RECYCLIZATION OF 4-METHYL(PHENYL)-2,3-DIHYDRO-1H-1,5-BENZODIAZEPIN-2-ONES

A. A. Gaponov, Z. F. Solomko, N. Ya. Bozhanova, and
E. I. Pantyukh

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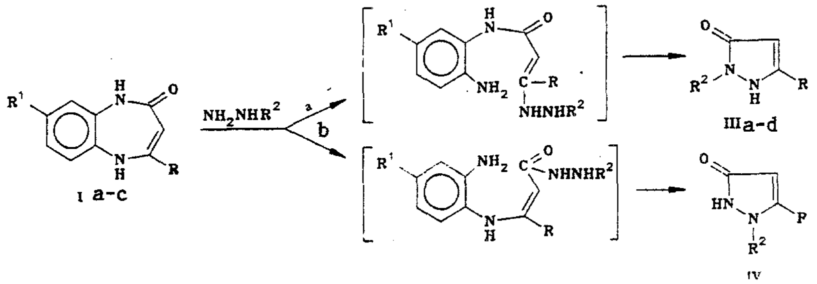
Depending on the reaction conditions, the hydrazinolysis of 4-(acetyl-methylene)-1,2,3,5-tetrahydro-1,5-benzodiazepin-2-one affords N-(2-aminophenyl)-5-methyl-3-pyrazolylacetamide or 2-benzimidazo-5-methyl-3-pyrazolylmethane [1]. In the presence of phenylhydrazine, 3,4,5-trimethyl-1,5-benzodiazepine is recyclized to 3,4,5-trimethyl-1-phenyl-2-pyrazole [2].

For 4-substituted 2,3-dihydro-1H-1,5-benzodiazepin-2-ones Ia-c, the reactions with hydrazine and phenylhydrazine were not investigated previously. We showed that during heating of diazepinones Ia and Ib with hydrazine hydrate IIa and phenylhydrazine IIb and of compound Ic with phenylhydrazine for 2-5 h, the recyclization of the seven-membered ring is accompanied by the formation of 3-monosubstituted IIIa and IIIb or 1,3-disubstituted 5-pyrazolones (IIIc and IIId). Apparently, the recyclization is accompanied by cleavage of the $C_{(4)}-N_{(5)}$ bond (direction a) with the formation of an acyclic intermediate, which subsequently is converted to the corresponding pyrazolone.



I a $R=CH_3$, $R^1=H$; b $R=C_6H_5$, $R^1=H$; c $R=C_6H_5$, $R^1=Cl$; III a $R=CH_3$, $R^2=H$; b $R=C_6H_5$, $R^2=H$; c $R=CH_3$, $R^2=C_6H_5$; d $R=R^2=C_6H_5$; IV $R=R^2=C_6H_5$

In the case of attack of hydrazines at the carbonyl carbon atom (direction b in the recyclization of compounds Ib and Ic in the presence of phenylhydrazine), pyrazolone isomer IV with mp 256°C [4] should be formed rather than pyrazolone IIId with mp 136-137°C [3]. The absence of isomer IV among the reaction products argues for direction a.

The IR and PMR spectra and melting points of the obtained compounds are similar to those described in the literature (see, e.g., [3]) and confirm the structure of the synthesized compounds. The structure of compound IIIc was also confirmed by back synthesis from acetoacetic ester and phenylhydrazine.

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