occurring. In such a complex, a secondary process, namely isomerization to *trans*-propenylbenzene, occurs. The free olefin may compete for ligand positions in separate or mixed sets of complex ions. However, it is required that the nature of the olefin complex be different from that of the cyclopropane complex as the products of each reactant are different.

When the ratio of palladium(II) chloride to phenylcyclopropane is 4:1, the yield of propiophenone is approximately 95% after 2 hr. No phenylacetone or *trans*-propenylbenzene is observed. Therefore, the oxidative cleavage reaction of phenylcyclopropane is enhanced, and this fact is consistent with the expected mass law effect on the formation of a complex ion containing one cyclopropane moiety.

Studies of the effect of structure are being undertaken in addition to experiments designed to elucidate further the structures of postulated intermediates. Deuterium-labeling experiments are being carried out in order to determine the origin and ultimate destination of the postulated hydride shifts in both the oxidation and isomerization reaction.

(8) Sinclair Oil Fellow, 1967–1968.

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The Alkylation of Diazoacetonitrile and Ethyl Diazoacetate by Means of Organoboranes. A New Synthesis of Nitriles and Esters

Sir:

We wish to report that trialkylboranes react with diazoacetonitrile and ethyl diazoacetate, respectively, with expulsion of nitrogen and provide, after hydrolysis, novel and facile routes to the corresponding homologated nitriles (1) and ethyl esters[1] (2). In concert

$$R_3B + N_2CHCN \xrightarrow{-N_2} \xrightarrow{\text{hydrolysis}} RCH_2CN \quad (1)$$

$$R_3B + N_2CHCOOC_2H_5 \xrightarrow{-N_2} \xrightarrow{\text{hydrolysis}} RCH_2COOC_2H_5 \quad (2)$$

with hydroboration, these reactions permit the over-all conversion of olefins into two-carbon-atom chain-extended derivatives possessing useful functionality.[2]

These reactions probably proceed by a mechanism analogous to that described earlier.[2] Both processes, however, occur with varying efficiency, and the following salient features have been noted.

Nitriles. The reactions of organoboranes derived from terminal olefins as well as cyclopentene proceed rapidly (as evidenced by complete nitrogen evolution) at ice-bath temperatures. Yields are excellent (93–100%). The product obtained from the organoborane derived from 1-hexene contained 95% octanenitrile and 5% 3-methylheptanenitrile. Since hydroboration of monosubstituted terminal olefins produces approximately 94% primary and 6% secondary alkyl groups,[3] it is apparent that in this reaction the primary and secondary alkyl groups migrate with equal facility.

More sterically hindered trialkylboranes react somewhat more sluggishly and give lower yields.[4] The results are summarized in Table I. Moreover, that triarylboranes also undergo this reaction was demonstrated by the conversion of triphenylborane to phenylacetonitrile (52%).

Table I. Functionalization of Olefins into Nitriles by Reaction of the Corresponding Trialkylboranes[a] with Diazoacetonitrile

Olefin	Product,[b] %	Yield,[c] %
1-Hexene	Octanenitrile, 95 3-Methylheptanenitrile, 5	100
1-Heptene	Nonanenitrile, 93[d]	93
Cyclopentene	Cyclopentylacetonitrile	99
2-Methyl-1-pentene	4-Methylheptanenitrile	97
trans-3-Hexene[e]	3-Ethylhexanenitrile	54

[a] Hydroboration was conducted such that complete conversion to R_3B was ensured.[3] [b] Structures were secured by direct comparison, comparison with literature constants, or acceptable compositional analyses and compatible spectral data. [c] By glpc analysis. Yield based on the utilization of one alkyl group of R_3B. A 50% excess of diazoacetonitrile was employed although we have not yet determined that this amount is necessary. A 1:1 molar ratio gives somewhat lower yields.[4] [d] Approximately 5% of another product, presumably 3-methyloctanenitrile, was also detected. [e] Reaction was conducted at 25° for 2 hr followed by a 4-hr reflux.

