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TRANSFER REACTIONS INVOLVING BORON. XXI
INTERMEDIATES FORMED IN THE ALKYLATION OF DIAZOCOMPOUNDS AND DIMETHYLSULFONIUM PHENACYLIDE VIA ORGANOBORANES

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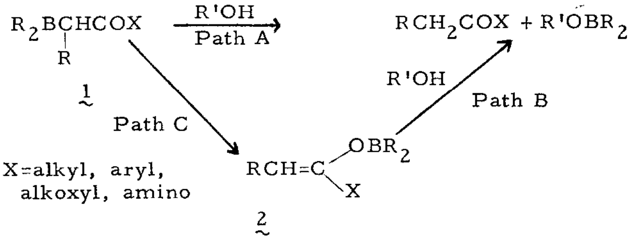
Numerous reports utilizing trialkylboranes for the alkylation of α-diazocarbonyl compounds (1), dimethylsulfuranylidene esters and amides (2), and α-halocarbonyl compounds (in the presence of base) (3) have appeared recently. These reports claim that β-ketoboranes of general structure 1 are the intermediates which undergo protonolysis to yield products (Path A). Our interest in the chemistry of substituted organoboranes (4) prompted us to attempt to prepare a β-ketoborane by utilizing these methods. Our studies to date of these reactions indicate that vinyloxyboranes 2 are the intermediates which undergo protonolysis (Path B) and not 1.



The reaction of tri-n-propylborane with diazoacetophenone in THF produces a mixture of 3 and 4[**] in nearly quantitative yield. Removal of the THF gave a viscous liquid

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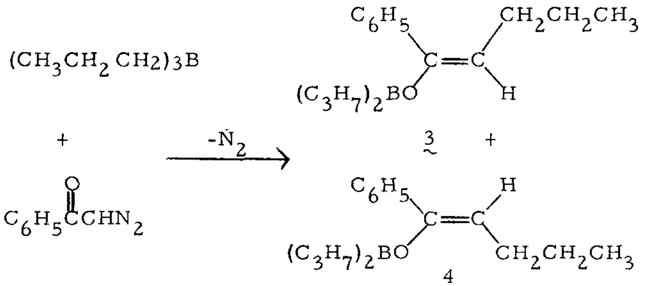
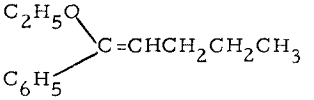
[**] The stereochemistry of 3 and 4 has been assigned using the correlation of vinyl hydrogen chemical shifts proposed by C. Pascual, J. Meier, and W. Simon, Helv. Chim. Acta, 49, 164 (1966).



(distillable in a molecular still, b. p. 75° at 0. 025-0. 05 mm)* which displayed no absorption in the carbonyl region of its infrared spectrum. The ^{11}B nmr spectrum displayed a single, broad peak at -52 ppm (relative to BF_3-etherate) characteristic of an alkaneborinate. The ^1H nmr spectrum displayed two triplets for the vinyl hydrogens of 3 and 4 at δ 5. 10 (J =7. 5H_z) and δ 5. 49 (J =7. 2Hz) of relative intensity 3:1, respectively. The remainder of the spectrum was in excellent agreement with the assigned structures. The UV spectrum (in ether) displayed a maximum at 249 nm compared to 250 nm for ethyl 1-phenyl-1-pentenyl ether, 5.



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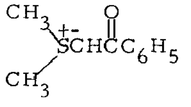

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Similarly, 4 (along with a trace of 3) can be slowly produced by refluxing dimethylsulfonium phenacylide, 6 (6), with tri-n-propylborane in THF.

The reaction of ethyl diazoacetate with tri-n-propylborane is slightly more complex in that both 7 and 8** are formed in a 9:1 ratio. The IR spectrum of the crude product displayed a peak of medium intensity at 1730 cm^{-1} (ester of 8). The ^{11}B nmr spectrum displayed a single peak at -53. 7 ppm. The ^1H nmr spectrum of the crude product displayed

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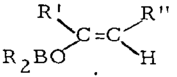
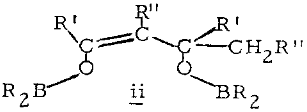
*Koster and Fenzl (5) have reported the preparation of vinyloxyboranes by treatment of ketones with trialkylboranes in an autoclave. These authors report that vinyloxyboranes of structure i undergo dimerization to ii at above 20°. We have not observed any tendency for dimerization in the systems similar to i we have prepared. Furthermore, the mechanism for Koster's dimerization is not clear. It seems more likely that ii is formed by a prior Lewis acid catalyzed ketol condensation, the β-hydroxyketone then reacting with the trialkylborane to give ii.



