SYNTHESIS OF IMIDAZOLINIUM SALTS BY CYCLIZATION OF AMINO ISONITRILES

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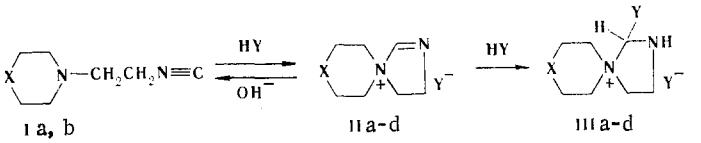
In a study of the possibility of obtaining stable salts of 2-amino isonitriles we observed a new heterocyclization reaction.

Thus spiro-imidazolinium salts II were obtained in 40-60% yields when amino isonitriles I were treated with an equimolar amount of acid in organic solvents at 20°C with subsequent isolation by the usual methods:



I a, b IIa-d IIIa-d

I a X=O, b X=CH_2; II a X=O, Y=Cl; b X=O, Y=TsO; c X=CH_2, Y=Cl; d X=CH_2, Y=TsO;
III a X=O, Y=Cl, Y=Cl; b X=O, Y=TsO, Y=Cl; c X=CH_2, Y=Cl, Y=Cl; d X=CH_2, Y=TsO, Y=Cl

The IR spectra of II (KBr) do not contain the band of vibrations of an isonitrile group at 2160, but a band at 1660 cm^{-1}, which is characteristic for the cyclic amidinium fragment of the molecule, is observed.

Compound IIa had mp 138°C and was obtained in 62% yield. PMR spectrum [$(CD_3)_2SO$, hexamethyldisiloxane (HMDS)]: 7.93 (s, 1H, $N^+CH=N$), 4.23 (t, 2H, $=NCH_2$), 3.84 (t, 4H, OCH_2), 3.49 (t, 2H, N^+CH_2), and 3.19 ppm (t, 4H, N^+CH_2). Compound IIb had mp 110-112°C and was obtained in 45% yield. PMR spectrum [$(CD_3)_2SO$, HMDS]: 7.99 (s, 1H, $N^+CH=N$); 7.5, 6.86 (two d, 4H, C_6H_4); 4.24 (t, 2H, $=NCH_2$); 3.86 (t, 4H, OCH_2); 3.49 (t, 2H, N^+CH_2); 3.23 (t, 4H, N^+CH_2); and 2.25 ppm (s, 3H, CH_3).

The results of elementary analysis were in agreement with the calculated values.

The structure of II was also confirmed by their ability to undergo conversion to the starting isonitrile upon treatment with 10% aqueous NaOH solution. On activity IV Al_2O_3 salt II (Y = Cl, TsO) undergoes partial conversion to starting I.

In connection with the fact that isonitriles are resistant to the action of salts of highly basic amines and strong acids [1], the reaction that we discovered may be related to the recently investigated heterocyclization of functionally substituted isonitriles with spatially close centers [2].

The reaction of isonitrile I with two equivalents of acid or of salt II with one equivalent of acid gave III, to which the structure of 2-substituted spiro-imidazolinium salts was assigned on the basis of the IR and PMR spectra. In the IR spectra of salts III the absorpiton band at 1660 cm^{-1} vanishes, and a band of stretching vibrations of the NH group appears at 3410 cm^{-1}.

Compound IIIa had mp 124-126°C and was obtained in 70% yield. PMR spectrum [$(CD_3)_2SO$, HMDS]: 8.74 (broad s, 1H, NH), 3.87 (t, 4H, CH_2O), and 3.08-3.6 ppm (m, 9H, CH_2N^+, CH_2N, N^+CHNH). Compound IIIb had mp 187-189°C and was obtained in 95% yield. PMR spectrum [$(CD_3)_2SO$, HMDS]: 8.15 (broad s, 1H, NH); 7.0, 7.39 (two d, 4H, C_6H_4); 3.80 (t, 4H, CH_2O); 3.00-3.45 (m, 9H, CH_2N^+, CH_2N, N^+CHNH); 2.21 ppm (s, 3H, CH_3). The results of elementary analysis were in agreement with the calculated values.

LITERATURE CITED

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