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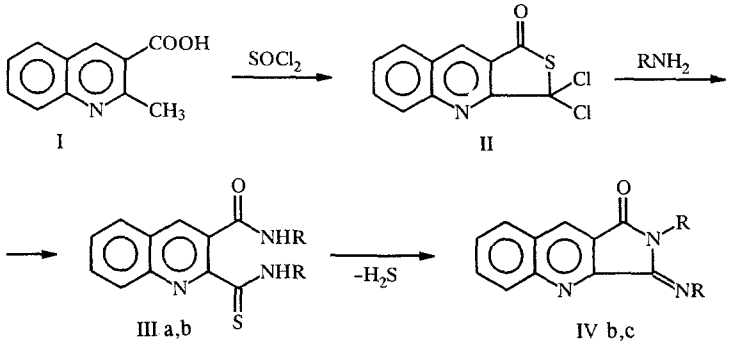
AMINOLYSIS OF THE PRODUCT OF THE OXIDATION OF 2-METHYLQUINOLINE-3-CARBOXYLIC ACID BY THIONYL CHLORIDE

V. P. Semenov, P. S. Lobanov, V. A. Gindin, and A. A. Potekhin

Thionyl chloride oxidizes methyl groups, whose hydrogen atoms display C—H acidity [1]. The product of the oxidation of 4-aryl-2-methylquinoline-3-carboxylic acid by thionyl chloride was found to be 3,3-dichloro-1,3-dihydrothieno[3,4-*b*]quinolin-1-one [2]. We carried out the oxidation of quinoline I by thionyl chloride and studied the reaction of the analogous oxidation product II with primary amines.

The structure of the products of this reaction depends on the nature of the R group in the primary amine. In the case of the bulky cyclohexyl radical, the reaction stops upon the formation of stable diamide IIIa. When the reaction was carried out with isobutylamine, diamide IIIb, which may be isolated, is also formed initially. However, diamide IIIb in chloroform slowly cyclizes to give 2-isobutyl-3-isobutylimino-2,3-dihydro-1H-pyrrolo[3,4-*b*]quinolin-1-one (IVb). NMR spectroscopy indicated that there is 50% conversion of IIIb to IVb in 30 days at room temperature. The cyclization of the intermediate diamide in the reaction of II with ethylamine occurs very rapidly and the only product of this reaction is pyrroloquinoline IVc.



IIIa R = *c*-C_6H_{11}; b R = *i*-C_4H_9; IVb R = *i*-C_4H_9; c R = C_2H_5

Thienoquinoline II. A mixture of 20 mmoles acid I and 15 ml thionyl chloride was heated at reflux until the precipitate disappeared and then for an additional 2 h. Excess thionyl chloride was evaporated in vacuum and the residue was washed with isooctane. The yield of II was 57%.

Reaction of II with Amines. A mixture of 3 mmoles primary amine and 3 mmoles triethylamine was added to a suspension of 1 mmole thienoquinoline II in 10 ml dioxane at 50°C. After 2 h, the reaction mixture was diluted with water. The precipitate was separated and recrystallized from xylene in the case of IIIa and IIIb and from octane in the case of IVc.

Diamide IIIa. Decomposed above 180°C with the liberation of hydrogen sulfide. PMR spectrum in DMSO-d_6: 1.0-2.2 (20H), 3.72 (1H, m), 4.37 (1H, m), 7.6-8.3 (6H, ArH, NH), 10.30 ppm (1H, NH). ^{13}C NMR spectrum in DMSO-d_6: 24.5, 25.1, 30.4, 32.1, 48.2, 53.6, 126.2, 127.1, 127.7, 128.5, 129.3, 130.3, 135.7, 145.8, 157.0, 165.6 (C=O), 194.5 ppm (C=S). The yield of IIIa was 47%.

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Diamide IIIb, mp 201.5-202°C (dec.). PMR spectrum in $CDCl_3$: 0.94 (6H, d), 1.08 (6H, d), 1.86 (1H, m), 2.22 (1H, m), 3.11 (2H, t), 3.67 (2H, t), 7.4-7.9 (5H), 6.85 (1H, t, NH), 9.65 ppm (1H, t, NH). ^{13}C NMR spectrum in $CDCl_3$: 20.2, 20.4, 27.3, 28.0, 47.6, 53.3, 126.4, 127.4, 127.5, 128.8, 129.0, 130.9, 136.3, 145.8, 154.7, 157.5 (C=O), 195.4 ppm (C=S). The yield of IIIb was 83%.

Pyrroloquinoline IVc, mp 134-13.43°C. PMR spectrum in $CDCl_3$: 1.23 (3H, t), 1.36 (3H, t), 3.84 (2H, q), 4.53 (2H, q), 7.55 (1H, t), 7.71 (1H, t), 7.81 (1H, d), 8.08 (1H, 1H, d), 8.38 ppm (1H, s). ^{13}C NMR spectrum in $CDCl_3$: 13.3, 16.6, 33.3, 44.5, 123.7, 127.0, 128.0, 129.1, 130.5, 130.8, 131.1, 149.7, 150.0, 147.1 (C=N), 164.6 ppm (C=O). The yield of IVc was 54%.

The elemental analysis data for II, IIIa, IIIb, and IVc corresponded to the calculated values.

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