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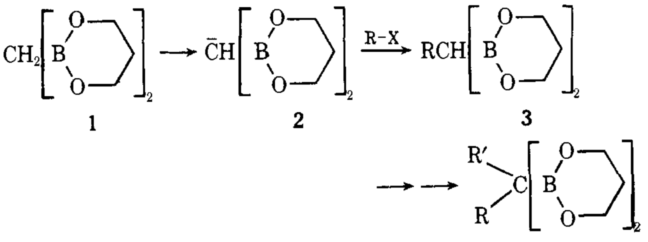
Carbanions from Deprotonation of *gem*-Diboronic Esters

Sir:

Deprotonation of bis(trimethylenedioxyboryl)methane (**1**) with lithium 2,2,6,6-tetramethylpiperidide yields the diborylcarbanion (**2**), which with alkyl halides gives high yields of *gem*-diboronic esters (**3**), which can in turn be deprotonated and alkylated.

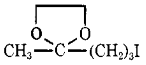
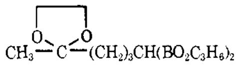


The carbanion from **3** (R = *n*-pentyl) converts esters, $R'CO_2CH_3$, to ketones, $R'COCH_2R$.

A close analogue of **2** has been shown previously to homologate aldehydes efficiently via alkeneboronic esters,[1] and several related boron substituted carbanions have been shown to have potential for synthetic applications,[2] but their use has been discouraged by the need to prepare them by deboronation of exotic tris- and tetrakis(dialkoxyboryl)methanes.[3] *gem*-Diboronic esters are accessible from the direct condensation of dichloromethane, lithium, and trimethyl borate[3] and also from dilithiomethane,[4] bis(iodomercuri)methane,[5] or, for higher members of the series, hydroboration.[6]

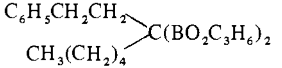
Bases normally attack boron in preference to carbon-bound protons,[1-3] but the success of Rathke and Kow in deprotonating *B*-methyl-9-borabicyclononane and alkenyldisiamylboranes with lithium 2,2,6,6-tetramethylpiperidide[7] prompted us to try this highly hindered base. Boronic esters offer more ways for the reaction to be diverted. The homologation of heptanal to octanal[1] was chosen as the test reaction. Low yields were obtained using the ethylene glycol ester, $CH_2(BO_2C_2H_4)_2$, and another ethylene glycol ester in a parallel study[8] gave no carbanion. The 1,3-propanediol ester **1** was then tested, and with inclusion of tetramethylethylenediamine in the reaction mixture the yield of octanal reached 62%. This is not as good as by the former procedure,[1] perhaps because the reaction medium is more basic. The problem is not in the conversion of **1** to the anion **2**, since reaction of **2** with 1-iodoheptane followed by oxidation[1] yielded 82% of octanal. The results of a series of alkylations of **2** are summarized in Table I.

Table I. Reactions of Lithium Bis(trimethylenedioxyboryl)methide (**2**)

Reactant	Product	% yield	Method
$CH_3(CH_2)_3I$	$CH_3(CH_2)_3CHO$	86	GLC
$CH_3(CH_2)_3Br$		79	GLC
$CH_3(CH_2)_4Br$	$CH_3(CH_2)_4CHO$	80	GLC
		62	Dist
	$CH_3(CH_2)_4CH(BO_2C_3H_6)_2$	71	Dist[a]
$CH_3(CH_2)_6I$	$CH_3(CH_2)_6CHO$	82	GLC
$CH_3(CH_2)_6OTs$		76	GLC
$C_6H_5CH_2Br$	$C_6H_5CH_2CHO$	71	GLC
$Cl(CH_2)_4I$	$Cl(CH_2)_4CHO$	83	GLC
$Br(CH_2)_4CN$	$(C_3H_6O_2B)_2CH(CH_2)_4CN$	49	Dist[a]
		57	Dist[a]

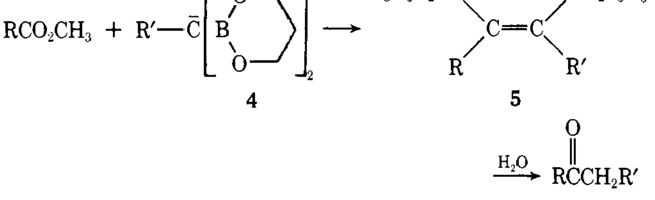
[a] Satisfactory analyses for C, H, B (and N).

