V. I. Vysotskii and M. N. Tilichenko

The product of the alkaline dimerization of 2-benzylidenecyclohexanone has the 4a-hydroxy-9-phenyl-5-benzylidene-1,2,3,4,4a,5,6,7,8,9a-decahydroxanthene structure.

One of us, together with Kharchenko [1], reported the dimerization of 2-benzylidenecyclohexanone (I) under the influence of alkali. The benzylidenebenzaldicyclohexanone structure (II) was assigned to the dimerization product on the basis of its ability to form a dioxime and on the basis of alternative synthesis from 2,6-dibenzylidenecyclohexanone and cyclohexanone. However, the absorption characteristic for a carbonyl group is absent in the IR spectrum of the dimer, but there is a band at 3620 cm⁻¹ which corresponds to the vibrations of a hydroxyl group.

This can be explained starting from the assumption that one of the carbonyl groups in II is enolized during the synthesis, and the keto enol (III or V) thereby formed cyclizes to a decahydroxanthene derivative (IV or VI). A choice can be made between these two structures on the basis of the UV spectrum of the dimer. The long-wave maximum in it appears at 292 nm, i.e., at higher wavelengths than in starting ketone I.* This indicates the existence of a developed system of conjugated bonds in the dimer molecule and makes it possible to conclude that formula IV is more suitable for the description of the dimer structure than formula VI. However, the substance with structure VI should absorb light in the same way as styrene, the long-wave maximum in the spectrum of which appears at 248 nm [2].

A number of chemical transformations confirm that the dimer actually has structure IV. The compound is readily methylated (via the Helferich method) with the formation of methoxy derivative VII. It is dehydrated to 9-phenyl-5-benzylidene-1,2,3,4,5,6,7,8-octahydroxanthene (VIII) by the action of acidic reagents.

An analysis of the PMR spectra of IV and VII makes it possible to draw a conclusion regarding the configuration of these compounds. The C_9 proton in these spectra appears as a doublet with a spin-spin interaction constant of 11 Hz, which corresponds to a trans diaxial orientation of the C_9 and C_{9a} hydrogen atoms. The olefinic proton of the benzylidene group appears at 6.8 and 6.87 ppm, respectively, in the PMR spectra of IV and VII. This sort of shift of the signal to the weak-field side is explained by the steric proximity of the proton of the benzylidene group and the oxygen atom of the xanthene ring. Finally, the facile dehydration of IV indicates that the C_{4a} hydroxyl group and the C_{9a} hydrogen atom have a trans diaxial orientation. On the basis of this the configurations of IV and VII can be represented as IVa and VIIa, respectively.

The authors thank V. V. Isakov for obtaining the PMR spectra and A. K. Dzizenko for his assistance in interpreting them.

EXPERIMENTAL

The IR spectra (0.15 M solutions in CCl_4 , layer thickness 0.25 mm) were obtained with a UR-20 spectrometer. The UV spectra were obtained for 0.002% solutions in hexane with a VSU-2P spectrometer for a layer thickness of 10 mm. The PMR spectra of CCl_4 solutions were obtained with a ZKR-60 spectrometer, and the chemical shifts are given in the δ scale.

* For ketone I, λ_{\max} 281.5 nm (log ε 4.08).

Far-Eastern State University, Vladivostok. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 3, pp. 299-300, March, 1971. Original article submitted March 11, 1970.

© 1973 Consultants Bureau, a division of Plenum Publishing Corporation, 227 West 17th Street, New York, N. Y. 10011. All rights reserved. This article cannot be reproduced for any purpose whatsoever without permission of the publisher. A copy of this article is available from the publisher for \$15.00.



<u>4a-Hydroxy-9-phenyl-5-benzylidene-1,2,3,4,4a,5,6,7,8,9a-decahydroxanthene (IV)</u>. This was obtained by dimerization of ketone I according to the method in [1] and had mp 143-144° (from benzene-hexane) (mp 139° [1], 142-143° [3]); it was chromatographically pure [activity II Al₂O₃, hexane-ethyl acetate (8:1)]. IR spectrum: 3620 cm⁻¹, no absorption at 1600-1800 cm⁻¹. UV spectrum λ_{max} , nm (log ϵ): 207, 292 (4.05, 4.16). PMR spectrum: 2.3 (singlet, OH), 3.05 (doublet, J 11 Hz, H₉), 6.8 (singlet, -CH=), 7.1, 7.17 ppm (C₆H₅).

<u>4a-Methoxy-9-phenyl-5-benzylidene-1,2,3,4,4a,5,6,7,8,9a-decahydroxanthene (VII)</u>. A suspension of 2.0 g (5 mmole) of IV in 40 ml of 0.25% HCl in absolute methanol was refluxed for 40 h, cooled, and the precipitate was filtered to give 1.74 g (83%) of VII with mp 130-130.5° (from methanol). Found %: C 83.9; H 7.9; CH₃O 7.5. C₂₇H₃₀O₂. Calculated %: C 83.9; H 7.8; CH₃O 8.0. IR spectrum: no absorption at 3200-3700 cm⁻¹ and 1600-1800 cm⁻¹; 1100 cm⁻¹ (strong). UV spectrum λ_{max} , nm (log ε): 207, 292 (4.19, 4.21). PMR spectrum: 3.05 (doublet, J = 11 Hz, H₃), 3.2 (singlet, CH₃O), 6.87 (singlet, -CH=), 7.1, 7.17 ppm (C₆H₅).

<u>9-Phenyl-5-benzylidene-1,2,3,4,5,6,7,8-octahydroxanthene (VIII)</u>. A. Dry HCl was bubbled through a solution of 2.95 g (8 mmole) of IV in 50 ml of absolute benzene. The solution became turbid after 2 min. Drops of water collected after the mixture stood for a day. The benzene solution was washed with sodium bicarbonate solution and water, 30 ml of benzene was removed by distillation, the residue was diluted with 125 ml of absolute alcohol, and 1.0 g of VIII crystallized out.

B. A solution of 10.0 g (27 mmole) of IV in 100 ml of absolute benzene was refluxed with 50 mg of ptoluenesulfonic acid in a flask equipped with a Dean-Stark trap for 3 h. A total of 0.45 ml of water (compared with the calculated value of 0.48 ml) was collected in the trap. The reaction product was isolated in the same way as in method A to give 4.3 g (46%) of VIII with mp 111-113° (from alcohol). Found %: C 88.0; H 7.4. $C_{26}H_{26}O$. Calculated %: C 88.1; H 7.4. IR spectrum: no absorption at 3200-3700 cm⁻¹, 1715 cm⁻¹,* 1640 cm⁻¹. PMR spectrum: 3.3 (singlet, H_9), 6.8 (singlet, -CH=), 7.1, 7.17 ppm (C_6H_5).

LITERATURE CITED

- 1. M. N. Tilichenko and V. G. Kharchenko, Dokl. Akad. Nauk SSSR, 110, 226 (1956).
- 2. V.S. Fikhtengol'ts, R.V. Zolotareva, and Yu. A. L'vov, Atlas of UV Absorption Spectra of Substances Used in the Manufacture of Synthetic Rubbers, Vol. 7 [in Russian], Moscow-Leningrad (1965), p. 10.
- 3. M. N. Tilichenko, V. G. Kharchenko, and T. I. Krupina, Zh. Obshch. Khim., <u>34</u>, 2721 (1964).
- 4. S. Masamune and N. T. Castelucci, J. Am. Chem. Soc., <u>84</u>, 2452 (1962).

^{*}Judging from [4], this frequency is due to vibrations of the pyran ring.