PYRROLES FROM KETOXIMES AND ACETYLENE.

40.* REACTION OF ALKYL HETARYL KETOXIMES WITH 1,2-DICHLOROETHANE IN SUPERBASE MEDIA

S. E. Korostova, R. N. Nesterenko, A. I. Mikhaleva,
R. I. Polovnikova, and N. I. Golovanova

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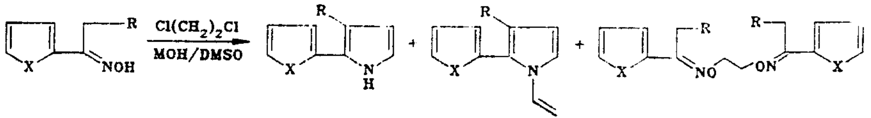
2-(2-Furyl)- and 2-(2-thienyl)pyrroles and their N-vinyl derivatives were synthesized by the reaction of alkyl furyl(thienyl) ketoximes with 1,2-dichloroethane in superbase media. 2-Chloroethyl and vinyl ethers of alkyl hetaryl ketoximes are intermediates in the reaction.

It is known that crypto forms of acetylene — 1,2-dichloroethane [2] or vinyl halides [3] — can be used in superbase media in a variant of the Trofimov synthesis of pyrroles.

In the present research it is shown that such systems can be used successfully for the synthesis of hetarylpyrroles and their N-vinyl derivatives from the corresponding ketoximes.



I a-g II a-g III a-g IV a-g

X=O, S; R=H, alkyl (see Table 1); M=Li, Na, K

This method for obtaining furyl(thienyl)pyrroles, the chief advantage of which is the replacement of acetylene by the accessible and conveniently recovered dichloroethane, is realized readily in the simplest apparatus with a stirrer at atmospheric pressure and 100-135°C. The yields of pyrroles IIa-g, N-vinylpyrroles IIIa-g, the intermediate ketoxime vinyl and 2-chloroethyl ethers Va,d and VId, and the side 1,2-bis(hetarylalkylideneiminoxy) ethanes IVa-g depend substantially on the conditions under which the reaction is carried out; as seen from Table 1, the reaction is sensitive to a change in the temperature conditions and the reaction time, as well as to the nature of the hydroxide and its concentration and the amount of water added. Thus the rate of pyrrolization of methyl furyl ketoxime (Ia) increases with an increase in the reaction temperature under other comparable conditions (experiments 2 and 4, Table 1): the yield of pyrrole IIa increases from 8% (120°C) to 23% (130-135°C). The rate of vinylation increases simultaneously: whereas vinylpyrrole IIIa is detected in the reaction mixture in only trace amounts (∿0.1%) at 120°C, at 130-135°C its yield increases to 20%, and the yield of side diether IVa decreases by a factor greater than five (from 51% in experiment 2 to 9% in experiment 4).

A similar dependence is observed in the reaction of propyl thienyl ketoxime (If) with dichloroethane in an NaOH—DMSO system containing 5% water (experiments 24 and 25). It follows from experiments 18 and 20 that a simultaneous increase in the temperature and an increase in the reaction time do not promote an increase in the yield of pyrrole IId; the yield of N-vinyl derivative IIId increases to 15%, but the overall yield of these pyrroles decreases. As in the case of the reaction between ketoximes and acetylene [2], to obtain a pyrrole that is free of the N-vinylpyrrole the reaction of alkyl hetaryl ketoximes with dichloroethane should be carried out in the presence of small amounts (5-10% of the mass of the DMSO) of added water, which usually slows down vinylation of NH heterocycles. For example, in the reaction between methyl furyl ketoxime and dichloroethane in the NaOH—DMSO

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*See [1] for Communication 39.

