Reaction of Oxo Acid III with Diazomethane. A 50-ml sample of a standard ether solution of diazomethane (from 3 g of nitrosomethylurea) was added at 0°C to a solution of 1.32 g of the reaction mixture (after irradiation of 1.36 g of diazo compound I) in 20 ml of ether, and the resulting mixture was allowed to stand for 30 min. After the usual workup and vacuum distillation, the yield of methyl ester IV was 0.88 g (63%, based on diazo compound I).

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TRICYANOVINYLATION OF PHENOXAZINE AND PHENOTHIAZINE

B. P. Bespalov

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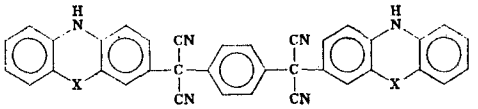
In the reaction of tricyanoethylene (TCE) with phenoxazine in DMF at 100°C, in addition to the principal reaction product — viz., 3-(tricyanovinyl)phenoxazine — 3-dicyanomethylene-3H-phenoxazine and 3-phenoxazinyl-3-(3H-phenoxazinylene)-cyanomethane are formed in small amounts. The latter two compounds were also obtained from phenoxazine and dibromomalononitrile. Phenothiazine reacts similarly with tetracyanoethylene. A reaction scheme is proposed, and in this scheme the formation of side products is explained by significant electron transfer in the tetracyanoethylene–heterocycle system. For the first time, 1,6 cleavage of HCN was detected, in which (in contrast to the known 1,6 cleavage of HCN from carbon atoms) the hydrogen is split out from the nitrogen atom.

In a previous study of the reaction of 7,7,8,8-tetracyanoquinodimethane (TCQD) with phenoxazine and phenothiazine it was found that the formation of a product of 1,6 addition to the quinoid system of TCQD (the principal product in the reaction of TCQD with anilines, phenols, pyrroles, and indoles) is observed only as an intermediate step [1]. The reaction results in the formation of I.



X=O, S I

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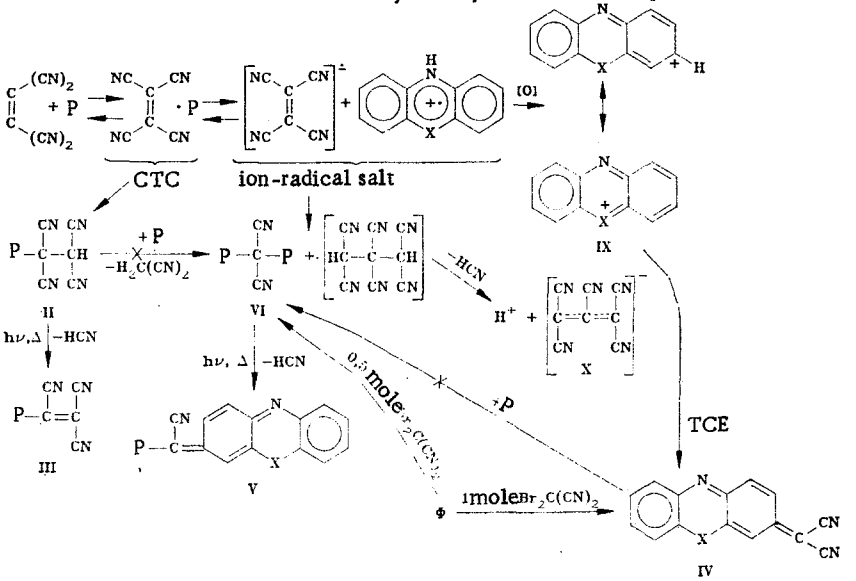
TABLE 1. Charge-Transfer Bands in the Electronic Spectra of Complexes of the Investigated Heterocycles with TCE

Heterocycle	Charge-transfer band, λ_{max}, nm	
	chloroform	acetonitrile
Phenoxazine	920	850
Phenothiazine	890	870
N-Methylphenothiazine	860	840
3,7-Dimethylphenothiazine	940	925

