Tetrahedron Letters,Vol.26,No.42,pp 5171-5172,1985
Printed in Great Britain

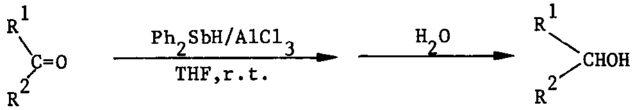
0040-4039/85 $3.00 + .00

SELECTIVE REDUCTION OF CARBONYL COMPOUNDS BY DIPHENYLSTIBINE[1]

Yaozeng Huang(Y.Z.Huang), Yanchang Shen, Chen Chen
Shanghai Institute of Organic Chemistry, Academia Sinica
345 Lingling Lu, Shanghai, People's Republic of China

Summary. Carbonyl compounds were selectively reduced by diphenylstibine in the presence of Lewis acid.

Numbers of metal hydrides and organometallic hydrides are able to reduce carbonyl compounds. Every hydrides has its own characteristic feature. However, no report is given in the literature concerning the reactivities of metal hydrides of main group V other than the addition of stibine with C≡C and N=N bonds[2,3]. We found that in the absence of Lewis acids, diphenylstibine alone did not react with carbonyl compounds, but in the presence of Lewis acid, it did react at mild conditions to afford, after hydrolysis, alcohols in excellent yields.



$$R^1R^2C{=}O \xrightarrow[\text{THF, r.t.}]{Ph_2SbH/AlCl_3} \xrightarrow{H_2O} R^1R^2CHOH$$

At the same conditions, diphenylstibine did not attack esters, acid chlorides, alkyl halides or olefins. Therefore, diphenylstibine would be expected to reduce carbonyls selectively.

With α,β-unsaturated cyclic ketones, diphenylstibine gave 1,2 or 1,4 reduction product (Entry 6 and 7), while with α,β-unsaturated aliphatic carbonyl compounds, reduction occurred at the C=O position (Entry 4 and 5). When a mixture of aldehyde and ketone, e.g. benzaldehyde and acetophene or 1-dodecanal and 4-methyl-3-cyclohexen-1-yl methyl ketone was allowed to react with diphenylstibine, aldehyde was reduced preferentially.

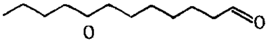
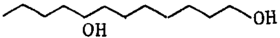
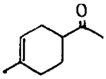
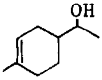
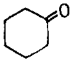
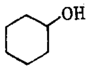
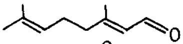
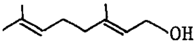
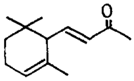
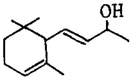
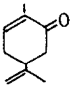
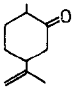
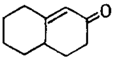
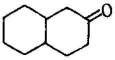
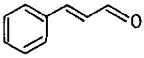
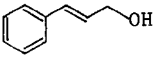
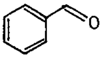
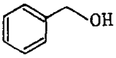
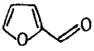
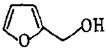
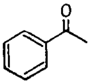
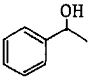
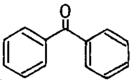
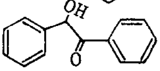
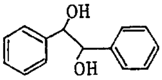
Several Lewis acids are effective for the diphenylstibine reduction. The effectiveness was roughly compared by the yield of following reaction:

$$C_6H_5CHO \xrightarrow[\text{r.t. 2h}]{Ph_2SbH/\text{Lewis acid}/THF} C_6H_5CH_2OH$$

$AlCl_3$(100%), $TiCl_4$(100%), $SnCl_4$(74%), $ZnCl_2$(25%).

The typical procedure was as follows:

1.0-1.1 mmol of diphenylstibine[4] was injected to a THF solution(2 ml) of 1.0 mmol of carbonyl compound under nitrogen. After adding 1.1 mmol of anhydrous $AlCl_3$, the mixture was stirred at room temperature and monitored the disappearance of reactant by NMR. The mixture was hydrolyzed either by 10% H_2SO_4 or by 10% NaOH solution. The resulting substance was extracted with ether or benzene and the organic layer was washed with water, dried and evaporated to remove the solvent. The residue was chromatographed on silica gel. The product was distilled or recrystallized and identified by comparison of physical constants, IR and ^{1}H-NMR, with the data reported in the literature. The results are shown in the following Table.

Entry	Substrate	Reaction Time (hr)	Product	Yield (%)	b.p.(m.p.) (°C/torr)
1		3		99	22-24(24)[a]
2		2		96	210(212-3)
3		2		92	161(160-1)
4		2		86	229(229.7)
5		2.5		95	128/15 (126.6-127/14.5)
6		2		68[b]	224(221-2)
7		2.5		47[c]	241(246)
8		2.5		90	256(257.5)
9		2		98	205(206.5)
10		4		79	170(171)
11		26		57[d]	202(203.6)
12		3		0	
13		3		89[e]	135.5-7(139-140)

[a] Data reported in literature.

[b] On the basis of NMR data, the ratio of dihydrocarvon : isodihydrocarvon is equal to 7:3[5].

[c] Accompanied with 20% β-decalol.

[d] Reactant recovered 29%.

[e] By comparison of NMR data of known configuration[6] with the product of entry 13 we assign that it is a meso form.

References and Notes

1. This paper is the 38th report on the studies of the application of elemento-organic compound of fifth and sixth group in organic syntheses.
2. A.N. Nesmeyanov, A.E. Borisov, N.V. Novikova, Dokl. Akad. Nauk. SSSR, Ser. Khim. 1965,763; 1967,815; 1972,1372; C.A.63,2998(1965);67,90900(1967);77,126784(1972).
3. K.H. Linke, W. Brandt, Z. Anorg. Allg. Chem., 433,119(1977).
4. K. Issleib, B. Hamann, Z. Anorg. Allg. Chem., 343,196(1966).
5. Y. Noma, S. Nonomura, H. Ueda. C. Tatsumi, Agric. Biol. Chem., 38,735(1974).
6. L.W. Trevoy, W.G. Brown, J. Amer. Chem. Soc., 71,1675(1949).

Thanks are due to the Science Fund of Academia Sinica for partial financial support.

(Received in Japan 27 July 1985)