SYNTHESES IN THE FIELD OF QUINOLINE DERIVATIVES

IV. Condensation of 5-Chloromethylquinolin-8-ol with Dialkyl Dithiocarbamates*

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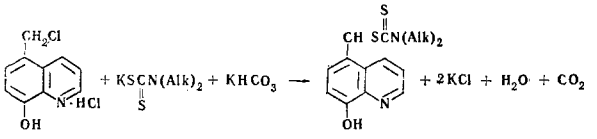
A number of 8-hydroxyquinolin-5-ylmethyl N, N-dialkyldithiocarbamates have been synthesized.

It is known that internally complexed dialkyldithiocarbamate compounds are used as pesticides [1]. Furthermore, both quinolin-8-ol and its internally complexed compound with copper (Bikvan) possess fungicidal properties [1]. Consequently, it appeared of interest to synthesize compounds combining the active principals of both types of substances. We have effected the synthesis of such compounds from 5-chloromethylquinolin-8-ol hydrochloride and salts of dialkyldithiocarbamates in accordance with the reaction:



Of a number of aprotic solvents tested (dioxane, benzene, ethyl acetate, petroleum ether), dioxane gave the best yields of dithiocarbamic acid derivatives. In dilute hydrochloric acid solution, the compounds synthesized form yellow-green hydrochlorides which are sparingly soluble in water.

The IR spectra of compounds I exhibit absorption bands characteristic for a quinoline ring and for a dithiocarbamate grouping. Thus, in addition to bands at 3420 cm^{-1} (stretching vibrations of an OH group) and at 1630, 1580, 1505, 1410, and 1380 cm^{-1} (stretching vibrations of C=C and C=N groups) and also at a weak band in the 2800–3100 cm^{-1} region (stretching vibrations of the CH groups of an aromatic ring), which are characteristic for the spectrum of quinolin-8-ol, the spectra of the substances obtained exhibit new bands. Thus, in the 2900–3100 cm^{-1} region the absorption is split into several bands, of which two (2950 and 2990 cm^{-1}) are the strongest. Absorption also appears in the 920–1145 cm^{-1} region which, according to literature data [2], is characteristic for the stretching vibrations of an aliphatic CN group. A strong band at 1300–1360 cm^{-1} is characteristic for the stretching vibrations of the C=S group [2]. The medium-intensity absorption at 1420–1440 cm^{-1} can be ascribed, on the basis of literature data, to the stretching vibrations of the N–Alk group [2]. Treatment of the absorption bands of the C=S group (705 cm^{-1}) and the NC=S group (1500 cm^{-1}) is difficult, since quinolin-8-ol itself also has strong absorption bands at 712 and 1505 cm^{-1} which are characteristic for the deformation vibrations of the CH group and of the stretching vibrations of the C=N group.

EXPERIMENTAL

8-Hydroxyquinolin-5-ylmethyl N, N-dialkyldithiocarbamates. With mechanical stirring, a carefully ground mixture of 4.6 g (0.02 mole) of 5-chloromethylquinolin-8-ol and 1.68 g (0.02 mole) of sodium bicarbonate was added to a solution of 3.42 g (0.02 mole) of sodium diethyldithiocarbamate in 30 ml of dioxane. The reaction mixture was heated until the solid matter had become colorless (1–2 hr). The solution was filtered hot, and the solvent was partially distilled off under reduced pressure. The residue was treated with water, and the precipitate that deposited was filtered off and recrystallized.

The other compounds given in the table were obtained similarly. The IR spectra of compounds I were recorded on a UR-10 instrument in the 700–3700 cm^{-1} region; the accuracy of the readings was ±5 cm^{-1}.

*For part III, see [3].

8-Hydroxyquinolin-5-ylmethyl N, N-dialkyldithiocarbamates (I)

Compound	N(Alk)₂	Mp, °C	Empirical formula*	N, % found	N, % calculated	Yield, %
1	$-N(CH_3)_2$	177—178	$C_{13}H_{14}N_2OS_2$	9.97	10.02	50—55
2	$-N(C_2H_5)_2$	113—114	$C_{15}H_{18}N_2OS_2$	9.07	9.05	50—55
3	$-N(C_3H_7)_2$	99—101	$C_{17}H_{22}N_2OS_2$	8.38	8.35	50—55
4	$-N(i\text{-}C_3H_7)_2$	96—98	$C_{17}H_{22}N_2OS_2$	8.32	8.35	40—45
5	$-N(i\text{-}C_4H_9)_2$	82—83	$C_{19}H_{26}N_2OS_2$	7.99	7.71	60
6	$-N\langle CH_2-CH_2\rangle O$ $\quad\quad CH_2-CH_2$	189—190	$C_{19}H_{16}N_2O_2S_2$	8.75	8.75	50—55
7	$-N\langle CH_2-CH_2\rangle N-$ $\quad\quad CH_2-CH_2$	208—209	$C_{26}H_{24}N_4O_2S_4$	10.25	10.01	40—45

*Compounds 1–6 were recrystallized from petroleum ether and compound 7 from dioxane or dimethylformamide.

The spectra of compounds **I–V** were measured in 5% chloroform solution and those of compounds **VI** and **VII** in tablets with potassium bromide.

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