

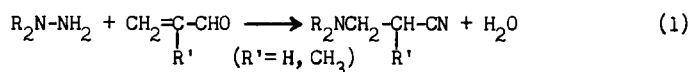
ON THE AMINONITRILIC REARRANGEMENT

B.V. Ioffe and K.N. Zelenin

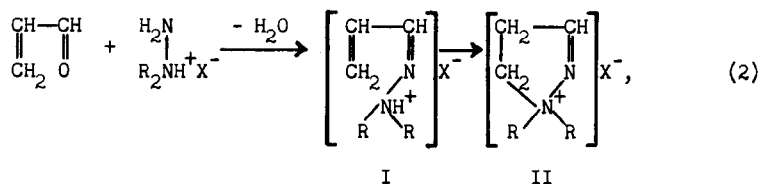
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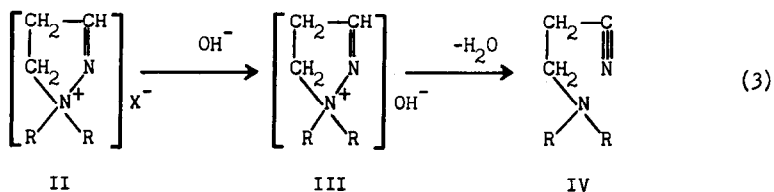
OUR recent reports<sup>1,2</sup> have shown the  $\beta$ -dialkylaminonitriles to be obtained by the interaction of salts of unsymmetrical dialkylhydrazines and acrolein or methacrolein followed by the alkalization of the reaction mixture:



We have established that such an "aminonitrilic rearrangement" passes through the stages of cyclization in pyrazolinium salts and of the decay of quarternary pyrazolinium bases:



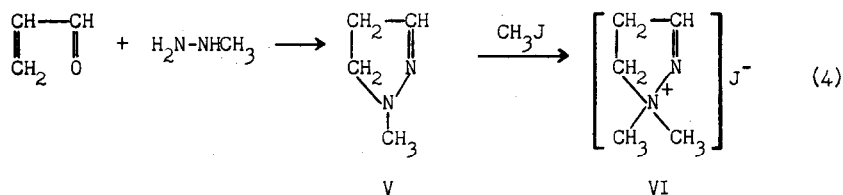
and then



<sup>1</sup> B.V. Ioffe and K.N. Zelenin, Dokl. Akad. Nauk SSSR **134**, 1094 (1960).

<sup>2</sup> B.V. Ioffe and K.N. Zelenin, Dokl. Akad. Nauk SSSR **141**, 1369 (1961).

Nobody has supposed the possibility of cyclization in heterocycles with the unsymmetrical dialkylhydrazines in reaction (2) under such mild conditions (cold mixing of reagents), and the simplest quarternary pyrazolinium salts (II) have been unknown. We proved their structure for 1,1-dimethylpyrazolinium iodide by the synthesis from methylhydrazine and acrolein according to the scheme:



Iodomethylate of 1-methylpyrazoline (VI) is identical with the interaction product of acrolein and water solution of hydroiodide of unsymmetrical dimethylhydrazine (II, R = CH<sub>3</sub>, X = J). Halides of quarternary pyrazolinium bases are very soluble in water and crystallize from it with difficulty. 1,1-Dimethylpyrazolinium iodide (VI) decomposes upon heating to 150-180°, the aminonitrile salt being contained in the transformation products. Corresponding quarternary bases (III) smoothly rearrange just at the moment of their formation. Thus, treatment of the concentrated water solution of 1,1-dimethylpyrazolinium iodide with 50 per cent alkali immediately yields β-dimethylaminopropionitrile (scheme 3; R = CH<sub>3</sub>, X = J).

The absence of the rearrangement in the condensation of acrolein with methoxyamine (unable to form stable onium ions) is the indirect evidence of the proposed mechanism.

The cyclization in quarternary pyrazolinium salts occurs readily only in the case of vinyl derivatives (acrolein, methylvinylketone). For homologues of acrolein the reaction (2) stops at the stage of the formation of unsaturated hydrazones (I).<sup>2</sup> Aminonitrilic rearrangement seems to occur under mild conditions only in the case of unsubstituted hydrogen atom in

position 3 of pyrazoline ring, and therefore pyrazolinium base from methyl-vynilketone and dimethylhydrazine decomposes to form polymers instead of aminonitrile.<sup>2</sup>

The elucidation of the mechanism of aminonitrilic rearrangement gives extensive possibilities for its practical application. In fact, quarternary pyrazolinium salts may be synthesized not only from unsymmetrical dialkylhydrazines but by the alkylation of various readily available pyrazolines. This second method will enable the preparation of pyrazolinium salts with various substituents in the ring and also the different  $\beta$ -aminonitriles, aminoacids,  $\beta$ -diamines and their derivatives otherwise difficult to obtain.

To illustrate preparative possibilities of aminonitrilic rearrangement we carried out the syntheses of  $\beta$ -dimethylaminoisobutyronitrile. At first, the unknown 1,4-dimethylpyrazoline and 1,1,4-trimethylpyrazolinium iodide have been obtained from methacrylic aldehyde and methylhydrazine [similarly to (4)], and then the pyrazolinium salt has been rearranged by the action of alkali at 0°C into the corresponding  $\beta$ -aminonitrile (53 per cent yield). This aminonitrile has also been isolated by condensation of methacrylic aldehyde and unsymmetrical dimethylhydrazine but its yield has been very poor.