On the Reaction of 1-Chloro-1-nitrosocyclohexane with Butadiene-1,3

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Abstract

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On the Reaction of 1-Chloro-1-nitrosocyclohexane with Butadiene-1,3

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It was shown earlier (1,2) that 1-chloro-1-nitrosocyclohexane reacts in the presence of alcohol with butadiene-1,3 to form the hydrochloride of 3,6-dihydro-1,2-oxazine. It was to be assumed that the reaction of butadiene with chloronitrosocyclohexane proceeds according to a diene-synthesis scheme. However, the primary product of the diene synthesis, I, evidently immediately rearranges into the quaternary immonium salt II, which then undergoes alcoholysis to form the hydrochloride of 3,6-dihydro-1,2-oxazine III and the acetal of cyclohexanone IV.

$$\mathrm{CH_2{=}CH - CH{=}CH_2 + O{=}N - C(Cl)(cyclohexyl)}$$

$$\longrightarrow \mathrm{I} \longrightarrow \mathrm{II} \xrightarrow{\mathrm{C_2H_5OH}} \mathrm{III} + \mathrm{IV}$$

I II III IV

Consequently, in the reaction of butadiene with chloronitrosocyclohexane in the presence of alcohol, the hydrochloride of 3,6-dihydro-1,2-oxazine and the acetal of cyclohexanone should be formed. We carried out the reaction of chloronitrosocyclohexane with butadiene in benzene medium in the presence of absolute ethanol at room temperature. From the reaction mixture there were isolated, in 78% yield, the hydrochloride of 3,6-dihydro-1,2-oxazine III and, in 58% yield, diethyl acetal of cyclohexanone IV.

An attempt was then made to isolate the immonium salt II that is formed as an intermediate in this reaction.

We carried out the reaction of chloronitrosocyclohexane with butadiene at room temperature in toluene medium and in the absence of alcohol. Under these conditions an insoluble, thick resin formed in toluene; on triturating it with absolute ethanol, we were unable to obtain the hydrochloride of 3,6-dihydro-1,2-oxazine.

Consequently, the immonium salt II formed as an intermediate is evidently very unstable and rapidly resinifies.* Therefore we attempted

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* Quaternary immonium salts can be obtained by alkylation of Schiff bases (3,4), by C-alkylation of tertiary vinylamines (5,6,7), by C-protonation of tertiary

vinylamines ([8]), and by a number of other methods ([9]). Many immonium salts proved to be extremely unstable compounds and were isolated only in the form of complex salts (hexachlorostannates, hexachloroantimonates). Immonium salts are readily hydrolyzed with formation of salts of secondary amines and carbonyl compounds.

to isolate this unstable immonium salt by carrying out the reaction at a temperature of −18°. Under these conditions, an almost colorless, wax-like substance, insoluble in toluene, is formed, which rapidly resinifies when the temperature is raised to room temperature. If, however, this wax-like substance is washed with absolute toluene cooled to −20° and then treated with absolute ethanol likewise cooled to −20°, the hydrochloride of 3,6-dihydro-1,2-oxazine III is formed.

Thus, we succeeded in separating the reaction of chloronitrosocyclohexane with butadiene into two stages: 1) preparation of the extremely unstable immonium salt II; 2) alcoholysis of this salt with formation of the hydrochloride of 3,6-dihydro-1,2-oxazine III and cyclohexanone acetal IV.

The reaction of other diene hydrocarbons (2,3-dimethylbutadiene-1,3 ([1]), cyclohexadiene-1,3 ([1]), 1-phenylbutadiene-1,3 ([10]), 2-chlorobutadiene-1,3 ([11])) with 1-chloro-1-nitrosocyclohexane in the presence of alcohol, leading to the formation of hydrochlorides of the corresponding substituted derivatives of 3,6-dihydro-1,2-oxazine, undoubtedly also proceeds through the intermediate formation of quaternary immonium salts.

Experimental Part

Reaction of 1-chloro-1-nitrosocyclohexane with butadiene-1,3 in the presence of ethanol. A mixture of 74.5 g of chloronitrosocyclohexane (b.p. 62–63° at 22 mm), 200 ml of absolute benzene, 75 ml of absolute ethanol, and 100 g of butadiene was left in the dark at room temperature for 48 hr. The precipitate of the hydrochloride of 3,6-dihydro-1,2-oxazine III that formed was filtered off under vacuum and washed with absolute ether. This gave 48.0 g (78% of theory) of III, m.p. 150–151° (with decomposition) ([1, 12]).

The mother liquor was washed with a 5% solution of sodium carbonate and with water. The benzene was distilled off, and the residue was fractionated in vacuum. This gave 50.0 g (58% of theory) of the diethyl acetal of cyclohexanone with the following constants: b.p. 61–62° (7 mm), d_4^{20} 0.9181, n_D^{20} 1.4370 ([13–15]).

Preparation of the addition product of 1-chloro-1-nitrosocyclohexane with butadiene-1,3. Experiment 1. A mixture of 9 g of chloronitrosocyclohexane, 25 ml of absolute toluene, and 15 g of butadiene was sealed in an ampoule, and the ampoule was left in the dark at room temperature. After 12 hr the initially blue solution had acquired a light-brown color, and a thick brown resin had settled at the bottom of the ampoule. The solution was decanted from the resin, and the resin was washed with absolute toluene. On grinding the resin with absolute ethanol, it was not possible to obtain the hydrochloride of 3,6-dihydro-1,2-oxazine.

Experiment 2. A mixture, cooled to −15°, of 9 g of chloronitrosocyclohexane, 25 ml of absolute toluene, and 15 g of butadiene was sealed in an ampoule. The ampoule was kept in a refrigerator at −18° for 5 days. Already after several hours, an almost colorless wax-like substance began to precipitate from the blue solution, the amount of which gradually increased. After 5 days the reaction had not gone to completion—the solution was blue in color. The ampoule was opened, the solution was decanted from the precipitate, and the precipitate was washed in the ampoule with absolute toluene cooled to −20°. This gave 5.8 g of a wax-like addition product of chloronitrosocyclohexane with butadiene. The addition product was covered with toluene (10 ml) cooled to −20°, and the temperature was raised to 0° over the course of 1 hr. At −10° the substance began to soften noticeably, and at 0° it turned into a thick viscous oil, which began to resinify. After the temperature was raised to room temperature, the substance rapidly resinified. In another experiment, the addition product (5.8 g), washed with toluene, was covered with absolute ethanol (10 ml) cooled to −20°. Crystals of the hydrochloride soon began to form.

3,6-dihydro-1,2-oxazine, the amount of which increased rapidly. On the following day the crystals were filtered off and washed with absolute ether. This gave 2.1 g of hydrochloride III, which after recrystallization from absolute ethanol had m.p. 150-151° (with decomposition).

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