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TRICYCLO[3.2.1.$0^{1,5}$]OCTANE - A HIGHLY STRAINED "PROPELLERANE"

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The recent communication by Wiberg and coworkers on the synthesis of 8-oxatricyclo-[3.2.1.$0^{1,5}$]octane[2] prompts us to report our synthesis of the parent hydrocarbon, tricyclo-[3.2.1.$0^{1,5}$]octane (1)[3]. Bicyclo[3.2.0]hept-1-ene[4] (2) could be converted into 1 in a one step process which involved the bubbling of diazomethane into an ethereal solution of 2

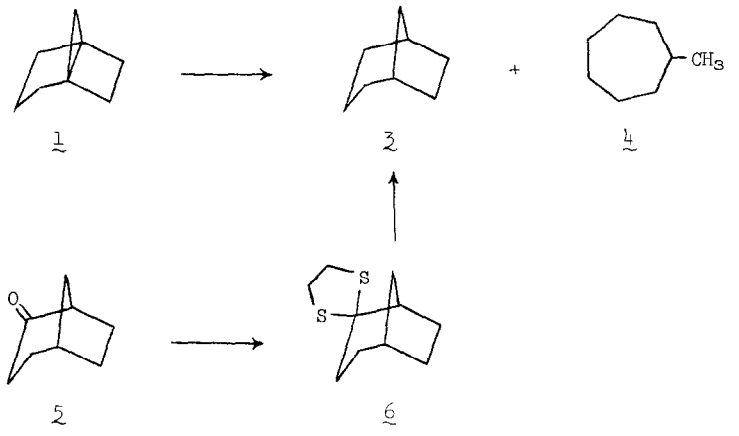
2 1

which also contained catalytic amounts of cuprous chloride[5]. When all of the olefin had reacted, as noted by vpc, the product could be isolated either by filtration through celite or by vacuum transfer, followed by fractional distillation. This method gave 1 in 50-65% yield, b.p. 45° (25 mm.). The tricyclic hydrocarbon polymerized rapidly at room temperature[6] and slowly at 0°.

The mass spectrum of 1 had the parent peak at m/e 108. The near infrared spectrum of 1 showed the typical cyclopropyl methylene absorption[7] at 1.647 μ (ε 0.237). The nmr spectrum of 1 showed a AB pattern with one proton at τ 9.43 and one proton at τ 9.08 with J_{AB} 6 cps. In addition a broad complex multiplet extended from τ 7.90 to τ 8.60 (10 protons).

On the basis of the spectroscopic evidence the structure assigned to 1 was reasonably

assured. Conclusive proof of the tricyclic structure was obtained from catalytic hydrogenation of 1 over 5% palladium on carbon in ether. We found that 1 took up 1.86 moles of hydrogen to yield a mixture of bicyclo[3.2.1]octane (3) and methylcycloheptane (4) in 10 and 74% yields, respectively. The bicyclo[3.2.1]octane was identified by a comparison of vpc retention times, infrared spectra, and nmr spectra with an authentic sample prepared



1 3 4

5 6

from commercially available 5 via conversion of 5 into the thioketal 6 and Raney nickel reduction of 6 according to the procedure of Newman and Yu[8]. Methylcycloheptane was similarly compared with an authentic sample.

The chemical reactivity of 1 was indicated by its ease of polymerization. In addition 1 reacted rapidly enough with bromine to permit titration at -60°. When 1 was mixed with dicyanoacetylene at room temperature a violent exothermic reaction occurred. At -78° the addition of dicyanoacetylene still occurred but at a controllable rate. We are currently investigating the structure of the bromination product and the products of the additions of acetylenes and olefins to 1. Since 1 is a bridged bicyclo[2.1.0]pentane derivative it will be interesting to elucidate whether 1 reacts with acetylenes in a manner similar to bicyclo[2.1.0]pentane[9] (to give derivatives of tetracyclo[3.2.2.$1^{1,5}$]-decane).

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2. K. B. Wiberg, J. E. Hiatt, and G. Burgmaier, Tetrahedron Letters, 5855 (1968).

3. We have recently learned that Professor Wiberg has indepentently synthesized 1. We thank Professor Wiberg for informing us of his results prior to publication.

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5. The procedure used was very similar to that of R. E. Pincock and J. I. Wells, J. Org. Chem., 29, 965 (1964).

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