Chemistry of acyl(imidoyl)ketenes. 3.* Synthesis and structure of 1-*p*-bromophenyl-2-*p*-methoxyphenyl-4-*p*-toluoyl-1,2-dihydropyrimidino[4,3-*c*][1,4]benzoxazine-3,5-dione

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Thermal decarbonylation of 3-*p*-toluoylpyrrolo[2,1-*c*][1,4]benzoxazine-1,2,4-trione affords (2-oxo-1,4-benzoxazin-3-yl)(*p*-toluoyl)ketene. The latter enters into the [4+2]-cycloaddition reaction with *p*-bromobenzylidene-*p*-anisidine to form 1-*p*-bromophenyl-2-*p*-methoxyphenyl-4-*p*-toluoyl-1,2-dihydropyrimidino[4,3-*c*][1,4]benzoxazine-3,5-dione. The molecular and crystal structure of the title compound was studied by X-ray diffraction analysis.

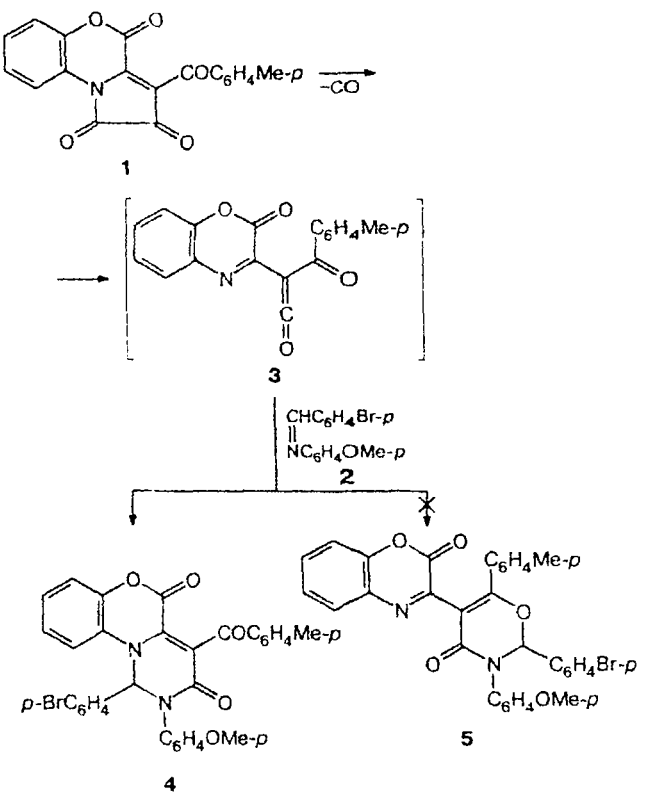
Key words: imidoylketene, acylketene, cycloaddition, molecular and crystal structure.

Acylketenes react with Schiff bases as dienes to form [4+2]-cycloaddition products, *viz.*, substituted 2,3-dihydro-1,3-oxazin-4-ones.[1,2] Analogous reactions of imidoylketenes with benzylideneisopropylamine afford substituted tetrahydropyrimidin-4-ones.[3] The reactions of ketenes, which contain simultaneously the acyl and imidoyl substituents and, therefore, can alternatively participate in [4+2]-cycloaddition as a diene, with azomethines have not been studied, because processes of stabilization through intramolecular cyclization are more typical of the majority of the known acyl(imidoyl)ketenes.[4,5]

Decarbonylation of 3-acylpyrrolo[2,1-*c*][1,4]benzoxazine-1,2,4-triones made it possible to generate substituted acyl(imidoyl)ketenes, which are structurally incapable of undergoing intramolecular cyclization but can participate in intermolecular processes.[6]

Thermolysis of 3-*p*-toluoylpyrrolo[2,1-*c*][1,4]benzoxazine-1,2,4-trione (**1**) at 156—159 °C in the presence of *p*-bromobenzylidene-*p*-anisidine (**2**) proceeded through intermediate formation of (2-oxo-1,4-benzoxazin-3-yl)(*p*-toluoyl)ketene (**3**), which entered into the [4+2]-cycloaddition reaction with the C=N group of Schiff base **2**. To elucidate which alternative isomer, **4** or **5**, was formed in the reaction, we carried out X-ray diffraction analysis of the product isolated.

