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A NEW CONVERSION OF N-(1-OXIMINO-1,2,3,4-TETRAHYDRONAPHTHYL-2)-HYDROXYLAMINE

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In our earlier publications (1) the synthesis and the chemistry of title compound (I) were reported. Now we wish to report of a new surprising conversion of I.

The ultraviolet spectrum I in the aqueous diluted alkali solution has shown the change in the character with time which indicated the instability of I under given conditions. In fact, on standing I in 5% sodium hydroxide solution over 3 days at room temperature and in access of air the complete disappearance of the initial compound could be observed. Two individual substances have been found among reaction products: liquid compound (II) (yield 47%), b.p. 181-183°/4 mm (found: C 63.1; H 5.3; N 14.8; calcd. for $C_{10}H_{10}N_2O_2$: C 63.2; H 5.3; N 14.8) and crystalline compound (III) (yield 12%), m.p. 109-110° (found: C 57.8; H 5.8; N 13.5; calcd. for $C_{10}H_{12}N_2O_3$: C 57.6; H 5.8; N 13.4).

II and III are insoluble in diluted acids but slowly dissolve in aqueous alkali solutions. Infrared spectrum

II showed the absorption at 2225 cm^{-1} which corresponds to the stretching mode C ≡ N group directly attached to the ring and the bands at 1570 and 1390 cm^{-1} indicating the presence of nitro group. In the out of plane C-H deformation vibration region (700-900 cm^{-1}) there exists the only band at 760 cm^{-1} characteristic for o-disubstituted benzene ring.

On the basis of the infrared spectrum and analytical data one might assume that II is benzonitrile which is substituted in o-position by aliphatic residue, containing nitro group ($C_3H_6NO_2$). This conclusion was supported by the good agreement of ultraviolet spectrum II (λ^{EtOH}_{max} 224 (logε3.95) 275 (3.05) and 283 mμ (3.04)) with that of o-tolunitrile (λ^{EtOH}_{max} 228 (logε 3.96), 276 (3.06) and 284 mμ (3.08)).

The structure of the aliphatic residue containing nitro group was established by means of n.m.r.spectrum x).The n.m.r. spectrum II obtained in $CDCl_3$ solution on JNM-3 spectrometer (40 Mc) consists of the three groups of bands: the singlet of the aromatic protons at $\tau = 2.55$ p.p.m., the triplet at $\tau=5.51$ p.p.m. with intensity ratio being 1:2:1 and the non-symmetrical multiplet centered at $\tau = 7.30$ p.p.m.. The ratio of the triplet and multiplet areas is 2:4. Thus, two of the six hydrogen atoms of the aliphatic residue corresponding to the triplet are more deshielded than the rest

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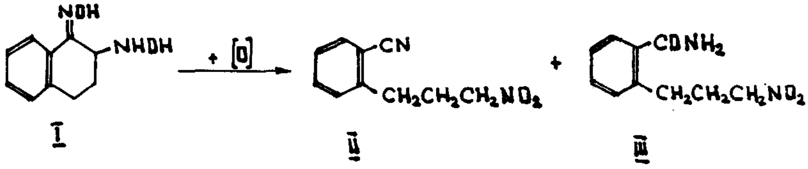
x) We wish to thank Yu.N.Molin for taking and discussing n.m.r. spectrum.

ones. It was quite natural to assume that the two protons are those of carbon atom adjacent to the nitro group, and the band at τ= 5.51 p.p.m. can be certainly assigned to the $-CH_2NO_2$ group (cp. (2)). The coupling of this band to the triplet with intensity ratio being 1:2:1 (J = 6.4 c.p.s.) indicates to the fact that $-CH_2NO_2$ group is attached to the methylene group. The n.m.r. results suggest that the aliphatic residue has the structure $-CH_2CH_2CH_2NO_2$ according to which the wide band at τ = 7.30 p.p.m. should be assigned to the two methylene groups which are not adjacent to the nitro group.

Proceeding from the above evidence II is assigned to the structure of the o-(γ-nitropropyl)-benzonitrile. The independent synthesis of this compound is carried out making use of the known o-(γ-chlorpropyl)-benzonitrile (3) by the action of NaI in acetone solution with the following treatment of the isolated iod-derivative with $AgNO_2$. Ultraviolet and infrared spectra of the produced specimen were found to be practically indentical to the spectra II.



According to their analytical data III differs from II by a water molecule. The infrared spectrum III (in $CHCl_3$) as well as the spectrum II have shown two bands of the nitro group (1570 and 1390 cm^{-1}) but no absorption of the nitrile group. The infrared spectrum III showed also C=O (1635 cm^{-1}) and NH_2 (3415 and 3530 cm^{-1}) stretching bands. The ultraviolet spectrum III (λ_{max}^{EtOH} 267 mμ(log 2.77)) fairly agrees with that of o-toluamide (λ_{max}^{EtOH} 269 mμ (log 2.81)). The spectral characteristics of II suggest that is has the structure of o-(γ-nitropropyl)-benzamide. This suggestion is supported by the formation of III when II is treated with 95% sulfuric acid at room temperature (yield 40%).

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