The reaction of phenoxazine and phenothiazine with tetracyanoethylene (TCE), which was studied in the present research, fits, with respect to the structure of the principal product, into the usual 1,2-addition reaction (similar to 1,6 addition); however, in this case compounds that are unusual for this scheme are formed in small amounts. In the first step TCE and phenoxazine give a molecular complex. The position of the charge-transfer bands for the investigated heterocycles is presented in Table 1. The subsequent reaction of TCE and phenoxazine proceeds at a satisfactory rate only in DMF at 100°C, and bands of a phenoxazine cation radical (λ_{max} = 530 nm) and a TCE anion radical (λ_{max} = 485 nm) appear in the electronic spectrum of the solution; the resulting product (II) of 1,2 addition ot TCE primarily is converted, with cleavage of HCN, to give tricyanovinylation product III. The addition of organic bases such as triethylamine accelerates this process. The catalytic action of bases both on the formation of the product of 1,2 addition to TCE and on the splitting out of HCN from it has been studied in quite some detail [2]. Thus, as a result of the reaction, III was obtained in ~65% yield; this was established on the basis of the results of elementary analysis and the mass spectrum. In order to determine the site of incorporation of the tricyanovinyl grouping in the heteroring under similar conditions we carried out the reaction of TCE with 3,7-dimethylphenothiazine. In this case we observed the formation only of a molecular complex. Consequently, the initial addition of TCE to the heteroring proceeds only in the para position with respect to the nitrogen atom of the heteroring. It should be noted that N-methylphenothiazine reacts with TCE also to give only a molecular complex. This can be explained by the fact that the N-alkyl derivatives of phenoxazine and its analogs, as noted in [3], have reduced reactivity with respect to electrophilic reagents. The decreased donor activity of N-methylphenothiazine as compared with phenothiazine also shows up in the hypsochromic shift of the band of the charge-transfer complex (CTC) with TCE (see Table 1).

General scheme of the reaction of tetracyanoethylene (TCE) with phenoxazine and phenothiazine

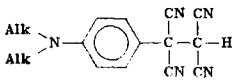


P = phenothiazine or phenoxazine;

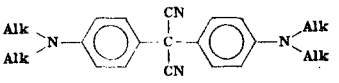
In the reaction of TCE with phenoxazine, in addition to III, we isolated chromatographically, in small amounts, two more colored compounds, red and blue, to which, on the basis of elementary analysis and spectral data, we assigned structures IV and V, respectively. In addition, in the reaction mixture we detected two other colorless compounds (according to TLC), which, upon UV irradiation with a chromatographic plate, were converted to the corresponding colored III and V. Assuming that these compounds are formed in the photochemical splitting out of HCN, we assigned structures II and VI to the colorless products.

In order to confirm the IV and V structures we obtained them by alternative synethesis by the reaction of dibromomalononitrile at a molar ratio of 1:1 in order to obtain red substance IV. When we used a twofold excess of phenoxazine, we observed the formation of a mixture of red compound IV and colorless VI, which was separated by chromatography. In the case of irradiation with UV light or heating in DMF at 100°C the isolated VI, which was identical (according to TLC) to the VI formed in the reaction medium, splits out HCN and is converted to V.

In a previous study of the reaction of TCE with N,N-dialkylanilines we obtained VII and VIII, which are similar to II and VI, respectively; it was assumed that VII is formed from a molecular charge-transfer complex (CTC), whereas VIII is formed from an ion-radical salt [2].



VII



VIII

Up until now the literature has not contained any new data that confirm or repudiate this scheme. On the basis of the results that we obtained, it is also not yet possible to draw any definite conclusions. One may only assume the formation of II from the CTC and the formation of VI from the ion-radical salt.

The formation of IV is explained by the reaction of the phenoxazine IX cation with TCE, and the cation itself is formed as a result of oxidation of the phenoxazine cation-radical by air oxygen. The reaction of the N-methylphenazine cation with TCE or malononitrile to give IV (X = N–Me) was recently observed [4]. In order to verify this scheme the phenoxazine cation-radicals were obtained by the action of copper(II) borofluoride on an acetonitrile solution of phenoxazine. In an inert atmosphere they do not react with TCE or malononitrile. After blowing of air for 2 min through a solution of the reagents or allowing the mixtures to stand in air (both with TCE and with malononitrile), IV (X = O) shows up along with the final product of the oxidation of the phenoxazine cation-radical, viz., 3H-phenoxazinyl-3-one (monitored by means of TLC). Compound IV is not formed when the reaction of TCE with phenoxazine is carried out in an inert atmosphere. On the other hand, the yield of IV increases in the case of a dry method of filling the chromatographic column, when the reaction mixture to be separated is applied to silica gel and is dried in air.

Three schemes are possible for the formation of VI. According to the first scheme, it is formed from the ion-radical salt, which exists in solution due to significant electron transfer in the TCE–heteroring system. This pathway has been previously proposed for the production of VIII in the TCE–N,N-dialkylaniline reaction, in which its yield increases as the aniline used for the reaction undergoes a decrease in its ionization potential, and, consequently, with an increase in the concentration in solution of the ion-radical salt; this was confirmed by EPR spectroscopy [2].

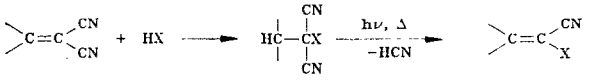
According to the second scheme, the phenoxazine adds to the dicyanomethylene carbon atom of iminoquinomethane IV to give VI. It was found that compounds VI and V are not formed when IV is heated with phenoxazine in DMF at 100°C. Thus V and IV are formed independently.

