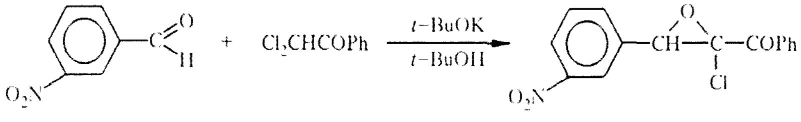
Chemistry of Heterocyclic Compounds, Vol. 30, No. 9, 1994

MOLECULAR STRUCTURE OF 1-PHENYL-2-CHLORO-3-(meta-NITROPHENYL)-2,3-EPOXYPROPANONE

I. A. Litvinov, V. A. Mamedov, and O. N. Kataeva

X-ray analysis was used to determine the structure of 1-phenyl-2-chloro-3-(m-nitrophenyl)-2,3-epoxypropanone, obtained by reacting phenacyl dihydrochloride with metanitrobenzaldehyde under Darzen's reaction conditions. The bulky m-nitrophenyl and benzoyl substituents were located in the trans position relative to the chloroepoxide fragment, which was found to stabilize when the m-nitrophenyl substituent was introduced.

In a previous report [1] we showed that the Cl_2C^-/COPh-type carbanion, generated *in situ* from phenacyl chloride under Darzen's reaction conditions, afforded 1-phenyl-2-chloro-3-(m-nitrophenyl)-2,3-epoxypropanone (1) on reacting with m-nitrobenzaldehyde.



I

Because of their instability the structure of α-chloro-epoxides is determined in most cases from the structure of derived isomers [2] or reaction products [3]. It is worth pointing out that in some cases the α-chloroepoxides and their isomers, namely the α-chloroketones, react with the same reagent to give the same product [4], while in other cases different reaction results are obtained [5]. In the absence of standard structures the use of spectroscopic methods (IR, NMR) cannot be relied upon to provide an unambiguous choice between the possible isomers that could be formed under the same conditions [6], so determining the structure of α-chloroepoxides with these methods cannot always be a clear-cut matter. We obtained stable crystals of compound I and we were able to establish its molecular and spatial structure using an x-ray analysis method.

From the diagrammatic representation of molecule I shown in Figure I it is clear that the oxirane ring geometry is distorted. There is a pronounced difference between the $C_{(2)}-O_{(2)}$ (1.402(3)) and $C_{(3)}-O_{(2)}$ (1.453(3) Å) bond lengths. The usual C–O bond length in the oxirane ring has an average statistical value of 1.446(11) Å [6] and varies within the range 1.438-1.456 Å [6]. Unfortunately none of the 498 crystalline structures containing oxirane rings include compounds with an α-chloroperoxide fragment, so we were not able to compare our results. The strong electron-accepting substituents at the $C_{(2)}$ atom in molecule (I) probably bring about a redistribution of electron density in the epoxide ring that manifests itself in the significant shortening of the $C_{(2)}-O_{(3)}$ bond length. In its turn the powerful electron-accepting substituent at the $C_{(3)}$ atom tends to lessen the effect of the substituents at $C_{(2)}$ and stabilizes the normally unstable α-chloroperoxide fragment.

It should be noted that replacing the m-nitrophenyl group in compound I with a less strong electron-accepting substituent such as a p-chlorophenyl, p-bromophenyl or phenyl group leads to isomerization of the product and the breaking of the epoxide ring (yielding α-chloroketones) [1]. The $C_{(2)}-Cl$ bond length (1.756(2) Å) is in line with that found in structures with chloro-substituted cyclopropyl groups (average of 1.755(11) Å [6]), while the $C_{(2)}-C_{(3)}$ bond length in molecule I (1.463(3) Å) corresponds with that found in oxirane rings (average of 1.466(15) Å [6]).

A. E. Arbuzov Institute of Organic and Physical Chemistry, Kazan Scientific Center, Russian Academy of Sciences, Kazan 420083. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 9, pp. 1172-1175, September, 1994. Original article submitted May 5, 1994.

