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CYCLODIMERIZATION OF ACYL-(3-OXO-2-QUINOXALINYL)KETENES

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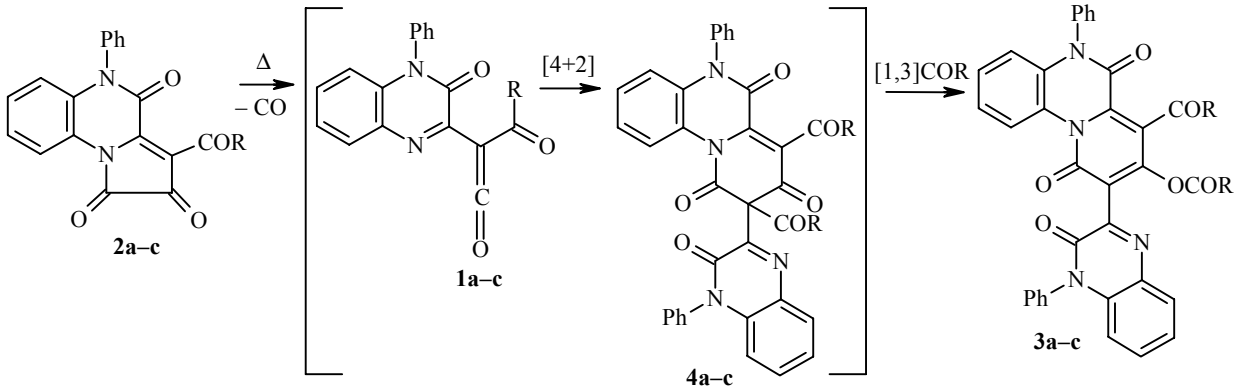
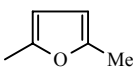
Two pathways have been described for the stabilization of acyl(imidoyl)ketenes, in which the imidoyl fragment is a part of the 1,2-dihydro-2-quinoxalone heterocyclic system. 3-Oxo-3,4-dihydro-2-quinoxalinyl(ethoxycarbonyl)ketene is stabilized by the transfer of the quinoxalone fragment from the amide to the hydroxyimine form with subsequent intramolecular acylation of the hydroxyimine OH group by the ketene fragment [1]. 3-Oxo-4-phenyl-3,4-dihydro-2-quinoxalinyl(ethoxycarbonyl)ketene is stabilized by undergoing a [4+2] cyclodimerization reaction, in which one ketene molecule acts as diene through the imidoylketene fragment, while the other acts as the dienophile by means of the C=C bond of the ketene fragment [2].

The formation of aroyl and heteroyl(3-oxo-4-phenyl-3,4-dihydro-2-quinoxalinyl)ketenes (**1a-c**) would be expected in the thermal decarbonylation of 3-aroyl- and 3-heteroyl-5-phenyl-1,2,4,5-tetrahydropyrrolo-[1,2-*a*]quinoxaline-1,2,4-triones (**2a-c**). However, the type of intramolecular cyclization described above [1] is impossible for ketenes **1a-c** and alternatives exist for the participation of both the acylketene and imidoylketene fragments in intermolecular cycloaddition.

Maintaining pyrroloquinoxalinetriones **2a-c** in decane, which is an inert, aprotic solvent, at 172-173°C for 30-60 min leads to the formation of 4-acyl-3-acyloxy-2-(3-oxo-4-phenyl-3,4-dihydro-2-quinoxalinyl)-6-phenyl-5,6-dihydro-1H-pyrido[1,2-*a*]quinoxaline-1,5-diones **3a-c**.



1–3 a R = *p*-MePh, **b** R = *p*-$MeOC_6H_4$,

c R = 

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The spectral indices for **3a-c** and model oxa analogs, whose structure was confirmed by X-ray diffraction structural analysis [3], were extremely similar.

Ketenes **1a-c** in the absence of reaction partners probably participate in [4+2] cyclodimerization as in the case described above [2] through the imidoylketene fragment. However, in contrast [1,3], acyl group shift occurs in the initial [4+2] cycloadducts **4a-c**, which is characteristic of oxa analogs of ketenes **1a-c** [3].

2-(3-Oxo-4-phenyl-3,4-dihydro-2-quinoxalinyl)-6-phenyl-4-*p*-tolyl-3-*p*-tolyloxy-5,6-dihydro-1H-pyrido[1,2-*a*]quinoxaline-1,5-dione (3a). Solution of compound **2a** (0.001 mol) in decane (4 ml) was maintained at 172-173°C for 60 min (until the color changed from violet to orange) and then cooled. The precipitate formed was filtered off to give 0.22 g (59%) of compound **3a**, which decomposes at 244-245°C (acetonitrile). IR spectrum in vaseline mull, ν, cm^{-1}: 1749 (CO_2), 1680 (CON), 1670 br ($C_{(4)}$–CO). ^{1}H NMR spectrum (DMSO-d_6, 400 MHz, HMDS as the standard), δ, ppm, *J* (Hz): 2.30 (3H, s, Me); 2.39 (3H, s, Me); 6.51-7.83 (25H, m, ArH); 9.17 (1H, d, *J* = 7.6, $C_{(10)}$H). Found, %: C 75.73; H 4.20; N 7.42. $C_{48}H_{32}N_4O_6$. Calculated, %: C 75.78; H 4.24; N 7.36.

2-(3-Oxo-4-phenyl-3,4-dihydro-2-quinoxalinyl)-6-phenyl-4-*p*-methoxyphenyl-3-*p*-methoxyphenyloxy-5,6-dihydro-1H-pyrido[1,2-*a*]quinoxaline-1,5-dione (3b) was obtained in 60% yield (0.24 g), it decomposes at 319-321°C (acetonitrile). IR spectrum, ν, cm^{-1}: 1749 (CO_2), 1680 (CON), 1668 br ($C_{(4)}$–CO). ^{1}H NMR spectrum (DMSO-d_6, 400 MHz, HMDS as the standard), δ, ppm, *J* (Hz): 3.77 (3H, s, MeO); 3.90 (3H, s, MeO); 6.51-7.62 (25H, m, ArH); 9.16 (1H, d, *J* = 7.9, $C_{(10)}$H). Found, %: C 72.78; H 4.10; N 7.11. $C_{48}H_{32}N_4O_8$. Calculated, %: C 72.72; H 4.07; N 7.07.

4-(5-Methyl-2-furoyl)-3-(5-methyl-2-furoyloxy)-2-(3-oxo-4-phenyl-3,4-dihydro-2-quinoxalinyl)-6-phenyl-5,6-dihydro-1H-pyrido[1,2-*a*]quinoxaline-1,5-dione (3c) was obtained in 72% yield (0.37 g), it decomposes at 325-327°C (toluene). IR spectrum, ν, cm^{-1}: 1759 (CO_2), 1682 (CON), 1656 br ($C_{(4)}$–CO). ^{1}H NMR spectrum (DMSO-d_6, 400 MHz, HMDS as the standard), δ, ppm, *J* (Hz): 2.31 (6H, s, 2Me); 6.20-7.86 (21H, m, ArH); 9.05 (1H, d, *J* = 8.0, $C_{(10)}$H). Found, %: C 71.30; H 3.83; N 7.60. $C_{44}H_{28}N_4O_8$. Calculated, %: C 71.35; H 3.81; N 7.56.

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