Dimethylvinylenedithio-1,3-dithiol-2-one (XI) was obtained in a yield of 80% in a similar way as compound Va. Colorless crystals, mp 120-122°C. Found, %: S 54.3. $C_7H_6OS_4$. Calculated, %: S 54.7.

bis(Dimethylvinylenedithio)tetrathiafulvalene (Ib) was obtained in a similar way as Ia. Yield 75%, yellow crystals (from pyridine), mp > 230°C (dec). Found, %: C 38.3, H 2.6, H 58.9. $C_{14}H_{12}S_8$. Calculated, %: C 38.5, H 2.8, S 58.7.

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5-SUBSTITUTED 2-METHYL- AND 2-METHYLENEINDOLINES

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A method for the synthesis of 5-substituted 1,3,3-trimethyl-2-methyleneindolines has been developed, in which the substituents are introduced into the benzene ring of 1,2,3,3-tetramethylindolines, followed by oxidation.

1,3,3-Trimethyl-2-methyleneindoline (the "Fischer base") and its quaternary salts are starting materials for the synthesis of dyes [1-4]. Therefore derivatives of this compound, including substituted derivatives in the benzene ring, are also of considerable interest. The latter compounds are usually obtained from the corresponding hydrazones by the Fischer reaction [2, 3], or by exhaustive methylation of substituted indoles [3, 4]. It appeared to us desirable to use a method which is employed primarily for the synthesis of substituted indoles, i.e., to carry out the reaction in the benzene ring of indoline, followed by oxidation [5, 6].

1,2,3,3-Tetramethylindoline (I) was obtained by catalytic hydrogenation of a technical grade Fischer base. For the synthesis of 5-bromo-, 5-formyl-, 5-dichlorophosphinyltetramethylindolines (II-IV) from compound I, we used electrophilic substitution reactions described for N,N-dimethylaniline [7-9].

In the thiocyanation of indoline I, instead of the expected 5-thiocyanato-1,2,3,3-tetramethylindoline, disulfide V was obtained, which possibly formed as the result of thermal decomposition of the expected thiocyanate during distillation. We should note that not all electrophilic substitution reactions which proceed smoothly with dimethylaniline, proceed so successfully with indoline I. Thus, we were unable to carry out the benzoylation of compound I, although a similar reaction with dimethylaniline is classical [10].

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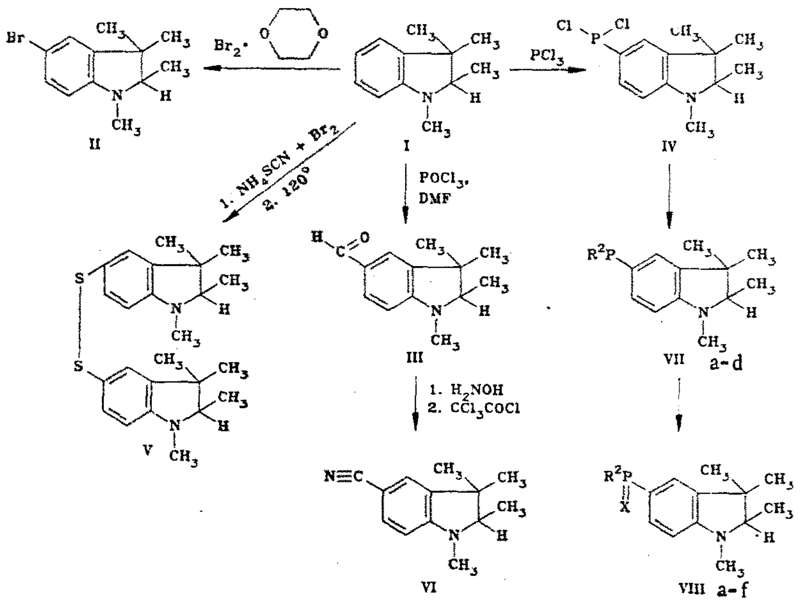
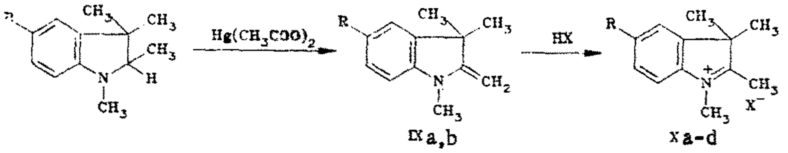


VII a R=Et, b R=Ph, c R=OEt, d R=N(CH$_3$)$_2$; VIII a R=Et, X=O, b R=Et, X=S, c R=Ph, X=O, d R=Ph, X=S, e R=OEt, X=O, f R=N(CH$_3$)$_2$, X=S

Nitrile VI was synthesized from aldehyde III that we obtained, while derivatives of tri- and pentavalent phosphorus (VIIa-d, VIIIa-f) were obtained from dichlorophosphine IV by the methods in [9, 11].

By oxidation with mercuric acetate, compounds II, VI, VIIIa,c are converted into the corresponding 2-methyleneindolines, which are isolated in the form of methylene bases IXa,b or their salts Xa-d.



