REACTION OF 1-VINYLPYRAZOLES WITH TETRACYANOETHYLENE

L. A. Es'kova, E. V. Petrova,
V. K. Turchaninov, E. S. Domnina, and
A. V. Afonin

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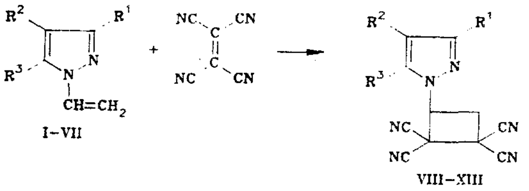
It was shown that in the reaction of tetracyanoethylene with 1-vinylpyrazoles in aprotic solvents, one of the first stages involves the formation of π—π complexes. The final products of the reaction are 1-(2,2,3,3-tetracyano-1-cyclobutyl)pyrazoles.

The reaction of tetracyanoethylene with nitrogen-containing heterocyclic compounds can occur in several ways. For example, indole [1], 1-phenyl-3-R-5-aminopyrazoles [2], methyl- and phenyl-substituted imidazoles [3], are 'tricyanovinylated' at specific positions of the heterocyclic ring. The imidazoles react to give imidazole 1,1,2,3,3-pentacyanopropenide [3] and also form complexes [4]. N-Vinylindole [5], N-vinylcarbazole [6], and 1-phenyl-4-vinylpyrazole [7] react with tetracyanoethylene under very mild conditions to give tetracyanocyclobutane derivatives. No work has been carried out on the reaction of tetracyanoethylene with N-vinylazoles containing competing reaction centers.

In the present work, the reaction of tetracyanoethylene with 1-vinylindazole (I), 1-vinylpyrazole (II), and its 3-methyl- (III), 5-methyl- (IV), 3,5-dimethyl- (V), 4-bromo-(VI), and 3,5-dimethyl-4-nitro derivatives (VII) has been studied. It was found that for the vinylpyrazoles I-VI, the reaction gives principally [2+2]-cyclo compounds. The 1-(2,2,3,3-tetracyano-1-cyclobutyl)pyrazoles (VIII-XIII) were obtained in 81-89% yield,



I, VIII $R^2+R^3=(CH)_4$, $R^1=H$; II, IX $R^1=R^2=R^3=H$; III, X $R^1=CH_3$, $R^2=R^3=H$;
IV, XI $R^1=R^2=H$, $R^3=CH_3$; V, XII $R^1=R^3=CH_3$, $R^2=H$; VI, XIII $R^1=R^3=H$, $R^2=Br$;
VII $R^1=R^3=CH_3$, $R^2=NO_2$

The vinylpyrazoles I and V reacted with tetracyanoethylene in benzene at room temperature; for the vinylpyrazoles III and IV it was necessary to heat the reactants to 80°C. The unsubstituted 1-vinylpyrazoles (II) did not give a cycloaddition product even after refluxing for 24 hours. Using a more polar solvent such as THF or without a solvent, excess vinylpyrazoles II—IV gave high yields of the corresponding 1-(2,2,3,3-tetracyano-1-cyclobutyl) pyrazoles (I-XI) at room temperature. Under the conditions employed, the nitropyrazole VII did not react with tetracyanoethylene to give a [2+2]-cycloaddition product. For the bromopyrazole VI, the yield of final product was 2-5%.

In the IR, compounds VIII-XIII absorb at 2260-2200 cm^{-1} (C≡N), and do not absorb at 1650-1640 cm^{-1} (C═C bond). In the PMR spectra of compounds VIII—XIII, in addition to signals from the heterocyclic protons there is a system of signals typical of cyclobutane derivatives (Table 1).

