SHORT PAPER

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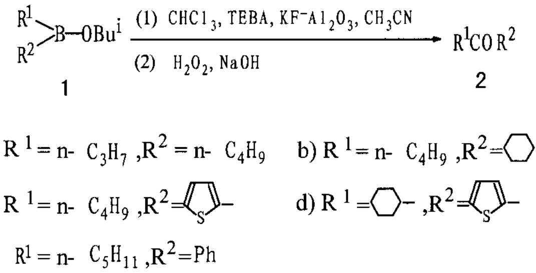
A convenient preparation of unsymmetrical ketones from borinates using phase transfer catalysis[†]

Feng Guo[ab], Shiwen Huang[a]*, Zixing Shan[a] and Dejie Zhao[a]

[a]*Department of Chemistry, Wuhan University, Wuhan 430072, P. R.China*
[b]*Department of Chemical Engineering, Hubei Polytechnic University, Wuhan 430068, P. R. China*

Unsymmetrical ketones were prepared from borinates via the insertion of dichlorocarbene into the C–B bond under solid–liquid phase transfer catalysis conditions and oxidation with alkaline hydrogen peroxide in 50–78% yields.

The importance of the preparation of ketones from di- or triorganyl boron compounds has been widely reported[1–5] and the phase transfer catalysis (PTC) technique has been applied extensively in organic synthesis. However, the reaction of organoboron compounds under PTC conditions has seldom been investigated.[6,7] In our previous papers,[8–10] we have combined the conversion of organoboron species with the PTC technique to accomplish the insertion of dichlorocarbene into the C–B bond of symmetrical borinates under PTC conditions followed by oxidation with alkaline hydrogen peroxide to afford symmetrical ketones.[8,9] We also observed that the yield of ketones from the solid–liquid reaction is high in comparison with a liquid-liquid system.[10] We herein report the preparation of unsymmetrical ketones **2** by the insertion of dichlorocarbene into the C–B bond of unsymmetrical borinates **1** under solid-liquid PTC[11] conditions. The results are listed in Table 1.



Firstly, the tricoordinated borinate **1** is easily converted into a tetracoordinated boron species, which is called an ate-complex, in the presence of a solid base such as KF–Al_2O_3. Dichlorocarbene is simultaneously generated from chloroform using KF–Al_2O_3 as a strong base and triethylbenzyl ammonium chloride (TEBA) as the phase transfer catalyst.[12] Then, insertion of the electrophilic :CCl_2 into the C–B bond of the nucleophilic ate-complex was readily achieved in the usual way[13] to form an α, α-dichloro borinate. This was followed by the migration of the alkyl group from the boron atom to the adjacent carbon atom to give an α-chloro boronate**,** which was oxidized with alkaline hydrogen peroxide to afford the expected product, namely the unsymmetrical ketone R^1COR^2 **2**. It is noteworthy that the insertion of :CCl_2 into R^1–B or R^2–B of **1** gave the same ketone after oxidation.

It has been reported that anhydrous zinc chloride accelerates the 1,2-shift of the α-chloroboron species derived from an alkyl boronate and $LiCHCl_2$.[18] In this paper, anhydrous zinc chloride was also used to facilitate the reaction and the results indicated that the yields of the unsymmetrical ketones increased by 6–15% using anhydrous zinc chloride under the same solid–liquid PTC conditions.

Table 1 Preparation of unsymmetrical ketones (**2**) via the insertion of dichlorocarbene into C–B bond of the borinates (**1**) and 1,2-shift and oxidation with hydrogen peroxide

Compd	b.p. (°C)	lit. (°C)	Yield (%) No $ZnCl_2$	Yield (%) with $ZnCl_2$
2a	64-65/660Pa	165–168[14]	50	65
2b	85-87/400Pa	85–86/400Pa[15]	60	75
2c	91-92/133Pa	258[16]	65	75
2d	125-127/66Pa	43–44(m.p.)[16]	70	78
2e	110-112/13Pa	265[17]	70	76

*All products were purified by distillation and identified by IR,^{1}HNMR and MS spectra.

In conclusion, the insertion of :CCl_2 into the C-B bond of unsymmetrical borinates under solid–liquid PTC conditions was achieved and the unsymmetrical ketones were prepared in satisfactory yields via such an insertion- shift-oxidation process. $ZnCl_2$, as a Lewis acid, was applied to facilitate the migration of the alkyl group from boron to the adjacent carbon and improve the yields of unsymmetrical ketones.