IX a R=Br, b R=Ph$_2$PO; X a R=Br; b R=CN, c R=Et$_2$PO, d R=Ph$_2$PO; a, b d X= =ClO$_4$, c X=I

At the same time, we were unable to convert several synthesized tetramethylindoles into the corresponding 2-methylene derivatives. In compounds VIIe,f, the phosphorus-containing groups were hydrolyzed, possibly, to the corresponding acid, while VIIIb,d were converted into the corresponding oxides Xc,d.

EXPERIMENTAL

The IR spectra were run on a Specord 75-IR spectrophotometer (in tablet or in thin layer), PMR spectra — on a Tesla BS-467 spectrometer (60 MHz), using TMS as internal standard, and the ^{31}P NMR spectra — on a Tesla BS 487B spectrometer (80 MHz), using 85% H_3PO_4 as external standard.

1,2,3,3-Tetramethylindoline (I). A 2 mole portion of 1,3,3-trimethyl-2-methyleneindoline, 500 ml of methanol, 10 g of Raney nickel, and 1 ml of concentrated HCl is stirred in autoclave for 3 h at 50 atm and 100°C. The catalyst is separated, methanol is evaporated, and the residue is distilled in vacuo, bp 134-135°C (15 mm). According to the data in [12], bp 279°C (749 mm). Yield 93%. PMR spectrum (without solvent): 1.02 (m, 9H, CH_3—C); 2.5 (s, 3H, CH_3—N); 2.67 (q, 1H, 2H, J = 6.5 Hz); 6.2 (d, 1H, 7-H), 6.5-6.8 ppm (m, Ar—H).

1,2,3,3-Tetramethyl-5-bromo- and 1,2,3,3-Tetramethyl-5-formylindolines (II, III). The bromination and formylation are carried out as described for dimethylaniline [7, 8]. The compounds are distilled twice in vacuo. The PMR spectra of compounds II, III in the 1-3 ppm region are similar to the spectrum of compound I. PMR spectrum of compound II (CCl_4): 6.08 (d, 1H, 7-H, J_{76} = 8.5 Hz); 6.90-7.12 ppm (s and d, 3H, 4-H and 6H, J_{67} = 8.5 Hz). PMR spectrum of compound III (CCl_4): 6.31 (d, 1H, 7-H, J_{76} = 8 Hz); 7.27-7.40 (s and d, 3H, 4-H and and 6-H, J = 8 Hz); 9.61 ppm (s, 1H, CHO). IR spectrum of compound III: 1680 cm^{-1} (C=O).

TABLE 1. Characteristics of Synthesized Compounds

Compound	bp[a], °C (mp, °C)	Found, %			Empirical formula	Calculated, %			Yield, %
		N	P(C)	S(H)		N	P(C)	S(H)	
IIa	98—101	5,4	31,21[b]		$C_{12}H_{16}BrN$	5,5	31,4[b]		65
III	121—123	6,8	(76,6)	(8,4)	$C_{13}H_{17}NO$	6.9	(76,8)	(8,4)	89
IV	(38—39)	5,0	11,0		$C_{12}H_{16}Cl_2NP$	5,1	11,2		96
V	117—118	6,7		15,8	$C_{24}H_{32}N_2S_2$	6,8		15,5	51
VI	120—122	13,8	(77,9)	(8,0)	$C_{13}H_{16}N_2$	14,0	(78,0)	(8,1)	78
VIIa	72—74	5,2	11,7		$C_{16}H_{26}NP$	5,3	11,8		61
VIIb	185—187 (44—45)	3,7	8,5		$C_{24}H_{26}NP$	3,9	8,6		66
VIIc	91—94	4,6	10,7		$C_{16}H_{26}NO_2P$	4,7	10,5		79
VIId	112—114	14,3	10,6		$C_{16}H_{28}N_3P$	14,3	10,6		76
VIIIa	142—146	4,8	11,0		$C_{16}H_{26}NOP$	5,0	11,1		80
VIIIb	132—138	4,8	10,4	10,8	$C_{16}H_{26}NPS$	4,7	10,5	10,9	69
VIIIc	(139—140)	3,5	8,2		$C_{24}H_{26}NOP$	3,7	8,3		83
VIIId	(118—119)	3,6	7,9	8,1	$C_{24}H_{26}NPS$	3,6	7,9	8,2	90
VIIIe	141—144	4,6	10,7		$C_{16}H_{28}NO_3P$	4,5	10,0		88
VIIIf	(70—71)	12,9	9,4	9,5	$C_{16}H_{28}N_3PS$	12,9	9,5	9,9	93
IXa	122—124	5,6	31,5[b]		$C_{12}H_{14}BrN$	5,6	31,7[b]		78
IXb	(156—158)	3,7	8,2		$C_{24}H_{24}NOP$	3,8	8,3		47
Xa	(210—218)	4,0	32,4[c]		$C_{12}H_{15}BrClNO_4$	4,0	32,7[c]		66
Xb	(198—206)	9,2	12,0[d]		$C_{13}H_{15}ClN_2O_4$	9.4	11,9[d]		32
Xc	(200—204)	3,5	7,5		$C_{16}H_{25}INP$	3,5	7,6		26
Xd	(220—224)	2,9	6,2		$C_{24}H_{25}ClNO_5P$	3,0	6,5		59

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[a] Pressure 0.05 mm Hg. [b] Br. [c] Br + Cl. [d] Cl.

