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TRICYCLO[3.2.1.$0^{1,5}$]OCTANE (1)

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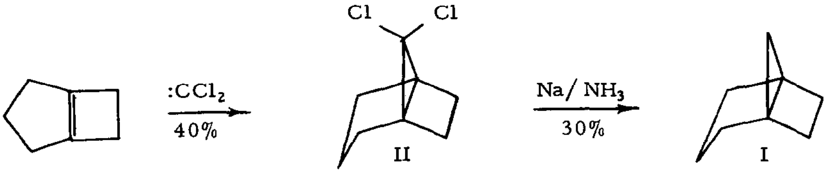
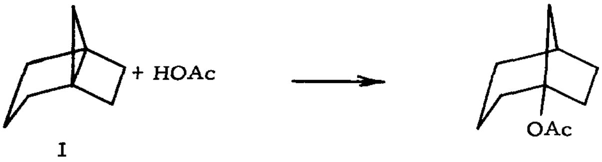
We have recently reported that 8-oxatricyclo[3.2.1.$0^{1,5}$]octane, in which the normal tetrahedral arrangement about the bridgehead atoms has been "inverted", is remarkably stable in thermal reactions despite the expected high strain energy (2). We now wish to report the preparation of the parent hydrocarbon (I) and to indicate its reactivity. The method of preparation was:



The addition of dichlorocarbene, generated from ethyl trichloroacetate and sodium methoxide, to bicyclo[3.2.0]hept-1(5)-ene (3) gave the dichloride, II, mp 29-30°. The nmr spectrum showed only a broad multiplet, τ = 6.80-7.75. The mass spectrum indicated two chlorines and gave m/e = 176 for the species having Cl^{35}. The elementary analysis of II was satisfactory, and the infrared spectrum was consistent with the assigned structure.

Dehalogenation of II gave I in a 30% yield. The nmr spectrum showed an AB quartet (J = 6 Hz) centered at τ 9.32 (2H) and a multiplet from τ 7.85-8.78 (10H). Elementary analysis combined with the mass spectrum indicated C_8H_{12}. The high field absorption indicated the presence of a cyclopropane ring, and the absence of low field nmr bands indicates the compound to be saturated, and hence tricyclic.

Important evidence for the assigned structure is obtained from its reaction with acetic acid. The reaction is rapid at room temperature and gives 1-acetoxybicyclo[3.2.1]octane as the only product. The latter was identified by a comparison of its nmr spectrum and vpc retention time with that of an authentic sample (4).



The hydrocarbon, I, has remarkable thermal stability. The half-life at 195° is in excess of 20 hrs. The high stability may result from its unique structure. Fragmentation of the cyclobutane ring to two double bonds in a concerted process is electronically forbidden (5). Because of the rigid structure, a two step process involving first the central bond would probably have the electronic characteristics of a concerted process. Similarly, cleavage of the central bond to a diradical cannot be followed by a hydrogen migration as is found with most cyclopropanes (6) because this will lead to a double bond to the bridgehead. Cleavage of one of the other cyclopropane ring bonds is probably not favored because it would have to be followed by an alkyl shift and such shifts are not common in free radical reactions.

Whereas bicyclo[2.1.0]pentane reacts relatively slowly with acetic acid (7), I reacts very rapidly (less than 5 min. at room temperature). This may in part result from the added alkyl substitution at the bridgehead in I, but probably also reflects a significant increase in strain over that in bicyclo[2.1.0]pentane (53 kcal/mole) (8). The heat of combustion of I is being determined in order to obtain the heat of formation and the strain energy. These data, as well as further information on the reactivity of I will be reported subsequently.

References

(1) This investigation was supported by the U.S. Army Research Office, Durham.

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