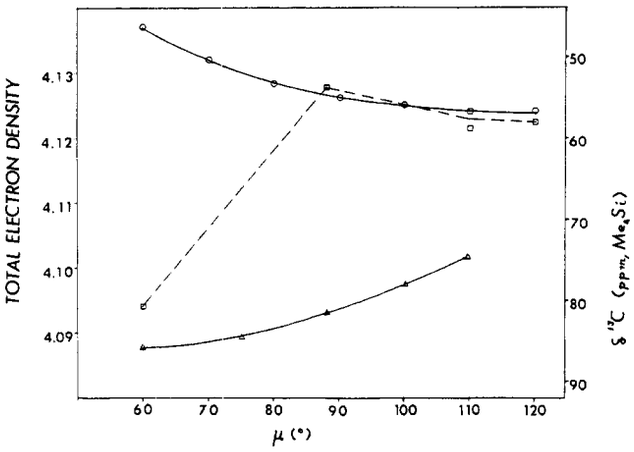

Figure 1. Variance of total electron density on the β carbon of vinylamine as a function of the HNH angle, μ, for ⊙ planar nitrogen, and △ pyramidal nitrogen. The dotted line shows the variance of ^{13}C chemical shift of carbon 1 in **2–6** as a function of μ.

pyramidal (sp^3) in **2** to essentially planar (sp^2) in **3–7** is being observed. Some support for this idea is provided by the work of Kamlet et al.[4] on *N*-(4-nitrophenyl)polymethylenimines. In that system, they found a pattern in the NMR for the ortho protons very similar to that mentioned in this paper, with supporting data from ultraviolet spectra and pK_a values.

In order to give further evidence for this notion, INDO SCF–MO calculations[7] were performed on a model system, vinylamine. Two functions were varied: (1) μ, the HNH angle, reflecting different ring sizes, and (2) θ, the angle between the HNH plane and the plane of the olefinic bond. Since ^{13}C chemical shifts are generally considered to correlate better with total electron density,[6] the latter vaues for the β carbon were plotted against μ for $\theta = 0$ (planar nitrogen) and $\theta = 54.7$ (~tetrahedral nitrogen). The two lines which resulted are shown in Figure 1. Also shown is a plot of the ^{13}C chemical shifts for **2–6** vs. μ (the dotted line).[9] From these data it is apparent that the deshielding of carbon 1 in **2** relative to **3–7** probably stems, in large part, from a pyramidal nitrogen. Deshielding of carbon 1 in **2** may also arise in part from angle strain rehybridization; however, the relative contribution of this effect is difficult to estimate from these calculations.

In conclusion, ^{13}C and ^1H spectra of the β-aminovinylphosphonium salts **3–7**, in conjunction with INDO SCF–MO calculations on vinylamine, seem to indicate structures with considerable enamine conjugation and essentially planar nitrogen atoms. Aziridine **2** appears to have considerably less enamine conjugation than **3–7** (albeit more conjugation than 8) and a pyramidal nitrogen. The nearly planar azetidine nitrogen, though observed previously in other systems,[4] is still quite surprising. The chemistry of these interesting compounds, in particular, derivatives of **2**, is presently under investigation and will be reported in a later publication.

Experimental Section

Carbon-13 spectra were obtained on a Bruker HFX-90 spectrometer equipped for Fourier transform pulsed NMR with a Nicolet 1085 data system. The ^{13}C data were taken at an operating frequency of 22.63 MHz. The ^{13}C chemical shifts are reported as referenced to Me_4Si. All samples were run in approximately 0.05 M solutions of $CDCl_3$ at 32 °C with broad band ^1H decoupling (except compound **2**, which was run at −5 °C). The proton spectra were obtained on either a Perkin-Elmer R-12 or Varian A-60A spectrometer and were referenced to Me_4Si. Concentrations used for the proton spectra were similar to those used for the ^{13}C spectra. The ^1H spectrum of compound **2** was taken at −10 °C; all others were taken at normal probe temperatures (~30–40 °C).

