formation. Primary alcohols form unsymmetrical ethers in the absence of structural features increasing the acidity of β protons.

(12) Fellow, National Institutes of Health, 1967–1971.

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The Reaction of Representative Organic Azides with Triethylborane. A New Route to Secondary Amines

Sir:

A wide variety of organic azides react readily with triethylborane in refluxing xylene. Nitrogen is evolved and an intermediate is produced which undergoes facile methanolysis or hydrolysis to the corresponding secondary amine (eq 1). This reaction opens up a new

$$RN_3 + BEt_3 \xrightarrow{\Delta} REtNBEt_2$$
$$\downarrow CH_3OH$$
$$REtNH + Et_2BOCH_3 \qquad (1)$$
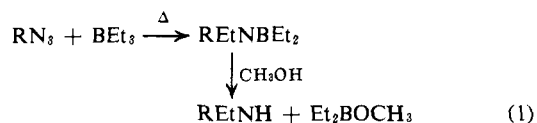
route to secondary amines.

Trialkylboranes react readily with carbenes and carbenoid intermediates.[1] Nitrenes are isoelectronic with carbenes, but no reaction between organoboranes and nitrenes has yet been described. Consequently, we decided to explore this possibility.

Nitrenes are produced in the thermal decomposition of organic azides[2] (eq 2). Such a nitrene might be expected

$$RN_3 \xrightarrow{\Delta} R\ddot{N}: + N_2 \qquad (2)$$
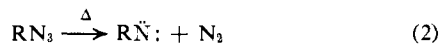
to react with an organoborane with migration of an alkyl group from carbon to nitrogen (eq 3). Such

$$R\ddot{N}: + BR'_3 \longrightarrow RR'NBR'_2 \qquad (3)$$

intermediates are known to undergo ready solvolysis to the corresponding secondary amines[3] (eq 4).

$$RR'NBR'_2 + CH_3OH \longrightarrow RR'NH + R'_2BOCH_3 \qquad (4)$$

Accordingly, a 1.0 *M* solution of triethylborane in tetrahydrofuran (THF) was heated under nitrogen with an equimolar quantity of *n*-butyl azide in an autoclave at 170°. After 3 hr the reaction mixture was oxidized with 30% hydrogen peroxide and 3 *M* sodium hydroxide to destroy residual organoborane. Analysis of the dried extract by glpc indicated a 55% yield of *n*-butylethylamine.

This result was encouraging. However, it would be far more convenient if the reaction could be carried out

at atmospheric pressure in a suitable high boiling solvent. To our surprise, even solvents boiling in the range of 135° were satisfactory. We finally selected xylene as a convenient solvent for the reaction.

n-Butyl azide proved to be quite stable in this solvent at reflux. Thus no significant nitrogen evolution was observed over 15 hr. However, the addition of an equimolar quantity of triethylborane to the refluxing solution of *n*-butyl azide resulted in a relatively rapid evolution of gas. Over a period of 6 hr 1 mol equiv of the gas, presumably nitrogen, was given off. Hydrolysis of the reaction mixture gave a 72% yield of *n*-butylethylamine.

Clearly the reaction does not involve an initial decomposition of the azide into the nitrene and nitrogen (eq 1). The rate of evolution of nitrogen follows second-order kinetics. The results, therefore, are in better agreement with a mechanism involving reversible coordination of the azide with triethylborane (eq 5), followed by loss of nitrogen from the intermediate (eq 6), with subsequent (or concurrent) migration of the ethyl group from boron to nitrogen (eq 7). Solvolysis

$$R-\bar{N}-\overset{+}{N}{\equiv}N + Et_3B \rightleftharpoons R-N-\bar{B}Et_3 \qquad (5)$$
$$\qquad\qquad\qquad\qquad\qquad |$$
$$\qquad\qquad\qquad\qquad {}_{+}N{\equiv}N$$

$$R-N-\bar{B}Et_3 \longrightarrow R-\overset{+}{N}-\bar{B}Et_3 + N_2 \qquad (6)$$
$$|$$
$${}_{+}N{\equiv}N$$

$$\qquad\qquad\qquad\qquad\qquad\qquad Et$$
$$\qquad\qquad\qquad\qquad\qquad\qquad |$$
$$R-\overset{+}{N}-\bar{B}Et_3 \longrightarrow R-N-BEt_2 \qquad (7)$$

produces the corresponding secondary amine (eq 4).

Phenyl azide and several representative alkyl azides were examined with triethylborane. The reaction rates for the more hindered azides were somewhat slower. However, all gave comparable yields, 72–80%, of the corresponding secondary amine. The results are summarized in Table I.

