effect. A more detailed discussion will be presented in the full paper.

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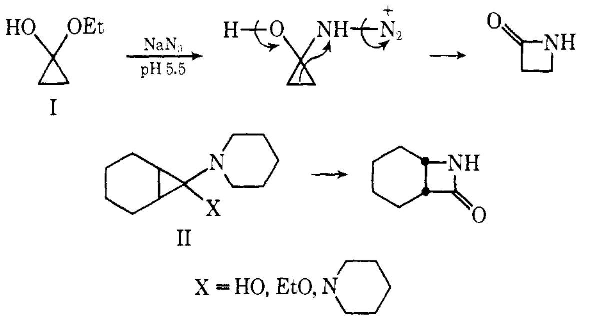
The Chemistry of Cyclopropanones. VI. A New Synthesis of β-Lactams[1]

Sir:

We have previously reported[2] that the ethyl hemiketal (I) of cyclopropanone reacts with sodium azide in buffered solution to form β-lactam, and we have recently[1] extended this reaction to the preparation of fused-ring β-lactams from 1,1-disubstituted cyclopropanones in the bicyclo[4.1.0] series (II).[3]

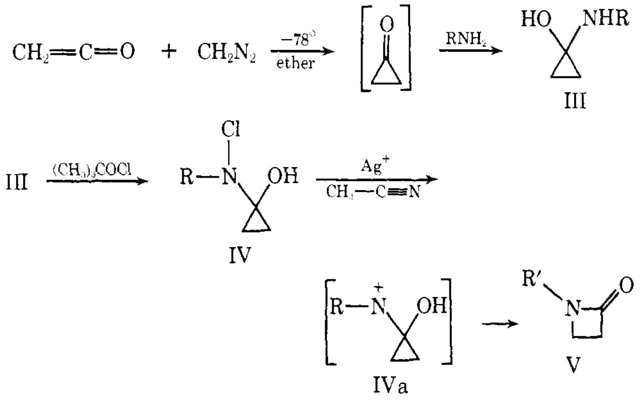


I

II

We now wish to report a more general application of this ring enlargement sequence taking place through the electron-deficient (nitrenium ion) species IVa analogous to the cyclopropylcarbinyl cation, or by the concerted process (IV → V) outlined in Scheme I.

Scheme I



III

IV

IVa

V

The reaction involves the formation of carbinolamines of type III which may be converted to *N*-chloro derivatives using *tert*-butyl hypochlorite according to Gassman's procedure.[4,5] Treatment of the *N*-halo derivative with silver ion in acetonitrile leads to β-lactam formation. Table I summarizes the results of our initial studies.

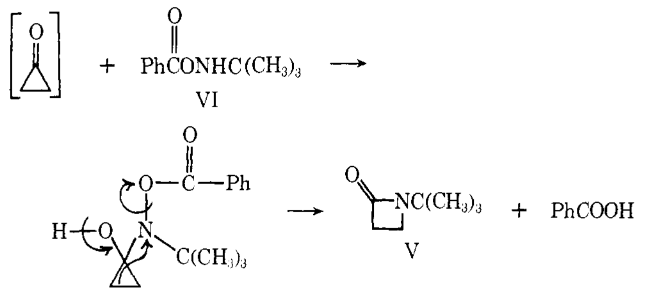
Table I[a]

Amine	Yield of β-lactam (V), %
$c\text{-}C_6H_{11}NH_2$	61
$CH_3(CH_2)_3NH_2$	43
$CH_3CH_2CH(\text{-}CH_3)NH_2$	38
$(CH_3)_3CNH_2$	52
$CH_3CH(\text{-}COOEt)NH_2$	65

[a] All new products gave satisfactory carbon, hydrogen, and nitrogen analyses and the expected parent peaks in the mass spectra.

