H_2SO_4 for 5-10 h at 70-80°C [2], after which the mixture was neutralized with ammonium hydroxide and extracted with ether. The extract was dried with magnesium sulfate, the ether was removed by distillation, and the residue was fractionated in vacuo (spirans XV and XVI) or chromatographed on activity II Al_2O_3 by elution with ether (spirans XIII, XIV, XVII, and XVIII).

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4-HYDROXY-2-QUINOLONES.

1. EFFICIENT METHOD FOR OBTAINING 3-ALKYL-4-HYDROXY-2-QUINOLONES

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3-Alkyl-4-hydroxy-2-quinolones were obtained in high yields via the Dieckmann intramolecular condensation of substituted malonic acid ethyl ester 2-carbalkoxyanilides.

It is known that 4-hydroxy-2-quinolone and its derivatives with alkyl substituents in the 3 position of the quinolone ring are intermediates in the biosynthesis of furoquinoline, acridone, and some other alkaloids [1], while the synthetic method for obtaining the alkaloids lunacridine and lunacrine that is based on refluxing substituted malonic esters with aromatic amines in diphenyl oxide leads to 3-alkyl-4-hydroxy-2-quinolones in rather low yields (up to 27%) and is accompanied by the formation of symmetrical dianilides of substituted malonic acids.

We have developed an efficient method for obtaining 3-alkyl-4-hydroxy-2-quinolones that makes it possible to synthesize these compounds preparatively in high yields.

For this, methyl (ethyl) anthranilate I was acylated with substituted malonic acid monoethyl ester chlorides II, obtained by a previously developed method [3], or with substituted malonic acid monoethyl esters III in the presence of dicyclohexylcarbodiimide. The resulting substituted malonic acid ethyl ester 2-carbalkoxyanilides IV were subjected, without isolation, to Dieckmann intramolecular condensation. Subsequent acidification of the reaction mixtures made it possible to isolate the corresponding 3-alkyl-4-hydroxy-2-quinolones VII in high yields.

It is interesting that The Dieckmann condensation of esters IV is accompanied by the elimination of the carbethoxy grouping of the malonic acid residue, probably in the form of carbonic acid esters.

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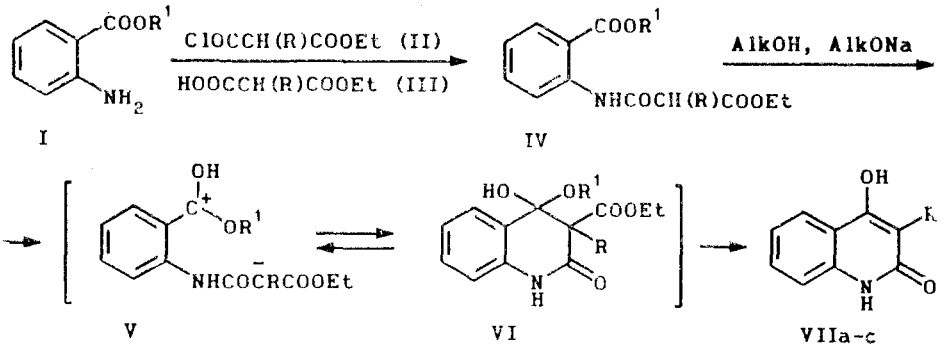

VII a R=CH_3; b R=C_3H_7; c R=$CH_2C_6H_5$

EXPERIMENTAL

The PMR spectra of solutions of the synthesized compounds in d_6-DMSO were recorded with a Bruker WP-100 SY spectrometer (100 MHz) with tetramethylsilane (TMS) as the internal standard.

The results of elementary analysis for C, H, and N were in agreement with the calculated values.

3-Methyl-4-oxo-2-quinolone (VIIa, $C_{10}H_9NO_2$). A 7.0-ml (0.05 mole) sample of triethylamine and 7.5 g (0.05 mole) of methylmalonic acid monoethyl ester chloride were added to a solution of 8.26 g (0.05 mole) of ethyl anthranilate in 20 ml of acetone. After 5 h, the acetone was removed, a solution of sodium ethoxide [from 4.6 g (0.2 mole) of sodium and 70 ml of absolute ethanol] was added to the residue, and the mixture was refluxed for 1 h. Ethanol (50 ml) was removed by distillation, the reaction mixture was cooled and treated with 100 ml of water, and the aqueous mixture was acidified to pH 4-5 with HCl. The precipitate was removed by filtration, washed with water, and dried to give a product with mp 264-266°C (from ethanol) (mp 265-268°C [4]). PMR spectrum, δ: 2.01 (3H, s, CH_3), 7.30 (3H, m, 6-8-H_{Ar}), 7.97 (1H, d, 5-H_{Ar}), 10.08 (1H, s, OH), 11.32 ppm (1H, s, NH). The yield was 8.32 g (95%).

3-Propyl-4-hydroxy-2-quinolone (VIIb, $C_{12}H_{13}NO_2$). This compound was similarly obtained and had mp 234-236°C (from ethanol). PMR spectrum, δ: 0.90 (3H, t, CH_3), 1.45 (2H, m, β-CH_2), 2.54 (2H, t, α-CH_2), 7.31 (3H, m, 6-8-H_{Ar}), 7.96 (1H, d, 5-H_{Ar}), 9.99 (1H, s, OH), 11.26 ppm (1H, s, NH). The yield was 9.35 g (92%).

3-Benzyl-4-hydroxy-2-quinolone (VIIc, $C_{16}H_{13}NO_2$). A 10.32-g (0.05 mole) sample of dicyclohexylcarbodiimide was added to a solution of 7.56 g (0.05 mole) of methyl anthranilate and 11.11 g (0.05 mole) of benzylmalonic acid monoethyl ester in 50 ml of dry methylene chloride. After 5 h, the dicyclohexylurea was removed by filtration, the solvent was removed from the filtrate by distillation, and a solution of sodium methoxide [from 4.6 g (0.2 mole) of sodium and 70 ml of absolute methanol] was added to the residue. The mixture was then worked up as described above to give a product with mp 218-219°C (from ethanol). PMR spectrum, δ: 3.94 (2H, s, CH_2), 7.00-7.59 (8H, m, 6-8-H_{Ar} + H_{Ph}), 7.98 (1H, d, 5-H_{Ar}), 10.38 (1H, s, OH), 11.39 ppm (1H, s, NH). The yield was 10.43 g (83%).

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