3,4-Dibromo-1-(4-nitrophenyl)pyrroline-2,5-dione (V). A 2.16-g (0.01 mole) sample of aldehyde I was dissolved by heating in 100 ml of CH_3COOH, and the warm solution was poured into 200 ml of water containing 2 ml of bromine. After 5 min, 1 liter of water was added, and the resulting crystals were removed by filtration, washed successively with 5% bisulfite solution and water, and air dried. The yield was 1.9 g (50%).

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REACTION OF 2-DICYANOMETHYLENEINDAN-1,3-DIONE WITH PYRROLES AND INDOLES

B. P. Bespalov and A. G. Abolin

UDC 547.742'753

The reaction of 2-dicyanomethyleneindan-1,3-dione with pyrrole, indole, and their methyl derivatives gives products of addition at the dicyanomethylene carbon atom, viz., pyrrolyl- and indolyl(1,3-dioxo-2-indanyl)malononitriles, which upon heating or irradiation with UV light irreversibly split out HCN to give deeply colored products of replacement of the nitrile group in the acceptor by a heterocyclic grouping. Data from the UV and PMR spectra of the compounds obtained are presented.

2-Dicyanomethyleneindan-1,3-dione is a strong organic π acid, and reactions involving nucleophilic addition at the dicyanomethylene carbon atom are characteristic for it. This acid reacts readily with nucleophiles such as aromatic and aliphatic amines to give products of addition to the double bond of the dicyanomethylene group [1]. 2-Dicyanomethyleneindan-1,3-dione is the weakest acceptor in series of related organic π acceptors such as tetracyanoethylene and tetracyanoquinodimethane, which also readily form addition products with organic nucleophiles. Its electron affinity (E_A) is 2.45 eV, as compared with 2.75 and 2.85 eV for tetracyanoethylene and tetracyanoquinodimethane, respectively [2].

The aim of the present research was to study the effect of the electrophilicity of the dicyanomethylene carbon atom on the direction of the reaction with pyrroles and indoles.

We found that 2-dicyanomethyleneindan-1,3-dione readily forms addition products with N-heterocyclic compounds that contain one nitrogen atom in a five-membered ring. The reaction proceeds through a step involving the formation of a charge-transfer complex (CTC), which is accompanied by characteristic coloring of the solution and the appearance of the absorption of a long-wave charge-transfer band in the electronic spectra.

After a few minutes, pyrrole and its methyl derivatives in polar solvents (for example, acetonitrile, acetone, and alcohol) at 20°C react with 2-dicyanomethylene-1,3-dione to give slightly colored addition products Ia-c.

It follows from a comparison of the PMR spectra of Ia-c with the spectra of the unsubstituted heterocycles and from an analysis of the integral intensities of the signals that the

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TABLE 1. Pyrrolyl- and Indolyl(1,3-dioxo-2-indanyl)malononitriles Ia-e

Compound	mp, °C	UV spectrum, λ_{max}, (CH_3OH)	Found, %			Empirical formula	Calculated, %			Yield, %
			C	H	N		C	H	N	
Ia	170—174*	258 269	69,9	3,5	15,0	$C_{16}H_9N_3O_2$	69,8	3,3	15,3	89
Ib	159—164*	255 264	71,0	4,4	13,8	$C_{18}H_{13}N_3O_2$	71,2	4,3	13,8	88
Ic	156—161*	254 263	71,2	4,3	13,5	$C_{18}H_{13}N_3O_2$	71,2	4,3	13,8	86
Id	162—170†	255 263	74,1	3,8	12,8	$C_{20}H_{11}N_3O_2$	73,8	3,4	12,9	84
Ie	178—182*	255 264	74,2	3,9	12,4	$C_{21}H_{13}N_3O_2$	74,3	3,9	12,9	88

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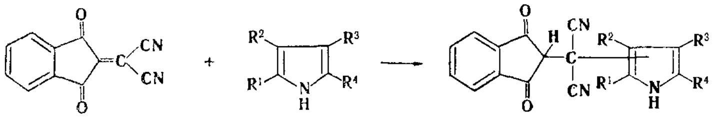
*From alcohol (dec.).
†From benzene (dec.).

reaction of dicyanomethyleneindan-1,3-dione with pyrrole and 2,4-dimethylpyrrole takes place in the 2 position of the heteroring or, if it is occupied (in the case of 2,5-dimethylpyrrole), in the 3 position relative to the nitrogen atom.