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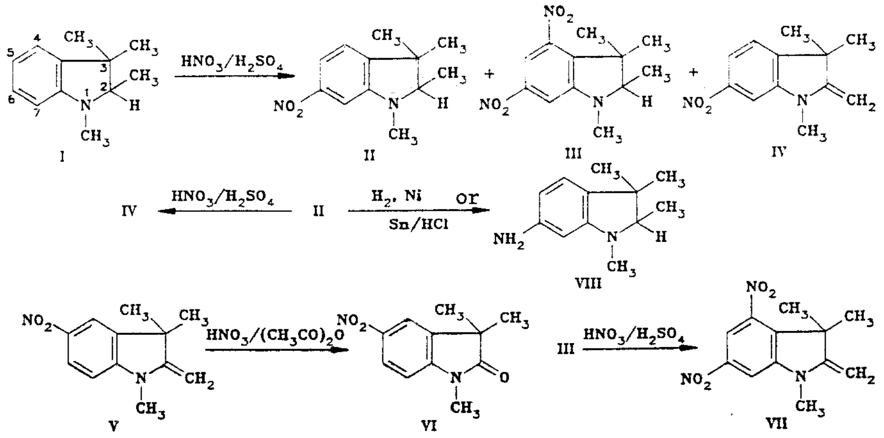
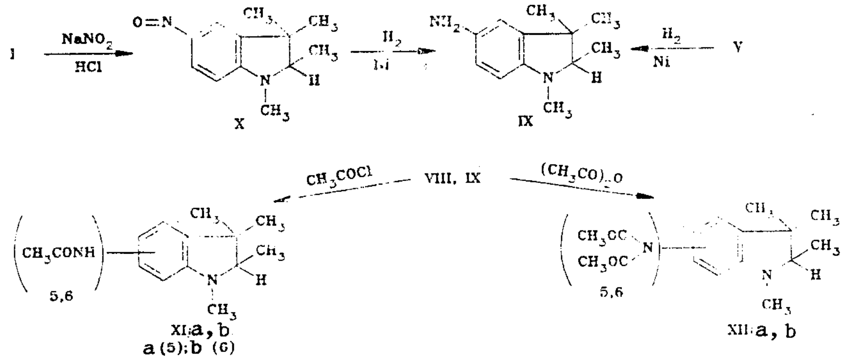


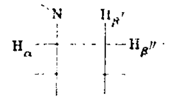
Diluting the nitrating mixture with water increased the yield of the indoline IV; when 75% sulfuric acid was used, an almost quantitative yield was obtained. In one case, compound III could not be isolated; possibly it is formed not by nitration of the indoline II, but by nitration of the unsaturated 1,2,3,3-tetramethyl-4-nitroindoline. In this compound, because of the proximity of a bulky group, the nitro group is removed from conjugation with the benzene ring [4], diminishing its electron-withdrawing properties; normally, a second nitro group should be introduced as easily as the first. Other attempts to introduce a second nitro group into mononitroindoline were also unsuccessful. For example, nitration in acetic anhydride of the available indoline V [5], resulted not in the introduction of a second nitro group, but to oxidation to the oxyindole VI. Examples of similar oxidation reactions of 2-methyleneindolines are described in the monograph [6]. Attempts to nitrate the indoline II, using methods of nitration which are used for the preparation of dinitrodimethylanilines from meta-nitrodimethylaniline [7, 8], gave only the oxidation product IV. The indoline IV was unaffected by attempts to introduce a second nitro group by these methods. The dinitroindoline III was also oxidized by a mixture of nitric and 75% sulfuric acid to 2-methyleneindoline VII, previously unobtainable by classical Fischer cyclization [9].

The dinitroindolines VII and III are very weakly basic, they do not dissolve in concentrated hydrochloric acid and do not give quaternary salts with p-toluenesulfonic acid in benzene. The nitroindoline II was reduced with hydrogen on Raney nickel, or tin and hydrochloric acid to 6-aminoindoline VIII. The isomeric 5-aminoindoline IX can be obtained either by reduction of the nitroso derivative of the tetramethylindoline X, or by the one-stage reduction of the nitro group and the double bond in 5-nitro-2-methyleneindoline V. The 6-aminoindoline VIII is a colorless oil which can be distilled in vacuum, and the 5-aminoindoline IX is a crystalline substance, which quickly darkens in air. They are readily converted to the monoacetyl (XI a and b) and diacetyl (XII a and b) derivatives by the usual methods.



The structures of all the compounds, including the site of introduction of the nitro group into the indolines II-IV, was confirmed from the PMR spectra of the indolines (Table 1). Thus, the presence of a meta-constant for aromatic proton signals is characteristic for the indolines III and V. The spectral data for the starting indolines are given in [1, 5].

TABLE 1. Compounds VIII–XIII



Compound	Empirical formula	mp, °C	Chemical shift, ppm			Coupling constant			Yield, %
			$H_{\beta'}$	$H_{\beta''}$	H_α	$^2J_{\beta'\beta''}$	$^3J_{\beta'\alpha}$	$^3J_{\beta''\alpha}$	
VIII	$C_{15}H_8N_6$	210...211	3,96	4,49	6,65	14,0	11,1	9,7	81
IX	$C_{11}H_6N_6$	173...174	3,98	4,36	6,23	13,9	9,2	8,8	86
X	$C_{12}H_8N_6$	151...152	3,93	4,30	6,09	13,19	9,1	9,3	70
XI	$C_{12}H_8N_6$	162...163	3,85	4,39	6,19	13,7	9,1	9,3	84
XII	$C_{13}H_{10}N_6$	148...150	3,80	4,37	6,07	13,5	9,1	9,3	89
XIII	—	—	4,06	4,35	6,27	14,1	9,4	9,4	—

