Homolytic Reductive Dehalogenation of Aryl and Alkyl Halides by Lithium Aluminium Hydride

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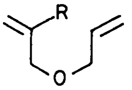
Photochemically induced reductions by lithium aluminium hydride of various halogeno-compounds including vinyl bromides, aryl chlorides and fluorides, neophyl chloride, cyclohexyl chloride, and 7,7-dichloronorcarane in the presence of di-t-butyl peroxide afford good yields of dehalogenated products.

Lithium aluminium hydride (LAH), in view of its ready availability, convenient handling, and ease of removal after completion of reactions, is an attractive alternative to other reagents (*e.g.* tin hydrides)[1] for the reductive dehalogenation of organic halides.[1,2] Unfortunately it lacks general utility because of the low reactivity of such families of substrates as aryl, vinyl, cyclopropyl, neopentyl, tertiary-alkyl, and bridgehead halides.[1-4] We now describe a photochemical procedure which enables the reduction of such compounds to be accomplished rapidly and in good yield.

Table 1

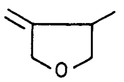
Halide[a]	Time /h	Product	Yield /%
p-Iodoanisole	1.5	Anisole	100
o-Bromoanisole	1.5	Anisole	86
o-Bromotoluene	2.2	Toluene	96
o-Allyloxybromobenzene	2.3	Mixture[b]	96
p-Bromochlorobenzene	1.0	Chlorobenzene	92
p-Chloroiodobenzene	0.7	Chlorobenzene	96
1-Bromonaphthalene[c]	2.3	Naphthalene	95
1-Chloronaphthalene[d]	2.0	Naphthalene	96
4-Bromobiphenyl[d]	1.2	Biphenyl	87
p-Bromo-*N*,*N*-dimethylaniline[e]	3.0	*N*,*N*-Dimethylaniline	93
p-Fluoroanisole[e]	1.9	Anisole	93
p-Fluorotoluene[e]	1.9	Toluene	90
2-Bromopropene	1.6	Propene	66
Allyl 2-bromoallyl ether	2.0	Mixture[f]	53
Neophyl chloride[e,g]	3.0	Mixture[h]	91
7,7-Dichloronorcarane[e,g]	0.5	Mixture[i]	93
Chlorocyclohexane[e,g]	2.5	Cyclohexane	72
Bromocyclohexane[e,g]	2.5	Cyclohexane	71

[a] Unless otherwise stated the reaction was conducted as described in the text for reduction of *o*-bromotoluene. [b] See ref 11. [c] 40 mmol of LAH. [d] 10 mmol of DTBP. [e] 20 mmol of DTBP. [f] Mixture contains compounds (**2**) (24%), (**3**) (29%), and (**4**) (47%). [g] Ether solvent. [h] Mixture includes compounds (**6**) (77%) and (**7**) (21%). [i] Mixture contains norcarane (10%), *syn*-7-chloronorcarane (25%), and *anti*-7-chloronorcarane (65%); after 3.5 h reaction time the relative yields were 95, 0.5, and 4.5% respectively.

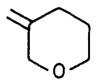


(1) R = Br

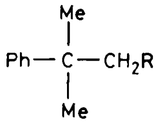
(2) R = H



(3)



(4)



$$\mathrm{Ph{-}\underset{Me}{\overset{Me}{C}}{-}CH_2R}$$

(5) R = Cl

(6) R = H

$Ph—CH_2—CHMe_2$

(7)

In a typical photostimulated reduction, a mixture of 10 mmole of *o*-bromotoluene, 5 mmole of di-t-butyl peroxide (DTBP) and 25 ml of a clear solution (1M) of LAH in tetrahydrofuran (THF) was irradiated with a 250 W high-pressure Hg lamp for 2.2 h, then cooled, diluted with dilute aqueous acid, extracted with pentane, and analysed by g.l.c., g.c.–mass spectrometry, and n.m.r. spectroscopy. The yield of toluene (96%) was much greater than that recorded for the conventional procedure (7% after 24 h).[4]

The results of experiments with other halides are summarised in Table 1. Chloro-, bromo-, and iodo-arenes are efficiently reduced, as are fluoroarenes, which were previously considered to be inert.[2] The order of reactivity is ArI > ArBr > ArCl > ArF, making possible the specific formation of chlorobenzene from *p*-bromochlorobenzene or from *p*-chloroiodobenzene. Preliminary experiments indicate that substituent effects on the rate of reaction are small. For example, when a mixture of *p*-bromochlorobenzene and *p*-bromo-*N*,*N*-dimethylaniline was reduced the two compounds were consumed at approximately equal rates.

When applied to vinyl bromides the method affords only modest yields, but alkyl and cycloalkyl halides are efficiently reduced. The successful dehalogenation of the normally sluggish chlorocyclohexane and neophyl chloride is noteworthy.

The formation of the rearrangement products (**3**) and (**4**) from the vinyl bromide (**1**),[5] and (**7**) from neophyl chloride (**5**),[6] is consistent with the free-radical mechanism previously proposed,[7] while the relatively small effect of substituents suggests that the chain-propagation step, $ArX + AlH_3^{\bullet -} \rightarrow Ar^{\bullet} + AlH_3X^-$, involves halogen-atom transfer rather than electron transfer.[8]

In further development of this procedure we are now examining the behaviour of other complex hydrides.

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