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THE REACTION OF LITHIUM TRIALKYLALKYNYLBORATES

A NOVEL METHOD OF SYNTHESIZING α,β-UNSATURATED KETONES

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Abstract—Treatment of lithium trialkylalkynylborates with acetyl chloride gave 2-oxa-3-borolenes (**2**). The enol borinates were oxidized by Jones reagent to highly substituted α,β-unsaturated ketones (**4**). The stability of **2** is ascribed to the steric hindrance of the B-alkyl groups and to the resonance contribution of the mesomeric structure **3**.

Trialkylboranes have been extensively used as alkylating agents since Brown's introduction of these compounds.[1] On the other hand, tetra-coordinated organoboron compounds,[2-7] i.e., borates, have little application in organic synthesis.[1] The reaction of trialkylalkynylborates with acyl chlorides gives 2-oxa-3-borolenes (**2**) and ketones RCOC≡CR',[4] but nothing further has been recorded. The present paper describes a reinvestigation of the 2-oxa-3-borolenes as listed in Table 1, and a novel synthesis of the highly substituted α,β-unsaturated ketones of Table 2.

Successive treatment of 1-heptyne in tetrahydrofuran (THF) with a hexane solution of n-butyllithium, and then with triisopropylborane gave a hexane–THF solution of lithium triisopropyl-1-heptynylborate (**1a**). Acetyl chloride was added and the mixture heated. GLC analysis indicated that 2-oxa-3-borolene (**2a**) was the only volatile product,† which was isolated in 65% yield.

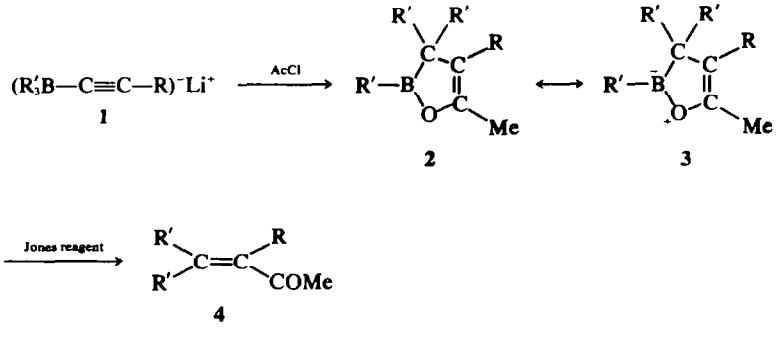
†In contrast to the reported case,[4] the formation of the alkynyl ketone was not observed in the present reaction. In other runs of this kind of reaction, the alkynyl ketones ($CH_3COC{\equiv}CR$, R = Am, Ph) were obtained in 15–25% yield.

Oxidation of **2** afforded α,β-unsaturated ketones (**4**) in fair yields. This is a convenient synthesis for α,β-unsaturated ketones and involves gem-dialkylation at C-1 and acylation at C-2 of the starting acetylene.

The oxidation of the oxaborolenes (**2b**, **2d**) with alkaline hydrogen peroxide[8] afforded **4b** (14%) and **4d** (23%), where R' was n-butyl. Under similar conditions, **2a** (R' = i-Pr) remained unchanged, whereas **2c** (R' = i-Pr) and **2f** (R' = sec-Bu) produced benzyl methyl ketone (**5**) possibly arising from **6** via the retroaldol cleavage.

Enol borinate **2a** also resisted oxidation with trimethyamine oxide,[9] or with triplet oxygen,[10] as well as protonolysis with propionic acid.[11] Attempted hydrogenation over Pd-C and PtO_2,[12] and hydroboration of **2a** resulted in the recovery of the starting material.