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TABLE 1. Yields of Products and Conditions of the Reaction of Alkyl Hetaryl Ketoximes with 1,2-Dichloroethane in MOH–DMSO Systems*

Expt. No.	Ketoxime (I)			M	Oxime:dichloroethane:MOH ratio (moles)	Reaction temp., °C	Reaction time,h	Yield,%			
	No.	X	R					pyrrole (II)	1-vinylpyrrole (III)	O-vinyl oxime (V)	diether (IV)
1	Ia	O	H	K	1 : 2 : 7	100	6	4	Not detected	Not detected	45
2	Ia	O	H	K	1 : 2 : 7	120	6	8	Traces	"	51
3	Ia	O	H	K	1 : 2 : 10 (5)**	120	7	47	5	"	12
4	Ia	O	H	K	1 : 2 : 8	130...135	6	23	20	"	9
5	Ia	O	H	Na	1 : 2 : 7 (5)**	120	8	19	Not detected	6	7
6	Ia	O	H	Na	1 : 2 : 7	120	6	36	Traces	Not detected	20
7	Ia	O	H	Na	1 : 3 : 10 (10)**	115...120	12	42	3	"	11
8	Ia	O	H	Li	1 : 2 : 7 (5)**	100...115	8	18	6	"	4
9	Ia	O	H	Li	1 : 2 : 7(5)**	120	6	12	Traces	Traces	30
10	Ib	O	Me	K	1 : 3 : 7	115...120	10	28	16	Not detected	43
11	Ib	O	Me	K	1 : 2 : 10	125...130	6	30	15	"	5
12	Ib	O	Me	Na	1 : 2 : 7 (10)**	120	7	32	6	Not detected	30
13	Ic	O	Et	Na	1 : 2 : 8	120	6	17	Traces	"	54
14	Ic	O	Et	Na	1 : 3 : 7	120	9	25	9	"	19
15	Id	S	H	K	1 : 2 : 7	120	6	13	Traces	"	65
16	Id	S	H	K	1 : 2 : 10	120	7	54	14	"	Traces
17	Id	S	H	K	1 : 31 : 37	110	3	4	Not detected	"	24***
18	Id	S	H	Na	1 : 2 : 7	120	6	46	Traces	"	18
19	Id	S	H	Na	1 : 2 : 7 (10)**	130...135	10	13	"	"	22
20	Id	S	H	Na	1 : 2 : 7	125...130	12	6	15	"	16
21	Id	S	H	Li	1 : 2 : 7	120	6	Traces	Not detected	20	63
22	Id	S	H	Li	1 : 2 : 7 (10)**	100	4	"	"	43	18
23	Ie	S	Me	Na	1 : 2 : 7	120	9	38	12	Not detected	7
24	If	S	Et	Na	1 : 2 : 7 (5)**	120	7	34	Traces	Not detected	7
25	If	S	Et	Na	1 : 2 : 7 (5)**	125...130	8	5	25	"	16
26	Ig	S	*n*-Bu	Na	1 : 2 : 7 (5)**	120	6,5	42	Traces	"	16
27	Ig	S	*n*-Bu	Na	1 : 2 : 8	120...130	10	13	20	"	46

*In all of the experiments the amount of DMSO used was a tenfold excess with respect to the mass of the ketoxime.

**The amount of water added (in percent of the volume of the DMSO) is indicated in parentheses.

***The yield of the 2-chloroethyl ether of ketoxime Id is presented.

TABLE 2. IR Spectra of 2-(2-Hetaryl)pyrroles

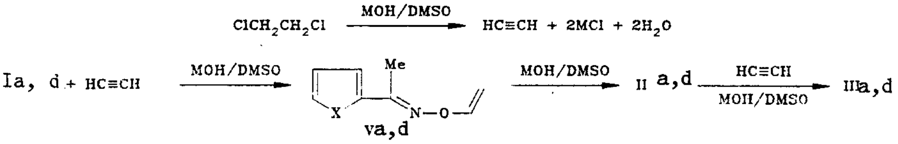
Compound	ν, cm^{-1}
IIb	460, 500, 570, 610, 665, 700, 770, 820, 860, 950, 970, 1000, 1045, 1080, 1120, 1175, 1230, 1270, 1370, 1380, 1415, 1450, 1495, 1530, 1595, 2850, 2910, 3010, 3400
IIc	470, 490, 580, 616, 700, 770, 830, 870, 950, 980, 1010, 1060, 1090, 1140, 1180, 1250, 1280, 1370, 1390, 1430, 1490, 1600, 2850, 2910, 3110, 3370
IIe	590, 695, 715, 800, 818, 847, 890, 907, 937, 1058, 1088, 1100, 1238, 1350, 1380, 1420, 1460, 1510, 1580, 2870, 2935, 2970, 3100, 3380
IIg	700, 815, 845, 890, 930, 1038, 1048, 1078, 1108, 1168, 1200, 1230, 1392, 1430, 1460, 1512, 1572, 1602, 2870, 2930, 2960, 3100, 3420

