CONVERSION OF α-AZOXYOXIMES TO 2H-1,2,3-TRIAZOLE N-OXIDE DERIVATIVES

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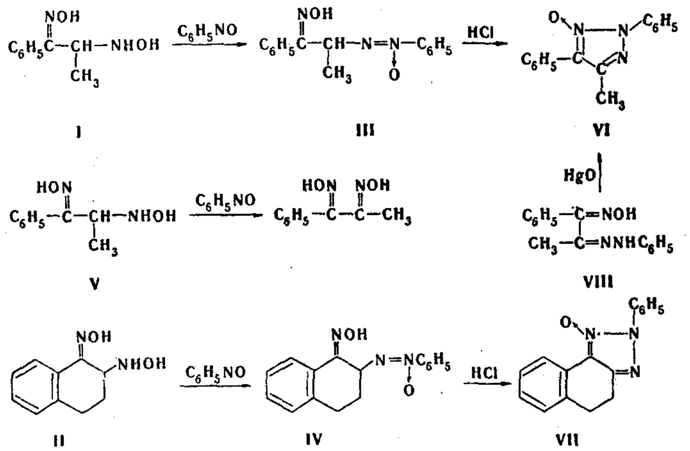
Reaction of the syn isomers of α-hydroxylaminooximes with nitrobenzene gives α-azoxyoximes, which undergo intramolecular cyclization to 2H-1,2,3-triazole N-oxide derivatives under the influence of hydrogen chloride.

It has been previously shown that α-hydroxylaminooximes react with aromatic aldehydes to give N-(1-oximino-2-alkyl)-α-arylnitrones [1]. The latter readily undergo intramolecular cyclization to imidazole derivatives. It was natural to attempt to obtain the previously unknown α-azoxyoximes and to study their capacity for intramolecular cyclization under similar conditions.

The reaction of N-(1-oximino-1-phenyl-2-propyl)hydroxylamine (I) and N-(1-oximino-1,2,3,4-tetrahydro-2-naphthyl)hydroxylamine (II), which have an oxime group with a syn configuration, with nitrobenzene gives, in a yield of ~30%, colorless crystalline III and IV, the composition of which corresponds to the products of condensation of I and II with nitrobenzene with splitting out of a molecule of water. The IR spectra of III and IV contain bands of the stretching vibrations of an azoxy group at 1270-1320 cm^{-1} and of an OH group at 3600 cm^{-1}. On the basis of these data, it might have been assumed that III and IV are α-azoxyoximes. Intense absorption bands are observed in the UV spectra at 242 nm (log ε 4.28) (III) and 254 nm (log ε 4.35) (IV). In conformity with the data in [2, 3] and UV spectroscopy, the 1-oximino-1-phenylpropyl-2-N,N,O-azoxybenzene and 1-oximino-1,2,3,4-tetrahydronaphthyl-2,N,N,O-azoxybenzene structures, respectively, can be assigned to III and IV.

It should be noted that 1-phenylpropane-1,2-diol dioxime is formed in the reaction of the anti isomer of N-(1-oximino-1-phenyl-2-propyl)hydroxylamine (V) with nitrobenzene.



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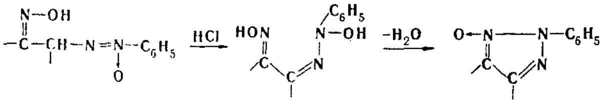
Colorless crystalline VI and VII, which correspond to the products of splitting out of water from the α-azoxyoximes, are formed by the action of dry hydrogen chloride on alcohol solutions of III and IV. The UV spectra of VI and VII contain intense absorption bands with maxima at 286 nm (log ε 3.95) and 301 nm (log ε 4.38), respectively, which attest to the formation of new chromophore systems that differ from the chromophore systems of the starting III and IV. The IR spectrum of VI does not contain bands of the azoxy and OH groups, but there are a group of signals of 10 aromatic hydrogen atoms at 7.2-8.0 ppm and a singlet of a methyl group at 2.44 ppm in the PMR spectrum. Signals of 10 aromatic hydrogen atoms at 7.2-8.4 ppm and a complex signal of two methylene groups at 2.96 ppm are present in the PMR spectrum of VII at weak field. These results make it possible to assign the substituted 2H-1,2,3-triazole N-oxide structure to VI and VII. However, the position of the N-oxide oxygen remained unexplained. Since VI did not prove to be identical to the previously described 4-methyl-2,5-diphenyl-2H-1,2,3-triazole 3-oxide [4], it might have been assumed that VI has the 5-methyl-2,4-diphenyl-2H-1,2,3-triazole 3-oxide structure. In fact, alternative synthesis of a compound with this structure by oxidation of 1-oximino-1-phenyl-2-phenylhydrazinopropane (VIII) with yellow mercuric oxide according to the method in [5] gave a product identical to VI. By analogy, the 2-phenyl-4,5-(3,4-dihydro-2,1-d)-2H-1,2,3-triazole 3-oxide structure was assigned to VII.



