The structure of 6-*tert*-butyl-4,5-dichloro-3-ethyl-4,5-dihydro-2,1-benzoisoxazole

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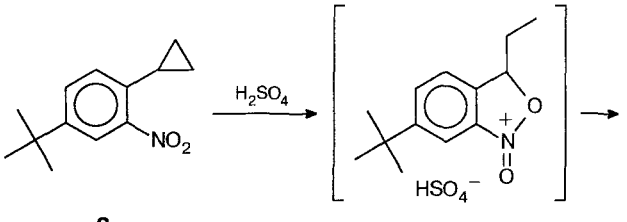
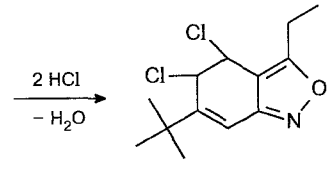
X-ray structural analysis revealed that the product of the reaction of 3,6-dialkyl-substituted *N*-oxo-2,1-benzoisoxazolinium sulfate with hydrochloric acid is 6-*tert*-butyl-4,5-dichloro-3-ethyl-4,5-dihydro-2,1-benzoisoxazole.

Key words: substituted 2,1-benzoisoxazole, crystal and molecular structure.

In the course of the study of the chemistry of heterocyclic ions, we demonstrated that the conversion of *N*-oxo-2,1-benzoisoxazolinium hydrosulfate under the action of hydrohalic acids depends substantially on the nature of the reagent.[1] Thus, the reaction of *N*-oxo-2,1-benzoisoxazolinium ions with hydrobromic acid affords mainly benzo[*c*]isoxazoles, which is attributable to the dominant reducing properties of HBr. When these ions react with hydrochloric acid, the nucleophilic addition of the chloride anion occurs at the electron-deficient position of the benzene ring, and chloro-substituted benzo[*c*]isoxazoles and substituted benzenes are formed as by-products. Unexpectedly, we obtained 6-*tert*-butyl-4,5-dichloro-3-ethyl-4,5-dihydro-2,1-benzoisoxazole (**1**) as a major product of the reaction of the heterocyclic ion **2** obtained from (4-*tert*-butyl-2-nitrophenyl)cyclopropane (**3**) with hydrochloric acid (see Ref. 2).



3 **2**



1

The synthesized compound can exist in several isomeric forms. Only X-ray diffraction allowed us to establish which of the isomers is formed as a result of this reaction.

Based on X-ray structural data, it may be concluded that in the course of the reaction the reductive addition of two chloride ions to the benzene ring (at two adjacent atoms C(8) and C(9)) occurs to form the *trans*-4,5-dihydrodichloro derivative of benzoisoxazole **1**. The isoxazole ring is planar with the localized N(4)=C(5) and C(10)=C(11) double bonds (Fig. 1).

All bond lengths and bond angles (Table 1) agree closely with those found in other isoxazoles.[3–5] The methyl group of the ethyl substituent is nearly normal to the plane of the five-membered cycle (the O(3)—C(11)—C(12)—C(13) torsion angle ~80°).

The C(6)—C(7) bond length (1.339 Å) in the six-membered ring corresponds to that of a double bond. The cycle has a distorted sofa conformation: the C(8) atom has the maximum deviation (0.59 Å) from the plane of the atoms C(5)C(6)C(10)C(9), the deviation of the C(7) atom is substantially smaller (0.02 Å). Both atoms, C(7) and C(8), are displaced from the plane in the same direction, namely, toward the Cl(1) axial substituent. Hence, the most favorable staggered conformation about the C(8)—C(9) bond is realized. The rotation about the C(6)=C(7) double bond is characterized by a C(5)—C(6)—C(7)—C(8) torsion angle of 7.2°. There are no shortened intermolecular contacts in the crystal.

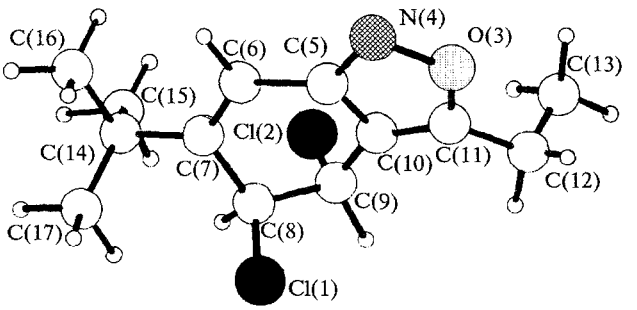


Fig. 1. Molecular structure of compound **1**.

