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SILVER-CATALYZED REDUCTIVE DEHALOGENATION OF 1,1-DIBROMOCYCLOPROPANES

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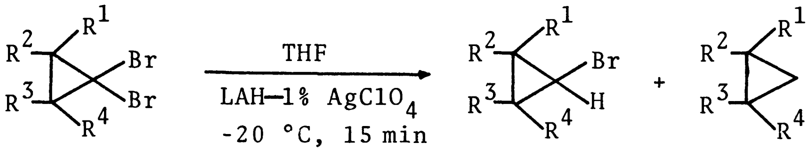
1,1-Dibromocyclopropanes underwent rapid reduction to the corresponding monobromides in high yields on treating with LiAlH$_4$–1 mol% silver perchlorate in THF, presumably via a silver-catalyzed radical chain mechanism.

Reductive dehalogenation of organic halides with lithium aluminum hydride (LAH) is normally slow for substrates which exhibit poor S$_N$2 reactivity.1,2) Here we show a marked rate accelerating effect of silver perchlorate on the reductive dehalogenation of cyclopropyl bromides with LAH.



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7,7-Dibromobicyclo[4.1.0]heptane (1a) reacted slowly with LAH (2 molar equiv) in THF at -20 °C, e. g., to only 59% completion even after 7 h; however, the reduction was completed within 15 min at that temperature affording 7-bromobicyclo-[4.1.0]heptane (2a, cis/trans = 4.4) in 77% yield when a catalytic amount (1 mol% of LAH) of silver perchlorate was added.3) This LAH–Ag(I) system was also effective for the reduction of the bromide 2a especially the trans-isomer, so delayed workup inevitably led to the formation of the fully reduced hydrocarbon 3a in a large quantity besides highly cis-enriched 2a. THF could be replaced by ether in which the reduction proceeded less rapidly but more stereoselectively than in the former solvent. Like 1a, representative 1,1-dibromocyclopropanes 1b—1g were converted to the corresponding monobromides with extreme ease when treated with LAH–1% AgClO$_4$ in THF and the results are given in Table 1.

The following additional observations characterize the present LAH–Ag(I) system.4) First, ease of the reduction depended sensitively on the halides and was found to be in the order: 1, 1-phenylethyl bromide,5) 1-bromo(and also chloro)-3-methyl-2-butene [100% (conversion after exposure to LAH–10% AgClO$_4$ in THF for 30 min at -20 °C)] $>$ 2-bromo-2-methyloctane (100%)6) $>$ 2-bromooctane (50%), 1-bromooctane (45%) $>$ β-bromostyrene, p-bromotoluene, 7,7-dichlorobicyclo[4.1.0]heptane, 2-chloro-2-methyloctane (<5%).7) Noteworthy is the fact that LAH–Ag(I) could easily reduce neophyl bromide (t-butylbenzene 95%; -20 °C, 1 h with 20% AgClO$_4$) as well as 1-bromoadamantane (adamantane 91%; -20 °C, 3 h with 15% AgClO$_4$) in contrast

Table 1. Reduction of 1,1-Dibromocyclopropanes with LAH–$AgClO_4$ (1 mol%)

	Dibromocyclopropane (1)				Conditions[a)]		Yield/%[b)]	
	R^1	R^2	R^3	R^4	Solvent	Time/h	2 (cis/trans)	3
1a	H	$-(CH_2)_4-$		H	THF	0.25	77 (4.4)	17
					THF	1.0	59 (7.8)	35
					THF	24	0	77
					ether[c)]	1.0	67 (13)	30
1b	H	$-(CH_2)_6-$		H	THF	0.25	75 (4.9)	12
					ether[c)]	1.0	26 (7.0)	71
1c	CH_3	CH_3	CH_3	CH_3	THF	0.25	96	d)
1d	CH_3	CH_3	CH_3	H	THF	0.25	89 (3.7)	d)
1e	$c\text{-}C_3H_5$	$c\text{-}C_3H_5$	H	H	THF	0.25	88	d)
1f	C_6H_5	H	H	H	THF	0.25	86 (7.9)	9
1g	$n\text{-}C_3H_7$	H	H	H	THF	0.25	93 (2.3)	d)

a) Reactions were carried out at -20 °C under nitrogen using 1 (5 mmol), LAH (10 mmol), and silver perchlorate (0.1 mmol) in THF or ether (10 ml). b) GLC yield. c) Using 0.5 mmol of $AgClO_4$. d) Not determined.

to LAH which was ineffective under these conditions. Clearly, the present system is quite useful for the reduction of tertiary or sterically hindered alkyl bromides which withstand LAH. Second, the reduction of 1a with LAD–$AgClO_4$ did not lead to D-incorporation in the products 2a and 3a. Third, the reduction of allyl halides accompanied the allylic rearrangement. For example, cinnamyl chloride gave allylbenzene in 61% yield together with 1-phenylpropene (28%) on treating with LAH–15% $AgClO_4$ (-50 °C, 15 min).[8)] These results are consistent with a radical chain mechanism (Eqs. 1—4), although it is uncertain whether silver hydride or its complex

$$\mathrm{AgClO_4} + \mathrm{LAH} \longrightarrow \mathrm{Ag^\circ} \quad (1) \qquad \mathrm{R{-}X} + \mathrm{Ag^\circ} \longrightarrow \mathrm{R\cdot} + \mathrm{AgX} \quad (2)$$

$$\mathrm{AgX} + \mathrm{LAH} \longrightarrow \mathrm{Ag^\circ} \quad (3) \qquad \mathrm{R\cdot} + \text{solvent} \longrightarrow \mathrm{R{-}H} \quad (4)$$

with aluminum hydride is involved as a reactive species.

References

1) S. Krishnamurthy and H. C. Brown, J. Org. Chem., 47, 276 (1982).
2) C. W. Jefford, D. Kirkpatrick, and F. Delay, J. Am. Chem. Soc., 94, 8905 (1972).
3) An admixture of LAH and silver perchlorate prepared prior to the addition of the halide was found to be equally effective. Silver chloride could be used as well.
4) For related reducing systems using transition metal salts see: S. Masamune, R. A. Rossy, and G. S. Bates, J. Am. Chem. Soc., 95, 6453 (1973); E. C. Ashby and J. J. Lin, J. Org. Chem., 43, 1265 (1978) and Tetrahedron Lett., 1977, 4481.
5) A mixture of ethylbenzene and 2,3-diphenylbutane (1 : 1.4) was obtained in 93% yield.
6) 2-Methyloctane and 2-methyl-1-octene were formed in 68 and 22% yields; the former alkane was the sole product (95%) when the reduction was carried out at -50 °C using LAH–30% $AgClO_4$ (2 h).
7) Relative rates of the reduction of 2-bromo-2-methyloctane, 2-, and 1-octyl bromides were found to be 9 : 1.3 : 1 for LAH–30% $AgClO_4$ but 0.03 : 0.3 : 1 for LAH in THF.
8) The LAH reduction of cinnamyl chloride (-20 °C, 6 h) gave a mixture of 1-phenylpropene and allylbenzene in the ratio 95 : 5 (91%).

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