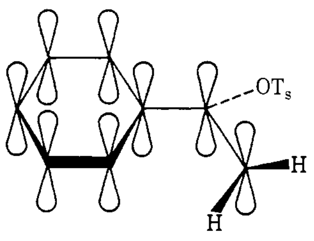
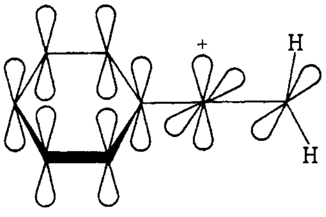
1-chloro-1-phenylethane to that of 2-chloropropane is 5000.[8] Accordingly the ability of a phenyl ring to stabilize a vinyl cation is shown to be less than that for a saturated cation. This result may be in part a consequence of the breaking of the conjugation of the vinyl p orbitals with those of the benzene ring in going from the ground state **1** to the transition state **2**. Grob has suggested the operation of similar effects in the solvolysis of bromides corresponding to **1** and of allylic vinyl bromides.[2,3]



1



2

Finally, from the ratio of the solvolysis rates of *cis*-2-buten-2-yl brosylate and cyclohexenyl brosylate (≥ 270) the predicted[9] preference for a linear over a bent vinyl cation is demonstrated. The absence of reactivity in 1-cyclohexenyl brosylate is analogous to that in phenyl tosylate[10a] and triflate.[10b] The phenyl data suggest that a *cis*-2-buten-2-yl to 1-cyclohexenyl rate ratio may be higher than the minimum of ~270 observed in our study, where no measurable reaction of 1-cyclohexenyl brosylate was observed.

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(8) Derived from the ratio of rates of *t*-butyl chloride and 1-chloro-1-phenylethane solvolyses at 50°, 80% aqueous ethanol, ~1, and isopropyl bromide and *t*-butyl bromide at 55°, 80% aqueous ethanol, ≃ 5000: A. Streitwieser, "Solvolytic Displacement Reactions," McGraw-Hill Book Co., Inc., New York, N. Y., 1963, pp 43 and 44.

(9) (a) P. E. Peterson and R. J. Kamat, *J. Am. Chem. Soc.*, **88**, 3152 (1966); (b) P. E. Peterson and R. J. Kamat, *ibid.*, **91**, 4521 (1969); (c) *cf.* R. Sustman, J. E. Williams, M. J. S. Dewar, L. C. Allen, and P. von R. Schleyer, *ibid.*, **91**, 5350 (1969).

(10) (a) J. D. Roberts and V. C. Chambers, *ibid.*, **73**, 5034 (1951); (b) T. M. Su, W. F. Sliwinski, and P. von R. Schleyer, *ibid.*, **91**, 5386 (1969).

(11) The award of a National Science Foundation Graduate Traineeship (1966–1969) is gratefully acknowledged by J. M. I.

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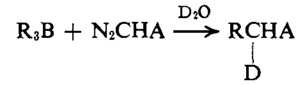
The Reaction of Organoboranes with Diazo Esters and Diazo Ketones in the Presence of Deuterium Oxide. A New Synthesis of α-Deuterio- and α,α-Dideuterio Esters and Ketones

Sir:

The facile alkylation of functionally substituted diazoalkanes with trialkylboranes (available from olefins *via* hydroboration[1]) affords a convenient synthesis of homologated nitriles,[2] esters,[2] ketones,[3] and diketones[4] (1) where A = CN, $COOC_2H_5$, $COCH_3$, COC_6H_5, and $CO(CH_2)_nCOCHN_2$, $n = 2, 3$.

$$R_3B + N_2CHA \xrightarrow{-N_2} \xrightarrow{\text{hydrolysis}} RCH_2A \qquad (1)$$

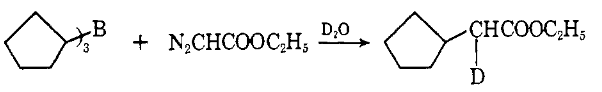
The observation that the intermediate functionalized organoborane underwent rapid cleavage by water[2] suggested the possibility[5] of specific deuterium incorporation by employing deuterium oxide as the hydrolytic medium. We wish to report that diazo esters and diazo ketones, such as ethyl diazoacetate, diazoacetone, and diazoacetophenone, react with organoboranes in the presence of deuterium oxide to produce high yields of site-specific monodeuterated esters and ketones with high isotopic purity (2). Consequently, this development provides a simple procedure for the synthesis of homologated monodeuterated derivatives unencumbered by the usual problems (polydeuteration, self-condensation) encountered in typical acid- or base-catalyzed exchange processes.[6]



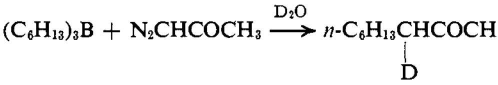
$$R_3B + N_2CHA \xrightarrow{D_2O} \underset{\displaystyle D}{\underset{|}{RCHA}} \qquad (2)$$

$A = COOC_2H_5, COCH_3, COC_6H_5$

Tricyclopentylborane, in the presence of deuterium oxide, reacts with ethyl diazoacetate to produce a 97% yield of ethyl α-d_1-cyclopentylacetate with virtually quantitative incorporation of one deuterium atom (3).



