Chemistry of acyl(imidoyl)ketenes
4.* Synthesis and crystal and molecular structure of 3-benzoyl-4-benzylamino-5-phenyl-5*H*-furan-2-one

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Intramolecular cyclization of [*N*-benzyl(arylglyoxylimidoyl)]ketenes generated upon thermal decarbonylation of 4,5-diaroyl-1-benzylpyrrole-2,3-diones is accompanied by redox processes to form 3-aroyl-5-aryl-4*H*-furo[3,2-*c*]isoquinolin-2-ones and 3-benzoyl-4-benzylamino-5-phenyl-5*H*-furan-2-one (**1**). The molecular and crystal structure of compound **1** was studied by X-ray diffraction analysis. Under conditions of thermolysis, the starting pyrrole-2,3-diones are partially reduced to 4,5-diaroyl-1-benzyl-3-hydroxy-5*H*-pyrrol-2-ones.

Key words: acyl(imidoyl)ketene, pyrroledione, crystal and molecular structure, cyclization.

The structural features of acyl(imidoyl)ketenes give grounds to expect that these unstable compounds will exhibit various reactivities due to which they are very attractive objects of investigations.[2,3]

Previously,[4] it has been reported that benzoyl[*N*-benzyl(phenylglyoxylimidoyl)]ketene (**2a**), which was generated by thermal decarbonylation of 4,5-dibenzoyl-1-benzylpyrrole-2,3-dione (**1a**) at 247—250 °C, underwent intramolecular cyclization to form 3-benzoyl-5-phenyl-4,5-dihydro-3*H*-furo[3,2-*c*]isoquinolin-2-one (**3a**). The latter was oxidized under conditions of thermolysis to 3-benzoyl-5-phenyl-4*H*-furo[3,2-*c*]isoquinolin-2-one (**4a**). A probable scheme was suggested, which involves 1,5-prototropic shift in the molecule of imidoylketene **2a** followed by intramolecular cyclization to 3-benzoyl-4-benzylidineamino-5-phenyl-3*H*-furan-2-one (**5a**). Since the question as to the reaction component which acts as an oxidizing agent remained to be answered, we studied thermolysis of pyrroledione **1a** at various temperatures, which allowed us to extend the scheme reported previously.

Thermolysis of compound **1a** at 233—236 °C in Dowtherm A afforded two minor products, *viz.*, 3-benzoyl-4-benzylamino-5-phenyl-5*H*-furan-2-one (**6**) and 4,5-dibenzoyl-1-benzyl-3-hydroxy-5*H*-pyrrol-2-one (**7**), along with furoisoquinolinone **4a**. Apparently, compounds **6a** and **7a** are products of reduction of iminofuranone **5a** and the starting pyrroledione **1a**, respectively.

The formation of furanone **6** confirmed the occurrence of the 1,5-prototropic migration in the molecule of acyl(imidoyl)ketene **2a** followed by intramolecular cyclization with the involvement of the ketene fragment and the enol OH group (Scheme 1).

Generally, cyclization of imines to form the hydrogenated isoquinoline system, analogous to cyclization of compounds **5a,b** to compounds **3a,b**, requires the presence of acid catalysts. In this case, a combination of favorable steric factors and high reaction temperature, apparently, suffices to perform cyclization. The introduction of a donor substituent (Me) at the *para* position of the aromatic ring involved in cyclization leads to somewhat of an increase in its nucleophilicity and, as a consequence, to an increase in the yield of the corresponding furoisoquinolinone **4b**.

Therefore, the initial compounds **1a,b** and intermediate iminofuranones **5a,b** act as oxidizing agents in the reactions proceeding upon thermolysis of 4,5-diaroyl-1-benzylpyrrole-2,3-diones **1a,b**.

Compound **6** was identified by X-ray diffraction analysis. The overall view of molecule **6** is shown in Fig. 1. All bond lengths and bond angles in the molecule are within ranges typical of the corresponding bond values (Tables 1 and 2) and need no comments. Noteworthy is only a substantial elongation of the C(6)=C(7) bond in the furan ring (1.383 Å) compared to the standard value of the double bond. However, according to the Cambridge Structural Database (struc-