system (experiment 6) in the absence of water the reaction mass contains, in addition to pyrrole IIa (36% yield), a small amount (∿0.1%) of N-vinylpyrrole IIIa, while when water in an amount that is 5% of the mass of the DMSO is added to the reaction mixture (experiment 5), vinylation is quenched completely, and the yield of pyrrole IIa is 19%. Pyrrole IId is formed in 13% yield from methyl thienyl ketoxime (NaOH–DMSO, 130-135°C, 10 h, experiment 19) in the presence of 10% water relative to the mass of the DMSO, and vinylpyrrole IIId is detected in the reaction mass only in traces. In the absence of water in the same system (125-130°C, 12 h, experiment 20) vinylpyrrole IIIa was obtained in 15% yield, while its unvinylated precursor was obtained in 6% yield. The overall yields of pyrroles IIa and IIIa even when water is present in the system (52% in experiment 3, 45% in experiment 7), pyrroles IIb and IIIb (45% in experiment 11), and pyrroles IId and IIId (68% in experiment 16) increase substantially when a tenfold (with respect to the ketoxime) molar excess of sodium or potassium hydroxide is used.

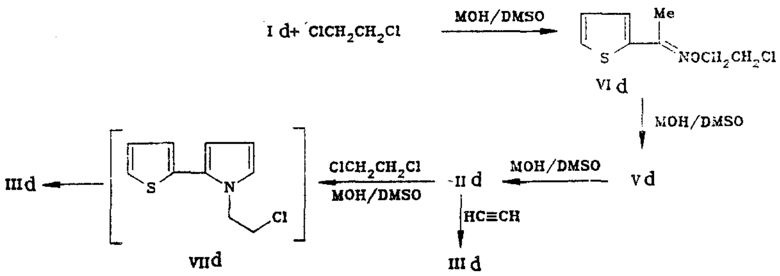
As in the reaction of ketoximes with acetylene [2], the hydroxides in this reaction differ not only with respect to catalytic activity but also with respect to the selectivity of their action (experiments 15, 18, 21). In contrast to the reaction of dialkyl [2, 4] and alkyl aryl [5] ketoximes with dichloroethane, which is catalyzed by the KOH–DMSO superbase and leads primarily to the corresponding pyrroles, the reaction with alkyl hetaryl ketoximes (Ia,d, experiments 2 and 15) in the same system under comparable conditions terminates with the formation of the corresponding diethers – 1,2-bis(hetarylalkylideneiminoxy)ethanes IVa, d; pyrroles IIa,d were obtained in low yields (8% and 13%, respectively). It is suprising that in the presence of NaOH under the same conditions (120°C, 6 h) and at the same reagent ratios (experiments 6 and 21) the tendency of ketoximes Ia and Id to undergo heterocyclization increases significantly and the selectivity of the process increases: the yields of pyrroles IIa and IId reach 36% and 46%, respectively, and their vinyl derivatives are detected in the reaction mass in only trace amounts; the yields of diesters IVa and IVd are 20% and 18%. It is remarkable that in the presence of water in the NaOH–DMSO system (120°C, 8 h, experiment 5) the reaction of dichloroethane with methyl furyl ketoxime or in the LiOH–DMSO system with methyl thienyl ketoxime (100°C, 4 h, experiment 22), as well as without water in the same system (120°C, 6 h, experiment 21), proceeds through an intermediate – the O-vinyl derivative of the corresponding oxime; the best yield (43%) of O-vinyl oxime Vd was obtained when the catalytic pair LiOH–DMSO with 10% H_2O (100°C, 4 h, experiment 22), which proved to be insufficiently active in the pyrrolization and vinylation of NH pyrrole IId under the investigated conditions, was used. An individual experiment showed that an O-(2-chloroethyl) oxime, for example, VId [KOH–DMSO (110°C, 3 h, experiment 17)], which is formed in 24% yield, may be another intermediate.

