Diazo-, Azo- and Azidoazoles, and Related Compounds. I. Synthesis of Naphthoazolo-*as*-triazines from Diazoazoles and 2-Naphthol.

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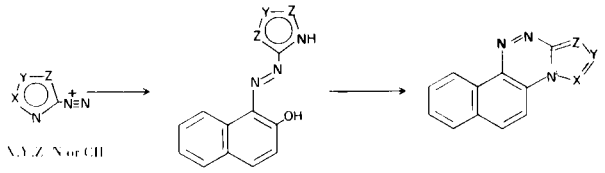
Azo derivatives prepared by coupling 2-diazoimidazole, 3(5)diazopyrazole, 3(5)diazo-*s*-triazole, 4(5)diazo-*v*-triazole and diazotetrazole with β-naphthol have been cyclized to the corresponding naphthoazolo-*as*-triazines, an heterocyclic system related to azasteroids. The structure of the products have been elucidated. A consistent mechanism for the cyclization is proposed.

This work deals with the detailed study of napthoazolo-*as*-triazines synthesis according to the following pathway:



X,Y,Z N or CH

Special emphasis has been made on the second step of this sequence.

Bamberger (1) was the first to describe this intramolecular condensation with 3-diazoindazole derivatives. More recently, Reimlinger *et al.* (2-3), and Mendoza and Garcia-Marquina (4) described the preparation of analogous compounds in the pyrazole series. A similar reaction with 2-aminonaphthalene (5) has been patented to protect the preparation of naphtho[2,1-*e*]-*s*-triazolo[5,1-*c*]-*as*-triazine and naphtho[2,1-*e*]tetrazolo[5,1-*c*]-*as*-triazine. Polya and Woodruff (6), as well as Reimlinger and Overstraeten (3), also applied these reactions to phenols other than β-naphthol. All of these authors, however, neither explained the mechanism nor studied the scope of the process as a general synthetic method.

Azo derivatives have been obtained by coupling freshly prepared diazonium salts with β-naphthol dissolved in excess aqueous sodium hydroxide. Since the diazonium group increases considerably the acidity of the ring (7), the electrophilic attack at position 1 in the β-naphthol molecule may be attributed to the diazoazole resulting from loss of the iminic proton in the azole ring.

Refluxing the azo derivatives I, III, V, VII and IX in polar solvents, compounds II, IV, VIA-VIB, VIIIB and X were obtained, respectively. Particularly fast cyclization was observed in imidazole cases, where a certain amount of II is already present in the dried raw coupling product.

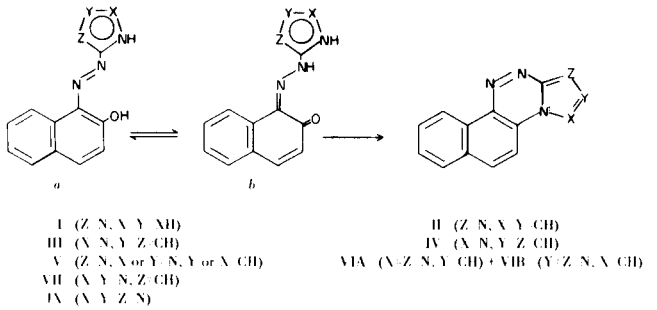
Comparison of the ir spectra in potassium bromide of the open (I, III, V, VII, IX) and the cyclic products shows in the latter, the absence of associated OH and/or NH bands, as well as the band at 1620-1630 cm^{-1} which would be only ascribed (8) to one carbonyl group with intramolecular hydrogen bond that suggest the presence of a hydrazone tautomer (*b*) in those open compounds. The azo-hydrazone tautomer has been studied by several authors (9) in a great number of azophenols and azonaphthols derivatives.

The cyclization of V either in glacial acetic acid or methanol gave only one product (VIA); when methanol with some drops of concentrated sulfuric acid was employed, a mixture of VIA and VIB was obtained. Identification of VIA and VIB was achieved by nmr spectroscopy. VIB is a stable compound, and no rearrangement to VIA was observed by refluxing it in acetic acid, trifluoroacetic acid (10) or ethylenglycol.

