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REDUCTION OF 4-ARYLAZOINDOLES

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It was established that 4-acetamido-5-hydroxyindole derivatives are formed in the reduction of 4-phenylazo-5-hydroxyindole derivatives with zinc dust in acetic acid in the presence of acetic anhydride and sodium acetate. However, p-semidine rearrangement of the intermediate hydrazo derivatives is observed in the analogous reduction of 4-arylazo-5-methoxyindoles, and 4-acetamido-5-methoxy-7-arylaminoindoles are formed. The latter are oxidized by oxygen and nitric acid to 4-oxo-7-arylimino-4,7-dihydroindoles; nitration of the arylimino ring occurs in some cases under the influence of nitric acid.

We have previously observed rearrangements of the o-benzidine and o-semidine type in the reduction of 3-arylazoindoles with zinc dust in acetic acid in the presence of acetic anhydride and sodium acetate [1-3]; it was established that the direction of the rearrangement depends on the character of the substituent attached to the nitrogen atom of the indole ring but is independent of the character and position of the substituents in the aryl ring of the arylazo group.

We have now found that rearrangement does not occur in the reduction of 1,2-dimethyl-3-carbethoxy-4-phenylazo-5-hydroxyindole (Ia) by the same method and that the only product is 1,2-dimethyl-3-carbethoxy-4-acetamido-5-hydroxyindole (II), which is converted to 1,2,5-trimethyl-3-carbethoxyoxazolo[4,5-e]indole (III) if the process is carried out under more severe conditions. However, p-semidine rearrangement of the intermediate hydrazo derivatives A is observed in the analogous reduction of 1,2-dimethyl-3-carbethoxy-4-arylazo-5-methoxyindoles (Ie-h) obtained from Ia-d by the action of dimethyl sulfate in an alkaline medium, and 1,2-dimethyl-3-carbethoxy-4-acetamido-5-methoxy-7-arylaminoindoles (IVa-d) are formed.

The direction of the rearrangement in the case of IVa was confirmed by the PMR spectrum. Two doublet signals at 6.92 and 7.2 ppm ($J \sim 9$ Hz), which are related to 6-H and 7-H of the indole ring, are observed in the PMR spectrum of the starting 4-phenylazo-5-methoxyindole derivative (Ie). The character of the signal of the proton of the indole ring (singlet at 6.64 ppm) in the PMR spectrum of rearrangement product IVa indicates replacement of one of the two ortho protons of the indole ring. This substituting group is a phenylamino residue, as evidenced by the signals of the remaining aromatic protons in the spectrum, viz., a doublet at 6.60 ppm (2H), a triplet at 7.13 ppm (2H), and a triplet at 6.72 ppm (1H), which correspond, respectively, to the ortho, meta, and para protons of the monosubstituted phenyl ring. Since the rearrangement cannot take place in the meta position relative to the amino group, 7-phenylamino-5-methoxyindole derivative IVa is formed.

If 1,2-dimethyl-3-carbethoxy-4-phenylazo-5-acetoxyindole (Ii), obtained by the action of acetic anhydride on Ia, is used in the investigated reaction, 1,2,5-trimethyl-3-carbethoxy-8-phenylaminooxazolo[4,5-e]indole (V) is formed. In this case the reaction evidently proceeds through a step involving the formation of a product (B) of semidine rearrangement, after which an oxazole ring is formed.

