CHEMISTRY LETTERS, pp. 2069 - 2070, 1984. © The Chemical Society of Japan 1984

A CONVENIENT METHOD FOR THE MILD REDUCTIVE DEBROMINATION OF α-BROMO KETONES AND OF *vic*-DIBROMOALKANES WITH STANNOUS CHLORIDE/DIISOBUTYLALUMINUM HYDRIDE

Takeshi ORIYAMA and Teruaki MUKAIYAMA
Department of Chemistry, Faculty of Science
The University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113

A new reducing agent prepared by the treatment of stannous chloride with diisobutylaluminum hydride was shown to be effective for debrominations of α-bromo ketones to ketones and of *vic*-dibromoalkanes to the corresponding alkenes under mild conditions.

The conversion of α-halo ketones into the parent ketones is one of the important reactions in organic synthesis.[1)] A number of reagents have been previously known to bring about such conversion under various reaction conditions.[2)]

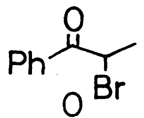
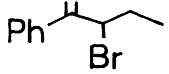
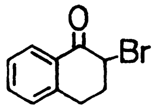
On the other hand, it is well known that organotin(IV) hydrides are useful reagents for the reduction of organic compounds such as halides, aldehydes, and ketones.[3)] However, the use of divalent tin hydrides in the above reduction process has never been reported in the literature. So we tried to prepare divalent tin hydride in situ by the treatment of stannous chloride with diisobutylaluminum hydride (DIBAH), and the hydride was applied to debrominations of α-bromo ketones and *vic*-dibromoalkanes.

In the first place, stannous chloride was treatd with DIBAH at -78 °C, followed by addition of α-bromopropiophenone. After 6 h at this temperature, work-up of the reaction mixture showed that propiophenone had been afforded in 56% yield. A screening of reaction conditions revealed that N,N,N′,N′-tetramethylethylenediamine (TMEDA) was an effective additive for the debromination of α-bromo ketones.

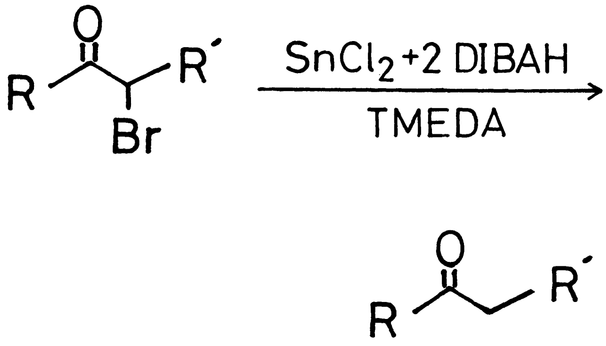
The key species of this reduction is assumed to be divalent tin hydride because metallic tin did not precipitate at -78 °C. On the other hand, when the temperature was raised to -30 °C, the evolution of hydrogen was observed probably due to the decomposition of the Sn(II) hydride to metallic tin.

The following experimental procedure is typical. To a suspension of anhydrous stannous chloride (140 mg, 0.738 mmol) and TMEDA (87 mg, 0.749 mmol) in 3 ml of THF was added dropwise diisobutylaluminum hydride (209 mg, 1.47 mmol) in 1.47 ml of toluene at -78 °C under argon atmosphere. Then α-bromopropiophenone (138 mg, 0.648 mmol) in 1.5 ml of THF was added dropwise at -78 °C and the resulting mixture was stirred for 10 min at this temperature. The reaction was

Table 1. Reductive Debromination of α-Bromo Ketones[a)]

α-Bromo Ketone	Yield/%[b)]
	81
	90
	90

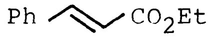
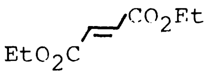
a) Reaction was carried out at -78 °C for 10 min. b) Isolated yield.



quenched with pH 7 phosphate buffer, and the precipitates were removed by filtration. The organic materials were extracted with dichloromethane and dried over Na_2SO_4. Propiophenone (71 mg, 81%) was isolated by thin layer chromatography on silica gel. The results are summarized in Table 1.

Next, the debromination of *vic*-dibromoalkanes to alkenes was studied. When the reducing agent, prepared as mentioned above, was applied to *meso*-1,2-dibromo-1,2-diphenylethane, *trans*-stilbene was obtained in 88% yield after 0.5 h at -78 °C. The results are summarized in Table 2. In these reductions, TMEDA was not so effective except in the case of ethyl dibromooleate.(Run 5, 6).

Table 2. Reductive Debromination of *vic*-Dibromoalkanes[a)]

vic-Dibromoalkane	Alkene	Conditions	Yield/%
1. *meso*$(PhCHBr)_2$		TMEDA/-78 °C/0.5 h	88
2.		-78 °C/0.5 h	85
3. $PhCHBrCHBrCO_2Et$		-78 °C/0.5 h	91
4. *meso*$(CHBrCO_2Et)_2$		-78 °C/0.5 h	84
5. $CH_3(CH_2)_7CHBrCHBr(CH_2)_7CO_2Et$	$CH_3(CH_2)_7CH=CH(CH_2)_7CO_2Et$	TMEDA/-78 °C → r.t./overnight	80
6.		-78 °C → r.t./overnight	26

a) Molar ratio of $SnCl_2$:DIBAH:*vic*-dibromoalkane=1:2:0.8-0.9 (Run 5,6;=1:2:0.2)

It should be noted that the present reductive debromination proceeds under extremely mild reaction conditions, without using any initiator, in comparison with the conventional organotin(IV) hydrides reduction.[3)]

References

1) For a example, see G. Stork and T. L. MacDonald, J. Am. Chem. Soc., 97, 1264 (1975). 2) D. L. J. Clive and P. L. Beaulieu, J. Org. Chem., 47, 1124 (1982); references cited therein. 3) For a review, see H. G. Kuivila, Synthesis, 1970, 499.

(Received September 7, 1984)