Intramolecular cyclization of ketene containing both acyl and *N*-alkylimidoyl substituents. Synthesis and crystal and molecular structure of 3-benzoyl-5-phenyl-2*H*,4*H*-furo[3,2-*c*]isoquinolin-2-one

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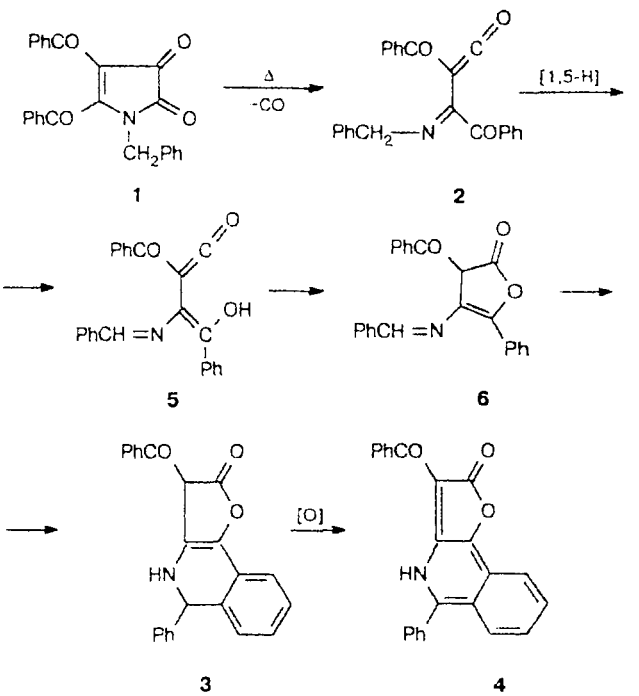
Thermal decarbonylation of 1-benzyl-4,5-dibenzoyl-2,3-dihydropyrrole-2,3-dione yields benzoyl[*N*-benzyl(phenylglyoxalimidoyl)]ketene. The latter undergoes intramolecular cyclization to 3-benzoyl-5-phenyl-2,3,4,5-tetrahydrofuro[3,2-*c*]isoquinolin-2-one, which is oxidized to 3-benzoyl-5-phenyl-2*H*,4*H*-furo[3,2-*c*]isoquinolin-2-one under the reaction conditions. The crystal and molecular structure of the title compound was studied by X-ray structural analysis.

Key words: imidoylketenes, acylketenes, intramolecular cyclization, crystal and molecular structure.

In the absence of reaction partners, acylketenes[1] and imidoylketenes[2,3] are not prone to intramolecular cyclization and undergo dimerization to substituted 3,4-dihydro-2*H*-pyran-2,4-diones and 2-imidoylmethylene-2,3-dihydro-6*H*-1,3-oxazin-6-ones, respectively. Intramolecular cyclizations of acyl(imidoyl)ketenes containing both acyl and imidoyl groups conjugated with the ketene fragment are poorly known.

Acyl(*N*-arylimidoyl)ketenes generated upon thermolysis of 1-aryl-3-acyl-2,3-dihydropyrrole-2,3-diones undergo cyclization through acylation, which occurs at the *ortho* position of the aryl group bonded to the imidoyl nitrogen atom, with the ketene fragment to form 3-acyl-1,4-dihydro-4-quinolones.[4,5] Introduction of one *ortho* substituent into the aryl group bonded to the nitrogen atom does not change the direction of the reaction (acylation occurs at the "free" *ortho* position[5]), whereas introduction of two *ortho* substituents excludes the possibility of this type of intramolecular cyclization. However, products were not isolated because of substantial resinification.[4] Reactions of acyl(*N*-alkylimidoyl)ketenes were not studied.

Thermolysis of 1-benzyl-4,5-dibenzoyl-2,3-dihydropyrrole-2,3-dione (**1**) at 247—250 °C generates benzoyl[*N*-benzyl(phenylglyoxalimidoyl)]ketene (**2**), which undergoes intramolecular cyclization to 3-benzoyl-5-phenyl-2,3,4,5-tetrahydrofuro[3,2-*c*]isoquinolin-2-one (**3**). Under the reaction conditions, the latter is oxidized to 3-benzoyl-5-phenyl-2*H*,4*H*-furo[3,2-*c*]isoquinolin-2-one (**4**). The crystal and molecular structure of **4** was studied by X-ray structural analysis.



