Experimental

Catalytic hydrogenation of 3, 3, 6, 6-tetramethyl-1, 2, 3, 4, 5, 6, 7, 8-octahydroacridine-1, 8-ione (Ia). 0.05 g PtO_2 in 50 ml ethanol are reduced with hydrogen for two hours, about 20 ml of the latter being consumed in the reduction and surface absorption. Then 0.5 g Ia (mp 149°) in 75 ml alcohol is introduced into the hydrogenation vessel. The solution immediately acquires a greenish fluorescence. Ia is hydrogenated for two hours, in which time 46 ml H_2 is used (theoretical 44 ml hydrogen [295° K] 770 mm). When hydrogenation ceases, the catalyst is filtered off, half of the alcohol distilled off in a vacuum, and an equal volume of water added to the residue. Yield 0.45 g (90%) IIa, mp 280°. Twice recrystallized from acetone-ethanol 296°. Undepressed mixed mp with IIa previously prepared [3].

Catalytic hydrogenation of 3, 3, 6, 6-tetramethyl-9-phenyl-1, 2, 3, 4, 5, 6, 7, 8-octahydroacridine-1, 8-dione (Ib). Carried out similarly. Yield 90% IIb. Identical with the compound previously [3] prepared.

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25 November 1964

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UDC 547.772+542.95

RING-OPENING OF QUATERNARY SALTS OF 1-ETHYLPYRAZOLINE WITH AN ELECTRON-ACCEPTING GROUP IN THE ETHYL RADICAL

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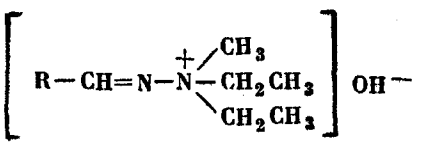
Khimiya Geterotsiklicheskikh Soedinenii, Vol. 1, No. 2, pp. 307-309, 1965

Electron-acceptor groups at the β position in the ethyl radical of quaternary salts of N-ethylpyrazoline do not facilitate rupture of the C-N bond in the Hofmann degradation, and the pyrazole ring opens to give β-cyanoethylamines.

It has recently been pointed out [1-5] that a resemblance exists between nitrile scission of pyrazoline and aldehyde hydrazone salts, and the Hofmann degradation of quaternary ammonium bases. As was shown by B. I. Ioffe and coworkers [4, 6], scission of the N-N bond and nitrile group formation with type I and II compounds takes place more readily than formation of ethylene in the Hofmann degradation of the C-N bond, and this was ascribed to special reactivity of the hydrogen atom at the C = N double bond.



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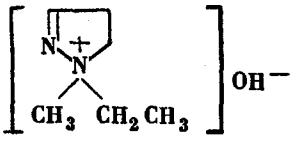
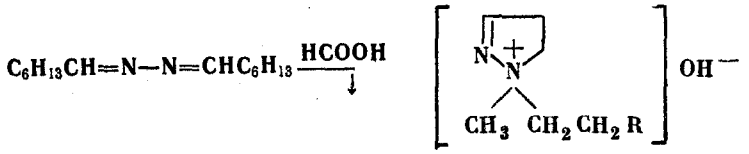


II

We have now synthesized pyrazolines with an ethyl group having additional electron-accepting substituents in the β position for the nitrogen atom, which considerably increased the susceptibility of structures III and IV to the Hofmann degradation.



However, under these conditions, scission occurred only at the N-N bond. Thus when the reaction products from degradation of III and IV in aqueous alkali were analyzed by thin-layer chromatography using alumina, spots corresponding to 1-methylpyrazoline, acrolein 1-methylcyanoethylhydrazone, and acrolein methyl (β-phenylethyl) hydrazone were not found. With various solvents, only one spot was discovered, that corresponding to methyl-di-(2-cyanoacetyl)

amine (or, as the case may be, methyl (2-cyanoethyl)-(2-phenylethyl) amine). Only the individual compounds formed by nitrile scission were isolated from the reaction products.

Hence the N-N bond is much more labile than the C-N one, even in the case of enhanced mobility of a hydrogen atom situated β to the substituting ethyl group.