The synthesis of a methylene-monodeuterated ketone is exemplified by the conversion of trihexylborane to 2-nonanone-3-d_1 in 99% yield (4).



$$(C_6H_{13})_3B + N_2CHCOCH_3 \xrightarrow{D_2O} n\text{-}C_6H_{13}\underset{\displaystyle D}{\underset{|}{C}}HCOCH_3 \qquad (4)$$

Dideuterio derivatives may also be prepared by a simple extension of this methodology. Diazoacetone-d_1 and deuteriodiazoacetic ester are readily available

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(1) (a) H. C. Brown, "Hydroboration," W. A. Benjamin, Inc., New York, N. Y., 1962; (b) G. Zweifel and H. C. Brown, *Org. Reactions*, **13**, 1 (1963).

(2) J. Hooz and S. Linke, *J. Amer. Chem. Soc.*, **90**, 6891 (1968).

(3) J. Hooz and S. Linke, *ibid.*, **90**, 5936 (1968).

(4) J. Hooz and D. M. Gunn, *Chem. Commun.*, 139 (1969).

(5) It should be emphasized that the mechanism suggested[2] has been employed purely as a working hypothesis, and has proven helpful in designing new experiments. However, our main efforts have been directed at the practical synthetic aspects of this reaction, and the suggested mechanism should not be regarded as firmly established.

(6) (a) H. Budzikiewicz, C. Djerassi, and D. H. Williams, "Structure Elucidation of Natural Products by Mass Spectrometry, Alkaloids," Vol. I, Holden-Day, Inc., San Francisco, Calif., 1964, Chapter 2; (b) A. Murray, III, and D. L. Williams, "Organic Syntheses with Isotopes, Part II," Interscience Publishers, Inc., New York, N. Y., 1958; (c) H. O. House, "Modern Synthetic Reactions," W. A. Benjamin, Inc., New York, N. Y., 1965, Chapter 7.

Table I. Formation of Deuterated Esters and Ketones by the Reaction of Diazo Derivatives with Organoboranes in the Presence of Deuterium Oxide

Olefin[a]	Diazo compound	Product	Yield, %[b]	Deuterium, %[c] d_1	Deuterium, %[c] d_2
1-Hexene	$N_2CHCOOC_2H_5$	Ethyl 2-deuteriooctanoate	98	100[d,e]	
Cyclopentene	$N_2CHCOOC_2H_5$	Ethyl α-d_1-cyclopentylacetate	97	100[d]	
1-Hexene	$N_2CHCOCH_3$	3-Deuterio-2-nonanone	99	94[d]	
1-Hexene	$N_2CHCOC_6H_5$	α-Deuterioheptyl phenyl ketone	100	95[d]	
1-Hexene	$N_2CDCOCH_3$	3,3-Dideuterio-2-nonanone	100		96[d]
1-Hexene	$N_2CDCOOC_2H_5$	Ethyl 2,2-dideuteriooctanoate	98		100[d,e]

[a] Each olefin was converted to the corresponding trialkylborane according to the method described in ref 1. The mole ratio of organoborane:diazo compound:deuterium oxide was 1.5:1:10, although we have not established that these excesses are necessary. Deuterium oxide, 99.7%, was obtained from Columbia Organic Chemicals Co., Inc. [b] Based on diazo compound and established by glpc analysis. [c] Established by mass spectroscopy (accurate to ±2%), and 100-MHz nmr spectroscopy (*ca.* ±4%). [d] By nmr spectroscopy. [e] By mass spectroscopy.

