

BICYCLO (2.1.1) HEX-2-ENE

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and

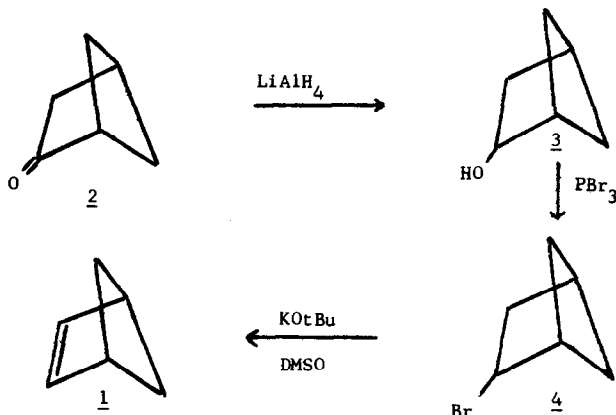
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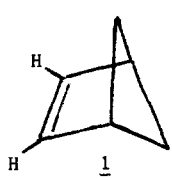
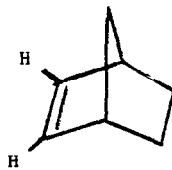
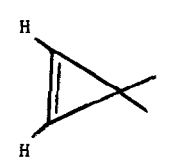
The recent communication by Meinwald and Uno (1) on the synthesis of bicyclo (2.1.1) hex-2-ene, 1, prompts us to report our alternate synthetic route and some preliminary studies of this most interesting, strained, symmetrical olefin. Our route to 1 also starts with bicyclo (2.1.1)-2-hexanone, 2 (2), and involves reduction to the alcohol 3, conversion to the bromide 4 in high yield with PBr_3 , and dehydrohalogenation with potassium t-butoxide/DMSO (3, 4) at 50° . The overall yield from 2 (ca 20%) is slightly lower than that reported



by Meinwald and Uno (1), but the method allows isolation of the olefin by distillation rather than preparative GLC. The crude dehydrohalogenation product was poured onto ice and extracted eight times with cyclooctane. The extracts were washed carefully, dried, and then carefully distilled through a spinning band column. The pure olefin, b.p. 60-62°, $n_D^{22} = 1.4376$ was collected in early fractions (5); later material was contaminated with *t*-butanol.

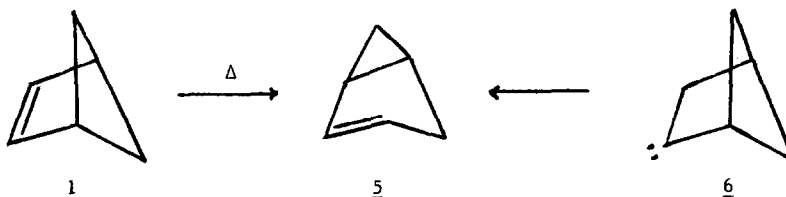
The structure of the olefin was confirmed by hydrogenation to the known bicyclo (2.1.1) hexane (6), and hydroboration-oxidation to the alcohol 3. Spectral properties of 1 were in general agreement with those reported (1), except that the NMR chemical shifts were all deshielded by 0.2 ppm, presumably a result of our using TMS as an internal standard. The olefinic protons at 6.82 ppm are downfield 0.86 ppm from those in norbornene (7), and deshielded almost as much as those in cyclopropenes (8). Of greater interest is the $^{13}\text{C-H}$ coupling measured from natural abundance on a neat sample and reported in Table I. The

TABLE I
Olefinic Proton

	δ	$J_{^{13}\text{C-H}}$	Ref.
<u>1</u>	6.82 ppm	177 cps	
	5.96	165	7
	7.00	220	8, 9

shape of the olefinic sateletes of 1 are quite similar to that reported for norbornene (7). Compound 1 has a coupling constant between the olefinic protons of 5 ± 1 cps.

One interesting feature of the chemistry of 1 is its thermolysis at $150-200^{\circ}$ to give predominantly (greater than 80%) bicyclo (3.1.0) hex-2-ene 5 (10). We had anticipated



this vinylcyclobutane rearrangement (11) from our investigation of the carbene 8 (generated thermally [190° required] from the sodium salt of the p-toluenesulfonylhydrazone of 2) which gave a mixture of products in which 5 was the major constituent. We have not yet identified minor products of the thermolysis nor measured the activation parameters, but it is interesting to note that the strain in 1 allows the isomerization to occur some 300 to 350° lower than that used for the 1-cyclobutylethyl acetate to cyclohexene rearrangement (11).

ACKNOWLEDGEMENTS

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4. The salt of a higher boiling tertiary alcohol would seem to be wise, since some samples of the olefin contained t-butanol.
5. Anal: Calcd. for C_6H_8 : C, 89.94; H, 10.06. Found: C, 89.62; H, 10.18.
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