Table I. The Reaction of Representative Organic Azides with Triethylborane

Organic azide[a] RN$_3$	Time, hr	Product[b]	Yield,[c] %
n-Butyl	6	*n*-Butylethylamine	72
Isobutyl	6	Isobutylethylamine	78
sec-Butyl	24	*sec*-Butylethylamine	80
Cyclopentyl	15	Cyclopentylethylamine	77
Cyclohexyl	24	Cyclohexylethylamine	73
Phenyl	9	*N*-Ethylaniline	78

[a] 10 mmol of RN$_3$ and 10 mmol of Et$_3$B in 10 ml of xylene, heated under reflux in a nitrogen atmosphere. [b] All products were isolated by glpc and exhibited analytical and spectral data in accordance with the assigned structures. [c] By glpc analysis, based on organic azide.

The reaction exhibits some features similar to those previously noted for the reaction of organoboranes with diazo compounds.[4] The diazo reactions exhibit considerable sensitivity to steric effects. This is also noted in the present azide reaction. Thus, organoboranes from α-olefins react smoothly with *n*-butyl azide. For example, yields of 80 and 73%, respectively, were

(1) D. Seyferth and B. Prokai, *J. Amer. Chem. Soc.*, **88**, 1834 (1966); G. Köbrich and H. R. Merkle, *Angew. Chem., Int. Ed. Engl.*, **6**, 74 (1967); G. Köbrich and H. R. Merkle, *Chem. Ber.*, **100**, 3371 (1967); A. Suzuki, S. Nozawa, N. Miyaura, M. Itoh, and H. C. Brown, *Tetrahedron Lett.*, 2955 (1969); H. C. Brown, B. A. Carlson, and R. H. Prager, *J. Amer. Chem. Soc.*, **93**, 2070 (1971).
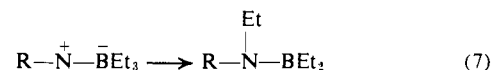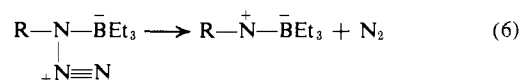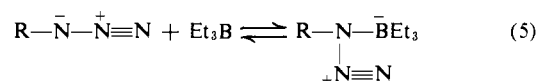
(2) P. Walker and W. A. Waters, *J. Chem. Soc.*, 1632 (1962); W. H. Saunders and J. C. Ware, *J. Amer. Chem. Soc.*, **80**, 3328 (1958).

(3) H. Steinberg and R. J. Brotherton, "Organoboron Chemistry," Vol. II, Wiley, New York, N. Y., 1966, p 27.

(4) J. Hooz and S. Linke, *J. Amer. Chem. Soc.*, **90**, 5936, 6891 (1968); J. Hooz and D. M. Gunn, *Chem. Commun.*, 139 (1969); J. Hooz and G. F. Morrison, *Can. J. Chem.*, **48**, 868 (1970).

realized in the reaction of tri-*n*-butylborane[5] and tri-*n*-hexylborane with *n*-butyl azide. However, as the steric effects are increased, either in the organoborane or in the azide, the reactions become more sluggish and the yields drop off. We are presently searching for a solution to this limitation.

The following procedure for the preparation of cyclo-pentylethylamine is representative. A dry 50-ml flask, equipped with a septum inlet, reflux condenser, and magnetic stirrer, was flushed with nitrogen. The flask was charged with 10 ml of xylene and 0.98 g, 1.42 ml (10 mmol), of triethylborane. The solution was then heated to reflux and attached to a gas buret. Then 1.11 g (10 mmol) of cyclopentyl azide[6,7] was added. After completion of the evolution of nitrogen, the solution was cooled, 30 ml of diethyl ether was added, and the amine was extracted with 6 *M* hydrochloric acid (two 20-ml portions). The aqueous phase was washed with ether to remove residual borinic acid. The solution was made strongly alkaline with potassium hydroxide and the amine was extracted with ether. Analysis by glpc (10% SE-30 column) revealed a 77% yield of cyclopentylethylamine of high purity.

Primary amines may be synthesized from the reactions of organoboranes with chloramine[8] or hydroxyl-amine-*O*-sulfonic acid.[8,9] The reaction of dimethyl-chloramine with organoboranes can evidently be controlled to provide a possible route to the corresponding tertiary amines.[10] The present development opens up a promising new route to the generally more difficultly synthesized secondary amines. We are actively exploring the full potentialities of this new route.

(5) The *n*-butylborane used contained 3% of *sec*-butyl groups. However, the product contained only a trace of *sec*-butyl-*n*-butylamine.

(6) Prepared from cyclopentyl bromide and sodium azide by the method of J. H. Boyer and J. Hamer, *J. Amer. Chem. Soc.*, 77, 951 (1955). The other alkyl azides were prepared similarly.

(7) Phenyl azide was prepared by the method of R. O. Lindsay and C. F. H. Allen, "Organic Syntheses," Collect. Vol. III, Wiley, New York, N. Y., 1955, p 710.

