Tetrahedron Letters No. 4, pp. 146-147, 1961. Pergamon Press Ltd. Printed in the United States of America.

A NOVEL SYNTHESIS OF BICYCLO (3·2·1)-3-OCTEN-2-OL

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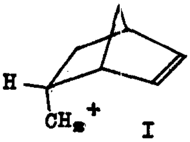
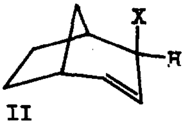
(Received 7 February 1961)

The abundance of rearrangements and non-classical ions implicit in the chemistry of bicyclo(2.2.1)heptane systems inspired an investigation of reactions involving the carbonium ion I and the corresponding exo isomer. We have investigated the gross features of one such reaction and have uncovered a novel rearrangement. Acetolysis at ca. 100° of the mixture of p-toluenesulfonate esters of the commercially available 2-hydroxymethylbicyclo(2.2.1)hept-5-ene led to a complex mixture in which the acetate IIa was the main component.



I



II
(a, X=OAc; b,X=OH)

III

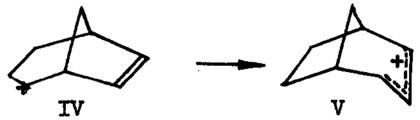
The structure of this compound is based on the evidence presented below. Fractional distillation of the solvolysis product gave IIa, b.p. 88.5-89°/11 mm, n_D^{25} 1.4807 (Found: C, 72.49; H, 8.59). Cleavage of the ester with lithium aluminum hydride in ether gave an alcohol (IIb)

whose properties were in agreement with those of a product assigned this structure by Wildman and Saunders;[1] p-nitrobenzoate, m.p. 84-85° (lit.[1] m.p. 81-81.5°), phenylurethan, m.p. 125-127° (lit.[1] m.p. 126-126.5°).

The allylic nature of the hydroxyl function was demonstrated by facile oxidation of the alcohol with manganese dioxide to an α,β-unsaturated ketone (III), b.p. 98.5°/20 mm λmax 227 mμ (ethanol), logϵ 3.9 (lit.[1] λ max 227 mμ, log ϵ 3.9); 2,4-dinitrophenylhydrazone, m.p. 140-142° (Found: C, 55.05; H, 4.73; N,18.96).

The trans stereochemistry of the product was inferred from the absence of infrared absorption at 1015 cm^{-1} in the spectrum of the bicyclo(3.2.1)octan-2-ol[2] obtained on catalytic reduction with hydrogen and palladium-charcoal.

This unusual rearrangement can best be rationalized by assuming the intervention of ion IV which could rearrange further to the allyl carbonium ion V. Attack of solvent from the exo side[2] would lead to the observed product.



IV V

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[1] W. C. Wildman and D. R. Saunders, *J. Amer. Chem. Soc.* **76**, 946 (1954).

[2] H. A. Youssef, M. E. Baum and H. M. Walborsky, *J. Amer. Chem. Soc.* **81**, 4709 (1959).