X-ray diffraction analysis demonstrated that the reaction yielded 1-*p*-bromophenyl-2-*p*-methoxyphenyl-4-*p*-toluoyl-1,2-dihydropyrimidino[4,3-*c*][1,4]benzoxazine-3,5-dione (**4**). Therefore, as in the case of the analogous reaction of ketene **3** with *p*-bromobenz-



* For Part 1, see Ref. 6; for Part 2, see Ref. 5.

† Deceased.

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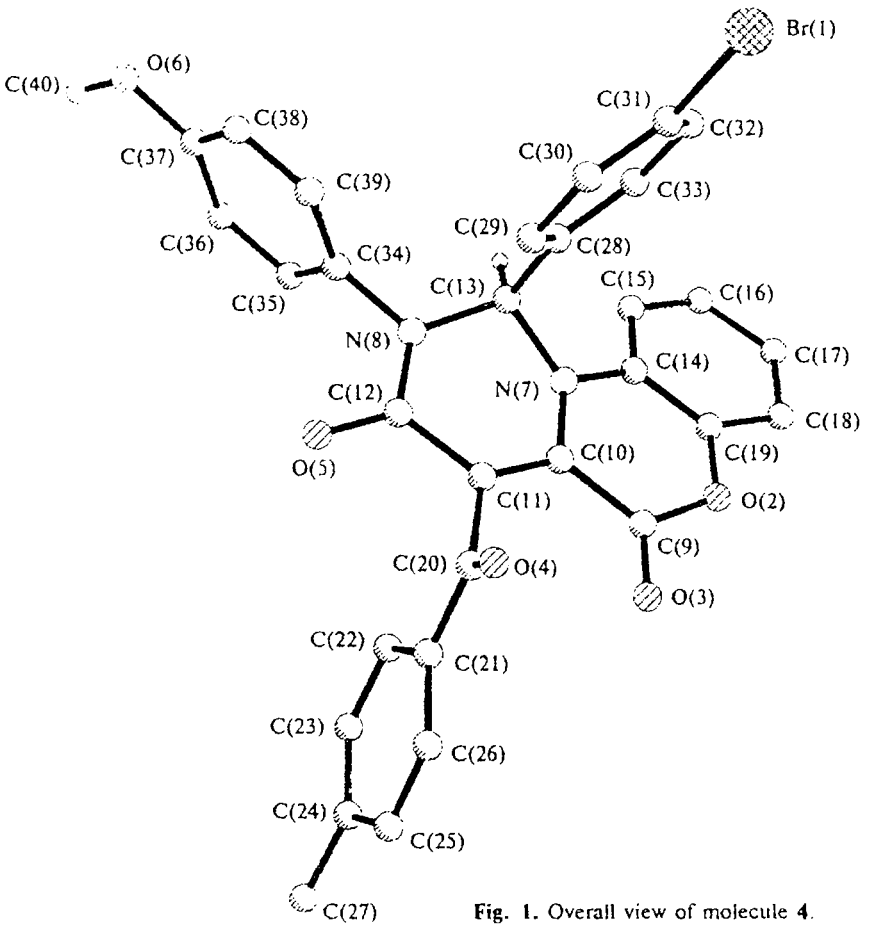

Fig. 1. Overall view of molecule **4**.

aldehyde,[6] [4+2]-cycloaddition proceeded with the participation of the imidoylketene rather than of the acylketene fragment. The fact that these reactions proceed similarly suggests that the benzoxazine system and the ketene fragment in intermediate **3** are coplanar and the C=O group of the toluoyl substituent apparently deviates from their plane. The overall view of molecule **4** is shown in Fig. 1. The bond lengths and bond angles are given in Tables 1 and 2.

All bond lengths and bond angles are in the ranges typical of the corresponding parameters and need no comments. The pyrimidine ring adopts a distorted boat conformation. The C(11) and C(13) atoms deviate from the plane through the remaining four atoms of the ring by 0.51 and 0.07 Å, respectively. The folding angles along the N(7)...N(8) and C(10)...C(12) lines are 36.6° and 6.4°, respectively. The *p*-bromophenyl substituent at the C(13) atom is in the axial orientation with respect to