The intermediates III were formed by treatment of ketene with diazomethane in ether at −78°[6] followed by the addition of 1 mol of primary amine to the reaction mixture. Evaporation of solvent below 30°, followed by repeated washing with cold petroleum ether, yielded the crude carbinolamines, which could be characterized by nmr and mass spectra. Because of the instability of the addition products of primary amines to cyclopropanone[7] we chose not to attempt isolation of the intermediates III, but found it advantageous to perform the halogenation directly on the crude carbinolamines after replacement of ether with acetonitrile. Thus, addition of 1 equiv of *tert*-butyl hypochlorite in the dark at 0° and stirring of the reaction mixture for 1 hr were followed by treatment with a threefold excess of silver nitrate and stirring for an additional 3 hr. After removal of silver chloride and evaporation of solvent, a residue was obtained which was treated with 6 *N* aqueous ammonia and extracted with ether. Evaporation of solvent yielded the crude β-lactam purified by column chromatography on silica gel. By this procedure, pure N-substituted β-lactams could be obtained in yields of *ca.* 50% based on the diazomethane employed.

In a further extension of this general method, we have investigated leaving groups other than Cl^- or N_2 in the ring enlargement. Thus, the *O*-benzoyl derivative of *N*-*tert*-butylhydroxylamine (VI)[8] reacts directly with cyclopropanone in ether at −78° to form the β-lactam V, R = *tert*-butyl (40%). To isolate the product, the ether solution was washed with bicarbonate and dried, the solvent was removed, and the residual liquid was purified by glc. The rearrangement is presumed to take place by the sequence shown below.



VI

V

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The β-lactams were identified by mass spectral, infrared, and nmr data. Characteristic β-lactam carbonyl peaks at *ca.* 1745 cm^{-1} [9] in the infrared were obtained for all products while the nmr spectra showed no vinyl protons, but instead the expected multiplets [*ca.* τ 6.80 (2 H) and 7.1 (2 H)] associated with the methylene protons in four-membered lactam rings.[10]

We are exploring cyclopropanone ring enlargements as methods for preparing β-lactam derivatives of amino acids, and as routes toward the synthesis of substances related to penicillin.

Acknowledgment. This work was supported by Grant No. GM-07874 from the National Institutes of Health.

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Germa- and Stannaundecaboranes

Sir:

Several examples of the insertion of representative elements other than carbon into boron hydride cages have been reported.[1-3] However, the absence of compounds containing group IVa elements below carbon has been surprising. Recently, we have found that reactions between $NaB_{10}H_{13}$ and $(CH_3)_3GeBr$ or $(CH_3)_3SnCl$ result in the formation of what appear to be the first examples of germa- and stannaundecaboranes, $(CH_3)_2GeB_{10}H_{12}$ and $(CH_3)_2SnB_{10}H_{12}$.

In a typical preparation of $(CH_3)_2SnB_{10}H_{12}$, $NaB_{10}H_{13}$ (3.0 mmol), obtained from the NaH deprotonation of $B_{10}H_{14}$, was allowed to react under N_2 at 1 atm of pressure with $(CH_3)_3SnCl$ (7.3 mmol) in diethyl ether. After 1.5 hr at 75° the reaction mixture was evaporated to dryness and extracted with benzene. Removal of the benzene *in vacuo* followed by repeated high-vacuum sublimation of the residue at 94° yielded pure $(CH_3)_2SnB_{10}H_{12}$ (mp 123–124°, yield 18%). *Anal.* Calcd for $C_2B_{10}SnH_{18}$: B, 40.19; C, 8.93; H, 6.75. Found: B, 39.96; C, 9.07; H, 6.73. Under similar reaction and purification conditions, $NaB_{10}H_{13}$ (5.0 mmol) and $(CH_3)_3GeBr$ (6.0 mmol) react to form $(CH_3)_2GeB_{10}H_{12}$ (mp 82–83%, yield <5%). *Anal.* Calcd for $C_2B_{10}GeH_{18}$: B, 48.52; C, 10.78; H, 8.14. Found: B, 47.48; C, 10.52; H, 8.31.

