

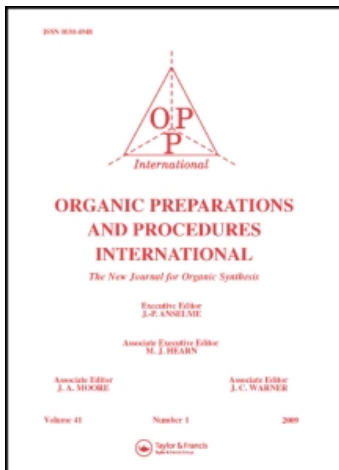
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SYNTHESIS OF 3,6-DIHYDROXY-4-PYRIMIDINONES (SYNTHESES OF HETEROCYCLES, 173.)

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SYNTHESIS OF 3,6-DIHYDROXY-4-PYRIMIDINONES

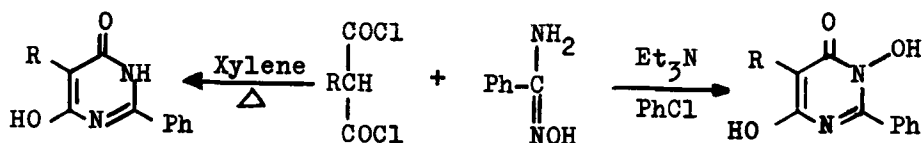
(SYNTHESES OF HETEROCYCLES, 173.)

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A previous communication¹ described the preparation of 3-alkoxy-6-hydroxy-4-pyrimidinones from the reaction of amidoxime ethers and malonyl chlorides in boiling xylene. The reaction between the free benzamidoxime² and benzylmalonyl chloride (Ia) under the same conditions gave, besides benzamide as the major product, benzamidoxime hydrochloride and 3,5-diphenyl-1,2,4-oxadiazole³, only 6-hydroxy-5-benzyl-2-phenyl-3,4-dihydro-4-pyrimidinone (IIa).⁴

However, in the presence of triethylamine and with chlorobenzene as solvent, reaction takes place between benzamidoxime and Ia to give 5-benzyl-2-phenyl-3,6-dihydroxy-3,4-dihydro-4-pyrimidinone (IIIa). Similarly, from methylmalonyl chloride (Ib) and benzamidoxime, 5-methyl-2-phenyl-3,6-dihydroxy-4-pyrimidinone (IIIb) can be isolated.



IIa: R=PhCH₂

Ia: R=PhCH₂

IIIa: R=PhCH₂

Ib: R=CH₃

IIIb: R=CH₃

W. STEIGER, A. ARGYRIDES AND E. ZIEGLER

When heated with acetic anhydride, compound IIIa gives a diacetate. The high infrared carbonyl absorption of this derivative at 1820 cm^{-1} is characteristic for acetates of hydroxamic acids.^{5,6}

Both IIIa and IIIb eliminate oxygen when heated or irradiated (daylight is sufficient), IIIa giving compound IIa and IIIb being converted to 6-hydroxy-5-methyl-2-phenyl-3,4-dihydro-4-pyrimidinone.⁴ Both compounds have been prepared by the procedure of Dox and Yoder⁴ and found to be identical with our substances in every respect (IR and chromatographic behaviour).

EXPERIMENTAL

5-Benzyl-2-phenyl-3,6-dihydroxy-3,4-dihydro-
-4-pyrimidinone (IIIa). A solution of 2.3 g (0.01 mole) of benzylmalonyl chloride (Ia), 2 g (0.015 mole) benzamidoxime and 3 ml triethylamine in 70 ml chlorobenzene was refluxed for 30 min. The reaction mixture was concentrated under reduced pressure to an oil, which was treated with water and a few drops of 5% HCl. The mixture was allowed to stand for 24 hrs. and an oil separated. After separation from the aqueous layer, the residue was triturated with a little methanol. Recrystallisation from ethanol afforded 1.0 g (34%) of IIIa, mp. 232° as pale yellow prisms.

Anal. Calcd. for $C_{17}H_{14}N_2O_3$: C, 69.38; H, 4.79; N, 9.52

Found: C, 69.19; H, 4.81; N, 9.60.

SYNTHESIS OF 3,6-DIHYDROXY-4-PYRIMIDINONES

Diacetate of IIIa . A solution of 0.5 g (0.0015 mole) of IIIa in 20 ml acetic anhydride was refluxed for 1 hour. Removal of the solvent in vacuo left a residue which was triturated with diethyl ether. The product was recrystallised from methanol to give 0.5 g (72%) of colorless needles, mp. 133°. Anal. Calcd. for $C_{21}H_{18}N_2O_5$: N, 7.40. Found: N, 7.65.

5-Methyl-2-phenyl-3,6-dihydroxy-3,4-dihydro-4-pyrimidinone (IIIb). A solution of 1.6 g (0.01 mole) of methylmalonyl chloride, 2.0 g (0.015 mole) of benzamidoxime and 3 ml triethylamine in 70 ml chlorobenzene was refluxed for 30 min. The solvent was removed and the mixture was worked up as described for IIIa. Recrystallisation from ethanol gave 1.2 g (55%) of pale yellow needles, mp. 260°. Anal. Calcd. for $C_{11}H_{10}N_2O_3$: N, 7.40. Found: N, 7.65.

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W. STEIGER, A. ARGYRIDES AND E. ZIEGLER

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