CYCLIZATION OF 2,2-DIMETHYLCYCLOPENTANE-1,3-DIONE MONOPHENYLHYDRAZONE

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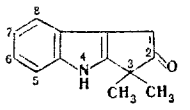
The behavior of cyclopentane-1,3-dione arylhydrazones in the Fischer reaction has not been previously investigated. In the present research it was shown that 3,3-dimethyl-1,2,3,4-tetrahydrocyclopenta[b]indol-2-one (I) is formed in the thermal cyclization of 2,2-dimethylcyclopentane-1,3-dione monophenylhydrazone.



I

The yield depends on the reaction temperature and time and reaches 24.5% in the case of refluxing for 4 h in ethylene glycol in a nitrogen atmosphere. A further increase in the reaction time leads to a decrease in the yield due to partial decomposition of I. A decrease in the yield to 14.7% was also observed in the case of cyclization in diethylene glycol (refluxing for 3 h) and also in the absence of an inert gas atmosphere (15.2 and 11.9% in the case of refluxing for 4 h in ethylene glycol and diethylene glycol, respectively).

Compound I was also obtained by refluxing phenylhydrazine and 2,2-dimethylcyclopentane-1,3-dione (II) in alcohol in the presence of acidic agents; however, the yields were lower – 6.5 and 7.5%, respectively – in the presence of zinc chloride and hydrogen chloride.

A mixture of 0.86 g (8 mmole) of phenylhydrazine and 1 g (8 mmole) of ketone II [1] was heated for 30 min on a water bath, after which the liberated water was removed by distillation with benzene, 20 ml of ethylene glycol was added to the residual oil, and the mixture was refluxed in a nitrogen atmosphere for 4 h. It was then cooled and treated with 150 ml of water, and the resulting precipitate was removed by filtration, washed with water, dried, and dissolved in the minimum amount of benzene. The benzene solution was chromatographed with a column filled with activity II Al_2O_3 (elutation with benzene). Workup of the eluate gave a fraction with R_f 0.57 [Silufol, benzene–methanol (10 : 1), evaporation of which gave 0.39 g (24.5%) of indole I with mp 172-172.5°C (from heptane). IR spectrum (in KBr): 1747 cm^{-1} (C=O). UV spectrum (in alcohol), λ_{max} (log ε): 217 (4.38) and 279 nm (3.94). PMR spectrum (in $CDCl_3$): 8.3 (1H, s, NH, broad signal), 6.99-7.64 (4H, m, aromatic protons), 3.57 (2H, s, CH_2), and 1.42 ppm (6H, s, CH_3). Found: C 78.5; H 6.6; N 6.9%. $C_{13}H_{13}NO$. Calculated: C 78.4; H 6.6; N 7.0%.

LITERATURE CITED

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