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Registry No.—**2,** 62460-44-0; **3,** 62460-45-1; **4,** 62460-46-2; **5,** 62460-47-3; **6,** 62460-48-4; **7,** 62460-49-5; 2-propynyltriphenylphosphonium bromide, 2091-46-5; aziridine, 151-56-4; azetidine, 503-29-7; pyrrolidine, 123-75-1; piperidine, 110-89-4; dimethylamine, 124-40-3; methylamine, 74-89-5.

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(8) Cf. M. Dewar, "The Molecular Orbital Theory of Organic Chemistry", McGraw-Hill New York, N.Y., 1969, p 408.
(9) The values of μ vs. $\delta^{13}C$ are 60° for aziridine [B. Bak and S. Skaaryp, *J. Mol. Struct.*, **10,** 385 (1971)], 88° for azetidine [V. S. Mastryukov, O. V. Dorofeeva, and L. V. Vilkov, *J. Chem. Soc., Chem. Commun.*, 772 (1973)], 110° for the five- and six-membered rings, and 120° for the dimethylamine derivative.

An Improved Synthesis of Bicyclo[4.2.1]nonan-2-one

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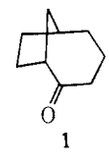
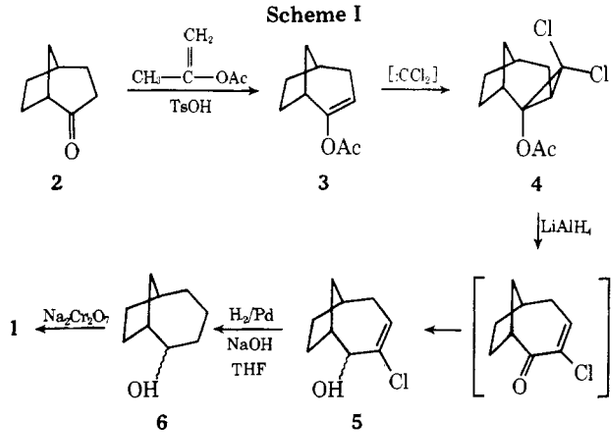
Our interest in the Favorskii rearrangement of bicyclic halo ketones[1] has prompted us to investigate the synthesis of bicyclo[4.2.1]nonan-2-one (**1**). Of the published routes to this



1

bicyclic ketone,[2–6] the method of Kraus et al.[6] is the only simple one. This involves treatment of bicyclo[3.2.1]octan-2-one[7] (**2**) with isopropenyl acetate and *p*-toluenesulfonic acid (TsOH) (Scheme I) to give bicyclo[3.2.1]oct-2-en-2-yl acetate (**3**). Dichlorocarbene addition to **3** yields 3,3-dichloro-*exo*-tricyclo[4.2.1.$0^{2,4}$]non-2-yl acetate (**4**), which undergoes re-

Scheme I



ductive fragmentation with lithium aluminum hydride in ether to give a mixture of exo and endo alcohols **5**. Hydrogenation and hydrogenolysis to alcohol **6** is routine and oxidation gives the desired ketone **1**.

A problem we encountered in the synthesis was the conversion of enol acetate **3** into cyclopropyl acetate **4**. Kraus stated that chloroform and 50% aqueous sodium hydroxide with catalytic amounts of benzyltriethylammonium chloride according to Makosza's procedure[8] gave a 67% yield of adduct **4**. He also mentioned that enol acetate **3** does not react with dihalocarbenes if they are generated from potassium *tert*-butoxide and trihalomethanes or from sodium trihaloacetates. This is probably due to the electron-deficient nature of the carbon–carbon double bond of **3**.

We have been unable to reproduce the addition of dichlorocarbene to acetate **3** by this procedure. Only nonvolatile products were obtained. However, use of Seyferth's reagent, (bromodichloromethyl)phenylmercury ($PhHgCCl_2Br$),[9] has been known for some time to be a mild method of generating dichlorocarbene.[10,11] Excess acetate **3** heated with this reagent in refluxing benzene for 4 h gives cyclopropyl adduct **4** in 57% yield and some **3**, easily separable by vacuum distillation, for a total recovery of 90%. The recovered enol acetate can be reused in the same reaction. The necessity of using excess **3** was not investigated, but a 1:1 stoichiometry has been found to be satisfactory for all but the least reactive olefins.[10] This change in the method of generating the dichlorocarbene makes bicyclo[4.2.1]nonan-2-one readily available through large-scale preparation.