The method illustrated for the conversion of cyclopentene to cyclopentylacetonitrile is representative. To an ice-cooled, magnetically stirred solution of tricyclopentylborane (prepared in the usual manner[3] from cyclopentene (63 mmol) in 15 ml of tetrahydrofuran and a solution of borane (20 mmol) in tetrahydrofuran) was added a solution of diazoacetonitrile[5] (30 mmol) in 15 ml of tetrahydrofuran over a period of 30 min. The solution was stirred for 2 hr at room temperature and then cooled in an ice bath, and 25 ml of a 3 *N* potassium hydroxide solution[6] was added. The reaction mixture was stirred at room temperature an additional 0.5 hr. After the addition of brine solution, glpc analysis of the organic extract indicated a 99% yield of cyclopentylacetonitrile. Evaporation of solvent and distillation of the residue afforded 1.76 g (81%) of cyclopentylacetonitrile, bp 85–86° (16 mm).

Esters. As in the nitrile synthesis, organoboranes derived from 1-alkenes liberate nitrogen smoothly at ice-bath temperature on treatment with ethyl diazoacetate. However, the organoborane–diazoacetic ester reaction appears to be considerably more sensitive to steric factors, as evidenced by the variation of yield (40–83%) with olefin structure.[4] Moreover, the tri-

(1) For alternative ester syntheses based on organoborane homologation, see: J. J. Tufariello, L. T. C. Lee, and P. Wojtkowski, *J. Am. Chem. Soc.*, **89**, 6804 (1967); H. C. Brown, M. M. Rogić, M. W. Rathke, and G. W. Kabalka, *ibid.*, **90**, 818, 1911 (1968).

(2) We have previously reported the functionalization of olefins into ketones *via* hydroboration; *cf.* J. Hooz and S. Linke, *ibid.*, **90**, 5936 (1968).

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

(4) A side reaction takes place which consumes diazo compound. We are investigating this in greater detail in an attempt to circumvent this difficulty.

(5) *Caution!* Although no difficulties were ever encountered in numerous reactions of this substance with a variety of organoboranes, the isolation of this diazo compound is occasionally fraught with capricious explosions. It is recommended that adequate safety precautions be observed in preparing this material. *Cf.* S. H. Harper and K. C. Sleep, *J. Sci. Food Agr.*, **6**, 116 (1955), and T. Curtius, *Ber.*, **31**, 2489 (1898).

(6) Subsequent experiments have indicated that the intermediate α-borylnitrile may be conveniently hydrolyzed by water in the absence of base, as described below for the ester synthesis.

alkylborane derived from 1-hexene gave rise exclusively to ethyl octanoate; no product corresponding to reaction of the 2-hexyl groups was observed.[7] Reactions with hindered organoboranes require a reflux period in order to complete the nitrogen evolution. The results are summarized in Table II.

Table II. Conversion of Olefins into Ethyl Esters by Treatment of the Corresponding Trialkylboranes with Ethyl Diazoacetate

Olefin	Product[a,4]	Yield,[b] %
1-Hexene	Ethyl octanoate	83
1-Octene	Ethyl decanoate	78
Cyclopentene[c]	Ethyl cyclopentylacetate	58
2-Methyl-1-pentene[d]	Ethyl 4-methylheptanoate	40

[a] Structures were proven by direct comparison or satisfactory elemental analyses. [b] By glpc analysis. Yield based on the consumption of one alkyl group of R_3B using a 1:1 molar ratio of ethyl diazoacetate to R_3B. [c] An additional 30-min reflux period was required for complete nitrogen evolution. [d] An additional 2-hr reflux period was necessary to liberate nitrogen completely.

The procedure for the functionalization of 1-hexene into ethyl octanoate is representative. A solution of ethyl diazoacetate (20 mmol) in 15 ml of tetrahydrofuran was added, over a period of 20 min, to an ice-cooled, magnetically stirred solution of trihexylborane[3] (20 mmol) in tetrahydrofuran. The solution was kept at ice-bath temperatures for an additional 30 min, then stirred at room temperature for 2 hr. The ice bath was replaced, and water (5 ml) was added dropwise (exothermic). The reaction mixture was refluxed for 1 hr. Glpc analysis indicated an 83% yield of ethyl octanoate. The solution was concentrated, then poured into water and extracted with pentane. Distillation of the dried (Drierite) organic extract yielded 2.40 g (70%) of ethyl octanoate, identical in all respects with an authentic sample.

