JOM 23486

On tertiary stibine

I. Reaction of ω-bromoacetophenone with aldehydes mediated by diphenylantimonyorganometallic reagents *

Li-Jun Zhang and Yao-Zeng Huang

Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 345 Lingling Lu, Shanghai 200032 (China)

(Received September 5, 1992; in revised form December 18, 1992)

Abstract

In the presence of diphenylantimonymagnesium, various aldehydes react readily with ω-bromoacetophenone to form α,β-unsaturated ketones in good yields.

1. Introduction

Many studies of the synthetic application of organoantimony compounds have been reported from our laboratory [1]. Most have concerned the reaction of pentavalent organoantimony compounds (pentaorganylstiborane, stibonium ylide, and quaternary stibonium halogenide) with carbonyl compounds. It was found that the quaternary stibonium halogenide is the least reactive towards aldehydes [2]. In continuation of our study, we found that the reaction was not promoted by Lewis acids, such as $AlCl_3$, $TiCl_4$, $BF_3 \cdot Et_2O$, because the bond polarized by the Lewis acid was the antimony–halogen bond (Sb–X), instead of the antimony–carbon bond (Sb–C). In contrast, the corresponding pentaorganylstiborane is highly reactive towards aldehydes, the reaction taking place readily even below −78°C, and its reaction stereoselectivity including diastereoselectivity was very low. We know of no published report concerning the reaction of tertiary stibines with carbonyl compounds. Generally, tertiary stibines are relatively stable, and their reactivity may be very different from that of the corresponding pentavalent organoantimony compounds. Hence our interest in the reactivity of tertiary stibines, and the present paper is our report of the first example of this type of reaction. In the presence of diphenylantimonymagnesium, various aldehydes react readily with ω-bromoacetophenone to form α,β-unsaturated ketones in good yields.

$$R_3Sb\begin{matrix}X\\R'\end{matrix} + MLn \longrightarrow [R_3\overset{+}{S}b-R'][MLnX]^-$$

2. Results and discussion

Diphenylantimonylithium can be readily obtained either by lithium cleavage of triphenylstibine [3] or by reaction of diphenylbromostibine with freshly cut strips of lithium. Diphenylantimonymagnesium must be prepared by reaction of diphenylbromostibine with magnesium shavings. The THF solution of diphenylantimonylithium or diphenylantimonymagnesium is deep red. To this solution, ω-bromoacetophenone was added (the colour faded immediately to light yellow) followed by aldehydes. After work-up as usual, α,β-unsaturated ketones were obtained as major products. The results are summarized in Table 1. In addition, small amounts of reductive and coupling products were formed as by-products.

A speculative mechanism is shown in Scheme 1. As no free radical was found by electron paramagnetic

Correspondence to: Dr. Y.-Z. Huang.

* Part CII of Studies of the synthetic application of elementoorganic compounds of Group 15 and 16.

0022-328X/93/$6.00

TABLE 1. Synthesis of α,β-unsaturated ketones via tertiary stibine

Entry	Aldehyde	Product 5	Yield (%) [a]
a	C_6H_5CHO	$C_6H_5CH=CHCOC_6H_5$	88
b	$p-CH_3C_6H_4CHO$	$p-CH_3C_6H_4CH=CHCOC_6H_5$	86
c	$p-ClC_6H_4CHO$	$p-ClC_6H_4CH=CHCOC_6H_5$	87 [b]
d	$CH_3(CH_2)_3CHO$	$CH_3(CH_2)_3CH=CHCOC_6H_5$	85
e	$CH_3(CH_2)_8CHO$	$CH_3(CH_2)_8CH=CHCOC_6H_5$	86
f	$CH_3CH=CHCHO$	$CH_3CH=CHCH=CHCOC_6H_5$	73
g			24 [c]

[a] Isolated yield based on aldehyde; [b] when diphenylantimonylithium was used, the yield was 66%; [c] determined by ^1H NMR.

