March, 1984] © *1984 The Chemical Society of Japan* NOTES *Bull. Chem. Soc. Jpn., 57, 885—886 (1984)* 885

Photoreductive Dehalogenation of Organic Halides in the Presence of Lithium Aluminum Hydride

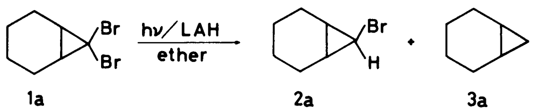
Nobujiro SHIMIZU,* Kenji WATANABE, and Yuho TSUNO
Department of Chemistry, Faculty of Science, Kyushu University 33, Higashi-ku, Fukuoka 812

(Received August 11, 1983)

Synopsis Lithium aluminum hydride markedly accelerates photoreductive dehalogenation of cyclopropyl, aromatic, and olefinic halides carried out in ether.

UV irradiation of organic halides in a hydrogen donating solvent often leads reductive dehalogenation.[1] Cyclopropyl bromides are thus obtainable by irradiating the corresponding *gem*-dibromides in ether, although in moderate to low yields.[2] We here report that irradiation in the presence of lithium aluminum hydride (LAH) results in significant improvement in the efficiency and yield of the photoreduction of halides including cyclopropylidene dihalides. Most of the experimental results are summarized in Table 1.

Figure 1 illustrates the photoreduction of 7,7-dibromonorcarane (**1a**) in the presence or absence of LAH carried out at 0 °C under nitrogen with a 100 W mercury lamp using *ca.* 0.02 M (1 M=1 mol dm^{-3}) ethereal solutions. Obviously, LAH exerts a marked rate accelerating effect which increases in keeping with the amount of LAH added. For example, **1a** disappeared practically in 15 min on irradiation in the presence of 2 molar amounts of LAH affording 7-bromonorcarane (**2a**, cis/trans=3.2) as the principal product (75%), whereas in the absence of the hydride, an incomplete photolysis resulted even after prolonged irradiation up to 4 h. LAH also facilitates the



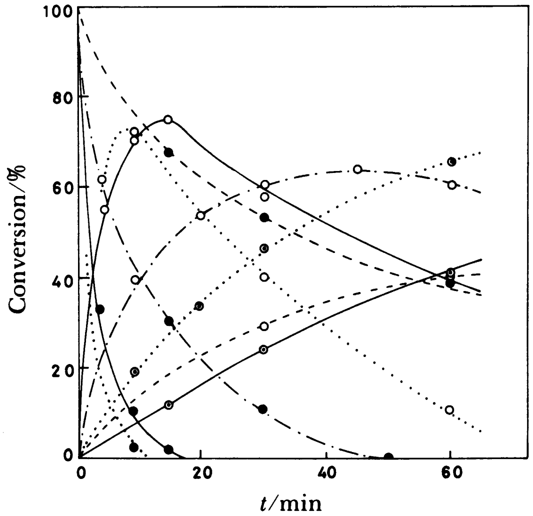


Fig. 1. Photoreduction of **1a** in ether in the presence of LAH.
[LAH]/[**1a**]: 4.0 (······), 2.0 (——), 1.0 (—·—), and 0 (----). ●: **1a**, ○: **2a**, ⊙: **3a**.

TABLE 1. PHOTOREDUCTIVE DEHALOGENATION IN THE PRESENCE OF LAH[a]

Halide **1**	Conditions		Yield/%[b]	
	[LAH]/[**1**]	Time/h	**2**[c]	**3** and others
7,7-Dibromonorcarane (**1a**)	2	8[d]	11 (3.0)	≈0 (86)[e]
	0	0.5	27 (3.3)	≈0 (51)[e]
	2	0.5	62 (3.2)	24 (0)[e]
	2	2.5	3 (3.5)	62
	4	0.5	46 (3.3)	44
9,9-Dibromobicyclo[6.1.0]nonane (**1b**)	2	0.5	71 (1.8)	7
7,7-Dichloronorcarane (**1c**)	0	8	19 (1.8)	≈0 (52)[e]
	4	8	77 (2.3)	5 (0)[e]
9,9-Dichlorobicyclo[6.1.0]nonane (**1d**)	4	8	88 (1.8)	7
1,1-Dichloro-2-hexylcyclopropane (**1e**)	4	8	94 (1.4)	5
1,1-Dichloro-2-phenylcyclopropane (**1f**)	4	8	55 (1.5)	5
Chlorobenzene (**1g**)	0	0.5		20 (benzene) (73)[e]
	2	0.5		96 (benzene) (0)[e]
Bromobenzene (**1h**)	2	0.25		95 (benzene)
p-Bromochlorobenzene (**1i**)	2	0.25		77 (**1g**) + 18 (benzene)
β-Bromostyrene	2	0.5		55 (styrene)

a) Each halide was irradiated in ether (*ca.* 0.02 M) with a 100 W medium pressure mercury lamp at 0 °C under nitrogen. b) Determined by GLC. c) Isomer ratio (cis/trans) was given in parentheses. d) Dark reaction. e) Recovery of the starting material.

photoreduction of the bromide **2a**; so prolonged irradiation leads to the formation of the fully reduced hydrocarbon **3a** in substantial quantity, especially so when large amounts of LAH are used.[3] LAH itself is capable of reducing most organic halides[4] but the contribution of this thermal process was negligibly small under the present photolysis conditions.