Table II. Reactions of 1-Lithio-1,1-bis(trimethylenedioxyboryl)hexane (**4**)

Reactant	Product	% yield
CH_3I	$CH_3(CH_2)_4COCH_3$	78
$C_6H_5CH_2CH_2I$	 $\begin{matrix} C_6H_5CH_2CH_2 \\ CH_3(CH_2)_4 \end{matrix} \Big> C(BO_2C_3H_6)_2$	70[a]
C_6H_5CHO	$C_6H_5CH_2CO(CH_2)_4CH_3$	84
$C_6H_5CO_2CH_3$	$C_6H_5CO(CH_2)_5CH_3$	99[b]
$CH_3(CH_2)_2CO_2CH_3$	$CH_3(CH_2)_2CO(CH_2)_5CH_3$	66

[a] By short-path distillation. Hydrolyzed to boronic acid, mp 66–147 °C dec, satisfactory C, H, and B anal. [b] Isolated 71% 2,4-DNP.

The alkylation product from **2** and 1-bromopentane (**3**, R = *n*-C_5H_{11}) was chosen to test anion formation with a higher homologue. Results are summarized in Table II. The resulting anion **4** was alkylated in the expected manner, and the efficient homologation of benzaldehyde to 1-phenyl-2-heptanone is analogous to aldehyde homologation. The remarkable conversions of methyl benzoate to 1-phenyl-1-heptanone and methyl butyrate to 4-decanone presumably involve enol borate intermediates (**5**), which would be immune to further attack by the carbanion (**4**) and would hydrolyze very rapidly.



$R = C_6H_5,\ C_3H_7;\ R' = C_5H_{11}$

The procedure for preparing **1** from bis(dimethoxyboryl)methane[3] and 1,3-propanediol was similar to previously reported transesterifications,[1] recrystallized from ether/pentane, 78%, mp 42–43 °C, satisfactory C, H, and B analyses. To form the carbanion **2**, 3.5 mmol of butyllithium converted 0.49 g of 2,2,6,6-tetramethylpiperidine to the lithio derivative in the presence of 0.41 g of tetramethylethylenediamine in 10 mL of rigorously dried THF, and this was stirred at −75 °C during the addition of 0.64 g (3.5 mmol) of **1** in 15 mL of THF. After 1 h at −75 °C the mixture was allowed to warm to 0 °C, resulting in precipitation of **2**, and stirred 1 h. The mixture was again cooled to −75 °C, 3.33 mmol of the alkyl halide was added, and reaction was continued 3 h at 25 °C. The solution was concentrated under vacuum. For boronic ester isolation, the residue was chromatographed on a short silica gel column with dichloromethane/pentane and the product **3** was further purified by short path distillation at ~100 °C (0.1 mm). For gas chromatographic analysis, the residue was dissolved in 20 mL of dichloromethane and oxidized with sodium perborate in water, using authentic comparison samples of carbonyl compounds and internal standards as previously described.[1a]

For the reactions with carboxylic esters, the anion **4** was prepared, the solvent was removed under vacuum, cyclohexane and the ester were added, and the mixture was refluxed overnight and worked up with aqueous acid.

Deprotonation of boronic esters may have wide-ranging synthetic utility, inasmuch as other types of substituted boronic esters can also be deprotonated to boron substituted carbanions.[8,9]

References and Notes

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Laser Induced Isotope Enrichment in a Rare Gas Matrix

Sir:

Since the initial report by King and Hochstrasser[1] on the first successful low temperature laser induced isotope separation in mixed molecular crystals of *s*-tetrazine, considerable attention has been given to this technique as well as to the photochemistry and spectroscopy of this interesting chromophore.[2-5] For example, King, Denny, Hochstrasser, and Smith[4] recently demonstrated that 1,4-nitrogen bonding plays a negligible role in the overall photochemical decomposition leading to nitrogen and HCN. Furthermore, it was noted that low temperature high resolution mixed crystal spectroscopy was a novel method for the nondestructive analysis of isotopic composition as well as a useful tool for the determination, at natural abundance, of spectroscopic parameters of rare isotopically substituted species.

