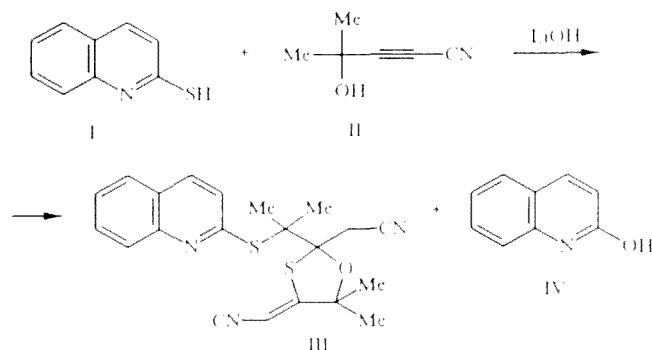


UNEXPECTED REACTION OF 2-MERCAPTOQUINOLINE WITH 4-HYDROXY-4-METHYL-2-PENTYNNITRILE

L. V. Andriyankova, A. G. Mal'kina, and B. A. Trofimov

During the reaction of 2-mercaptoquinoline (I) with 4-hydroxy-4-methyl-2-pentyne nitrile (II), the previously unknown 2-[1-methyl-1-(5,5-dimethyl-4-cyanomethylene-2-cyanomethyl-1,3-oxathiolan-2-yl)]ethylthioquinoline (III) was formed in a single stage instead of the expected cyanovinyl derivative. 2-Hydroxyquinoline (IV) was isolated as a side product. The products (III) and (IV) are probably formed through a stage involving the addition of the thiol (I) at the triple bond of the alcohol (II) followed by transformation of the cyanovinyl derivative into the oxathiolane ring.



To a solution of 0.32 g (2 mmole) of mercaptoquinoline (I) and 0.025 g (0.1 mmole) of lithium hydroxide in 10 ml of dioxane, we added 0.22 g (2 mmole) of the cyanoalkynyl alcohol (II). The mixture was stirred for 30 h. The dioxane was distilled, and the residue was chromatographed on a column of aluminum oxide with a 20:4:1 mixture of chloroform, benzene, and ethanol as eluant. The yield was 0.28 g (72%); mp 122-124°C (from a 5:1 mixture of hexane and acetone). The product was a mixture of the Z and E isomers in a ratio of 1.5:1.0. IR spectrum, cm^{-1} : 2210, ($\text{CNC}=\text{C}$), 2250 (CNCH_2). PMR spectrum (deuteriochloroform): 1.57, 1.71, 1.68, 1.84, 1.92, 1.96, 2.09 (24H, s, CH_3), 3.21, 3.30, 3.40, 3.47, 3.66 (4H, m, CH_2CN), 5.10, 5.21, (2H, s, $\text{C}=\text{CHCN}$), 6.8-8.0 ppm (6H, m, aromatic protons).

In addition, 0.03 g (10%) of the hydroxyquinoline (IV) was isolated from the column; mp 198-200°C. Published data: mp 199-200°C [1].

The elemental analysis of compound (III) for C, H, N, and S agreed with the calculated data.

REFERENCES

1. Beilstein, Handbuch der Organischen Chemie, Springer Verlag, Berlin (1931), Vol. 27, p. 77.