i



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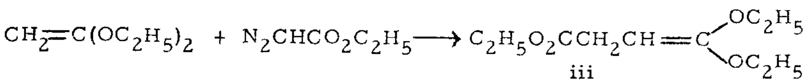
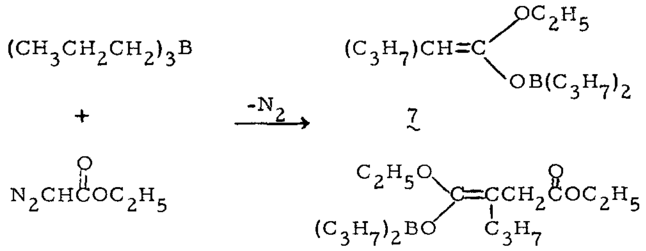
**The structure of 8 has not been demonstrated unambiguosly. The structure is assigned by analogy with the report of M. F. Dull and P. G. Abend (J. Amer. Chem. Soc., 81, 2588 (1959)) on the reaction of 1, 1-diethoxyethylene with ethyl diazoacetate to give ethyl 4, 4-diethoxy-3-butenoate (iii). The mechanism of formation of 8 has not been investigated.



$$CH_2{=}C(OC_2H_5)_2 + N_2CHCO_2C_2H_5 \longrightarrow C_2H_5O_2CCH_2CH{=}C(OC_2H_5)_2$$

iii



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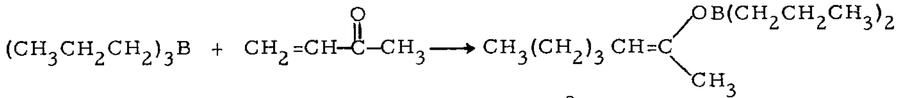
8

a complex multiplet centered at δ 4.0 for the $-OC\underline{H}_2CH_3$ and vinyl hydrogen of 7. Glpc analysis of the crude product showed no ethyl valerate or diethyl n-propylsuccinate; however, on hydrolysis both compounds were shown to be present and were isolated by preparative glpc and fully characterized.

The spectral properties of 3, 4, 7, and 8 compare favorably with the spectral properties we have measured for the vinyloxyborane 9 produced by reaction of methyl vinyl ketone with tri-n-propylborane (7) (^{11}B nmr, -53.4 ppm; ^{1}H nmr, δ 4.59 triplet (J=6.5**Hz**).



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It should be noted that our results do not preclude the intermediacy of a β-ketoborane. It is possible that an α-boryl derivative is the kinetically controlled product which then rearranges rapidly to the vinyloxyborane (Path C). In any case, the very rapid formation and intermediacy of the vinyloxyborane could explain the apparent inability of these reactions to proceed beyond the stage of transfering only one alkyl group from boron and the relatively facile protonolysis of the intermediate already noted (1, 2, 3). It will be necessary to prepare an authentic β-ketoborane to answer these questions. We are currently actively pursuing this problem.

References

1. (a) J. Hooz and S. Linke, J. Amer. Chem. Soc., **90**, 5936, 6891 (1968); (b) J. Hooz and D. M. Gunn, Chem. Commun., 139 (1969); (c) J. Hooz and D. M. Gunn, Tetrahedron Lett., 3455 (1969); (d) J. Hooz and D. M. Gunn, J. Amer. Chem. Soc., **91**, 6195 (1969).
2. J. J. Tufariello, L. T. C. Lee, and P. W. Wojtkowski, J. Amer. Chem. Soc, **89**, 6804 (1967).

3. (a) H. C. Brown, M. M. Rogic, M. W. Rathke, and G. W. Kabalka, *ibid.*, **90**, 818, 1911 (1968); (b) H. C. Brown, M. M. Rogic, and M. W. Rathke, *ibid.*, **90**, 6218 (1968); (c) H. C. Brown and M. M. Rogic, *ibid.*, **91**, 2146, 3942 (1969); (d) H. C. Brown, M. M. Rogic, H. Nambu, and M. W. Rathke, *ibid.*, **91**, 2147 (1969); (e) H. C. Brown, M. M. Rogic, M. W. Rathke, and G. W. Kabalka, *ibid.*, **91**, 2150 (1969).

4. D. J. Pasto, V. Balasubramaniyan, and P. W. Wojtkowski, *Inorg. Chem.*, **8**, 549 (1969); and previous articles in this series.

5. R. Köster and W. Fenzl, *Angew. Chemie, Int. Ed.*, **7**, 735 (1968).

6. B. M. Trost, *J. Amer. Chem. Soc.*, **89**, 138 (1967).

7. A. Suzuki, A. Arase, H. Matsumoto, M. Itoh, H. C. Brown, M. M. Rogic, and M. W. Rathke, *ibid.*, **89**, 5708 (1967).