SYNTHESIS AND STRUCTURE OF THE π COMPLEX OF CHROMIUM WITH 2-PHENYLINDOLIZINE

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The π complexing of indolizines was investigated. The first π complex of a transition metal (chromium) with a phenylindolizine ligand was synthesized. It was proved by IR, PMR, and mass spectroscopy that coordination of the metal atom is realized through the benzene ring of the molecule.

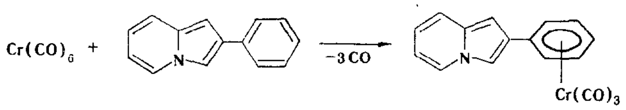
Although indolizines were obtained long ago [1, 2], no data are available regarding π complexes of indolizines and their derivatives with transition metals [3]. It is known [4] that the presence of linearly annelated rings and a "pyridine" nitrogen atom hinders the synthesis of π complexes of condensed heterocycles. This explains the complexity of the synthesis of π complexes of quinoline and isoquinoline [5].

Indolizine contains a nitrogen atom that is essentially of the "pyridine" type in the nodal plane of two rings. According to the results of x-ray diffraction analysis, the indolizine two-ring system is planar [6,7]. The aim of our investigation was to shed some light on the following problems: 1) the possibility of coordination of indolizine through the heterocyclic ring to give a stable π complex; 2) the possibility of coordination through the benzene ring of substituted indolizines such as phenylindolizines.

The subjects of the investigation were 2-methylindolizine and 2-phenylindolizine.

An unstable yellow complex, which decomposed rapidly to the starting 2-methylindolizine during isolation, was formed in the reaction of 2-methylindolizine with chromium carbonyl in refluxing dioxane, 15 min after the start of the reaction. A π-indolizine complex also was not formed under conditions of prolonged thermal reaction (in refluxing n-octane).

In contrast to 2-methylindolizine, a π complex, the structure of which was proved by IR, PMR, and mass spectroscopy and the results of **elemental analysis, was** obtained in the reaction of 2-phenylindolizine with $Cr(CO)_6$ in a high-boiling coordinating solvent (dibutyl ether; 6 h):



The mass-spectral fragmentation of the complex under the influence of electron impact includes the successive detachment of three CO groups and the phenylindolizine ligand:

$$C_{14}H_{11}NCr(CO)_3^+ \xrightarrow[-2CO]{} C_{14}H_{11}NCr(CO)^+ \xrightarrow[-CO]{} C_{14}H_{11}NCr^+ \xrightarrow[-C_{14}H_{11}N]{} Cr^+$$

The dependence of the logarithm (Z) of the ratio of the intensities of the Cr^+ and $C_{14}H_{11}NCr^+$ peaks in the mass spectrum on the number of vibrational degrees of freedom of the ligand (N) satisfies the equation [8] obtained for π-arene chromium complexes: $\log Z = -0.022N + 1.595$.

The IR spectra of the complex contain two characteristic [for π-arene$Cr(CO)_3$ complexes [9]] bands of carbonyl groups at 1895 and 1973 cm^{-1}.

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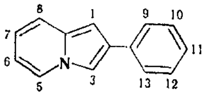
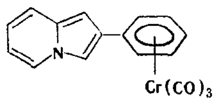
TABLE 1. PMR Spectra of Phenylindolizine and Its π Complex

Compound	Spectrum, ppm						
	1-H	3-H	5-H	6-& 7-H	8-H	9-& 13-H	10-, 11- & 12-H
	6,75	7,83	8,05	6,55	7,20	7,70	7,40
	6,70	7,81	8,10	6,50	7,27	5,95	5,60

A shift of the signals of the benzene ring to the strong-field region (5.6-5.95 ppm) is observed in the PMR spectrum (Table 1).