Table 1. Bond lengths (*d*) in molecule **4**

Bond	*d*/Å	Bond	*d*/Å	Bond	*d*/Å	Bond	*d*/Å
Br(1)—C(31)	1.891(8)	N(8)—C(34)	1.434(8)	C(16)—C(17)	1.369(11)	C(28)—C(33)	1.386(9)
O(2)—C(9)	1.352(10)	N(8)—C(13)	1.460(8)	C(17)—C(18)	1.384(12)	C(28)—C(29)	1.397(10)
O(2)—C(19)	1.398(10)	C(9)—C(10)	1.481(10)	C(18)—C(19)	1.377(10)	C(29)—C(30)	1.397(10)
O(3)—C(9)	1.196(9)	C(10)—C(11)	1.348(10)	C(20)—C(21)	1.475(10)	C(30)—C(31)	1.349(10)
O(4)—C(20)	1.216(10)	C(11)—C(12)	1.465(10)	C(21)—C(22)	1.393(11)	C(31)—C(32)	1.386(12)
O(5)—C(12)	1.228(8)	C(11)—C(20)	1.509(11)	C(21)—C(26)	1.395(10)	C(32)—C(33)	1.380(11)
O(6)—C(37)	1.358(8)	C(13)—C(28)	1.515(10)	C(22)—C(23)	1.399(11)	C(34)—C(35)	1.380(10)
O(6)—C(40)	1.414(10)	C(14)—C(19)	1.388(10)	C(23)—C(24)	1.378(12)	C(34)—C(39)	1.391(10)
N(7)—C(10)	1.376(9)	C(14)—C(15)	1.391(10)	C(24)—C(25)	1.393(13)	C(35)—C(36)	1.385(10)
N(7)—C(14)	1.408(8)	C(15)—C(16)	1.369(10)	C(24)—C(27)	1.503(11)	C(36)—C(37)	1.401(10)
N(7)—C(13)	1.469(8)	C(38)—C(39)	1.370(10)	C(25)—C(26)	1.380(11)	C(37)—C(38)	1.367(12)
N(8)—C(12)	1.364(10)						

Table 2. Bond angles (ω) in molecule **4**

Angle	ω/deg	Angle	ω/deg	Angle	ω/deg
C(9)—O(2)—C(19)	121.3(6)	N(7)—C(13)—C(28)	109.9(5)	C(26)—C(25)—C(24)	120.8(8)
C(37)—O(6)—C(40)	118.7(7)	C(19)—C(14)—C(15)	117.7(7)	C(25)—C(26)—C(21)	121.4(9)
C(10)—N(7)—C(14)	121.4(5)	C(19)—C(14)—N(7)	118.2(6)	C(33)—C(28)—C(29)	118.0(7)
C(10)—N(7)—C(13)	116.3(6)	C(15)—C(14)—N(7)	124.1(6)	C(33)—C(28)—C(13)	119.4(7)
C(14)—N(7)—C(13)	120.1(6)	C(16)—C(15)—C(14)	120.2(8)	C(29)—C(28)—C(13)	122.5(6)
C(12)—N(8)—C(34)	121.5(6)	C(15)—C(16)—C(17)	121.3(9)	C(30)—C(29)—C(28)	120.2(6)
C(12)—N(8)—C(13)	121.1(6)	C(16)—C(17)—C(18)	119.9(8)	C(31)—C(30)—C(29)	120.5(7)
C(34)—N(8)—C(13)	116.3(5)	C(19)—C(18)—C(17)	118.5(8)	C(30)—C(31)—C(32)	120.3(7)
O(3)—C(9)—O(2)	119.0(8)	C(18)—C(19)—C(14)	122.2(8)	C(30)—C(31)—Br(1)	120.2(7)
O(3)—C(9)—C(10)	122.9(8)	C(18)—C(19)—O(2)	117.2(7)	C(32)—C(31)—Br(1)	119.4(6)
O(2)—C(9)—C(10)	118.0(6)	C(14)—C(19)—O(2)	120.5(7)	C(31)—C(32)—C(33)	119.6(7)
C(11)—C(10)—N(7)	120.9(6)	O(4)—C(20)—C(21)	122.0(7)	C(32)—C(33)—C(28)	121.3(8)
C(11)—C(10)—C(9)	121.0(7)	O(4)—C(20)—C(11)	120.2(7)	C(35)—C(34)—C(39)	118.7(7)
N(7)—C(10)—C(9)	118.1(6)	C(21)—C(20)—C(11)	117.7(7)	C(35)—C(34)—N(8)	120.0(7)
C(10)—C(11)—C(12)	120.6(7)	C(22)—C(21)—C(26)	117.7(7)	C(39)—C(34)—N(8)	121.3(7)
C(10)—C(11)—C(20)	124.0(7)	C(22)—C(21)—C(20)	121.8(7)	C(34)—C(35)—C(36)	121.4(7)
C(12)—C(11)—C(20)	115.3(6)	C(26)—C(21)—C(20)	120.4(7)	C(35)—C(36)—C(37)	118.8(8)
O(5)—C(12)—N(8)	122.1(7)	C(21)—C(22)—C(23)	120.6(8)	O(6)—C(37)—C(38)	115.8(7)
O(5)—C(12)—C(11)	122.1(7)	C(24)—C(23)—C(22)	121.2(9)	O(6)—C(37)—C(36)	124.6(8)
N(8)—C(12)—C(11)	115.7(6)	C(23)—C(24)—C(25)	118.2(7)	C(38)—C(37)—C(36)	119.7(7)
N(8)—C(13)—N(7)	109.3(5)	C(23)—C(24)—C(27)	122.1(9)	C(37)—C(38)—C(39)	121.1(8)
N(8)—C(13)—C(28)	114.3(6)	C(25)—C(24)—C(27)	119.7(8)	C(38)—C(39)—C(34)	120.3(8)