Factors of Nonhydrogen Atoms*2 and Isotropic Temperature Factors of H Atoms (B_{iso}, Å^2)

Atom	*x*	*y*	*z*	*B*
Cl	0,64106(6)	0,16727(8)	0,04448(4)	4,58(1)
$O_{(1)}$	0,4518(2)	0,1379(2)	0,2163(1)	6,68(5)
$O_{(2)}$	0,7033(1)	0,2363(2)	0,2045(1)	4,13(3)
$O_{(3)}$	1,0693(2)	0,5155(2)	0,0817(1)	6,52(5)
$O_{(4)}$	1,1991(2)	0,3846(3)	0,0052(2)	8,82(6)
N	1,1142(2)	0,3884(3)	0,0549(2)	5,39(5)
$C_{(1)}$	0,5237(2)	0,0474(3)	0,1805(1)	3,79(5)
$C_{(2)}$	0,6488(2)	0,1172(2)	0,1518(1)	3,37(4)
$C_{(3)}$	0,7710(2)	0,0833(3)	0,1930(1)	3,51(4)
$C_{(4)}$	0,8943(2)	0,0895(3)	0,1508(1)	3,37(4)
$C_{(5)}$	0,9439(2)	0,2357(3)	0,1210(1)	3,54(4)
$C_{(6)}$	1,0603(2)	0,2335(3)	0,0846(1)	3,96(5)
$C_{(7)}$	1,1292(2)	0,0916(3)	0,0744(2)	4,64(5)
$C_{(8)}$	1,0801(2)	-0,0528(3)	0,1036(2)	4,61(5)
$C_{(9)}$	0,9638(2)	-0,0538(3)	0,1423(2)	4,01(5)
$C_{(10)}$	0,4964(2)	-0,1271(3)	0,1640(1)	3,34(4)
$C_{(11)}$	0,5816(2)	-0,2293(3)	0,1252(1)	3,65(4)
$C_{(12)}$	0,5523(4)	-0,3929(3)	0,1120(2)	4,33(5)
$C_{(13)}$	0,4379(2)	-0,4527(3)	0,1387(2)	5,08(6)
$C_{(14)}$	0,3818(2)	-0,35623(3)	0,1770(2)	4,95(6)
$C_{(15)}$	0,3814(2)	-0,1907(3)	0,1906(2)	4,14(5)
$H_{(3)}$	0,769(2)	0,013(2)	0,242(1)	3,7(4)*
$H_{(5)}$	0,899(2)	0,327(2)	0,126(1)	3,8(5)*
$H_{(7)}$	1,209(2)	0,097(3)	0,046(2)	5,9(6)*
$H_{(8)}$	1,123(2)	-0,151(2)	0,096(1)	4,5(5)*
$H_{(9)}$	0,928(2)	-0,153(2)	0,162(1)	4,1(5)*
$H_{(11)}$	0,660(2)	-0,192(2)	0,110(1)	3,4(4)*
$H_{(12)}$	0,610(2)	-0,458(3)	0,080(2)	5,5(6)*
$H_{(13)}$	0,419(2)	-0,552(3)	0,130(2)	6,4(6)*
$H_{(14)}$	0,271(2)	-0,388(3)	0,196(2)	6,5(7)*
$H_{(15)}$	0,325(2)	-0,122(2)	0,220(1)	4,8(5)*

---

*Atoms checked isotropically.

*2 $B_{iso}^{equiv} = 4/3 \sum_{i=1}^{3} \sum_{j=1}^{3} (a_i a_j)\, B(i, j)$ (Å^2).

