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FREE RADICAL CHLORINATION OF BICYCLO[2.1.0]PENTANE[*]

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Reaction of chlorine with bicyclo[2.1.0]pentane in chloroform at -25°C has been reported to occur by electrophilic addition to the three membered ring leading to a 1,3-chloronium ion and to give predominantly dichlorides (1). Free radical chlorinations of several strained bicyclic systems (2) have been reported to occur primarily without rupture of the bicyclic ring systems. We have investigated the chlorination of bicyclo[2.1.0]pentane and wish to report on the novel course of this reaction.

Bicyclo[2.1.0]pentane, free of cyclopentene, was prepared by the method of Criegee (3) and was photochlorinated in a modification of the vapor phase chlorination apparatus described by Roberts and Mazur (4). The hydrocarbon vapors were boiled up through a pyrex spiral irradiated with two Sylvania 275 watt sunlamps, where they were mixed with chlorine, which was added slowly so that there was always a large excess of substrate to chlorine. The vapors were then condensed and returned to the boiler. Samples were withdrawn from the boiler during the course of the reaction, quenched in pyridine, washed with sodium bisulfite solution and water, examined spectroscopically and analyzed by vapor phase chromatography on several different columns. A complex mixture was obtained, whose components were identified by comparison of their v.p.c. retention times, indices of refraction and infrared and n.m.r. spectra with those of authentic samples. In a typical run, after complete reaction has occurred the relative percentages of detected products were: cyclopentene (27.8%)[⁎], 4-chlorocyclopentene (6.5%), chlorocyclopentane (36.1%), *trans*-1,2-dichlorocyclopentane (22.3%), *trans*-1,3-dichlorocyclopentane (3.8%), *cis*-1,3-dichlorocyclopentane (2.8%) and *cis*-1,2-dichlorocyclopentane (0.7%)[#]. No other simple products could be

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[⁎] Bicyclo[2.1.0]pentane alone does not isomerize to cyclopentene under these conditions.

[#] Not enough of this material could be obtained for spectra, but its v.p.c. retention times on three different columns were identical to those of authentic *cis*-1,2-dichlorocyclopentane.

detected.

This product mixture differs from that obtained in the low temperature ionic chlorination (1) in several important respects. Two new products, cyclopentene and 4-chlorocyclopentene, have appeared, and the relative percentage of chlorocyclopentane has increased significantly. The formation of 4-chlorocyclopentene seems to require the intermediacy of a free radical, most probably the Δ^3-cyclopentenyl radical. One way in which this intermediate can be formed is by chlorine atom abstraction of a 2-hydrogen of bicyclo[2.1.0]pentane, followed by rearrangement of the resultant bicyclic radical to the much less strained Δ^3-cyclopentenyl radical†. Our failure to detect chlorinated bicyclic products contrasts with the results obtained in less strained systems‡. Cyclopentene is present in large amounts even in the early stages of the reaction. At least some cyclopentene arises from the action of HCl on the bicyclic hydrocarbon. We have found that reaction of bicyclo[2.1.0]pentane with gaseous or aqueous HCl leads to as much as 46% of cyclopentene in addition to the expected chlorocyclopentane (5), in contrast to the report (6) that reaction of bicyclo[2.1.0]pentane with p-toluenesulfonic acid in acetic acid yields only cyclopentyl acetate. Chlorocyclopentane is formed mainly by addition of HCl to the starting material or to cyclopentene but alternate modes of formation via direct attack of a chlorine atom on the internal bridgehead carbon carbon bond are possible.

All of the products formed can react further. For instance it can be observed that the 1,2-dichloride builds up at the expense of cyclopentene. The relative percent of 4-chlorocyclopentene decreases somewhat after the early stages of the reaction suggesting that it undergoes further chlorination to yield undetected polychlorinated products. We are currently attempting to elucidate further details about the mechanism of formation of all the products of this reaction.

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† Loosening of the internal bridgehead carbon carbon bond may well occur concomitantly with carbon hydrogen bond breaking providing additional driving force due to relief of strain.

‡ Bicyclo[4.1.0]heptane yields chlorides from both the bicyclic radical and the ring opened cyclohexenylmethyl radical. R. S. Boikess and M. D. Mackay, unpublished results.

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