Intermediacy of Aryl Radicals and Arylmetal Compounds in Reductive Dehalogenation of Halogenoarenes with Lithium Aluminium Hydride

Athelstan L. J. Beckwith* and Swee Hock Goh

Research School of Chemistry, Australian National University, Canberra, A.C.T. 2601, Australia

Reduction of *o*-allyloxybromobenzene (**1**) with lithium aluminium hydride proceeds by two competing pathways; one involving aryl radicals is promoted by oxygen, the other affords initially an arylmetal compound.

Previous studies[1–8] of the reductive dehalogenation of halogenoarenes by $LiAlH_4$ (LAH) have afforded discordant results. Thus aryl halides have been described as 'generally resistant'[1] and as displaying 'considerable reactivity',[2] while evidence has been adduced in support of radical,[3–6] anionic,[3] four-centre,[2] and S_N2 mechanisms.[2] We now show that the reaction under normal conditions involves two mechanistically distinct competing processes, the relative importance of which determines the rate and outcome of the reduction. One involves free-radical intermediates, detected in our experiments by the diagnostic ring closure (**2**)→(**3**),[9] while the other initially affords arylmetal species which are converted into deuteriated compounds upon quenching with D_2O. The results are summarised in Table 1.

The reduction of the bromide (**1**) with a clear solution of LAH or LAD in tetrahydrofuran (THF)[8] is very slow when oxygen is scrupulously excluded from the mixture (runs 1 and 2), and affords mainly the uncyclised compound (**6**) containing D (or H) from the quenching solvent. We conclude that reactions conducted in the absence of oxygen do not involve aryl radicals and afford initially an arylmetal intermediate (**5**, M = Li or an Al-centred group).

When limited amounts of oxygen are admitted both the overall rate and the yield of cyclised product (**7**) are increased (runs 3 and 4). When oxygen is present in larger amount, products (*e.g.* **4**), formed by coupling of the radical (**3**) with oxygen are obtained. The change in the ratio (**7**)/(**6**) with time (run 5) indicates that the relative importance of the radical pathway increases during the course of the reaction.

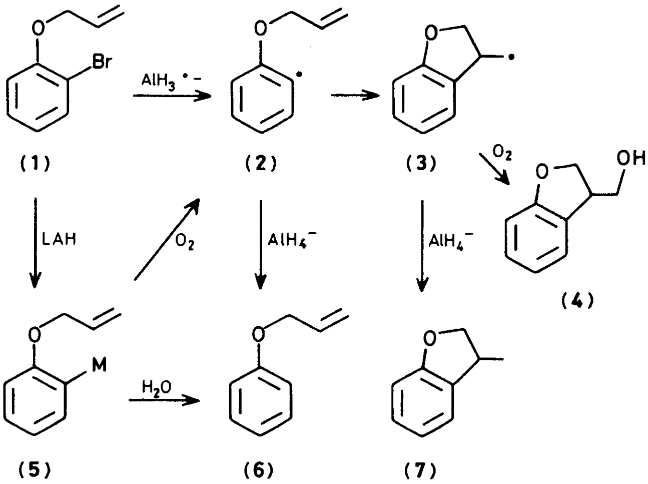

Table 1

							$^2H_1$ content/%[c]	
Run	[LAH]/M	Conditions[a]	Time/h	% Reduction[b]	(7)/(6)	Quench	(6)	(7)
1	1.2	N_2	28	18	0.03	D_2O	91	–[d]
2	0.5(LAD)	N_2	64	17	0.1	H_2O	19	71
						D_2O	91	76
3	0.95	N_2, air admitted after 26 h	26	33	0.02			
			28	40	0.2			
4	0.95	N_2, air[e]	21	100	2.5			
5	1.0	N_2, air[f]	0.5	23	1.5			
			2.0	56	1.8			
			22	100	2.6			
6	1.0	N_2, $h\nu$	1.0	14	0.7			
7	1.1	N_2, DTBP, $h\nu$	1.6	100	2.2	D_2O	0	0
8	0.85	N_2, DTBP, $h\nu$	1.5	78	3.1			
9	0.60(LAD)	N_2, DTBP, $h\nu$	1.3	65	4.3	D_2O	81	80
						H_2O	–[d]	80
10	0.09	N_2, DTBP, $h\nu$	1.5	23	5.7	D_2O	30	0
11	1.0(slurry)	N_2, DTBP, $h\nu$	2.1	33	0.31	D_2O	66	1
12	1.0(slurry)	N_2	2.1	21	0.01	D_2O	58	–[d]

