the literature[6] required TiCl$_4$ catalyst in refluxing THF. We now report the first quantitative, uncatalyzed LiAlH$_4$ reduction of an aryl chloride in THF at 25°C, wherein *Z*-2-chlorostilbene 1 yielded a mixture of phenanthrene 5 and *Z*-stilbene 6 by a mechanism which, we believe, involves initial transfer of an electron from LiAlH$_4$ to 1. Subsequently, 6 undergoes LiAlH$_4$ induced isomerization giving *E*-stilbene 7.

On the addition of LiAlH$_4$ contained in THF[7] to a solution of 1 in the same solvent at ambient temperature under dry nitrogen, with magnetic stirring, the reaction commenced with evolution of dihydrogen. The reaction mixtures in different runs, on work-up after 12 or 24 hr, gave the results summarized in the Table.

It is evident from these data that 5 and 6 are formed first and 7 arises from the latter in a secondary process involving LiAlH$_4$. A comparison of the combined yields of 6 and 7 with those of 5 in runs 2-6 reveals that the reductive cyclization predominates over the simple dechlorination process; but this trend is reversed in runs 7 and 8 where cyclohexene and cumene respectively, are present. The reported[4] order of reactivities in the LiAlH$_4$ reductions of halobenzenes i.e., I > Br > Cl > F, is same as that observed[8] in electron transfer reductions using several different electron donor reagents. All these observations become discernible when intervention of radicals formed by dissociative electron capture on 1 is considered significant as shown in the Scheme.

Conditions favoring electron transfer from LiAlH$_4$[9] to 1 in step 1 do exist in the present study. The extended conjugation in 1 presumably provides ABMO of low enough energy for acceptance of an electron from LiAlH$_4$ made available

TABLE: Reaction of 1 (0.01 mol) with $LiAlH_4$ in 50 ml THF at 25°C

Run	$LiAlH_4$ mol	Time hr	% Yield of products[a]			H_2[b] ml
			Phenanthrene 5	Z-Stilbene 6	E-Stilbene 7	
1	0.00625	12	33	16	nil	20
2	0.0125	12	65	30	nil	32
3	0.0125	24	66	29	nil	32
4	0.025	12	66	25	5	38
5	0.025	24	68	20	8	40
6	0.04	24	68	5	22	62
7[c]	0.025	12	32	52	12	48
8[d]	0.025	12	37	50	9	46

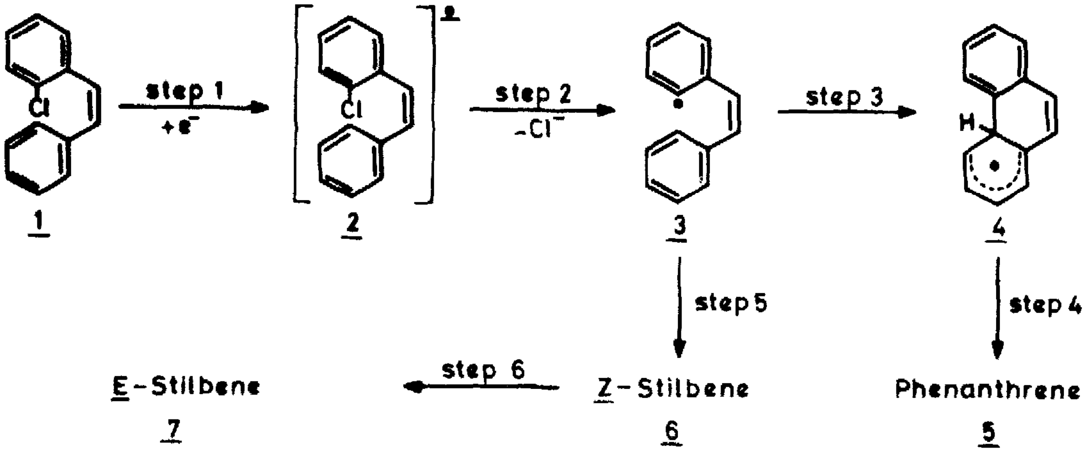
[a] Crude products were separated into 5 and a mixture of 6 and 7 by elution with petroleum-ether (bp 60-80°) over activated silica gel column. Yields of 6 and 7 were estimated by glc (calibration method) using 10 ft. silicone rubber SE-30 column.

[b] 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.

[c] In presence of cyclohexene (0.15 mol).

[d] In presence of cumene (0.15 mol).

