SYNTHESIS OF MONOXIMES OF 2-ARYL-2H-NAPHTHO[1,2-d]TRIAZOLE-4,5-QUINONES AND THEIR REARRANGEMENT TO TRIAZOLYLCARBOXYLIC ACID

A. P. Stankyavichyus and P. B. Terent'ev

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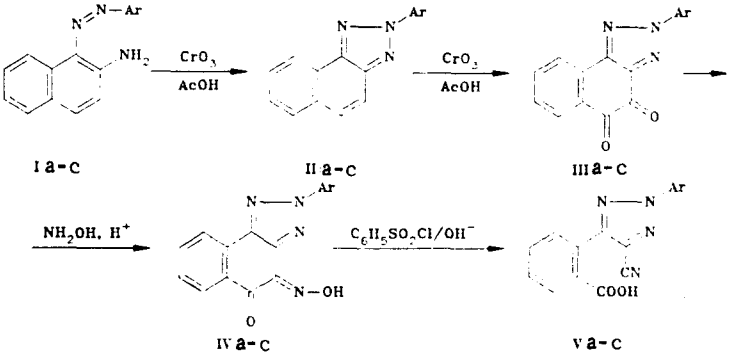
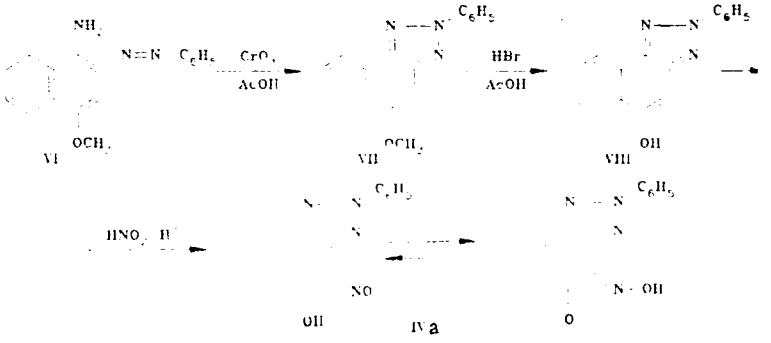
Oximation of 2-aryl-2H-naphtho[1,2-d]triazole-4,5-quinones gave the 4-oximes. The rearrangement of the latter in alkaline medium in the presence of benzenesulfonyl chloride to triazolylcarboxylic acids was studied, and derivatives were obtained. UV and mass spectral data are presented.

We recently showed [1] that 5-hydroxy-4-nitroso-2-phenyl-2H-1,2,3-benzotriazole, which exists predominantly as the orthoquinone monoxime, undergoes rearrangement when treated with benzenesulfonyl chloride in alkaline medium to form 3-(2-phenyl-5-cyano-2H-1,2,3-triazolyl-4)acrylic acid. It was of interest to determine whether the analogous rearrangement could take place in the naphthothiazole series. The starting monoximes of the ortho-quinones IVa-c were obtained by oxidative cyclization of the arylazonaphthylamines Ia-c as follows:



I-V a Ar=C_6H_5; b Ar=$C_6H_3Cl_2$-2,5; c Ar=$C_6H_3(CH_3)_2$-2,4

Monooximation of the unsymmetrical ortho-quinones IIIa-c with hydroxylamine hydrochloride proceeded smoothly, but the location of the hydroxyimino group had to be established. In [2], using N-unsubstituted naphtho[1,2-d]triazole-4,5-quinone it was shown that the oxime and the hydrazone are formed at position 4; i.e., the orientation typical of 1,2-naphthoquinone was preserved [3]. In work on the analogous 2-aryl-substituted ortho-quinones [4, 5] the location of the oxime group was not established. The data of [6] concern benzo- and naphthotriazolequinones in which the redox potential depends on N-substitution and the location of the substituent; from these data it follows that 2-phenyl-2H-1,2,3-benzotriazole-quinones are most comparable to naphthoquinones, so that a similar direction can be assumed for oximation. To solve this problem we synthesized monoxime IV by a well known procedure, viz., the nitrosation of 2-phenyl-2H-5-hydroxynaphtho-[1,2-d]triazole VIII.



