SHORT COMMUNICATIONS

Studies of 2-Azabicyclo[3, 2, 2]nonanone-3. I. A New Synthesis of 2-Azabicyclo[3, 2, 2]nonanone-3

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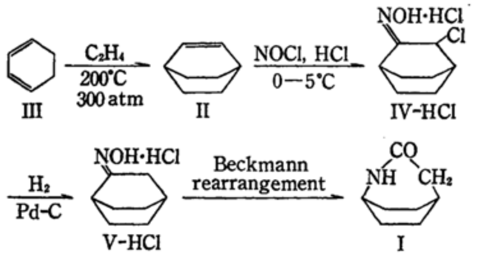
Although 2-azabicyclo[3, 2, 2]nonanone-3 (I)[1-3] seems to be an interesting modifier for the polyamide obtained from ε-caprolactam, no detailed report has yet been published on the copolymerization of I with ε-caprolactam.

In the course of our studies of the copolymerization, we have achieved a new synthesis of I, starting from bicyclo[2, 2, 2]octene-2 (II). II has been obtained by the reaction of 1, 3-cyclohexadiene (III) with excess ethylene under pressure in an pressure vessel at 200°C.[4]

The addition of nitrosyl chloride to II in the presence of hydrogen chloride at 0—5°C in triclene afforded 3-chlorobicyclo[2, 2, 2]octanone-2-oxime hydrochloride (IV-HCl), mp 127.5—130°C (dec.), in a 80% yield.



The treatment of IV-HCl with dilute NH_4OH gave the free chloroxime (IV), mp 106—106.5°C. The structures of IV-HCl and IV have been confirmed by elemental analysis, and by a study of their NMR and IR spectra.

The chlorine in the chloroxime was replaced with hydrogen under an atmospheric pressure, using Pd-C as the catalyst. Surprisingly enough, both IV and IV-HCl were smoothly hydrogenated at room temperature in ethanol. Bicyclo[2, 2, 2]octanone-2-oxime-hydrochloride (V-HCl) was obtained in an excellent yield, upon neutralization, this afforded the free oxime (V).

The Beckmann rearrangements of both V and V-HCl were carried out with benzenesulfonyl chloride in an alkaline solution. The product had a melting point identical with that of the lactam obtained from bicyclo[2, 2, 2]octanone-2 and hydroxylamine.[1]

The structure of the lactam was further confirmed by a study of the NMR spectrum and by the reduction of the carbonyl group with $LiAlH_4$.

Interesting polyamides have been obtained by the copolymerization of I with ε-caprolactam in various molar ratios. More detailed studies, including that of the copolymerization of I, will be published in the near future.

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1) H. K. Hall, Jr., *J. Am. Chem. Soc.*, **82**, 1209 (1960).
2) Swiss Pat. 276924 (1949).
3) G. Reinisch, H. Bara and H. Klare, *Chem. Ber.*, **99**, 856 (1966).
4) H. M. Walborsky and D. F. Loncrini, *J. Am. Chem. Soc.*, **76**, 5396 (1954).