SCHEME



by the process outlined in eq 1 alone or in combination with that symbolized in eq 2.

$$AlH_4^- \rightleftharpoons AlH_3 + H^- \; ; \quad H^- \longrightarrow \tfrac{1}{2} H_2 + e^- \qquad \ldots (1)$$

$$AlH_4^- \longrightarrow \cdot AlH_4 + e^- \qquad \ldots (2)$$

The radical 3, obtainable from the anion-radical 2 in the usual manner, is known[10] to prefer intramolecular phenylation (giving 5) over hydrogen atom abstraction.[11] The favorable distance[12] of the order of 1.5 Å between the two positions to be linked in 3 significantly contributes to cyclization.[13] Evidently, the life-time of radical 3 must be long compared to the time of rotation or oscillation of the rings. However, enhanced yields of stilbenes in runs 7 and 8 reflect the known[14] ease of hydrogen atom donation by cyclohexene and cumene respectively, to aryl radicals. The carbanion corresponding to radical 3, even if formed, would not have cyclized.[15]

Electron donation by $LiAlH_4$, as seen from the volume of H_2 evolved, generates only a fraction of the total amount of 3 that actually produces 5, 6 and 7. It is, therefore, considered likely that besides reacting by step 3, radical 3 picks up a hydrogen atom[16] from AlH_4^- producing 6 and anion-radical $AlH_3^{\dot{-}}$ (eq 3). At this stage, $AlH_3^{\dot{-}}$ intervenes as electron donor[17] in step 1 which

$$3 + AlH_4^- \longrightarrow 6 + AlH_3^{\dot{-}} \qquad \ldots (3)$$

continues giving 3 as long as both 1 and AlH_4^- are present. Consequently, eq 3 must account for a major portion of stilbenes obtained in runs 1-6. Indeed, run 3 conducted with $LiAlD_4$ instead of $LiAlH_4$ yielded 5 (65 %) and 6 (28 %) which contained largely the monodeuterated component (nmr). That 7 is produced by $LiAlH_4$ induced isomerization of 6 is evident from a comparison of the yields of the two stilbenes in runs 4-8 with those in runs 1-3. This conclusion receives support from the following results obtained by reacting an authentic sample of 6 (0.01 mol) with $LiAlH_4$ in 50 ml THF at 25°C under nitrogen for 24 hr:

$LiAlH_4$, mol	0.005	0.01	0.02	0.05	0.10
Yield of 7 (glc), %	50	55	80	93	96

The possible role of $LiAlH_4$ as an electron donor in this and similar isomerizations[18] as well as cyclizations leading to the synthesis of a variety of carbocyclic and heterocyclic systems is under investigation.

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

References and Notes

(1) A preliminary account was presented at the International Symposium on Nucleophilic Substitution, Pocono Manor, Pennsylvania, U.S.A., April 1975, Abstract No. 51.

(2) Present address: Chief Chemist, Kind & Knox, Division of Knox Gelatine, Inc., P.O.Box 725, Sioux City, Iowa 51102, U.S.A.

(3) G.J. Karabatos, R.L. Shone and S.E. Scheppele, *Tetrahedron Lett.*, 2113 (1964).

(4) H.C. Brown and S. Krishnamurthy, *J. Org. Chem.*, *34*, 3918 (1969).

(5) P. Olavi, I. Virtanen and P. Jaakkola, *Tetrahedron Lett.*, 1223 (1969).

(6) T. Mukaiyama, M. Hayashi and K. Narasaka, *Chemistry Lett.*, 291 (1973).

(7) Each dried batch was distilled over $LiAlH_4$ before use.

(8) J.F. Bunnett, *Acc. Chem. Res.*, *11*, 413 (1978).

(9) Conclusions regarding electron transfer from $LiAlH_4$ to some benzylic chlorides and bromides under similar conditions, based on esr and other evidence are reported in ref. 1 and to other conjugated systems in E.M. Gause and J.R. Rowlands, *Spectroscopy Lett.*, *9*, 219 (1976) and in ref. 16.

(10) R.M. Elofson and F.F. Gadallah, *J. Org. Chem.*, *36*, 1769 (1971).

(11) Results obtained in acetonitrile medium (ref. 10) are considered more or less valid when THF is the solvent.

(12) The distance between the same two positions in α-phenylcinnamic acid has been calculated by D.H. Hey and R.D. Mullay, *J. Chem. Soc.*, 2276 (1952).

(13) Other radical species present in the medium may pick up a hydrogen atom from 4 in step 4. Abstraction of a hydrogen atom by AlH_3 produced in the medium, in this step giving 5 and $\cdot AlH_4$ is also a possibility worth consideration.

(14) R.F. Bridger and G.A. Russell, *J. Am. Chem. Soc.*, *85*, 3754 (1963).

(15) P.R. Singh and Ramesh Kumar, *Ind. J. Chem.*, *11*, 692 (1973).

(16) Sung-Kee Chung and Fu-fan Chung, *Tetrahedron Lett.*, 2473 (1979).

(17) Analogous species $BH_3^{\dot{-}}$ produced by the loss of a hydrogen atom from BH_4^- in the $NaBH_4$ reduction of 7,7-dibromonorcarane acts as electron donor: see J.T. Groves and K.W. Ma, *J. Am. Chem. Soc.*, *96*, 6527 (1974).

(18) Isomerization of 6 and similar compounds in the presence of electron donors has been reported previously: M.A. Doran and R. Waack, *J. Organomet. Chem.*, *3*, 94 (1965); Ref. 15; M. Prashad, M. Seth and A.P. Bhaduri, *Ind. J. Chem.*, *18B*, 176 (1979).

(Received in UK 15 September 1980)