# SYNTHESIS AND STRUCTURE OF O-(ARYLCARBAMOYL)BUTYRHYDROXIMOYL CHLORIDES

V. B. Sokolov, A. N. Chekhlov,
T. A. Epishina, and I. V. Martynov

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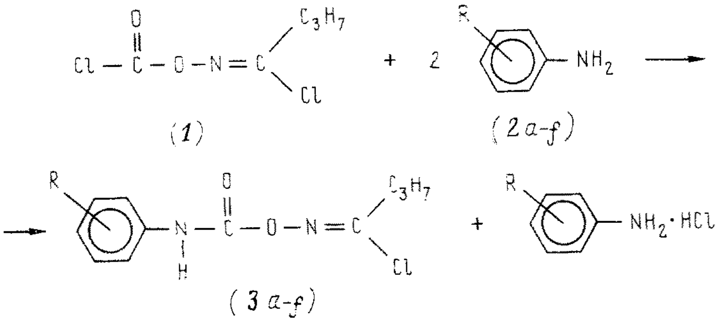
The O-(arylcarbamoyl)butyrhydroximoyl chlorides were synthesized, and the x-ray structural analysis (XSA) of one of them – O-(o-tolylcarbamoyl)butyrhydroximoyl chloride – was performed. It was established from the data of the XSA and the PMR spectra that all synthesized compounds are the Z isomers.

Keywords: O-(arylcarbamoyl)butyrhydroximoyl chlorides, synthesis, molecular structure, (Z, E) isomerism, PMR spectra, x-ray structure analysis.

The O-substituted acylhydroximoyl chlorides can be regarded as promising biologically active substances [1, 2], exhibiting pesticidal properties in particular [3]. In the present work, the synthesis of a new series of compounds of such a type is described. We showed that the interaction of O-(chloroformyl)butyrhydroximoyl chloride (1) with aniline (2a) or the substituted anilines (2b-f) results in the formation of the corresponding O-(arylcarbamoyl)butyrhydroximoyl chlorides (3a-f) with the yield of 44-79%



R = H (a), o-$CH_3$ (b), m-$CH_3$ (c), p-$CH_3$ (d), p-Br (e), 3,4-$Cl_2$ (f).

The compounds (3a-f) are colorless or colored crystalline substances, the composition and structure of which were confirmed by the data of the elemental analysis and the PMR spectra (Tables 1 and 2). The structure of one of them – O-(o-tolylcarbamoyl)butyrhydroximoyl chloride (3b) – was studied in detail by us using the method of x-ray structural analysis (XSA), whereby it was established unambiguously that the compound (3b) is the Z isomer. Since the PMR spectra of the compounds (3a-f) did not reveal the splitting off of the signals by analogy to that found for the initial compound (1), it is evident that the compounds (3a-f) are obtained only in the form of one isomer (Z or E). From the data of the XSA of the compound (3b) and the analysis of the PMR spectra of the compounds (1) and (3a-f) (Table 2), it can be concluded that all of the molecules of (3a-f) have the same configuration, i.e., they are the Z isomers, and the initial compound (1) is the mixture of the Z and E isomers in the ratio of 7.5:1.

The structure of the molecule (3b) found as the result of the XSA is shown in Fig. 1. The main bond lengths and the bond and torsion angles are given in Table 3. It can be seen that the molecule (3b) has the Z configuration in relation to the $N^1{=}C^1$ double bond and the trans conformation in relation to the $O^1{-}N^1$ single bond. The analogous Z configuration

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TABLE 1. Yield, Melting Points, and the Results of the Elemental Analysis of the Compounds (3a-f)

| Compound | Yield, % | mp, °C | Empirical formula | Found/Calculated, % | | |
|---|---|---|---|---|---|---|
| | | | | C | H | N |
| **3a** | 50.7 | 83–84 | $C_{11}H_{13}ClN_2O_2$ | 54.67/54.89 | 5.26/5.44 | 12.29/11.64 |
| **3b** | 71.4 | 61–63 | $C_{12}H_{15}ClN_2O_2$ | 56.63/56.59 | 6.09/5.94 | 11.65/11.00 |
| **3c** | 43.7 | 99–100 | $C_{12}H_{15}ClN_2O_2$ | 55.90/56.59 | 5.82/5.94 | 11.97/11.00 |
| **3d** | 79.1 | 85–87 | $C_{12}H_{15}ClN_2O_2$ | 56.36/56.59 | 5.99/5.94 | 11.66/11.00 |
| **3e** | 71.1 | 81–83 | $C_{11}H_{12}BrClN_2O_2$ | 41.30/41.34 | 4.29/3.78 | 8.72/8.77 |
| **3f** | 48.7 | 129–130 | $C_{11}H_{11}Cl_3N_2O_2$ | 42.12/42.68 | 3.39/3.58 | 8.73/9.05 |