TABLE 2. Ionization Potentials of Pyrazoles and Charge Transfer Bands of Their Tetracyanoethylene Complexes

Compound	I_1,eV	I_2,eV	CCl_4[*1] (benzene)		$\Delta_{1,2}$, eV	
			$\nu_1 \cdot 10^{-3}$, cm^{-1}	$\nu_2 \cdot 10^{-3}$, cm^{-1}	photoelectric spect.	charge transfer
I	8,01	8,90	17,5	24,0	0,89	0,81
II	8,81	9,50	23,0(*2)	28,0	0,69	0,62
III	8,59	9,11	22,0[*3] (21,5)	24,5	0,52	0,30
IV	8,48	9,23	20,25 (21,0)	26,0	0,75	0,71
V	8,23	8,87	19,5 (18,8)	23,4	0,64	0,48
VI	8,68	9,47	22,20 (*2)	28,0	0,79	0,72
XIV	8,73	9,20	23,0[*4] (*2)	25,8[*4]	0,47	0,35
XV	8,41	8,80	20,0[*4] (20,2)	—	0,39	—

[*1] Mixed with donor in ratio 10:1.

[*2] Overlapped charge transfer bands of complex of tetracyanoethylene with benzene.

[*3] Obtained from an analysis of the shape of the line.

[*4] Overlapped with spectrum of pentacyanopropenide-anion (25,000, 23,900 cm^{-1}), the position of the bands was obtained by separating the overall spectra into components.

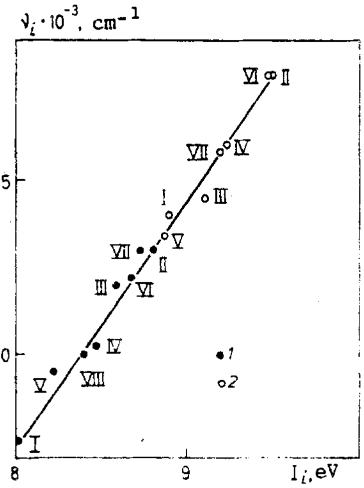


Fig. 1. Relationship between the charge transfer band in the UV spectrum and the ionization potentials: 1) long-wave band, 2) short-wave band.

When the reagents were mixed, the solutions immediately became colored. In the case of the vinylpyrazoles II–VI, the color persisted for an extended period; for the indazole I the reaction mixture faded within 20-30 min. The color was due to the formation of two new absorption bands at 17,000-28,000 cm^{-1} (Table 2). A linear relationship exists between the position of these UV absorption bands (see Fig. 1) and the first two ionization potentials (I_1, I_2) of the azoles I–VI, XIV, and XV, and also between the difference of the energies of the bands (Δ_{CT}) and the difference I_2–I_1, which confirms the formation of the donor-acceptor complex of the π–π type [10], and which agrees with the idea of a stepwise reaction mechanism possibly including donor-acceptor complexes [6, 9, 10]. In the donor-acceptor system 1,5-dimethyl- (XIV) and 1-ethyl-3,5-dimethylpyrazole (XV), the charge transfer band for the complex overlaps with the bands at 25,000 and 23,900 cm^{-1}, indicating the formation of pentacyanopropenide-anion (Table 2), the spectrum of which the authors [4, 11] mistakenly attribute to the complex. The formation of this ion is also observed in the reaction of tetracyanoethylene with the imidazole [3].

EXPERIMENTAL

Electronic absorption spectra were taken on a Specord M-40 spectrophotometer at 18-25°C. Photoelectric spectra were obtained on an ÉC-3201 electronic spectrometer at 30-100°C. The He (I) resonance band (21.21 eV) was used for excitation. The energy scale was calibrated at the first ionization potential of Ar (1576 eV) and chlorobenzene (9.06 eV). Errors in the determination of the ionization potentials were +0.05 eV. PMR spectra were recorded on a Tesla BS-497 spectrometer (100 MHz) using $CDCl_3$ as solvent. The vinylpyrazoles were obtained by the method given in [12]. Silica gel L 100/250 was used for chromatography.

Elemental analysis data (C, H, and N) for compounds VIII–XIII were in agreement with the calculated values.

1-(2,2,3,3-Tetracyano-1-cyclobutyl)pyrazoles (VIII-XIII) were obtained by mixing equimolar amounts of solutions of tetracycloethylene and 1-vinylpyrazoles I and V in benzene, II–IV, and VI in THF for 0.5-5 h. Compounds VIII and XII precipitated and were filtered off and washed. The cyclobutane derivatives IX–XI were precipitated with hexane. Compounds were purified by column chromatography; a 1:1:2 mixture of benzene–chloroform–ethyl acetate was used for compounds X and XI, and chloroform for the pyrazole IX.

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