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An unexpected reaction of 2-(cyclopent-2-enyl)aniline hydrochloride with dimethyldioxirane

D. I. D'yachenko,* A. G. Mustafin, V. V. Shereshovets, N. N. Kabal'nova, V. P. Kazakov, I. B. Abdrakhmanov, and G. A. Tolstikov

Institute of Organic Chemistry, Ufa Research Center of the Russian Academy of Sciences, 71 prosp. Oktyabrya, 450054 Ufa, Russian Federation.
Fax: +7 (347 2) 35 6066

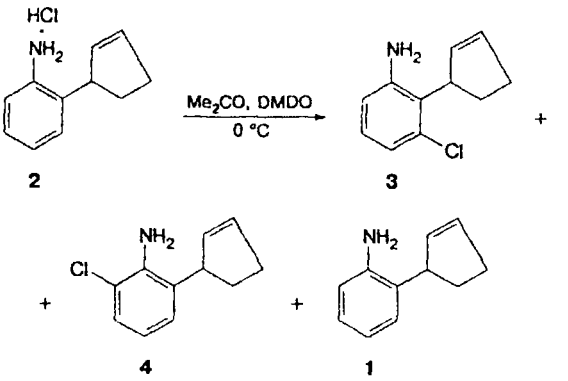
An unusual direction of the reaction of 2-(cyclopent-2-enyl)aniline hydrochloride with dimethyldioxirane was found: the formation of two isomeric products, *viz.*, 3- and 6-chloro-2-(cyclopent-2-enyl)anilines, was observed.

Key words: 2-(cyclopent-2-enyl)aniline hydrochloride, dimethyldioxirane, 3-chloro-2-(cyclopent-2-enyl)aniline, 6-chloro-2-(cyclopent-2-enyl)aniline.

It has recently been shown that dimethyldioxirane (DMDO) can be used for selective epoxidation of primary and secondary *N*-alkenylamines,[1–3] which is achieved after preliminary protection of the amino group as an ammonium salt or a complex with BF_3. Hydrochlorides of aliphatic amines are oxidized by DMDO to nitro compounds.[4,5]

We studied the possibility of epoxidation of *ortho*-alkenylarylamines, in particular, 2-(cyclopent-2-enyl)aniline (**1**), with the aim of further using this methodology as the key stage in the synthesis of hardly accessible nitrogen-containing heterocycles. The amino group was protected by converting amine **1** into hydrochloride **2**, which is well soluble in organic solvents. When we studied the reaction of salt **2** with DMDO, we found that it occurs in an unusual direction leading to the formation of 3-chloro-2-(cyclopent-2-enyl)aniline (**3**) and 6-chloro-2-(cyclopent-2-enyl)aniline (**4**) in 21 and 27% yields, respectively. The structures of the compounds obtained were established by ^{1}H NMR and IR spectroscopy and mass spectrometry and confirmed by the data of elemental analysis.

For example, the mass spectra of compounds **3** and **4** indicate that each of them contains one chlorine atom in the molecule. The identity of the high-field portions of the ^{1}H NMR spectra of compounds **1**, **3**, and **4** due to the protons of the cyclopentenyl fragment[6] is evidence for the localization of the chlorine atom in the aromatic ring of molecules **3** and **4**. The absence of singlet signals in the region of aromatic protons (at δ 6.5—7.5) and the appearance of a doublet of doublets in the same region indicate that the chlorine atom is located in positions 3 or 6 of the aromatic ring. For isomers **3** and **4**, the signals confirming this position were assigned by the double resonance method. Irradiation of a doublet of doublets at δ 7.00 results in the appearance of singlets at δ 6.66 and 6.86 in the ^{1}H NMR spectrum of compound



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3. Irradiation of a doublet of doublets at δ 6.85 results in the appearance of singlets at δ 7.07 and 7.09 in the ^{1}H NMR spectrum of compound **4**.

It is noteworthy that free arylamine **1** (48%) is found in the reaction mixture. This probably accounts for the unique direction of the reaction studied, whose nature should be further investigated.