Z. Yanushkyavichyus Scientific Research Institute of Physiology and Pathology of the Cardiovascular System, Kaunas 233009. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 10, pp. 1364-1368, October, 1988. Original article submitted November 9, 1987.

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TABLE 1. Properties of Synthesized Compounds

Compound	R_f*1	mp, °C	UV spectrum, λ_{max}, nm (log ε)	% N (Cl), found	Empirical formula	% N (Cl), calculated	Yield, %
Ib	0,82 (A)	164...165	242 (4,52), 276 (4,28), 360 (3,85), 482 (4,23)	13,0 (22,2)	$C_{16}H_{11}Cl_2N_3$	13,3 (22,5)	76
Ic	0,75 (A)	128...129	232 (4,47), 248 (4,50), 278 (4,20), 346 (4,01), 452 (4,21)	15,3	$C_{18}H_{17}N_3$	15,3	50
IIa	0,46 (A)	107	222 (4,60), 278 (4,49), 336 (4,30)	17,8	$C_{16}H_{11}N_3$	18,0	81
IIb	0,68 (B)	170...171	268 (4,54), 320 (4,07)	13,2 (22,3)	$C_{16}H_9Cl_2N_3$	13,4 (22,6)	51
IIc	0,63 (B)	86...87	224 (4,54), 264 (4,43), 326 (4,05)	15,3	$C_{18}H_{15}N_3$	15,4	82
IIIa	0,74 (C)	208...209	296 (4,40)	15,7	$C_{16}H_9N_3O_2$	16,0	78
IIIb	0,75 (C)	262...263	338 (3,56)	12,3 (20,3)	$C_{16}H_7Cl_2N_3O_2$	12,4 (20,6)	72
IIIc	0,71 (C)	190...191	258 (4,37), 386 (3,47)	13,7	$C_{18}H_{13}N_3O_2$	13,9	70
IVa	0,44 (D)	232...233	226 (4,29), 302 (4,41), 266 (4,43), 334 (4,38), 400 (4,07)*2	19,5	$C_{16}H_{10}N_4O_2$	19,3	70
IVb	0,60 (D)	227...228	228 (4,63), 284 (4,42)	15,4 (19,7)	$C_{16}H_8Cl_2N_4O_2$	15,6 (19,6)	42
IVc	0,58 (D)	224...225	230 (4,44), 260 (4,38), 288 (4,41)	17,4	$C_{18}H_{14}N_4O_2$	17,6	85
Va	0,72 (D)	175...176	284 (4,36)	19,5*3	$C_{16}H_{10}N_4O_2$	19,3	43
Vb	0,71 (D)	226...227	256 (4,14)	15,4 (19,4)	$C_{16}H_8Cl_2N_4O_2$	15,6 (19,6)	62
Vc	0,71 (D)	190...191	264 (4,21)	17,4	$C_{18}H_{14}N_4O_2$	17,6	66
VI	0,69 (E)	121...123	232 (4,46), 322 (4,36), 500 (4,17)	14,9	$C_{17}H_{15}N_3O$	15,2	43
VII	0,73 (E)	134...135	232 (4,60), 278 (4,48), 342 (4,38)	15,0	$C_{17}H_{13}N_3O$	15,3	60
VIII	0,44 (E)	241	232 (4,52), 280 (4,48), 348 (4,30)	16,3	$C_{15}H_{11}N_3O$	16,1	80
IX	0,69 (F)	134...135	284 (4,37)	18,4*4	$C_{17}H_{12}N_4O_2$	18,4	56
X	0,35 (D)	238...240*5	284 (4,33)	13,2*6	$C_{15}H_{11}N_3O_4$	13,6	65
XI	0,42 (D)	251...252	282 (4,31)	18,5*7	$C_{16}H_{12}N_4O_3$	18,3	55

*1 Solvent systems: 3:1 hexane–bezene, A; 10:1 hexane–benzene, B; 5:1 benzene–ethanol, C; 4:1 isopropanol–5% aqueous ammonia, D; 10:1 benzene–ethanol, E; 20:1 benzene–chloroform, F.