The set of data obtained in our research provides evidence that coordination of the chromium atom is realized through the benzene ring of the molecule. The π complex of chromium with 2-phenylindolizine is stable in air. In organic solvents (benzene, tetrahydrofuran, and chloroform) it undergoes rapid decomposition to the starting 2-phenylindolizine. It is stable in deoxygenated weakly coordinating solvents (CH_3CN and CH_3NO_2).

The activation of 2-phenylindolizine in a π complex is of interest for the synthesis of new phenyl-substituted indolizines that are difficult to obtain by traditional methods [10].

EXPERIMENTAL

The mass spectra* were obtained with an MS-30 spectrometer with direct introduction of the samples into the ion source; the ionizing voltage was 70 eV, and the ionization-chamber temperature was 200°C. The IR spectra of solutions in nitromethane were recorded with a UR-20 spectrometer. The PMR spectra of solutions in acetonitrile and deuteroacetone were recorded with Varian FT-80A (80 MHz) and Varian XL-100 (100 MHz) spectrometers with hexamethyldisiloxane as the internal standard.

The 2-methyl- and 2-phenylindolizines were obtained by known methods [2, 11]. The solvents used in this research were dried over sodium and distilled just prior to use. The π complex was synthesized in an atmosphere of dry purified argon.

A flask equipped with a bubbling tube and a reflux condenser was charged with 0.68 g (3.1 mmole) of $Cr(CO)_6$, 0.4 g (2.05 mmole) of 2-phenylindolizine, and 25 ml of dibutyl ether. The reaction was monitored by thin-layer chromatography (TLC) on Silufol plates with ether as the eluent. The reaction mixture was cooled to room temperature, as a result of which yellow acicular crystals precipitated. The solution was filtered, the solvent was removed from the filtrate by vacuum evaporation, and the dry residue and crystals were recrystallized twice from hexane to give 0.26 g (39%) of a complex with mp 168-170°C. Found: C 62.2; H 3.38%. $C_{17}H_{11}NO_3Cr$. Calculated: C 62.0; H 3.35%.

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REACTION OF TETRACYANOETHYLENE WITH 1-VINYLINDOLE

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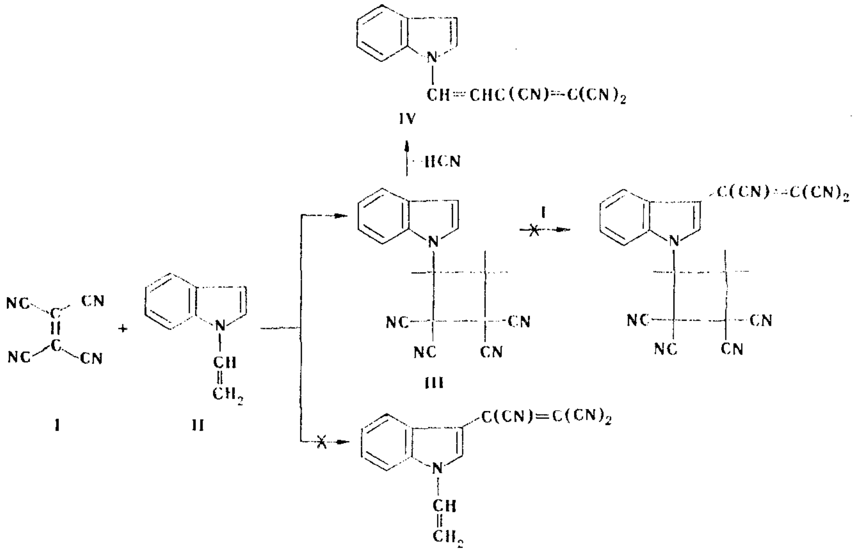
It was established that [2 + 2] cycloaddition at the N vinyl group proceeds selectively in the reaction of tetracyanoethylene with 1-vinylindole in aprotic solvents. The resulting 1-(2,2,3,3-tetracyano-1-cyclobutyl)indole upon heating in aqueous media and in alcohols undergoes stereospecific conversion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