1 **2** **5** **6** **3** **4**

Apparently, in ketene **2**, a [1,5]-prototropic shift occurs to yield the corresponding hydroxyethenylketene (**5**) followed by cyclization to 2,3-dihydrofuran-2-one (**6**). In turn, compound **6** undergoes cyclization to furo[3,2-*c*]isoquinolin-2-one **3** because the electron-de-

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya*, No. 3, pp. 563—565, March, 1997.

1066-5285/97/4603-0543 $18.00

Table 1. Bond lengths (d) and bond angles (ω) in molecule **4**

Bond	d/Å	Bond	d/Å
O(1)—C(5)	1.35(1)	C(13)—C(14)	1.33(2)
O(1)—C(8)	1.44(1)	C(14)—C(15)	1.37(1)
O(2)—C(8)	1.20(1)	C(16)—C(17)	1.45(2)
O(3)—C(9)	1.25(1)	C(16)—C(21)	1.45(1)
N(4)—C(6)	1.35(1)	C(17)—C(18)	1.34(2)
N(4)—C(22)	1.36(1)	C(18)—C(19)	1.37(2)
C(5)—C(6)	1.38(1)	C(19)—C(20)	1.38(2)
C(5)—C(16)	1.38(2)	C(20)—C(21)	1.42(2)
C(6)—C(7)	1.40(1)	C(21)—C(22)	1.40(2)
C(7)—C(8)	1.44(2)	C(22)—C(23)	1.44(2)
C(7)—C(9)	1.46(2)	C(23)—C(24)	1.38(2)
C(9)—C(10)	1.49(1)	C(23)—C(28)	1.41(1)
C(10)—C(11)	1.37(2)	C(24)—C(25)	1.36(2)
C(10)—C(15)	1.39(1)	C(25)—C(26)	1.39(2)
C(11)—C(12)	1.39(2)	C(26)—C(27)	1.37(2)
C(12)—C(13)	1.39(1)	C(27)—C(28)	1.37(1)

Angle	ω/deg	Angle	ω/deg
C(5)—O(1)—C(8)	107.5(6)	C(13)—C(14)—C(15)	123.0(12)
C(6)—N(4)—C(22)	123.4(10)	C(14)—C(15)—C(10)	117.5(11)
O(1)—C(5)—C(6)	110.1(9)	C(5)—C(16)—C(17)	124.0(10)
O(1)—C(5)—C(16)	128.7(10)	C(5)—C(16)—C(21)	117.8(10)
C(6)—C(5)—C(16)	121.0(10)	C(17)—C(16)—C(21)	118.1(10)
N(4)—C(6)—C(5)	119.8(11)	C(18)—C(17)—C(16)	120.7(11)
N(4)—C(6)—C(7)	131.0(11)	C(17)—C(18)—C(19)	120.4(12)
C(5)—C(6)—C(7)	109.0(10)	C(20)—C(19)—C(18)	123.8(12)
C(6)—C(7)—C(8)	106.1(9)	C(19)—C(20)—C(21)	118.2(11)
C(6)—C(7)—C(9)	121.1(9)	C(22)—C(21)—C(16)	119.9(11)
C(8)—C(7)—C(9)	132.7(10)	C(22)—C(21)—C(20)	121.4(11)
O(2)—C(8)—C(7)	136.0(12)	C(16)—C(21)—C(20)	118.7(10)
O(2)—C(8)—O(1)	117.1(11)	N(4)—C(22)—C(21)	118.0(11)
C(7)—C(8)—O(1)	106.7(7)	N(4)—C(22)—C(23)	114.6(10)
O(3)—C(9)—C(7)	116.5(9)	C(21)—C(22)—C(23)	127.4(11)
O(3)—C(9)—C(10)	118.9(9)	C(24)—C(23)—C(28)	117.5(10)
C(7)—C(9)—C(10)	124.6(9)	C(24)—C(23)—C(22)	121.7(9)
C(11)—C(10)—C(15)	120.5(10)	C(28)—C(23)—C(22)	120.7(10)
C(11)—C(10)—C(9)	116.9(9)	C(25)—C(24)—C(23)	121.1(10)
C(15)—C(10)—C(9)	122.5(10)	C(24)—C(25)—C(26)	121.2(11)
C(10)—C(11)—C(12)	120.7(11)	C(25)—C(26)—C(27)	118.2(10)
C(11)—C(12)—C(13)	117.8(11)	C(28)—C(27)—C(26)	121.1(10)
C(14)—C(13)—C(12)	120.4(12)	C(27)—C(28)—C(23)	120.5(11)