*2 In 0.01 N KOH in ethanol.

*3 Found: C 65.6; H 3.4%. Calculated: C 66.2; H 3.4%.

*4 Found: C 66.9; H 4.0%. Calculated: C 67.1; H 3.9%.

*5 According to [12], mp = 242°C.

*6 Found: C 62.2; H 3.4%. Calculated: C 62.1; H 3.6%.

*7 Found: C 62.4; H 3.8%. Calculated: C 62.7; H 3.9%.

In the UV spectra of these compounds, (Table 1), in going from azo derivatives Ia-c and VI to triazoles IIa-c, VII, and VIII the absorption maximum in the visible disappears, and remaining three bands, which are typical of the benzene ring, overlap the heterocycle absorption [7]. In the UV spectrum of o-quinones IIIa-c, analogous to phenanthrenequinone-9,10 [8], there is a notable benzene band that often has a complex structure, and a quinoid band that is very diffuse but is more distinct in alkaline medium.

When monooximes IV a-c are heated in alkaline medium in the presence of benzenesulfonyl chloride, the quinoid ring is cleaved to form the cyanoacids Va-c. Esterification of Va with methanol in the presence of sulfuric acid gives ester IX; in alkaline medium the nitrile group of Va is hydrolyzed to form dicarboxylic acid X or amide XI.

The UV spectrum of cyanoacid Va, its ester IX, and its hydrolysis products X and XI (see Table 1) retain the absorption band that is typical of 2-substituted 1,2,3-triazoles and overlaps the benzene band.

The mass spectra of monooxime IVa and its rearrangement product Va are characterized by intense peaks of molecular ions (M^+); the former is more stable (W_M = 18.6) than the latter (W_M = 13.1). Common to the dissociative ionization of both compounds is $[M-OH]^+$ (273)*; this ion is typical of the fragmentation of both oximes and of arylcarboxylic acids, as well as $C_6H_5N^+$ (91) and C_6H_5 (77) that are formed by decomposition of the hetero ring. The decomposition of acid Va is characterized also by a high probability of formation of the ion $[M - CO_2]$ (246, confirmed by a metastable ion), which demonstrates the presence of a carboxyl group in M^+. On the other hand the mass spectrum of IVa shows an intense peak of $[M - OH, - CO]^+$ (245), which is typical of other ortho-quinone monoximes [1]. From these data we can conclude that before it decomposes, M^+ of oxime IV does not undergo the rearrangement to M^+ of acid Va that is found in the isatine monoxime series [10].

EXPERIMENTAL

UV spectra were obtained in ethanol with a SF-16 instrument. Mass spectra were recorded with MAT-212 and MKh 1303 instruments at 70 and 50 eV ionization energies respectively, with direct introduction of sample into the ion source. The identities of the compounds and the course of the reactions were monitored by TLC on an unattached layer of aluminum oxide of grade II activity, with development by iodine vapor.

2-Amino-1-phenylazonaphthalene (Ia) was obtained by the procedure of [11] in 82.2% yield. mp 101-103°C, from ethanol (lit., 102-104°C). 1-(2,5-dichlorophenylazo)-2-aminonaphthalene (Ib) and 1-(2,4-dimethylphenylazo)-2-aminonaphthalene (Ic) were synthesized analogously (Table 1).

2-Aryl-2H-naphtho[1,2-d]triazoles IIa-c were obtained by oxidation of amines Ia-c by chromic acid in acetic acid [4].

2-Aryl-4,5-dioxo-2H-[1,2-d]triazoles IIIa-c were obtained by oxidation of naphthotriazoles IIa-c with chromic acid in acetic acid by the procedure of [5], but without addition of acetic anhydride, and with subsequent holding of the reaction mixture for 1 h at 40°C. Thus the yield was increased to 78%.