The main product obtained in the cyclization of VII gives the expected elemental analysis, but its nmr spectrum differs from the spectra of II, IV, VIA and VIB, suggesting the possibility of rearrangement to naphtho[2,1-*e*]-*v*-triazolo[1,5-*b*]-*as*-triazine (VIIIB). Our efforts to isolate VIIIA in appreciable amounts by reducing the time of heating or trying out various solvents were unsuccessful.

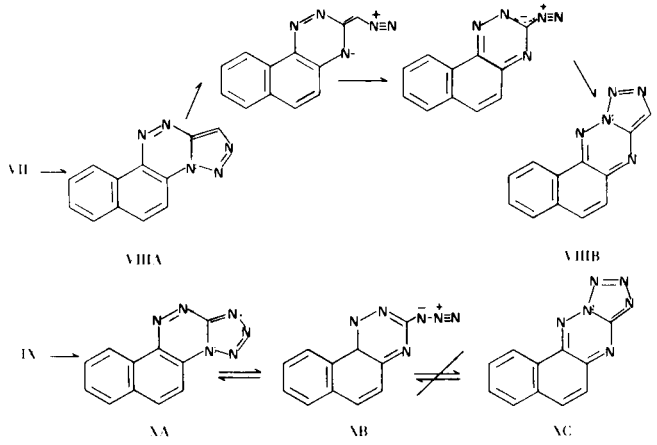
Compound X is a new example of azide-tetrazole equilibrium. In solid state no azide bands are present in its ir spectrum. In chloroform, however, two strong bands appear at 2160 and 2130 cm^{-1}. In dimethylsulfoxide the azide bands are weak but their intensity (in relation to the other bands) increases with the temperature.

Since in the solid state and in dimethylsulfoxide solu-



I (Z N, X Y NH)
III (X N, Y Z CH)
V (Z N, X or Y N, Y or X CH)
VII (X Y N, Z CH)
IX (X Y Z N)

II (Z N, X Y CH)
IV (X N, Y Z CH)
VIA (X Z N, Y CH) + VIB (Y Z N, X CH)



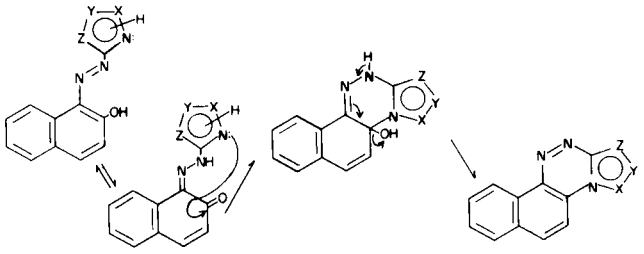
VIIIA VIIIB

XA XB XC

tion at room temperature, tetrazole form is favoured, it is interesting to know which would be the actual structure (XA or XC) of this compound in those conditions. Unfortunately, the solubility of the product in dimethylsulfoxide at 20° is insufficient for the nmr study with ordinary instruments. Nevertheless, the visible spectrum of X was very similar to those of II, IV, VIA and VIB, and different from that of VIIIB. Therefore, structure XC must be discarded.

According to the results summarized in Table I, hydroxylic solvents are the more suitable to carry out the reaction, favoured by acid catalysis.

The experimental observation that the ease of cyclization of azo derivatives depends upon the relative basic character of the heterocycle (imidazole ≫ pyrazole > *s*-triazole > *v*-triazole > tetrazole) and the fact that their ir spectra shows the appearance of the tautomeric oxo-hydrazone form, suggest for this process the following mechanism:



The effect of the heterocyclic nature on the equilibrium $a \rightleftharpoons b$ seems to be irrelevant, except in the case of imidazole derivative (11), as demonstrated by the visible spectra of compounds III, V, VII and IX which are very similar, both in methanol and in chloroform at room temperature (Table II). The lower λ max may be attributed to the azo form and the higher to the hydrazone form, according to assignments sufficiently discussed by previous authors (9) (12-13) in several aromatic and heteroaromatic azonaphthols.

