# REACTION OF 2,2',3,3'-TETRACHLORO-6,6'-DIQUINOXALYL WITH NUCLEOPHILIC REAGENTS

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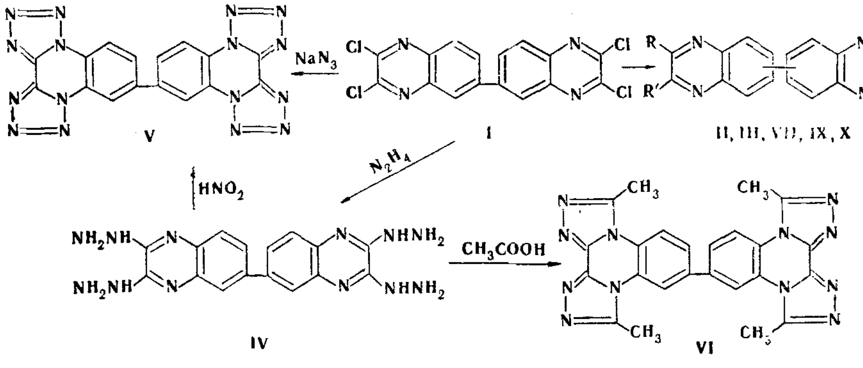
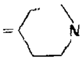
The corresponding tetrasubstituted diquinoxalyls were synthesized by reaction of 2,2',3,3'-tetrachloro-6,6'-diquinoxalyl with sodium methoxide, piperidine, and hydrazine. Tetrahydrazinodiquinoxalyl reacts with nitrous acid to give tetrakistetrazolodiquinoxalyl, which is also obtained by the action of sodium azide on tetrachlorodiquinoxalyl. Tetrahydrazinodiquinoxalyl undergoes cyclization with acetic acid to give tetrakistriazolodiquinoxalyl. A competitive effect of nucleophiles [CN and $N(CH_3)_2$] was observed in the reaction of tetrachlorodiquinoxalyl with cuprous cyanide in dimethylformamide.

2,2',3,3'-Tetrachloro-6,6'-diquinoxalyl (I) [1] is used for the synthesis of thermally stable polymers [2, 3] by condensation with aromatic tetrafunctional hydroxy, mercapto, and amino derivatives.

The extremely high lability of the chlorine atoms in 2,3-dichloroquinoxaline [4] made it possible to hope that we would also be able to obtain tetrasubstituted 6,6'-diquinoxalyl derivatives free of incomplete substitution products in the reactions of I with nucleophilic reagents.

In fact, tetrasubstituted II-IV were obtained by reaction of I with excess sodium methoxide, piperidine, and hydrazine. We also obtained a tetrasubstituted product by reaction of diquinoxalyl I with sodium azide, as in the reaction of 2-chloroquinoxaline [2]. However, its IR spectrum both in the solid state and in dimethylformamide (DMF) did not have the characteristic bands (2050-2200 $cm^{-1}$) of asymmetrical stretching vibrations of an azide group; in addition, bands of vibrations of tetrazole rings (1090, 1065, and 1040 $cm^{-1}$) were observed, i.e., the product of this reaction was tetrakistetrazolo[4,5-a; 5,4-c; 4',5'-a'; 5',4'-c']-9,9'-diquinoxalyl (V).



II R = R' = R'' = $CH_3O$; III R = R' = R'' =  N– ; VII R = CN, R' = R'' = $N(CH_3)_2$; IX R = CN, R' = $N(CH_3)_2$, R'' = Cl; X R = R' = R'' = $N(CH_3)_2$

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When we changed the polarity of the solvent, we did not observe for V the ring—chain tautomerism between the open azomethine and tetrazole forms that is well known for some monoazide derivatives [6].

We also obtained the same V by the action of nitrous acid or nitrosylsulfuric acid on hydrazino derivative IV.

Tetrahydrazinodiquinoaxalyl IV can also be used in other cyclization reactions. For example, we obtained 1,1',6,6'-tetramethyltetrakis-sym-triazolo[4,5-a; 5,4-c:4'5'-a'; 5'4'-c']-9,9'-diquinoxalyl (VI) by reaction with acetic acid.