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TABLE 1. 4-Arylazoindoles (Ia-i)

Compound	R	R'	mp, °C	Found, %			Empirical formula	Calc., %			Yield, %
				C	H	N		C	H	N	
Ia	H	H	190–191[a]	67,6	5,7	12,7	$C_{19}H_{19}N_3O_3$	67,6	5,7	12,5	98
Ib	CH_3	H	201–202[a]	68,4	6,0	12,1	$C_{20}H_{21}N_3O_3$	68,4	6,0	12,0	99
Ic	OCH_3	H	184–185[b]	65,6	5,8	11,4	$C_{20}H_{21}N_3O_4$	65,4	5,8	11,4	97
Id	Cl	H	186–187[a]	61,6	5,0	11,4	$C_{19}H_{18}ClN_3O_3$[c]	61,4	4,9	11,3	99
Ie	H	CH_3	159–160[d]	68,2	6,2	12,2	$C_{20}H_{21}N_3O_3$	68,4	6,0	12,0	77
If	CH_3	CH_3	151,5–153[d]	69,0	6,4	11,6	$C_{21}H_{23}N_3O_3$	69,0	6,3	11,5	75
Ig	OCH_3	CH_3	130–131[e]	66,3	6,1	11,0	$C_{21}H_{23}N_3O_4$	66,1	6,1	11,0	57
Ih	Cl	CH_3	178–179[d]	62,0	5,1	11,1	$C_{20}H_{20}ClN_3O_3$[f]	62,3	5,2	10,9	50
Ii	H	$COCH_3$	206–207[a]	66,2	5,6	11,0	$C_{21}H_{21}N_3O_4$	66,5	5,6	11,1	91

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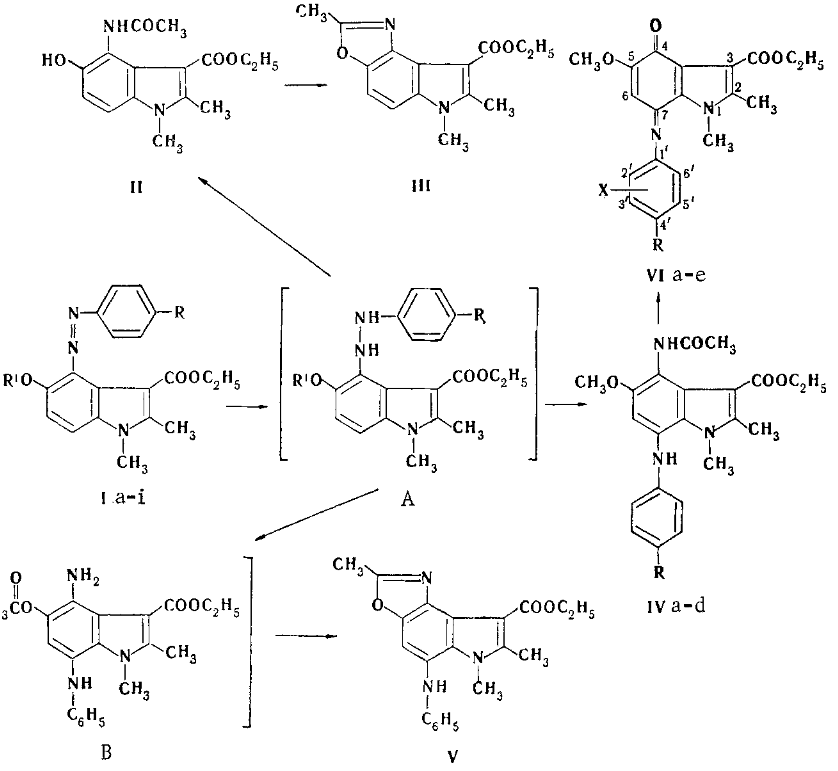
[a] From dimethylformamide (DMF)–methanol (1:1). [b] From DMF. [c] Found: Cl 9.4%. Calculated: Cl 9.5%. [d] From methanol. [e] From isopropyl alcohol. [f] Found: Cl 9.4%. Calculated: Cl 9.2%.



