2-Isopropylamino-4, 5-dimethylthiazole was prepared in 85% yield. Colorless needles, mp 100.5-102°(from aqueous alcohol). Found N 16.40; S 18.75%. Calculated for $C_8H_{14}N_2S$: N 16.45; S 18.83%.

The product of reaction of 3-chlorobutan-2-one with 1-isopropylthiourea melts at 101-102°. Mixed mp undepressed.

The picrate forms yellow transparent prisms, mp 215° (decomp.) (from alcohol-acetic acid). Found: N 17.12%. Calculated for $C_8H_{14}N_2S \cdot C_6H_3N_3O_7$: N 17.05%.

2-Cyclohexylamino-4, 5-dimethylthiazole. Viscous yellow oil, bp 124° (3-4 mm), $n_D^{20}$ 1.5578; $d_4^{20}$ 0.8688. Yield 41%. Found: N 13.29; S 15.10%. Calculated for $C_{11}H_{18}N_2S$: N 13.3; S 15.24%.

The picrate forms long yellow fibrous needles, mp 238-239° (decomp.) (from acetic acid). Found: N 15.95%. Calculated for $C_{11}H_{18}N_2S \cdot C_6H_3N_3O_7$: N 16.15%.

The reaction product from 3-chlorobutan-2-one and 1-cyclohexylthiourea give a picrate, mixed mp with the picrate above 238°.

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30 November 1963



Dnepropetrovsk Chemical Engineering Institute



UDC 547.835+542.941


# POLYNUCLEAR HETEROCYCLIC COMPOUNDS. XIX*. REDUCTION OF 3, 3, 6, 6-TETRAMETHYLOCTAHYDROACRIDINE-1, 8-DIONES


E. I. Stankevich, and G. Ya. Vanag

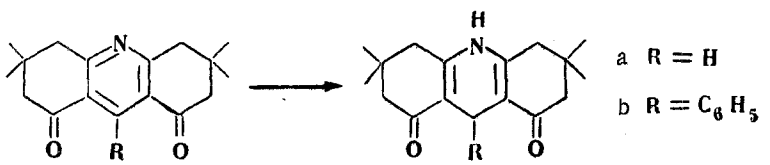


Khimiya Geterotsiklicheskikh Soedinenii, Vol. 1, No. 2, pp. 305-306, 1965



Reduction in alcohol solution, using hydrogen at atmospheric pressure and platinum oxide catalyst, of 3, 3, -6, 6-tetramethyl-1, 2, 3, 4, 5, 6, 7, 8-octahydroacridine-1, 8-dione and its 9-phenyl derivative gives the corresponding 3, 3, 6, 6-tetramethyl-1, 2, 3, 4, 5, 6, 7, 8, 9, 10-decahydroacridine-1, 8-dione and its 9-phenyl derivative.


The present authors [2] have previously described borohydride and sodium hydrosulfite reduction of 3, 3, 6, 6-tetramethyl-1, 2, 3, 4, 5, 6, 7, 8-octahydroacridine-1, 8-dione (Ia), to 3, 3, 6, 6-tetramethyl-1, 2, 3, 4, 5, 6, 7, 8, 9, 10-decahydroacridine-1, 8-dione (IIa).




I a, b II a, b

In the reactions described the yields of the corresponding dihydropyridines were not very high, so further attempts were made to improve the yields and quality of the dihydro-derivatives. The best results were obtained by catalytically hydrogenating Ia, b over platinum oxide. In ethanol solution the necessary amount (1 mole) of hydrogen is taken up in two hours, and under the particular conditions the yields of decahydroacridinediones IIa, b amount to 80-90%. Under the reaction conditions used, there is no further reduction of the decahydroacridinediones, and no hydrogen is taken the next 24 hr. The IIa, b, thus prepared, are identical with the compounds previously synthesized [2].

*For part XVIII see [1].

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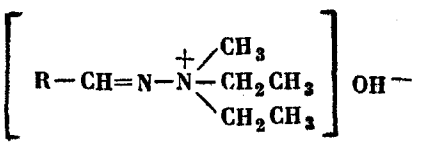
Khimiya Geterotsiklicheskikh Soedinenii, Vol. 1, No. 2, pp. 307-309, 1965



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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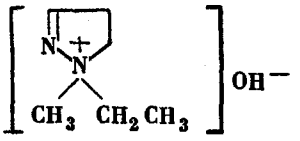
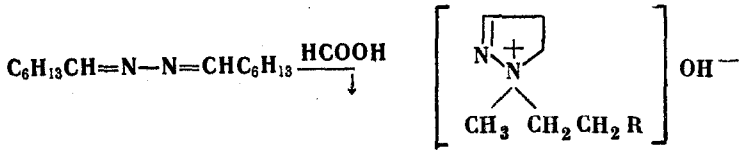


II

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)