TABLE 2. Parameters of the PMR Spectra of the Compounds (1) and (3a-f)

| Compound | δ, ppm |
|---|---|
| **1** | 0.99 and 1.03 t ($CH_3$, ratio of intensities 7.5 : 1), 1.75 m and 1.76 ($CH_2$, ratio 1 : 7.5), 2.65 m and 2.79 m ($\bar{C}H_2$, ratio 7.5 : 1) |
| 3a | 0.98 t ($CH_3$), 1.72 m ($CH_2$), 2.64 t ($CH_2$), 7.1–7.62 m ($C_6H_5$), 9.18 s (NH) |
| **3b** | 0.98 t ($CH_3$), 1.74 m ($CH_2$), 2.30 s ($CH_3$), 2.64 t ($CH_2$), 7.1–7.62 m ($C_6H_4$), 9.1 s (NH) |
| **3c** | 1.00 t ($CH_3$), 1.75 m ($CH_2$), 2.34 s ($CH_3$), 2.64 t ($CH_2$), 6.92–7.42 m ($C_6H_4$), 9.1 s (NH) |
| **3d** | 0.98 t ($CH_3$), 1.75 m ($CH_2$), 2.30 s ($CH_3$), 2.65 t ($CH_2$), 7.15–7.48 m ($C_6H_4$), 9.13 s (NH) |
| 3e | 0.99 t ($CH_3$), 1.72 m ($CH_2$), 2.62 t ($CH_2$), 7.41–7.68 m ($C_6H_4$), 9.12 s (NH) |
| 3f | 0.98 t ($CH_3$), 1.76 m ($CH_2$), 2.65 t ($CH_2$), 7.56–7.92 m ($C_6H_3$), 9.1 s (NH) |

and the trans conformation are possessed by the previously studied hydroximoyl chlorides: $HON{=}C(Cl)C_6H_4NO_2$-p (4) [4], $CH_3OH{=}C(Cl)C_6H_4NO_2$-p (5) [5], $Ph_2P(O)ON{=}C(Cl)Pr$-i (6) [6], $H_2NC(O)ON{=}C(Cl)CH_3$ (7) [7], and $HON{=}C(Cl)CONH_2$ (8) [8]. As far as is known to the authors, only one structure – $HON{=}C(Cl)CH{=}NOH$ (9) [9] – with the E configuration of the O–N=C–Cl fragment has been studied.

In the oxime fragment of the molecule (3b), the lengths of the $O^1$–$N^1$ and $N^1{=}C^1$ bonds and the $O^1N^1C^1$ bond angle have values intermediate between those found in the structure (6) [1.420(5) Å, 1.248(6) Å, and 113.6(4)°] [6] and the structure (7) [1.404(2) Å, 1.256(2) Å, and 111.8(1)°] [7]. Thereby, the $O^1$–$N^1$ bond in (3b) is close in length, and the $N^1{=}C^1$ bond is somewhat shortened, in relation to the average lengths for oxime fragments of 1.416(6) Å for O–N and 1.281(13) Å for N=C [10]. The length of the $O^1$–$C^5$ and $O^2{=}C^5$ bonds in (3b) agree with the mean statistical values of 1.362(18) Å and 1.190(14) Å for the ester fragments $C^*$–C(=O)–O–C=C [10], and the $N^2$–$C^5$ bond in (3b) agrees in its length with the mean statistical value of 1.334(11) Å in the amide fragments $C^*$–NH–C=O [10]. The $N^2$ amide nitrogen atom in (3b) has the usual trigonal planar hybridization. The length of the $N^2$–$C^6$ bond in (3b) occurs in the range of values 1.392(3)-1.425(3) Å [11], characteristic of different derivatives of acetanilide. According to [11], this length hardly correlates with the angle of the turning of the Ph ring in relation to the plane of the adjoining amide group. In the molecule of (3b), the length of the $C^1$–$C^2$ bond almost agrees with the mean length of the $C_{sp^2}$-$C_{sp^3}$ bond which equals 1.507(15) Å [10], and the lengths of the Cl–$C^1$, $C^3$–$C^4$, and $C^7$–$C^{12}$ bonds are somewhat reduced in relation to the corresponding mean lengths: Cl–$C_{sp^2}$ = 1.734(19) Å, $C_{sp^3}$–$C_{sp^3}$ = 1.530(15) Å, and $CH_3$–$C_{ar}$ = 1.506(11) Å [10]; this is probably due to the effect of increased thermal vibrations of the terminal atoms of Cl,