* For Part 3, see Ref. 1.
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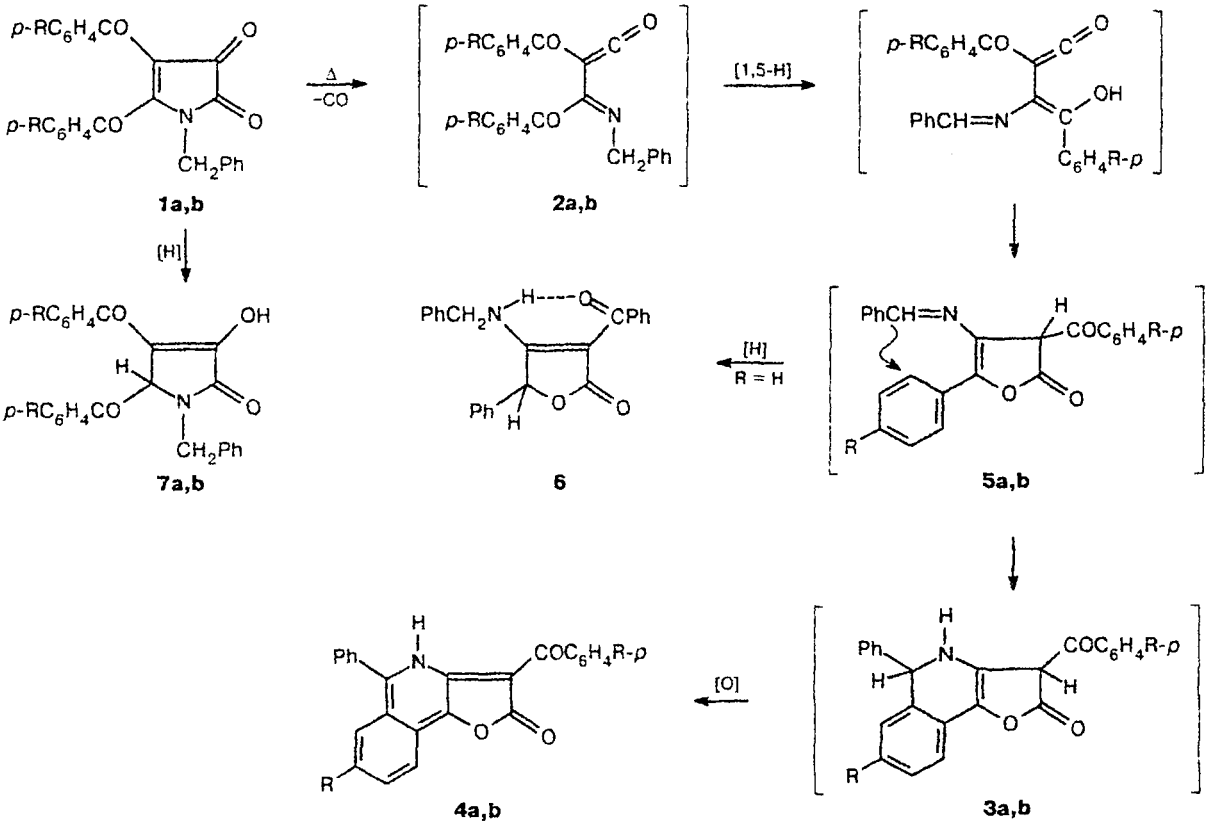
Scheme 1



R = H (**a**), Me (**b**)

tures characterized by $R \leq 0.06$ were considered), this bond in furanone derivatives varies in a wide range (1.291—1.399 Å).

The orientations of the benzoyl and benzylamine substituents with respect to the furan ring are primarily determined by the intramolecular N(4)—H(4)...O(3) hydrogen bond [2.77 Å, d(O...H) = 2.16 Å]. The C(15)N(4)C(7)C(6) and C(7)C(6)C(22)O(3) torsion angles are 179.4° and 7.7°, respectively.

Apparently, the rotation of the benzoyl fragment about the C(6)—C(22) bond is determined by the molecular packing in the crystal. The phenyl ring and two hydrogen atoms at the C(15) atom are on the opposite sides of the plane of the furan ring. The

