SOME CHARACTERISTICS OF REDUCTION OF NITRO GROUP IN 3-CYCLOHEXENE DERIVATIVES

G. M. Nikolaev and L. D. Konyushkin

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In a search for new plant growth regulators the trans-6-methyl-1-amino-3-cyclohexene (I) and trans-2-methyl-1-aminocyclohexane (II) were obtained by the reduction of the corresponding nitro compounds (III) [1] and (IV) with powdered tin [2, 3] in conc. CH_3COOH . At the same time, attempts have been made to use other methods for reducing the nitro group [2, 4-9], but in nearly all cases they failed to accomplish the desired result



It is known that the reduction of a nitro group in unconjugated nitroolefins or nitrocyclenes with metals in an acid medium, or with lithium aluminum hydride, proceeds, as a rule, in a selective manner [10], and leads to the formation of unsaturated amines. Only in the case of the reduction of 4-nitro-1-phenyl-1-buten-3-ol [11] and 1-(nitromethyl)-1-cyclohexene [10] with LiAlH₄ was reduction of both the nitro group and the double bond observed. Together with (I), a certain amount of (II) is formed when (III) is reduced with LiAlH₄. The structure of amines (I) and (II) was corroborated by the IR, NMR, and mass spectra. The presence of a multiplet at δ 2.53 (W_{1/2} 17.5 Hz) in the NMR spectrum of (I), corresponding to the H₁ proton, characterizes its axial orientation (H₁ = δ 2.61, W_{1/2} ~ 20 Hz for amine II) [12], and its width testifies to the axial orientation of the vicinal H₂ and H₆ protons, in this way indicating the transposition of the NH₂ and CH₃ groups. As a result, the reduction of (III) with tin in CH₃COOH proceeds stereospecifically, without a change in the configuration; this result is in agreement with the data given in [2-5]. It should be mentioned that the peak of the molecular ion in the mass spectra of the studied compounds has a low intensity (7-17 rel. %).

EXPERIMENTAL METHOD

The NMR spectra were taken on a JNM-4H-100 spectrometer in CCI_4 and CD_3OD , using TMS as the internal standard. The IR spectra were taken on a UR-10 spectrophotometer in CCI_4 (5.6%) or as KBr pellets.

trans-6-Methyl-1-amino-3-cyclohexene (I). To a solution of 11.3 g of (III) in 160 ml of conc. CH₃ · COOH, with vigorous stirring, was added 24 g of Sn powder in portions, and at the same time the temperature was raised up to 100°C, after which the mixture was stirred for 1.5 h at the same temperature, cooled to ~20°, and made alkaline with 40% KOH solution (to pH 10). The precipitate was separated, the filtrate was extracted well with ether, and the extract was washed with water, dried over Na₂SO₄, filtered, and saturated with dry HCl. We obtained 4 g (33.8% when based on the amine) of the hydrochloride of amine (I), mp 232.5-233.5° (methanol: ether, 1:2). Found: C 56.94; H 9.57; N 9.52; Cl 24.16%. C₇H₁₄NCl. Calculated: C 56.95; H 9.56; N 9.47; Cl 24.01%. Mass spectrum (m/e): 111, 94, 82, 57, 42, 36, 30. The hydrochloride was made alkaline with 20% KOH solution, extracted with ether, dried over Na₂SO₄, the solvent was removed, and the residue was vacuum-distilled in an N₂ stream. Here we obtained (I), bp 47-47.5° (13 mm); n_D²⁰ 1.4778. Infrared spectrum (CCl₄, cm⁻¹): 3400, 3320, 3032, 2960, 1660. NMR spectrum (δ, ppm; J, Hz): CH₃-(3H, 0.99, 5.2); -HC=C-(2H, 5.54, 2.1); H₂N-(2H, 1.71, 3).

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The N-acetyl derivative corresponding to amine (I) has mp 93-94° (ether). Found: N 9.18; O 10.25%. $C_{9}H_{15}NO.$ Calculated: N 9.14; O 10.44%. NMR spectrum (δ , ppm; J, Hz): $CH_{3}-C$ (3H, 0.98, 5.2); $CH_{3}CO-(3H, 1.96)$; >CH-N (H, 3.69, $W_{1/2} \sim 14.9$); -HC=C-(2H, 5.60, 1.5). Mass spectrum (m/e): 153, 99, 94, 79, 60, 57, 43, 32.

The N-benzoyl derivative has mp 113-114° (hexane). Found: N 6.22%. $C_{14}H_{17}NO$. Calculated: N 6.51%. Infrared spectrum (KBr pellet, cm⁻¹): 3275, 3090, 3030, 2970, 2885, 1632, 1605, 1580. Mass spectrum (m/e): 215, 161, 122, 105, 79, 77.

 $\frac{\text{trans-2-Methyl-1-aminocyclohexane (II).}}{\text{of Sn powder and 160 ml of conc. CH₃COOH we obtained 4.8 g (40.2% when based on the amine) of the hydrochloride of amine (II), mp 279-280° (decompn.) (1:2 methanol-ether). Found: C 56.15; H 10.73; N 9.44; Cl 24.06%. C₇H₁₆NCl. Calculated: C 56.11; H 10.84; N 9.36; Cl 23.68%. Mass spectrum (m/e): 113, 92, 70, 57, 56, 43, 41.$

When the hydrochloride was made alkaline we obtained amine (II), bp 48° (19 mm); n_D^{20} 1.4568. Infrared spectrum (CCl₄, cm⁻¹): 3390, 3315, 1460. The N-acetyl derivative corresponding to this amine has mp 122.5-123° (ether). Found: N 8.99; O 10.64%. C₉H₁₇NO. Calculated: N 9.02; O 10.31%. NMR spectrum (δ , ppm; J, Hz): CH₃-C (3H, 0.90, 7); CH₃CO-(3H, 1.92). Mass spectrum (m/e): 155, 112, 98, 96, 81, 70, 60, 56, 43, 32.

The N-benzoyl derivative has mp 148-148.5° (hexane). Found: N 6.44; O 7.40%. $C_{14}H_{19}NO$. Calculated: N 6.45; O 7.32%. Infrared spectrum (in KBr, cm⁻¹): 3244, 3088, 2970, 2875, 1635, 1605, 1580. Mass spectrum (m/e): 217, 160, 123, 122, 105, 77, 32.

<u>trans-2-Methyl-1-nitrocyclohexane (IV)</u>. The hydrogenation of 14.1 g of (III) in 14 ml of alcohol in the presence of 0.2 g of Pd/CaCO₃, followed by distillation, gave 13.5 g (94%) of (IV), bp 79-80° (9 mm), n_D²⁰ 1.4552. Infrared spectrum (as a film, cm⁻¹): 2965, 2870, 1555, 1380. NMR spectrum (δ , ppm; J, Hz): CH₃-(3H, 0.95, 5.5); >CH-N (4.07 W_{1/2} ~ 24.8).

CONCLUSIONS

The reduction of the nitro group in 3-cyclohexene derivatives proceeds stereospecifically, but not selectively.

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