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CHEMISTRY OF ACYL(IMIDOYL)KETENES. 8*. THERMOLYSIS OF 3-ALKOXYCARBONYL-5-PHENYL-1,2,4,5-TETRAHYDROPYRROLO[1,2-*a*]-QUINOXALINE-1,2,4-TRIONES. STRUCTURE OF 2-(3-OXO-4-PHENYL-3,4-DIHYDRO-2-QUINOXALINYL)-2,4-DI(ETHOXYCARBONYL)-6-PHENYL-2,3,5,6-TETRAHYDRO-1H-PYRIDO[1,2-*a*]QUINOXALINE-1,3,5-TRIONE

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3-Alkoxycarbonylmethylene-1-phenyl-1,2,3,4-tetrahydro-2-quinoxalones, obtained by the interaction of dialkyl esters of oxaloacetic acid and N-phenyl-o-phenylenediamine, react with oxalyl chloride with the formation of 3-alkoxycarbonyl-5-phenyl-1,2,4,5-tetrahydropyrrolo[1,2-a]quinoxaline-1,2,4-triones. Alkoxycarbonyl(2-oxo-1-phenyl-1,2-dihydro-3-quinoxalinyl)ketenes, generated on thermal decarbonylation of the latter, are stabilized by participation in a [4+2] cyclodimerization reaction with the formation of 2,4-di(alkoxycarbonyl)-2-(3-oxo-4-phenyl-3,4-dihydro-2-quinoxalinyl)-6-phenyl-2,3,5,6-tetrahydro-1H-pyrido[1,2-a]quinoxaline-1,3,5-triones. The crystal and molecular structure of the di(ethoxycarbonyl) derivative have been investigated by X-ray structural analysis.

Keywords: alkoxycarbonyl(imidoyl)ketene, acyl(imidoyl)ketene, pyrroledione, crystal and molecular structure, [4 + 2] cyclodimerization.

Two routes have been described for the stabilization of acyl(imidoyl)ketenes in which the imidoyl fragment is part of a heterocyclic system.

Alkoxycarbonyl(2-oxo-1,2-dihydro-3-quinoxalinyl)ketenes **A** are cyclized intramolecularly as a result of acylation of the hydroxy group of the tautomeric hydroxyimine form by the ketene fragment [2]. Aroyl(2-oxo-3,4-dihydro-2H-1,4-benzoxazin-3-yl)ketenes **B** and aroyl(3-aryl-2-quinoxalinyl)ketenes **C**, in the absence of partners for interaction, participates in a [4 + 2] cyclodimerization reaction [1,3,4]. The role of diene is played by the imidoylketene fragment of one ketene molecule, and the role of dienophile by the C=C bond of the ketene fragment of the other molecule. A [1,3]-migration of the aroyl group occurs in the [4 + 2] cycloadducts formed initially.

The thermolytic conversion of 3-alkoxycarbonyl-5-phenyl-1,2,4,5-tetrahydropyrrolo[1,2-*a*]quinoxaline-1,2,4-triones **2a,b** has been investigated in the present work.

* For Part 7 see [1].