1,2,3,3-Tetramethyl-5-cyanoindoline (VI). A mixture of 0.31 mole of compound III and 0.6 mole of hydroxylamine hydrochloride, 95 ml of pyridine, and 180 ml of ethanol is heated for 3 h on a boiling water bath. When cool, the mixture is mixed with water (0.5 liter), saturated NaCl solution, and a small amount of ether. The ether layer is separated, and the aqueous layer is extracted by ether (2•75 ml). The ether extracts are combined and dried over $MgSO_4$. Ether is evaporated, and the remaining oil is held for a few hours in vacuo (0.05 mm) at 60°C. The residue is dissolved in 250 ml of dry methylene chloride and 0.6 mole of triethylamine is added, and then a solution of 0.33 mole of trichloracetyl chloride in 250 m of methylene chloride is added dropwise. The mixture is stirred at 20°C for 1 h, methylene chloride is evaporated, and 500 ml of ether are added. Triethylamine hydrochloride is filtered, the ether solution is washed with water, ether is evaporated, and the residue is distilled in vacuo. PMR spectrum (the aromatic region) (CCl_4): 6.31 (d, 7-H, J_{76} = 8 Hz); 7.08 (d, 1H, 4-H, J_{46} = 1.5 Hz); 7.21 ppm (d. d, 1H, 6-H, J_{67} = 8, J_{64} = 1.5 Hz). IR spectrum: 220 cm^{-1} (C≡N).

1,2,3,3-Tetramethyl-5-dichlorophosphinoindoline (IV). A mixture of 0.5 mole of phosphorus trichloride and 0.5 mole of compound I is allowed to stand at 20°C for 24 h, and then heated, gradually raising the temperature in the bath to 150°C in the course of 2 h. Compound IV is extracted by petroleum ether (2•400 ml). The salt of indoline I is dissolved in 150 ml of benzene and precipitated by 400 ml of petroleum ether. The solvents are evaporated. The residue, a practically pure dichlorophosphine, is dissolved in heptane and frozen by liquid nitrogen. ^{31}P NMR spectrum: 157.2 ppm.

Di-1,2,3,3-tetramethylindolinium-5-disulfide (V). A 0.06 mole portion of Br in 15 ml of acetic acid is added in the course of 20 min with stirring and cooling to an emulsion of 0.06 mole of compound I and 0.12 mole of ammonium thiocyanate in 35 ml of acetic acid. The mixture becomes thicker. The temperature is raised to 20°C, and the mixture is left to stand for 30 min, with grinding from time to time the lumps formed. It is then treated with 70 ml water, bringing the mixture to a weakly alkaline reaction, and the oil that separates is extracted by chloroform (3•50 ml). The extract is dried over $MgSO_4$, evaporated to dryness, and the disulfide is distilled twice in vacuo.

Phosphorylated Indolines VIIa-d and VIIIa-f are obtained by methods described in [9-11]. Compounds VIIa-d are distilled in vacuo, while compound VIIc is crystallized from a mixture of benzene with heptane. Compound VIIId is ground with methanol and crystallized from benzene, VIIId [sic] from hexane (with freezing). ^{31}P NMR spectrum (chemical shift of ^{31}P, ppm): VIIa 17.8; VIIb 5.7; VIIc 158.0; VIId 100.0; VIIIa 43.6; VIIIb 50.2; VIIIc 28.7; VIIId 43.4; VIIIe 21.4; VIIIf 82.5.

Indolines IXa,b and Indolenine Salts Xa-d. A 0.022 mole portion of mercuric acetate is added to a solution of 0.01 mole of compounds II, VI, VIIIa in 30 ml of 70% acetic acid, and the mixture is heated on a boiling water bath for 15 min, with periodical shaking. The mixture is cooled by cold water. The white precipitate of mercurous monoacetate is filtered. A large excess of sodium sulfide is rapidly added. The precipitate that separates in centrifuged, washed with methanol, and centrifuged again. A large excess of alkali is added, the indolines are extracted by benzene, and benzene is evaporated. Compound IXa is distilled in vacuo, compound IXb is ground with hexane, and crystallized from propanol. The compounds obtained are dissolved in concentrated HCl, the solution is washed with benzene, the acid is evaporated in vacuo, the salts are dissolved in water and precipitated by excess sodium perchlorate or sodium iodide. Salts Xa-c are crystallized from methanol; Xd is repeatedly washed with hot methanol. In the PMR spectra of compounds Xa,b, signals of methylene groups are observed at 3.3-3.8 ppm. In the ^{31}P NMR spectra of compounds IXb, Xc, Xd, there are signals at 29.0; 44.1; 28.3 ppm, respectively. IR spectrum of compound Xb: 2250 cm^{-1} (C≡N).

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