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LETTERS TO THE EDITOR

ADDITION OF AROYLKETENES AT THE C=N BOND OF ASYMMETRICAL AZINES

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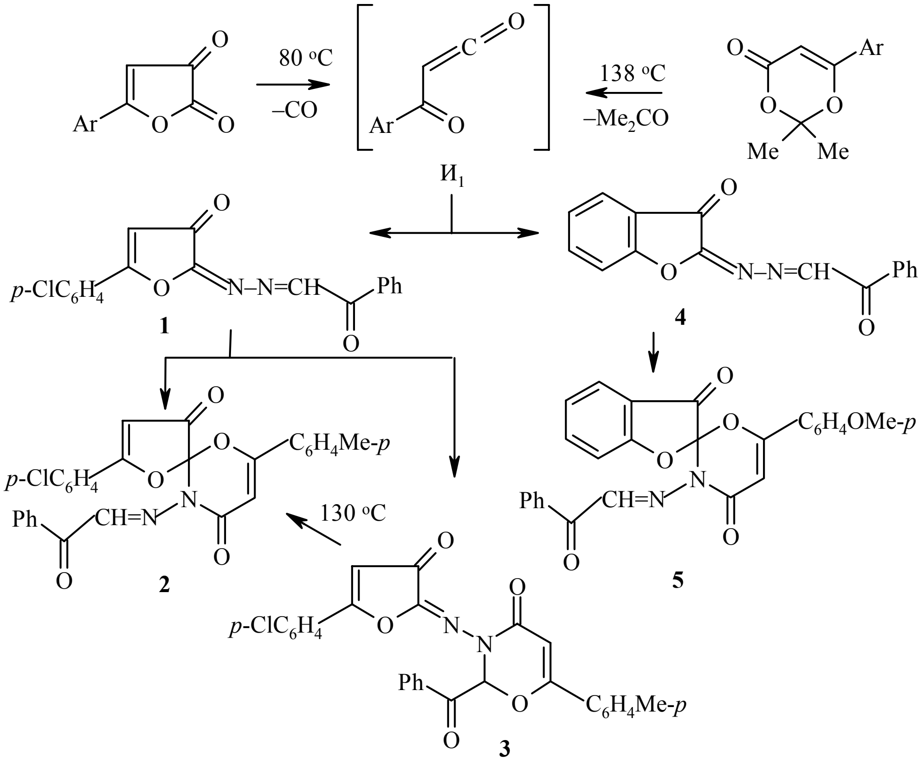
We have established that the reaction of the aroylketene (I_1) generated in the thermolysis of 5-(4-methylphenyl)-2,3-dihydro-2,3-furandione [1] with 2-benzoylmethylenehydrazono-5-(4-chlorophenyl)-2,3-dihydro-3-furanone (**1**) gives a mixture of products, of which 3-benzoylmethylenamino(4-chlorophenyl)-3'H-3'-furanone (**2**) and 2-benzoyl-3-[5-(4-chlorophenyl)-3-oxo-2,3-dihydro-2-furanyliden]amino-6-(4-methylphenyl)-3,4-dihydro-2H-1,3-oxazin-4-one (**3**) were isolated.



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Furanone **2** and oxazinone **3** are products of the [2+4] cycloaddition of the aroylketene at the C=N bonds of **1**, acting as dienophiles. The composition of the reaction products depends on the means of generation of the aroylketene and stability of the compounds formed. Thus, thermolysis of the furanedione at 80°C leads to **2** in 49% yield and **3** in 32% yield. These two products are both probably formed in the thermolysis of 1,3-dioxin-4-one at 130°C [2] but **3**, as a result of its lower stability in comparison with **2** and the reversibility of the cycloaddition, likely eliminates aroylketene and the thermodynamically more stable spiro compound **2** is observed as the final product. This hypothesis was supported by the formation of **2** upon prolonged heating of **3** at 130°C.

Only spiro compound 3-benzoylmethylenamino-6-(4-methoxyphenyl)spiro[benzofuran-2(3H),2-[2H][1,3]oxazine]-3,4-(3H)-dione (**5**) is formed in the thermolysis of 2,2-dimethyl-6-(4-methoxyphenyl)-1,3-dioxin-4-one in the presence of 2-benzoylmethylenehydrazono-2,3-dihydro-3-benzofuranone (**4**).

Furanone 2 was obtained in 49% yield; mp 219-220°C (toluene). IR spectrum, ν, cm^{-1}: 1715, 1678, 1655 (C=O). ^1H NMR spectrum (DMSO-d_6), δ, ppm: 2.38 (3H, s, CH_3); 6.65 (1H, s, CH); 6.85 (1H, s, CH); 7.55 (13H, m, $2C_6H_4+C_6H_5$); 8.25 (1H, s, CH=N).

Oxazinone 3 was obtained in 32% yield; mp 198-199°C (acetonitrile). IR spectrum, ν, cm^{-1}: 1705, 1685, 1660 (C=O). ^1H NMR spectrum (pyridine-d_5), δ, ppm: 2.01 (3H, s, CH_3); 6.25 (1H, s, CH); 6.45 (1H, s, CH); 6.60 (1H, s, CH); 7.38 (13H, m, $2C_6H_4+C_6H_5$).

Dione 5 was obtained in 79% yield; mp 179-180°C (toluene). IR spectrum, δ, cm^{-1}: 1710, 1670, 1658 (C=O). ^1H NMR spectrum (DMSO-d_6), δ, ppm: 3.71 (1H, s, CH_3O); 6.38 (1H, s, $C_{(5)}H$); 7.28 (13H, m, $2C_6H_4+C_6H_5$); 9.08 (1H, s, CH=N).

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