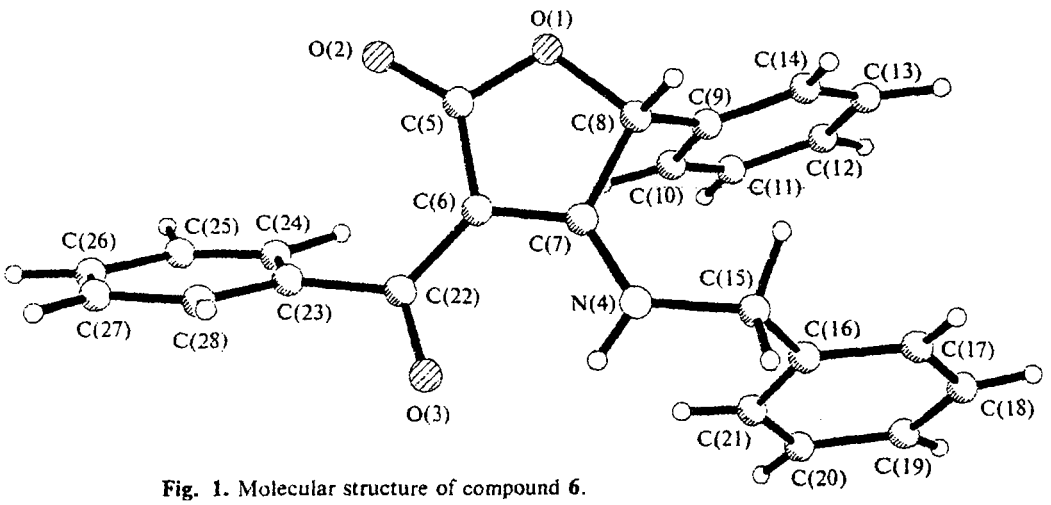


Fig. 1. Molecular structure of compound **6**.

Table 1. Bond lengths (*d*) in compound **6**

Bond	*d*/Å	Bond	*d*/Å	Bond	*d*/Å	Bond	*d*/Å
O(1)—C(5)	1.369(3)	C(6)—C(22)	1.430(3)	C(13)—C(14)	1.380(4)	C(22)—C(23)	1.501(3)
O(1)—C(8)	1.454(3)	C(7)—C(8)	1.513(3)	C(15)—C(16)	1.505(4)	C(23)—C(28)	1.366(5)
O(2)—C(5)	1.207(3)	C(8)—C(9)	1.503(3)	C(16)—C(21)	1.366(4)	C(23)—C(24)	1.393(5)
O(3)—C(22)	1.233(3)	C(9)—C(14)	1.380(3)	C(16)—C(17)	1.368(4)	C(24)—C(25)	1.385(5)
N(4)—C(7)	1.307(3)	C(9)—C(10)	1.391(4)	C(17)—C(18)	1.391(6)	C(25)—C(26)	1.390(8)
N(4)—C(15)	1.462(3)	C(10)—C(11)	1.381(4)	C(18)—C(19)	1.352(7)	C(26)—C(27)	1.340(8)
C(5)—C(6)	1.447(3)	C(11)—C(12)	1.366(5)	C(19)—C(20)	1.355(6)	C(27)—C(28)	1.405(6)
C(6)—C(7)	1.383(3)	C(12)—C(13)	1.379(5)	C(20)—C(21)	1.388(6)		

Table 2. Bond angles (ω) in compound **6**

Angle	ω/deg	Angle	ω/deg	Angle	ω/deg	Angle	ω/deg
C(5)—O(1)—C(8)	110.6(2)	O(1)—C(8)—C(9)	109.3(2)	N(4)—C(15)—C(16)	114.5(2)	C(6)—C(22)—C(23)	121.6(2)
C(7)—N(4)—C(15)	126.4(2)	O(1)—C(8)—C(7)	103.0(2)	C(21)—C(16)—C(17)	118.1(3)	C(28)—C(23)—C(24)	120.1(3)
O(2)—C(5)—O(1)	118.9(2)	C(9)—C(8)—C(7)	115.8(2)	C(21)—C(16)—C(15)	123.3(3)	C(28)—C(23)—C(22)	119.7(3)
O(2)—C(5)—C(6)	131.6(2)	C(14)—C(9)—C(10)	119.2(3)	C(17)—C(16)—C(15)	118.6(3)	C(24)—C(23)—C(22)	120.1(3)
O(1)—C(5)—C(6)	109.4(2)	C(14)—C(9)—C(8)	120.2(2)	C(16)—C(17)—C(18)	120.4(4)	C(25)—C(24)—C(23)	120.1(4)
C(7)—C(6)—C(22)	124.5(2)	C(10)—C(9)—C(8)	120.5(2)	C(19)—C(18)—C(17)	121.0(4)	C(24)—C(25)—C(26)	118.8(5)
C(7)—C(6)—C(5)	107.6(2)	C(11)—C(10)—C(9)	120.0(3)	C(18)—C(19)—C(20)	118.8(4)	C(27)—C(26)—C(25)	121.2(4)
C(22)—C(6)—C(5)	127.4(2)	C(12)—C(11)—C(10)	120.1(3)	C(19)—C(20)—C(21)	120.8(4)	C(26)—C(27)—C(28)	120.5(5)
N(4)—C(7)—C(6)	127.8(2)	C(11)—C(12)—C(13)	120.4(3)	C(16)—C(21)—C(20)	120.9(3)	C(23)—C(28)—C(27)	119.3(5)
N(4)—C(7)—C(8)	123.0(2)	C(12)—C(13)—C(14)	119.7(3)	O(3)—C(22)—C(6)	120.1(2)		
C(6)—C(7)—C(8)	109.1(2)	C(9)—C(14)—C(13)	120.4(3)	O(3)—C(22)—C(23)	118.4(2)		

C(7)N(4)C(15)C(16) torsion angle is −94.5°. The plane of the phenyl substituent at the C(8) atom is orthogonal to the plane of the five-membered ring and has a bisector orientation with respect to the latter and the *cis* orientation with respect to the phenyl substituent of the benzylamine group.

