Aziridines. XI. The *cis*- and *trans*-Cyclododecenimines

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BOTH *cis*- and *trans*-cyclododecenimine (13-azabicyclo-[10.1.0] tridecane) have now been prepared by the conventional Wenker synthesis, as suggested by observations on the similar steric requirements for the Wenker ring closure of aziridines and the Hofman ring closure of epoxides (*1, 2, 4*). On treatment with methyl iodide, each imine gave a stable quaternary salt. On treatment with methyl iodide, cycloheptenimine also gave a stable quaternary salt without opening of the aziridine ring, thus resembling cycloöctenimine rather than cyclohexenimine (*1*).

EXPERIMENTAL

***cis*- and *trans*-2-Aminocyclododecyl Hydrogen Sulfate.** The sulfate esters were prepared in the usual way (*5*) from the known amino alcohols (*3*). Analytical samples were not obtained because of the extreme insolubility of both compounds.

***trans*-Cyclododecenimine.** A solution of 6.0 grams of crude *cis*-sulfate and 12 grams of sodium hydroxide in 175 ml. of water was gently refluxed for three days. A portion of the product solidified in the condenser and was removed daily by washing with ether. The residual liquid was then extracted with ether. Distillation of the combined ether solutions and sublimation of the residue gave 1.08 gram (30%) of white solid, m.p. 50–55° C.

ANAL. Calcd. for $C_{12}H_{23}N$: C, 79.49; H, 12.79; N, 7.72.
Found: C, 79.69; H, 12.88; N, 7.22.

A picrolonate melted at 235° with decomposition.

ANAL. Calcd. for $C_{22}H_{31}N_5O_5$: C, 59.31; H, 7.01; N, 15.72.
Found: C, 59.03; H, 7.22; N, 15.75.

***trans*-13,13-Dimethyl-13-azoniabicyclo[10.1.0]tridecane Iodide.** A solution of 0.10 grams of *trans*-imine and 0.20 grams of methyl iodide in 5 ml. of benzene was allowed to stand in the dark for a day at room temperature. The yield of colorless, crystalline product was 50 mg., m.p. 198–203° dec. Conclusive evidence for the structure was provided by an x-ray diffraction study (*6*).

ANAL. Calcd. for $C_{14}H_{28}NI$: C, 49.85; H, 8.38; N, 4.15.
Found: C, 49.84; H, 8.55; N, 4.06.

***cis*-Cyclododecenimine.** The same procedure was used. From 380 mg. of crude *trans*-sulfate, was obtained after sublimation 120 mg. of colorless solid, m.p. 85–90°.

ANAL. Calcd. for $C_{12}H_{23}N$: C, 79.49; H, 12.79; N, 7.72.
Found: C, 79.58; H, 12.64; N, 8.12.

The infrared spectra (CCl_4) of the isomeric imines were nearly identical in the 4000–1600 cm.$^{-1}$ region, but differed greatly below 1600 cm.$^{-1}$

***cis*-13,13-Dimethyl-13-azoniabicyclo[10.1.0]tridecane Iodide.** A solution of 116 mg. of *cis*-imine and 232 mg. of methyl iodide in 5 ml. of benzene was allowed to stand in the dark for two days at room temperature. The yield of colorless, crystalline product was 70 mg., m.p. 206–209° with decomposition.

ANAL. Calcd. for $C_{14}H_{28}NI$: C, 49.85; H, 8.38; N, 4.15.
Found: C, 50.29; H, 8.26; N, 4.01.

8,8-Dimethyl-8-azoniabicyclo[5.1.0]octane Iodide. A solution of 0.89 gram of cycloheptenimine (*5*) and 2.8 gram of methyl iodide in 20 ml. of benzene was allowed to stand overnight at room temperature. The colorless, crystalline solid was collected and recrystallized from ethanol, giving colorless plates, m.p. 165–167°.

ANAL. Calcd. for $C_9H_{18}NI$: C, 40.46; H, 6.79; N, 5.20.
Found: C, 40.37; H, 6.81; N, 5.53.

The compound was readily soluble in water and the solution remained clear when it was made strongly alkaline by addition of sodium hydroxide solution, as expected for a quaternary salt. Furthermore, the infrared spectrum (KBr) closely resembled that of the homologous 9,9-dimethyl-9-azoniabicyclo[6.1.0]octane iodide, with bands near 3000 and 0450 cm.$^{-1}$ assigned to CH, as well as sharp, unassigned bands at 1345, 1270, and 1245 cm.$^{-1}$.

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