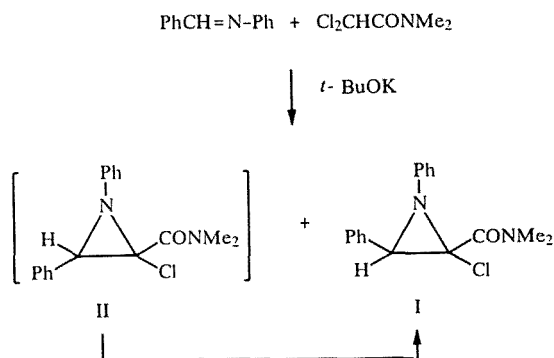# STRUCTURE OF THE CONDENSATION PRODUCT OF BENZALANILINE WITH N,N-DIMETHYLAMIDE OF DICHLOROACETIC ACID UNDER DARZENS REACTION CONDITIONS

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Condensation of benzalaniline with N,N-dimethylamide of dichloroacetic acid under Darzens reaction conditions was used to obtain r-1, t-3-diphenyl-c-2-chloro-2-(N,N-dimethylcarbamoyl)aziridine. The structure was established by x-ray diffraction analysis. Stabilization of the position of the substituents at the atoms of the aziridine ring by the hyperconjugation interaction of the unshared electron pair of the nitrogen atom with the antibonding orbital of the C−Cl bond is discussed.

The Darzens condensation is successfully used in the synthesis of glycide esters [1], α-halo epoxides [2], α-halo ketones [3], α,α-dihalohydrins [4], etc. Use of this reaction in the synthesis of aziridines by the reaction of α-halo carbanions with imines is limited to the work of Deyrup [5], who was able to isolate the cis and trans isomers of substituted aziridines in low yields, and to the work of Wartski [6], who showed that for such reactions, the yields can be raised by using meta-chlorobenzylideneaniline. In the only work [7] dealing with the condensation of isopropyl dichloroacetate with various imines, it was found that regardless of the nature of the radical in the azomethine fragment, the same stereoisomer is always obtained.

To understand the nature of the formation of a single isomer in such reactions, we here studied the condensation of benzalaniline with N,N-dimethylamide of dichloroacetic acid in the presence of dry t-BuOK in 1,2-dimethoxyethane and THF.

In the PMR spectrum of the reaction mixture obtained in dimethoxyethane, in addition to the signals of the amide groups and phenyl substituents, there are singlet signals at 4.16 and 3.78 ppm of the protons of the aziridine ring from different stereoisomers. On standing or during recrystallization (i-PrOH), the signal at 4.16 ppm disappears. In the PMR spectrum of the reaction mixture obtained by condensation in THF, the signal of the aziridine ring proton at 4.16 ppm is absent. This can be
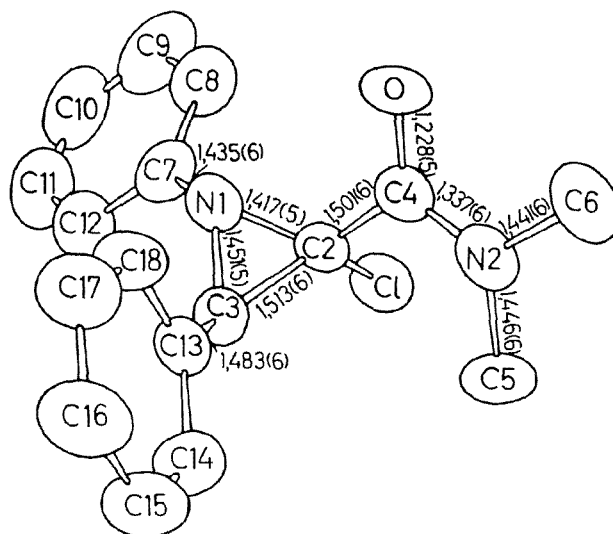

Fig. 1. Geometry of molecule I and bond lengths in it (d, Å). The hydrogen atoms are not shown. The bond lengths in the benzene rings are normal.