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

Bond	d/Å	Angle	ω/deg
Cl(1)—C(8)	1.841(4)	N(4)—O(3)—C(11)	109.7(3)
Cl(2)—C(9)	1.825(4)	O(3)—N(4)—C(5)	104.5(3)
O(3)—N(4)	1.410(5)	N(4)—C(5)—C(6)	126.1(3)
O(3)—C(11)	1.342(4)	N(4)—C(5)—C(10)	112.5(3)
N(4)—C(5)	1.294(3)	C(6)—C(5)—C(10)	121.4(3)
C(5)—C(6)	1.462(4)	C(5)—C(6)—C(7)	120.3(3)
C(5)—C(10)	1.415(4)	C(6)—C(7)—C(8)	117.6(3)
C(6)—C(7)	1.339(3)	C(6)—C(7)—C(14)	124.4(3)
C(7)—C(8)	1.534(4)	C(8)—C(7)—C(14)	118.0(3)
C(7)—C(14)	1.512(5)	Cl(1)—C(8)—C(7)	108.1(2)
C(8)—C(9)	1.497(4)	Cl(1)—C(8)—C(9)	104.7(2)
C(9)—C(10)	1.480(3)	C(7)—C(8)—C(9)	116.6(2)
C(10)—C(11)	1.350(4)	Cl(2)—C(9)—C(8)	106.4(2)
C(11)—C(12)	1.471(5)	Cl(2)—C(9)—C(10)	109.4(2)
C(12)—C(13)	1.485(5)	C(8)—C(9)—C(10)	111.1(2)
C(14)—C(15)	1.561(5)	C(5)—C(10)—C(9)	120.3(3)
C(14)—C(16)	1.514(5)	C(5)—C(10)—C(14)	104.5(3)
C(14)—C(17)	1.508(5)	C(9)—C(10)—C(11)	135.1(3)
		O(3)—C(11)—C(10)	108.8(3)
		O(3)—C(11)—C(12)	116.7(3)
		C(10)—C(11)—C(12)	134.5(3)
		C(11)—C(12)—C(13)	113.0(3)
		C(7)—C(14)—C(15)	106.4(3)
		C(7)—C(14)—C(16)	111.9(3)
		C(7)—C(14)—C(17)	110.3(3)
		C(15)—C(14)—C(16)	111.5(3)
		C(15)—C(14)—C(17)	108.5(3)
		C(16)—C(14)—C(17)	108.2(3)

Table 2. Fractional atomic coordinates ($\times 10^4$ for non-hydrogen atoms, $\times 10^3$ for H atoms) in structure **1**.

Atom	x	y	z	Atom	x	y	z
Cl(1)	9456(1)	4846(3)	810(2)	H(6)	636(1)	407(1)	546(1)
Cl(2)	6793(2)	8397(2)	1811(2)	H(8)	896(1)	773(1)	115(1)
O(3)	8366(3)	7529(3)	6779(3)	H(9)	763(1)	586(1)	6(1)
N(4)	7687(3)	6190(3)	6827(3)	H(121)	998(1)	954(1)	557(1)
C(5)	7574(3)	6053(3)	5150(3)	H(122)	975(1)	973(1)	333(1)
C(6)	6918(3)	4852(3)	4479(3)	H(131)	898(1)	1192(1)	524(1)
C(7)	7007(3)	4718(3)	2654(3)	H(132)	802(1)	1073(1)	690(1)
C(8)	7931(3)	5737(3)	1301(3)	H(133)	779(1)	1093(1)	466(1)
C(9)	8112(3)	7281(3)	1991(3)	H(151)	480(1)	389(1)	48(1)
C(10)	8153(3)	7237(3)	3962(3)	H(152)	587(1)	537(1)	2(1)
C(11)	8629(3)	8129(4)	5060(4)	H(153)	476(1)	525(1)	221(1)
C(12)	9291(3)	9573(4)	4791(4)	H(161)	499(1)	308(1)	446(1)
C(13)	8471(4)	10884(4)	5439(4)	H(162)	623(1)	183(1)	374(1)
C(14)	6258(3)	3634(4)	1842(4)	H(163)	503(1)	179(1)	265(1)
C(15)	5353(3)	4614(4)	1082(4)	H(171)	757(1)	358(1)	−80(1)
C(16)	5576(4)	2504(4)	3276(4)	H(172)	652(1)	206(1)	−39(1)
C(17)	7081(4)	2778(4)	232(4)	H(173)	774(1)	210(1)	71(1)

Experimental

The colorless platelet-like crystals of $C_{13}H_{17}NOCl_2$ are monoclinic: a = 11.299(2) Å, b = 8.881(3) Å, c = 7.438(2) Å, β = 74.28(2)°, V = 782.0 Å^3, M = 548.4, d_{calc} = 1.164 g cm^{-3}, Z = 2, the space group is $P2_1$. The unit-cell parameters and intensities of reflections were measured on a four-circle KM-4 (KUMA DIFFRACTION) diffractometer operated in the χ mode using the $\theta/2\theta$-scanning technique in the angle range $4° < \theta < 80°$ the (λ(Cu-Kα) radiation, graphite monochromator); 1706 independent reflections with $I > 3\sigma(I)$ were used in the calculations. The structure was solved by the direct statistical method. The H atoms were unambiguously located from difference electron density syntheses. The anisotropic (isotropic for H atoms) full-matrix least-squares refinement converged to R = 0.064 (R_w = 0.062). All calculations were performed on a PC-AT personal computer using the CSD program package.[6] Atomic coordinates are given in Table 2.

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