2-Aryl-4-hydroximino-2H-5-oxonaphtho[1,2-d]triazoles IVa-c. To a hot solution of 0.04 mole of dioxocompound IIIa-c in 400 ml of propanol and 80 ml of chloroform was added 0.04 mole of hydroxylamine hydrochloride. The mixture was boiled for 2 h, then cooled. The precipitate was filtered off by suction, washed with propanol, and dried. Mass spectrum of triazole IVa, m/z (%): 290 (72), 273 (64), 246 (20), 245 (45), 118 (25), 91 (100), 77 (49), 64 (31), 51 (21).

3-(2-Carboxyphenyl)-2-aryl-4-cyano-2H-1,2,3-triazoles Va-c. To a mixture of 2.9 g (0.01 mole) of monoxime IVa, 120 ml of dioxane, and 1.55 ml of benzenesulfonyl chloride, heated to boiling, was added to a solution of 1.4 g (0.025 mole) of sodium hydroxide in 14 ml of water, in small portions. The mixture should boil steadily. It was cooled and acidified with glacial acetic acid† (5 ml), and the solvent was evaporated. To the residue were added 5%

*The number that characterizes the ion is determined by m/z.

†If the mixture is not acidified before evaporation, then amide XI will be obtained. Mass spectrum, m/z (%): 308 (46), 264 (80), 263 (95), 248 (14), 235 (5), 91 (100), 77 (56), 64 (35), 51 (28).

sodium bicarbonate solution to weak alkalinity, and activated carbon. The mixture was boiled, filtered, cooled, and acidified with glacial acetic acid to pH 2-3. The precipitate was filtered off, dried, and crystallized from 50% aqueous ethanol. Mass spectrum, m/z(%): 290 (84), 273 (95), 247 (16), 246 (41), 167 (39), 113 (22), 111 (28), 91 (70), 77 (100), 64 (25), 51 (37). Compounds Vb, c were obtained analogously.

3-(2-Methoxycarbonylphenyl)-2-phenyl-4-cyano-2H-1,2,3-triazole (IX). A solution of 2.9 g (0.01 mole) of acid Va and 1.5 ml of concentrated sulfuric acid in 20 ml of absolute methanol was boiled under a reflux condenser for 3 h. The solution was cooled and diluted with water, and the resulting precipitate was filtered off and crystallized from ethanol.

3-(2-Carboxyphenyl)-4-carboxy-2-phenyl -2H-1,2,3-triazole (X). A solution of 2.9 g (0.01 mole) of cyanoacid Va in 20 ml of 10% sodium hydroxide was boiled 4 h. The resulting precipitate was dissolved in hot water. Activated carbon was added, the mixture was boiled and filtered, and the filtrate was acidified with dilute sulfuric acid to pH 2-3. The precipitate was filtered by suction, washed with water, and crystallized from 50% ethanol.

1-Amino-4-methoxy-2-phenylazonaphthalene (VI) was obtained from 1-amino-4-methoxy-naphthalene hydrochloride analogously to the 4-ethoxy derivative [13].

5-Methoxy-2-phenyl-2H-naphtho[1,2-d]triazole (VII) was synthesized from 27.7 g (0.1 mole) of amino derivative VI (see the synthesis of triazoles IIa-c). The light rose crystals that separated were crystallized from acetic acid; zinc dust was added for decolorization.

5-Hydroxy-2-phenyl-2H-naphtho[1,2-d]triazole (VIII). A solution of 13.75 g (0.05 mole) of methoxy compound VII in 300 ml of glacial acetic acid and 400 ml of hydrobromic acid was boiled for 56 h. It was evaporated to half its volume and cooled, and 25% aqueous ammonia was added to pH 5-6. The precipitate was filtered off by suction, washed with water, and crystallized from nitromethane.

4-Hydroxyimino-5-oxo-2-phenyl-2H-naphtho[1,2-d]triazole (IVa). To a solution of 3.9 g (0.015 mole) of hydroxy derivative VII in 600 ml of glacial acetic acid* was added a solution of 0.5 g of sodium nitrite in 10 ml of water. The mixture was stirred for 30 min, then diluted with water, and the precipitate was filtered off and crystallized from dioxane. mp 231-233°C. The melting point of a mixture of authentic sample with this product was not depressed.

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*The dissolution is accelerated by heating.