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3-(2-Chloropropyl)-2-oxa-3-azabicyclo[2.2.2]oct-5-ene and 2-oxa-3-azabicyclo[2.2.2]oct-5-ene hydrochloride have been prepared by cycloaddition of 2-chloro-2-nitrosopropane to 1,3-cyclohexadiene and their structure determined by nmr, using a ^1H nmr shift reagent.

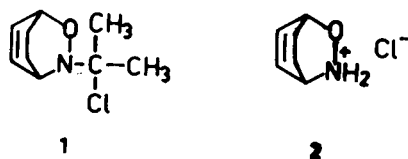
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Aromatic nitroso compounds readily form 1,4-cycloadducts with conjugated dienes (1,2). Aliphatic nitroso compounds do not form cycloadducts with conjugated dienes unless the α -carbon carries an electron-withdrawing substituent (3). Aliphatic chloro-nitroso compounds decompose easily and are reported to form unstable cycloadducts (2).

The reaction of 2-chloro-2-nitrosopropane with 1,3-butadiene (4) and of 1-chloro-1-nitrosocyclohexane with a variety of conjugated dienes have been studied earlier (5,6). In the course of our experiments 2-oxa-3-azabicyclo[2.2.2]oct-5-ene hydrochloride **2** was prepared by cycloaddition of 2-chloro-2-nitrosopropane and 1,3-cyclohexadiene in ether, followed by alcoholysis of the unstable addition product **1**.

This result confirms the mechanism of cycloaddition previously proposed for the Diels-Alder reaction of 1-chloro-1-nitrosocyclohexane with 1,3-cyclohexadiene. In this preparation of **2** alcoholysis, by the solvent ethanol, occurred "in situ" (6).

The melting point of our compound **2** was considerably higher than reported (6), but nmr, ir, ms and the elemental analyses showed that the structure was indeed **2**.



EXPERIMENTAL

General.

Melting points were determined on a Reichert apparatus and are uncorrected. A Perkin-Elmer 257 ir spectrometer was used for ir spectra. ^1H Nmr spectra were recorded on a Varian A-60 (compound **1**) and on a JEOL MH 100 spectrometer (compound **2**). The elemental analyses were carried out by the Department of Analytical Chemistry at the University of Lund, Sweden.

Starting Materials.

2-Chloro-2-nitrosopropane was obtained by chlorination of acetoxime with nitrosyl chloride in ether (7) and with chlorine in 10% sodium hydroxide solution (8).

Cyclohexa-1,3-diene was prepared by bromination of cyclohexene with

N-bromosuccinimide to give 3-bromocyclohexene (b.p. 61-68°/12 mm), followed by elimination of hydrogen bromide by means of quinoline at 140-180°, b.p. 79-81°/760 mm (9).

3-(2-Chloropropyl)-2-oxa-3-azabicyclo[2.2.2]oct-5-ene (**1**).

Cyclohexa-1,3-diene (2.69 g., 0.033 mole) was added at 0° (ice) to 2-chloro-2-nitrosopropane (3.05 g., 0.028 mole) in dry ether (20 ml.) with stirring. The reaction mixture was stirred for another hour (a crystalline precipitate began to appear within a 0.5 hour) and allowed to stand for 24 hours at 0°. The precipitate was collected and washed with cold dry ether, giving 5.65 g. (theoretical yield) of a crystalline, yellowish product. At room temperature the compound **1** changed to a brown oil and it was therefore stored on dry ice; $\text{C}_8\text{H}_{14}\text{ClNO}$ (187.667); nmr and ir spectra indicate the structure to be **1**; ir (potassium bromide): 1360 cm^{-1} , 1380 cm^{-1} ($\text{C}(\text{CH}_3)_2$), 780 cm^{-1} ($\text{C}-\text{Cl}$), 1450 cm^{-1} ($\text{CH}=\text{CH}$); nmr (deuteriochloroform): δ 1.27-2.58 (m, 4H, CH_2), 2.40 (s, 3H, CH_3), 2.60 (s, 3H, CH_3), 5.43-5.76 (m, 1H, CH sat.), 5.76-6.09 (m, 1H, CH sat.), 6.63-7.12 (m, 2H, CH unsat.).

2-Oxa-3-azabicyclo[2.2.2]oct-5-ene hydrochloride (**2**).

A solution of 1.0 g. of **1** in methanol (20 ml.) was refluxed with active carbon, filtered and the filtrate was treated with ether, precipitating 0.6 g. (76.8%) of white, glistening crystals, m.p. 164-168° dec., lit. value (6): 147-147.5°. A sample for analyses was recrystallized from methanol-ether and dried over calcium chloride in vacuum at 56°; nmr ($\text{DMSO}-d_6$): δ 1.20-1.60 (m, 2H, CH_2), 1.81-2.59 (m, 2H, CH_2), 4.42-4.61 (m, 1H, CH sat.), 4.88-5.09 (m, 1H, CH sat.), 6.61 (0, 1H, $\text{J}_{\text{CH}=\text{CH}} = 8.3$ Hz, $\text{J}_{\text{allyl}} = 5.9$ Hz, $\text{J}_{\text{CH}=\text{CH}} = 1.7$ Hz, CH unsat.), 6.86 (0, H, J = same for both vinyl protons, CH unsat.), 11.75 (s, 2H, NH_2^+).

Anal. Calcd. for $\text{C}_8\text{H}_{10}\text{ClNO}$: C, 48.82; H, 6.83; N, 9.49; Cl, 24.02. Found: C, 48.90; H, 6.81; N, 9.61; Cl, 24.00.

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