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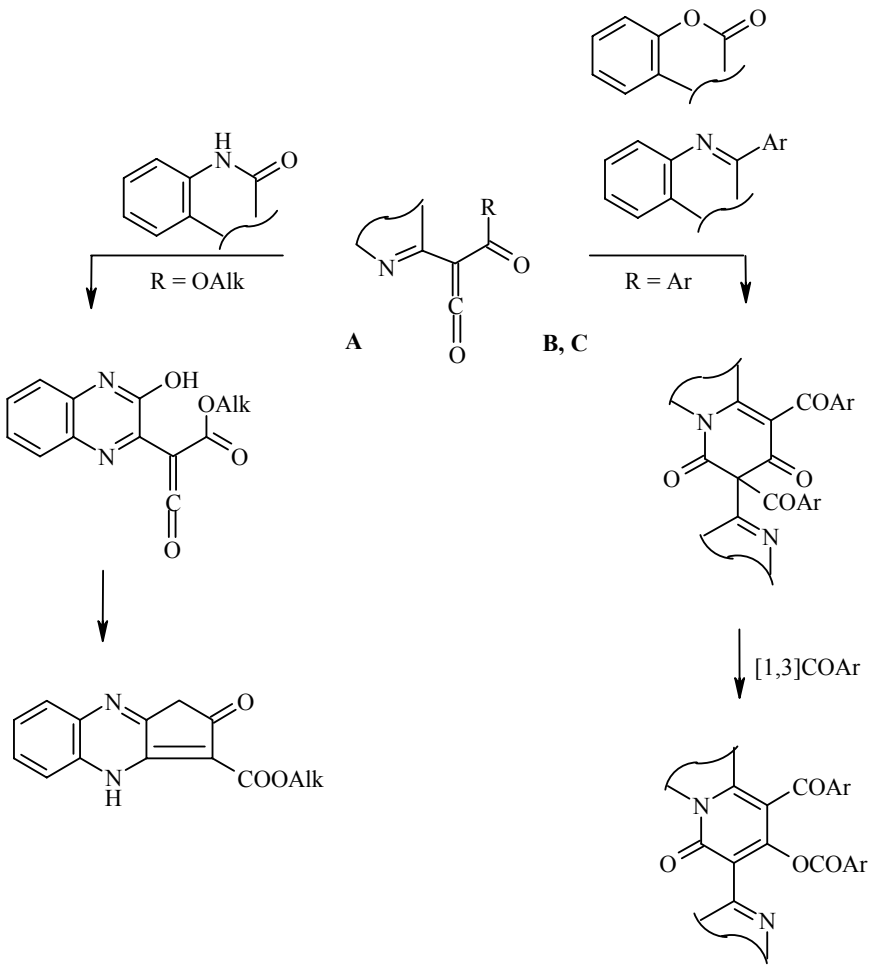
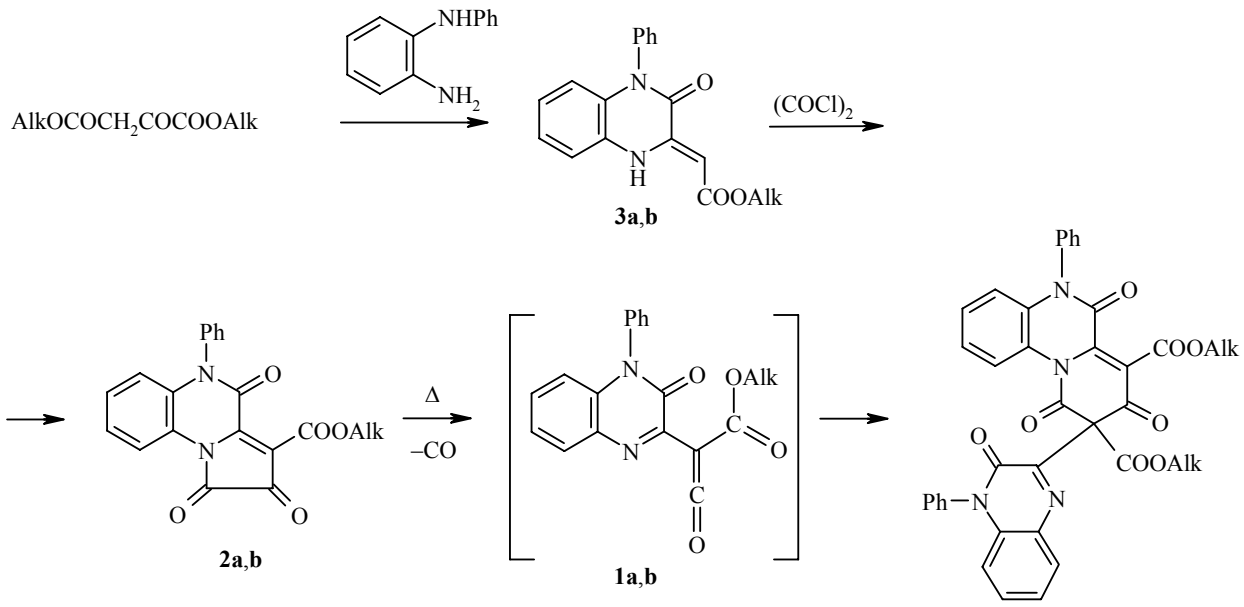


For alkoxycarbonyl(2-oxo-1-phenyl-1,2-dihydro-3-quinoxalinyl)ketenes **1a,b**, generated by the thermal decarbonylation of compounds **2a,b,** an intramolecular cyclization of the type described above [2] is structurally impossible and there are alternative possibilities for participation in intramolecular cycloaddition reactions for both the alkoxycarbonylketene and the imidoylketene fragments. Synthesis of the pyrroloquinoxalinetriones **2a,b** was carried out by the known method by the interaction of oxalyl chloride and *Z*-3-alkoxycarbonylmethylene-1-phenyl-1,2,3,4-tetrahydro-2-quinoxalones **3a,b**, obtained in turn, by the reaction of dialkyl esters of oxaloacetic acid and N-phenyl-*o*-phenylenediamine.