In the crystal, the oxygen and nitrogen atoms form (in addition to the intramolecular hydrogen bond) an intermolecular hydrogen bond (2.90 Å) with the molecule, related by a center of symmetry. Hence, it can be stated that in the crystal, the molecules exist as centrosymmetrical dimeric associates linked *via* hydrogen bonds.

Experimental

The IR spectra of the synthesized compounds were recorded on a UR-20 spectrophotometer. The ^{1}H NMR spectrum was obtained on a Bruker-80 instrument (80 MHz). The mass spectra (EI) were measured on an MKh-1320 instrument; ionizing voltage was 70 eV. Thermolysis was performed in Dowtherm A, *i.e.*, in a eutectic mixture of biphenyl and diphenyl ether.[5]

3-Benzoyl-5-phenyl-4*H*-furo[3,2-*c*]isoquinolin-2-one (4a), 3-benzoyl-4-benzylamino-5-phenyl-5*H*-furan-2-one (6), and 4,5-dibenzoyl-1-benzyl-3-hydroxy-5*H*-pyrrol-2-one (7a). A solution of compound **1a** (1.98 g, 0.005 mol) in Dowtherm A (5 mL) was kept at 233—236 °C for 25 min and then cooled. The red precipitate of compound **4a** that formed was filtered off; the yield was 0.40 g (22%), m.p. 281—283 °C (with decomp., from dioxane).[4] Hexane (30 mL) was added to the mother liquor and the resinous precipitate that formed was filtered off. Compounds **6** and **7a** were isolated by fractional recrystallization from a 1 : 1 $CHCl_3$—hexane mixture. Compound **6** was obtained in a yield of 0.1 g (5%), m.p. 207—209 °C. MS, *m/z*: 369 $[M]^+$. IR, ν/cm^{-1}: 3260 (NH), 1720 (C(2)=O), 1620 (C(3)C=O). Compound **7a** was obtained in a yield of 0.1 g (5%), m.p. 201—203 °C (with decomp.). Found (%): C, 74.97; H, 5.03; N, 3.48. $C_{25}H_{19}NO_4$. Calculated (%): C, 75.55; H, 4.82; N, 3.52. MS, *m/z*: 397 $[M]^+$. IR, ν/cm^{-1}: 3110 (OH), 1685 (C(2)=O), 1630 (PhCO).

7-Methyl-5-phenyl-3-*p*-toluoyl-4*H*-furo[3,2-*c*]isoquinolin-2-one (4b) and 1-benzyl-4,5-di-*p*-toluoyl-3-hydroxy-5*H*-pyrrol-2-one (7b). A solution of compound **1b** (2.12 g, 0.005 mol) in Dowtherm A (5 mL) was kept at 239—240 °C for 25 min and then cooled. The red precipitate of compound **4b** that formed was filtered off; the yield was 0.63 g (32%), m.p. 288—289 °C (with decomp., from dioxane). IR, ν/cm^{-1}: 1728 (C(2)=O), 1630 (C(3)C=O), 1600 (C=C). Hexane (15 mL) was added to the mother liquor and the precipitate that formed was filtered off and crystallized from a 1 : 1 $CHCl_3$—hexane mixture. Compound **7b** was obtained in a yield of 0.45 g (21%), m.p. 199—201 °C (with decomp.). MS, *m/z*: 425 $[M]^+$. IR, ν/cm^{-1}: 3120 (OH), 1670 (C(2)=O), 1625 (C(4)CO, C(5)CO). ^{1}H NMR ($CDCl_3$), δ: 2.28 (s, 3 H, CH_3(C(5))); 2.31 (s, 3 H, CH_3(C(4))); 4.48 (q, 2 H, CH_2, J = 15 Hz); 5.76 (s, 1 H, C(5)—H); 7.32 (m, 13 H, Ar).