Table III summarizes the nmr spectra of the cyclic compounds in dimethylsulfoxide-d_6 and trifluoroacetic acid as solvents. First, it may be observed that in dimethylsulfoxide the signal of proton H_7 occurs at analogous chemical shifts in II, IV, VIA and VIB. The paramagnetic deshielding of this proton by the neighbour lone pair of electrons on nearest nitrogen atom is stressed and related with that observed by Donkt *et al.* (14) in benzoquinoleines. In contrast, the proton H_7 in the *v*-triazole derivative occurs at higher fields; H_2 and H_3 also appear at higher fields and the coupling constant $J_{2\,3}$, greater than in compounds IV and VI, indicates major double bond character between the

(TABLE I)

Cyclization of *s*-triazole[3-azo-1]-2-naphthol by Different Means (a)

	Temperature °C	Percent of Cyclic Product after 10 minutes	after 1 hour
2*N* Hydrochloric acid	*ca.* 100	60-70	100
2*N* Sodium hydroxide	*ca.* 100	---	---
2-Butanol	108	---	10
Pyridine	116	---	---
Glacial acetic acid	118	80-90	100
Chlorobenzene	132	---	20-30
Tetrachloroethane	145	---	50-60
Ethylene glycol	197	100	

(a) Twenty-five mg. in 30 ml. of solvent.

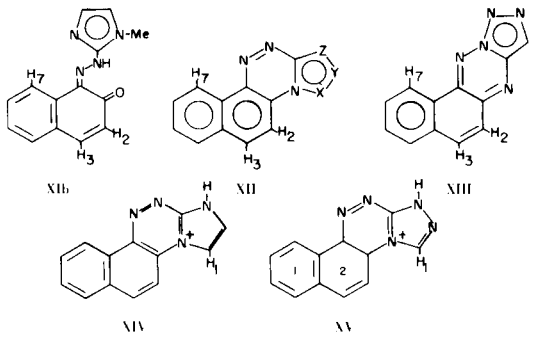
corresponding carbon atoms. The proposed structure VIIIB justifies these differences, if one considers that II, IV, VIA and VIB can be represented schematically by XII and VIIIB by XIII, and in consequence the proton H_7 of VIIIB is only under the influence of one aromatic ring. This effect is also evident in the proton H_4. Moreover, from molecular models of structures XII and XIII it is obvious that H_7 and the nitrogen atom which are responsible for the deshielding are somewhat more separated in XIII than in XII. The ultraviolet-visible spectrum of VIIIB in several solvents also differs from the corresponding to II, IV, VIA and VIB; for example, VIIIB in methanol shows a maximum at 438 nm (15), as long as II, IV, VIA and VIB have the greater λ max at 388, 398, 388 and 386 nm, respectively.

(TABLE II)

Visible Absorption Spectra of the Open Chain Products

	In Methanol λ max in nm (log ε)	In Chloroform λ max in nm (log ε)
XI	476 (3.89)	480 (4.10)
	422 (3.90)	430 (3.86)
III	445 (3.76)	445 (3.86)
	406 (3.83)	409 (3.87)
V	450 (3.99)	456 (4.08)
	410 (3.98)	420 (4.05)
VII	448 (3.91)	449 (3.95)
	413 (3.88)	412 (3.93)

Compound X affords another difficulty already mentioned: to enhance its solubility in dimethylsulfoxide it is necessary to register the nmr spectrum by raising the temperature or adding trifluoroacetic acid to the dimethylsulfoxide. In those conditions (which favours, as is known, the azido form), only one isomer is present in the spectrum, and this is presumably XB. In fact, the proton H_7 at 9.00 should suggest the structure XC, but H_2 and H_3 appear at lower fields than in the VIIIB. Also, compared with II, IV, VIA and VIB, XA must be discarded in those conditions; coupling constants $J_{2\,3}$ is moreover between the expected for XA and XC. At room temperature, however, XA predominates in non-acidic polar solvents, as demonstrated the visible spectrum of X in methanol (λ max, 406 nm), and in dimethylsulfoxide (λ max, 409 nm), which resembles these of II, IV, VIA and VIB, and differs from VIIIB (16).