I a $R=R^1=H$; b $R=CH_3$, $R^1=H$; c $R=OCH_3$, $R^1=H$; d $R=Cl$, $R^1=H$; e $R=H$, $R^1=CH_3$; f $R=R^1=CH_3$; g $R=OCH_3$, $R^1=CH_3$; h $R=Cl$, $R^1=CH_3$; i $R=H$, $R^1=COCH_3$; IV a $R=H$; b $R=CH_3$; c $R=OCH_3$; d $R=Cl$; VI a $R=X=H$; b $R=OCH_3$, $X=H$; c $R=OCH_3$, $X=2'\text{-}NO_2$; d $R=H$, $X=4'\text{-}NO_2$; e $R=CH_3$, $X=2'\text{-}NO_2$

The absence of rearrangement in the case of Ia, which contains an unprotected OH group, is probably associated with the existence of a hydrogen bond between the hydroxy group and the nitrogen atom of the arylhydrazo group in compound A, which prevents rearrangement.

Compounds IVa, c are oxidized by oxygen in DMF in the presence of copper acetate to 1,2-dimethyl-3-carbethoxy-5-methoxy-4-oxo-7-phenylimino-4,7-dihydroindole (VIa) and 1,2-dimethyl-3-carbethoxy-5-methoxy-4-oxo-7-(4-methoxyphenylimino)-4,7-dihydroindole (VIb), respectively. Like the oxidation with oxygen, the oxidation of IVa with concentrated nitric acid at 30°C leads to VIa, whereas 1,2-dimethyl-3-carbethoxy-5-methoxy-4-oxo-7-(2-nitro-4-methoxyphenylimino)-4,7-dihydroindole (VIc) is formed from IVc under these conditions, i.e., the arylimino substituent undergoes nitration. The oxidation of IVa with concentrated nitric acid at 100°C leads to 1,2-dimethyl-3-carbethoxy-5-methoxy-4-oxo-7-(4-nitrophenylimino)-4,7-dihydroindole (VId), while the oxidation of IVb leads to 1,2-dimethyl-3-carbethoxy-5-methoxy-4-oxo-7-(2-nitro-4-methylphenylimino)-4,7-dihydroindole (VIe).

TABLE 2. 7-Arylaminoindoles (IVa-d)

Compound	R	mp, °C	Found, %			Empirical formula	Calculated, %			Yield, %
			C	H	N		C	H	N	
IVa	H	222—222,5[a]	66,8	6,5	10,6	$C_{22}H_{25}N_3O_4$[b]	66,8	6,4	10,6	22
IVb	CH_3	209—210[c]	67,7	6,6	10,3	$C_{23}H_{27}N_3O_4$	67,5	6,7	10,3	17
IVc	OCH_3	200—201[c]	65,1	6,4	9,8	$C_{23}H_{27}N_3O_5$	64,9	6,4	9,9	25
IVd	Cl	239—240[c]	61,6	5,7	10,0	$C_{22}H_{24}ClN_3O_4$[d]	61,5	5,6	9,8	16

[a] From ethanol. [b] M^+ 395. [c] From methanol. [d] Found: Cl 8.2%. Calculated: Cl 8.3%.

The structure of VId, particularly the presence of a nitro group in the 4' position, i.e., in the para position relative to the imino group, follows from the PMR spectrum, in which the signals of the protons of the arylimino ring form a multiplet of the AA'BB' type.

In contrast to VId, the position of the nitro group in VIc, e cannot be determined from the type of spectrum of the protons of the arylimino ring of these compounds, since it, in conformity with a 1,2,4-trisubstituted benzene, does not depend on the mutual orientation of the nitro and imino groups. However, a comparison of the chemical shifts of the protons of the arylimino rings in VIa, e (Table 4) provides evidence in favor of an ortho orientation of the indicated groups. The chemical shift of the proton in the meta position relative to the nitro group (6.83 ppm) for the proposed structure of VIe is in good agreement with an ortho orientation of this proton relative to the imino group (in particular, with the chemical shift 6.89 ppm of the analogous proton in VIa) and with the mutually compensating effect on its chemical shift of the m-NO_2 and m-CH_3 substituents. The assumption of a meta orientation of the imino and nitro groups in VIe would lead (with allowance for a similar compensating effect of the o-CH_3 and m-NO_2 groups) to an abvious discrepancy between the chemical shift of the proton in the meta position relative to the nitro group (6.83 ppm), to which a meta orientation relative to the nitro group also should have been assigned in this structure, and the chemical shift of the proton in the meta position relative to the imino group in VIa (7.41 ppm).