Table 3. Atomic coordinates (×10⁴) and isotropic thermal parameters (×10³) in molecule **4**

Atom	*x*	*y*	*z*	*U*/Å²	Atom	*x*	*y*	*z*	*U*/Å²
Br(1)	6395(2)	10039(1)	10482(1)	55(1)	C(33)	1216(14)	9834(3)	9169(4)	39(2)
O(2)	1873(11)	10553(2)	6841(3)	47(2)	C(34)	−532(12)	8008(3)	8331(3)	30(2)
O(3)	4116(8)	9952(3)	6280(3)	52(1)	C(35)	−2474(13)	7785(3)	8122(4)	39(2)
O(4)	6411(10)	8778(3)	6751(3)	50(1)	C(36)	−3496(14)	7325(3)	8503(4)	40(2)
O(5)	2498(10)	7824(2)	7291(3)	47(1)	C(37)	−2521(14)	7085(3)	9111(4)	38(2)
O(6)	−3346(11)	6631(2)	9526(3)	50(1)	C(38)	−599(15)	7308(4)	9318(4)	46(2)
N(7)	277(10)	9549(2)	7577(3)	31(1)	C(39)	401(14)	7763(3)	8938(4)	41(2)
N(8)	475(10)	8488(2)	7929(3)	34(1)	C(40)	−5294(15)	6364(4)	9329(5)	55(2)
C(9)	2698(13)	9990(4)	6697(4)	41(2)	H(13)	−1272(12)	9146(3)	8378(3)	38
C(10)	1905(13)	9452(3)	7105(4)	31(2)	H(15)	−3386(13)	9866(3)	8173(4)	49
C(11)	2795(13)	8889(3)	7036(4)	35(2)	H(16)	−4900(16)	10827(3)	8221(4)	63
C(12)	1953(13)	8356(3)	7425(4)	37(2)	H(17)	−3353(16)	11660(4)	7678(5)	64
C(13)	156(12)	9120(3)	8182(3)	31(2)	H(18)	−269(16)	11528(3)	7027(4)	58
C(14)	−834(12)	10113(3)	7593(3)	34(2)	H(22)	945(14)	8429(4)	5940(4)	50
C(15)	−2733(13)	10199(3)	7950(4)	41(2)	H(23)	221(17)	8093(4)	4796(4)	61
C(16)	−3641(16)	10774(3)	7975(4)	52(2)	H(25)	6289(14)	8299(4)	4276(4)	60
C(17)	−2732(16)	11271(4)	7645(5)	53(2)	H(26)	7049(16)	8588(4)	5421(4)	55
C(18)	−888(16)	11195(3)	7261(4)	48(2)	H(27a)	4036(18)	7920(5)	3408(5)	99
C(19)	11(14)	10615(3)	7232(4)	38(2)	H(27b)	1721(18)	8172(5)	3450(5)	99
C(20)	4601(14)	8749(3)	6539(4)	39(2)	H(27c)	2229(18)	7497(5)	3705(5)	99
C(21)	4082(12)	8551(3)	5810(4)	32(2)	H(29)	3993(13)	8689(3)	8588(4)	42
C(22)	2033(14)	8398(4)	5610(4)	42(2)	H(30)	6266(12)	9038(3)	9469(4)	45
C(23)	1597(17)	8198(4)	4919(4)	51(2)	H(32)	2254(14)	10389(4)	9956(4)	55
C(24)	3169(15)	8152(4)	4415(4)	46(2)	H(33)	−58(14)	10039(3)	9101(4)	47
C(25)	5213(14)	8314(4)	4612(4)	50(2)	H(35)	−3111(13)	7946(3)	7717(4)	47
C(26)	5663(16)	8498(4)	5298(4)	46(2)	H(36)	−4805(14)	7179(3)	8357(4)	48
C(27)	2751(18)	7914(5)	3678(5)	66(3)	H(38)	40(15)	7149(4)	9724(4)	56
C(28)	1683(13)	9321(3)	8757(3)	32(2)	H(39)	1710(14)	7908(3)	9086(4)	49
C(29)	3621(13)	9028(3)	8865(4)	35(2)	H(40a)	−5680(15)	6053(4)	9670(5)	83
C(30)	5002(12)	9244(3)	9388(4)	38(2)	H(40b)	−5163(15)	6178(4)	8867(5)	83
C(31)	4517(15)	9750(3)	9775(4)	40(2)	H(40c)	−6361(15)	6679(4)	9315(5)	83
C(32)	2602(14)	10048(4)	9679(4)	46(2)					