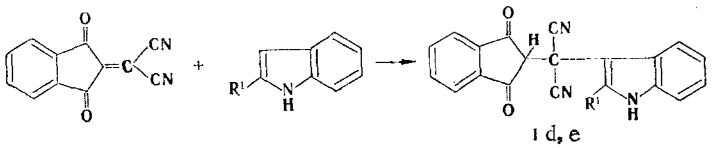
Scheme A



2-dicyanomethyleneindan-1,3-dione

I a-c

The reaction with indole and 2-methylindole takes place just as readily but, in contrast to pyrrole, in the 3 position of the heteroring, as one should expect:



I d, e

The reaction of pyrroles and indoles with tetracyanoquinodimethane takes place similarly [3]; however, in our case we were unable to isolate a product of addition of skatole to dicyanomethyleneindan-1,3-dione, since severe conditions are required for its occurrence; this can be explained by the lower electron affinity for this compound as compared with tetracyanoquinodimethane. Under these conditions the corresponding dye is formed in addition to the addition product, and the resulting resinous mixture could not be separated.

Thus, the reaction of dicyanomethyleneindan-1,3-dione with pyrroles and indoles is similar with respect to the direction of the reaction to certain positions of the heterocyclic ring to electrophilic substitution in pyrroles and indoles. This can be explained by the fact that the dicyanomethylene carbon atom in the molecule of this compound can be regarded as a strong electrophilic center that attacks the donor molecule.

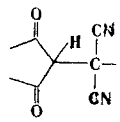
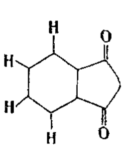
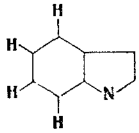
Compounds Ia-e are slightly colored crystalline substances; their constants are presented in Table 1, and their PMR spectra are presented in Table 2.

All addition products Ia-e have photosensitivity and thermal sensitivity. When they are irradiated with UV light or heated, they split out HCN irreversibly and are converted to deeply colored products of replacement of one nitrile group in the dicyanomethyleneindan-1,3-dione by a heterocyclic residue (Table 3). (See Scheme B following page.)

EXPERIMENTAL

A PRK-2 UV lamp was used in carrying out the photochemical reactions. The UV spectra were recorded with a Hitachi MSP-50L spectrophotometer. The PMR spectra were recorded with a Tesla BS-487B spectrometer (60 MHz).

TABLE 2. Chemical Shifts of the Protons in Ia-e (δ scale, acetonitrile, 20°C)*

Compound			Heteroring			
			>N–H	αC–H	βC–H	
Pyrrole Ia	4,27	7,89	9,03 9,54	6,75 6,74 (1 proton)	6,17 6,12 (2 protons)	
2,4-Dimethylpyrrole Ib	4,10	7,90	8,23 8,77 8,42	6,38	5,74 5,49 5,70	
2,5-Dimethylpyrrole Ic	4,00	7,85	8,77		5,39	
Indole Id	4,32	7,80	9,17 9,62	7,08 7,20	6,48	6,94—7,65 7,00—7,45
2-Methylindole Ie	4,15	7,75	9,00 9,49		6,11	6,86—7,46 6,85—7,56

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*The signal of the solvent (δ = 1.92 ppm) served as the internal standard.

TABLE 3. Pyrrolyl- and Indolyl(1,3-dioxo-2-indanylidene)acetonitriles IIa-e

Compound	mp, °C	UV spectrum, λ_{max}, nm (CH_3OH)	Found, %			Empirical formula	Calculated, %			Yield, %
			C	H	N		C	H	N	
IIa	228—230*	465	72,9	3,8	11,3	$C_{15}H_8N_2O_2$	72,6	3,6	11,3	61
IIb	220—221*	509	74,1	4,2	10,3	$C_{17}H_{12}N_2O_2$	73,9	4,4	10,1	46
IIc	245—246*	483	73,6	4,6	9,9	$C_{17}H_{12}N_2O_2$	73,9	4,4	10,1	44
IId	270—272†	513	76,1	3,7	9,7	$C_{19}H_{10}N_2O_2$	76,5	3,4	9,4	48
IIe	298—300†	512	76,6	4,1	8,9	$C_{20}H_{12}N_2O_2$	76,9	3,9	9,0	54

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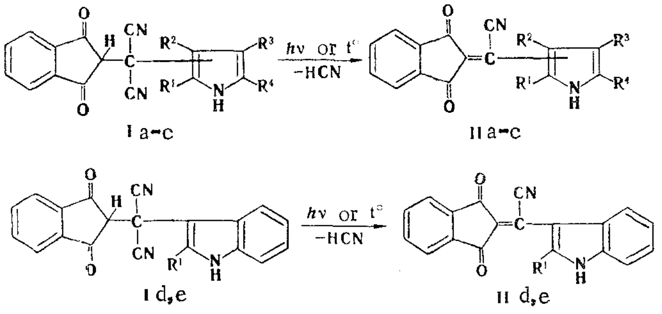
*From alcohol.