TABLE 1. Coordinates of Nonhydrogen Atoms of Structure I and Their Equivalent Isotropic Thermal Factors

Atom	x	y	z	B_{iso}^{eq}
Cl	0,0085(1)	0,2492(3)	0,45758(7)	5,01(3)
O	0,2170(4)	-0,1956(6)	0,4548(2)	5,6(1)
$N_{(1)}$	0,1172(4)	0,0711(8)	0,3669(2)	3,9(1)
$N_{(2)}$	0,2834(5)	0,1020(8)	0,5039(2)	5,1(1)
$C_{(2)}$	0,1352(5)	0,1449(9)	0,4235(2)	3,3(1)
$C_{(3)}$	0,1762(5)	0,2836(9)	0,3753(2)	3,6(1)
$C_{(4)}$	0,2160(5)	0,0044(9)	0,4622(2)	4,1(1)
$C_{(5)}$	0,879(8)	0,337(1)	0,5143(3)	6,6(2)
$C_{(6)}$	0,3521(7)	-0,030(1)	0,5453(3)	7,3(2)
$C_{(7)}$	-0,0005(5)	0,042(1)	0,3378(2)	4,4(1)
$C_{(8)}$	-0,0671(6)	-0,144(1)	0,3542(3)	5,9(2)
$C_{(9)}$	-0,1775(6)	-0,184(1)	0,3241(3)	8,5(2)
$C_{(10)}$	-0,2229(7)	-0,041(1)	0,2785(3)	7,6(2)
$C_{(11)}$	-0,1543(6)	0,134(1)	0,2652(3)	7,0(2)
$C_{(12)}$	-0,0415(6)	0,178(1)	0,2943(3)	5,1(1)
$C_{(13)}$	0,3051(5)	0,3001(9)	0,3604(2)	3,6(1)
$C_{(14)}$	0,3661(6)	0,3640(4)	1,0779(4)	5,0(1)
$C_{(15)}$	0,4850(6)	0,519(1)	0,3530(3)	5,5(2)
$C_{(16)}$	0,5416(5)	0,348(1)	0,3275(3)	5,3(2)
$C_{(17)}$	0,4808(5)	0,150(1)	0,3195(3)	5,0(1)
$C_{(18)}$	0,3630(5)	0,1282(9)	0,3361(3)	4,1(1)

explained by the fact that in THF, the transition of one isomer to the other takes place so fast that both isomers cannot be recorded at the same time by means of PMR spectroscopy.

In addition to the signal of the hydrogen atom, manifested at 3.78 ppm, the PMR spectrum contains singlet signals, at 2.63 and 7.20 ppm, from the dimethylamide and phenyl groups in the 3 position of the aziridine ring, respectively, and a multiplet signal at 6.76-7.13 ppm from the phenyl group at the nitrogen atom. The single hydrogen atom in the aziridine ring does not permit one to determine the structure of one of the two possible stereoisomers by means of the PMR spectrum.

TABLE 2. Valence Angles in Molecule I, ω (deg)

Angle	ω	Angle	ω
$C_{(2)}N_{(1)}C_{(3)}$	63,6(3)	$N_{(1)}C_{(2)}C_{(3)}$	59,3(3)
$C_{(2)}N_{(1}C_{(7)}$	124,2(4)	$N_{(1)}C_{(2)}C_{(4)}$	116,2(4)
$C_{(3)}N_{(1)}C_{(7)}$	123,6(4)	$C_{(3)}C_{(2)}C_{(4)}$	126,0(4)
$C_{(4)}N_2C_{(5)}$	125,1(4)	$N_{(1)}C_{(3)}C_{(2)}$	57,1(3)
$C_{(4)}N_{(2)}C_{(6)}$	120,0(4)	$N_{(1)}C_{(3)}C_{(13)}$	116,8(3)
$C_{(5)}N_{(2)}C_{(6)}$	114,8(5)	$C_{(2)}C_{(3)}C_{(13)}$	123,5(4)
$ClC_{(2)}N_{(1)}$	118,7(3)	$OC_{(4)}N_{(2)}$	122,3(5)
$ClC_{(2)}C_{(3)}$	115,3(3)	$OC_{(4)}C_{(2)}$	119,0(5)
$ClC_{(2)}C_{(4)}$	111,9(3)	$N_{(2)}C_{(4)}C_{(2)}$	118,6(4)

TABLE 3. Torsion Angles in Molecule I, τ (deg)

