LETTERS TO THE EDITOR

# FORMATION OF TRIPYRROLYLMETHANE DERIVATIVES

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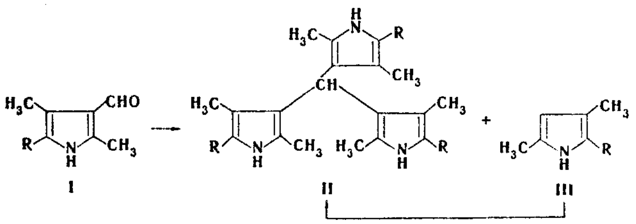
UDC 547.748.745

In a study of the possibility of protection of the formyl group in formylpyrroles by means of ethylene glycol in the presence of p-toluenesulfonic acid, we observed that even brief heating of 2,4-dimethyl-3-formyl-5-carbethoxypyrrole (I) leads to the formation of a tripyrrolylmethane derivative (II). 2,4-Dimethyl-5-carbethoxypyrrole (III) was also isolated from the reaction mixture. When I is heated in ethylene glycol in acidic media, the formyl group is split out, as a result of which β-unsubstituted pyrrole III is formed. The subsequent condensation of III with the starting formylpyrrole gives tripyrrolylmethane II. No changes whatsoever were observed when I was heated in ethylene glycol in the absence of p-toluenesulfonic acid, and the starting pyrrole was isolated.

To prove the structure of the tripyrrolylmethane, it was synthesized from I and III. The samples obtained by the two routes have identical IR spectra and do not differ with respect to their mobilities on aluminum oxide and silica gel; no melting-point depression was observed for mixtures of them.

In contrast to dipyrrolylmethanes [1], the most intense peak in the mass spectrum of II is the molecular ion peak with m/e 511, which attests to the increased stability of such compounds.



$R = COOC_2H_5$

## EXPERIMENTAL

Tris(2,4-dimethyl-5-carbethoxy-3-pyrrolyl)methane (II). A. A 0.05-g sample of p-toluenesulfonic acid was added to a solution of 1 g of I in 40 ml of ethylene glycol, and the mixture was heated on a steam bath for 20 min. It was then poured into 100 ml of 5% KOH solution, and the resulting precipitate was removed by filtration. The product was applied to a column filled with silica and eluted with chloroform to give, initially, pyrrole III and then 0.37 g of II with mp 241-242° (from alcohol). IR spectrum: 3300 (NH), 1660 cm$^{-1}$ (C=O). Mass spectrum, m/e (intensity, %): 511 (M$^+$, 100), 496 (53), 466 (18), 450 (22), 438 (60), 392 (24), 358 (19), 329 (47). Found: C 65.6; H 7.4; N 8.4%. $C_{28}H_{37}N_3O_6$. Calculated: C 65.7; H 7.3; N 8.2%.

B. A solution of 1 g of I and 1.7 g of III in 20 ml of alcohol was heated with 0.15 ml of concentrated hydrochloric acid on a steam bath for 20 min and was then poured into water. The precipitate was removed by filtration and recrystallized from alcohol to give 1.4 g (53%) of a product with mp 241.5-242°.

## LITERATURE CITED

1. A. H. Jackson, G. W. Kenner, H. Budzikiewicz, C. Djerassi, and J. M. Wilson, Tetrahedron, 23, 603 (1967).

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M. V. Lomonosov Moscow Institute of Precision Chemical Engineering. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 9, p. 1291, September, 1972. Original article submitted January 5, 1972.