XIb XII XIII

XIV XV

VIA and VIB were identified by the knowledge of the nmr spectra of triazolo-*as*-triazines (10) and triazolopyrimidines (17). Thus, the compound in which H_1 resonates to 8.93 ppm has the structure VIA. Differences between 10.23 and 8.93, higher than that expected (*ca.* 0.8 ppm), may be attributed to ring currents originated in the naphthalenic system over the H_1 proton in VIB.

H_0 and H_1 assignments in II are resolved by comparison with VIA and VIB. In the imidazo[1,2-*a*]pyrimidine system (18) downfield signals were attributed to proton H_0 but the difference between H_0 and H_1 is small (*ca.* 0.1 ppm). Nevertheless, in this case, H_1 is the more downfield shifted proton for its approach to naphthalene ring.

Attribution of H_2 and H_3, in some cases, is not problematic because long-range coupling with H_7 allows to distinguish it (small $J_{3\,7}$ is even greater than the inappreciable $J_{2\,7}$, and signals corresponding to H_3 are more broad).

Protonation in trifluoroacetic acid often displaces signals downfield. However, some exceptions must be justified. First, if compounds II, IV, VIA and VIB are compared, an anomalous shift of H_7 in IV is observed. As is presumable, in opposition to II, VIA and VIB, protonation takes place in IV over one N of the triazine ring, instead of over N azolic. The chemical shift of H_2 in IV is also in good agreement: it is analogous to δ H_2 in VIA and at downer fields than H_2 of II and VIB where protonation practically does not affect δ H_2 (19). The slight shift of H_1 toward higher fields in II and VIB (represented by XIV and XV, respectively), probably as a results of electronic density decreases into ring 2 when aromaticity of triazine ring increases, is also interesting.

EXPERIMENTAL

Melting points were determined on a Buchi apparatus and are uncorrected. Elemental analysis were carried out by the Service of "Patronato Juan de la Cierva", C.S.I.C., Barcelona. The infrared and visible spectra have been obtained in Perkin-Elmer 457 and 124 instruments, respectively. The magnetic resonance spectra have been enregistered in a Perkin-Elmer R-12A and, in some cases, repeated in a Varian A-60 and HA-100 instruments of the "Laboratoire de Synthèse et Etude Physicochimique des Hétérocycles Azotes", Montpellier.

Aminoazoles.

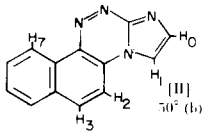
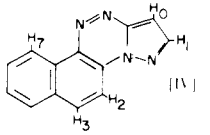
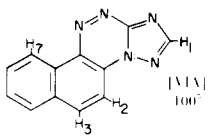
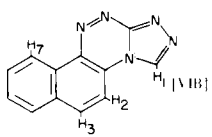
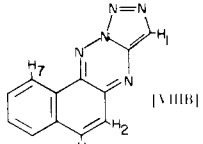
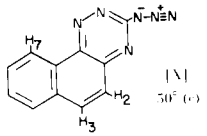
2-Aminoimidazole was prepared according to (20) but using aminoacetaldehyde dimethylacetal as starting material. 2-Amino-1-methylimidazole was obtained by the method of Storey *et al.* (21), 3(5)aminopyrazole by the Dorn *et al.* system, and 4(5)amino-*v*-triazole according to the Hoover and Day method (23). 3(5)Amino-*s*-triazole and 5-aminotetrazole were purified commercial products.

Azo Derivatives.

