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REARRANGEMENT OF AZIDOXIMES TO TETRAZOLE DERIVATIVES

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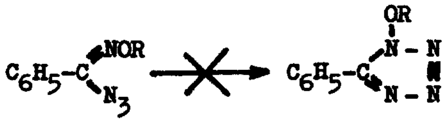
Products obtained in the reaction of chloroximes (hydroxamic acid chlorides) with azide ion were originally formulated as 1-hydroxytetrazoles[1,2]. Infrared spectroscopy investigations by Eloy[3] indicate, however, that these compounds exist as open-chain azides (I) and do not isomerise to tetrazoles (II).



$R = H, CH_3, COC_6H_5$

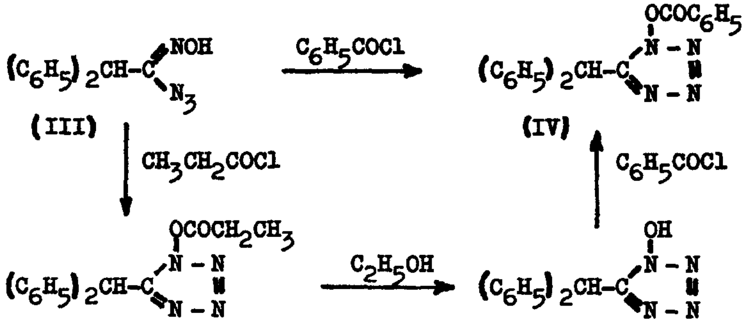
(I) (II)

This statement is supported by other authors[4,5].

I have found, however, that the azidoximes can be converted into the appropriate tetrazoles; both types of compounds are reasonably stable and easy to isolate in pure form. Diphenylacetazidoxime (III) was used as a model compound for this study. It was obtained in the reaction of diphenylacetohydroxamic acid chloride with sodium azide in a water/methanol solution at room temperature. The compound was stable and was purified by recrystallisation from ethanol. Mp.146° with decomp. IR(KBr): 3270 (O-H), 2160 and 2137 (N_3); mol. wt. by mass spectrometry 252.

Reaction of the azidoxime (III) with benzoyl chloride at elevated temp. (75-80°) gave the appropriate benzoyl derivative (IV), mp.131-2°, IR(KBr): 1805 (C = O), mol.wt. by MS - 356. IR spectrum of IV showed no absorption bands in the 2500-1900 cm^{-1} region. This fact suggested that cyclization to tetrazole ring occurred during the reaction.

Reaction of the azidoxime (III) with propionyl chloride in cyclohexane soln. at room temp. yielded the appropriate propionyl derivative (V), mp.131--2°; IR(KBr) 1853 (C = O); mol.wt. by MS - 308. V underwent deacylation when refluxed in ethanol. The deacylated product, 5-diphenylmethyl-1-hydroxytetrazole (VI), mp.196.5-197.5°, mol.wt. by MS - 252, revealed no IR absorption bands in the region characteristic for the azido group. VI treated with benzoyl chloride at 75-80° gave the benzoyl derivative (IV), identical with that prepared from III.



Phenylazidoxime[1] (I, R = H) mp.123-4° with decomp.; IR(KBr) 2157 (N_3); mol.wt. by MS - 162, was prepared analogously as described for III.

Reaction of phenylazidoxime (I, R = H) with acetyl chloride or propionyl chloride in cyclohexane solution at room temp. gave 1-hydroxy-5-phenyltetrazole (II, R = H), mp.151-2° with decomp.; mol.wt. by MS - 162.

Further investigation of the chemical and spectral properties of these compounds is in progress.

References:

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