In contrast to VIe, the structure of VIc cannot be established by a comparison of the chemical shifts of the protons of the arylimino rings in VIa and VIc because of the similar effect of the imino and methoxy groups on the chemical shifts of the protons of the benzene ring; this effect is manifested in particular in the close chemical shifts of all of the protons of the arylimino ring in VIb. To establish the structure of VIc we therefore compared the chemical shifts in the ^{13}C NMR spectra of the CH groups of the arylimino rings in VIa, b, c* (Table 5).

With allowance for the relative intensities of the signals, as well as the effect of a substituent on the ^{13}C chemical shifts in substituted benzenes [4], the signals at 120.2, 128.7, and 124.2 ppm in the ^{13}C NMR spectrum of VIa were assigned, respectively, to the carbon atoms in the ortho, meta, and para positions relative to the imino group, while the signals at 122.0 and 114.2 ppm in the ^{13}C NMR spectrum of VIb were assigned to the carbon atoms, respectively, in the ortho and meta positions relative to the imino group. The latter values, as well as the contribution to the ^{13}C chemical shifts due to the effect of a nitro group in series of substituted benzenes ($\Delta\delta_{ortho} = -4.8$ ppm, $\Delta\delta_{meta} = +0.9$ ppm, and $\Delta\delta_{para} = +5.8$ ppm) [4], were used to calculate the expected ^{13}C chemical shifts of the CH groups of the arylimino ring of VIc under the assumption of an ortho orientation of the imino and nitro groups ($C_{3'}$ 109.4 $C_{5'}$ 120, and $C_{6'}$122.9) or a meta orientation of the same groups ($C_{2'}$ 117.2, $C_{5'}$ 115.1, and $C_{6'}$ 127.8 ppm). The chemical shifts of the corresponding ^{13}C atoms found from the spectrum of VIc (108.8, 120.9, and 123.0 ppm) are in good agreement with the first set of calculated chemical shifts; this constitutes evidence for another orientation of the imino and nitro groups in VIc, as well as in VIe.

EXPERIMENTAL

The PMR spectra of solutions of the compounds in deuterochloroform were recorded with JNM-4H-100 (Jeol) (IVa and VIa-e) and C-60HL (Jeol) (Ie) spectrometers with hexamethyldisiloxane as the internal standard. The ^{13}C NMR spectrum of VIa was recorded with an XL-100A-

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*The signals of the quaternary carbon atoms in these compounds were not assigned unambiguously.

TABLE 3. 7-Arylimino-4,7-dihydroindoles (VIa-e)

Compound	R	X	mp, °C	Found, %			Empirical formula	Calc., %			Yield, %
				C	H	N		C	H	N	
VI a	H	H	171—173[a]	67,8	5,7	7,8	$C_{20}H_{20}N_2O_4$	68,2	5,7	8,0	48
VIb	OCH_3	H	182—183[b]	65,6	5,6	7,5	$C_{21}H_{22}N_2O_5$	66,0	5,8	7,3	21
VIc	OCH_3	2′-NO_2	219—220[a]	59,2	5,1	9,8	$C_{21}H_{21}N_3O_7$	59,0	5,0	9,8	74
VId	H	4′-NO_2	212—214[a]	60,4	4,7	10,3	$C_{20}H_{19}N_3O_6$	60,5	4,8	10,6	23
VIe	CH_3	2′-NO_2	213—214[a]	61,2	5,2	10,2	$C_{21}H_{21}N_3O_6$	61,3	5,2	10,2	60

[a] From methanol. [b] From hexane—ethyl acetate (1:1).

