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trans-BICYCLO[5.1.0]OCTANE (1)

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Our interest in bond angle deformation and considerations similar to those suggested by Gassman (2) have led us to investigate bicyclic compounds with a *trans*-fused cyclopropane ring. The acid catalyzed ring opening reactions (carried out in 0.005*M* p-toluenesulfonic acid in acetic acid) of the *cis*- and *trans*-bicyclo[6.1.0]nonanes (3) were found to proceed at nearly the same rate, and only the product distribution was different for the two compounds (Table I). The product distribution will be considered in more detail at a later time. The similarity in rates of reaction suggests that the energy difference is small, unlike the difference in energy between *cis*- and *trans*-cyclooctene (4, 5).

Since *trans*-fusion of an eight membered ring onto cyclopropane appeared to introduce only a small increase in strain, one might expect that the next smaller homolog, *trans*-bicyclo[5.1.0]octane, should be reasonably stable and *trans*-bicyclo[4.1.0]heptane might be isolable. We wish to report the synthesis of the former hydrocarbon via the route:

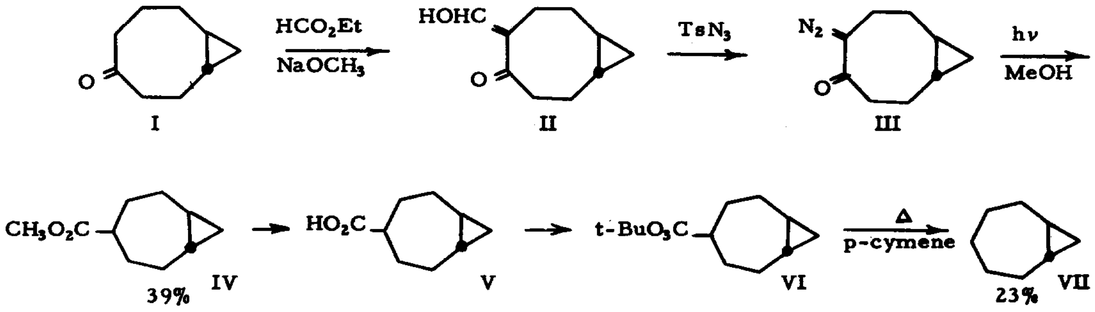
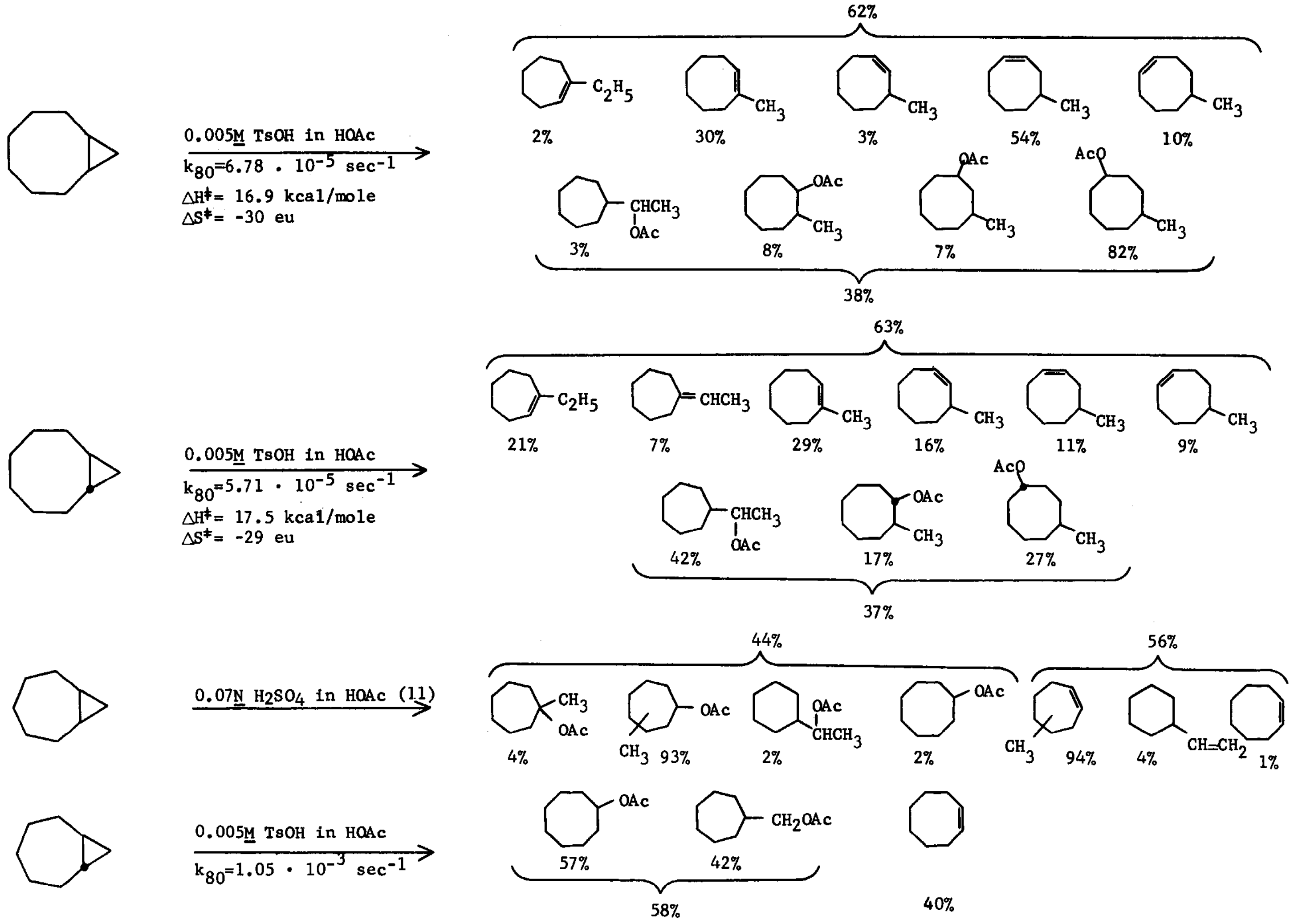