According to the third scheme, VI is formed from II due to splitting out from the latter of a malononitrile anion and the reaction of the carbonium ion with a second phenothiazine molecule. Since II is formed as a result of the reaction of the hetercycle with TCE only in trace amounts, we selected VII (Alk = Et) for the experiment. Heating of this compound in DMF in the presence of N,N-diethylaniline leads rapidly to 4-tricyanovinyl-N,N-diethylaniline; however, it is impossible to detect even traces of VIII, although it is easily detected by TLC by means of irradiation, for several seconds, of a chromatographic place with the full light of a mercury lamp. Compound VIII on the adsorbent surface, under

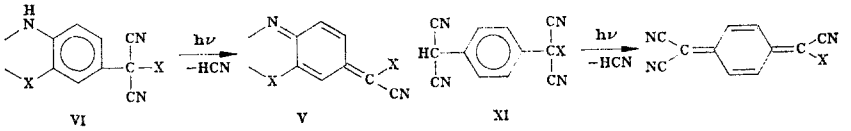
the influence of UV light, splits out CN, thereby undergoing transformation to a green diphenylmethane dye cation. It follows from what we have stated above that the formation of VI also does not take place via the third scheme. Thus we are left with the first scheme, in which the malononitrile, which is split out in the formation of VI from the ion-radical salt, reacts with TCE and is visible on the chromatogram in the form of a pentacyanopropene anion. Malononitrile has similarly been detected in the formation of VIII in the reaction of TCE with dialkylanilines [2].

The formation of small amounts of compounds of the IV and V type is also observed in the case of the reaction of phenothiazine with TCE.

It should be noted that, ordinarily in light- or heat-sensitive reaction products formed in the reaction of polycyanine acceptors with neutral nucleophilic donors (ND) under irradiation with UV light or under thermal action, HCN is split out to give intensely colored products of substitution of one nitrile group by the nucleophile:



In the case of VI we observed a new instance of this sort of transformation in which splitting out of hydrogen via splitting out of HCN occurs from the nitrogen atom. Yet another peculiarity of this system is the high thermal sensitivity, as compared with the thermal sensitivity of products of 1,2 addition to TCE, in which splitting out of HCN takes place from the vicinal carbon atoms.



VI V XI

The carbon analog of the light-sensitive VI system, viz., the product of 1,6 addition of HX to 7,7,8,8-tetracyanoquinodimethane (XI), in contrast to VI, has virtually no thermal sensitivity, and the splitting out of HCN from it usually proceeds photochemically.

EXPERIMENTAL

The tetracyanoethylene was purified by sublimation *in vacuo*, and the phenoxazine, phenothiazine, N-methylphenothiazine, and 3,7-dimethylphenothiazine were purified by recrystallization from benzene with activated charcoal. The UV spectra of 96% ethanol solutions of the compound were recorded with a Hitachi EPS-3T spectrophotometer. The IR spectra of KBr pellets were recorded with a UR-20 spectrometer. Chromatography was carried out on L-40-100 μ silica gel, and TLC was carried out on Silufol chromatographic plates.

3-(Tricyanovinyl)phenoxazine (IIIa). A mixture of 0.4 g (3.1 mmoles) of TCE and 0.57 g (3.1 mmoles) of phenoxazine in 3 ml of DMF was heated at 100°C for 3 h, after which the mixture was allowed to stand overnight at room temperature. The precipitate was removed by filtration and dried to give 0.48 g (54.3%) of needles with a green metallic luster, which, after recrystallization from acetone, gave a product with mp 267°C (dec.). IR spectrum: 2210 (C≡N) and 3500 cm^{-1} (N–H). UV spectrum, λ_{max}: 330 and 650 nm. Found: C 71.7; H 2.8; N 19.8%; M 284. $C_{17}H_8N_4O$. Calculated: C 71.8; H 2.8; N 19.7%. The DMF mother liquor was poured into water, and the precipitate was removed by filtration, dried, and chromatographed on silica gel by elution with benzene to give, in succession, three colored compounds: a red compound [0.045 g (5.3%)], 3-dicyanomethylene-3H-phenoxazine (IVa) [mp 266.5-267°C (acetonitrile); IR spectrum: 2210 cm^{-1} (C≡N); UV spectrum λ_{max}: 260 and 550 nm; Found: C 73.9; H 2.8; N 17.3%; M 245. $C_{15}H_7N_3O$. Calculated: C 73.5; H 2.9; N 17.1%], a blue compound, 0.090 g (10.4%), identified as 3-(tricyanovinyl)phenoxazine, identical to the compound obtained above, and another blue compound, 0.030 g (4.8%, identified as (3-phenoxazinyl)-[3-(3H-phenoxazinylidene)cyanomethane (V), mp 284-285°C (acetonitrile); IR spectrum: 2200 (C≡N) and 3350 cm^{-1} (N–H); UV spectrum, λ_{max}: 330, 440, and 670 nm; Found: C 77.9; H 3.7; N 10.3%; M 401. $C_{26}H_{15}N_3O_2$. Calculated: C 77.8; H 3.8; N 10.5%].

