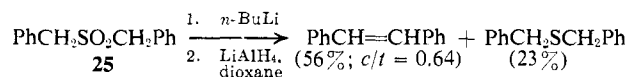


sulfonic acid group could complete the conversion to the strained olefin, but such considerations remain to be established by experiment.

Finally, we note the similarities of the present procedure with two other methods capable of supplanting a sulfur atom by a carbon-carbon double bond, namely the Ramberg-Bäcklund¹³ and Stevens rearrangements.¹⁴ The new scheme is clearly superior for the generation of strained tetrasubstituted double bonds, and as illustrated by the behavior of dibenzyl sulfone (**25**) could prove to



be at least equally convenient in a variety of simpler synthetic transformations.¹⁵

(13) L. A. Paquette, "Mechanisms of Molecular Migrations," Vol. I, B. S. Thyagarajan, Ed., Interscience, New York, N. Y., 1968, pp 121-156; L. A. Paquette, *Accounts Chem. Res.*, **1**, 209 (1968); F. G. Bordwell, *ibid.*, **3**, 281 (1970).

(14) For a leading reference, see R. H. Mitchell and V. Boekelheide, *J. Amer. Chem. Soc.*, **96**, 1547 (1974).

(15) This investigation was supported in part by a grant from the National Cancer Institute.

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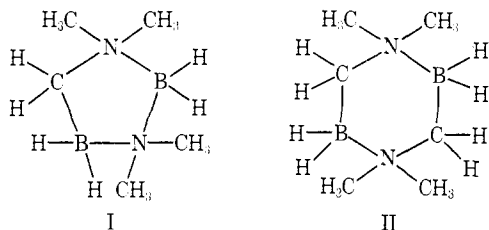
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Synthesis of a New Small Ring Heterocyclic Boron Compound

Sir:

We wish to report the synthesis of a new five-membered boron heterocycle, 1,1,3,3-tetramethyl-1,3-diazonia-2,4-diboracyclopentane, $\text{B}_2\text{C}_3\text{N}_2\text{H}_{18}$ (I). The new compound is isomeric with the cyclic adduct of dimethylaminoborane and dimethylaminomethylborane prepared by Haubold and Schaeffer,¹ and links structurally the four-membered ring systems derived from dimeric aminoboranes to the six-membered heterocycle 1,1,4,4-tetramethyl-1,4-diazonia-2,5-diboracyclohexane, $\text{B}_2\text{C}_6\text{N}_2\text{H}_{20}$ (II).² Compound I was pre-



pared in better than 30% yield from the reaction of bis(trimethylamine)boronium iodide with a Na-K alloy in 1,2-dimethoxyethane. Its reactivity appears to be similar to II.

The compound is a liquid immiscible with water but soluble in most organic solvents. It shows no sign of decomposition after 3 weeks at room temperature in an inert atmosphere or in CH_2Cl_2 solution. Methylene chloride solutions of I show little degradation after 24-hr contact with water but are rapidly decomposed on contact with strong aqueous hydrochloric acid and so-

(1) W. Haubold and R. Schaeffer, *Chem. Ber.*, **104**, 513 (1971).

(2) N. E. Miller and E. L. Muetterties, *Inorg. Chem.*, **3**, 1196 (1964).

dium hydroxide solutions. The compound reacts readily with bromine or iodine.

To synthesize I, 7.16 g of $[(\text{CH}_3)_3\text{N}]_2\text{BH}_2\text{I}$ and 2.29 g of Na-K alloy (25% Na) were slurried with 50-75 ml of 1,2-dimethoxyethane. The mixture was gently refluxed over an oil bath for 2 hr, when gas evolution ceased abruptly. After filtration the clear colorless solution was then concentrated by vacuum evaporation to about 5 ml, and the remaining liquid was fractionated by repeated evaporation and passage through a -23° trap, until the proton nmr spectrum showed that all the solvent had been removed from the product, which tended to collect in the -23° trap.

Since the compound has a vapor pressure of about 1 mm at 25° removal of solvent by trap-to-trap fractionation entails a concomitant not insignificant loss of product. Nevertheless, a total of 0.5 g, 30% yield of analytically pure I was obtained.

Anal. Calcd for $\text{B}_2\text{C}_3\text{N}_2\text{H}_{18}$: C, 46.98; H, 14.19; N, 21.91; B, 16.91. Found: C, 47.07; H, 14.12; N, 21.77; B, 16.85.³

The ir spectrum from 4000 to 600 cm^{-1} , obtained as a thin film between NaCl plates, gave the following bands in cm^{-1} : 3000 ms, 2940 s bd, 2415 s, 2340 s bm, 2265 ms, 1463 s bd, 1402 w, 1360 vw, 1290 m, 945 m bd, 878 w, 830 w bd, 791 ms, 720 vw.