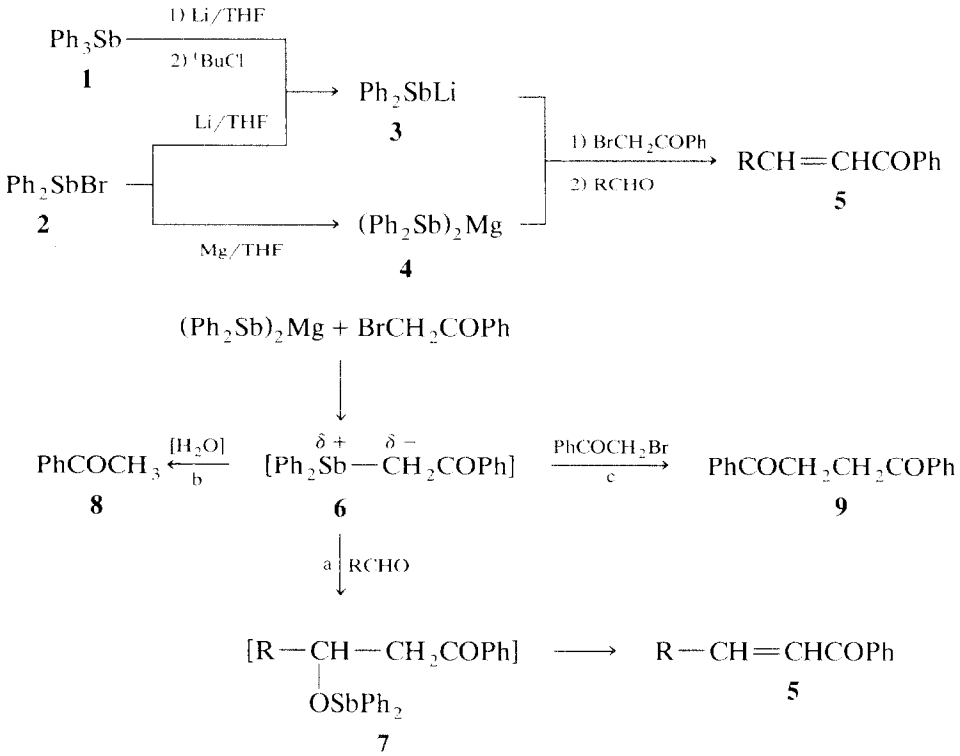
resonance (EPR), it is believed that the reaction was by an ionic mechanism. Diphenylantimonylithium reacted with ω-bromoacetophenone to result in an intermediate tertiary stibine **6**, which then reacted with aldehydes to give another intermediate **7** (path a). The major products, α,β-unsaturated ketone **5**, was obtained by elimination of Ph_2SbOH from intermediate **7**. Meanwhile, the tertiary stibine **6** may suffer from hydrolysis (path b) and coupling (path c) reactions to give reductive product **8** and coupling product **9** respectively.

3. Experimental Section

IR spectra were obtained on a Shimadzu IR-440 spectrophotometer and are reported in cm^{-1} units. Mass spectra were measured on a Finnigan GC-MC 4021 spectrometer. ^1H NMR spectra were recorded on a Varian EM-360L instrument in CCl_4 solution with TMS as an internal standard and are reported in δ units (ppm). Boiling and melting points are uncorrected. Diphenylbromostibine was prepared according to the literature method [4].

3.1. Chalcone (5a): Typical procedure

A mixture of diphenylbromostibine 997 mg (Ph_2SbBr, 2.8 mmol) and magnesium 120 mg (Mg, 5.0 mmol) was stirred in THF at r.t. for 6 h, resulting in a deep red solution. After removal of unreacted Mg, ω-bromoacetophenone 458 mg ($BrCH_2COPh$, 2.3 mmol) and benzaldehyde 212 mg (RCHO, 2.0 mmol)



Scheme 1.

were added sequentially with vigorous stirring. The resulting solution was stirred at r.t. for 1 h. After chromatography on a silica column, 365 mg (88%) chalcone was obtained. Mp 59–60°C (authentic sample: 57–58°C); ^{1}H NMR 7.20–7.80 (m, 10H), 8.0 (m, 2H); IR (KBr) 1660, 1602; MS 208 (M^+, 45). The data are the same as from an authentic sample.