†From acetonitrile.

2-Dicyanomethyleneindan-1,3-dione. A 10-g (0.056 mole) sample of ninhydrin and 5 g (0.076 mole) of malononitrile were stirred in 100 ml of water at 50°C for 1 h, after which the precipitated acceptor was removed by filtration, washed with two 10-ml portions of water, and dried. The yield was 12.4 g (98%). Recrystallization from dioxane gave 10.6 g (84%) of a product with mp 281-282°C.

Scheme B



a R^1 = bond, $R^2=R^3=R^4$=H; b $R^1=R^3=CH_3$, R^2=H, R^4= bond; c $R^1=R^4=CH_3$, R^2= bond R^3=H; d R^1=H; e $R^1=CH_3$

Pyrrolyl- and Indolyl(1,3-dioxo-2-indanyl)malononitriles (Ia-e). A mixture of 0.5 mmole of dicyanomethyleneindan-1,3-dione and 0.6 mmole of the corresponding heterocycle was stirred in 50 ml of dry acetone or acetonitrile at 20°C for 20-30 min, after which the solvent was removed by vacuum distillation to a volume of 5 ml, and the product was precipitated with hexane or petroleum ether. The solid product was crystallized from alcohol or benzene. The yield was 84-89%.

Pyrrolyl- and Indolyl(1,3-dioxo-2-indanylidene)acetonitriles (IIa-e). A solution of 0.5 mmole of reaction product I in 50 ml of acetonitrile was irradiated from above with the full light of the UV lamp, which was situated at a distance of 10 cm from the surface of the solution. The corresponding dye, which precipitated in the form of a finely crystalline substance, was removed periodically by filtration and was recrystallized from acetonitrile. Irradiation was carried out for 20-30 h until I was converted almost completely to the dye, which was verified by chromatography. The dyes were obtained in 44-61% yields.

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PYRROLOINDOLES.

6.* NEW SYNTHESIS OF 1H,5H-PYRROLO[2,3-f]INDOLE AND 3H,6H-PYRROLO[3,2-e]INDOLE

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E. N. Gordeev, V. E. Zhigachev,
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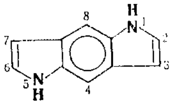
UDC 547.759.3'5.07:541.
63:543.422.25.4.6

Ethyl pyruvate 1-acetyl-5-indolinylhydrazone was obtained by diazotization of 1-acetyl-5-aminoindoline with subsequent reduction of the diazonium salt and condensation of the hydrazine with ethyl pyruvate. A mixture of hydrogenated derivatives of linear and angular pyrroloindoles is formed as a result of cyclization of the hydrazone in polyphosphoric acid esters. Subsequent hydrolysis, decarboxylation, and dehydrogenation lead to 1H,5H-pyrrolo[2,3-f]indole and 3H,6H-pyrrolo[3,2-e]indole.

Unsubstituted linear pyrroloindoles are difficult to obtain, and little study has therefore been devoted to them. The literature contains only two reports describing the synthesis of 1H,5H-pyrrolo[2,3-f]indole (I) [2] and 1H,7H-pyrrolo[3,2-f]indole (II) [3], which were obtained by closing of two pyrrole rings with the benzene ring. Pyrroloindole II is formed only as an impurity in angular 1H,6H-pyrrolo[2,3-e]indole (III) in the cyclization of the corresponding hydrazone obtained from m-phenylenediamine (with subsequent hydrolysis and decarboxylation) [3]. Only angular 3H,6H-pyrrolo[3,2-e]indole (IV) was synthesized by the same method when p-phenylenediamine was used as the starting amine [4]. Pyrroloindole I is obtained as the principal product in the cyclization of 2,5-bis(β-aminoethyl)hydraquinone hydrobromide (with subsequent dehydrobromination [2]. However, the difficulty with which starting hydroquinone V is obtained, the large number of steps, and the low overall yield make this method unsuitable for the synthesis of pyrroloindole I.



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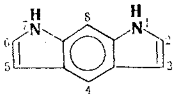
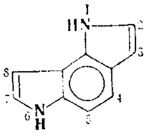
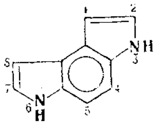


II



III



IV

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*See [1] for Communication 5.

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