The proton nmr spectrum in methylene chloride, referred to internal tetramethylsilane, shows two broad incompletely resolved peaks and a shoulder. The width at one-half the peak height for the absorption at -2.64 ppm is 5 Hz and the width at one-half the peak height of the absorption at -2.40 ppm is 9 Hz. The shoulder appears to be centered at -2.23 ppm and is assigned to the methylene carbon in position five of the ring based on position and relative intensity to the other two peaks.

Based on peak broadness we assign the absorption at -2.64 ppm to the methyl groups attached to the nitrogen in position one of the ring and the absorption at -2.40 ppm to the methyl groups attached to the nitrogen in position three of the ring.

The mass spectrum was obtained at 70 V and showed the presence of a molecular ion at m/e 128, as expected for the heaviest isotopic variant of $\text{B}_2\text{C}_3\text{N}_2\text{H}_{18}$ and no peaks at higher masses. As is the case for trimethylamine-borane, loss of one and more protons occurs easily on electron impact so that the pattern of molecular ion fragments becomes complex in the mass region immediately below the parent peak. Table I

Table I. Mass Spectrum of $\text{B}_2\text{C}_3\text{N}_2\text{H}_{18}$

m/e	Relative intensity, %	Species	Abundance, %
128	5.7	$\text{B}_2\text{C}_3\text{N}_2\text{H}_{18}^+$	6.3
127	34.6	$\text{B}_2\text{C}_3\text{N}_2\text{H}_{17}^+$	52
126	27.2	$\text{B}_2\text{C}_3\text{N}_2\text{H}_{16}^+$	17
125	20.0	$\text{B}_2\text{C}_3\text{N}_2\text{H}_{15}^+$	21
124	8.7	$\text{B}_2\text{C}_3\text{N}_2\text{H}_{14}^+$	3.0
123	2.7		
122	1.2		

shows the fragmentation pattern and the relative abundance of species calculated on the basis of statistical

(3) Analysis was done by Galbraith Laboratories, Inc., Knoxville, Tenn.

distribution of the isotopes of boron, carbon, and hydrogen. In agreement with observation in our laboratory on the 70-V mass spectra of other amine boranes, the positive ion derived by hydrogen loss from the parent molecule is the most abundant species.

The molecular weight obtained in a vapor pressure osmometer with benzene as solvent was 135.

The ^{11}B spectrum gave two 1:2:1 triplets with $A_{\text{B-H}} = 110$ Hz at +12.3 ppm for one triplet and $A_{\text{B-H}} = 97$ Hz at +25.2 ppm for the remaining triplet (trimethyl borate reference).

The triplet at +12.3 ppm is assigned to the boron in position 2 of the ring based on a similar chemical shift to the boron atoms in $[(\text{CH}_3)_2\text{NBH}_2]_2$. The triplet at +25.2 ppm is assigned to the boron atom in position 4 of the ring based on a similar chemical shift and coupling constant to the boron atoms in compound II.

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A Remote, Anodic Rearrangement-Substitution Reaction of Aliphatic Ketones

Sir:

A conceptually useful analogy between mass spectrometry and anodic chemistry is emerging from studies of the anodic chemistry of aliphatic compounds. Recent studies have, for example, demonstrated that branched alkanes¹ and α -branched ketones^{2,3} anodically mimic the fragmentations observed by mass spectrometry. We, therefore, reasoned that ketones without α -branching should anodically give an intramolecular hydrogen abstraction and perhaps β -cleavage in analogy with the McLafferty rearrangement.⁴ This paper reports an initial investigation of that hypothesis. To our knowledge, there are no literature reports of the anodic oxidation of such aliphatic ketones in aprotic media. The results obtained reveal a unique and potentially useful reaction which should be general for ketones.

The ketones investigated were 4,4-dimethyl-2-pentanone (I), 4-methyl-2-pentanone (II), 2,6-dimethyl-4-heptanone (III), and 2-hexanone (IV). The reactions were performed potentiostatically, in a three-compartment cell,⁵ at room temperature, in acetonitrile at platinum. The reference electrode was $\text{Ag}|0.1\text{ N AgNO}_3$ in acetonitrile. The solvent was twice distilled from phosphorus pentoxide and lithium perchlorate (0.1 N) was the supporting electrolyte. Further information on the oxidations and $E_{\text{p},2}$ values for the ketones is shown in Table I.

The oxidations were arbitrarily terminated after passage of ~ 2 faradays/mol of added ketone. The anolyte was worked up by distillation of the acetonitrile (note to dryness, contains HClO_4). Then, 10% aqueous NaHCO_3 was added and the mixture extracted

(1) T. M. Siegel, L. L. Miller, and J. Y. Becker, *J. Chem. Soc., Chem. Commun.*, in press.