*3.2. 4-Methylchalcone (**5b**)*

From 4-methylbenzaldehyde, 380 mg (86%). Mp 95–96°C (ref. 5: 96.5°C); ^{1}H NMR 2.30 (s, 3H), 7.20–7.80 (m, 9H), 8.05 (m, 2H); IR (KBr) 1658, 1600; MS 222 (M^+, 42).

*3.3. 4-Chlorochalcone (**5c**)*

From 4-chlorobenzaldehyde, 420 mg (87%). Mp 114–115°C (ref. 6: 115–116°C); ^{1}H NMR 7.15–7.70 (m, 9H), 7.90 (m, 2H); IR (KBr) 1662, 1605; MS 242 (M^+, 52).

*3.4. 1-Phenyl-2-hepten-1-one (**5d**)*

See ref. 7. From valeraldehyde, 320 mg (85%). Bp 112–114°C/2 mmHg; ^{1}H NMR 0.90 (t, $J = 7.0$ Hz, 3H), 1.40 (m, 4H), 2.20 (m, 2H), 6.85 (m, 2H), 7.40 (m, 3H), 7.80 (m, 2H); IR (neat) 1670, 1620; MS 188 (M^+, 15).

*3.5. 1-Phenyl-2-dodecen-1-one (**5e**)*

See ref. 8. From decyl aldehyde, 440 mg (86%). Bp 158–160°C/2 mmHg; ^{1}H NMR 0.90 (t, $J = 7.0$ Hz, 3H), 1.30 (m, 14H), 2.20 (m, 2H), 6.90 (m, 2H), 7.40 (m, 3H), 7.80 (m, 2H); IR (neat) 1670, 1620; MS 258 (M^+, 5).

*3.6. 1-Phenyl-2,4-hexendien-1-one (**5f**)*

See ref. 9. From crotonaldehyde, 250 mg (73%). Bp 90–92°C/2 mmHg; ^{1}H NMR 1.90 (d, $J_1 = 6.0$ Hz, 3H), 6.20 (m, 3H), 6.70 (d, $J_2 = 14.0$ Hz, 1H), 7.40 (m, 3H), 7.90 (m, 2H); IR (neat) 1660, 1630; MS 172 (M^+, 30).

*3.7. 2-Cyclohexylidene-1-phenyl-ethanone (**5g**)*

See ref. 10. From cyclohexanone. ^{1}H NMR 1.98 (m, 6H), 2.60 (m, 4H), 6.50 (s, 1H), 7.40 (m, 3H), 7.80 (m, 2H); IR 1665, 1620.

Acknowledgement

Thanks are due to the National Natural Science Foundation of China and Academia Sinica for financial support.

References

1 Y.Z. Huang, *Acc. Chem. Res., 25* (1992) 182, and references cited therein.
2 For example, see: Y.Z. Huang, L.J. Zhang, C. Chen and G.Z. Guo, *J. Organomet. Chem., 412* (1991) 47.
3 D. Wittenberg and H. Gilman, *J. Org. Chem., 23* (1958) 1063.
4 S. Samaan, in E. Muller (ed.) *Houben-Weyl, Methoden der Organischen Chemie*, 4th ed., Vol. XIII/8, Georg Thieme Verlag, Stuttgart, 1978, p. 497.
5 H. Stobbe and K. Bremer, *J. Prakt. Chem., 123* (1929) 52.
6 W. Dilthey, L. Neubaus, E. Reis and W. Schommer, *J. Prakt. Chem., 124* (1929) 126.
7 R.C. Larock and J.C. Berhardt, *J. Org. Chem., 43* (1978) 710.
8 K. Inomata, Y. Murata, H. Kato, Y. Tsukahara, H. Kinoshita and H. Kotake, *Chem. Lett.*, (1985) 931.
9 I. Rhee, I. Ryu, H. Omura, S. Murai and N. Sonoda, *Chem. Lett.*, (1979) 1435.
10 N. Matsumura, A. Kunugihara and S. Yoneda, *Tetrahedron Lett.*, 24 (1983) 3239.