Chemistry of Heterocyclic Compounds, Vol. 39, No. 1, 2003

REGIOSELECTIVE CYCLOADDITION OF CYCLIC KETONES TO ACYL(IMIDOYL)KETENES

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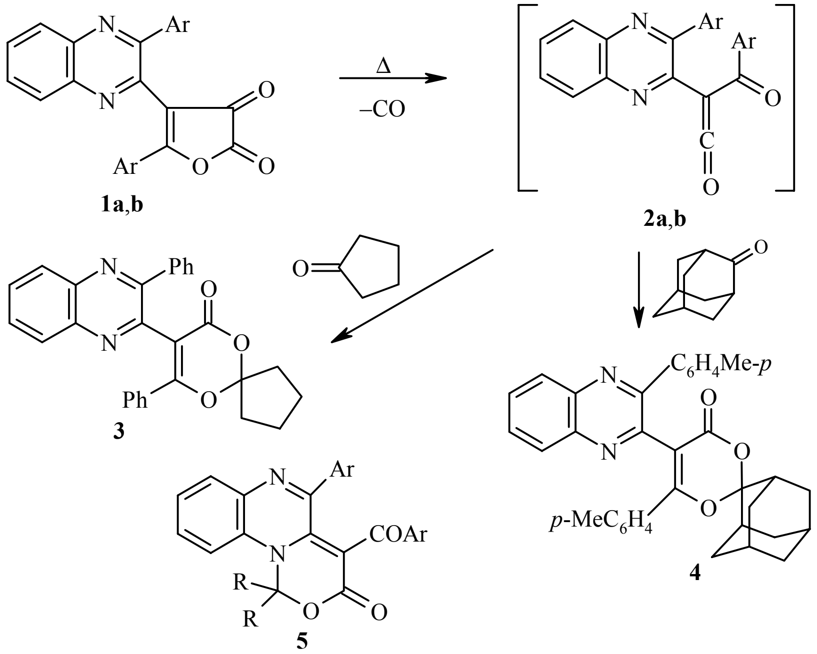
Keywords: aroyl(imidoyl)ketenes, aroyl(quinoxalinyl)ketenes, 2,3-dihydro-2,3-furandiones, cyclic ketones, cycloaddition.

The thermolysis of substituted 5-aryl-4-quinoxalinyl-2,3-dihydro-2,3-furandiones [3-aryl-2-(2-aryl-4,5-dioxo-4,5-dihydro-3-furyl)quinoxalines **1a** and **1b** leads to decarbonylation and formation of 3-aryl-2-quinoxalinyl(aroyl)ketenes **2a** and **2b**, which are representatives of aroyl(imidoyl)ketenes). Ketenes **2a** and **2b** in the absence of other reaction partners undergo [4+2] cyclodimerization. One ketene molecule acts as a dienophile by means of the ketene C=C bond, while the other ketene molecule acts as the diene by means of the conjugated C=C–C=N bond system of the imidoylketene fragment [1].

We were able to capture aroyl(imidoyl)ketenes **2a** and **2b** using cyclic ketones such as cyclopentanone and adamantanone to give the corresponding [4+2] cycloadducts, namely, substituted 6-aryl-5-quinoxalinyl-4H-1,3-dioxin-4-ones **3** and **4**.



1, 2 a Ar = Ph, **b** Ar = *p*-MeC_6H_4

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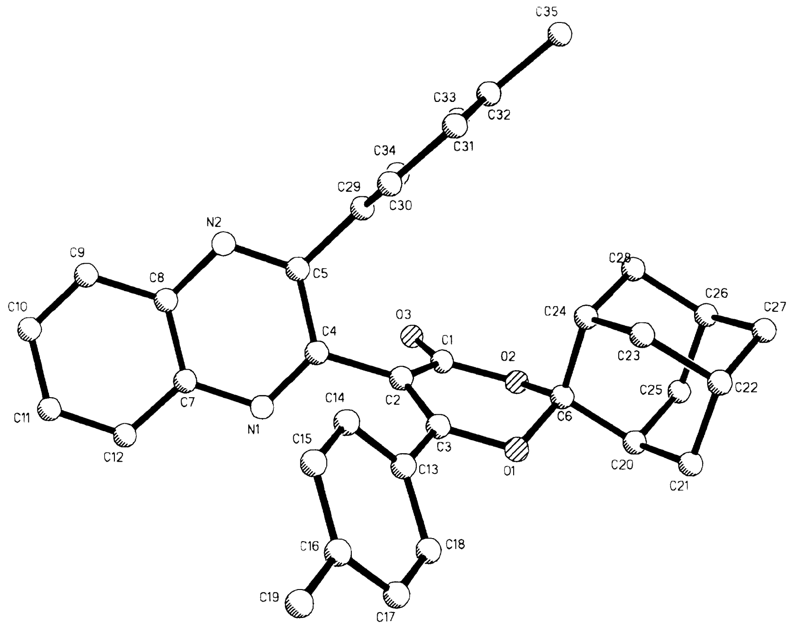

Fig. 1. General view of **4**.

