EXPERIMENTAL

The experiments were carried out with furoyl peroxide and hydroperoxide synthesized by known methods [13]. The purity of the samples, checked by iodometry, was 99% and the mp of the FP was 85° C (decomp.) and that of the FHP 59° C (decomp.). According to the literature [13], mp of FP 86° C, mp of FHP 60° C.

The determination of the hydrogen peroxide in the presence of the organic peroxides was carried out cerimetically by a method that we have developed. The sum of the organic peroxides and H_2O_2 was determined iodometrically. The spectra of the conversion products of the FP and FHP at various stages of the reaction were recorded on an SF-4 instrument. The mixtures of acids in the final products were separated by descending paper chromatography [14] and column adsorption chromatography on silica gel [15].

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12 December 1966

Krasnodar Polytechnic Institute

LETTERS TO THE EDITOR

REACTION OF sym-OCTAHYDROTHIOXANTHYLIUM PERCHLORATES WITH A GRIGNARD REAGENT

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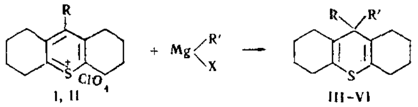
Khimiya Geterotsiklicheskikh Soedinenii, Vol. 4, No. 4, p. 762, 1968

UDC 547.818.6:542.957.2:543.422.4

We have established for the first time that sym-octahydrothioxanthylium perchlorate and its 9-alkyl derivatives smoothly react with a Grignard reagent forming 9-alkyl(aralkyl)-sym-octahydrothioxanthenes with yields of 80–85%;



I, II

I R = H;

II R = CH_3

X = Cl, Br

III–VI

III R = H, R' = CH_3;

IV R = H, R' = C_2H_5;

V R = H, R' = $CH_2C_6H_5$;

VI R = CH_3, R' = $CH_2C_6H_5$

This reaction is of scientific and practical interest, since it opens up the possibility of the synthesis of hydrothioxanthenes of new homologous series. The structures of III and IV are confirmed by the absence of a depression in mixtures of them with authentic 9-methyl- and 9-ethyl-sym-octahydrothioxanthenes, which have been obtained by independent syntheses. [1]. The structures of V and VI are confirmed by the results of elementary and spectral analyses and also by the analysis of their sulfones.

9-Ethyl-sym-octahydrothioxanthene (IV).– colorless crystals mp 23°–25° C (from a mixture of ethanol and ether, 2 : 1), yield 88%. Main frequencies in the IR spectrum: 675, 768, 820, 845, 1008, 1075, 1342, 1350 (shoulder), 1380, 1455, 1650, 1675 and a strong broad band at 2830–2980 with peaks at 2840, 2860, 2935, and 2970 (shoulder) cm^{-1} (the UV spectra were taken on a UR-10 instrument in paraffin oil). Sulfone–mp 126°–127° C (from petroleum ether). Found, %: C 67.70, 67.63; H 8.13, 8.29; S 11.70. Calculated for $C_{15}H_{22}SO_2$, %: C 67.67; H 8.27; S 12.03.

9-Benzyl-sym-octahydrothioxanthene (V). Yield 95.2%. Colorless crystals, mp 108°–110° C (from ethanol). Found, %: C 81.52, 81.46; H 7.80, 8.19; S 10.38, 10.74. Calculated for $C_{20}H_{24}S$, %: C 81.11; H 8.11; S 10.81. Main frequencies in the IR spectrum; 611, 671, 695, 747, 955, 1002, 1070, 1132, 1240, 1261, 1271, 1305, 1317, 1331, 1345, 1375, 1440, 1453, 1492, 1548, 1581, 1600, 1632, 1654 cm^{-1}.

Sulfone – colorless crystals, mp 173°–175° C (from ethanol). Fround, %: 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; 9.36.

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24 July 1967

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

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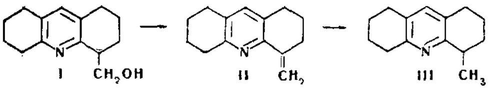
Khimiya Geterotsiklicheskikh Soedinenii, Vol. 4, No. 4, p. 763, 1968

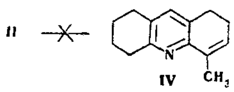
UDC 547.835

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.

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9 February 1968

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