

Notes

Insertion of Dichlorocarbene into C—B Bond of Borinates under Liquid-Liquid Phase Transfer Catalysis Conditions: A Convenient Preparation of Unsymmetrical Ketones

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Unsymmetrical ketones were conveniently prepared from the unsymmetrical diorganyl borinates *via* the insertion of dichlorocarbene into C—B bond under liquid-liquid phase transfer catalysis conditions and oxidation with alkaline hydrogen peroxide in 35—67% yields.

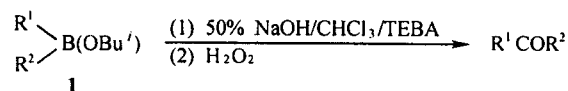
Keywords Dichlorocarbene, insertion, borinate, phase transfer catalysis, unsymmetrical ketone

The conversion of organic boron compounds into various functional products is important in organic synthesis. For example, the ketones were obtained from interaction of triorganyl borane or diorganyl borinate with CO,¹ NaCN,² (PhS)₃CH,³ Cl₂CHOCH₃ (DCME)⁴ and CHCl₃/MeONa,⁵ *etc.* On the other hand, the phase transfer catalysis (PTC) technique is often superior to the conventional methods and has wide application in organic synthesis. However, the reaction of organic boron species under PTC conditions has seldom been reported in literature.^{6,7} In our previous papers,⁸⁻¹⁰ it has been reported that symmetric ketones were simply prepared from trialkyl boranes, dialkyl borinates and diheteroaromatic borinates *via* dichlorocarbene insertion and oxidation under liquid-liquid and liquid-solid PTC conditions. Here we report a convenient preparation of unsymmetrical ketones from the unsymmetrical borinates *via* the same insertion-oxidation process and discuss the possible mechanism of the insertion of dichlorocarbene into C—B

bond.

The insertion of dichlorocarbene into C—B bond of unsymmetrical diorganyl borinates (1) under liquid-liquid PTC condition and oxidation with alkaline hydrogen peroxide afforded the corresponding unsymmetrical ketones. It is shown in Scheme 1. The results are listed in Table 1.

Scheme 1



TEBA: triethylbenzylammonium chloride

The possible mechanism of the insertion of dichlorocarbene into C—B bond and 1,2-shift and oxidation with alkaline hydrogen peroxide is shown in Scheme 2.

Tricoordinated organic boron species can not react with dichlorocarbene because they both are electron deficient. The electrophilic tricoordinated boron compound changes into the nucleophilic ate-complex (such as 2 in Scheme 2) under alkaline condition. Thus it becomes possible that electrophilic dichlorocarbene inserts into C—B bond of the nucleophilic intermediate 2 to afford α,α -dichloroalkyl boron species 3, which is easily con-

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Received April 3, 2000; accepted August 3, 2000.

Project supported by the National Natural Science Foundation of China (No. 2937206).

verted into the intermediate **4** via 1,2-shift. We made an effort to separate the intermediate **4**. Unfortunately it is not successful. α -Hydroxy alkyl boron species **5** was obtained by the nucleophilic substitution of α -chloro of the intermediate **4** with hydroxy group. It was confirmed by the protonolysis of **5** with acetic acid to afford the cor-

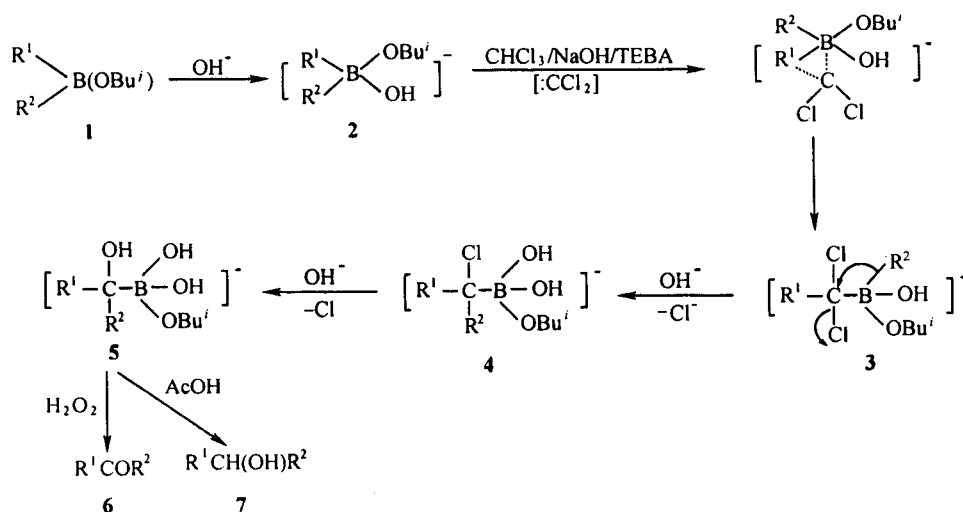
responding secondary alcohol **7**. For example, the insertion of dichlorocarbene into C—B bond of the borinate **1** ($R^1 = n$ -butyl, $R^2 =$ phenyl) under the above condition and protonolysis with AcOH yielded 1-phenyl-1-pentanol (**7**, $R^1 =$ butyl, $R^2 =$ phenyl).