Angle	τ	Angle	τ
$C_{(3)}N_{(1)}C_{(2)}Cl$	104,10	$C_{(3)}N_{(1)}C_{(7)}C_{(8)}$	-152,9
$C_{(3)}N_{(1)}C_{(2)}C_{(4)}$	-118,0	$C_{(5)}N_{(2)}C_{(4)}O$	179,0
$C_{(7)}N_{(1)}C_{(2)}Cl$	-10,0	$C_{(5)}N_{(2)}C_{(4)}C_{(2)}$	-1,7
$C_{(7)}N_{(1)}C_{(2)}C_{(3)}$	-114,2	$C_{(6)}N_{(2)}C_{(4)}O$	-5,7
$C_{(7)}N_{(1)}C_{(2)}C_{(4)}$	127,8	$C_{(6)}N_{(2)}C_{(4)}C_{(2)}$	173,6
$C_{(2)}N_{(1)}C_{(3)}C_{(13)}$	114,2	$ClC_{(2)}C_{(4)}O$	108,0
$C_{(7)}N_{(1)}C_{(3)}C_{(2)}$	115,1	$ClC_{(2)}C_{(4)}N_{(2)}$	-71,2
$C_{(7)}N_{(1)}C_{(3)}C_{(13)}$	-130,8	$N_{(1)}C_{(2)}C_{(4)}O$	-32,6
$ClC_{(2)}C_{(3)}N_{(1)}$	-109,7	$N_{(1)}C_{(2)}C_{(4)}N_{(2)}$	148,0
$ClC_{(2)}C_{(3)}C_{(13)}$	147,8	$C_{(3)}C_{(2)}C_{(4)}O$	-102,4
$N_{(1)}C_{(2)}C_{(3)}C_{(13)}$	-102,5	$C_{(3)}C_{(2)}C_{(4)}N_{(2)}$	78,3
$C_{(4)}C_{(2)}C_{(3)}N_{(1)}$	101,7	$N_{(1)}C_{(3)}C_{(13)}C_{(14)}$	-178,9
$C_{(4)}C_{(2)}C_{(3)}C_{(13)}$	-0,8	$C_{(2)}C_{(3)}C_{(13)}C_{(14)}$	-112,2
$C_{(2)}N_{(1)}C_{(7)}C_{(8)}$	-74,0		

The method of x-ray diffraction analysis (XDA) was used to establish the structure of r-1, t-3-diphenyl-c-2-chloro-2,N,N-dimethylcarbamoyl)aziridine (see Fig. 1) for compound I. Thus, the aryl substituents at the $N_{(1)}$ and $C_{(3)}$ atoms of the aziridine ring are in the trans position to the plane of the three-membered ring. The dimethylamide group at the $C_{(2)}$ atom is in the cis position to the phenyl substituent at the $C_{(3)}$ atom. These substituents are positioned in such a way as to reduce the steric interactions between them. Nevertheless, the repulsion of these substituents is manifested in a appreciable increase of the valence angles $C_{(3)}C_{(2)}C_{(4)}$ [126.0(4)°] and $C_{(2)}C_{(3)}C_{(13)}$ [123.5(4)°]. In the aziridine ring, an appreciable difference of the bond lengths $N-C$ [1.417(5) and 1.451(5) Å] is observed, the shorter bond being the one with the disubstituted carbon atom $C_{(2)}$. These differences may be due to the $n-\sigma^*$ interaction of the unshared electron pair of the nitrogen atom $N_{(1)}$ with the antibonding orbital of the $C-Cl$ bond. In the planar dimethylamide group, conjugation of the unshared electron pair of the nitrogen atom with the π system of the $C=O$ bond is observed, manifested in an appreciable shortening of the $N_{(2)}-C_{(4)}$ bond to 1.337(6) Å and a lengthening of the $C_{(4)}=O$ bond [1.228(5) Å].

Thus it may be assumed that the reaction of N,N-dimethylamide of dichloroacetic acid with benzalaniline takes place by analogy with the reactions of dihaloacetate anions with carbonyl compounds [7]. The great stability of structure I compared to structure II can apparently be explained by the hyperconjugational $n-\sigma^*$ interaction of the unshared electron pair of the $N_{(1)}$ atom with the antibonding orbital of the $C-Cl$ bond, this interaction taking place in structure I but not in structure II.