The preparation of I, XI, III, V, VII and IX was carried out by a common method: the amines (10-20 mmoles) were diazotized in 15-30 ml. of 4*M* sulfuric acid with slight excess of sodium nitrite dissolved in a few ml. of water, at *ca.* -5°. As an exception, 2-aminoimidazole was diazotized between -15° and -10°, and aminotetra-

(TABLE III)

Nmr Spectra (a)

	Dimethylsulfoxide-d_6							Trifluoroacetic Acid						
	H_0	H_1	H_2	H_3	$H_4H_5H_6$	H_7		H_0	H_1	H_2	H_3	$H_4H_5H_6$	H_7	
 [III] 50° (b)	8.26(d)	8.95(d)	8.52(s)	8.52(s)	8.3-7.8(m)	9.42(m)	J_{01} = 1.2	8.51(d)	8.87(d)	8.43(d)	8.94(d)	8.3-8.1(m)	9.65(m)	J_{01} = 2.5 J_{23} = 9.2
 [IV]	7.64(d)	8.53(d)	8.45(d)	8.62(d)	8.3-7.8(m)	9.40(m)	J_{01} = 2.5 J_{23} = 9.0	7.87(d)	8.93(d)	8.79(d)	8.93(d)	8.3-8.1(m)	9.24(m)	J_{01} = 2.5 J_{23} = 9.2
 [VIA] 100°	---	8.93(s)	8.40(d)	8.65(d)	8.3-7.8(m)	9.42(m)	J_{23} = 9.0	---	9.42(s)	8.72(d)	9.03(g)	8.3-8.2(m)	9.70(m)	J_{23} = 9.2 J_{37} = 1.0
 [VIB]	---	10.23(s)	8.45(d)	8.70(d)	8.3-8.0(m)	9.38(m)	J_{23} = 9.0	---	10.12(s)	8.45(d)	8.96(d)	8.3-8.1(m)	9.65(m)	J_{23} = 9.2
 [VIIIB]	---	8.72(s)	7.58(d)	8.08(d)	7.9-7.8(m)	8.88(m)	J_{23} = 9.7	---	9.22(s)	7.81(d)	8.40(d)	8.2-8.0(m)	9.28(m)	J_{23} = 9.7
 [X] 50° (c)	---	---	7.80(d)	8.40(d)	8.1-7.9(m)	9.00(m)	J_{23} = 9.5	---	---	7.92(d)	8.48(d)	8.1-8.0(m)	9.25(m)	J_{23} = 9.5

(a) Chemical shifts in ppm (δ) with TMS as the internal reference and at 32°, otherwise are indicated; multiplicity within parenthesis; coupling constants in hertz. (b) The spectrum is identical at 32°. (c) Signals are the same in dimethylsulfoxide at 80° and in dimethylsulfoxide with trifluoroacetic acid at 32°.

zole was handled in more dilute solutions, to guard against possible explosions. These solutions were dropped into β-naphthol (1.44-2.88 g.) in excess of 10% aqueous sodium hydroxide magnetically stirred, with external cooling. Then, the excess of base was neutralized with diluted sulfuric acid until adequate *p*H (depending on the acidity of the heterocycle) was reduced. The precipitates were recovered and dried *in vacuo*. The yields were 65-75% of I (including product transformed into II) and 85-90% of XI and III; V, VII and IX were obtained with almost quantitative yields. The samples for analytical data were purified by column chromatography over silica gel. To avoid its easy cyclization, I was purified by cellulose column chromatography using mixtures of *n*-hexane and methylene chloride as eluents.

I, m.p. 270-271° (at *ca.* 170° the product turns yellow, then melts at the temperature of II); ir ν max cm^{-1} in potassium bromide: 1624 (C=O).

Anal. Calcd. for $C_{13}H_{10}N_4O$: C, 65.53; H, 4.23; N, 23.51. Found: C, 65.88; H, 4.11; N, 23.82.

XI, m.p. 134-137°; ir ν max cm^{-1} in potassium bromide: 1622 (C=O).