Crystals of compound **6** belong to the monoclinic system: a = 13.727(3), b = 12.281(2), c = 12.071(2) Å, β = 104.43(3)°, V = 1971.4(6) Å^3, M = 368.39, d_{calc} = 1.241 g cm^{-3}, Z = 4, space group $P2_1/c$. The X-ray diffraction data set was collected on an automated four-circle KM-4 diffractometer (KUMA DIFFRACTION) with the χ geometry using the θ—2θ scan-

Table 3. Atomic coordinates ($\times 10^4$) and equivalent isotropic thermal parameters ($U_{eq} \cdot 10^3/Å^2$) in compound **6**

Atom	*x*	*y*	*z*	U_{eq}	Atom	*x*	*y*	*z*	U_{eq}
O(1)	8464(1)	2080(1)	5426(1)	46(1)	C(25)	6520(5)	980(4)	753(4)	110(2)
O(2)	7860(1)	2505(2)	3596(2)	58(1)	C(26)	5650(5)	1497(5)	143(4)	122(2)
O(3)	5359(1)	550(2)	4014(2)	81(1)	C(27)	4966(4)	1873(6)	669(4)	130(2)
N(4)	6616(2)	386(2)	6199(2)	47(1)	C(28)	5095(3)	1714(4)	1849(3)	94(1)
C(5)	7757(2)	1984(2)	4407(2)	43(1)	H(4)	6032(23)	163(25)	5785(26)	61(8)
C(6)	6969(2)	1252(2)	4545(2)	43(1)	H(8)	8106(20)	1975(25)	6904(23)	59(8)
C(7)	7179(2)	954(2)	5685(2)	40(1)	H(10)	8938(24)	−155(28)	5288(31)	80(10)
C(8)	8180(2)	1437(2)	6307(2)	40(1)	H(11)	10179(28)	−1446(32)	6032(32)	95(12)
C(9)	9001(2)	633(2)	6791(2)	41(1)	H(12)	11037(34)	−1443(39)	8008(36)	124(15)
C(10)	9262(2)	−162(3)	6098(3)	60(1)	H(13)	10503(33)	−154(37)	9201(39)	123(15)
C(11)	10018(2)	−897(3)	6553(4)	74(1)	H(14)	9248(22)	1217(25)	8357(25)	69(9)
C(12)	10500(2)	−854(3)	7687(4)	80(1)	H(15A)	6186(22)	102(25)	7655(24)	65(8)
C(13)	10246(2)	−71(4)	8385(3)	81(1)	H(15B)	7341(20)	677(23)	7839(23)	57(8)
C(14)	9504(2)	677(3)	7932(2)	61(1)	H(17)	7748(41)	−822(42)	9284(42)	149(21)
C(15)	6866(2)	76(2)	7406(2)	50(1)	H(18)	8583(41)	−2435(41)	9794(46)	144(18)
C(16)	7335(2)	−1034(2)	7653(2)	51(1)	H(19)	8609(33)	−3678(39)	8464(35)	115(15)
C(17)	7798(3)	−1297(4)	8760(3)	89(1)	H(20)	7755(41)	−3319(48)	6486(47)	167(22)
C(18)	8229(4)	−2320(4)	9026(4)	117(2)	H(21)	7075(30)	−1639(34)	6059(35)	111(13)
C(19)	8223(4)	−3064(4)	8199(4)	106(2)	H(24)	7354(32)	527(32)	2451(37)	112(14)
C(20)	7742(5)	−2819(4)	7106(4)	113(2)	H(25)	7136(43)	778(41)	262(48)	168(19)
C(21)	7302(3)	−1805(3)	6829(3)	84(1)	H(26)	5482(40)	1610(43)	−778(51)	164(19)
C(22)	6062(2)	982(2)	3713(2)	52(1)	H(27)	4295(50)	2273(48)	359(55)	180(23)
C(23)	5941(2)	1201(3)	2463(2)	59(1)	H(28)	4615(38)	2090(39)	2276(41)	139(18)
C(24)	6667(3)	844(3)	1921(3)	79(1)					

ning technique and monochromated Cu-Kα radiation in the angle range of $3° < \theta < 80°$. A total of 4314 independent reflections were measured. Absorption was ignored ($\mu = 0.660$ mm^{-1}). The structure was solved by the direct statistical method followed by a series of successive electron density maps. The positions of the hydrogen atoms were located from the difference electron density synthesis calculated after isotropic refinement of the nonhydrogen atoms. The full-matrix least-squares refinement with anisotropic thermal parameters for nonhydrogen atoms converged to $R = 0.045$ using 1611 reflections with $I \geq 2\sigma(I)$. The atomic coordinates are given in Table 3. (The parameters of anisotropic thermal vibrations can be obtained from the authors.) All calculations were carried out on a PC/AT computer using the SHELX 86[6] and SHELXL 93[7] program packages.

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