The $(CH_3)_2GeB_{10}H_{12}$ and $(CH_3)_2SnB_{10}H_{12}$ are thermally stable and exhibit reasonable stability in air. The mass spectra of these compounds exhibit fragmentation envelopes which are entirely consistent with those expected for heteroatom-substituted decaboranes. The highest mass peaks in the low-energy (15 eV) spectra of $(CH_3)_2GeB_{10}H_{12}$ and $(CH_3)_2SnB_{10}H_{12}$ occur at *m/e* 228 and 276, respectively, and can be assigned to the $(CH_3)_2{}^{76}Ge^{11}B_{10}H_{12}^+$ and $(CH_3)_2{}^{124}Sn^{11}B_{10}H_{12}^+$ molecular ions. Absorption peaks in the infrared spectrum of $(CH_3)_2GeB_{10}H_{12}$ at 2950, 2590, and 1970 cm^{-1} and in the spectrum of $(CH_3)_2SnB_{10}H_{12}$ at 2900, 2550, and 1910 cm^{-1} suggest the presence of B–H,[4-6] C–H,[4] and B–H–B[5,6] groups. The lack of absorptions in the 2060–2100- and 1820–1870-cm^{-1} regions[4,7] indicates the absence of Ge–H or Sn–H bonded units, respectively.

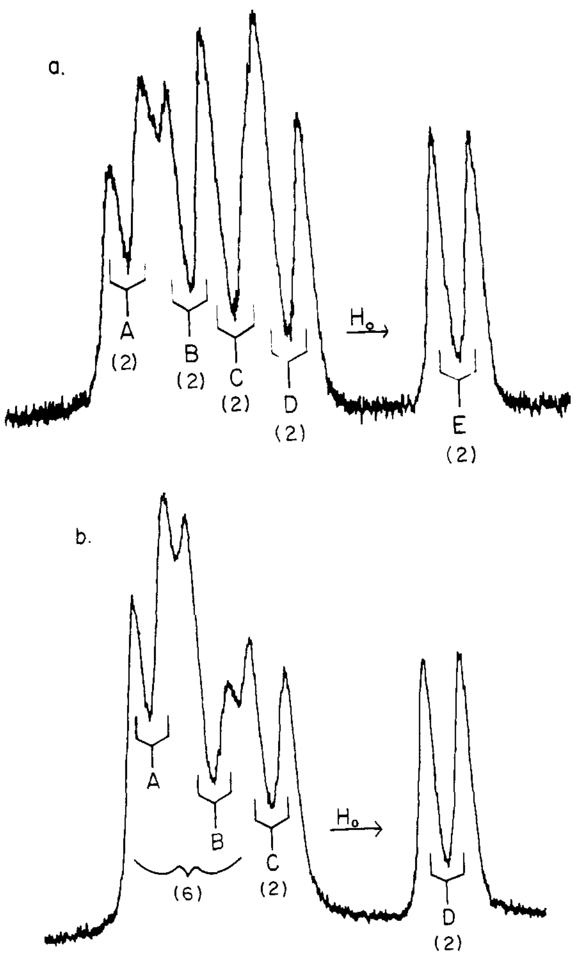

Figure 1. The 32-MHz ^{11}B nmr spectrum of (a) $(CH_3)_2GeB_{10}H_{12}$ and (b) $(CH_3)_2SnB_{10}H_{12}$ in benzene solvent. Chemical shifts (ppm relative to $BF_3 \cdot O(C_2H_5)_2$) and coupling constants (Hz) are, for a (A) −13.3, 145; (B) −5.5, 160; (C) +0.7, est 170; (D) +6.9, 170; and (E) 29.4, 160; and for b (A) −10.4, 148; (B) −2.4, 167; (C) 5.4, 148, and (D) 29.1, 157. Numbers in parentheses refer to relative resonance areas.

The 32.1-MHz ^{11}B nmr spectra of the new compounds are shown in Figure 1, and spectral parameters are given in the figure legend. From ^{11}B-[^1H] double-resonance experiments and examination of the 70.6-MHz high-field spectra, the spectra appear to consist of doublet resonances only, suggesting that each boron atom is terminally bonded to a single hydrogen atom. The presence of an area 2 doublet in the region of the

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