12 (Varian) spectrometer with a frequency for ^{13}C nuclei of 25.2 MHz, while the ^{13}C NMR spectra of VIb and VIc were recorded with a WH-90 (Bruker) spectrometer with a frequency for the ^{13}C nuclei of 22.63 MHz; the spectra were recorded with complete and partial decoupling of the protons, and deuterochloroform (δ 76.9 ppm) was used as the solvent and standard [5]. The individuality of the substances was monitored on a Silufol UV-254 plate in a benzene—methanol system (9:1) in the case of Ia-i, II, III, IVb-d, V, and VIc-e and in an acetone—hexane system (1:1) in the case of IVa and VIa, b.

1,2-Dimethyl-3-carbethoxy-4-arylazo-5-hydroxyindoles (Ia-d). A diazonium salt obtained by the usual method from 0.26 mole of the arylamine, 60 ml of concentrated HCl, and 0.3 mole of sodium nitrite was added at —5 to 0°C to a solution of 0.2 mole of 1,2-dimethyl-3-carbethoxy-5-hydroxyindole in a mixture of 400 ml of dioxane and 400 ml of 5% solutions of sodium hydroxide, and the mixture was stirred at 0°C for 3 h. The resulting precipitate was removed by filtration, washed with water, and dried. Data for Ia-d are presented in Table 1.

1,2-Dimethyl-3-carbethoxy-4-arylazo-5-methoxyindoles (Ie-h). A 200-ml sample of a 2 N solution of sodium hydroxide was added dropwise at 5-6°C to a suspension of 0.1 mole of 1,2-dimethyl-3-carbethoxy-4-arylazo-5-hydroxyindole (Ia-d) in a mixture of 300 ml of dioxane and 100 ml of acetone, after which 19 ml of dimethyl sulfate was added immediately. The mixture was stirred for 1 h, and the temperature was gradually raised to room temperature. The resulting precipitate was removed by filtration, washed with water and methanol, and dried. Data for Ie-h are presented in Table 1.

PMR spectrum of Ie: 0.87 (t, $COOCH_2\mathbf{CH_3}$); 2.48 (s, 2-CH_3); 3.55 (s, N—CH_3); 3.77 (q, $COO\mathbf{CH_2}CH_3$); 3.92 (s, OCH_3); 6.92, 7.2 (two d, 6-H and 7-H of the indole ring); 7.35-8.0 ppm (m, five aromatic protons).

1,2-Dimethyl-3-carbethoxy-4-phenylazo-5-acetoxyindole (Ii). A solution of 3.37 g (0.01 mole) of Ia in 4 ml of acetic anhydride was refluxed for 2 h, after which it was cooled, and the resulting precipitate was removed by filtration. Data for Ii are presented in Table 1.

1,2-Dimethyl-3-carbethoxy-4-acetamido-5-hydroxyindole (II). A 3.2-g (0.039 mole) of fused sodium acetate, 8.5 ml (0.09 mole) of acetic anhydride, and (in portions) 11.7 g (0.18 mole) of zinc dust were added successively to a suspension of 10 g (0.03 mole) of Ia in 60 ml of glacial acetic acid while maintaining the temperature of the reaction mixture at 55-60°C. At the end of the addition of the zinc dust, the reaction mixture was stirred at 30 min, and the temperature was gradually lowered to room temperature. The unchanged zinc dust was removed by filtration, and the mother liquor was poured into water. The resulting precipitate was removed by filtration, washed with water, and dried to give 5 g (58%) of II with mp 163-164°C (from methanol). Found: C 62.0; H 6.2; N 9.6%. $C_{15}H_{18}N_2O_4$. Calculated: C 62.1; H 6.3; N 9.7%.

1,2,5-Trimethyl-3-carbethoxyoxazolo[4,5-e]indole (III). This compound was obtained from 3.37 g (0.01 mole) of Ia, 1.07 g (0.013 mole) of fused sodium acetate, 2.9 ml (0.03 mole) of acetic anhydride, and 3.9 g (0.06 mole) of zinc dust. The reaction and isolation of the substance were carried out under the conditions of the synthesis of II, except that the reaction mixture was refluxed for 30 min after the addition of the zinc dust. The yield of III, with mp 161-162°C (from methanol), was 1.8 g (66%). Found: C 66.3; H 5.9; N 10.3%. $C_{15}H_{16}N_2O_3$. Calculated: C 66.2; H 5.9; N 10.3%.

