

Sulfone — colorless crystals, mp 173°–175° C (from ethanol). Found, %: C 73.54; H 7.72; S 9.40. Calculated for $C_{20}H_{24}O_2S$, %: C 73.17; H 7.32; S 9.75.

9-Benzyl-9-methyl-sym-octahydrothioxanthene (VI). Yield 80%. Colorless crystals, mp 52°–53° C (from ethanol). Found, %: C 81.52, 81.61; H 8.42, 8.35; S 9.93, 10.25. Calculated for $C_{21}H_{26}S$, %: C 81.23; H 8.44; S 10.33. **Sulfone**—colorless rods, mp 138.5°–140.5° C. Found, %: C 73.41, 73.44; H 7.94, 7.83; S 9.34, 9.21. Calculated for $C_{21}H_{26}SO_2$, %: C 73.64; H 7.65; S 9.36.

REFERENCE

1. V. G. Kharchenko, T. I. Krupina, and S. K. Klimenko, *ZhOrKh*, 2, 1899, 1966.

24 July 1967

Saratov Polytechnic Institute

SYNTHESIS OF 4-METHYL- AND 4-METHYLENE-sym-OCTAHYDROACRIDINES

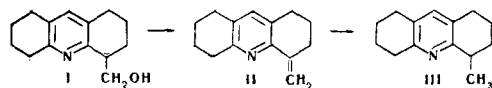
V. A. Stonik, V. I. Vysotski, and M. N. Tilichenko

Khimiya Geterotsiklicheskih Soedinenii, Vol. 4, No. 4, p. 763, 1968

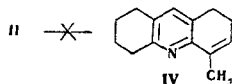
UDC 547.835

Of all the theoretically possible methyl-sym-octahydroacridines, only one — 9-methyloctahydroacridine — is known [1, 2]; homologs of octahydroacridine with unsaturated side chains are completely unknown.

By the dehydration of the 4-hydroxymethyloctahydroacridine (I) that we have described previously [3], we have obtained 4-methyleneoctahydroacridine (II), and by the hydrogenation of the latter we have obtained 4-methyloctahydroacridine (III).



The dehydration of I takes place readily both under the action of polyphosphoric acid (yield of II is 40%) and when it is heated with KOH (yield 45%). The latter method is more convenient preparatively. The absence of migration of the semicyclic double bond into the endocyclic position (II → IV) follows from a consideration of the PMR spectrum of 4-methyleneoctahydroacridine. The spectrum has no signals of methylene protons but has peaks at 4.80 and 6.10 ppm ascribed to the protons of a methylene group located, respectively, in the trans- and cis-positions with respect to the nitrogen atom.



4-Methylene-sym-octahydroacridine (II), bp 138°–142° C (1 mm), n_D^{20} 1.5850, d_4^{20} 1.0680. Found, %: C 84.82; H 8.72; N 7.11; MR_D

62.44. Calculated for $C_{14}H_{17}N$, %: C 84.36; H 8.61; N 7.02; MR_D 62.32. IR spectra (UR-10, carbon tetrachloride): 3080, 900 cm^{-1} ($=CH_2$). 1630 cm^{-1} ($C=C$), no hydroxyl absorption. Picrate mp 157.5°–159° C (acetone). Found, %: N 13.04. Calculated for $C_{14}H_{17}N \cdot C_6H_3N_3O_7$, %: N 13.08.

4-Methyl-sym-octahydroacridine (III) was obtained by the hydrogenation of II in ethanol over Adams catalyst at room temperature and atmospheric pressure. Yield 84%. Colorless crystals in the form of needles, mp 26°–28° C (petroleum ether), n_D^{20} 1.5563, d_4^{20} 1.0290 (supercooled melt). Found, %: C 83.58; H 9.43; MR_D 63.63. Calculated for $C_{14}H_{19}N$, %: C 83.54; H 9.43%; MR_D 63.79. In the PMR spectrum the signal of a CH_3 group is observed in the form of a doublet (1.11 and 1.25 ppm). Picrate mp 144°–145° C (ethanol). Found, %: N 13.00. Calculated for $C_{14}H_{19}N \cdot C_6H_3N_3O_7$, %: N 13.02. A mixture with the picrate of II melted at 126° C.

REFERENCES

1. M. N. Tilichenko, M. A. Abramova, and M. E. Egorova, *Izv. V. Sh., Khim. i khim. tekhnol.*, 3, 130, 1960.
2. N. Berbulesku, G. Beditse, and M. N. Tilichenko, *ZhOrKh*, 33, 4028, 1963.
3. M. N. Tilichenko, V. A. Stonik, and V. I. Vysotski, *KhGS [Chemistry of Heterocyclic Compounds]*, 4, 570, 1968.

9 February 1968

Far Eastern State University, Vladivostok