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REACTION OF TETRACYANOETHYLENE WITH 1-VINYLINDOLE

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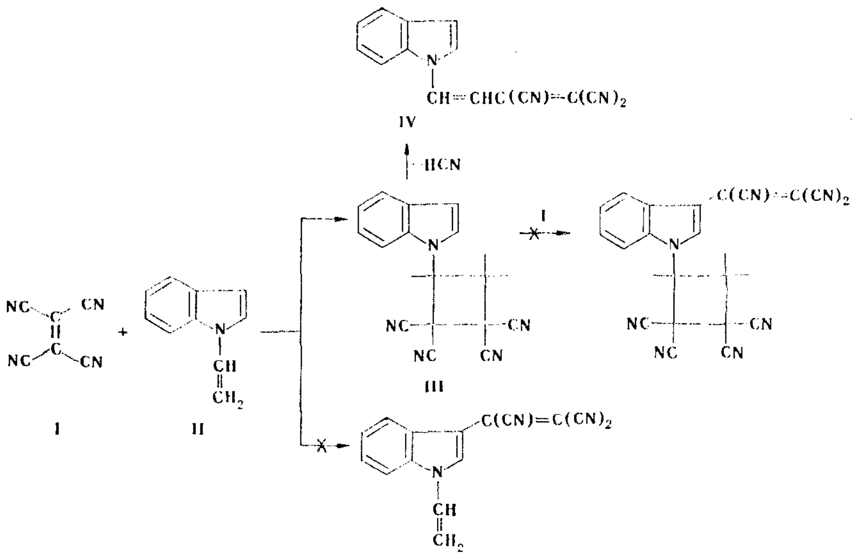
It was established that [2 + 2] cycloaddition at the N vinyl group proceeds selectively in the reaction of tetracyanoethylene with 1-vinylindole in aprotic solvents. The resulting 1-(2,2,3,3-tetracyano-1-cyclobutyl)indole upon heating in aqueous media and in alcohols undergoes stereospecific conversion to trans-1-(3,4,4-tricyano-1,3-butadien-1-yl)indole.

Indole and 1-methylindole readily undergo tricyanovinylation in the 3 position of the heteroring upon reaction with tetracyanoethylene (I) [1, 2]. The intermediates in these reactions are 3-(1,1,2,2-tetracyano-1-ethyl)indoles [3].

Processes that are characteristic for N-vinyl heterocyclic monomers, viz., homopolymerization and cycloaddition, theoretically become possible with the introduction of a vinyl group in the 1 position of the indole molecule [4, 5]. The material presented in the present paper is devoted to the elucidation of pathways in the reaction of ethylene I with the 1-vinyl derivative of indole.

We observed that selective [2 + 2] cycloaddition at the N-vinyl group to give 1-(2,2,3,3-tetracyano-1-cyclobutyl)indole (III) occurs in the reaction of ethylene I with 1-vinylindole (II):



In addition to the signals of the heterocyclic ring protons [7.83 (d, J_{23} = 3 Hz, 2-H), 6.66 (d, J_{32} = 3 Hz, 3-H), and 7.05-7.75 ppm (m, 4-, 5-, 6-, 7-H)], the PMR spectrum of indole III contains an ABX system that is typical for cyclobutane compounds [6, 7]. The AB

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part of the spectrum consists of eight lines, the X part comprising four of these lines. The signal of the resonance absorption of the proton of the X part of the spectrum, which is located in the weak-field region, is overlapped with the absorption of the proton in the 3 position of the heteroring. We obtained the following set of parameters from an analysis of the ABX spectrum: X—H 6.65, A—H 4.49, and B—H 3.96 ppm; J_{XA} = 11.1, J_{XB} = 9.7, and J_{AB} = 14 Hz.

The maximum yield (78-97%) of III was achieved with an excess of ethylene I or indole II. The reaction proceeds smoothly at room temperature in benzene, methylene chloride, chloroform, THF, and acetonitrile and is complete in 15-30 min. Despite variations in the experimental conditions, viz., an increase in the dielectric permeability of the medium from 2.2 (benzene) to 36.2 (acetonitrile) and increasing the synthesis times from 0.5 to 20 h, we were unable to obtain a product of addition of ethylene I or a product of tricyanovinylation in the 3 position of indole II. An attempt to add ethylene I to the 3 position of cyclobutylindole III (at 20°C) was also unsuccessful; only starting I and III were isolated from the reaction mixture in this case. Raising the temperature to 60°C leads to destruction of the butane ring in indole III.