3-(Tricyanovinyl)phenothiazine (IIIb). A mixture of 0.4 g (3.1 mmoles) of TCE and 0.62 g (3.1 mmoles) of phenothiazine in 3 ml of DMF was heated at 100°C for 3 h, after which it was allowed to stand overnight at room temperature. The precipitate was removed by filtration and dried to give a 0.5 g (53.3%) of blue needles, which, after recrystallization

from acetonitrile, had mp 231-232°C. IR spectrum: 2220 (C≡N) and 3330 cm^{-1} (N–H). UV spectrum, λ_{max}: 330 and 650 nm. Found: C 68.2; H 3.0; N 18.8%. $C_{17}H_8N_4S$. Calculated: C 68.0; H 2.7; N 18.7%.

3-Dicyanomethylene-3H-phenoxazine (IVa). A 1.89-g (5.5 mmoles) sample of the solid complex of dibromomalononitrile with potassium bromide [5] was added all at once with stirring to a suspension of 1 g (5.5 mmoles) of phenoxazine and 0.61 g (11 mmoles) of potassium oxide in 10 ml of acetonitrile, after which the solution was stirred at room temperature for 1 h and then poured into 200 ml of cold water. The precipitate was removed by filtration, dried, and recrystallized twice from a small amount of benzene to give 0.6 g (45.1%) of a product with mp 256-257°C. According to TLC and the IR spectrum, the substance was identical to the compound isolated in the reaction of TCE with phenoxazine.

Di(3-phenoxazinyl)malononitrile (VI). A 0.95-g (2.25 mmoles) sample of the solid complex of dibromomalononitrile with potassium bromide was added in small portions with stirring in the course of 10 min to a suspension of 1 g (5.5 mmoles) of phenoxazine and 0.61 g (11 mmoles) of potassium oxide in 10 ml of acetonitrile, after which the solution was stirred at room temperature for 1 h. The inorganic mixture and the precipitated IV were removed by filtration, and the mother liquor was chromatographed on silica gel by elution with benzene–acetone (4:1) with protection of the column and the solutions from direct sunlight to give 0.1 g of red IV and 0.4 g of colorless VI, which, according to TLC, was identical to VI detected in the reaction mixture, for a total yield (34.2%) of a substance with mp 118-120°C (heptane). Found: C 75.6; H 4.0; N 12.9%. $C_{27}H_{16}N_4O_2$. Calculated: C 75.7; H 3.8; N 13.1%.

3-Phenoxazinyl-[3-(3H-phenoxazinylene)]cyanomethane (V). Thermal production from VI. A 0.1-g sample of VI in 5 ml of DMSO was stirred at 100°C for 10 min, after which the mixture was cooled and poured into 100 ml of water. The precipitate was removed by filtration, washed with water, dried, and recrystallized from acetonitrile to give 0.5 g (53.4%) of a product with mp 283-284°C. The IR spectrum was identical to the spectrum of V obtained from the reaction mixture.

Photochemical production from VI. A 0.1-g sample of VI was dissolved in 5 ml of acetonitrile, and the solution was irradiated with stirring with the UV light of a PRK-2 lamp at a distance of 15 cm from the surface of the solution until the starting compound in it vanished according to TLC (2h). The precipitated V was removed by filtration to give 0.8 g (85.4%) of a product with mp 238-284°C. The IR spectrum of the product was identical to the spectrum of V obtained from the reaction mixture.

3-Dicyanomethylene-3H-phenothiazine (IVb). A 1.89-g (5.5 mmoles) sample of the solid complex of dibromomalononitrile with potassium bromide was added all at once with stirring to a suspension of 1.1 g (5.5 mmoles) of phenothiazine and 0.61 g (11 mmoles) of calcium oxide in 10 ml of acetonitrile, after which the solution was stirred at room temperature for 1 h. It was then poured into 200 ml of cold water, and the precipitate was removed by filtration, dried, and recrystallized from acetonitrile–benzene (1:1) to give 0.55 g (38.2%) of a product with mp 293-295°C. IR spectrum: 2220 (C≡N) and 3330 cm^{-1} (N–H). UV spectrum, λ_{max}: 250 and 590 nm. Found: C 68.8; H 2.8; N 16.0%; M 261. $C_{18}H_7N_3S$. Calculated: C 69.0; H 2.7; N 16.1%.

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