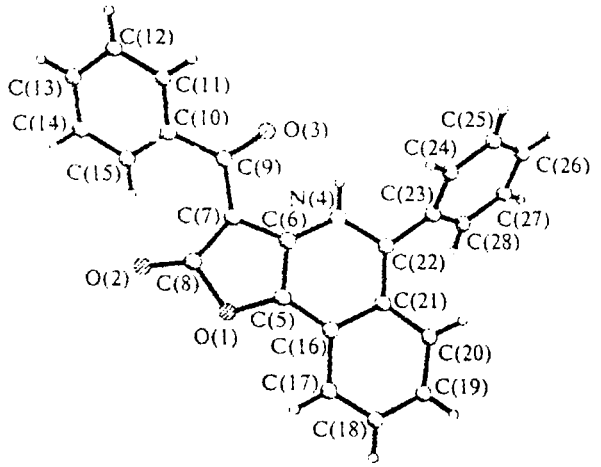


Fig. 1. Overall view of molecule **4**.

Table 2. Atomic coordinates ($\times 10^4$) and isotropic equivalent temperature factors ($U_{iso}^{eq} \cdot 10^3$/Å^2) for nonhydrogen atoms in molecule **4**

Atom	x	y	z	U_{iso}^{eq}
O(1)	602(3)	658(4)	0	46(2)
O(2)	1308(3)	59(4)	1169(11)	59(2)
O(3)	230(3)	−925(4)	4903(8)	51(2)
N(4)	−387(3)	−1497(4)	2574(11)	36(2)
C(5)	137(4)	−1119(6)	417(12)	38(3)
C(6)	71(4)	−1100(6)	1928(12)	34(3)
C(7)	562(4)	−697(6)	2539(12)	36(3)
C(8)	897(4)	−385(6)	1320(15)	41(3)
C(9)	640(5)	−639(5)	4131(12)	37(3)
C(10)	1174(4)	−276(5)	4872(11)	39(3)
C(11)	1069(5)	66(6)	6201(16)	53(3)
C(12)	1549(5)	372(6)	7019(13)	55(3)
C(13)	2133(5)	324(6)	6428(14)	52(3)
C(14)	2224(5)	−11(5)	5127(14)	53(3)
C(15)	1761(5)	−321(6)	4304(13)	50(3)
C(16)	−272(5)	−1513(6)	−455(13)	42(3)
C(17)	−220(5)	−1578(7)	−2044(14)	53(3)
C(18)	−615(5)	−2001(7)	−2812(14)	55(3)
C(19)	−1078(6)	−2379(7)	−2111(15)	63(4)
C(20)	−1172(5)	−2355(6)	−605(15)	51(3)
C(21)	−756(5)	−1932(6)	270(11)	42(3)
C(22)	−811(5)	−1904(6)	1807(12)	43(3)
C(23)	−1273(5)	−2261(6)	2703(14)	44(3)
C(24)	−1633(4)	−1838(6)	3650(14)	54(3)
C(25)	−2056(4)	−2185(6)	4522(16)	66(4)
C(26)	−2172(5)	−2966(6)	4416(15)	60(3)
C(27)	−1815(5)	−3395(6)	3486(14)	61(4)
C(28)	−1384(5)	−3055(6)	2607(14)	52(3)

ficient carbon atom of the azomethine group attacks the *ortho* position of the phenyl ring at the C(5) atom of the dihydrofuran ring.