The resistance of **2a** toward oxidation is mainly ascribed to the steric hindrance around the boron atom. Examination of framework molecular models shows clearly that the boron atoms of **2a**, **2c** and **2e** with secondary R' groups attached are more shielded from attack by any reagents than those of **2b** and **2d** having the primary R' groups. Phenyl-substituted oxaborolenes with secondary R' groups



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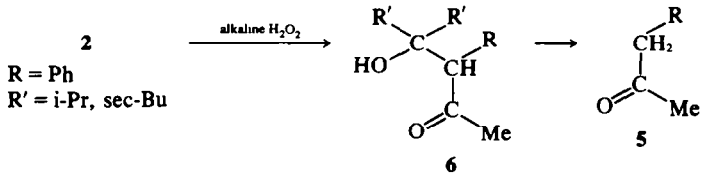

(2)

Table 1. Cyclic enol borinates 2

	R	R'	b.p. °C(mm)	Yield (%) (based on RC≡CH)
2a	Am	i-Pr	118–121 (5)	65[a]
2b	Am	n-Bu	116–118 (5)	—[b]
2c	Ph	i-Pr	126–129 (6)	58[a]
2d	Ph	n-Bu	138–143 (5)	—[b]
2e	Ph	sec-Bu	137–139 (5)	49[a]

[a] Isolated yield.
[b] These products are so unstable that yields could not be calculated. Distilled products of these runs always contained a fair amount of 4.

Table 2. α,β-Unsaturated ketones 4

	R	R'	b.p. °C(mm)	Yield (%) (based on RC≡CH)
4a	Am	i-Pr	106–110 (10)	42
4b	Am	n-Bu	90–100 (4)	36
4c	Ph	i-Pr	105–110 (6)	36
4d	Ph	n-Bu	120–130 (6)	30
4e	Ph	sec-Bu	127–129 (6)	28

(2c and 2e), however, are not as stable as 2a having an alkyl instead of the phenyl group. The extreme stability of 2a is ascribed to the predominant contribution of the mesomeric form 3. This is reflected in the UV max (λ_{max} 238 nm, log ε 3·45), which is close to that of cyclopentadiene (λ_{max} 238 nm, log ε 3·53).[11] On the other hand, the UV max of 2c and 2d do not show any appreciable bathochromic and hypsochromic shift as observed in 1- and 3-phenylcyclopentadiene.[14] The UV data of phenyl substituted oxaborolenes (2c, 2d and 2e) indicate the absence of the conjugation between the styryl group and O—B linkage. The absence of the conjugation facilitates the oxidation of 2.

EXPERIMENTAL

All b.ps were uncorrected. Gas chromatography was performed on Shimadzu GC-4BPT with 3 m × 3 mm column packed with 20% polyethyleneglycol and 25% HVSG on Chromosorb W-AW (80–100 mesh). Mass spectra were obtained on a Hitachi RMS-4 and RMU-6L with 70 eV ionization potential, NMR Me_4Si internal standard and CCl_4 solvent on JEOL C-60-H and Varian EM-360, UV on Hitachi EPS-2 and IR on Shimadzu IR-27G spectrometer.

3-Methyl-1,4,5,5-tetraalkyl-2-oxa-3-borolenes (2),

General procedures. To a stirred soln of 1-alkyne (5·0 mmol) in THF (5·0 ml) at 0° under N_2, a hexane soln of n-BuLi (5·0 mmol in 5·0 ml) was added and the resulting mixture stirred at room temp for 30 min. The mixture was cooled to 0° and trialkylborane (5·0 mmol) was added, and the resulting mixture stirred at room temp for 1 h. The mixture was cooled in an ice-salt bath, and then acetyl chloride (0·47 g, 6·0 mmol) was added. After the addition, the ice-salt bath was removed and the mixture heated under reflux for 10 h. Distillation under reduced pressure gave 2.

3 - Methyl - 4 - pentyl - 1,5,5 - triisopropyl - 2 - oxa - 3 - borolene (2a). The preparation of lithium triisopropyl - 1 - heptynylborate (20·0 mmol) and its reaction with acetyl chloride (2·36 g, 30·0 mmol) was performed by the general procedure. After standard work-up, distillation and chromatography (silica gel–hexane) 2a (3·61 g; 64·9%) was obtained: b.p. 118–121° (5 mm); IR (neat) 1675 cm^{-1} ($\nu_{c=c}$); NMR (CCl_4) δ 0·8 (d, 6 H, J = 5 Hz), 0·9 (d, 6 H, J = 5 Hz), 0·95 (t, 3 H, J = 3 Hz), 1·0 (d, 6 H, J = 5 Hz), 1·3 (m, 6 H), 1·7 (m, 2 H), 1·9 (s, 3 H), 2·0 (m, 2 H); MS *m/e* (rel. intensity %) 278 (M^+, 8), 235 (100), 193 (78), 109 (99), 95 (100); UV (EtOH) λ_{max} 238 nm, log ε 3·45. (Found: C, 77·42; H, 12·78. Calc for $C_{18}H_{35}BO$: C, 77·69; H, 12·68%).

