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SHORT COMMUNICATIONS

Two Pathways in the Cycloaddition of 4-Nitrobenzaldehyde to Acyl(imidoyl)ketene

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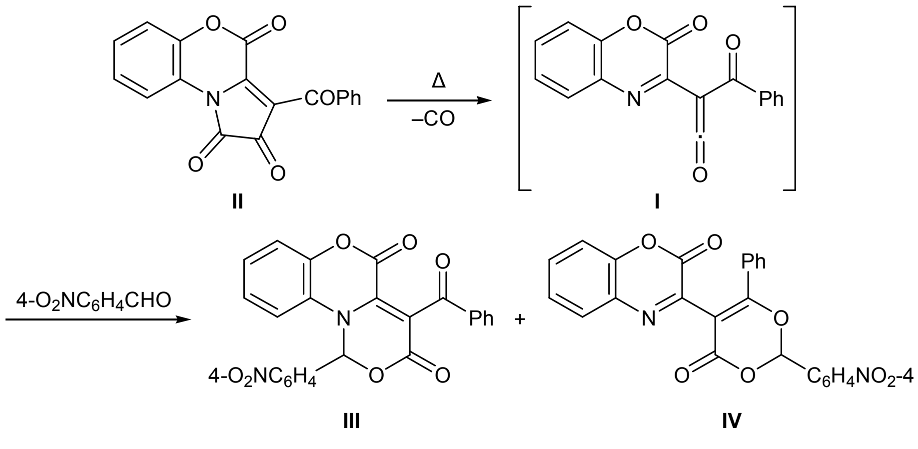
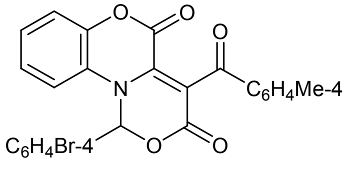
Aroyl(benzoxazinyl)ketenes **I** generated by thermal decarbonylation of 3-aroylpyrrolo[2,1-*c*][1,4]benzoxazine-1,2,4-triones **II** undergo [4+2]-cyclodimerization in the absence of other reaction partners. In this transformation, one molecule **I** acts as dienophile via the ketene C=C bond, and the other acts as diene through the conjugated C=C–C=N bond sequence in the imidoylketene fragment [1]. Attempts to trap aroyl(benzoxazinyl)ketenes **I** with 4-bromobenzaldehyde or Schiff base lead to the formation of the corresponding [4+2]-cycloadducts with participation of the C=C–C=N fragment in imidoylketene **I** and C=O bond of 4-bromobenzaldehyde [2] or C=N bond of Schiff base [3]. On the other hand, [4+2]-cycloaddition of *N*,*N*′-dicyclohexylcarbodiimide to ketenes **I** involves the C=C–C=O bond sequence of the aroylketene fragment in **I** and the C=N bond of *N*,*N*′-dicyclohexylcarbodiimide [4]. According to the TLC data, all the above reactions are regioselective.

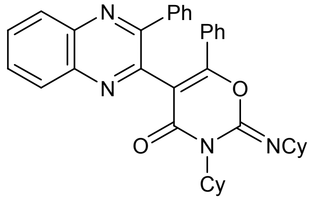
By heating a solution of 3-benzoylpyrrolo[2,1-*c*][1,4]benzoxazine-1,2,4-trione (**II**) and 4-nitrobenzaldehyde in pseudocumene at 168–169°C over a period of 15 min (until disappearance of violet color typical of initial compound **II**) we obtained a mixture of 4-benzoyl-1-(4-nitrophenyl)-1,3-dihydro-5*H*-[1,3]oxazino[4,3-*c*][1,4]benzoxazine-3,5-dione (**III**) and 3-[2-(4-nitrophenyl)-4-oxo-6-phenyl-4*H*-1,3-dioxin-5-yl]-2*H*-1,4-benzoxazin-2-one (**IV**) at a ratio of ~5:3.