1,2-Dimethyl-3-carbethoxy-4-acetamido-5-methoxy-7-arylaminoindoles (IVa-d). These compounds were obtained from 0.05 mole of Ie-h, 0.07 mole of fused sodium acetate, 0.15 mole of acetic anhydride, and 0.3 mole of zinc dust. The reaction was carried out under

TABLE 4. PMR Spectra of 7-Arylimino-4,7-dihydroindoles (VIa-e)

Compound	Position									
	1	2	3	5	6	2′	3′	4′	5′	6′
VIa	3,60 s	2,49 s	1,42 t 4,39 q	4,04 s	5,87 s	6,89	7,41	7,17	7,41	6,89
VIb	3,62 s	2,46 s	1,40 t 4,38 q	3,96 s	5,98 s	—[a]	—[a]	3,83	—[a]	—[a]
VIc	3,61 s	2,47 s	1,39 t 4,36 q	3,94 s	5,68 s	—	7,61	3,88	7,25	6,81
VId	3,61 s	2,61 s	1,39 t 4,36 q	3,99 s	5,62 s	—[a]	—[a]	—	—[a]	—[a]
VI	3,61 s	2,47 s	1,39 t 4,37 q	3,96 s	5,67 s	—	7,92	2,44	7,43	6,83

[a] The multiplet of the AA'BB' type at 6.70-6.95 ppm in the PMR spectrum of VIb and at 6.94-8.22 ppm in the PMR spectrum of VId corresponds to the protons in the 2', 3', 5', and 6' positions.

TABLE 5. ^{13}C Chemical Shifts in the Spectra of VIa-c (δ, ppm)

Compound	Group			
	CH$_3$	CH$_2$	CH	=C<
IVa	10,8; 14,1 33,6; 55,7	60,6	96,7; 120,2 124,2; 128,7	112,0; 120,1; 131,7; 140,1 149,5; 151,4; 156,6; 164,9; 175,1
VIb	10,7; 14,0 33,5; 55,6; 55,3	60,5	96,7; 114,2 122,0	111,9; 120,0; 132,0; 140,2; 142,7 151,3; 156,6; 157,0; 165,1; 175,3
VIc	10,5; 13,8; 33,6 55,7; 55,7	60,3	96,5; 108,8 120,9; 123,0	112,0; 120,1; 131,2; 137,5; 140,6 140,6; 151,9; 156,2; 156,9; 164,6; 174,8

the conditions of the synthesis of II. The unchanged zinc dust was removed by filtration,* and the mother liquor was poured into water.† The precipitate was washed with water, and dried. Data for IVa-d are presented in Table 2.

PMR spectrum of IVa: 1.39 (t, COOCH$_2$CH$_3$), 2.18 (s, COCH$_3$), 2.52 (s, 2-CH$_3$), 3.64 (s, N-CH$_3$), 3.77 (s, OCH$_3$), 4.38 (%, COOCH$_2$CH$_3$), 5.82 (s, 1'-NH), 9.40 (s, NHCOCH$_3$), 6.64 (s, indole ring proton), and 6.60-7.13 ppm (m, five aromatic protons).

1,2,5-Trimethyl-3-carbethoxy-8-phenylaminooxazolo[4,5-e]indole (V). This compound was obtained from 1.9 g (0.005 mole) of Ii, 0.6 g (0.007 mole) of fused sodium acetate, 1.4 ml (0.015 mole) of acetic anhydride, and 2 g (0.03 mole) of zinc dust. The reaction and isolation of the substance were carried out under the conditions of the synthesis of III. Recrystallization of V from ethanol gave 0.6 g (33%) of a product with mp 211-212°C. Found: C 69.1; H 5.9; N 114.%. C$_{21}$H$_{21}$N$_3$O$_3$. Calculated: C 69.4; H 5.8; N 11.6%.