3 - Methyl - 4 - pentyl - 1,5,5 - tributyl - 2 - oxa - 3 - borolene (2b). The preparation of 2b was according to the general procedure. This enol borinate was so unstable that the isolated yield could not be calculated. The distilled product always contained a fair amount of 4b. A pure sample was obtained by preparative GLC: b.p. 116–118° (5 mm); IR (neat) 1686 cm^{-1} ($\nu_{c=c}$); MS *m/e* (rel. intensity %) 320 (M^+, 12), 263 (100), 207 (93), 95 (45); UV (EtOH) λ_{max} 249 nm. (High resolution MS. Found: *m/e* 320·3266. Calc for $C_{21}H_{41}BO$: *m/e* 320·3250).

3-Methyl - 4 - phenyl - 1,5,5 - triisopropyl - 2 - oxa - 3 - borolene (**2c**). The compound, obtained as described, gave on distillation **2c** (0·82 g; 58%): b.p. 126–129° (6 mm); IR (neat) 1686 cm^{-1} ($\nu_{c=c}$); NMR (CCl_4) δ 0·7 (d, 6H, J = 6 Hz), 1·1 (d, 6H, J = 6 Hz), 1·4 (m, 1 H), 1·9 (s, 3 H), 2·3 (hept, 2 H, J = 6 Hz), 7·2 (m, 5 H); MS *m/e* (rel. intensity %) 284 (M^+, 8), 241 (68), 199 (28), 171 (100); UV (EtOH) λ_{max} 250 nm, log ϵ 3·87. (Found: C, 79·99; H, 10·58. Calc for $C_{19}H_{29}BO$: C, 80·28; H, 10·28%).

3-Methyl - 4 - phenyl - 1,5,5 - tributyl - 2 - oxa - 3 - borolene (**2d**). The enol borinate was also unstable and the yield could not be calculated. A pure sample was prepared by GLC: b.p. 138–143° (5 mm); IR (neat) 1684 cm^{-1} ($\nu_{c=c}$); MS *m/e* (rel. intensity %) 326 (M^+, 8), 269 (100), 213 (98), 175 (50), 153 (53), 105 (69), 91 (80); UV (EtOH) λ_{max} 251 nm. (High resolution MS. Found: *m/e* 326·2786. Calc for $C_{22}H_{35}BO$: *m/e* 326·2781).

3 - Methyl - 4 - phenyl - 1,5,5 - tri - sec - butyl - 2 - oxa - 3-borolene (**2e**). The compound on distillation gave **2e** (0·80 g; 49%): b.p. 137–139° (5 mm); IR (neat) 1664 cm^{-1} ($\nu_{c=c}$); NMR (CCl_4) δ 0·6–2·2 (m, 27 H), 1·9 (s, 3 H), 7·2 (m, 5 H); MS *m/e* (rel. intensity %) 326 (M^+, 8), 269 (100), 213 (94), 157 (80); UV (EtOH) λ_{max} 251 nm, log ϵ 4·05. (Found: C, 81·10; H, 10·99. Calc for $C_{22}H_{35}BO$: C, 80·97; H, 10·81%).

3,4-Dialkyl-3-alken-2-one (**4**)

General procedure. In these reactions **2** was not isolated. After 20 h heating under reflux, the precipitated LiCl was filtered off, and the filtrate concentrated under reduced pressure. The residue was dissolved in 10 ml acetone, then Jones reagent (8 N)[15] was added dropwise to the soln until a reddish-brown colour remained. The stirring was continued for a further 15 min, and acetone was then removed under reduced pressure. The remainder was extracted with hexane, the extract was washed, dried (Na_2SO_4) and the solvent evaporated. The residue was chromatographed (silica gel–benzene) to give **4**.

