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SYNTHESIS OF 5-BENZOYL-6-PHENYL-1,3-OXAZINONES⁺ (SYNTHESES OF HETEROCYCLES, 179.)

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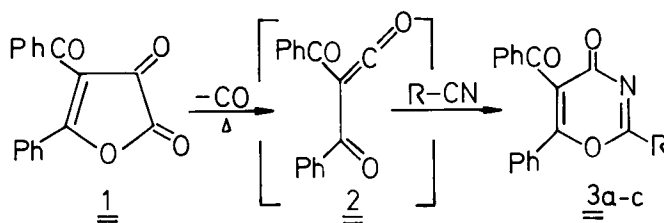
SYNTHESIS OF 5-BENZOYL-6-PHENYL-1,3-OXAZINONES[†]

(Syntheses of Heterocycles, 179.)

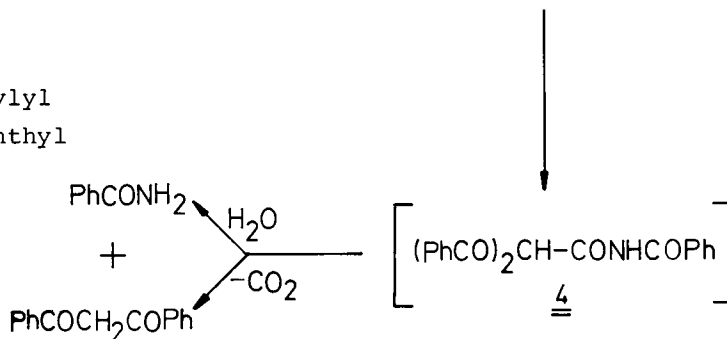
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The thermal decomposition of 4-benzoyl-5-phenyl-furan-2,3-dione (1) leads to the α -acylketene 2 as an intermediate which undergoes cycloaddition reactions with hetero-cumulenes like arylisocyanates or carbodiimides¹. In a similar way, the C \equiv N bond of nitriles should also react with 2 to form the corresponding 1,3-oxazinones. This paper reports the formation of 1,3-oxazinones (3) from the reaction of 2 with aromatic nitriles.



- a) R= Ph
- b) R= 3,4-Xylyl
- c) R= 1-Naphthyl



Our experiments show that attention must be paid to special reaction conditions in order to prevent 2 from undergoing dimerisation reactions²: a) The nitrile must be used in excess and as solvent; b) the temperature must be carefully controlled. In this way, benzonitrile, 3,4-dimethylbenzonitrile and 1-naphthonitrile reacted with 2 to give the corresponding 1,3-oxazinones 3a - c.

Hydrolysis of 3a in the presence of acids leads to ring opening and formation of the unstable intermediate 4, which finally after cleavage of the C-C bond and loss of CO₂ gives dibenzoylmethane and benzamide as final stable compounds. Other oxazinones such as substituted 1,3-benzoxazinones show the same behaviour toward acid hydrolysis³. The instability of high acylated derivatives of acetic acid e.g. 4 toward hydrolysis is also well known⁴.

EXPERIMENTAL⁵

5-Benzoyl-6-aryl-4H-1,3-oxazin-4-ones (3). - The general procedure is illustrated for 3a. - A mixture of 0.005 mole 1 and 0.025 mole aromatic nitrile was heated at 130° until the evolution of CO has subsided (15 min.). The cooled reaction mixture was treated with ether (50 ml) by which a solid was formed. This crude product was dissolved in hot ethanol and the insoluble dimerisation product of 2 was separated by filtration. The filtrate was concentrated in vacuo to give 3a.

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3a: 47 % yield as colorless needles from ethanol, mp. 195-196°; IR 1685 m, 1645 s cm⁻¹ (C=O).

Anal. Calcd for C₂₃H₁₅NO₃: C, 78,17; H, 4,27; N, 3,96.

Found: C, 77,87; H, 4,32; N, 3,91.

3b: 44 % yield as colorless needles from ethanol, mp. 198-99°; IR 1685 m, 1645 s cm⁻¹ (C=O).

Anal. Calcd for C₂₅H₁₉NO₃: C, 78,70; H, 5,02; N, 3,67.

Found: C, 78,41; H, 5,04; N, 3,83.

3c: 35 % yield as colorless needles from ethanol, mp. 187-88°; IR 1680 m, 1645 s cm⁻¹ (C=O); mass spectrum M⁺ 403 (calcd. 403).

Anal. Calcd for C₂₇H₁₇NO₃: C, 80,38; H, 5,25; N, 3,47.

Found: C, 80,33; H, 5,31; N, 3,41.

Hydrolysis of 3a . - A mixture of 0.3 g 3a, 15 ml dioxane, 0.5 ml water and 5 mg p-toluenesulfonic acid was refluxed for 1 hour. After evaporation of the solvents, the residue was triturated with 5 ml methanol in order to separate from 0.05 g of undecomposed 3a; then 5 ml of water was added to the methanolic solution to yield 0.1 g (63 %) colorless needles, pm. 78° (from methanol), identified as dibenzoylmethane. Removal of the methanol in vacuo gave 0.05 g (62 %) of a colorless substance, mp. 130°, identified as benzamide.

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 5. Melting points are corrected. IR spectra were determined as KBr disks. The mass spectrum of 3c was obtained on a AEI MS-20 mass spectrometer.

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