[a] Reactions were conducted at 20—24 °C with 1.0 mmol of halogenoarene and 5.0 mmol of LAH in clear solution in THF (except runs 11 and 12); for photoinitiation 1.0 mmol of DTBP was added and the mixture in a Pyrex flask was irradiated with a 250 W high pressure mercury lamp. [b] Determined by g.c. analysis on 2 m 3% OV-17 and SE-30 columns; all products were characterised by appropriate n.m.r. and mass spectral measurements. [c] Determined by mass spectrometry. [d] Not determined. [e] Small quantity of air leaked into the mixture. [f] Air containing 1.0 mmole of oxygen admitted into reaction vessel.

Ultraviolet irradiation of the reaction mixture with exclusion of oxygen modestly increases the relative importance of the radical pathway (run 6). However, irradiation of mixtures containing di-t-butyl peroxide (DTBP) initiates a rapid chain reaction, equations (1)–(3) in which one step involves formation of the aryl radical either by S_H2 at halogen or by electron transfer.[10] As expected, the ratio (7)/(6) is greatest when [LAH] is low (run 10), but under these conditions chain transfer is inefficient, the overall rate is reduced, and formation of the arylmetal (5) begins to intervene.

$$Bu^tO^\bullet + AlH_4^- \rightarrow Bu^tOH + AlH_3^{\bullet -} \tag{1}$$

$$AlH_3^{\bullet -} + ArX \rightarrow AlH_3X^- + Ar^\bullet \tag{2}$$

$$Ar^\bullet + AlH_4^- \rightarrow ArH + AlH_3^{\bullet -} \tag{3}$$

The mode of formation of (5) may involve direct hydride attack on the halogen, two-electron transfer, or a four-centre process. The reaction occurs better with slurries than with clear solutions (compare runs 1, 11, and 12) and may well involve surface phenomena, and/or reactions of insoluble impurities. Experiments with ultrasound support these hypotheses.[11] Reactions of arylmetal compounds with molecular oxygen involve radical intermediates;[12] we believe that the free-radical component of reactions conducted under normal conditions is initiated in this manner.

Finally, we note that the quenching experiments give no indication of direct S_N2 attack of hydride on halogenoarene. Our suggestion that reductions of bromoarenes with LAH involve two competing pathways, the relative importance of which depends critically on experimental conditions, rationalises previous discordant observations, while the finding that the free-radical process can be efficiently initiated allows the development of a useful method for the reduction of halogenoarenes (including fluorides).[13]

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References

1 E. Wiberg and E. Amberger, 'Hydrides of the Elements of Main Groups 1—4,' Elsevier, Amsterdam, 1971.
2 H. C. Brown and S. Krishnamurthy, *J. Org. Chem.*, 1969, **34**, 3918.
3 S.-K. Chung and K. L. Filmore, *J. Chem. Soc., Chem. Commun.*, 1983, 358.
4 S.-K. Chung and F.-f. Chung, *Tetrahedron Lett.*, 1979, 2473.
5 S.-K. Chung, *J. Org. Chem.*, 1980, **45**, 3513.
6 P. R. Singh, A. Nigam, and J. M. Khurana, *Tetrahedron Lett.*, 1980, 4753.
7 G. J. Karabatsos and R. L. Shone, *J. Org. Chem.*, 1968, **33**, 619.
8 S. Krishnamurthy and H. C. Brown, *J. Org. Chem.*, 1982, **47**, 276.
9 A. L. J. Beckwith and W. B. Gara, *J. Am. Chem. Soc.*, 1969, **91**, 5689.
10 J. R. M. Giles and B. P. Roberts, *J. Chem. Soc., Chem. Commun.*, 1981, 1167.
11 B. H. Han and P. Boudjouk, *Tetrahedron Lett.*, 1982, **23**, 1643.
12 K. U. Ingold and B. P. Roberts, 'Free-Radical Substitution Reactions,' Wiley–Interscience, New York, 1971, ch. 3, 4; J. K. Kochi, 'Organometallic Mechanisms and Catalysis,' Academic Press, New York, 1978, ch. 17.
13 A. L. J. Beckwith and S. H. Goh, *J. Chem. Soc., Chem. Commun.*, 1983, following communication.