Chemistry of Heterocyclic Compounds, Vol. 30, No. 8, 1994

UNEXPECTED MIGRATION OF THE BENZYL GROUP IN N-BENZYLINDOLES

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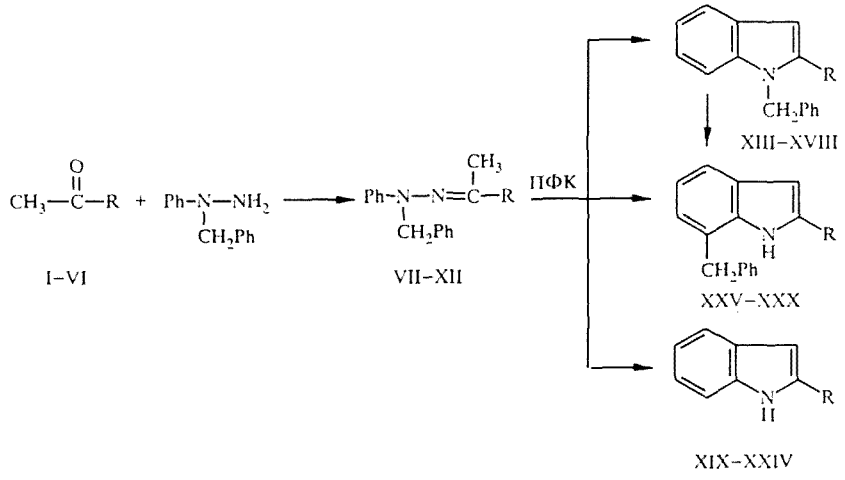
In an attempt to synthesize the N-benzyl derivatives of certain 2-phenylindoles we observed an unexpected migration of the benzyl group.

On heating hydrazones VII-XII or a mixture of N-benzylphenylhydrazine and methyl ketones I-VI in polyphosphoric acid, besides the expected N-benzyl derivatives XIII-XVIII, split-off products (compounds XIX-XXIV) and migration products of the benzyl group (compounds XXV-XXX) are formed.

It was found (chromatographic control) that in all cases the benzyl group splits off at 50-60°C, while a rearrangement takes place at a higher temperature — at 90-110°C.



I, VII, XIII, XIX, XXV R = C_6H_5; II, VIII, XIV, XX, XXVI R = *p*-$C_6H_4NO_2$; III, IX, XV, XXI, XXVII R = *p*-$C_6H_4OCH_3$; IV, X, XVI, XXII, XXVIII R = *p*-C_6H_4Br; V, XI, XVII, XXIII, XXIX R = Alk; VI, XII, XVIII, XXIV, XXX R = $COOC_2H_5$

The split-off products of the benzyl group XIX-XXIV were identified by comparison of R_f, the melting points and the IR spectra with the data for the previously synthesized 2-phenylindoles.

On heating the authentically pure N-benzyl derivatives in PPA it was found that the rearrangement occurs after the cyclization. The rearrangement proceeds to completion with R = Ar or $COOC_2H_5$ without side processes occurring, while with R = Alk the reaction mixture resinifies before completion of the rearrangement.

Compounds XXV-XXX with the Ehrlich reagent give a color characteristic for an indole unsubstituted at the β-position. In the IR spectra of these compounds there are absorption bands in the 3500-3400 cm^{-1} region characteristic for the indole NH group.

The Tbilisi State University of the Georgian Republic, Tbilisi 380028. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 8, pp. 1146-1147, August, 1994. Original article submitted July 5, 1994.

0009-3122/94/3008-0993$12.50

In the PMR spectra (in DMSO-D_6) of the rearrangement products the two doublets at 7.61 and 7.85 ppm (J = 8.7 Hz) are assigned to the 2-phenyl ring protons. The benzyl group protons appear in the form of a singlet at 4.26 (CH_2) and a multiplet in the region of 7.30-7.11 ppm (C_6H_5), the NH signal at 11.38 ppm, and the doublet at 6.89 ppm (J = 2.2 Hz) can be assigned to the 3-H proton. The 4-H and 6-H proton signals appear in the form of two doublets of doublets (J_{ortho} = 7.6; J_{meta} = 1.4 Hz) at 6.80 and 6.76 ppm, respectively, while the 5-H proton appear in the form of a triplet at 6.88 ppm (J_{ortho} = 7.4 Hz). Thus, the benzyl substituent is present at the 7-position of the indole ring.

The elemental analysis and mass-spectral data agree well with the proposed structures.