(2) V. Koch and L. L. Miller, *J. Amer. Chem. Soc.*, **95**, 8631 (1973).

(3) Unpublished results of T. M. Siegel and J. Y. Becker.

(4) H. Budzikiewicz, C. Djerassi, and D. Williams, "Mass Spectrometry of Organic Compounds," Holden-Day, San Francisco, Calif., 1967, Chapter 3.

(5) E. A. Mayeda, L. L. Miller, and J. F. Wolf, *J. Amer. Chem. Soc.*, **94**, 6812 (1972).

Table I. Voltammetric Data

Substrate (mmol)	$E_{\text{p},2}^a$	E^b	n^c	i_0^d mA	Product (% yield) ^e
I (4.0)	2.45	2.25	2.2	270	V (50)
(2.0)		2.30	3.3	130	V (40)
I (1.0) + $(\text{CH}_3)_2\text{CHCH}(\text{CH}_3)_2$ (10.0)		2.25	2.2	130	V (50)
II (5.3)	2.40	2.20	2.0	120	VI (20) VII (20)
III (3.65)	2.50	2.25	2.0	120	VIII (20) IX (20)
IV (1.65)	2.45, 2.60	2.30	2.2	80	X (40)

^a Potentials are quoted vs. $\text{Ag}|0.1\text{ N AgNO}_3$ reference electrode at a voltammetric sweep rate of 0.5 V/sec. ^b The controlled potential used in preparative experiments. ^c Number of electrons transferred per molecule of added substrate. ^d Initial current. The background current for all experiments was 2-3 mA at 2.3 V. ^e Yields based on isolated products compared to added reactant.

Table II. Products of Electrooxidation and Spectroscopic Data

Substrate	Product	Nmr ^a and mass spectra
I	4-Acetamido-4-methyl-2-hexanone (V)	Nmr: 0.75 (t, 3 H), 1.27 (s, 3 H), 1.80 (oct, 2 H, $J = 2.5$ Hz), 1.85 (s, 3 H), 1.91 (s, 3 H), 2.88 (AB quartet, 2 H, $J = 16.5$ Hz), 5.91 (s, 1 H). Mass spectral: 171.1277 (M^+), 156, 142, 128, 114, 113, 100, 58, 57, 43
II	4-Acetamido-4-methyl-2-pentanone (VI)	Nmr: 1.40 (s, 6 H), 1.95 (s, 3 H), 2.10 (s, 3 H), 2.98 (s, 2 H), 6.20 (s, 1 H). Mass spectral: 157.1090 (M^+), 114, 100, 58, 57, 43
	4-Acetamido-2-hexanone (VII)	Nmr: 0.9 (t, 3 H), 1.5 (m, 2 H), 2.0 (s, 3 H), 2.2 (s, 3 H), 2.65 (d, 2 H), 4.2 (m, 1 H), 6.2 (s, 1 H). Mass spectral: 157.1111 (M^+), 128, 114, 100, 58, 43
III	2-Acetamido-2,6-dimethyl-4-heptanone (VIII)	Nmr: 0.9 (d, 3 H), 1.4 (s, 6 H), 1.95 (s, 3 H), 2.0-2.4 (m, 3 H), 2.9 (s, 2 H), 6.8 (s, 1 H). Mass spectral: 199 (M^+), 184, 157, 142, 114, 100, 58, 43
	6-Acetamido-2-methyl-4-octanone (IX)	Nmr: 0.8-1.1 (m, 9 H), 1.5 (m, 2 H), 1.98 (s, 3 H), 2.3 (3 H), 2.65 (d, 2 H), 4.1 (m, 1 H), 6.2 (s, 1 H). Mass spectral: 199 (M^+), 170, 157, 142, 128, 114, 100, 86, 58, 43
IV	5-Acetamido-2-hexanone (X)	Nmr: 1.17 (d, 3 H), 1.93 (s, 3 H), 2.18 (s, 3 H), 1.57-2.17 (m, 2 H), 2.37-2.77 (m, 2 H), 3.65-3.93 (m, 1 H), 6.10 (s, 1 H). Mass spectral: 157 (M^+), 114, 100, 86, 58, 57, 43

^a Nmr data are given in ppm. ^b Broad singlet.

several times into chloroform. The chloroform solution was dried over anhydrous magnesium sulfate, filtered, and evaporated, and the products were isolated by preparative glc on a 10% SE-30 on Chromosorb W column. All the isolated products were ketamides which were characterized spectrally (Table II).

The ir spectra of V-X gave bands near 3300, 1660, and 1550 cm^{-1} characteristic of *N*-alkylacetamides and a ketone band at 1710 cm^{-1} . Nmr and mass spectral