Experimental Section

Melting and boiling points are uncorrected. Gas chromatography was performed on an SE-30 column at 190 °C.

3,3-Dichloro-*exo*-tricyclo[4.2.1.$0^{2,4}$]non-2-yl Acetate (4). Bicyclo[3.2.1]oct-2-en-2-yl acetate (**3**, 90% pure by GC, 24.39 g, 0.147 mol) and (bromodichloromethyl)phenylmercury (32.41 g, 0.0735 mol) were magnetically stirred and refluxed for 4 h with dry benzene (150 mL) under nitrogen. After the mixture was cooled, the phenylmercuric bromide (mp 275–280 °C, lit.[11] mp 283–285 °C) was suction filtered and washed with petroleum ether (bp 30–60 °C, 100 mL). The solvents were rotary evaporated and the yellow oil was vacuum distilled. The first fraction had bp 50–90 °C (0.12–0.18 mm) and was identified as enol acetate **3** (15.02 g, 0.0905 mol). The second fraction distilled as a colorless liquid with bp 93–108 °C (0.15–0.20 mm) and was found to be 3,3-dichloro-*exo*-tricyclo[4.2.1.$0^{2,4}$]non-2-yl acetate [**4**, 10.37 g, 0.0416 mol, 57%, lit.[6] bp 96 °C (0.5 mm)]: IR (neat) 3070 (cyclopropyl C–H), 2990 and 2930 (C–H), 1765 (C=O), 1445 (CH_2), 1355, 1200 (C–O), 1150, 1120 (C–O), 1015, 810 cm^{-1} (C–Cl); NMR (CCl_4) δ 3.0–3.2 (m, 1, $CHCCl_2$), 2.03 (s, 3, CH_3COO), 1.0–2.4 (m, 10). The starting material **3** plus product **4** represents a total recovery of 90%.

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Registry No.—**1**, 3850-55-3; **3**, 37678-33-4; **4**, 37678-34-5; $PhHgCCl_2Br$, 3294-58-4.

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Synthesis of the Torsionally Strained Monocyclic Polythiaether 1,4,7-Trithiacyclononane

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In a previous paper, we had reported convenient synthetic methods[1] for macrocyclic polythiaether ligands, which were subsequently exploited in our continuing investigation of macrocyclic polythiaether coordination chemistry with copper and mercury.[2] In the course of current crystallographic studies of the metal complexes as a function of ring size and sulfur atom donor number, we required the 1,4,7-trithiacyclononane **2** ligand. Whereas the oxa, aza, and the mixed oxa–aza–thia nine-membered cyclic ligand syntheses have been reported[3] by methods analogous to those illustrated in Scheme I, often in excellent yields, the corresponding trithia ligand **2** in our hands proved to be frustratingly inaccessible.

Compound **2** had been reported in 1920 by Ray as a by-product from the synthesis of ethanedithiol by the reaction of ethylene bromide in alcoholic potassium hydrogen sulfide.[4] We have reinvestigated this reaction and found that the main cyclic product is *p*-dithiane **1**, without the slightest trace of **2** being detectable by analytical high-pressure liquid chromatography.

We had previously reported the absence of **2** from the cyclization of sodium mercaptides of either 3-thiapentane-1,5-dithiol with ethylene bromide or 1,2-ethanedithiol with 1,5-dichloro-3-thiapentane in butanol media at 60 °C.[1] Rather, in both of these reactions, the major direct cyclization product was the hexathia macrocycle **4** along with *p*-dithiane **1** and the tetrathia macrocycle **3**, both of the latter being formed by intrachain cyclization. The absence of **2** was reasonably rationalized by the prohibitive torsional ring strain of the cyclononane structure.[5] Analysis of the structure with CPK space-filling models reveals that the most stable conformation of **2** requires nearly completely eclipsed conformations of the ethylene bridges.

However, when we reacted the sodium dimercaptide of 3-thiapentane-1,5-dithiol with ethylene chloride in ethanol media below 5 °C, the desired product **2** was isolated in 0.04% yield from a preparative scale reaction. This low yield was not

Scheme I