EXPERIMENTAL

X-Ray Diffraction Analysis. Crystals of compound I, $C_{17}H_{17}ClN_2O$, monoclinic; at 20°C, $a = 10.968(4)$, $b = 6.073(3)$, $c = 23.753(9)$ Å, $\beta = 93.71(3)°$, $d_{calc} = 1.27$ g/cm^3, $Z = 4$, space group $P2_1/c$. The cell parameters and intensities of 1103 independent reflections with $F^2 \geq 3\sigma$ were measured with an ENRAFNONIUS CAD-4 automatic four-circle

diffractometer (λMoKα, graphite monochromator, $\omega/2\theta$ scanning, $\theta \geq 25°$). The structure was solved by the direct method using the MULTAN program and was refined anisotropically. All the hydrogen atoms were located from a difference Fourier map, and their contribution to the structure factors was taken into account in the final cycles of the refinement with fixed positional and isotropic thermal parameters ($B_{iso} = 4$ Å^2). The final values of the agreement factors were $R = 0.056$, $R_W = 0.078$. All the calculations were carried out with a PDP 11/23 computer using programs of the SDP system.

The coordinates of the nonhydrogen atoms of the structure are listed in Table 1; the geometry of the molecule and the bond lengths in it are shown in Fig. 1, and the valence and torsion angles are listed in Tables 2 and 3, respectively.

The IR spectra were recorded with a UR-20 spectrometer in Vaseline oil, and the PMR spectra were recorded with a Varian T-60 instrument, with TMS as the internal standard.

The data of the elemental analysis for C, H, N, Cl correspond to the calculated data.

Reaction of Benzalaniline with N,N-Dimethylamide of Dichloroacetic Acid. To a mixture of powdered t-BuOK [prepared by evaporating at 100°C and 12 Torr a solution of 2.2 g (0.056 g-atom) of K in 50 ml of t-BuOH] and 5.3 g (0.29 mole) of benzalaniline in 200 ml of freshly distilled dimethoxyethane is added 8.2 g (0.052 mole) of dimethylamide of dichloroacetic acid in a stream of argon at $-40°C$ for 1 h. The reaction mixture is heated to 20°C and stirred for another 1.5 h at this temperature. Dimethoxyethane is driven off in a vacuum to dryness. The residue is treated with saturated NaCl solution. The extraction is carried out with ether (3 $\times$ 50 ml), and MgSO$_4$ is used for drying. The PMR spectrum of the raw substance after the ether (CD$_3$CN) has been driven off is as follows: 2.63 (6H, s, N(CH$_3$)$_2$; 2.66 (3H, s, NCH$_3$), 3.08 (3H, s, NCH$_3$); 3.78 (1H, s, CH); 4.16 (1H, s, CH); 6.76-7.86 ppm (signals from phenyl groups). After recrystallization from i-PrOH, 5.4 g (62%) of compound I is obtained in the form of wet crystals, mp 131-133°C. IR spectrum: 3060, 3045, 1665, 1600, 1495, 1465, 1400, 1330, 1270, 835, 780, 705 cm^{-1}. PMR spectrum (CD$_3$CN): 2.63 (6H, s, N(CH$_3$)$_2$); 3.78 (1H, s, CH); 6.76-7.13 (5H, m, N$-$C$_6$H$_5$); 7.20 ppm (5H, s, C$_6$H$_5$).

The same reaction was carried out in THF under similar conditions.

REFERENCES

1. General Organic Chemistry [Russian translation], Vol. 2, Khimiya, Moscow (1982), p. 728.
2. V. A. Mamedov and I. A. Nuretdinov, Izv. Akad. Nauk SSSR, Ser. Khim., No. 9, 2159 (1992).
3. V. A. Mamedov, V. G. Malaev, F. G. Sibgatullina, I. A. Nuretdinov, and Yu. P. Kitaev, Izv. Akad. Nauk SSSR, Ser. Khim., No. 2, 438 (1992).
4. V. A. Mamedov, V. N. Valeeva, L. A. Antokhina, and I. A. Nuretdinov, Izv. Akad. Nauk SSSR, Ser. Khim., No. 8, 1870 (1992).
5. I. A. Deyrup, J. Org. Chem., **34**, 2724 (1969).
6. L. Wartski, J. Chem. Soc. Chem. Commun., No. 17, 602 (1977).
7. Ph. Coutrot and A. El Gadi, J. Organomet. Chem., No. 280, C11 (1985).
8. R. N. McDonald and P. A. Schwab, J. Org. Chem., **29**, 2459 (1964).