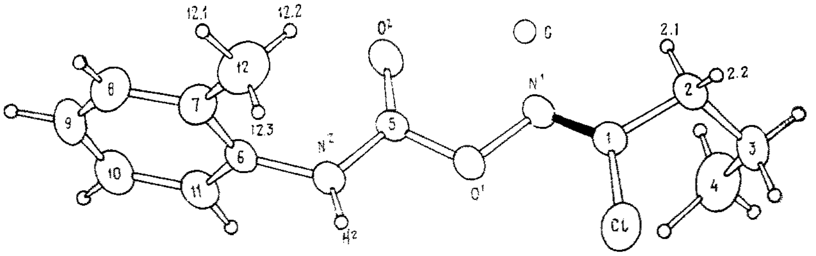

Fig. 1. The structure of the molecule (3b) according to the data of XSA. The non-hydrogen atoms are represented with probabilities of 30% by ellipsoids of thermal vibrations.

TABLE 3. Main Bond Lengths d (Å), and Bond Angles φ and Torsion Angles τ (deg) in the Molecule of (3b)

| Bond | d | Angle | φ | Angle | τ |
|---|---|---|---|---|---|
| $Cl-C^1$ | 1.714(2) | $N^1O^1C^5$ | 110.8(1) | $ClC^1N^1O^1$ | −0.3 |
| $O^1-N^1$ | 1.410(2) | $O^1N^1C^1$ | 112.9(1) | $ClC^1C^2C^3$ | 62.5 |
| $O^1-C^5$ | 1.366(2) | $C^5N^2C^6$ | 122.1(1) | $C^1N^1O^1C^5$ | 173.3 |
| $O^2-C^5$ | 1.192(2) | $ClC^1N^1$ | 123.9(1) | $C^1C^2C^3C^4$ | 59.3 |
| $N^1-C^1$ | 1.251(2) | $ClC^1C^2$ | 116.5(1) | $N^1O^1C^5N^2$ | 177.6 |
| $N^2-C^5$ | 1.338(2) | $N^1C^1C^2$ | 119.6(2) | $N^1C^1C^2C^3$ | −117.5 |
| $N^2-C^6$ | 1.419(2) | $C^1C^2C^3$ | 113.0(2) | $O^1N^1C^1C^2$ | 179.7 |
| $C^1-C^2$ | 1.502(3) | $C^2C^3C^4$ | 114.1(2) | $O^1C^5N^2C^6$ | 178.0 |
| $C^2-C^3$ | 1.515(3) | $O^1C^5O^2$ | 124.4(1) | $O^2C^5O^1N^1$ | −1.9 |
| $C^3-C^4$ | 1.474(4) | $O^1C^5N^2$ | 108.9(1) | $O^2C^5N^2C^6$ | −2.4 |
| $C^6-C^7$ | 1.383(3) | $O^2C^5N^2$ | 126.8(2) | $C^5N^2C^6C^7$ | −85.7 |
| $C^7-C^{12}$ | 1.490(4) | $N^2C^6C^7$ | 119.8(2) | $C^5N^2C^6C^{11}$ | 96.3 |
| $H^2-N^2$ | 0.86(3) | $C^6C^7C^{12}$ | 120.4(2) | $N^2C^6C^7C^{12}$ | 2.8 |

$C^4$, and $C^{12}$. The mean length of the C⩦C bond in the Ph ring of (3b) is 1.375(3) Å; this is also a little shorter than the mean statistical value of 1.384(13) Å [10].

In the central fragment of the molecule (3b), the chain of atoms O=C–O–N=C–Cl has the S-type form as in the structure (7) [7]. In (3b), the almost planar [with the accuracy of ±0.015(2) Å] fragment of the $C^6$, $N^2$, $H^2$, $C^5$, $O^2$, and $O^1$ atoms forms the angle of 8.0° with the plane of the $O^1$, $N^1$, $C^1$, Cl, and $C^2$ atoms and the angle of 86.4° with the plane of the Ph ring. Since the plane of the ortho-substituted Ph ring is almost perpendicular to the plane of the amide group, there is no conjugation between their π systems in (3b). The terminal $C^1–C^2–C^3–C^4$ fragment of the molecule (3b) has the gauche conformation with the twisted orientation of the H atoms in relation to the $C^2–C^3$ and the $C^3–C^4$ single bonds. The $H^{2.1}$ and $H^{12.1}$ atoms of hydrogen have the shielded conformation in relation to $C^1–C^2$ and $C^7–C^{12}$ bonds (the torsion angles: $H^{2.1}C^2C^1N^1 = -6°$, and $H^{12.1}C^{12}C^7C^8 = 0°$).

