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Abstract

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CHEMISTRY

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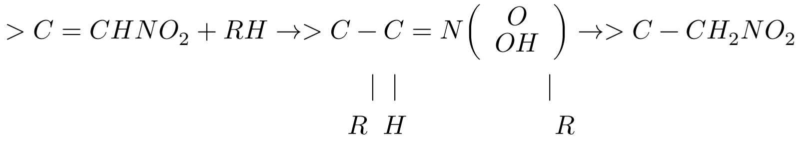
INTERACTION OF UNSATURATED NITRO COMPOUNDS WITH ORGANIC BASES

Nitroolefins in which the nitro group is attached to an unsaturated carbon atom contain a conjugated system of double bonds capable of adding substances containing a mobile hydrogen atom: alcohols, bisulfite, hydrocyanic acid, organic bases, etc. The reaction proceeds according to the scheme



$$>C=CHNO_2+RH\rightarrow>\underset{R}{\underset{|}{C}}-\underset{H}{\underset{|}{C}}=N\left(\begin{matrix}O\\OH\end{matrix}\right)\rightarrow>\underset{R}{\underset{|}{C}}-CH_2NO_2$$

The interaction of unsaturated nitro compounds with organic bases was first observed by Posner (^{1}). Treating ω-nitrostyrene with an alcoholic solution of hydroxylamine, Posner obtained α-nitro-β-phenyl-β-hydroxylaminoethane—a crystalline substance readily soluble in dilute HCl and dilute NaOH. A detailed study of the reactions of ω-nitrostyrene with organic bases was carried out by Uorrol (^{2}), who established that nitrostyrene reacts with the following bases: aniline, n-toluidine, phenylhydrazine, diphenylhydrazine, β-naphthylhydrazine, n-tolylhydrazine, semicarbazide, thiosemicarbazide, and piperidine.

Wieland and Sakellarios (^{3}) were the first to obtain the product of addition of aniline to a lower nitroolefin—nitroethylene. Later, in the work of Hass and Rose (^{4}), data were presented on the addition of ammonia, diethylamine, and aniline to lower nitroolefins: nitroethylene, nitropropylene, and nitrobutylene. Several years ago, in connection with an investigation of the nitration reaction of cyclohexene, we were the first to obtain the product of addition of semicarbazide to an unsaturated nitro compound of the naphthene series—1-nitrocyclohexene (^{5}). For a more detailed study of the interaction of unsaturated nitro compounds of the naphthene and olefin series with organic bases, we investigated the reactions of 1-nitrocyclohexene with the following organic bases: phenylhydrazine, urea, thiosemicarbazide, hydroxylamine, aniline, and n-toluidine.

The investigation showed that aniline and hydroxylamine do not form crystalline derivatives upon interaction with 1-nitrocyclohexene. When 1-nitrocyclohexene was treated with phenylhydrazine, urea, thiosemicarbazide, and *n*-toluidine, new crystalline compounds not described in the literature were obtained: 2-nitrocyclohexylphenylhydrazine, 2-nitrocyclohexylurea, 2-nitrocyclohexylthiosemicarbazide, and 2-nitrocyclohexyl-*n*-toluidine.

When nitroisobutylene was treated with semicarbazide and phenylhydrazine, crystalline addition products were obtained: nitroisobutylsemicarbazide and nitroisobutylphenylhydrazine.

Experimental Part

As has already been reported in our earlier work (5), when 1-nitrocyclohexene is treated with an alcoholic solution of acetic acid semicarbazide, 2-nitrocyclohexylsemicarbazide is formed—a crystalline product of the addition of semicarbazide to 1-nitrocyclohexene. The yield of the semicarbazide derivative is 75% of theory.

In the present work it was shown that, by using an alcoholic solution of free semicarbazide instead of acetic acid semicarbazide, the yield of 2-nitrocyclohexylsemicarbazide can be increased to 89% of theory. The starting 1-nitrocyclohexene was synthesized by the method of Levy, Baldock, and Scaife (6). The constants of 1-nitrocyclohexene were as follows: b.p. 71.5° (3 mm), n_D^{20} 1.5051; d_4^{20} 1.1280; MR found 33.43 (calculated 32.85).

