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REACTION OF 6-QUINOLINE ALDEHYDE WITH RHODANINES AND 2, 6-DIMETHYLQUINOLINE

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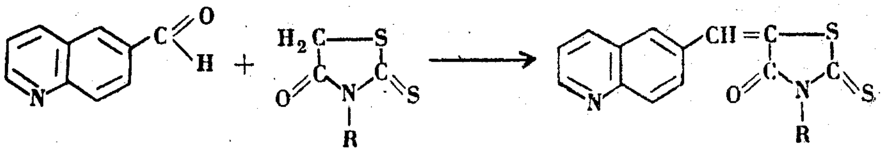
The crotonaldehyde type of condensation of 6-quinolylaldehyde and its methiodide with 3-methyl-3-ethyl-, and 3-allylrhodanines is investigated. 5-(Quinolidene-6-)-3-alkylrhodanines and their monomethiodides are synthesized. 2-[2-(Quinolyl-6) ethenyl]-6-methylquinoline is prepared by condensing 6-quinolylaldehyde with 2, 6-dimethylquinoline.

Extending previously published work [1-3], a study has been made of the reaction of 6-quinolylaldehyde and its methiodide with 3-methyl-, 3-ethyl-, 3-allylrhodanines and 2, 6-dimethylquinolines, where only the α-CH_3 group is active [4].

5-(Quinolidene-6)-3-methylrhodanine (I), 5-(quinolidene-6)-3-ethylrhodanine (II), and 5-(quinolidene-6)-3-allylrhodanine (III) are obtained in good yield by carrying out condensation at room temperature in methanol solution in the presence of pyridine.



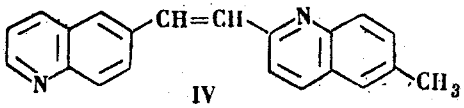
I II III

R=CH_3 (I), C_2H_5 (II), C_3H_5 (III)

6-Quinolylaldehyde methiodide condenses with the same rhodanines when they are heated together in glacial acetic acid, to give the methiodides of compounds I-III, which can be prepared by treating the bases I-III with methyl iodide.

The quinolidenerhodanines synthesized are fairly stable when stored in air, and their methiodides are even more stable.

The reaction of 6-quinolylaldehyde with 2, 6-dimethylquinoline on heating is analogous to the condensation with 2-methylquinoline [1], and gives 2-[2-(quinolyl-6)-ethenyl]-6-methylquinoline (IV).



IV

It is interesting to note that reaction of base IV with methyl iodide at room temperature gives a dimethiodide, whereas under the same conditions 2-[2-(quinolyl-6)-ethenyl] quinoline gives just the monomethiodide [1].

Experimental

5-(quinolidene-6)-3-methylrhodanine (I). 1.15 g (7.3 mmole) 6-quinolylaldehyde (mp 74-76°) and 1.15 g (7.8 mmole) 3-methylrhodanine were heated together for 3 min (until evolution of water ceased) in a metal bath at 165-170°. For recrystallizing, the product was dissolved in 15 ml boiling glacial acetic acid.

When 0.8 g (5.1 mmole) of the same aldehyde, 0.8 g (5.4 mmole) 3-methylrhodanine in 2 ml methanol, and 0.2 g freshly-distilled piperidine were mixed, there was spontaneous heating, a crystalline precipitate quickly formed, and this was filtered off, and washed with alcohol. Yield 1.3 g (89.6%) I, mp 239-240° (from glacial acetic acid). It was very sparingly soluble in methanol, ethanol, soluble in chloroform and glacial acetic acid, less soluble in benzene, insoluble in ether and hot water. Found: S 22.57%. Calculated for $C_{14}H_{10}N_2OS_2$: S 22.40%.

The methiodide, mp 264-266°* (from 60% acetic acid) was prepared by refluxing together for 45 min, 0.6 g

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*In most instances the mp of methiodides were determined by heating the capillaries from 150°.

(2 mmole) 6-quinoline-aldehyde methiodide and 0.3 g (2 mmole) 3-methylrhodanine in 6 ml glacial acetic acid. The next day the precipitate was filtered off, and washed with anhydrous ethanol. Yield 0.62 g (72.0%), dark red crystals. The substance was sparingly soluble in methanol, ethanol and glacial acetic acid, but dissolved in hot water. Found: 29.91%. Calculated for $C_{15}H_{13}IN_2OS_2$: I 29.64%.