In the crystal structure, the molecules of (3b) are joined along the c axis in infinite chains by intermolecular hydrogen bonds $N^2–H^2...O^2(i)$. The corresponding spacings are: $N^2...O^2(i) = 3.028(2)$ Å and $H^2...O^2(i) = 2.29(3)$ Å. The angle $N^2–H^2...O^2(i) = 144(2)°$. In the structure of (3b), there are also two more reduced intermolecular contacts having the participation of the H atoms: $H^2...H^1(i) = 2.48(2)$ Å and $H^{2.2}...O^2(ii) = 2.45(3)$ Å. The symmetrical transforms are: (i) X, $^1/_2 - Y$, $^1/_2 + Z$, and (ii) $1 - X$, $Y - {}^1/_2$, $^1/_2 - Z$.

## EXPERIMENTAL

The PMR spectra were taken on the "Bruker CXP-200" instrument using the solution in $CDCl_3$ relative to TMS.

O-(Chloroformyl)butyrhydroximoyl Chloride (1). This compound was obtained by the method of [7] on heating O-(trimethylsilyl)butyrhydroximoyl chloride [12] with phosgene. The yield of (1) was 73.7%; it had the bp 69-70°C (7 mm) and the $n_D^{20}$ 1.4616. For the PMR spectrum, compare Table 2.

O-(Phenylcarbamoyl)butyrhydroximoyl Chloride (3a). To the solution of 1.84 g (0.01 mole) of (1) in 100 ml of ether were added, at −15 to −10°C with stirring, 1.86 g (0.02

TABLE 4. Coordinates of the Atoms ($\times 10^4$, $\times 10^3$ for H) of the Structure (3b)

| Atom | X | Y | Z | Atom | X | Y | Z |
|---|---|---|---|---|---|---|---|
| Cl | 3102,3(6) | 335.1(6) | 4552,8(7) | $C^{12}$ | 8479(3) | 2438(3) | 7453(4) |
| $O^1$ | 4727(1) | 2002(1) | 4811(1) | $H^2$ | 562(2) | 283(2) | 691(2) |
| $O^2$ | 6061(1) | 3007(1) | 4083(1) | $H^{2.1}$ | 342(2) | 85(2) | 114(2) |
| $N^1$ | 4330(2) | 1612(1) | 3391(2) | $H^{2.2}$ | 332(2) | −42(2) | 195(3) |
| $N^2$ | 5953(2) | 3125(1) | 6334(2) | $H^{3.1}$ | 126(2) | 3(2) | 172(3) |
| $C^1$ | 3587(2) | 855(2) | 3215(2) | $H^{3.2}$ | 145(3) | 11(3) | 26(3) |
| $C^2$ | 3070(2) | 351(2) | 1758(2) | $H^{4.1}$ | 39(2) | 163(2) | 50(3) |
| $C^3$ | 1662(2) | 448(2) | 1118(3) | $H^{4.2}$ | 138(2) | 191(2) | 206(3) |
| $C^4$ | 1203(3) | 1543(3) | 928(4) | $H^{4.3}$ | 160(3) | 192(2) | 28(3) |
| $C^5$ | 5638(2) | 2747(2) | 4993(2) | $H^8$ | 979(2) | 418(2) | 847(3) |
| $C^6$ | 6907(2) | 3890(2) | 6862(2) | $H^9$ | 928(2) | 594(2) | 833(3) |
| $C^7$ | 8140(2) | 3574(2) | 7441(2) | $H^{10}$ | 722(2) | 646(2) | 737(3) |
| $C^8$ | 9022(2) | 4364(3) | 7997(3) | $H^{11}$ | 571(2) | 513(2) | 645(3) |
| $C^9$ | 8685(3) | 5402(2) | 7951(3) | $H^{12.1}$ | 942(3) | 234(3) | 792(3) |
| $C^{10}$ | 7467(3) | 5692(2) | 7367(3) | $H^{12.2}$ | 822(3) | 221(3) | 644(4) |
| $C^{11}$ | 6576(2) | 4940(2) | 6827(2) | $H^{12.3}$ | 819(3) | 207(3) | 808(4) |

mole) of aniline. The precipitated residue was filtered off. The filtrate was concentrated, and the residue was recrystallized from hexane. The yield of 1.22 g of the colorless crystals of (3a) was obtained.