On maintaining solutions of pyrroloquinoxalinetriones **2a,b** in dowtherm A [5] at 185-187°C for 5-7 min 2,4-di(alkoxycarbonyl)-2-(3-oxo-4-phenyl-3,4-dihydro-2-quinoxalinyl)-6-phenyl-2,3,5,6-tetrahydro-1H-pyrido[1,2-*a*]quinoxaline-1,3,5-triones **4a,b*** are formed. The structure of the di(ethoxycarbonyl) derivative **4b** was identified on the basis of data of X-ray structural analysis.

Probably ketenes **1a,b**, formed on thermal decarbonylation of pyrroloquinoxalinetriones **2a,b**, are stabilized by participating in a [4 + 2] cyclodimerization reaction analogously [1, 4]. The [1,3]-acylotropic shift of alkoxycarbonyl groups, described in [1, 3, 4] for the aroyl analogs, does not occur in the resulting cycloadducts **4a,b**, probably as a result of their lower stability compared with the readily migrating aroyl groups.

* See preliminary communication [6].



1–4 a Alk = Me, **b** Alk = Et

As a result of an X-ray structural investigation it became clear that specially grown crystals of compound **4b** cocrystallized with benzene and water molecules in a ratio of 1:1:1. The general shape of the compound **4b** molecule is shown in Fig. 1. The tricyclic fragment of the molecule deviates significantly from a planar structure. The pyrazine ring has a *boat* conformation. Twists along the line C(8)···C(11) and C(9)···C(10) were 19.8 and 13.2° respectively, and the deviations of the N(1) and N(2) atoms from the plane of the four carbon atoms were 0.24 and 0.15 Å. The phenyl substituent at the N(2) atom has a strictly bisecting orientation. The pyridine ring is also non-planar and has an *envelope* conformation. The twist along the N(1)···C(2) line was 28.6°. The deviation of the C(1) atom from the plane of the remaining five ring atoms was 0.37 Å to the side of the quinoxaline substituent at the C(2) atom. The orientations of the ethoxycarbonyl groups are characterized by

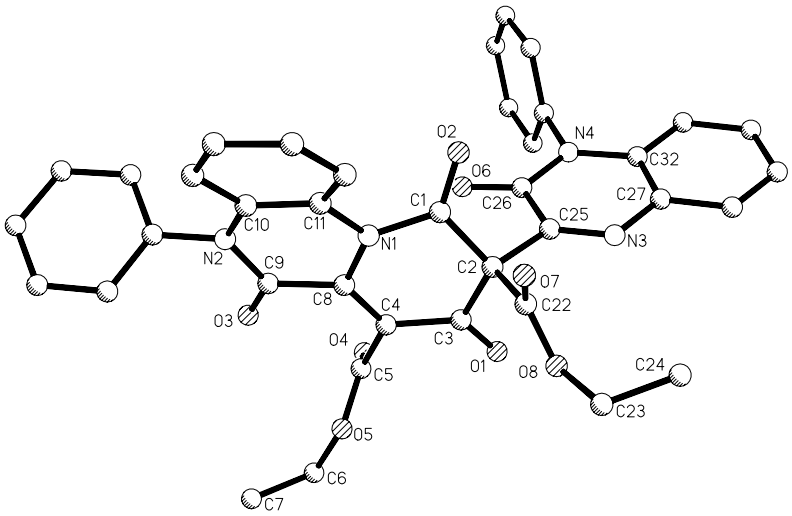


Fig. 1 Structure of the compound **4b** molecule.

torsion angles C(3)C(4)C(5)O(4) of 72.7 and C(3)C(2)C(22)O(7) of 144.9°. The quinoxaline group at C(2) was planar. The torsion angle C(3)C(2)C(25)N(3) was equal to 112.6° and the plane of the phenyl substituent at the N(4) atom was orthogonal to the plane of the quinoxaline. The C(4)=C(8) and N(3)=C(25) double bonds [1.350(3) and 1.273(3) Å respectively] were localized, without significant participation in conjugation. The remaining bond lengths in the molecule have the usual values and require no comment.