Table I

Rates and Products of Acetolysis of Bicyclo[n.1.0]alkanes



trans-Bicyclo[6.1.0]nonan-4-one has been described (6). Condensation with ethyl formate gave only one of the two possible isomers (II), which reacted with tosyl azide (7) to give the diazoketone (III). Photolysis of III in methanol gave the ester (IV) (39% yield based on I). The acid V was found by its melting point (mp 84-86°C) and nmr spectrum to be identical with the trans-bicyclo[5.1.0]octane-4-carboxylic acid prepared by Gassman et al. (8) via a different route.

The acid was converted to the t-butyl perester (VI). On heating in p-cymene (9), VI was converted to trans-bicyclo[5.1.0]octane (VII). The structure of VII was established based on the following data. The nmr spectrum showed two cyclopropane protons at high field (9.73τ). This is characteristic of trans-fused cyclopropane derivatives (6). cis-Bicyclo[5.1.0]octane has a band at high field (10.06τ) corresponding to only one proton (10). The nmr spectrum of VII indicated no vinyl protons, and both the mass spectrum and elemental analysis agreed with C_8H_{14}.

The reaction of VII with 0.005M p-toluenesulfonic acid in acetic acid at 80° occurred about 18 times faster than for trans-bicyclo[6.1.0]nonane. The product distribution is given in Table I along with the corresponding data for the cis-fused isomer determined by LaLonde and Forney (11). The unique feature of the product distribution is the predominant cleavage of the bridging bond (75%) whereas the other compounds in Table I react mainly by cleavage of one of the external cyclopropane bonds.

The small rate enhancement suggests that the increase in strain on going from the trans-[6.1.0] to the trans-[5.1.0] system is only on the order of a few kcal/mole. This is consistent with the remarkable thermal stability of the trans-[5.1.0] system. When the ester IV was heated at 280° for 39 hrs only 60-70% rearrangement to an unidentified olefinic product occurred. One might then expect trans-bicyclo[4.1.0]heptane to be reasonably stable and attempts are being made to prepare it.

References

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

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5. The difference in energy between *cis*- and *trans*-bicyclo[6.1.0]nonan-2-ones has been found to be 3.5±0.5 kcal/mole by equilibration (6).

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