4 - Isopropyl - 5 - methyl - 3 - pentyl - 3 - hexen - 2 - one (**4a**). After the general procedure, chromatography gave **4a** (0·47 g; 42%): b.p. 106–110° (10 mm); IR (neat) 1693 cm^{-1} ($\nu_{c=o}$); NMR (CCl_4) δ 0·9 (t, 3H, J = 5 Hz), 1·0 (d, 6H, J = 7 Hz), 1·1 (d, 6H, J = 7 Hz), 1·3 (m, 6H), 2·1 (s, 3H), 2·5 (m, 4H); MS *m/e* (rel. intensity %) 224 (M^+, 8), 181 (40), 43 (100). (Found: C, 80·01; H, 12·47. Calc for $C_{15}H_{28}O$: C, 80·29; H, 12·58%).

4 - Butyl - 3 - pentyl - 3 - octen - 2 - one (**4b**). After the general procedure, distillation and chromatography gave **4b** (0·45 g; 36%): b.p. 90–100° (4 mm); IR (neat) 1690 cm^{-1} ($\nu_{c=o}$); NMR (CCl_4) δ 0·9 (m, 9 H), 1·3 (m, 14 H), 2·0 (m, 6 H), 2·1 (s, 3 H); MS *m/e* (rel. intensity %) 252 (M^+, 9), 43 (100). (Found: C, 80·59; H, 12·71. Calc for $C_{17}H_{32}O$: C, 80·88; H, 12·78%).

4 - Isopropyl - 5 - methyl - 3 - phenyl - 3 - hexene - 2 - one (**4c**). After the general procedure, chromatography gave **4c** (0·41 g; 36%): b.p. 105–110° (6 mm); IR (neat) 1691 cm^{-1} ($\nu_{c=o}$); NMR (CCl_4) δ 0·9 (d, 6 H, J = 7 Hz), 1·2 (d, 6 H, J = 7 Hz), 2·0 (s, 3H), 2·5 (hept, 2H, J = 7 Hz), 7·2 (m, 5H); MS *m/e* (rel. intensity %) 230 (M^+, 8), 187 (40), 145 (50), 43 (100). (Found: C, 83·18; H, 9·71. Calc for $C_{16}H_{22}O$: C, 83·43; H, 9·63%).

4 - Butyl - 3 - phenyl - 3 - octen - 2 - one (**4d**). After the general procedure, chromatography gave **4d** (0·39 g, 30%): b.p. 120–130° (6 mm); IR (neat) 1687 cm^{-1} ($\nu_{c=o}$); NMR (CCl_4) δ 0·9 (m, 6 H), 1·3 (m, 8 H), 1·9 (s, 3 H), 2·2 (m, 4 H), 7·2 (m, 5 H); MS *m/e* (rel. intensity %) 258 (M^+, 19), 201 (22), 91 (43), 43 (100). (Found: C, 83·39; H, 10·42. Calc for $C_{18}H_{26}O$: C, 83·66; H, 10·43%).

5-Methyl-3-phenyl - 4 - sec - butyl - 3 - hepten - 2 - one (**4e**). After the general procedure, chromatography gave **4e** (0·36 g; 28%): b.p. 127–129° (6 mm); IR (neat) 1687 cm^{-1} ($\nu_{c=o}$); NMR (CCl_4) δ 0·7 (t, 3 H, J = 7 Hz), 0·9 (t, 3 H, J = 7 Hz), 0·9 (d, 3 H, J = 7 Hz), 2·1 (m, 2 H), 7·2 (m, 5 H); MS *m/e* (rel. intensity %) 258 (M^+, 13), 201 (76), 43 (100). (Found: C, 83·85; H, 10·38. Calc for $C_{18}H_{26}O$: C, 83·66; H, 10·43%).

Alkaline hydrogen peroxide oxidation of 2

General procedure. The compounds **2** were not isolated. To a mixture containing **2**, 5 ml of 6 N NaOH was added, then 5 ml of 30% H_2O_2 was added dropwise during 15 min. The mixture was stirred for an additional 3 h at room temp. The resulting mixture was extracted with hexane, the extract was washed with water, dried (Na_2SO_4) and concentrated under reduced pressure. To the residue, 1,1-diphenylethylene (0·36 g, 2·0 mmol) was added as an internal standard. The yield of **4** was obtained by GLC.

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