The overall view of molecule **4** is shown in Fig. 1. The bond lengths and bond angles are given in Table 1. The tricyclic fragment of the molecule is virtually planar (to within 0.03 Å). In spite of the presence of the intramolecular N(4)—H(4)...O(3) hydrogen bond (r(N—H) = 0.86 Å, r(O...H) = 2.13 Å, and the N—H—O angle is 123.6°), the O(3) atom of the benzoyl group deviates substantially from the plane of the tricyclic fragment. The O(3)C(9)C(7)C(6) torsion angle is 4.3°. The deviation of the O(3) atom from the plane of the benzene ring, to which O(3) is bonded, is even larger (the O(3)C(9)C(10)C(11) torsion angle is 31.9°). The

Table 3. Atomic coordinates ($\times 10^4$) of hydrogen atoms in molecule **4**

Atom	x	y	z
H(4)	−411(3)	−1492(4)	3518(11)
H(11)	674(5)	96(6)	6564(16)
H(12)	1481(5)	600(6)	7930(13)
H(13)	2461(5)	527(6)	6944(14)
H(14)	2619(5)	−36(5)	4761(14)
H(15)	1837(5)	−553(6)	3401(13)
H(17)	92(5)	−1322(7)	−2532(14)
H(18)	−575(5)	−2040(7)	−3828(14)
H(19)	−1345(6)	−2669(7)	−2679(15)
H(20)	−1500(5)	−2610(6)	−179(15)
H(24)	−1586(4)	−1308(6)	3693(14)
H(25)	−2272(4)	−1892(6)	5201(16)
H(26)	−2482(5)	−3192(6)	4960(15)
H(27)	−1867(5)	−3925(6)	3452(14)
H(28)	−1165(5)	−3352(6)	1942(14)

angles between the mean plane of the tricyclic fragment and the planes of the phenyl ring at the C(22) atom and the benzoyl group are 55.9 and 35.1°, respectively. There are no intermolecular hydrogen bonds and shortened contacts in the crystal.

Experimental

The IR spectrum of compound **4** was obtained on an UR-20 instrument (Nujol mulls). The ^{1}H NMR spectrum was recorded on a RYa-2310 instrument (60 MHz) in DMSO-d_6 with HMDS as the internal standard. The purity of compound **4** was confirmed by TLC on Silufol plates in a 3 : 2 benzene—ether system.

3-Benzoyl-5-phenyl-2*H*,4*H*-furo[3,2-*c*]isoquinolin-2-one (4). A solution of compound **1** (0.005 mol) in Dowtherm A (5 mL) was kept at 247—250 °C for 20 min and then cooled. Compound **4** was filtered off. The yield was 0.44 g (24%), m.p. 281—283 °C (with decomp., from dioxane). Found (%): C, 79.03; H, 4.36; N, 3.66. $C_{24}H_{15}NO_3$. Calculated (%): C, 78.89; H, 4.14; N, 3.83. IR (ν/cm^{-1}): 1730(C(2)=O), 1630 (COPh), 1598 (C=C). ^{1}H NMR, δ: 7.62 (m, Ph).

The crystals of compound **4** belong to the orthorhombic system: a = 21.965(4), b = 17.417(3), c = 9.090(2) Å, V = 3477.5 Å, Z = 8, d_{calc} = 1.396 g cm^{-3}, space group *Aba*2. The unit cell parameters and intensities of 982 independent reflections with $I > 3\sigma(I)$ (max $\sin\theta/\lambda$ = 0.51) were measured on an automated DAR-UM diffractometer (Cu-Kα radiation, graphite monochromator). Absorption was ignored. The structure was solved by the direct method and refined anisotropically by the full-matrix least-squares method. Hydrogen atoms were located from the difference electron density synthesis. For hydrogen atoms, only positional parameters were refined, whereas their thermal parameters were fixed half as large as those of the corresponding nonhydrogen atoms. The final value of the R factor was 0.056. All calculations were carried out on a PC AT computer using the AREN program package.[6] The atomic coordinates and thermal parameters are given in Tables 2 and 3.

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Received June 26, 1996;
in revised form January 24, 1997