REACTION OF DIHYDROPYRAN WITH PHENYL AZIDE

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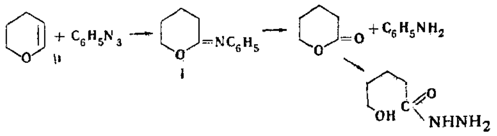
Khimiya Geterotsiklicheskikh Soedinenii, Vol. 5, No. 1, pp. 24–25, 1969

UDC 547.811'812.5

The reaction of dihydropyran with phenyl azide leads to the formation of N-phenyliminotetrahydropyran.

Reaction of aromatic azides with olefins takes place in two main directions depending on the strain of the double bond: with formation of triazolines in the case of strained olefins [1–4] and with the formation of arylimino derivatives for ordinary olefins [1, 2, 5]. For cyclic vinyl ethers with an unstrained double bond, this reaction should lead to aryliminolactones. The latter play an important part in processes of the cleavage of peptide bonds [6, 7].

We have found that the reaction of dihydropyran with phenyl azide does actually lead to an unstable, readily polymerizing, phenyliminolactone (I). The structure of I was shown by its hydrolytic decomposition.



The acid hydrolysis of I gives valerolactone, identified in the form of 5-hydroxyvaleric hydrazide. The alkaline saponification of I leads to the formation of aniline.

EXPERIMENTAL

Valerolactone phenylimide (I). A mixture of 4.25 g of phenyl azide and 10 g of dihydropyran was boiled for 10 hr. Vacuum distillation yielded 3.2 g of I with bp 135–140° C (3 mm). An analytical sample was obtained after two distillations, bp 130–132° C (2.5 mm), n_D^{20} 1.5707, d_4^{20} 1.100. MR_D 52.31. $C_{11}H_{13}NO$. Calculated: MR_D 51.97. Found, %: C 75.30; 75.28; H 7.67; 7.30; N 7.73; 7.89. Calculated for $C_{11}H_{13}NO$, %: C 75.40; H 7.48; N 7.99. The IR spectrum of I has an absorption band at 1667 cm^{-1} (C=N) and lacks absorption bands in the 2170–2120 cm^{-1} region (azide group).

A solution of 1 g of I in 7 ml of methylene chloride was shaken with 5 g of 25% sulfuric acid, the organic layer was separated off, the acid layer was extracted with 3 ml of methylene chloride, and the combined extracts were distilled in vacuum to give 0.21 g of δ-valerolactone with bp 112° C (13 mm), n_D^{20} 1.4691, d_4^{20} 1.079. According to the literature: bp 88° C (4 mm), mp 12.5° C, d_4^{20} 1.1081, n_D^{20} 1.4568 [8]; bp 83–85° C (3 mm), d_4^{20} 1.1439, n_D^{20} 1.4869 [9].

A 0.2 g quantity of δ-valerolactone was treated with 0.2 g of hydrazine hydrate. The crystals that deposited were pressed out on the filter, and recrystallization from a mixture of acetonitrile and benzene (1 : 1) gave 5-hydroxyvaleric hydrazide with mp 103–105° C. According to the literature: mp 107° C [10].

A mixture of 0.8 g of I and 5 g of 30% KOH solution was boiled for 18 hr and extracted with ether, and 1 ml of acetic anhydride was added to the ethereal extracts, which gave 0.32 g of acetanilide.

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9 December 1966

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