When III is heated in aqueous acetonitrile or alcohol, it is converted to 1-(3,4,4-tricyano-1,3-butadien-1-yl)indole (IV).

The opening of the butane ring is a stereospecific process. For example, the trans isomer of IV was isolated in 84% yield after indole III was refluxed in methanol for 3 h. The spin—spin coupling constant (J_{trans} = 13 Hz) indicates the trans orientation of the tricyanovinyl grouping and the heterocyclic substituent with respect to the exocyclic CH=CH bond. The magnitudes of the chemical shifts of the vinylene protons (8.39 and 7.04 ppm) and the intense absorption band (K band [8]) in the visible region of the spectrum (λ_{max} = 454 nm, ε = $33 \cdot 10^3$) constitute evidence for the existence of a common system of conjugation between the donor (indolyl) and acceptor (tricyanovinyl grouping) fragments of IV. For this reason, indole IV can be classified as an organic dye.

The literature contains contradictory data regarding the ability of indole II to undergo homopolymerization under the influence of ethylene I. The synthesis of poly(1-vinylindole) in the presence of organic electron acceptors (chloranil and ethylene I) has been reported in a patent [9]. At the same time, the absence of polymerization in the indole II—ethylene I system is indicated in [10].

We have shown that the addition of ethylene I to indole II is not accompanied by homopolymerization of the latter, in contrast to the analogous reactions of 9-vinylcarbazole and 10-vinylphenothiazine [4, 5]. We did not obtain a homopolymer, even in the case of induction of polymerization of indole II by means of cycloaddition product III.

Thus the reaction between tetracyanoethylene and 1-vinylindole leads exclusively to the formation of 1-(2,2,3,3-tetracyano-1-cyclobutyl)indole. The production of trans-1-(3,4,4-tricyano-1,3-butadien-1-yl)indole is possible via stereospecific opening of the butane ring in III.

EXPERIMENTAL

The IR spectra of the compounds were recorded with a UR-20 spectrometer. The UV spectra were recorded with a Specord UV-VIS spectrophotometer. The PMR spectra of solutions of the compounds in acetone and DMSO were obtained with a Tesla BS-487C spectrometer (80 MHz) with hexamethyldisiloxane as the internal standard. The signals of the protons of the cyclobutane fragment in the spectrum of III and of the protons of the exocyclic and endocyclic CH=CH bonds in the spectrum of IV were assigned by means of the homonuclear INDOR method. The mass spectra were recorded with direct introduction of the samples into the ion source with a Varian Mat-212 spectrometer at 120-170°C and an ionizing-electron energy of 70 eV.

1-Vinylindole (II). The vinylation of indole by means of acetylene was carried out in a KOH/DMSO superbase medium by the method in [11]. The synthesized indole II was distilled *in vacuo* in the form of an azeotropic mixture with DMSO, after which the mixture was washed with water. The organic layer was combined with the ether extracts obtained by extraction of the aqueous layer, and the combinate was dried with potassium carbonate and distilled *in vacuo* [bp 72°C (1.33 hPa)], the distillate was crystallized from n-hexane to give indole II (75% yield) in the form of white crystals with mp 30°C (according to the data in [12], indole II had mp 29-30°C).

