to be unstable with respect to its dissociation into methylene and ethylene. For the heat of dissociation of cyclopropane into ethylene and methylene we calculate a value of 105 kcal/mol (exptl value 93 kcal/mol).

By appropriate variation of geometrical parameters it was ensured that III and IV are energetically the highest points on the corresponding paths for the isomerization of cyclopropane. The two structures III and IV are of like symmetry (C_s) and the occupied orbitals can be correlated. Thus, III can be transferred to IV passing a barrier for which we calculated an upper limit of only 7 kcal/mol.

3. In addition, one of the possible trimethylene transition states was also calculated. According to the *ab initio* results,[2,3] the different conformations of trimethylene are of only slightly different energies. We have chosen for our study the trimethylene with two coplanar CH_2 groups (V).

Its ground state cannot be described adequately with one determinant. Hence, the interaction with one doubly excited configuration was taken into account (corresponding to the transfer of two electrons from the highest π to the lowest π^* orbital). As was shown earlier,[7] such a configuration interaction treatment of a "broken" bond is equivalent to the half-electron method.[13] This method yields consistent heats of formation and geometries of radicals.[7,13] Thus, one can expect to get reasonable results for the trimethylene by the procedure described above.

In this manner, an energy of 63 kcal/mol above cyclopropane was obtained for trimethylene. This value compares well with those calculated with *ab initio* methods (61[3] and (with a 3 × 3 CI treatment) 52[2] kcal/mol). Since CI was used in the calculation of V, and also because of the artificial favoring of small ring stability by the modified CNDO method,[5] the direct comparison of its energy with the energies of III and IV is subject to some reservations. In IV the interaction with the most important doubly excited configurations lowers the energy by an additional 8 kcal/mol. The corresponding value for cyclopropane is only 6 kcal/mol. The optimized structure of V is characterized by a C–C bond length of 1.50 Å and a CCC valence angle of 120°.

Although the quantitative results of our calculations may be of questionable accuracy, the following conclusions can be drawn. According to the calculations, the transition states III, IV, and V have comparable energies, *i.e.*, 73, 67, and 63 kcal/mol, respectively, relative to cyclopropane. The experimental value for the activation energy of the isomerization process of cyclopropane is reported to be 64 kcal/mol.[14]

Thus, one can expect that the mechanism for the isomerization of a substituted cyclopropane derivative will be determined by electronic factors as given by its substituents. An electron withdrawing substituent R might favor the transition state IV because of the stabilization of the lone pair in the carbene CHR. On the other hand, appropriate 1,2 substitution could stabilize the trimethylene. Finally, carbenoids might isomerize *via* a state which is analogous to III.

More generally, reactions proceeding with a high activation energy (50 kcal/mol) may be expected to involve a greater variety of possible transition states than do thermally "allowed" reactions.

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(14) B. S. Rabinovitch, E. W. Schlag, and K. B. Wiberg, *J. Chem. Phys.*, **28**, 504 (1958).

Vinyloxyboranes as Synthetic Intermediates

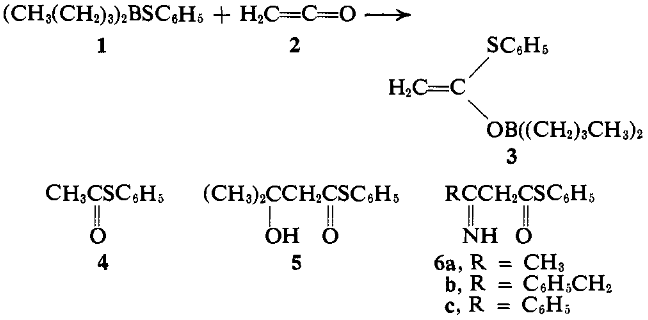
Sir:

We recently reported a convenient method for preparation of β-hydroxyalkanethioates by the reaction of thioboronite and carbonyl compounds with ketene, and it was suggested that the reaction proceeded by initial formation of a coordination complex of a carbonyl compound with thioboronite, followed by a nucleophilic attack of the thiolate anion on ketene.[1] However, the present investigation shows that the key intermediate of this reaction is vinyloxyborane (**3**) formed from thioboronite and ketene.

When nearly 1 equiv of gaseous ketene (**2**) was passed into a solution of phenyl di-*n*-butylthioboronite (**1**) in CCl_4 at −20 to −30° under argon, the formation of **3** was confirmed by the pmr spectrum of the reaction mixture which displayed two doublets for the vinyl hydrogens (H_A and H_B) at δ 4.57 and 4.63 (J_{AB} = ~1.5 Hz). On hydrolysis of this reaction mixture, phenyl thioacetate (**4**) was isolated by preparative tlc.

It was further established that the treatment of **3** with acetone in ether, followed by hydrolysis and preparative tlc of the crude product, afforded phenyl β-hydroxyisovalerothioate (**5**, oil, ir 3410, 1685 cm^{-1}; pmr (CCl_4) δ 1.22 (s, 6 H), 2.70 (s, 2 H), 3.28 (s, 1 H), 7.23 (s, 5 H)) in 67% yield.

