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INTERMOLECULAR CYCLODIMERIZATION OF AROYL(IMIDOYL)KETENES GENERATED BY THERMOLYSIS OF 5-ARYL-4-IMIDOYL-2,3-DIHYDRO-2,3-FURANDIONES

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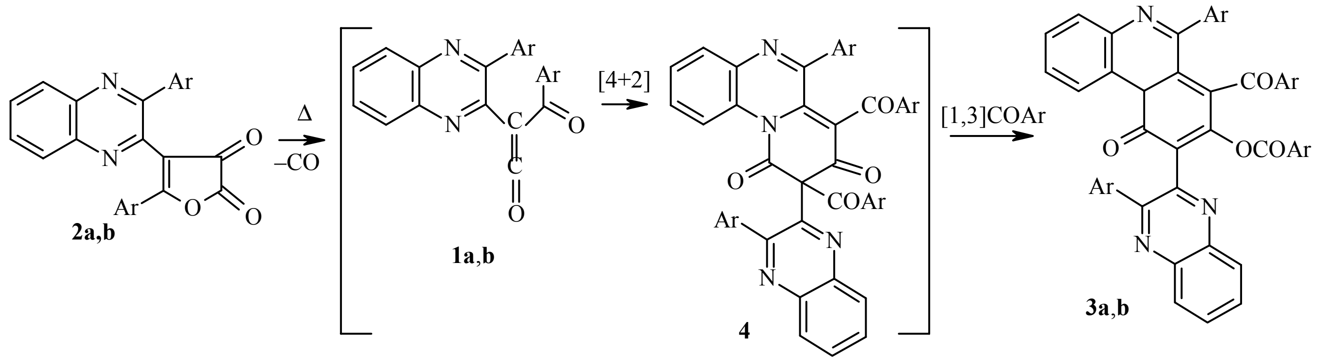
The methods for stabilizing acylketenes generated by the thermolytic decarbonylation of substituted 2,3--dihydro-2,3-furandiones depend on the nature of the substituents in the furandione ring. Aroylketenes formed from 5-aryl-, 5-aryl-4-halo-, 5-aryl-4-methyl-, 4-benzoyl-5-phenyl-, and 4,5-diaryl-2,3-dihydro-2,3-furandiones are stabilized by intermolecular [4+2] cycloaddition [1-4]. The aroylketene fragment of one ketene molecule plays the role of the diene, while the C=C bond of the ketene fragment of the other molecule acts as the dienophile. In the case of cycloadducts from 5-aryl-, 4-benzoyl-5-phenyl-, and 4,5-diaryl-2,3-dihydro-2,3-furandiones, the reaction is usually accompanied by [1,3] migration of a hydrogen atom or aroyl group. In the case of di(pivaloyl)ketene obtained from 5-*tert*-butyl-4-pivaloyl-2,3-dihydro-2,3-furandione, the C=O bond of the pivaloyl or ketene fragment participates in the analogous [4+2] cyclodimerization.



1–4 a Ar = Ph, **b** Ar = p-MeC$_6$H$_4$

Aroyl(imidoyl)ketenes formed from 4-[α-(arylimino)benzyl]-5-phenyl-2,3-dihydro-2,3-furandiones are stabilized by intramolecular cyclization due to acylation of the *ortho* position of the N-aryl ring by the ketene fragment [6].

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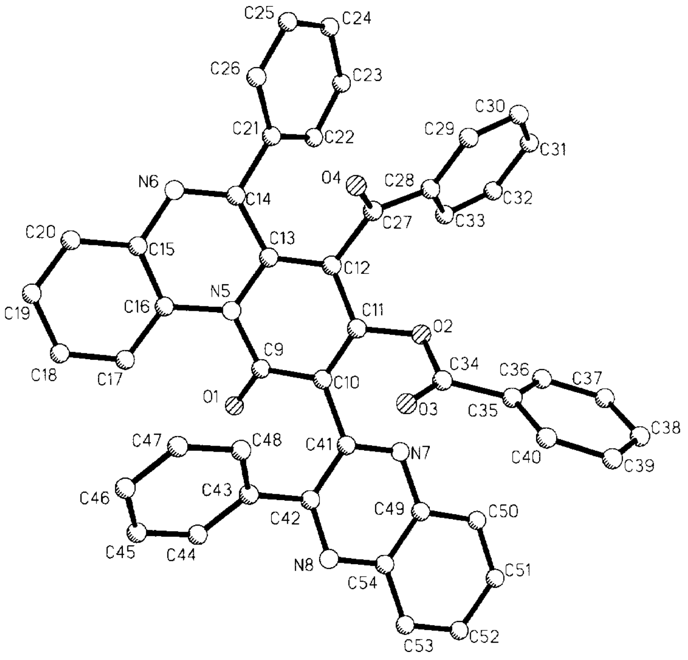

Molecular structure of compound **3a**.