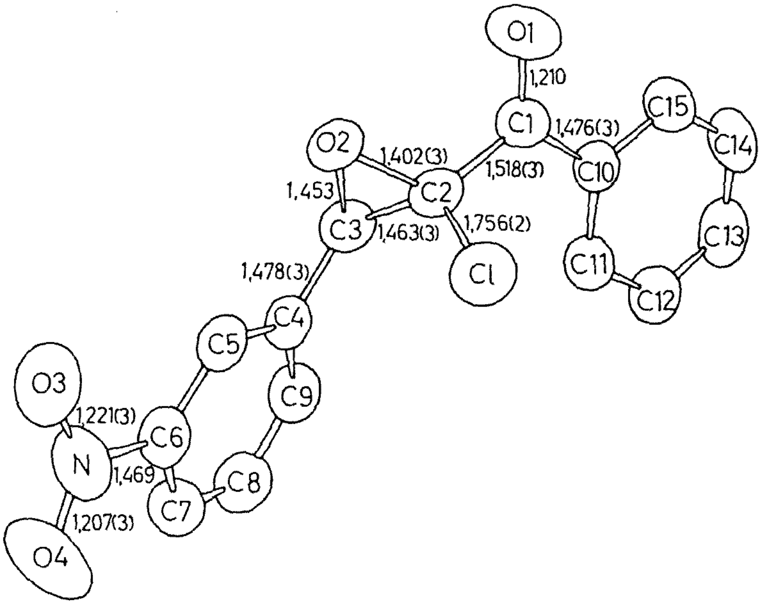


Fig. 1. Geometry and bond lengths for molecule I. H atoms are not shown.

TABLE 2. Valence Angles ω (deg)

Angle	ω	Angle	ω
$C_{(2)}O_{(2)}C_{(3)}$	61,6(1)	$O_{(2)}C_{(2)}C_{(1)}$	115,6(2)
$O_{(1)}C_{(1)}C_{(2)}$	118,0(2)	$O_{(2)}C_{(2)}C_{(3)}$	60,9(1)
$O_{(1)}C_{(1)}C_{(10)}$	123,4(2)	$C_{(1)}C_{(2)}C_{(3)}$	124,0(2)
$C_{(2)}C_{(1)}C_{(10)}$	118,5(2)	$O_{(2)}C_{(3)}C_{(3)}$	57,5(1)
$ClC_{(2)}O_{(2)}$	115,5(2)	$O_{(2)}C_{(3)}C_{(4)}$	117,9(2)
$ClC_{(2)}C_{(1)}$	110,8(2)	$C_{(2)}C_{(3)}C_{(4)}$	124,5(2)
$ClC_{(2)}C_{(3)}$	120,4(2)		

The geometry of the benzoyl and m-nitrophenyl substituents was normal.

Short intermolecular contacts were observed for $C_{(3)}$ and $O_{(2)}'$ (3/2-x, y-1/2, 1/2-z): $C_{(3)}...O_{(2)}'$ 3.279(3) Å, $C_{(3)}-H_{(3)}$ 0.97(2) Å, $H_{(3)}...O_{(2)}'$ 2.43(2) A, $C_{(3)}-H...O_{(2)}'$ angle 146(1) deg. These distances satisfy the hydrogen bond criteria.

EXPERIMENTAL

Crystals of compound I, $C_{15}H_{10}NO_4Cl$, mp 117-118.5°C, monoclinic. At 20°C a = 10.564(2), b = 8.170(2), c = 15.909(4) Å, β = 91.04(2) deg, Z = 4, d_{calc} = 1.47 g/cm^3, space group $P2_1/n$.

Nuclear parameters and the intensity of 3092 reflections, 1511 with $F^2 \geq 3\sigma$ were measured on an automatic four-circle diffractometer with ENERAF-NONIUS CAD-4 K-geometry (λMoKα, graphite monochromator, ω(5/3 θ)-scanning, $\theta \leq 27$ deg). The structure was interpreted by direct method using the NULTAN program and checked first in isotropic, then anisotropic approximation. All the hydrogen atoms were identified from a differential series and checked isotropically in conclusive cycles. Final divergence factor values R = 0.0315, R_w = 0.0451 from 1511 reflections with $F^2 \geq 3\sigma$. All computations were performed on a PDP-11/23 computer using the SDP programs.

Atomic coordinates are shown in Table 1 and molecular geometry and bond lengths in Figure 1. Valence angles are given in Table 2.

REFERENCES

1. V. A. Mamedov, V. L. Polushina, F. F. Mertsalova, and I. A. Nuretdinov, Izv. Akad. Nauk. Ser. Khim., No. 1, 204 (1992).
2. S. Tsuboi, H. Furutani, and A. Takeda, Synthesis, No. 3, 292 (1987).
3. P. Catsoulacos and Ch. Camoutsis, J. Heterocycl. Chem., **18**, 1485 (1981).
4. P. Catsoulacos and D. Kallias, J. Heterocycl. Chem., **16**, 763 (1979).
5. J. Gasteiger and Ch. Herzig, Tetrahedron Lett., **21**, 2687 (1980).
6. F. H. Allen, O. Kennard, and D. G. Watson, J. Chem. Soc. Perkin Trans. II, No. 12, (1987).