Experimental

IR spectra were recorded on a UR-20 instrument (film). ^{1}H NMR spectra were recorded on a Bruker AM-300 instrument (300.13 MHz) using $CDCl_3$ as the solvent and $SiMe_4$ as the internal standard. Mass spectra (EI, 70 eV) were obtained on a Hewlett Packard 5890A-5972A instrument. Chromatography was performed on columns filled silica gel LS 40/100 μm and Silpearl. TLC control was performed on Silufol UV-254 and UV-254/366 plates in the CH_2Cl_2—MeOH (95 : 5) system.

Dimethyldioxirane[7,8] and 2-(cyclopent-2-enyl)aniline hydrochloride (**2**)[6,9] were obtained by the described procedures.

A solution of DMDO (0.01 mol) in acetone (30 mL) was added with stirring at 0 °C to a solution of compound **2** (1.95 g, 0.01 mol) in acetone (10 mL). The solvent was evaporated *in vacuo*, and the residue was subjected to column chromatography to obtain compound **3** (0.41 g, 21%) and compound **4** (0.52 g, 27%).

3-Chloro-2-(cyclopent-2-enyl)aniline (3). Oil, R_f 0.81. IR, ν/cm^{-1}: 3460; 2960; 1620; 760. ^{1}H NMR ($CDCl_3$), δ: 1.75 (m, 2 H, CH_2); 2.35—2.60 (m, 2 H, CH_2); 3.48 (s, 2 H, NH_2); 4.00 (m, 1 H, CH); 5.8—6.0 (m, 2 H, CH=CH); 6.66 (d, 1 H, HC(6), J = 6.41 Hz); 6.86 (d, 1 H, HC(4), J = 7.71 Hz); 7.00 (dd, 1 H, HC(5), J_1 = 6.41 Hz, J_2 = 7.71 Hz). MS, *m/z*: 193 $[M]^+$. Calculated (%): C, 68.21; H, 6.25; N, 7.23; Cl, 18.30. $C_{11}H_{12}ClN$. Found (%): C, 67.76; H, 7.00; N, 7.22; Cl, 18.10.

6-Chloro-2-(cyclopent-2-enyl)aniline (4). Oil, R_f 0.63. IR, ν/cm^{-1}: 3460; 2940; 1615; 760. ^{1}H NMR ($CDCl_3$), δ: 1.80 (m, 2 H, CH_2); 2.35—2.60 (m, 2 H, CH_2); 3.42 (s, 2 H, NH_2); 4.05 (m, H, CH); 5.8—6.0 (m, 2 H, CH=CH); 6.85 (dd, 1 H, HC(4), J_1 = 6.34 Hz, J_2 = 7.58 Hz); 7.07 (d, 1 H, HC(3), J = 6.34 Hz); 7.09 (d, 1 H, HC(5), J = 7.58 Hz). MS, *m/z*: 193 $[M]^+$. Calculated (%): C, 68.21; H, 6.25; N, 7.23; Cl, 18.30. $C_{11}H_{12}ClN$. Found (%): C, 67.70; H, 7.08; N, 7.05; Cl, 18.13.

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Synthesis of volatile alkoxygallium hydrides and study of their thermostability

V. V. Gavrilenko and L. A. Chekulaeva*

A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences,
28 ul. Vavilova, 117813 Moscow, Russian Federation.
Fax: +7 (095) 135 5085

A method for the synthesis of alkoxygallium hydrides ($ROGaH_2$ and $(RO)_2GaH$, where R = Pr^i, Bu^t) was proposed. The method is based on the reaction of gallane GaH_3 with one or two equivalents of the corresponding alcohol. Thermolysis of these compounds was studied by differential thermogravimetry.

Key words: mono- and dialkoxygallium hydrides, isopropoxygallium dihydride, di(isopropoxy)gallium hydride, *tert*-butoxygallium dihydride, di(*tert*-butoxy)gallium hydride, synthesis, thermolysis.

Aluminum and gallium alkoxides $M(OR)_3$ (M = Al, Ga)[1] find use in the production of ceramic materials, active oxides, and oxide films in microelectronics obtained by epitaxial technology from the gas phase. In

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