Unlike the benzene molecule the water of crystallization molecule was randomized statistically at two crystallographic positions. Since both these positions are close to the center of inversion with coordinates 0.5 0 0, the water molecule is in fact randomized statistically with a weighting of 1/4 at four positions at the corners of a square with side 1.70 Å. Hydrogen bonds and other shortened contacts were absent from the crystal.

EXPERIMENTAL

The IR spectra of the synthesized compounds were recorded on a UR 20 spectrometer in nujol, the ^{1}H NMR spectra on a Bruker DRX 400 (400 MHz) instrument in DMSO-d_6, internal standard was HMDS (δ 0.05 ppm), and the mass spectrum on a MX 1410 instrument with ionising voltage 70 eV. The homogeneity of the obtained compounds was confirmed by TLC on Silufol plates in the system benzene–ethyl acetate, 5:1.

***Z*-3-Methoxycarbonylmethylene-1-phenyl-1,2,3,4-tetrahydro-2-quinoxalone (3a).** A solution of N-phenyl-*o*-phenylenediamine (10 mmol) in dioxane (15 ml) was added to a solution of oxaloacetic acid dimethyl ester (10 mmol) in dioxane (5 ml). The mixture was boiled for 1 h 30 min, cooled, and the precipitated solid compound **3a** filtered off. Yield 2.65 g (90%); mp 194-195°C (dioxane). IR spectrum, ν, cm^{-1}: 2980 br (NH), 1680 ($C_{(2)}$=O), 1612 br (COO). ^{1}H NMR spectrum, δ, ppm: 3.71 (3H, s, CH_3O); 5.59 (1H, s, CH); 6.25-7.95 (9H, m, C_6H_5 + C_6H_4); 11.15 (1H, s, NH). Found, %: C 69.40; H 4.83; N 9.45. $C_{17}H_{14}N_2O_3$. Calculated, %: C 69.38; H 4.79; N 9.52.

***Z*-3-Ethoxycarbonylmethylene-1-phenyl-1,2,3,4-tetrahydro-2-quinoxalone (3b).** Yield 2.62 g (85%); mp 161-163°C (toluene). IR spectrum, ν, cm^{-1}: 3015 br (NH), 1685 ($C_{(2)}$=O), 1630 (COO). ^{1}H NMR spectrum, δ, ppm: 1.31 (3H, t, CH_3); 4.21 (2H, q, CH_2); 5.61 (1H, s, CH); 6.32 (1H, d, *o*-CH in C_6H_5); 6.81-7.69 (8H, m, $2C_6H_4$); 11.22 (1H, s, NH). Found, %: C 70.07; H 5.18; N 9.14. $C_{18}H_{16}N_2O_3$. Calculated, %: C 70.12; H 5.23; N 9.09.

3-Methoxycarbonyl-5-phenyl-1,2,4,5-tetrahydropyrrolo[1,2-*a*]quinoxaline-1,2,4-trione (2a). A solution of compound **3a** (10 mmol) and oxalyl chloride (10 mmol) in absolute chloroform (50 ml) was boiled for 1 h, cooled, and the precipitated solid compound **2a** filtered off. Yield 3.13 g (90%); mp 187-189°C (chloroform). IR spectrum, ν, cm^{-1}: 1770 ($C_{(1)}$=O), 1750 (COO), 1730 ($C_{(2)}$=O), 1690 ($C_{(4)}$=O). ^{1}H NMR spectrum, δ, ppm: 3.74 (3H, s, CH_3O); 6.69 (1H, d, *o*-CH in C_6H_5); 7.39-8.35 (8H, m, $2C_6H_4$). Found, %: C 65.50; H 3.51; N 8.01. $C_{19}H_{12}N_2O_5$. Calculated, %: C 65.52; H 3.47; N 8.04.