1-Nitrocyclohexylsemicarbazide. To 1.75 g of acetic acid semicarbazide was added a saturated aqueous solution of KOH (calculated for 0.9 g KOH). The liberated free semicarbazide was dissolved in methyl alcohol and filtered off from the KCl precipitate. The filtrate was added to 1 g of nitrocyclohexene. Mixing of the liquids was accompanied by heating. Immediately, a white finely crystalline precipitate began to separate, and within half an hour the entire mass crystallized. The crystals of 2-nitrocyclohexylsemicarbazide, filtered off the following day, were thoroughly washed with water and ethyl ether and dried in a desiccator over $CaCl_2$. The amount of precipitate was 1.4 g, corresponding to 89% of theory. 2-Nitrocyclohexylsemicarbazide melted with decomposition at 162–162.5°. After recrystallization from ethyl alcohol, m.p. 163°. Found N 28.15%; calculated 27.73%.

2-Nitrocyclohexylphenylhydrazine. A solution of 1.1 g of phenylhydrazine in 2 ml of ethyl alcohol was added to 0.63 g of 1-nitrocyclohexene. The liquid became orange, and rather strong heating was observed. After several minutes, yellow lustrous crystals began to separate. The next day, 0.85 g of precipitate was filtered off. After another day, a further 0.18 g of crystalline substance separated. After recrystallization from ethyl alcohol, the crystals melted at 115–115.5° to a yellow liquid. The preparation of 2-nitrocyclohexylphenylhydrazine purified by recrystallization is a finely crystalline powder with a faint yellow shade. On storage, the intensity of the color increases. Deepening of the color is accompanied by a lowering of the melting point. A preparation that had stood in the light for 2 months turned into a bright-yellow liquid. 2-Nitrocyclohexylphenylhydrazine is soluble in organic solvents and 10% H_2SO_4 and insoluble in aqueous alkali. Dissolution in 10% alcoholic NaOH is accompanied by the appearance of a yellow color, indicating the formation of the salt of the isoform.

When equimolecular amounts of an alcoholic solution of phenylhydrazine and 1-nitrocyclohexene are mixed, the yield of 2-nitrocyclohexylphenylhydrazine is 88% of theory.

Found %: C 61.23; H 7.35; N 18.03
Calculated %: C 61.25; H 7.28; N 17.86

Hydrochloride of 2-nitrocyclohexylphenylhydrazine. 0.1 g of 2-nitrocyclohexylphenylhydrazine was dissolved in several milliliters of ethyl ether. The liquid was cooled with ice water, and an ethereal solution of HCl was added to it. Immediately, a light amorphous precipitate began to separate. The precipitate was filtered off, washed several times with ether, and recrystallized from a mixture of CCl_4-C_2H_5OH. On heating, the precipitate gradually darkened and at 138–140° melted to a dark-red liquid.

Found %: Cl 12.84%
Calculated %: Cl 13.05%

2-Nitrocyclohexylthiosemicarbazide. 0.46 g of thiosemicarbazide was dissolved, with heating, in 15 ml of a mixture of water and ethyl alcohol (2 : 1). The warm solution was added to 0.63 g of 1-nitrocyclohexene. On cooling the mixture, a finely crystalline precipitate began to separate. On the following day the precipitate was filtered off and washed with water and ether. The precipitate melted with decomposition at 153.5°. After recrystallization from ethyl alcohol, m.p. 155°.

Found, %: C 38.31; H 6.58; S 15.36
Calculated, %: C 38.52; H 6.46; S 14.69

The yield of 2-nitrocyclohexylthiosemicarbazide is 70% of theory.

2-Nitrocyclohexyl-*p*-toluidine. When equimolecular amounts of 1-nitrocyclohexene and *p*-toluidine are mixed, formation of a crystalline addition product is not observed. The appearance of crystals cannot be induced either by cooling or by prolonged standing of the reaction mixture.

On addition of conc. HCl to the reaction products, a precipitate of the hydrochloride of 2-nitrocyclohexyl-*p*-toluidine separates. The crystalline base was obtained by neutralizing the HCl salt with a 1 *N* NaOH solution.