The spectral characteristics of compounds **3** and **4** as well as the X-ray diffraction data for **4** provided evidence for the elimination of isomeric structures **5** and suggest that, in contrast to the cyclodimerization reaction in our previous work [1], aroyl(imidoyl)ketenes **2a** and **2b** participate in cycloaddition with cyclic ketones at the ketonic C=O bonds only as dienes by means of the conjugated C=C–C=O system of the aroylketene fragment.

Well-defined triclinic crystals of $C_{35}H_{32}N_2O_3$ have the following unit cell parameters: a = 10.678(2), b = 11.288(2), c = 13.363(3) Å; α = 108.070(3), β = 110.97(3), γ = 95.02(3)°; V = 1393.6(5) Å^3; M = 528.63; Z = 2; d_{calc} = 1.260 g/cm^3; space group P-1. The unit cell parameters and experimental reflections were measured with a Kuma Diffraction KM-4 automatic, 4-θ-circle diffractometer, Cu$K\alpha$ radiation in the range $3.8 < \theta < 80.2°$. The structure was determined by the direct statistical method. All the hydrogen atoms including the methyl group hydrogen atoms were located objectively from the electron density difference maps. Full-matrix anisotropic least squares refinement for the non-hydrogen atoms and isotropic refinement for the hydrogen atoms was carried out to R = 0.421 using 3343 reflections with $I > 2\sigma(I)$ from the total set of 5200 measured reflections. *GOOF* = 0.966. Absorption corrections were not introduced (μ = 0.635 mm^{-1}). All the calculations were carried out using the SHELX 97 program package.

The bond lengths of the dioxin ring ($O_{(1)}$–$C_{(2)}$, 1.433; $C_{(2)}$–$O_{(3)}$, 1.437; $O_{(3)}$–$C_{(4)}$, 1.338; $C_{(4)}$–$C_{(5)}$, 1.457; $C_{(5)}$–$C_{(6)}$, 1.354; $C_{(6)}$–$O_{(1)}$, 1.357 Å) and the two spiro bonds of the adamantyl fragment (1.511 and 1.525 Å) are close to ordinary values.

4-Oxo-6-phenyl-5-(3-phenyl-2-quinoxalinyl)-4H-1,3-dioxin-2-spirocyclopentane (3). A solution of furandione **1a** (1 mmol) and cyclopentanone (1.1 mmol) in absolute *p*-xylene (5 ml) was maintained for 20 min at 138-140°C. The precipitate formed was filtered off to give 0.35 g (81%) of **3**; mp 141-142°C (cyclohexane). IR spectrum (vaseline oil), ν, cm^{-1}: 1725 (C=O), 1620 w (C=N). ^{1}H NMR spectrum (DMSO-d$_6$, 400 MHz, with HMDS as the internal standard), δ, ppm (J, Hz): 1.77-2.29 (8H, m, C_5H_8); 6.98-8.11 (14H, m, $2C_6H_5 + C_6H_4$). Found, %: C 77.41; H 5.13; N 6.41. $C_{28}H_{22}N_2O_3$. Calculated, %: C 77.40; H 5.10; N 6.45.

4-Oxo-6-*p*-tolyl-5-(3-*p*-tolyl-2-quinoxalinyl)-4H-1,3-dioxin-2-spiro-2-adamantane (4) was obtained in 92% yield (0.49 g); mp 229-230°C (ethyl acetate). IR spectrum (vaseline oil), ν, cm^{-1}: 1720 (C=O), 1662 w (C=N). ^{1}H NMR spectrum (DMSO-d$_6$, 400 MHz, with HMDS as the internal standard), δ, ppm: 1.54-2.04 (14H, m, AdH); 1.23 (3H, m, Me); 2.36 (3H, s, Me); 7.04-8.14 (12H, m, 3C$_6$H$_4$). Found, %: C 79.60; H 6.10; N 5.25. $C_{35}H_{32}N_2O_3$. Calculated, %: C 79.52; H 6.10; N 5.30.

This work was carried out with the financial support of the Russian Basic Research Fund (Grant No. 01-03-32641).

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