The spectral parameters of compounds **III** and **IV** were fairly similar to those of structurally related 1-(4-bromophenyl)-4-(4-methylphenyl)-1,3-dihydro-5*H*-[1,3]oxazino[4,3-*c*][1,4]benzoxazine-3,5-dione (**V**) [2] and 2-(3-cyclohexyl-2-cyclohexylimino-4-oxo-6-phenyl-3,4-dihydro-2*H*-1,3-oxazin-5-yl]-3-phenylquinoxaline (**VI**) [5] whose structure was unambiguously determined by X-ray analysis. Obviously, compounds **III** and **IV** are formed as a result of thermal decarbonylation of 3-benzoylpyrrolo[2,1-*c*][1,4]benzoxazine-1,2,4-trione (**II**) with generation of benzoyl(benzoxazinyl)ketene **I** which reacted with 4-nitrobenzaldehyde according to the [4+2]-cycloaddition pattern involving the aldehyde C=O bond and both C=C–C=O and C=C–C=N conjugated bond systems in aroyl(imidoyl)ketene **I**.





V



VI

Thus the described reaction is an example of two concurrent [4+2]-cycloaddition pathways in reactions of ambident dienes [acyl(imidoyl)ketenes **I** in which the imidoyl fragment is a part of a heterocyclic system], and it may be regarded as a new method of synthesis of difficultly accessible polyfunctionalized oxazinylbenzoxazinones.

4-Benzoyl-1-(4-nitrophenyl)-1,3-dihydro-5*H*-[1,3]oxazino[4,3-*c*][1,4]benzoxazine-3,5-dione (III) and 3-[2-(4-nitrophenyl)-4-oxo-6-phenyl-4*H*-1,3-dioxin-5-yl]-2*H*-1,4-benzoxazin-2-one (IV). A solution of 3.0 mmol of compound **II** and 3.0 mmol of 4-nitrobenzaldehyde in 10 ml of anhydrous pseudocumene was heated for 15 min under reflux. The mixture was cooled, and the yellow precipitate (compound **III**) was filtered off. Yield 50%, mp 227–228°C (decomp., from toluene). IR spectrum, ν, cm^{-1}: 1770 (C^5=O), 1716 (C^3=O), 1675 (COPh). ^{1}H NMR spectrum, δ, ppm: 7.26–7.65 m (9H, Ph, 7-H, 8-H, 9-H, 10-H), 7.87 d (2H, 3′-H, 5′-H, J = 8.7 Hz), 8.23 s (1H, 1-H), 8.33 d (2H, 2′-H, 6′-H, J = 8.7 Hz). Found, %: C 65.56; H 3.22; N 6.29. $C_{24}H_{14}N_2O_7$. Calculated, %: C 65.16; H 3.19; N 6.33.

Petroleum ether (bp 40–70°C), 2 ml, was added to the mother liquor, the precipitate was filtered off, the filtrate was kept for 2 days, and the colorless precipitate was filtered off. Yield of **IV** 30%, mp 183–184°C (decomp., from benzene). IR spectrum: ν 1737 cm^{-1} (C^2=O, $C^{4'}$=O). ^{1}H NMR spectrum, δ, ppm: 7.41 s (1H, 2′-H), 7.44–7.80 m (9H, Ph, 5-H, 6-H, 7-H, 8-H), 8.09 d (2H, 3″-H, 5″-H, J = 8.7 Hz), 8.42 d (2H, 2″-H, 6″-H, J = 8.7 Hz). Found, %: C 65.52; H 3.17; N 6.33. $C_{24}H_{14}N_2O_7$. Calculated, %: C 65.16; H 3.19; N 6.33.

The IR spectra were recorded on a Perkin Elmer Spectrum Two spectrometer from samples dispersed in mineral oil. The ^{1}H NMR spectra were measured on a Bruker AM-400 instrument at 400 MHz from solutions in DMSO-d_6 using tetramethylsilane as internal reference. The purity of the isolated compounds was checked by TLC on Silufol plates using benzene–ethyl acetate (5 : 1) and ethyl acetate as eluents.

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