The scope of solid state isotope separation and analysis, however, has been severely limited by the general requirement for high quality mixed crystals. It is a difficult problem to find a suitable host species for each new chromophore. With this consideration in mind we report here on high resolution optical spectroscopy of a photochemically unstable species in a rare gas matrix at low temperature. In addition, the results of laser induced isotope enrichments and photochemical studies are presented. The system chosen for study was *s*-tetrazine in argon.

Matrices of *s*-tetrazine[6] in argon were deposited on a polished LiF window, maintained at 10 K, via three techniques: slow uniform deposition at a rate of ca. 0.5 L Torr h^{-1}, rapid deposition at 5-10 L Torr h^{-1}, and pulsed deposition in 10 μmol aliquots. Typical argon:tetrazine mole ratios (M/R) were ca. 1000. Examination of the $^1B_{3u} \leftarrow {}^1A_g$ (n π^*) band region of a fresh *s*-tetrazine-argon matrix at moderate resolution revealed the presence of several sites. However, approximately 90% of the observed spectral intensity was due to *s*-tetrazine chromophores with their origin band at 17 926 cm^{-1}. The bandwidths of these unannealed spectra were 3-5 cm^{-1} regardless of the method used for the deposition. Annealing to 40 K produced two dramatic changes. First, there was a considerable decrease in the observed vibronic transition line widths to ca. 0.5 cm^{-1}. Second, an additional set of absorption bands which were reduced in intensity in matrices of M/R ~ 2000, appear to higher energy than the O-O and vibronic bands in matrices of M/R = 1000. These new bands result from aggregation.

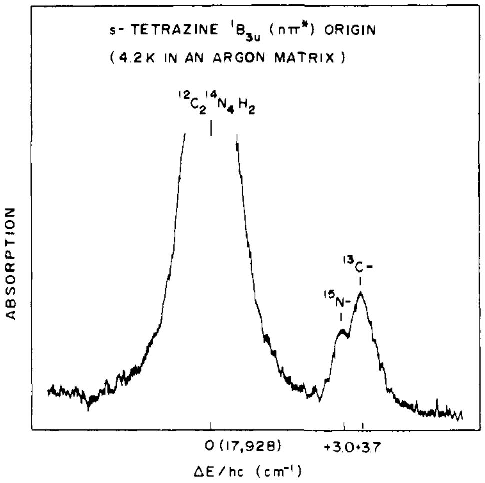

Figure 1. The absorption of the *s*-tetrazine $^1B_{3u} \leftarrow {}^1A_g$ O-O band in an argon matrix at 4.2 K. The spectrum was photographed on a 2-m Jarrell-Ash spectrometer in 15th order. A 450-W Xe lamp was used as the background continuum.

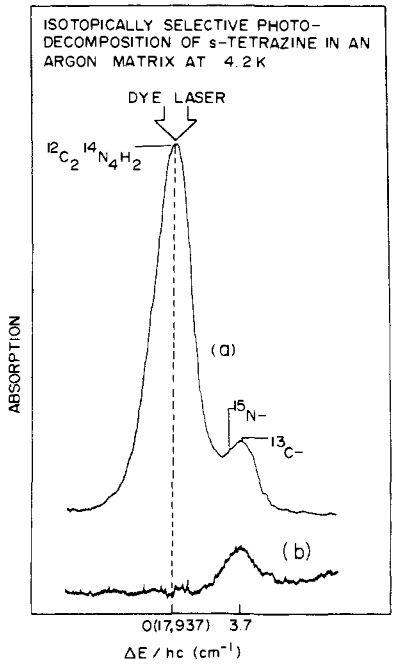

Figure 2. Absorption spectra of the isotopically selective photodecomposition of *s*-tetrazine in an argon matrix at 4.2 K. The photolysis source was a 0.6 cm^{-1} N_2 pumped tunable dye laser tuned to the region of the $^{12}C_2{}^{14}N_4H_2$ absorption. Absorption spectra were recorded photoelectrically on a Spex scanning monochromator.

The strongest O-O band site of annealed *s*-tetrazine in argon (M/R = 1000) at 4.2 K was measured at 17 928.4 cm^{-1} (cf. Figure 1). Two sharp spectral features associated with this peak at 17 931.4 and 17 932.1 cm^{-1} were observed with relative intensities of 0.71:1. These are the O-O transitions of *s*-tetrazine-$^{15}N_1$ and *s*-tetrazine-$^{13}C_1$ in argon, respectively.