It seemed of interest to us to verify the possibility of replacing the halogen in I by a cyano group by the Rosenmund—Braun reaction [7]. In DMF solution we isolated 2,2'-(3,3')-dicyano-3,3'-(2,2')bis(dimethylamino)-6,6'-diquinoxalyl (VII) (31% yield) as the principal product. Cyano substitution evidently takes place in both rings, since the same reaction with 2,3-dichloroquinoxaline leads to 2-cyano-3-dimethylaminoquinoxaline (VIII). In addition to product VIII, we detected the copper complex of tetraquinoxalinoporphyrazine, which was identical to the complex obtained previously in [8]; this complex is evidently formed by subsequent transformation of the intermediate 2,3-dicyanoquinoxaline.

In addition to VIII, we isolated incomplete substitution product IX in 6% yield from the products of the reaction of I with cuprous cyanide. 2,2',3,3'-Tetrakis(dimethylamino)-6,6'-diquinoxalyl (X) is obtained when I is refluxed with DMF in the absence of cuprous cyanide.

The conversions to VII and VIII constitute the first example of simultaneous reaction of halo derivatives of quinoxaline with two competitive nucleophiles: dimethylamino derivatives ([9], for example) or nitriles [7] were previously obtained by this reaction.

## EXPERIMENTAL

The UV spectra were recorded with an SP-500 spectrophotometer. The IR spectra of KBr pellets of the compounds were recorded with a UR-20 spectrometer.

2,2',3,3'-Tetramethoxy-6,6'-diquinoxalyl (II). A 0.15-g (0.38 mmole) sample of I was dissolved by refluxing in 20 ml of toluene, and the solution was mixed with 2.3 ml of 0.836 M sodium methoxide solution. The mixture was refluxed for 7 h, after which it was cooled, and the toluene was removed by distillation. The yellow residue was washed with water and dried to give 0.14 g (98%) of a product with mp 284° (from alcohol). Found: C 63.8; H 4.7; N 14.9%. $C_{20}H_{18}N_4O_4$. Calculated: C 63.5; H 4.8; N 14.8%.

2,2',3,3'-Tetrapiperidino-6,6'-diquinoxalyl (III). A 0.15-g (0.38 mmole) sample of I was dissolved in 15 ml of freshly distilled piperidine, and the solution was refluxed for 8 h. The solvent was removed by distillation, and the residue was diluted with water. Workup gave 0.21 g (97%) of a product with mp 259-260° (from alcohol). Found: C 72.9; H 7.8; N 18.9%. $C_{36}H_{46}N_8$. Calculated: C 73.2; H 7.8; N 19.0%.

2,2',3,3'-Tetrahydrazino-6,6'-diquinoxalyl (IV). A 0.58-g (1.5 mmole) sample of I was dissolved in 30 ml of freshly distilled hydrazine hydrate, and the solution was refluxed for 12 h. It was then cooled and diluted with water, and the yellow precipitate was removed by filtration and washed with water and alcohol in a Soxhlet apparatus to give 0.49 g (96%) of a product with mp 308-309°. IR spectrum 3200 cm$^{-1}$ ($NH_2$). Found: C 50.6; H 4.9; N 44.7%. $C_{16}H_{18}N_{12}$. Calculated: C 50.8; H 4.8; N 44.4%.

Tetrakistetrazolo[4,5-a; 5,4-c:4',5'-a';5',4'-c']-9,9'-diquinoxalyl (V). A) A 0.41-g (1.4 mmole) sample of I was dissolved by heating in 30 ml of DMF and a solution of 0.31 g (4.6 mmole) of sodium azide in 2 ml of water was added dropwise. The mixture was refluxed for 6 h, after which the precipitated NaCl was removed by filtration and washed with DMF. The filtrate was diluted with water, and the yellow precipitate was washed with water to give 0.43 g (94%) of a product with mp 264° (dec., from pyridine with subsequent washing with alcohol in a Soxhlet apparatus). UV spectrum, $\lambda_{max}$ (in DMF), nm (log ε): 292 (4.34), and 323 (4.41). IR spectrum: 1090, 1065, and 1030 cm$^{-}$. Found: C 45.6; H 1.5; N 52.9%. $C_{16}H_6N_{16}$. Calculated: C 45.5; H 1.4; N 53.1%. The product decomposed on standing.

B) A 0.26-g (0.686 mmole) sample of IV was dissolved with cooling in 8 ml of concentrated $H_2SO_4$, 0.38 g (5.5 mmole) of sodium nitrite was added, and the mixture was stirred for 6 h. It was then poured over ice, and the aqueous mixture was worked up to give 0.16 g (69%) of V.