Such intramolecular cyclization is structurally impossible for aroyl(imidoyl)ketenes **1a** and **1b** generated by the thermolytic decarbonylation of 3-aryl-2-(2-aryl-4,5-dioxo-4,5-dihydro-3-furyl)-quinoxalines **2a** and **2b**. Alternative pathways involve participation of both the aroylketene and imidoylketene fragments in intermolecular cycloaddition. Maintaining furandiones **2a** and **2b** at 140-144°C for 20 min gave 5-aryl-2-(3-aryl-2-quinoxalinyl)-4-aroyl-3-aroyloxy-1H-pyrido[1,2-*a*]quinoxalin-1-ones **3a** and **3b**, which were identified by X-ray diffraction structural analysis.

Ketenes **1** formed upon the thermal decarbonylation of furandiones **2** are stabilized due to [4+2] cyclodimerization. A ketene molecule acts as the diene by means of the imidoylketene fragment, while the other acts as the dienophile by means of the C=C bond of the ketene fragment; [1,3]-migration of the aroyl group occurs in cycloadducts **4**.

4-Benzoyl-3-benzoyloxy-5-phenyl-2-(3-phenyl-2-quinoxalinyl)-1H-pyrido[1,2-*a*]quinoxalin-1-one (3a). A solution of furandione **2a** (0.38 g, 0.001 mol) [7] in absolute *p*-xylene (5 ml) was maintained for 20 min at 140-144°C and then cooled. The precipitate formed was filtered off to give 0.28 g (80%) **3a**; mp 270-271°C (from acetonitrile). IR spectrum (vaseline mull), ν, cm^{-1}: 1745 (CO$_2$), 1662 (CO). ^{1}H NMR spectrum at 400 MHz (DMSO-d$_6$) with HDMS as the standard, δ, ppm: 7.00-7.94 (27H, m, 4C$_6$H$_5$+C$_6$H$_4$+C$_6$H$_3$); 8.12 (1H, d, C$_{(10)}$H). Found, %: C 78.83; H 4.00; N 7.99. $C_{46}H_{28}N_4O_4$. Calculated, %: C 78.84; H 4.03; N 8.00.

X-ray diffraction structural analysis of **3a**. A sample of **3a** was further recrystallized from *p*-xylene for the diffraction study to give well-formed, yellow, four-sided, monoclinic prisms $C_{46}H_{28}N_4O_4 \cdot 0.5(p\text{-}CH_3C_6H_4CH_3)$: a = 20.812(4), b = 16.202(3), c = 11.857 Å; β = 98.03°; V = 3958.9(12) Å^3; M = 753.80; d_{calc} = 1.265 g/cm$_3$; Z = 4; space group $P2_1/n$. The unit cell parameters and set of experimental reflections were measured on a KUMA Diffraction KM-4 automatic four-circle diffractometer with χ-geometry using ω-2θ scanning with monochromatic CuKα radiation at $3.47 < 2\theta < 80.24°$. A total of 7723 reflections were measured, of which 3099 with $I \geq \sigma(I)$. An absorption correction was not introduced (μ = 0.649 mm^{-1}) The structure was solved by the direct method with a subsequent series of electron density map calculations.

The hydrogen atoms were introduced geometrically after obtaining R = 0.065 by anisotropic least squares refinement. The final refinement gave R = 0.039. GOOF = 0.902, All the calculations were carried out on a PCA/AT using the SHELX97 program package.

5-*p*-Tolyl-2-(3-*p*-tolyl-2-quinoxalinyl)-4-*p*-toluoyl-3-*p*-toluoyloxy-1H-pyrido[1,2-*a*]quinoxalin-1-one (3b) was obtained in 74% yield (0.28 g); mp 310-311°C (acetonitrile). IR spectrum (vaseline mull), ν, cm^{-1}: 1750 (CO_2), 1665 (CO). ^{1}H NMR spectrum at 250 MHz (DMSO-d_6) with TMS as the internal standard, δ, ppm: 2.20 (3H, s, Me); 2.28 (3H, s, Me); 2.36 (3H, s, Me); 2.45 (3H, s, Me); 6.70-8.10 (24H, m, $6C_6H_4$). Found, %: C 79.34; H 4.79; N 7.41. $C_{50}H_{36}N_4O_4$. Calculated, %: C 79.35; H 4.79; N 7.40.

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