Compounds (3b-f). These compounds were obtained analogously to (3a) from (1) and the corresponding substituted anilines (2b-f). The yield, mp, and the results of the elemental analysis of the compounds (3a-f) are presented in Table 1. The PMR spectra are presented in Table 2.

The XSA of the Compound (3b). The analysis was performed using the automatic diffraction system "Enraf-Nonius CAD4—LSI11/02—PDP11/23" ($MoK_\alpha$-radiation, graphite monochromator). The pale blue-green transparent crystals of (3b) are monoclinic: $C_{12}H_{15}ClN_2O_2$, M = 254.72; $a = 11.317(2)$, $b = 12.690(3)$, $c = 9.836(3)$ Å, $\beta = 109.07(2)°$, $V = 1335(1)$ Å$^3$, $Z = 4$, $d_{calc} = 1.267$ g/cm$^3$, $\mu(MoK_\alpha) = 2.76$ cm$^{-1}$, space group $P2_1/c$.

The intensities of 2615 reflections were measured in the quadrant of reverse field ($2\theta \le 50°$) by the method of $\omega/2\theta$-scanning. Of these, 1732 independent observed reflections with $I \ge 2\sigma(I)$ were utilized in concluding calculations. Absorption was not taken into account. The structure of (3b) was decoded by direct methods and specified by the complete-matrix method of least squares (MLS) using the anisotropic (isotropic for the H atoms) approximation and with consideration of the secondary extinction ($g = 7(2)\cdot 10^{-7}$). The initial positions of all the H atoms were determined from the difference Fourier synthesis. In the final cycle of the complete matrix specification for all 215 parameters being varied: $|\Delta|\sigma < 0.01$. The final coordinates of the atoms in the structure (3b) are presented in Table 4.

The final R-factors, calculated from the 1732 observed reflections, are as follows: $R = 0.048$ and $R_W = 0.068$. The quality factor of the "adjustment" was $S = 1.54$. In the final difference synthesis of Fourier, $\Delta\rho < 0.37$ eÅ$^{-3}$. The weight scheme for the reflections in the MLS, the f-criteria utilized, and the anomalous dispersion corrections to them ($\Delta f'$ and $\Delta f''$) are shown, e.g., in [13]. All calculations were carried out on a PDP11/23 mini-computer using the scheme of the SDP-PLUS programs of the firm "Enraf-Nonius."

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# X-RAY INVESTIGATION OF bis(2-DIMETHYLAMINOMETHYLCYCLOPENTADIENYLMANGANESETRICARBONYL)MERCURY: THE REACTION PATH OF AMINE MERCURATION

L. G. Kuz'mina

UDC 548.737

The structure of the centrosymmetric complex $\{[(CO)_3MnC_5H_3(CH_2NMe_2)]_2Hg\}$ (1), obtained in the reaction of $\{[C_5H_3(CH_2NMe_2)Mn(CO)_3]Li\}$ with mercuric chloride, was determined by a diffractometric experiment (diffractometer, $MoK_\alpha$ radiation, $R = 0.027$, in 2311 reflections). In the centrosymmetric molecule of compound (1) the Hg—C bond length [2.042(6) Å] is short compared with the mean value of 2.07 Å as a result of the contribution from π conjugation in the $C_5H_4$‒‒‒Hg‒‒‒$C_5H_4$ system. The orientation of the dimethylaminomethyl substituent at position 2 of the cyclopentadienyl is favorable for the formation of a weak intramolecular secondary Hg...N bond [2.933(5) Å], which closes a five-membered chelate ring. Investigation of the geometry features of the structurally related molecules of the Q—HgX type [$Q = L_nM(\eta{-}C_5H_3{-}CH_2NMe_2)$, X = Cl or Q; $L_nM$ = CpFe, $(CO)_3Mn$] makes it possible to propose a possible amine mercuration path for the investigated model molecules and to predict a dimeric structure of a molecular salt-type complex for the second unstable asymmetric product from the above-mentioned reaction.

Keywords: X-ray crystallographic investigation, bis(2-methylaminomethylcyclopentadienylmanganesetricarbonyl)mercury, secondary bond, mapping of the reaction path.

In the present work we undertook an x-ray crystallographic investigation of the symmetrical complex $[(CO)_3MnC_5H_3(CH_2NMe_2)]Hg$ (1), which belongs to the following series of previously investigated complexes (2) [1], (3) [2], and (4) [3]:

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