Anal. Calcd. for $C_{14}H_{12}N_4O$: C, 66.64; H, 4.80; N, 22.21. Found: C, 66.42; H, 4.93; N, 22.45.

III, m.p. 193-194°; ir ν max cm^{-1} in potassium bromide: 1628 (C=O).

Anal. Calcd. for $C_{13}H_{10}N_4O$: C, 65.53; H, 4.23; N, 23.51. Found: C, 65.60; H, 4.37; N, 23.56.

V, m.p. 269-272° (at *ca.* 220° the product takes yellow colour and had a m.p. near to VIA), lit. (24) 225°; ir ν max cm^{-1} in potassium bromide: 1626 (C=O).

Anal. Calcd. for $C_{12}H_9N_5O$: C, 60.24; H, 3.79; N, 29.28. Found: C, 60.22; H, 3.75; N, 29.37.

VII, m.p. 175-176° dec., (25); ir ν max cm^{-1} in potassium bromide: 1629 (C=O).

Anal. Calcd. for $C_{12}H_9N_5O$: C, 60.24; H, 3.79; N, 29.28. Found: C, 60.30; H, 3.81; N, 29.32.

IX, m.p. 184-186° dec., lit. (26) 165°; ir ν max cm^{-1} in potassium bromide: 1625 (C=O).

Anal. Calcd. for $C_{11}H_8N_6O$: C, 54.99; H, 3.35; N, 34.99. Found: C, 54.90; H, 3.32; N, 35.18.

In contrast to cyclic products, all these open-chain products gives coloured complexes with 1% methanolic ferric chloride.

Nahptho[2,1-*e*]imidazolo[2,1-*c*]-*as*-triazine (II).

The precipitate obtained from 2-diazoimidazole (1.32 g. of 2-aminoimidazole sulfate) and 2-naphthol was heated in ethanol. Rapid change in colour was observed. The solvent was evaporated and the solid dissolved in chloroform. This solution was washed with aqueous sodium hydroxide, then with water, and finally dried over anhydrous magnesium sulfate. Evaporation of solvent gave 1.36 g. (62% of yield referred to the amine) of II, m.p. 270-271°, ir ν max cm^{-1} in potassium bromide: 3140m, 3100w, 3050w, 1600s, 2576s, 1529s, 1478s, 1454s, 1402s, 1330s, 1320s, 1310s, 1128s, 898s, 840s, 764s, 753s.

Anal. Calcd. for $C_{13}H_8N_4$: C, 70 89; H, 3.66; N, 25.44. Found: C, 70.92; H, 3.50; N, 25.61.

Naphtho[2,1-*e*]pyrazolo[5,1-*c*]-*as*-triazine (IV).

Compound III (0.66 g.) in 50 ml. of glacial acetic acid was refluxed during 20-30 minutes, until a change in colour was observed. The solvent was evaporated to dryness and the residue recrystallized from carbon tetrachloride giving IV (95%), m.p. 193-194°, lit. (2) 192-194°; ir ν max cm^{-1} in potassium bromide: 3120m, 3080w, 1590s, 1568s, 1532s, 1430s, 1406s, 1175s, 1137s, 819s, 799s, 783s, 750s, 730s.

Naphtho[2,1-*e*]-*s*-triazolo[5,1-*c*]-*as*-triazine (VIA).

Compound V (1.00 g.) was refluxed either overnight in methanol or for one hour in glacial acetic acid. The solvent was eliminated and the residue recrystallized in ethanol giving VIA (90%), m.p. 272-274°, ir ν max cm^{-1} in potassium bromide: 3092m, 3070w, 1590s, 1532s, 1470s, 1445s, 1402s, 1393s, 1335s, 1315s, 1285s, 1250s, 1246s, 1195s, 1133s, 845s, 765s.

Anal. Calcd. for $C_{12}H_7N_5$: C, 65.15; H, 3.18; N, 31.66. Found: C, 65.33; H, 3.10; N, 31.82.

Naphtho[2,1-*e*]-*s*-triazolo[3,4-*c*]-*as*-triazine (VIB).