(8) H. C. Brown, W. R. Heydkamp, E. Breuer, and W. S. Murphy, *J. Amer. Chem. Soc.*, 86, 3568 (1964).

(9) M. W. Rathke, N. Inoue, K. R. Varma, and H. C. Brown, *ibid.*, 88, 2870 (1966).

(10) A. G. Davies, S. C. W. Hook, and B. P. Roberts, *J. Organometal. Chem.*, 23, C11 (1970).

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Acetylenic Bond Participation in Biogenetic-Like Olefinic Cyclizations. I. Formation of Five-Membered Rings in Model Systems

Sir:

Since acetylenic bonds can assist the solvolysis of sulfonate esters with concomitant ring formation,[1] we were intrigued by the possibility that these bonds might also participate in polyolefinic cyclizations. The present preliminary communication describes basic studies prob-

(1) See P. E. Peterson and R. J. Kamat, *J. Amer. Chem. Soc.*, 91, 4521 (1969), and references cited therein.
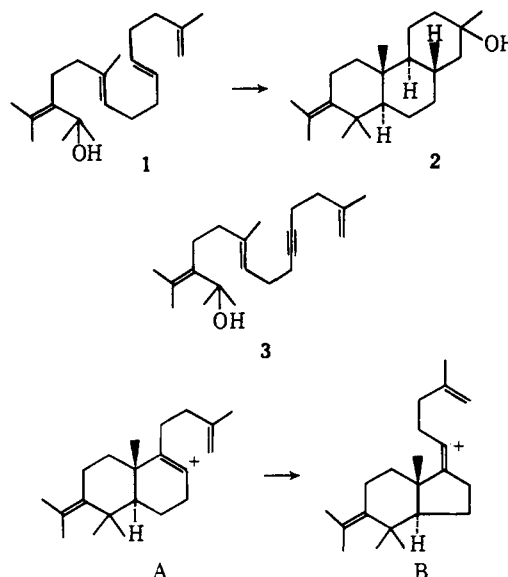
ing this question which has now been answered in the affirmative.

Since the tetraenol **1** has been shown[2] to undergo facile acid-catalyzed cyclization to give good yields of tricyclic material **2** having the rings fused exclusively in the "natural" trans,anti,trans configuration, we elected first to examine the cyclization of the trienynol **3** in order to look for participation of the acetylenic bond. In that event, it was not clear, *a priori*, whether there would be a preference for formation of a six- or five-membered ring *via* the vinyl cations A or B, respectively.[1]

When a mixture of the trienynol **3**,[3] contaminated with 9% of the isomeric homoallylic alcohol (formula **3** with an isopropenyl in place of the isopropylidene group), in methylene chloride containing 2% by weight of trifluoroacetic acid was allowed to stand for 5 min at −70°, the substrate **3** was largely converted (*ca.* 70% yield, by vpc) into a product which proved to be the tricyclic triene **4**.[4] This substance was purified by preparative tlc on silica gel (1:4 EtOAc–pentane, under N$_2$), and the structure was deduced by the following evidence. The mass spectrum showed a parent peak at *m/e* 284 (M$^+$), and the uv spectrum, λ_{max}^{MeOH} 245 mμ (ϵ 10,000), was consistent with the conjugated dienic chromophore shown in **4**.[5] The ir spectrum showed no absorption for the terminal methylene group and the nmr spectrum (60 MHz, CDCl$_3$, TMS internal standard) included singlets at δ 0.96 (3 H), 1.12 (3 H), and 1.37 (3 H) for the three methyl groups attached to quaternary carbon atoms, and at 1.68 (3 H) and 1.78 (3 H) for the isopropylidene methyl groups; in addition there was a broad singlet ($W_{h/2} = 4$ Hz) at 2.17 (3 H) for the methyl group attached to the olefinic bond in

(2) W. S. Johnson and T. K. Schaaf, *Chem. Commun.*, 611 (1969).

(3) The allylic alcohol substrates 3, 10, and 12 were prepared by a modification of a general method that has already been described,[2] namely alkylation of the bis anion of β,β-dimethylacrylic acid (produced by the action of lithium diisopropylamide on the acid in THF) with the appropriate homoallylic bromide, followed by esterification (CH$_2$N$_2$), isomerization (KO-*tert*-Bu in *tert*-BuOH) of the resulting β,γ- into the α,β-unsaturated ester, and finally treatment with excess methyllithium in ether. This modification resulted in an increase in yield (*ca.* 85 instead of 50%) at the alkylation step.

(4) The geometrical configuration about the exocyclic olefinic bond at C-1 of the hydrindane ring system is not known.

(5) Calcd: 244 mμ. *Cf.* A. I. Scott, "Ultraviolet Spectra of Natural Products," Pergamon Press, Oxford, 1964, pp 45–52.