The reactions of organoboranes with functionally substituted diazoalkanes thus appear to possess very broad synthetic potential, and we are continuing to pursue these possibilities.

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(7) We could have detected <1% ethyl 3-methylheptanoate under our analytical conditions.

(8) Postdoctoral Research Fellow, 1967–1968.

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Catalysis of Hydrolysis of N-Benzyl-3-cyanopyridinium Bromide. A Model for the Nitrilase Reaction[1]

Sir:

A substantial variety of plant and bacterial species are known to possess enzymes, nitrilases, capable of catalyzing the hydrolysis of a variety of organic nitriles to the corresponding carboxylic acids.[2,3] In each case, reactions catalyzed by these enzymes are susceptible to inhibition by reagents which react with thiol groups of the enzymes. This behavior has led to the suggestion that thiol groups of the enzymes may function as nucleophilic catalysts in these reactions.[2] Among the various nitriles acted upon by these enzymes is 3-cyanopyridine.[2b] An investigation of the catalysis of hydrolysis of a related nitrile, N-benzyl-3-cyanopyridinium ion, by a simple thiol, mercaptoethanol, reveals a substantial number of parallels between the mercaptoethanol-promoted reaction and the enzyme-promoted reactions. Since the nonenzymatic reaction mechanism may shed substantial light on that of the enzymatic reactions, we are prompted to report our findings at this time.

Catalysis of hydrolysis of N-benzyl-3-cyanopyridinium bromide by mercaptoethanol is characterized by the following. First, under neutral or slightly acidic conditions, the predominant reaction product is the corresponding amide. Under conditions more acidic than pH 3 appreciable amounts of the corresponding acid are formed as well. Second, first-order rate constants for disappearance of the nitrile at fixed concentrations of mercaptoethanol exhibit a rate maximum near pH 7. Third, between pH 3.6 and pH 8.9 first-order rate constants for disappearance of the nitrile exhibit saturation with respect to mercaptoethanol concentration. This point and that developed just above are illustrated by the collection of rate constants for this reaction in Table I. Fourth, at the values of pH near 10 excess mercaptoethanol causes inhibition of the reaction.

Table I. First-Order Rate Constants for the Disappearance of N-Benzyl-3-cyanopyridinum Bromide in the Presence of Mercaptoethanol in Aqueous Solution at 25° and Ionic Strength 0.60[a]

	Mercaptoethanol concentration, M		
pH	0.04	0.08	0.15
3.63			0.061
3.88			0.112
4.28	0.075	0.154	0.277
4.90	0.25	0.56	1.03
5.45	1.05	2.09	4.04
6.26	3.77	6.28	8.63
6.54	3.50	6.90	9.20
7.00	4.76	7.15	8.20
7.31	4.95	5.96	5.8
7.88	4.29	5.32	5.6
7.46	4.66	6.33	7.6
7.64	3.84	5.45	6.55
7.66	3.02	3.83	
7.85	2.65	3.90	4.57
8.25	2.63	3.52	4.10
8.55	2.43	3.23	4.06
8.89	2.06	2.58	

[a] Rate constants in units of min^{-1}, multiplied by 10^2. The reaction was followed spectrophotometrically at 332 mμ by the periodic withdrawal of aliquots of the reaction mixtures and addition of these to a 0.1 M solution of mercaptoethanol, at pH 10.3 ± 0.1. Under these conditions, only the nitrile adds mercaptoethanol to form a 332-mμ chromophore.

(1) Supported by Grant GE 3277 from the National Science Foundation and by Grant AM08232-05 from the National Institutes of Health. Publication No. 1626 from the Department of Chemistry, Indiana University.

(2) (a) K. V. Thimann and S. Mahadevan, *Arch. Biochem. Biophys.*, 105, 133 (1964); (b) S. Mahadevan and K. V. Thimann, *ibid.*, 107, 62 (1964).

(3) R. H. Hook and W. C. Robinson, *J. Biol. Chem.*, 239, 4263, 4257 (1964).