

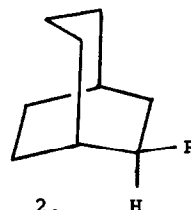
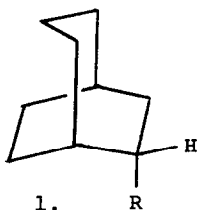
DEAMINATION OF THE EPIMERIC 6-AMINOMETHYLBICYCLO(3,2,2)NONANES

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(Received in UK 30 January 1970; accepted for publication 5 February 1970)

Bicyclo(3,3,2)decan-3-one and the corresponding epimeric 3-ols were required as part of our examination<sup>(1)</sup> of this ring system. Condensation of cyclohepta-1,3-diene and acrylonitrile<sup>(2)</sup> in a sealed tube at 165° furnished a 3:2 mixture of the epimeric 6-cyanobicyclo(3,2,2)non-8-enes which were separated by preparative thin-layer chromatography and hydrogenated to give 1 and 2, (R = CN). Comparison of the



corresponding p.m.r. spectra with that of the endo-acid<sup>(3)</sup> (1, R = CO<sub>2</sub>H) suggests that the exo-epimer (2, R = CN) predominates.

Lithium aluminium hydride reduction of the mixture<sup>(2)</sup> (1 and 2, R = CN) and subsequent treatment with HCl gas gave the corresponding hydrochlorides (1 and 2, R = -CH<sub>2</sub>NH<sub>3</sub><sup>+</sup>Cl<sup>-</sup>), which on treatment with nitrous acid at 100° and isolation of the product by steam distillation<sup>(2)</sup> gave a mixture of alcohols only poorly resolved by gas liquid chromatographic analysis.

Alder<sup>(2)</sup> assumed that this ring expansion deamination produced only bicyclo-(3,3,2)decan-3-ols, whereas a recent publication<sup>(4)</sup> describes a single alcohol which was characterised spectrally as the corresponding amine<sup>(5)</sup> and assigned the bicyclo-(3,3,2)decan-3-ol structure (of unknown configuration).

Acetylation of the above mixture and gas liquid chromatographic analysis\* with authentic samples<sup>(6)</sup>, revealed a product distribution consisting of mainly epimeric bicyclo(3,3,2)decan-2-ols. (See Table 1)

\* 50 metre, .01" diameter, T.C.E.P., capillary column.

TABLE 1

Product distribution (%) from Deamination of mixed *exo/endo*  
6-aminomethylbicyclo(3,2,2)nonanes

<u><i>exo</i></u> -2-bicyclo(3,3,2)decanol	16
<u><i>endo</i></u> -2-bicyclo(3,3,2)decanol	36
<u><i>exo</i></u> -3-bicyclo(3,3,2)decanol	6
<u><i>endo</i></u> -3-bicyclo(3,3,2)decanol	12
six unidentified components	30†

† Present in ca. equal amounts, all of shorter retention times than the 2 and 3-bicyclodecyl acetates.

An unambiguous determination of the stereochemistry of 1 and 2 (R = CN) and isolation and structural determination of the six minor components is now in progress with a view to elucidating the competing roles played by preferred conformation and "memory effects"<sup>(7)</sup> in determining the product distribution.

REFERENCES

- (1) M.P. Doyle and W. Parker, Chem. Comm., 1969, 319.
- (2) K. Alder, S. Hartung and G. Hausmann, Ber., 1956, 1972.
- (3) A.B. Penrose, Ph.D. Thesis, Glasgow University, 1969.
- (4) B.P. 1, 104, 058; A.P. 3, 427, 353; Chem. Abst., 1968, 69, 51739e.
- (5) Dr. A. Chow, personal communication.
- (6) Jones oxidation of *exo*-2-bicyclo(3,3,2)decanol<sup>(1)</sup> gave the corresponding 2-one ( $\nu_{\max} \text{CCl}_4$  1706  $\text{cm}^{-1}$ , incorporation of three deuterium atoms on treatment with 0.1 M. NaOD/Dioxan.  $M^+ m/e$  155). Subsequent lithium aluminium hydride reduction proceeded non-stereoselectively giving a 65:35 mixture of *exo:endo* 2-ols.  
Oxidation of *exo*-3-bicyclo(3,3,2)decanol<sup>(1)</sup> gave the 3-one ( $\nu_{\max} \text{CCl}_4$  1698  $\text{cm}^{-1}$ , incorporation of four deuterium atoms,  $M^+ m/e$  156). Similar reduction of this ketone gave a 2:3 mixture of *exo:endo* 3-ols.
- (7) J.A. Berson, Angew. Chem. Int., 7, 1968, 779.