the heterocycle, and the angle between this substituent and the N(7)N(8)C(13) plane is 112.2°. The C(29)C(28)C(13)N(8) torsion angle is 20.9°. The planar methoxyphenyl fragment (the C(38)C(37)O(6)C(4) torsion angle is 177.7°) is orthogonal to the C(13)N(8)C(12) plane and has a bisector orientation with respect to this plane. The orientation of the toluoyl group (the O(4)C(20)C(21)C(22) torsion angle is 166.8°) with respect to the heterocycle is characterized by the following torsion angles: C(10)C(11)C(20)C(21), −89.8° and C(11)C(20)C(21)C(22), −10.5°. The oxazine ring adopts a highly flattened boat conformation. The O(2) and N(7) heteroatoms deviate from the plane through the four carbon atoms by 0.14 and 0.12 Å, respectively. The folding angles are 11.9° and 10.2°. There are no intermolecular hydrogen bonds and shortened contacts in the crystal.

Experimental

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

1-*p*-Bromophenyl-2-*p*-methoxyphenyl-4-*p*-toluoyl-1,2-dihydropyrimidino[4,3-*c*][1,4]benzoxazine-3,5-dione (4). A solution of compound **1** (5 mmol) and compound **2** (10 mmol) in Dowtherm A (17 mL) was kept at 156—159 °C for 10 min and then cooled. Compound **4** was filtered off. The yield was 1.50 g (48%), m.p. 279—280 °C (with decomp., from MeCN). Found (%): C, 64.38; H, 3.71; Br, 13.53; N, 4.58. $C_{32}H_{23}BrN_2O_5$. Calculated (%): C, 64.55; H, 3.89; Br, 13.42; N, 4.70. IR, ν/cm^{-1}: 1760 (C(5)=O), 1665 (COAr), 1645 (C(3)=O). ^{1}H NMR, δ: 2.35 (s, 3 H, CH_3); 3.77 (s, 3 H, OCH_3); 7.48 (m, 17 H, 4 C_6H_4+C(1)H).

Crystals of compound **4** belong to the orthorhombic system: a = 6.342(1), b = 21.608(4), c = 18.812(4) Å, V = 2578.0(8) Å^3, M = 595.43, d_{calc} = 1.534 g cm^{-3}, Z = 4, space group $P2_12_12_1$. The X-ray intensity data were collected on an automated four-circle KM-4 diffractometer (KUMA DIFFRACTION) with the χ geometry using the θ-2θ scanning technique and monochromatic Cu-Kα radiation in the angle range of 3 < θ < 80°. A total of 3071 independent reflections were measured. Absorption was ignored (μ = 2.569 mm^{-1}). The structure was solved by the direct statistical method followed by a series of successive calculated electron density maps. The positions of the hydrogen atom were located from the difference electron density synthesis calculated after isotropic refinement of the nonhydrogen atoms. The full-matrix least-squares anisotropic refinement converged to R = 0.036 using 1493 reflections with $I \geq 2\sigma(I)$. The coefficients of the thermal vibrations of the hydrogen atoms were not refined and were set 1.2 (1.5 for the methyl groups) times as large as the corresponding values of the nonhydrogen atoms. The atomic coordinates are given in Table 3. The parameters of the anisotropic thermal vibrations can be obtained from the authors. All calculations were carried out on a PC/AT computer using the SHELX86[7] and SHELXL93[8] program packages.

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