5-(quinolidene-6)-3-ethylrhodanine (II). A mixture of 0.7 g (4.5 mmole) 6-quinolinealdehyde and 0.71 g (4.5 mmole) 3-ethylrhodanine was heated for 5 min in a metal bath at 150-155°. While hot the products were dissolved in 5 ml ethanol. Yield 1.12 g (84.2%) pale yellow crystals mp 183° (from benzene). When reaction was carried out in methanol with addition of piperidine, the yield was 93.2% mp 182-183° (from glacial acetic acid). The substance was sparingly soluble in methanol, ethanol, ether, more soluble in acetone, glacial acetic acid and benzene, readily soluble in chloroform, insoluble in water. Found: S 21.93%. Calculated for $C_{15}H_{12}N_2OS_2$: S 21.36%.

Methiodide, mp 207-208° (from 60% acetic acid), was obtained by refluxing for 1 hr a mixture of 0.5 g (1.7 mmole) 6-quinolinealdehyde methiodide and 0.3 g (1.9 mmole) 3-ethylrhodanine in 6 ml glacial acetic acid. Yield 0.6 g (81.0%). The same compound (in 69% yield) was obtained when 0.4 g (1.3 mmole) free base II and 2 ml methyl iodide were mixed and allowed to stand for three weeks. It was soluble in methanol, ethanol, glacial acetic acid, and water. Found: I 28.39%. Calculated for $C_{16}H_{15}IN_2OS_2$: I 28.72%.

The ethiodide of II could not be obtained by heating the aldehyde ethiodide with 3-ethylrhodanine in glacial acetic acid.

5-(quinolidene-6)-3-allylrhodanine (III). 0.2 ml piperidine was added to 0.5 g (3.2 mmole) aldehyde and 0.6 g (3.5 mmole) 3-allylrhodanine in 2 ml methanol, when a precipitate rapidly separated. Yield 0.95 g (95.9%) III. Yellow crystals mp 176-177° (from benzene). The compound was sparingly soluble in methanol and ether, more soluble in acetone and benzene, readily soluble in glacial acetic acid and chloroform, insoluble in water. Found: S 20.80%. Calculated for $C_{16}H_{12}N_2OS_2$: S 20.54%.

Methiodide was obtained in 86.8% yield from 0.7 g (2.3 mmole) aldehyde methiodide and 0.45 g (2.6 mmole) 3-allylrhodanine in 5 ml glacial acetic acid (30 min refluxing). Orange crystals, mp 180-182° (from dilute acetic acid). The same methiodide was obtained from 0.4 g (1.3 mmole) free base III and 2 ml methyl iodide by mixing and allowing to stand for three weeks at room temperature. Yield 94.8%. Reddish-orange crystals mp 179-182° (mixed mp). Soluble in methanol, ethanol, glacial acetic acid, and water. Found: I 27.56%. Calculated for $C_{17}H_{15}IN_2OS_2$: I 27.94%. III ethiodide could not be prepared by heating the aldehyde ethiodide with 3-allylrhodanine in glacial acetic acid.

2-[2-(quinolyl-6)-ethenyl]-6-methylquinoline (IV). 2.8 g (18 mmole) 6-quinolinealdehyde and 2.8 g (18 mmole) 2,6-dimethylquinoline were heated together for 15 min in a metal bath at 240-250°, then while still hot, dissolved in 5 ml ethanol. Yield 3.45 g (65.4%) pale yellow crystals mp 177-178° (from alcohol), soluble in methanol, ethanol, and benzene, more sparingly soluble in acetone and ether, readily soluble in chloroform and glacial acetic acid, insoluble in water. If allowed to stand for a week, the substance gradually turned green. Found: N 9.53%. Calculated for $C_{21}H_{16}N_2$: N 9.46%.

Dimethiodide, mp 277-278° (from 60% acetic acid), was prepared in 70% yield from 0.92 g (3.1 mmole) compound IV and 2 ml methyl iodide (refluxed 15 min in 10 ml acetic acid), or in 88% yield by allowing these reactants to stand for a week. Dark yellow crystals, soluble in methanol, ethanol, and hot water, very sparingly soluble in glacial acetic acid. Found: I 43.47%. Calculated for $C_{23}H_{22}I_2N_2$: I 43.76%.

Diethiodide, mp 270-273° (decomp. from dilute acetic acid), was prepared in 61% yield from 0.4 g (1.4 mmole) compound IV and 2 ml ethyl iodide in 5 ml glacial acetic acid (refluxed 8 hr). Dark yellow crystals, soluble in methanol and ethanol, very sparingly soluble in glacial acetic acid, sparingly soluble in water. Found: I 41.72%. Calculated for $C_{25}H_{26}I_2N_2$: I 41.74%.

Only solid resins were obtained when attempts were made to synthesize the dimethiodide and diethiodide by heating the appropriate 6-quinolinealdehyde and 2,6-dimethylquinoline alkhalides together in glacial acetic acid.

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