The detection of O-vinyl oximes Va,d and O-(2-chloroethyl) oxime VId among the principal reaction products makes it possible to propose two possible pathways for the formation of pyrroles and N-vinylpyrroles:

1) A previously proposed [2] pathway in which dichloroethane in the superbase medium acts as a supplier of acetylene:



2) Nucleophilic substitution of one chlorine atom in dichloroethane by an oximate anion with the formation of O-(2-chloroethyl) oxime VId with the subsequent elimination of HCl and the formation of O-vinyl oxime Vd, which undergoes cyclization to pyrrole IId:



The possibility of the formation of 1-(2-chloroethyl) pyrrole VIId under the investigated conditions is in agreement with the data in [6].

With respect to their physicochemical constants, the synthesized pyrroles IIa,b,d,f, N-vinylpyrroles IIIa-g [2], and O-vinyl oxime Vd [7] are identical to those obtained from the corresponding alkyl hetaryl ketoximes and free acetylene.

The IR spectrum of 2-(2-furyl)pyrrole IIa, N-vinyl-2-(2-furyl)pyrroles IIIa-c were presented in [2, 8, 9], the IR spectra of 2-(2-thienyl)pyrroles IId,f were presented in [2, 9, 10], the IR spectra of N-vinyl-2-(2-thienyl)-pyrroles IIId-f were presented in [9], and the IR spectrum of O-vinyl oxime Vd was presented in [7]. The ^1H NMR spectra of IIb and IIIb,c were described in [11], and the ^1H NMR spectrum of Vd was described in [2, 7]. The ^{13}C NMR spectrum of vinylpyrrole IIId was presented in [2, 10].

The characteristics of the side 1,2-bis(hetarylalkylideneiminoxy)ethanes IVa,d,g were given in [12].

EXPERIMENTAL

The IR spectra of microlayers of the liquid compounds or KBr pellets of the crystalline compounds were obtained with UR-20 and Specord-75 IR spectrometers and are presented in Table 2. The ^1H and ^{13}C NMR spectra of solutions of the compounds in CCl_4 or $CDCl_3$ were recorded with Bruker WP-200 SY, Tesla BS-487C, and Tesla BS-567 spectrometers with hexamethyldisiloxane (HMDS) or tetramethylsilane (TMS) as the internal standard. The results of elementary analysis of the undescribed compounds for C, H, N, Cl, and S were in agreement with the calculated values.

2-(2-Furyl)pyrrole (IIa) and 1,2-Bis[1-(2-furyl)methylideneiminoxy]ethane (IVa). A 3-g (0.027 mole) sample of methyl furyl ketoxime, 29 ml of DMSO, and 1.9 g (0.048 mole) of NaOH were placed in a flask equipped with stirrer, reflux condenser, dropping funnel, and thermometer, and the mixture was heated to 120°C. A solution of 5 g (0.05 mole) of dichloroethane in 10 ml of DMSO was added slowly (in the course of 5 h and 30 min) with vigorous stirring with the simultaneous addition in small portions of another 5 g (0.125 mole) of NaOH. The mixture was stirred at the same temperature for another 30 min, cooled to room temperature, and poured into cold water. The aqueous mixture was extracted with ether, and the ether extracts were washed with water and dried with potassium carbonate. The ether was removed, and the residue was chromatographed on thin loose layers of Al_2O_3 [hexane–ether (1:1)] to give 1.2 g (36%) of pyrrole IIa [8]. ^{13}C NMR spectrum ($CDCl_3$): 124.1 $C_{(2)}$, 105.5 $C_{(3)}$, 109.7 $C_{(4)}$, 118.1 $C_{(5)}$, 148.5 $C_{(2')}$, 102.2 $C_{(3')}$, 111.3 $C_{(4')}$, 140.3 $C_{(5')}$. Also obtained was 0.7 g (20%) of diether IVa [12].

2-(2-Furyl)-3-methylpyrrole (IIb) and 1-Vinyl-2-(2-furyl)-3-methylpyrrole (IIIb). A 1.4-g (32%) sample of pyrrole IIb [8] and 0.3 g (6%) of vinylpyrrole IIIb [8] were obtained from 4.2 g (0.034 mole) of ethyl furyl ketoxime and 6.3 g (0.064 mole) of dichloroethane in 45 ml of DMSO and 4.5 ml of water and 8.4 g (0.21 mole) of NaOH at 120°C after 7 h after workup as described above.