Other halides **1b**—**j**— they were thermally almost inert toward LAH under the photolysis conditions given in the table for each halide — also underwent rapid reduction on irradiation in the presence of LAH. The reduction proceeded more rapidly for bromides than for chlorides and a selective dehalogenation was feasible for a mixed halide **1i**. For preparative purpose, concentrated solutions could be used as well. For example, **2a** was prepared in 70% isolated yield by irradiating a 0.2 M ethereal solution of **1a** in the presence of 2 molar amounts of LAH (0 °C, 1.5 h).[5]

Two additional observations are worth stating. First, 2,3-diethoxybutane (**4**) was formed in substantial quantity in all LAH-assisted photoreductions. Second, the photolysis of **1a** using lithium aluminum deuteride led no D-incorporation in the products **2a** and **3a**. These results suggest that LAH does not act as a hydrogen donor toward an alkyl (or aryl) radical in contrast to sodium borohydride.[6] Presumably, LAH would

$$\text{R-X} \overset{h\nu}{\rightleftharpoons} \text{R}\cdot + \cdot\text{X} \xrightarrow{\text{LAH}} \text{R}\cdot + \text{HX} + \text{LiAlH}_3{}^{-}\cdot$$

$$\text{R-X} + \text{LiAlH}_3{}^{-}\cdot \longrightarrow \text{R}\cdot + \text{LiX} + \text{AlH}_3$$

$$\text{R}\cdot + \text{ether} \longrightarrow \text{R-H} + \mathbf{4}$$

depress the recombination between an alkyl and a halogen radicals *vis* efficient capture of the latter. Moreover, aluminum hydride anion radical which would result may induce homolysis of another molecule of a halide. Besides, LAH suppressed the formation of a polymeric material, especially in the photolyses of cyclopropylidene dibromides, and this would also be partly responsible for the observed rate acceleration.

Experimental

Lithium aluminum hydride (Wako Pure Chemical) was used directly as slurries in ethereal solutions. Photolyses were carried out with a 100 W medium pressure mercury lamp (Eikosha Halos PIH-100) at 0 °C under nitrogen. All products **2**—**4** were characterized by comparison of their spectral data with those reported or those of authentic samples prepared separately. The following photolysis was representative.

Photolysis of 7,7-Dibromonorcarane (1a) in the Presence of LAH. To a cold stirred solution of LAH (965 mg) in ether (500 ml) was added a mixture of **1a** (3.23 g, 12.7 mmol) and tridecane (0.20 ml as an internal standard). The mixture was irradiated with stirring for 30 min at 0 °C and quenched with cold hydrochloric acid. GLC analysis of the crude oil obtained after workup indicated the formation of 7-bromonorcarane (**2a**, cis/trans=3.2) and norcarane (**3a**) in 62 and 24% yields, respectively. The oil was fractionated under reduced pressure to give **2a** (cis/trans=3.35, 1.17 g, 53%), bp 83—85 °C/20 Torr (1 Torr=133.3 Pa) [lit,[7] bp 84—86 °C/23 Torr], together with a low-boiling fraction (760 mg) which was shown to be a mixture of **3a** and 2,3-diethoxybutane (1:1 mixture of two diastereoisomers) in the ratio 1:3.

References

1) J. R. Siegman and J. J. Houser, *J. Org. Chem.*, **47**, 2773 (1982); N. Mitsuo, T. Kunieda, and T. Takizawa, *ibid.*, **38**, 2255 (1972); J. T. Pinhey and R. D. G. Rigby, *Tetrahedron Lett.*, **1969**, 1267.

2) N. Shimizu and S. Nishida, *Chem. Lett.*, **1977**, 839.

3) The isomer ratio of **2a** did not change significantly during the photolysis, suggesting little difference in photochemical behavior between the cis and trans stereoisomers.

4) S. Krishnamurthy and H. C. Brown, *J. Org. Chem.*, **47**, 276 (1982); C. W. Jefford, D. Kirkpatrick, and F. Delay, *J. Am. Chem. Soc.*, **94**, 8905 (1972).

5) The photolysis did not proceed appreciably in the absence of LAH mainly because of the formation of polymeric materials on the surface of the lamp at the very early stage.

6) J. T. Groves and K. W. Ma, *J. Am. Chem. Soc.*, **96**, 6527 (1974); J. A. Barltrop and D. Bradbury, *ibid.*, **95**, 5085 (1973).

7) D. Seyferth, D. L. Lambert, Jr., and M. Massol, *J. Organomet. Chem.*, **88**, 255 (1975).