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THE REACTION OF B-VINYLIC- AND B-ALKYL-9-BORABICYCLO[3.3.1]NONANE DERIVATIVES WITH ETHYL DIAZOACETATE AND DIAZOACETONE

J. Hooz and D. M. Gunn
Department of Chemistry, University of Alberta, Edmonton, Alberta, Canada

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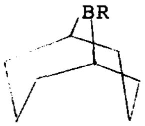
Numerous studies have attested to the synthetic value of trialkylboranes as intermediates for the alklation of ylides[1], carbanions[2], and diazo compounds[3], although a problem inherent in such systems (illustrated for diazoalkanes) is that but one alkyl group of R_3B is constructively utilized.

$$R_3B + N_2CHX \longrightarrow \longrightarrow RCH_2X$$

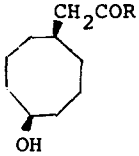
$$X = COCH_3,\ COC_6H_5,\ CN,\ COOC_2H_5,\ CO(CH_2)_nCOCHN_2 \text{ where } n = 2,3.$$

Attempts to circumvent this difficulty in the carbonylation reaction[4] have prompted studies of the migratory aptitudes of various alkyl groups of mixed organoboranes[5] (R_2BR'). Recently, this problem has been solved by using 9-borabicyclo[3.3.1]nonane (9-BBN, 1a) as a hydroborating agent[6] and establishing that for the carbonylation process the resultant B-alkyl-9-borabicyclo [3.3.1]nonane (B-R-9BBN, 1b) derivatives undergo preferential B-alkyl[4,6c]



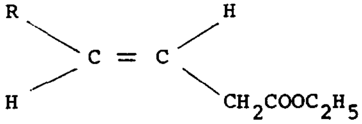
1a: R = H

b: R = alkyl, cycloalkyl



2a: R = OC_2H_5

b: R = CH_3



3a: R = C_6H_5

b: R = n-C_4H_9

(rather than B-cyclooctyl) bond migration. As part of our continuing interest in this area[3], we report our preliminary results on the reactions of diazo compounds with B-substituted-9-BBN derivatives which contrast markedly with the results of carbonylation studies[4].

Hydroboration of phenylacetylene with 9-BBN[7a], followed by the addition of ethyl diazoacetate[7b] (rapid nitrogen liberation) and subsequent processing with alkaline hydrogen peroxide, afforded a total ester yield[7c] of 65%. The ratio of ethyl(cis-5-hydroxycyclooctyl)acetate (2a)[7d] to the desired trans-β,γ-unsaturated ester (3a)[7e] was 1.6. Similar treatment of 1-hexyne yielded 75% of ester products in which the ratio of 2a:3b = 2.6. Although the formation of β,γ-unsaturated ester is sterospecific, the predominance of B-cyclooctyl bond migration permitted a maximum yield (3a) of 25%, and 21% (3b), respectively.

B-Alkyl-9-BBN derivatives (1b), on the other hand, react with diazoacetone and ethyl diazoacetate, respectively, to give products derived from exclusive B-cyclooctyl bond migration. Thus, oxidation of the reaction mixture derived from B-hexyl-9-BBN (1b, R=n-C_6H_{13}) with diazoacetone[7b] gave cis-1,5-cyclooctanediol (20%, from unhomologated organoborane), 1-hexanol[7f] (100%) and ketone[7d] 2b (80%). 2-Nonanone, the anticipated product of B-hexyl bond migration, could not be detected by glpc analysis[7g]. In a similar manner, ethyl diazoacetate reacts with 1b (R=n-C_6H_{13}) to provide, after oxidation, cis-1,5-cyclooctanediol (23%), 1-hexanol (100%), and ester 2a (77%). The latter was isolated as the acetate (61%) by direct fractional distillation of the crude acetylated (acetic anhydride-pyridine) reaction mixture. Ethyl octanoate could not be detected (glpc)[7g].

Although the unfavorable B-cyclooctyl bond migration mitigates against the effective employment of alkyl moieties in this reaction, it should be noted that the present results do fortuitously provide a facile, stereospecific synthesis of cis-functionalized 1,5-cyclooctanol derivatives in good yields. Efforts thus far have been directed at the practical applications of this reaction; current investigations will hopefully provide further insight into the reasons for the different behavior of B-R-9BBN compounds toward diazo substrates as contrasted with the carbonylation reaction[8].

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7. (a) Conducted according to the method outlined in ref. 5b; (b) From 7-14% excess of organoborane was employed in all reactions; (c) Yields of ester and ketone are based on diazo compound and were established by glpc; (d) Gross structure secured by correct compositional analysis and compatible spectral data. Stereochemistry is tentatively assigned by analogy to numerous previous demonstrations (cf. ref. 4) of retention of configuration at the carbon atom undergoing reaction; (e) Stereochemistry assigned on

the basis of IR absorption at 968cm^{-1} (trans-CH=CH-); (f) Yield based on 1b (R=n-C_6H_{13}); (g) We could have detected <1% under our analytical conditions.

8. In a recent series of communications [(a) H. C. Brown, E. F. Knights, and R. A. Coleman, J. Am. Chem. Soc., **91**, 2144 (1969); (b) H. C. Brown and M. M. Rogić, ibid., **91**, 2146 (1969); (c) H. C. Brown, M. M. Rogić, H. Nambu, and M. W. Rathke, ibid., **91**, 2147 (1969)] it has been demonstrated that B-R-9-BBN derivatives may be very advantageously employed for the alkylation of α-halocarbanions as well as in the carbonylation reaction. Brief mention is also made (ref. 8b) of the tentative identification of compound 2a (80% yield), from reaction of ethyl diazoacetate with B-n-butyl-9-BBN, a result in excellent accord with the present study.