1-(2,2,3,3-Tetracyano-1-cyclobutyl)indole (III). A) A solution of 0.38 g (2.6 mmole) of indole II in 5 ml of benzene was added with stirring to a solution of 0.17 g (1.3 mmole) of ethylene I in 11 ml of benzene. When the black-blue color of the reaction mixture disappeared, the resulting precipitate was removed by filtration, washed with benzene, and dried *in vacuo* at room temperature to give indole III [98% (0.35 g)] in the form of an amorphous white powder with mp 141°C (dec.). IR spectrum (KBr pellet): 2260 (unconjugated $C{\equiv}N$); 2295, 2985, and 3035 cm^{-1} (CH, CH_2). UV spectrum (in THF), λ_{max} (log ε): 211 (4.34), 260 (3.86), and 291 nm (3.59). Mass spectrum, m/z (relative intensity, %): M^+ 271 (20.6), $[M^+ - HCN]$ 244 (6.0), $[M^+ - HCN, CN]$ 218 (10.0), $[M^+ - CH_2C(CN)_2]$ 193 (26.0), $[M^+ - C(CN)_2C(CN)_2]$ 143 (100), $[C(CN)_2C(CN)_2]^+$ 128 (34.0), and $[M^+ - CHCH_2C(CN)_2C(CN)_2]$ 116 (25.3). Found: C 70.7: H 3.5; N 25.0%. $C_{16}H_9N_5$. Calculated: C 70.8; H 3.3; N 25.8%; M 271.

B) A solution of 0.38 g (2.6 mmole) of indole II in 5 ml of acetonitrile was added to a solution of 0.17 g (1.3 mmole) of ethylene I in 11 ml of acetonitrile, and the mixture was stirred at room temperature for 30 min. The solvent was removed by distillation *in vacuo*, and the residue was washed with benzene and dried *in vacuo* to give 0.31 g (88%) of indole III.

C) A solution of 0.38 g (2.6 mmole) of indole II in 2 ml of acetonitrile was added to a solution of 0.17 g (1.3 mmole) of ethylene I in 5 ml of acetonitrile, after which the reaction mixture was maintained at room temperature for 30 min and at −15°C for 2 h. The precipitated crystals were removed by filtration, washed with cold acetonitrile, and dried *in vacuo* to give 0.15 g (42%) of indole III.

D) A solution of 0.25 g (1.7 mmole) of indole II in 2 ml of THF was added to a solution of 0.44 g (3.4 mmole) of ethylene I in 6 ml of THF, and the mixture was stirred at room temperature for 20 h. The solvent was separated *in vacuo*, and the residue was washed with benzene and dried *in vacuo* to give 0.36 g (79%) of indole III.

1-(3,4,4-Tricyano-1,3-butadien-4-yl)indole (IV). A) A solution of 0.5 g of III in 30 ml of methanol was refluxed for 3 h, and the precipitated orange crystals were removed by filtration, washed with methanol, and dried *in vacuo* to give 0.38 g (84%) of indole IV with mp 268-269°C. IR spectrum (KBr pellet): 2220 (conjugated $C{\equiv}N$); 1590 and 1620 cm^{-1} (butadiene fragment $C{=}C$). UV spectrum (in THF), λ_{max} (log ε): 2.10 (4.50), 256 (3.97), 292 (3.77), and 454 nm (4.51). PMR spectrum: 8.08 (d, J_{23} = 2 Hz, 2-H), 6.96 (d, J_{32} = 2 Hz, 3-H), 7.26-7.86 (m, 4-H, 5-H, 6-H, 7-H), 8.39 (d, $J_{\alpha\beta}$ = 13 Hz, α-H), and 7.04 ppm (d, $J_{\beta\alpha}$ = 13 Hz, β-H). Mass spectrum, m/z (relative intensity, %): M^+ 244 (100), $[M^+ - HCN]$ 217 (30), $[M^+ - C(CN)_2]$ 180 (13.7), $[CN{=}CHC(CN){=}C(CN)_2]^+$ 128 (3.7), and $[M^+ - CH{=}CHC(CN){=}C(CN)_2]$ 116 (5). Found: C 73.6; H 3.2; N 23.4%. $C_{15}H_8N_4$. Calculated: C 73.7; H 3.2; N 22.9%; M 244.

B) Water (2 ml) was added to a solution of 0.5 g of III in 12 ml of acetonitrile, and the mixture was heated in a sealed ampul at 60°C for 3 h. The precipitated crystals were removed by filtration, washed with water and alcohol, and dried *in vacuo* to give 0.10 g (22%) of indole IV.

The polymerization of indole II in the presence of ethylene I and of III in solution in benzene and acetonitrile was carried out by the method in [5].

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