2-(2-Furyl)-3-ethylpyrrole (IIc, $C_{10}H_{11}NO$). A 1-g (25%) sample of pyrrole IIc, with bp 159°C (10 mm Hg), d_4^{20} 1.1483, and n_D^{20} 1.5107, was obtained from 3.7 g (0.024 mole) of propyl furyl ketoxime, 7.35 g (0.07 mole) of dichloroethane, 40 ml of DMSO, and 6.7 g (0.17 mole) of NaOH (120°C, 9 h).

O-(2-Vinyl) Methyl 2-Furyl Ketoxime (Va, $C_8H_9NO_2$) and 1,2-Bis[1-(2-furyl)methylideneiminoxy]ethane (IVa). A 0.6-g (19%) sample of pyrrole IIa, 0.25 g (7%) of diether IVa, and 0.22 g (6%) of O-vinyl oxime Va, with bp 105°C (2 mm Hg), d_4^{20} 1.0350, and n_D^{20} 1.5391, were obtained from 3 g (0.024 mole) of methyl furyl ketoxime, 5 g (0.05 mole) of dichloroethane, and 6.65 g (0.17 mole) of NaOH in 20 ml of DMSO and 1.5 ml of water (120°C, 8 h) by the method described for the synthesis of 2-(2-furyl)pyrrole. IR spectrum: 1642 ($\nu C{=}C$ in $OCH{=}CH_2$); 3070 (ν_{as} $=CH_2$); 982 (δ CH_2); 916 ($\nu C{-}O$); 1147, 1150 cm^{-1} ($\nu C{-}O$). ^1H NMR spectrum (CCl_4): 2.15 (3H, s, CH_3), 4.06 (1H, dd, β-H_{cis}, J_{cis} = 6.8 Hz, $OCH{=}CH_2$), 4.59 (1H, dd, β-H_{trans}, J_{trans} = 14.2, J_{gem} = 1.7 Hz, $OC\underline{H}{=}CH_2$), 6.88 (1H, q, α-H, $OCH{=}CH_2$), 6.63 (1H, dd, 3-H), 6.29 (1H, dd, 4-H), 7.35 ppm (1H, dd, 5-H, furan ring).

2-2(2-Thienyl)pyrrole (IId). A 3.5-g (0.025 mole) sample of methyl thienyl ketoxime, 1.4 g (0.025 mole) of KOH, and 30 ml of DMSO were placed in the apparatus described for the preparation of pyrrole IIa, after which the mixture was heated to 120°C, and a solution of 5.3 g (0.054 mole) of dichloroethane in 10 ml of DMSO was added with vigorous stirring in the course of 6 h. It was then stirred for another hour and worked up as described above. The residue was distilled in vacuo to give a mixture consisting of pyrrole IId [7] and vinylpyrrole IIId [7], which was thiylated by the method in [13]. Fractionation in vacuo gave 2 g (54%) of pyrrole IId that was free of vinylpyrrole IIId, which was converted to a 1-(2-alkylthioethyl)-2-(2-thienyl)pyrrole. ^{13}C NMR spectrum ($CDCl_3$): 126.8 $C_{(2)}$, 106.9 $C_{(3)}$, 110.1 $C_{(4)}$, 118.5 $C_{(5)}$, 136.5 $C_{(2')}$, 121.0 $C_{(3')}$, 127.6 $C_{(4')}$, 126.6 ppm $C_{(5')}$.

2-(2-Thienyl)-3-butylpyrrole (IIg, $C_{12}H_{15}NS$), 1-Vinyl-2-(2-thienyl)-3-butylpyrrole (IIIg), and 1,2-Bis[1-(2-thienyl)amylideneiminoxy]ethane (IVg). A mixture of IIg, IIIg, and IVg was obtained from 5.8 g (0.03 mole) of amyl thienyl ketoxime, 6.3 g (0.06 mole) of dichloroethane, 9.6 g (0.24 mole) of NaOH, and 60 ml of DMSO at 120-130°C for 10 h. Chromatography of this mixture on thin loose layers of Al_2O_3 [hexane–ether (4:2.5)] gave 0.8 g (13%) of pyrrole IIg, with bp 145°C (1.5 mm Hg), d_4^{20} 1.0956, and n_D^{20} 1.5342; 1.4 g (20%) of vinylpyrrole IIIg [7] [^1H NMR spectrum ($CDCl_3$): 6.03 (1H, d, 4-H), 6.93 (1H, d, 5-H), 6.78 (1H, dd, 3'-H), 7.02 (1H, dd, 4'-H), 7.31 (1H, dd, 5'-H), 4.47 (1H, dd, β-H_{cis}, ^2J = 0.9 Hz, $NCH{=}CH_2$), 4.96 (1H, dd, β-H_{trans}, ^3J = 15.4 Hz, $NCH{=}CH_2$), 6.72 (1H, dd, α-H, $NCH{=}CH_2$), 2.38 (2H, t, α-CH_2 in Bu), 1.38 (4H, m, β, γ-CH_2 in Bu), 0.85 ppm (3H, t, CH_3 in Bu)], and 2 g (46%) of diether IVg.