1,1',6,6'-Tetramethyltetrakis-sym-triazolo[4,5-a; 5,4-c:4',5'-a'; 5',4'-c']-9,9'-diquinoxalyl (VI). A 0.19-g (0.5 mmole) sample of IV was refluxed for 4 h in 25 ml of acetic acid, after which the mixture was diluted with water and filtered. The precipitate was washed with water and alcohol in a Soxhlet apparatus to give 0.22 g (88%) of a product with mp >300°. Found: C 60.4; H 34.9%. $C_{24}H_{20}N_{12}$. Calculated: C 60.7; H 3.8; N 35.4%.

Reaction of 2,2'3,3'-Tetrachloro-6,6'-diquinoxalyl with Cuprous Cyanide. A mixture of 0.83 g (2 mmole) of I, 0.9 g (10 mmole) of cuprous cyanide, and 30 ml of DMF was refluxed in a steam of nitrogen for 8 h, after which it was evaporated to a small volume and treated with 5% $NH_4OH$. The precipitate was removed by filtration, and the red-brown substance was washed with water and heated with 35 ml of dilute aqueous ethylenediamine solution to 50°. It was then cooled and extracted with benzene. The extract was evaporated and chromatographed twice on Silufol with elution with chloroform-petroleum ether (1:40). The first fraction contained 0.05 g (6%) of IX ($R_f$ 0.14) with mp 218-222° [from heptane–benzene (2:1)]. IR spectrum: 2230 cm$^{-1}$ (CN). Found: C 62.7; H 3.4; N 25.0%. $C_{20}H_{12}ClN_7$. Calculated: C 62.3; H 3.1; N 25.4%. The second fraction contained 0.25 g (31%) of yellow crystals of VII ($R_f$ 0.07) with mp 247-252° (from benzene). IR spectrum: 2230 cm$^{-1}$ (CN). Found: C 66.7; H 4.6; N 28.8%. $C_{22}H_{18}N_8$. Calculated C 67.0; H 4.6; N 28.4%. The third fraction contained 0.1 g of a red substance ($R_f$ 0.02) with mp 277-280° (from benzene). Found: C 62.1; H 4.4; N 25.4%. The structure was not established.

Reaction of 2,3-Dichloroquinoxaline with Cuprous Cyanide. A mixture of 1.36 g (15 mmole) of cuprous cyanide and 7 ml of DMF was added to a solution of 0.8 g (4 mmole) of 2,3-dichloroquinoxaline in 10 ml of DMF, and the mixture was refluxed for 8 h. It was then evaporated to a small volume, and the residual solution was heated at 40° with 10 ml of ethylenediamine in 50 ml of water for 1 h. It was then cooled and extracted with benzene. The extract was evaporated to a small volume, washed with 10% NaCl and water, dried, and chromatographed on silica gel. A mixture of chloroform and petroleum ether (100:1) eluted 0.4 g (51%) of yellow crystals of VIII with mp 117-118° (from pentane). IR spectrum: 2230 cm$^{-1}$ (CN). Found: C 66.6; H 5.2; N 28.1%. $C_{11}H_{10}N_4$. Calculated: C 66.7; H 5.1; N 28.3%. Acetone eluted 0.04 g of a substance with mp 125-130° (from benzene) that is possibly 2-dimethylaminoquinoxaline-3-carboxamide. IR spectrum: 1680 cm$^{-1}$ (CO). This substance could not be purified for analysis. The solid material (0.2 g) remaining after extraction with benzene was heated in DMSO, and the mixture was filtered to give a blue Cu complex with tetraquinoxalinoporphyrazine with $\lambda_{max}$ 715 nm [8].

2,2',3,3'-Tetrakis(dimethylamino)-6,6'-diquinoxalyl (X). A solution of 0.8 g (2 mmole) of I in 20 ml of DMF was refluxed for 27 h, after which it was cooled and diluted with water. The yellow precipitate was washed with water and chromatographed in a benzene–acetone mixture (400:1) on silica gel to give 0.44 g (51%) of a product with mp 218-220° (benzene–chloroform). Found: C 67.3; H 7.2; N 25.9%. $C_{24}H_{30}N_8$. Calculated: C 67.0; H 7.0; N 26.0%.

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