Compound V (1.00 g.) was refluxed in 50 ml. of methanol and 5 ml. of concentrated sulfuric acid for 3-4 hours. The solution was neutralized with aqueous sodium hydroxide and concentrated *in vacuo*. The precipitate was collected and washed with aqueous sodium hydroxide, then with water, and finally dried, giving 0.84 g. (90%) of VIA and VIB mixture, which were separated by column chromatography over silica gel: VIA was eluted with benzene/methylene chloride and methylene chloride, the more polar VIB with chloroform and chloroform/ethanol 98/2. About 70% of mixture consists in VIB, m.p. 310-312°, ir ν max cm^{-1} in potassium bromide: 3100m, 3060w, 1590s, 1573s, 1522s, 1462s, 1383s, 1344s, 1320s, 1178s, 1095s, 1030s, 968s, 840s, 755s.

Anal. Calcd. for $C_{12}H_7N_5$: C, 65.15; H, 3.18; N, 31.66. Found: C, 65.22; H, 3.20; N, 31.81.

Naphtho[2,1-*e*]-*v*-triazolo[1,5-*b*]-*as*-triazine (VIIIB).

a) Compound VII (0.60 g.) was refluxed during two days in methanol. The solution was evaporated to dryness and the residue dissolved in methylene chloride. This solution was washed with 10% aqueous sodium hydroxide then dried and concentrated. Addition of *n*-hexane gave 0.45 g. (80%) of VIIIB, m.p. 198-200° dec; ir ν max cm^{-1} in potassium bromide: 3100w, 1600s, 1512m, 1444s, 1357s, 1332s, 1298s, 1286s, 1268s, 1245s, 1220s, 1085s, 1000s, 943s, 828s, 760s.

Anal. Calcd. for $C_{12}H_7N_5$: C, 65.15; H, 3.18; N, 31.66. Found: C, 65.10; H, 3.22; N, 31.86.

b) Compound VII (0.60 g.) was heated at 150-160° in 30 ml. of ethylenglycol during 15 minutes. An identical volume of 10% aqueous sodium hydroxide was added and the mixture extracted with methylene chloride. The resulting solution was concentrated and columnated over silica gel. Compound VIIIB was separated (60-65%) but VIIIA was not obtained.

The cyclization of VII by refluxing it in glacial acetic acid also gives VIIIB as major product. In methanol/sulfuric acid or in 2*M* sulfuric acid at 50-60° no isolation of VIIIA was achieved.

Nahptho[2,1-*e*]tetrazolo[5,1-*c*]-*as*-triazine (X).

Compound IX (1.00 g.) was cyclized by refluxing it either overnight in methanol with a few drops of sulfuric acid or in 2*M* sulfuric acid for two hours. Solutions were basified with excess of 10% aqueous sodium hydroxide and treated with chloroform (previous elimination of methanol *in vacuo* in the first case). In both the same product was obtained evaporating the dried chloroform extract, with similar yields (80-85%), m.p. 190-191° dec.; ir ν max cm^{-1} in potassium bromide: 3085w, 3050w, 1600s, 1570w, 1548s, 1517s, 1452s, 1411s, 1353s, 1280s, 1236s, 1078s, 985s, 383s, 752s; in chloroform: 2160s, 2130s, 1380s; in dimethylsulfoxide: 2140w, 1600s, 1540s, 1280s.

Anal. Calcd. for $C_{11}H_6N_6$: C, 59.45; H, 2.72; N, 37.82. Found: C, 59.40; H, 2.81; N, 37.97.

Cyclization of Compound V by Different Means.

Compound V (25 mg.) was added in various flasks containing 30 ml. of different liquids at reflux (see Table I). After 10 minutes solutions were cooled and the solvent eliminated at reduced pressure. The non-cyclized product was separated with the help of 2*N* aqueous sodium hydroxide and the residue, when dried, was weighed. Solutions refluxed during 1 hour were handled analogously.

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