2-(2-Thienyl)-3-methylpyrrole (IIe, C_9H_9NS). This compound was similarly synthesized and had bp 112°C (1 mm Hg), d_4^{20} 1.0812, and n_D^{20} 1.6078.

O-(2-Chloroethyl) Methyl 2-Thienyl Ketoxime VId, $C_8H_{10}ClNOS$). A 1.2-g (24%) sample of 2-chloroethyl ether VId in the form of a yellow immobile liquid with bp 98-100°C (3 mm Hg) and d_4^{20} 1.2249 was obtained from 3.5 g (0.025 mole) of methyl thienyl ketoxime and 81.4 g (0.83 mole) of dichloroethane in 40 ml of DMSO and 52.5 g (0.94 mole) of KOH after 4 h at 120°C and the standard workup (see above) and fractionation in vacuo.

O-(2-Vinyl) Methyl 2-Thienyl Ketoxime (Vd) and 1,2-Bis-[1-(2-thienyl)methylideneiminoxy]ethane (IVd). A 2.6-g (43%) sample of O-vinyl oxime Vd [7] and 0.96 g (18%) of diether IVd [12] were obtained from 4.9 g (0.04 mole) of methyl thienyl ketoxime, 8.4 g (0.08 mole) of dichloroethane, and 6.7 g (0.28 mole) of LiOH in 50 ml of DMSO and 5 ml of water at 100°C after 4 h by the method described for O-vinyl oxime IVa.

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PHOTOCHROMIC FULGIDES BASED ON 1-METHYL-2-FORMYLINDOLE

I. Yu. Grishin, N. M. Przhiyalgovskaya,
Yu. M. Chunaev, V. F. Mandzhikov,
L. N. Kurkovskaya, and N. N. Suvorov

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The reactions of 1-methyl-2-formylindole with the diethyl esters of alkyl- and phenylmethylene-substituted itaconic acids led to the production of photochromic fulgides, which formed deeply colored 5,8b-dihydrocarbazole derivatives during UV irradiation. It was found by PMR that the fulgides also undergo E,Z isomerization during UV irradiation.

As reported in [1], heterocyclic fulgides (Ia-d), obtained from 1,2-dimethyl-3-formylindole, do not exhibit photochromic characteristics resulting from the formation of the more deeply colored 8,8a-dihydrocarbazole derivatives (IIIa-e) during UV irradiation but only undergo E,Z-isomerization with the formation of compounds (IIa-e). At the same time fulgides based on 1-methyl-3-formyl- and 1-methyl-3-acetylindole exhibit photochromism [2]. The absence of photochromic characteristics in compounds (Ia-e) is evidently due to steric hindrances created by the methyl group at position 2 of the indole ring [1] and also

TABLE 1. The Synthesized Compounds

Compound	Molecular formula	Color of crystals	T_{mp}, °C*	λ_{max}, nm	log ε	M** found	M calc.	Yield,*** %
IIf	$C_{17}H_{15}NO_3$	Yellow	171...172	414	4,1	281	281	63
Ig	$C_{18}H_{17}NO_3$	Bright-yellow	205...207	418	4,1	295	295	68
Ih	$C_{27}H_{19}NO_3$	Orange	241...242	480	4,1	405	405	3
IIh	$C_{27}H_{19}NO_3$	Dark-red	181...183	484	4,2	405	405	25
VII	$C_{20}H_{19}NO_3$	Light-yellow	132...134	330	3,7	321	321	23

*Compounds (IIf, h, Ig, VII) were crystallized from ethanol, (Ih) from isopropanol.
**Measured by mass spectrometry on a Varian MAT-311A instrument.
***Calculated on the initial 1-,ethyl-2-formylindole.

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