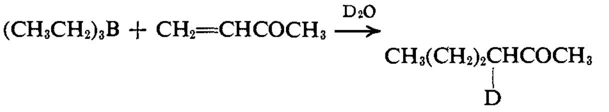
materials.[7] Utilization of these reagents in this synthesis providesa unique and convenient route to dideuteriomethylene ketones and α,α-dideuterio esters. For example, treatment of a mixture of trihexylborane and deuterium oxide with diazoacetone-d_1 produced an essentially quantitative yield of 3,3-dideuterio-2-nonanone (5). The results are summarized in Table I.

$$(C_6H_{13})_3B + N_2CDCOCH_3 \xrightarrow{D_2O} n\text{-}C_6H_{13}CD_2COCH_3 \qquad (5)$$

The procedure illustrated for the preparation of ethyl 2-deuteriooctanoate is representative. A solution of trihexylborane (60 mmol) in tetrahydrofuran was prepared by the hydroboration[1] of 1-hexene. To the magnetically stirred solution was added 7.2 ml (400 mmol) of deuterium oxide, followed by the dropwise addition (2 hr) of a solution of 4.56 g (40 mmol) of ethyl diazoacetate in 25 ml of tetrahydrofuran. The reaction temperature was maintained below 20° by means of an ice bath. After stirring for an additional hour at 25°, the nitrogen evolution was quantitative. At this stage, glpc analysis indicated a 98% yield of product. The solution was concentrated, D_2O (3 ml) was added, and the mixture was extracted with pentane (three 20-ml portions). The extract was dried (Na_2SO_4), and the residue that remained after removal of solvent was distilled to afford 5.32 g (77%) of ethyl 2-deuteriooctanoate, bp 95–97° (17 mm), n_D^{25} 1.4158, spectroscopically identical with a sample independently synthesized by the reaction of deuteriodiazoacetic ester with trihexylborane in the presence of H_2O.

It has recently been demonstrated that trialkylboranes react with methyl vinyl ketone,[8] cyclic α,β-unsaturated ketones,[9] acrolein,[10] and 2-bromo- and 2-methylacrolein.[11] These reactions produce intermediates, presumably enol borinates, which are also readily cleaved by water to yield the corresponding alkylated carbonyl derivatives.

We examined the reaction of methyl vinyl ketone with triethylborane in the presence of deuterium oxide. A quantitative yield of 3-deuterio-2-hexanone (93% d_1 by nmr) was obtained (6). This result is in keeping with



$$(CH_3CH_2)_3B + CH_2{=}CHCOCH_3 \xrightarrow{D_2O} CH_3(CH_2)_2\underset{\displaystyle D}{\underset{|}{C}}HCOCH_3 \qquad (6)$$

the suggestion of a vinyloxyborane intermediate,[10] and by analogy with mechanistically related processes should render readily available α-deuterio-α-alkylated cyclic ketones, α-deuterio aldehydes, α-deuterio-α-bromo aldehydes, and α-deuterio-α-methylated aldehydes, materials which at present would be accessible with considerable difficulty.

Acknowledgment. We wish to thank the National Research Council of Canada for financial support of this work.

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(7) Diazoacetone-d_1 was prepared by the reaction of dideuteriodiazomethane with acetyl chloride. Deuteriodiazoacetic ester was synthesized by the heterogeneous exchange (D_2O–ether) of ethyl diazoacetate using potassium carbonate as catalyst, followed by extraction with methylene chloride. We wish to thank Professor S. Masamune and Mr. K. Hojo for kindly providing the details of this efficient exchange procedure.

(8) A. Suzuki, A. Arase, H. Matsumoto, M. Itah, H. C. Brown, M. M. Rogić, and M. W. Rathke, *J. Amer. Chem. Soc.*, **89**, 5708 (1967).

(9) H. C. Brown, M. W. Rathke, G. W. Kabalka, and M. M. Rogić, *ibid.*, 90, 4166 (1968).

(10) H. C. Brown, M. M. Rogić, M. W. Rathke, and G. W. Kabalka, *ibid.*, **89**, 5709 (1967).

(11) H. C. Brown, G. W. Kabalka, M. W. Rathke, and M. M. Rogić, *ibid.*, 90, 4165 (1968).

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Vibrational Quenching of Triplet States

Sir:

During the course of triplet counting experiments with *cis*-piperylene,[1] we observed that 1,4-cyclohexadiene (D) reduced without chemical reaction the quantum yield for *cis–trans* isomerization of piperylene using acetophenone (**1**) or β-chloropropiophenone (**2**) as sensitizers.

The triplet energy of 1,4-cyclohexadiene can be estimated at >80 kcal[2] while the triplet energy of β-chloro-

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(1) A. A. Lamola and G. S. Hammond, *J. Chem. Phys.*, **43**, 2129 (1965). All experiments were run using 0.01 *M* sensitizer in benzene and variable concentrations of piperylene and D.

(2) The triplet energy of planar ethylene was measured by Evans to be 82 kcal/mole, and he reports that alkyl substituents had little effect on the triplet energy levels of unsaturated compounds.[3] The unconju-