Table 1 Insertion of dichlorocarbene into C—B bond of unsymmetric diorganyl borinates **1** and oxidation with alkaline peroxide

Entry	Borinate 1		Product *	Yield (%)	
	R^1	R^2		No ultrasonic irradiation	ultrasonic irradiation
1	<i>n</i> -propyl	<i>n</i> -butyl	4-octanone	35	40
2	<i>n</i> -butyl	cyclohexyl	butyl cyclohexyl ketone	45	50
3	<i>n</i> -butyl	2-thienyl	butyl 2-thienyl ketone	55	67
4	cyclohexyl	2-thienyl	cyclohexyl 2-thienyl ketone	50	54
5	<i>n</i> -pentyl	phenyl	<i>n</i> -pentyl phenyl ketone	55	67

* All products were purified by distillation under reduced pressure and identified by IR, ^1H NMR and MS spectra.

Scheme 2



The preparation of unsymmetrical ketones via the insertion-shift-oxidation process is convenient, however, the reaction time is too long (24 h). It has been reported¹¹ that the ultrasonic irradiation accelerates the generation of dichlorocarbene. Here, the ultrasonic technique was applied to increase the rate and yield of above reaction. The results are also listed in Table 1.

The results indicated that the reaction rates were increased rapidly and the yields were somewhat increased by the ultrasonic irradiation. The insertion reaction was completed within 0.5 h under the ultrasonic irradiation.

Experimental

The IR spectra were recorded on a NICOLET

170SX FT-IR spectrophotometer. The ^1H NMR spectra were recorded on a JEOL FX-90 (90 MHz) NMR spectrometer for samples in CDCl_3 solution with TMS as internal reference. The mass spectra were taken on a ZAB-3F mass spectrometer.

*Preparation of 4-octanone via the insertion of dichlorocarbene into C—B bond of the borinate **1** ($R^1 = n$ -Pr, $R^2 = n$ -Bu) and oxidation with alkaline hydrogen peroxide*

Typical procedure To the mixture of borinate **1** ($R^1 = n$ -Pr, $R^2 = n$ -butyl, 3.1 g, 16.3 mmol),¹² TEBA (0.84 g), chloroform (6.7 mL) and ethyl ether (30

mL) in 100 mL three-necked flask was dropped freshly prepared ice-cooled 50% sodium hydroxide solution (6.8 mL) under ice-bath with vigorously stirring. The reaction temperature gradually rose to room temperature and the mixture was stirred for 24 h at this temperature and 1 h at 50–60°C, then cooled to room temperature and oxidized with 30% hydrogen peroxide (8 mL) at 25°C for 2 h and 50–60°C for 0.5 h, then cooled and water (30 mL) was added, the organic layer was separated and the water layer was extracted with ethyl ether (20 mL × 2). The combined organic layer was washed three times with water and dried with anhydrous sodium sulfate. The solvent was evaporated and the residue was distilled under reduced pressure to afford 4-octanone (0.72 g, 35%). b. p.: 63–64°C/660 Pa (Lit.¹³ 165–168°C). ¹H NMR (CDCl₃, TMS = 0) δ: 0.86 (t, *J* = 7.0 Hz, 6H, 2 × CH₃), 1.00–1.60 (m, 6H, 3 × CH₂), 2.2 (t, *J* = 7.0 Hz, 4H, CH₂COCH₂). IR ν: 2930, 2875, 1712, 1461, 1375 cm⁻¹. *m/z* (%): 128 (M⁺), 85 (C₄H₉CO⁺), 71 (C₃H₇CO⁺), 57 (C₄H₉⁺), 43 (C₃H₇⁺).

Preparation of 4-octanone via the insertion-shift-oxidation process under ultrasonic irradiation

All apparatus, materials and details are the same as the above procedure except that the insertion reaction time was 0.5 h under ultrasonic irradiation. 4-Octanone

(0.86 g, 40%) was obtained. The IR, ¹H NMR and MS spectra of the products are the same as those in the above example.

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(E200004078 SONG, J.P.; LING, J.)