Hydrochloride of 2-nitrocyclohexyl-*p*-toluidine. To 0.63 g of 1-nitrocyclohexene, 0.54 g of *p*-toluidine was added. As the crystals of *p*-toluidine dissolved, the nitro adduct turned orange. On the following day the liquid became viscous. When 2 ml of conc. HCl was added to it, after a short time a light-colored crystalline precipitate of the hydrochloride of 2-nitrocyclohexyl-*p*-toluidine began to separate. Amount of precipitate: 0.82 g. Yield 60.8% of theory. On heating, the precipitate begins to darken at 142° and at 147–148° melts to a black liquid. M.p. after recrystallization from a mixture of benzene and C_2H_5OH: 150–150.5°.

Found, %: Cl 13.04; N 10.10; C 57.60; H 6.70
Calculated, %: Cl 13.09; N 10.25; C 57.67; H 6.70

2-Nitrocyclohexyl-*p*-toluidine. To 0.1350 g of the hydrochloride of 2-nitrocyclohexyl-*p*-toluidine, 2 ml of 1 *N* NaOH solution was added from a microburet. The crystals were thoroughly ground in a porcelain dish with the alkali solution, then suction-filtered and washed with several portions of distilled water. Amount of precipitate dried in a desiccator: 0.1070 g. Yield 91% of theory. M.p. of the base 71°.

Found, %: C 66.58; H 7.75; N 11.97
Calculated, %: C 66.64; H 7.74; N 11.96

2-Nitrocyclohexyl-*p*-toluidine is soluble in 10% H_2SO_4; insoluble in water and aqueous alkali. It is readily soluble in organic solvents (alcohol, benzene, acetone, and CCl_4).

2-Nitrocyclohexylurea. To 0.63 g of 1-nitrocyclohexene, a solution of 0.6 g of urea in 3 ml of ethyl alcohol was added. On mixing the liquids, no heating and no disappearance of the sharp odor of 1-nitrocyclohexene were observed. After standing for 30 days, the mixture was diluted with water. On dilution, drops of a yellow oil collected at the bottom of the flask; on standing, this crystallized. The crystals were suction-filtered and washed with ethyl ether. M.p. of the substance 190°. After recrystallization from ethyl alcohol, the m.p. rose to 193.5°. Melting is accompanied by decomposition of the substance.

Found, %: C 44.83; H 6.94; N 22.52
Calculated, %: C 44.91; H 7.00; N 22.45

2-Nitrocyclohexylurea forms white, light crystals. It is soluble in organic solvents; on heating it dissolves in water.

1-Nitroisobutylene was obtained by the method of Levy, Baldock, and Wilder-Smith (7) by elimination of nitrous acid from 2-methyl-1,2-dinitropropane, which had been synthesized by the action of N_2O_4 on isobutylene.

The constants of 1-nitroisobutylene were as follows: b.p. 61–62.5° at 10 mm; n_D^{20} 1.4690; d_4^{20} 1.0423; MR found 27.02 (calculated 25.82).

Found, %: C 47.48; H 7.01; N 13.83
Calculated, %: C 47.56; H 6.98; N 13.87

Nitroisobutyl semicarbazide. To 0.5 g of nitroisobutylene, with ice cooling, was added the theoretical amount of semicarbazide dissolved in methyl alcohol. After several minutes the reaction mixture crystallized. The crystals were filtered off and washed with ethyl ether. Amount of crystals 0.72 g, m.p. 129–130.5°; after recrystallization from ethyl alcohol, 132.5–133°. Yield 82.8%. Nitroisobutyl semicarbazide is soluble in organic solvents.

Found, %: C 34.08; H 6.84; N 31.73
Calculated, %: C 34.08; H 6.86; N 31.80

Nitroisobutyl phenylhydrazine. To 0.5 g of nitroisobutylene was added 0.54 g of phenylhydrazine. Several minutes after the reagents were mixed, the liquid crystallized. The precipitate was filtered off and washed with ethyl ether. Amount of precipitate 0.99 g, m.p. 68.5–69°.

After washing with ether, the amount of precipitate was 0.77 g, m.p. 71–71.5°. Yield 72% of theory. The substance is soluble in organic solvents.

Found, %: C 57.58; H 7.22; N 19.90
Calculated, %: C 57.40; H 7.23; N 20.08

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