1,2-Dimethyl-3-carbethoxy-5-methoxy-4-oxo-7-arylimino-4,7-dihydroindoles (VIa, b). A 0.03-g sample of copper acetate dihydrate and 3 ml of water were added to a solution of 0.01 mole of IVa, c in 50 ml of distilled DMF, and a stream of oxygen was passed through the mixture at 50°C for 16 h. The mixture was diluted with a double volume of water, and the precipitate was removed by filtration, washed with water, and dried. Data for VIa, b are presented in Table 3.

1,2-Dimethyl-3-carbethoxy-5-methoxy-4-oxo-7-arylimino-4,7-dihydroindoles (VIa, c). A 2-ml sample of concentrated HNO$_3$ was added dropwise with stirring at room temperature to a suspension of 0.01 mole of IVa, c in 50 ml of glacial acetic acid, and the reaction mixture was stirred at 30°C for 10 min. It was then poured into water, and the precipitate was removed by filtration, washed with water, and dried. Data for VIa, c are presented in Table 3.‡

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*Some IVa precipitated on the unchanged zinc dust.

†In the case of IVb, the mother liquor was evaporated, and the residue was diluted with water.

‡Compound VIa was obtained in 25% yield by this method.

1,2-Dimethyl-3-carbethoxy-5-methoxy-4-oxo-7-arylimino-4,7-dihydroindoles (VId, e). These compounds were obtained from IVa, b. The reaction and isolation were carried out under the conditions of the synthesis of VIa, c, except that the reaction mixture after the addition of nitric acid was heated at 100°C for 10 min. Data for VId, e are presented in Table 3.

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BENZINDOLES.

21.* STRUCTURES OF THE PRODUCTS OF THE WITTIG REACTION IN THE ANGULAR BENZINDOLE SERIES

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α-Phenyl-β-(1H-benzo[g]indol-3-yl)ethylene and α-phenyl-β-(3H-benzo[e]indol-1-yl)-ethylene were obtained in the form of two geometrical isomers by reaction of 3-formyl-1H-benzo[g]- and 1-formyl-3H-benzo[e]indoles with benzylidenetriphenylphosphorane in tert-butyl alcohol containing potassium tert-butoxide. The configurations of the compounds obtained were established on the basis of data from the PMR spectra.

The Wittig reaction with 3-formylindole, as a result of which α-phenyl-β-(3-indolyl)-ethylene was obtained was previously studied in [2]. However, the authors were unable to establish its configuration unambiguously. We have carried out the reaction of 3-formyl-1H-benzo[g]- and 1-formyl-3H-benzo[e]indoles with benzylidenetriphenylphosphorane in tert-butyl alcohol containing potassium tert-butoxide. In both cases we obtained a complex mixture, from which by means of column adsorption chromatography we were able to isolate α-phenyl-β-(1H-benzo[g]indol-3-yl)ethylene (I) and α-phenyl-β-(3H-benzo[e]indol-1-yl)ethylene (II) (Table 1) in low yields. We found that fusion of the indole ring with a benzene ring, particularly in the [e] position, hinders the Wittig reaction. By means of thin-layer chromatography (TLC) we observed that I and II are mixtures of two isomers with very close R_f values. Only one structural isomer of each of the olefins (Ia and IIa) was isolated in individual form by preparative TLC. We were unable to isolate the second minor isomers (Ib and IIb) in individual form.

The configurations of the compounds obtained were established from data from the PMR spectra (Table 2). To simplfy the interpretation of the PMR spectrum of a sample of Ia we obtained α-(p-toyl)-β-(1H-benzo[g]indol-3-yl)ethylene (III) in the form of one isomer via the Wittig reaction.

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*See [1] for Communication 20.

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