In a similar way, β-imino thiol esters (**6a–c**) were obtained by the reaction of **3** with nitriles at room temperature under argon (**6a**, 35%, oil; **6b**, 39%, mp 74°; **6c**, 37%, mp 111–112°). On the other hand, it was found that a coordination complex[2] formed from **1** and benzyl cyanide did not react with ketene.



$(CH_3(CH_2)_3)_2BSC_6H_5 + H_2C{=}C{=}O \longrightarrow H_2C{=}C(SC_6H_5)OB((CH_2)_3CH_3)_2$

1 **2** **3**

$CH_3C(=O)SC_6H_5$ **4**

$(CH_3)_2C(OH)CH_2C(=O)SC_6H_5$ **5**

$RC(=NH)CH_2C(=O)SC_6H_5$ **6a**, R = CH_3; **b**, R = $C_6H_5CH_2$; **c**, R = C_6H_5

Next, in order to study further the reactions of vinyloxyborane, the preparation of the borane from thioboronite and vinyl methyl ketone was tried. Vinyl methyl ketone was allowed to react with an equimolar

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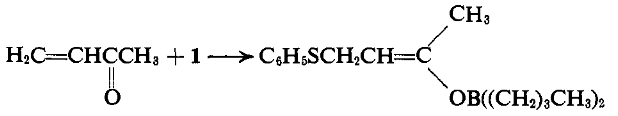
(1) T. Mukaiyama and K. Inomata, *Bull. Chem. Soc. Jap.*, **44**, 3215 (1971).

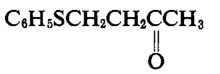
(2) (a) T. Mukaiyama, K. Inomata, and S. Yamamoto, *Tetrahedron Lett.*, 1097 (1971); (b) T. Mukaiyama, S. Yamamoto, and K. Inomata, *Bull. Chem. Soc. Jap.*, **44**, 2807 (1971).

amount of **1** in ether at room temperature for 30 min to give the 1,4-addition product (**7**, pmr (CCl_4) δ 1.78 (s, 3 H), 3.36 (d, $J = 8$ Hz, 2 H), 4.77 (t, $J = 8$ Hz, 1 H)), which was hydrolyzed with aqueous methanol to 4-phenylthiobutan-2-one (**8**) in 86% yield.



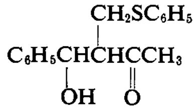
$$H_2C{=}CH\underset{\underset{O}{\|}}{C}CH_3 + 1 \longrightarrow C_6H_5SCH_2CH{=}C\begin{matrix}CH_3\\ OB((CH_2)_3CH_3)_2\end{matrix}$$

7



$$C_6H_5SCH_2CH_2\underset{\underset{O}{\|}}{C}CH_3$$

8

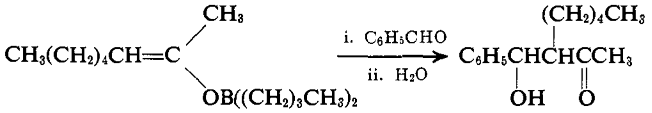


$$C_6H_5\underset{\underset{OH}{|}}{C}H\overset{\overset{CH_2SC_6H_5}{|}}{C}H\underset{\underset{O}{\|}}{C}CH_3$$

9

The treatment of the above new vinyloxyborane-type intermediate (**7**) with benzaldehyde in ether at room temperature, followed by hydrolysis, afforded the corresponding β-hydroxy ketone (**9**, 92.5%, oil, ir 3440, 1700 cm^{-1}; pmr (CCl_4) δ 1.97 (s, 3 H), 3.20 (d, 2 H), 2.9–3.4 (m, 2 H), 4.80–4.95 (m, 1 H), 7.1–7.4 (m, 10 H)).

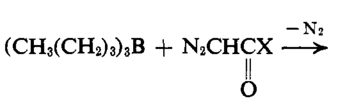
Similarly, it was found that the vinyloxyborane (**10**), prepared from tri-*n*-butylborane[3] and vinyl methyl ketone according to the method of Brown and Suzuki, *et al.*,[4] reacted with benzaldehyde to give diastereomeric β-hydroxy ketones **11a**, **11b** (3:1, separated with preparative tlc) in 91% yield (**11a**, oil, ir 3420, 1695 cm^{-1}; pmr (CCl_4) δ 0.6–1.8 (m, 11 H), 1.83 (s, 3 H), 2.70 (m, 1 H), 3.15 (s, 1 H), 4.70 (d, 1 H), 7.23 (s, 5 H); **11b**, oil, ir 3420, 1700 cm^{-1}; pmr (CCl_4) δ 0.6–1.8 (m, 11 H), 2.06 (s, 3 H), 2.73 (m, 1 H), 3.32 (s, 1 H), 4.56 (d, 1 H), 7.23 (s, 5 H)).