Experimental

1-(2-phenylethyl) pyrazoline. 5.6 g freshly distilled acrolein is added gradually to a mixture of 13.6 g 2-phenylethylhydrazine, 30 ml water, and 15.6 g monosodium dihydrogen phosphate at 0°. The reaction mixture is left for four hours, 6 g KOH in 50 ml water are then added, and the whole extracted with ether. The ether extract is dried over KOH and distilled. Yield 6.2 g (35.6%) of 1-(2-phenylethyl, pyrazoline, bp 137-140° (14 mm), n_D^{20} 1.5457. Found: C 75.63, 75.60; H 7.92, 7.84%. Calculated for $C_{11}H_{14}N_2$: C 75.82; H 8.09%.

1-(2-phenylethyl) pyrazoline methiodide. A mixture of 4.8 g 1-(2-phenylethyl) pyrazoline, 20 ml dry ether, and 4.3 g methyliodide is refluxed together for eight hours. The precipitate of quaternary salt is separated off. Yield 5.7 g (67%), mp 118-120° (from dry methanol). Found: C 45.48, 45.50; H 5.47, 5.54%. Calculated for $C_{12}H_{17}N_2I$: C 45.58; H 5.42%.

Degradation of 1-(2-phenylethyl) pyrazoline methiodide. 10 ml water, and then 20 ml 40% sodium hydroxide solution are added to 4.8 g 1-(2-phenylethyl) pyrazoline methiodide. The oil which separates is extracted with ether, and the extract dried over K_2CO_3. When the ether is removed, styrene is not found. At 166-170°/20 mm, 2 g (71.4%) methyl(2-phenylethyl) (2-cyanoethyl) amine distill over as a colorless liquid having n_D^{20} 1.5170, d_4^{25} 0.9835. Found: C 76.17, 76.12; H 8.75, 8.79%. Calculated for $C_{12}H_{16}N_2$: C 76.55; H 8.56%.

Thin-layer chromatography was carried out using grade IMP, DKhR (2nd degree of activity, layer 0.5 mm thick) alumina, and systems benzene : methanol (60 : 1), benzene : acetone (4 : 1), and acetone : cyclohexane (1 : 1), one spot being obtained with R_f = 0.70, 0.57, and 0.68 respectively. An intense band was found at 2254 cm^{-1} (nitrile group) in the ir spectrum (IKS-14, vaseline). Picrate, mp 97° (from alcohol). Found: C 52.03, 51.98; H 4.68, 4.69%. Calculated for $C_{18}H_{19}O_7N_5$: C 51.79; H 4.59%.

1-(2-cyanoethyl)pyrazoline. 10 g (22.6%) 1-(2-cyanoethyl)pyrazoline, bp 100-103° (6 mm), n_D^{20} 1.4802, are prepared by the method above from 0.4 mole 2-cyanoethylhydrazine and 0.4 mole acrolein (but the extraction is with benzene). The pyrazoline is used without further purification for preparing the methiodide.

1-(2-cyanoethyl) pyrazoline methiodide. A mixture of 8.5 g 1-(2-cyanoethyl) pyrazoline, 20 ml dry ether, and 12.8 g methyl iodide is refluxed for eight hours. An oil separates out on the bottom of the flask. This crystallizes on rubbing with a glass rod. The quaternary salt weighs 17.8 g (97.2%), mp 123-124° (from absolute methanol). Found: C 31.94, 31.73; H 4.57, 4.69%. Calculated for $C_7H_{12}N_3I$: C 31.71; H 4.56%.

Degradation of 1-(2-cyanoethyl) pyrazoline methiodide. 20 ml water and 50 ml 40% NaOH solution are added, with stirring, to 17.5 g 1-(2-cyanoethyl) pyrazoline. After 30 min the mixture is carefully extracted with ether, and the extract dried over K_2CO_3. After taking off the ether the residue is distilled, when 1-methylpyrazoline and acrylonitrile are not found in the low-boiling material. Yield 5 g (53.2% on the pyrazoline) methyldi(2-cyanoethyl) amine, bp 144-146° (3 mm); n_D^{20} 1.4602. The literature [7] gives 148° (3 mm), n_D^{25} 1.4584. The ir spectrum (IKS-14, vaseline) shows absorption at 2248 cm^{-1}, corresponding to the nitrile group. The identity of the two preparations was also demonstrated by thin-layer chromatography using the conditions described. With the systems chloroform : methanol (60 : 1), benzene : acetone (4 : 1), and acetone : cyclohexane (1 : 1) R_f was, respectively, 0.63, 0.60, and 0.80. Picrate, mp 164-165° (from methanol), undepressed mixed mp with methyldi(2-cyanoethyl) amine prepared by means of the reverse synthesis, i.e. by dicyanoethylating methylamine [7].

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11 December 1964

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