3-Ethoxycarbonyl-5-phenyl-1,2,4,5-tetrahydropyrrolo[1,2-*a*]quinoxaline-1,2,4-trione (2b). Yield 3.26 g (90%); mp 185-187°C (chloroform). IR spectrum, ν, cm^{-1}: 1765 ($C_{(1)}$=O), 1725 (COO, $C_{(2)}$=O), 1675 ($C_{(4)}$=O). ^{1}H NMR spectrum, δ, ppm: 1.31 (3H, t, CH_3); 4.27 (2H, q, CH_2); 6.56 (1H, d, *o*-CH in C_6H_5); 7.00-7.70 (7H, m, C_6H_4 + C_6H_3); 7.85 (1H, d, *o*-CH in C_6H_5). Found, %: C 66.28; H 3.87; N 7.76. $C_{20}H_{14}N_2O_5$. Calculated, %: C 66.30; H 3.89; N 7.73.

2,4-Di(methoxycarbonyl)-2-(3-oxo-4-phenyl-3,4-dihydro-2-quinoxalinyl)-6-phenyl-2,3,5,6-tetrahydro-1H-pyrido[1,2-*a*]quinoxaline-1,3,5-trione (4a). A solution of compound **2a** (1 mmol) in dowtherm A (4 ml) was maintained at 185-187°C for 7 min, cooled, and the precipitated solid compound **4a** filtered off. Yield 0.33 g (52%); mp 235-237°C (decomp., from benzene). IR spectrum, ν, cm^{-1}: 1740, 1720 ($COOCH_3$), 1675 (CO). ^{1}H NMR spectrum, δ, ppm: 3.30 (6H, s, $2CH_3$); 6.42-7.80 (18H, m, $2C_6H_5$ + $2C_6H_4$). Found, %: C 67.48; H 3.77; N 8.72. $C_{36}H_{24}N_4O_8$. Calculated, %: C 67.50; H 3.78; N 8.75.

2,4-Di(ethoxycarbonyl)-2-(3-oxo-4-phenyl-3,4-dihydro-2-quinoxalinyl)-6-phenyl-2,3,5,6-tetrahydro-1H-pyrido[1,2-*a*]quinoxaline-1,3,5-trione (4b). A solution of compound **2b** (1.66 mmol) in dowtherm A (4 ml) was maintained at 185-187°C for 5 min, cooled, and the precipitated solid **4b** filtered off. Yield 0.27 g (40%); mp 209-211°C (decomp., from benzene). IR spectrum, ν, cm^{-1}: 1720 ($COOC_2H_5$), 1645 (CO). ^1H NMR spectrum, δ, ppm, (*J*, Hz): 1.24 (3H, t, *J* = 7.0, CH_3); 1.42 (3H, t, *J* = 7.0, CH_3); 4.17 (2H, q, *J* = 7.0, CH_2); 4.50 (2H, q, *J* = 7.0, CH_2); 6.40-8.03 (18H, m, $2C_6H_5 + 2C_6H_4$). Mass spectrum, *m/z* (*I*, %): 668 $[M]^+$. Found, %: C 68.31; H 4.25; N 8.41. $C_{38}H_{28}N_4O_8$. Calculated, %: C 68.26; H 4.22; N 8.38.

X-ray Structural Investigation of Compound 4b. For the X-ray structural investigation compound **4b** was repeatedly crystallized from aqueous benzene. The yellow well-defined crystals of $C_{38}H_{28}N_4O_8 \cdot C_6H_6 \cdot H_2O$ were triclinic: *a* = 13.556(3), *b* = 17.452(3), *c* = 9.244(2) Å; α = 95.70(3), β = 104.29(3), γ = 100.28(3)°; *V* = 2061.5(7) $Å^3$; M = 764.77; *Z* = 2; d_{calc} = 1.232 g/cm^3; space group *P*1. Unit cell parameters and the set of experimental reflections were measured with an automatic 4-circle KM-4 diffractometer (Kuma Diffraction) with Cu*K*α radiation in the angle range 2.6 < θ < 80.3°. The structure was determined by the direct statistical method. Hydrogen atoms were fixed geometrically. A full-matrix anisotropic (for non-hydrogen atoms) refinement by the method of least squares was carried out to *R* = 0.0612 for 5041 reflections with $I > 2\sigma(I)$ from the overall group of 8498 reflections measured. GooF = 1.065. No corrections for absorption were introduced (μ = 0.719 mm^{-1}). All calculations were carried out with the SHELX-97 set of programs [7].

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