The formation of VI and VII from α-azoxyoximes apparently commences with inverstion of the configuration of the oxime group [1] with subsequent splitting out of a proton from the oxime group and a hydroxyl group from the azoxy group in the tautomeric form (see [6]). This sort of cyclization was recently observed for α-diazooximes [7].

EXPERIMENTAL

The IR spectra were recorded from CCl_4 solutions and KBr pellets with a UR-10 spectrometer. The UV spectra of alcohol solutions were recorded with a Unicam SP 700 C spectrophotometer. The PMR spectra of CCl_4 solutions were recorded with a Varian A-56/60A (60 MHz) spectrometer.

1-Oximino-1-phenylpropyl-2-N,N,O-azoxybenzene (III). A solution of 5.4 g (0.03 mole) of I in 20 ml of dimethylformamide was added with stirring to a cooled (to 0°) solution of 4.8 g (0.045 mole) of nitrobenzene in 35 ml of dimethylformamide. The solution turned light-green and then yellow 15 min after the end of the addition. It was then diluted with water, and the oily precipitate was removed by filtration and washed with cold petroleum ether. The residual solid III [2.4 g (30%)] was crystallized from CCl_4 to give a product with mp 160-160.5°. Found: C 67.1; H 5.7; N 15.8%. $C_{15}H_{15}N_3O_2$. Calculated: C 67.0; H 5.6; N 15.7%.

Under the same conditions, 3.21 g (0.03 mole) of nitrobenzene and 3.6 g (0.02 mole) of V gave 3.3 g (93%) of 1-phenylpropane-1,2-dioldioxime with mp 237-240°. This product did not depress the melting point of a sample of 1-phenylpropane-1,2-dioldioxime, and their IR spectra were identical.

1-Oximino-1,2,3,4-tetrahydronaphthyl-2-N,N,O-azoxybenzene (IV). A 1.92-g (0.01 mole) sample of II and a suspension of 1.07 g (0.01 mole) of nitrobenzene in 30 ml of methanol were added to a cooled (to −10°) solution of sodium methoxide (from 1.15 g of sodium metal and 20 ml of methanol), and the mixture was stirred for 20 min and poured over ice. The aqueous mixture was neutralized with acetic acid and extracted with ether. The ether was evaporated to give 0.9 g (30%) of IV with mp 125-126° (from petroleum ether). Found: C 68.2; H 5.5; N 14.6%. $C_{16}H_{15}N_3O_2$. Calculated: C 68.3; H 5.4; N 14.9%.

5-Methyl-2,4-diphenyl-2H-1,2,3-triazole 3-Oxide (VI). A suspension of 1.31 g (0.005 mole) of III in 30 ml of anhydrous alcohol was cooled with ice, saturated with dry hydrogen chloride, and allowed to stand for 48 h at room temperature. The alcohol was partially evaporated, and the residue was diluted with water and extracted with ether. The extract was dried, the solvent was evaporated, and the residual solid VI [0.5 g (40%)] was crystallized from petroleum ether to give a product with mp 74-75°. Found: C 72.2; H 5.4; N 16.8%. $C_{15}H_{13}N_3O$. Calculated: C 71.7; H 5.2; N 16.6%. UV spectrum of VI, λ_{max}, nm (log ε); 203 (4.55), 246 (3.90), 286 (3.95). Compound VI did not depress the melting point of a sample of 5-methyl-2,4-diphenyl-2H-1,2,3-triazole 3-oxide obtained from VIII via the method in [5], and their IR spectra were identical.

2-Phenyl-4,5-(3,4-dihydronaphtho-2,1-d)-2H-1,2,3-triazole 3-Oxide (VII). This compound [0.15 g (37%)] was obtained under the same conditions from 0.45 g of IV and had mp 109-110° (from petroleum ether). Found: C 72.8; H 4.6; N 16.3%. $C_{16}H_{13}N_3O$. Calculated: C 73.0; H 4.9; N 15.9%. UV spectrum, λ_{max}, nm (log ε): 205 (4.59), 252 (4.21), 301 (4.38).

1-Oximino-1-phenyl-2-phenylhydrazinopropane (VIII). A 4.35-g (0.025 mole) sample of 1-oximino-1-phenylacetone and 2.48 g (0.023 mole) of phenylhydrazine were dissolved in 25 ml of butyl alcohol, and the solution was refluxed for 33 h. The butanol was vacuum evaporated, and the residue was crystallized successively from benzene and alcohol to give 0.24 g (4%) of VIII with mp 141°. In [8], a melting point of 154° is given, but the yield is not indicated. Found: C 70.9; H 5.9; N 16.6%. $C_{15}H_{15}N_3O$. Calculated: C 71.1; H 5.9; N 16.6%.

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