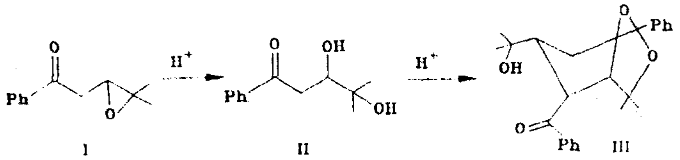
# SYNTHESIS OF A SUBSTITUTED 6,8-DIOXABICYCLO[3.2.1]OCTANE

**P. U. Posas, L. S. Novikov, and V. A. Mezhentsev**

UDC 547.915

The literature data on the conversion of epoxy ketones to the corresponding 5-phenyl-2,3-dihydro-3-furanones [1, 2] open up the possibility of using 4-methyl-1-phenyl-3,4-epoxy-1-pentanone (I) in the synthesis of the natural compound 2,2-dimethyl-5-phenyl-3(2H)-furanone (bulatenone) [3] by cyclization of ketone I in an acidic medium.

However, we have found that in the presence of sulfuric, oxalic, trifluoroacetic, and other acids in THF epoxy ketone I undergoes isomerization to 3,4-dihydroxy-4-methyl-1-phenyl-1-pentanone (II) in 87% yield, while 2-benzoyl-3-(1-hydroxy-1-methylethyl)-7,7-dimethyl-5-phenyl-6,8-dioxabicyclo[3.2.1]octane (III) is formed in 58% yield when the solution is refluxed. The bicyclic product contains a skeletal fragment that lies at the foundation of some natural pheromones [4, 5].



A solution of 0.19 g (1 mmole) of epoxy ketone I in 15 ml of THF and 3 ml of 30% $H_2SO_4$ was refluxed for 45 min, after which it was cooled, diluted with water, and extracted with ether. The ether extract was dried with $MgSO_4$, the ether was removed by distillation, and the residue was crystallized from methanol to give 0.11 g (58%) of III in the form of colorless crystals with mp 153-154°C. IR spectrum (KBr): 1657 (C=O), 3471 $cm^{-1}$ (O—H). PMR spectrum ($CDCl_3$), ppm: 1.00, 1.12, 1.37, and 1.53 (3H each, s, $CH_3$); 4.47 (1H, d, J = 8.2 Hz, CHO—); 3.03 (1H, dd, $J_1$ = 8.2 Hz, $J_2$ = 10 Hz, CHCO—); 1.97 (1H, m, $J_1$ = 10.0 Hz, $J_2$ = 12.0 Hz, $J_3$ = 4.0 Hz, CHC—); 2.38 (1H, dd, $J_1$ = 10.0 Hz, $J_2$ = 12.0 Hz, $CH_2$); 2.53 (1H, dd, $J_1$ = 12.0 Hz, $J_2$ = 4.0 Hz, $CH_2$); 2.88 (1H, s, OH); 7.14-7.56 (10H, m, $C_6H_5$). $M^+$ 380.

It follows from the Karplus correlation that the experimental $J_{12}$ value of 8.2 Hz corresponds to a dihedral angle of 30°, and, on the basis of an analysis of Dreiding models, one may therefore state that the configuration presented above for III is the preferred configuration.

## LITERATURE CITED

1. F. Bohlmann, F. Stohr, and J. Staffeldt, *Chem. Ber.*, **111**, 3146 (1978).
2. K. Gupinath, P. K. Mahanta, F. Bohlmann, and C. Zdero, *Tetrahedron*, **32**, 737 (1976).
3. W. Parker, R. A. Raphael, and D. I. Wilkinson, *J. Chem. Soc.*, No. 16, 3871 (1958).
4. K. Mori and Y. B. Seu, *Tetrahedron*, **42**, 5901 (1986).
5. P. F. Hundrlik, A. M. Hundrlik, T. Yimenu, and M. A. Waugh, *Tetrahedron*, **44**, 3791 (1988).

---

A. M. Gor'kii Minsk Pedagogical Institute, Minsk 220809. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 5, pp. 692-693, May, 1991. Original article submitted March 27, 1990.