$$CH_3(CH_2)_4CH{=}C\begin{matrix}CH_3\\ OB((CH_2)_3CH_3)_2\end{matrix} \xrightarrow[\text{ii. } H_2O]{\text{i. } C_6H_5CHO} C_6H_5\underset{\underset{OH}{|}}{C}H\overset{\overset{(CH_2)_4CH_3}{|}}{C}H\underset{\underset{O}{\|}}{C}CH_3$$

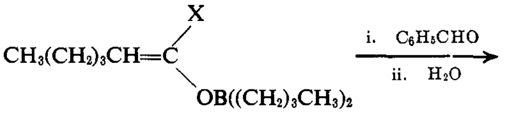
10 **11a, b**

Vinyloxyboranes can also be produced by an alternative pathway from trialkylborane and diazo ketone (**12a**) or ester (**12b**). This reaction was developed by Hooz and his coworkers[5] and the structure of the intermediate, vinyloxyborane, was confirmed by Pasto and Wojtkowski by means of nmr and uv spectra.[6] The vinyloxyboranes (**13a,b**) thus obtained were further treated with benzaldehyde in THF at room temperature for 10 min followed by hydrolysis to afford the expected products, β-hydroxy ketone (**14a**, 98%, oil, ir 3440, 1660 cm^{-1}; pmr (CCl_4) δ 0.3–2.0 (m, 9 H), 3.4–3.9 (m, 2 H), 4.6–4.9 (m, 1 H), 6.8–7.4 (m, 8 H), 7.5–8.0 (m, 2 H)) and β-hydroxy ester (**14b**, 75%, oil, ir 3450, 1710 cm^{-1}; pmr ($CDCl_3$) δ 0.6–1.6 (m, 9 H), 1.18 (t, 3 H), 2.5–2.9 (m, 1 H), 3.05 (broad s, 1 H), 4.15 (q, 2 H), 4.75 (d, 1 H), 7.25 (s, 5 H)).



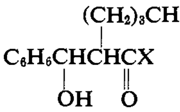
$$(CH_3(CH_2)_3)_3B + N_2CH\underset{\underset{O}{\|}}{C}X \xrightarrow{-N_2}$$

12a, X = C_6H_5
b, X = OC_2H_5



$$CH_3(CH_2)_3CH{=}C\begin{matrix}X\\ OB((CH_2)_3CH_3)_2\end{matrix} \xrightarrow[\text{ii. } H_2O]{\text{i. } C_6H_5CHO}$$

13a,b

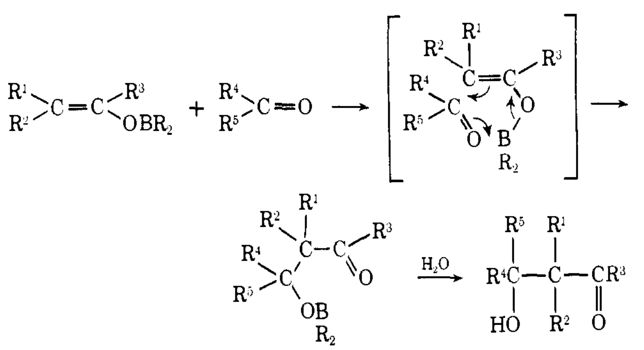


$$C_6H_5\underset{\underset{OH}{|}}{C}H\overset{\overset{(CH_2)_3CH_3}{|}}{C}H\underset{\underset{O}{\|}}{C}X$$

14a, b

From the above findings, we considered that vinyloxyboranes reacted with carbonyl compounds according to Scheme I. Vinyloxyboranes should be very useful intermediates in organic synthesis because of their high reactivity with carbonyl compounds[7] and the ease of their preparation in many ways.[6,8,9] Further work is in progress to explore the full synthetic potential of this new reaction.

Scheme I



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[3] Prepared from *n*-butylmagnesium bromide and boron trifluoride methyl etherate in ether.

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[6] D. J. Pasto and P. W. Wojtkowski, *Tetrahedron Lett.*, 215 (1970).

[7] We found that other aldehydes and ketones reacted with vinyloxyboranes in the same way (to be submitted for publication elsewhere).

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One-Proton Catalysis in the Deacetylation of Acetyl-α-chymotrypsin

Sir:

The rate of deacetylation of acetyl-α-chymotrypsin decreases linearly with the atom fraction of deuterium (n) in mixtures of protium and deuterium oxides (Table I, Figure 1) which shows that *one proton in the catalytic transition state* produces the solvent isotope effect $k_{H_2O}/k_{D_2O} = 2.4$. Mechanisms involving multiple proton switches are thus excluded and any suspicion is removed that the moderate solvent isotope effects[1] in these reactions might arise only from changes in protein or substrate hydration or other sources involving small alterations in the binding states of many protons.

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