Experimental

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

*The preparation of 4-octanone (***2a***) is typical: general procedure in the absence of anhydrous zinc chloride:* A mixture of borinate **1a** (3.9g, 21mmol), anhydrous acetonitrile (30ml), KF-Al_2O_3 [12] (6.6g, 41mmol), chloroform (3.3mL, 41mmol) and TEBA (0.46g) in a 100mL three-necked flask was stirred vigorously at room temperature for 24 h , then filtered to remove the precipitate. The filtrate was oxidized with 3N sodium hydroxide solution (5mL) and 30% hydrogen peroxide (5mL) at 40°C for 2 h, cooled and diluted with water and extracted with ether three times. The combined ether layer was washed successively with water and brine and dried over anhydrous sodium sulfate. The mixture was then filtered and the solvent was removed. The residue was distilled under reduced pressure to obtained colorless 4-octanone (1.34g, 50%), bp: 64–65°C/660Pa. IR: 2930, 2875, 1712, 1461, 1375cm^{-1}; ^{1}HNMR ($CDCl_3$, TMS=0) δ (ppm): 0.86 (t ,6H, $2CH_3$), 1.0-1.6 (m, 6H, $3CH_2$), 2.2 (t, 4H, CH_2COCH_2); MS(EI), *m/e:* 128 (M^+), 85 ($C_4H_9CO^+$), 71 ($C_3H_7CO^+$), 57 ($C_4H_9^+$), 43 ($C_3H_7^+$).

General procedure in the presence of anhydrous zinc chloride: All apparatus, materials and details were same as that in the above process except that anhydrous zinc chloride (0.5g) was added to the reaction mixture before the reaction began. 4-octanone (1.95g, 65%) was obtained by distillation under reduced pressure, and was characterised by IR, ^{1}HNMR and MS spectra.

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* To receive any correspondence. E-mail: swhuang@public.wh.hb.cn

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References

1 H.C. Brown and M.W. Rathke, *J. Am. Chem. Soc.*, 1967, **89**, 2738.
2 A. Pelter, K. Smith, M.G. Hutching and K. Rowe, *J. Chem. Soc. Perkin Trans. 1*, 1975,129.
3 A. Pelter and J.M. Rao, *J. Chem. Soc. Chem. Commun.*, 1981, 1149.
4 B.A. Carlson and H.C. Brown, *J. Am. Chem. Soc.*, 1973, **95**, 6876.
5 C. Narayana and M. Periasamy, *Tetrahedron Lett.*, 1985, **26**, 6361.
6 L. Akimoto and A. Suzuki, *Synth. Commun.*, 1981, **11**, 475.
7 C. Bedel and A. Foucaud, Tetrahedron Lett., 1993, **34**, 311.
8 D. Zhao, T. Ke, C. Ke and Z. Shan, *Chin. Chem. Lett.,* 1993, **4**, 471.
9 T. Ke, Z. Shan and D. Zhao, .*J. Wuhan Univ. (Nat. Sci. Ed.)*, 1995, **41**, 702.
10 D. Zhao, J. Huang and Z. Shan, *Chin. Chem. Lett.*, 1993, **4**, 385.
11 E.V. Dehmlow and S.S. Dehmlow, *Phase Transfer Catalysis*. Verlag Chemie, Weinheim, 1980.
12 X. Ting and C. Liu, *Youji Huaxue*, 1988, **8**, 511.
13 I. Tabushi, Z. Yoshida and N. Takahashi, *J. Am. Chem. Soc.*, 1970, **92**, 6670.
14 R.F. Smith, *J. Org. Chem*., 1960, 25, 453.
15 N.K. Nelson and H.H. Morris, *J. Am. Chem. Soc*., 1953, **75**, 3337.
16 J.J. Spurlock, *J. Am Chem. Soc*., 1953, **75**, 1115.
17 R.L. Shriner and T.A. Turner, *J. Am. Chem. Soc.*, 1930, **52**, 1267.
18 D. S. Matteson and K. M. Sadhu, *J. Am. Chem. Soc.*, 1983, **105**, 2077.