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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TABLE 1. Characteristics of Benzindole Analogs of Stilbene

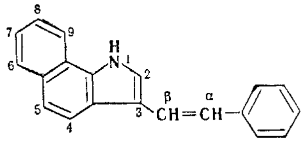
Compound	mp, °C	IR spectrum, ν, cm^{-1}	UV spectrum, λ_{max} (log ε)	Found, %			Empirical formula	Calculated, %		
				C	H	N		C	H	N
I	226—233	3420, 1670, 1640	205 (4,58), 225 (4,66), 274 (4,59), 325 (4,51)	89,0	5,7	4,9	$C_{20}H_{15}N$	89,2	5,6	5,2
Ia	245—246	3420, 1660, 1620	206 (4,49), 225 (4,60), 278 (4,50), 322 (4,52)							
II	88—93	3390, 1660, 1630	204 (4,59), 228 (4,68), 319 (4,38)	89,0	5,8	4,9	$C_{20}H_{15}N$	89,2	5,6	5,2
IIa	104,5—105	3370, 1660, 1640	206 (4,60), 227 (4,91), 317 (4,41)							
III	263—265	3420, 1660, 1640	207 (4,52), 226 (4,59), 277 (4,50), 323 (4,47)	88,2	6,05	4,6	$C_{21}H_{17}N$	89,0	6,05	4,9

The PMR spectra of Ia and III indicate a trans orientation of the olefin protons ($J_{\alpha,\beta}$ = 15.8 and 16.4 Hz, respectively). In this case a planar structure with both a transoid and a cisoid orientation of the $C_2{=}C_3$ and $C_\alpha{=}C_\beta$ bonds is possible. Interconversion of these orientations is not difficult. The absence of $J_{2,\beta}$ more likely indicates a cis orientation of 2-H and β-H and, consequently, predominance under the given conditions of a transoid orientation of the $C_2{=}C_3$ and $C_\alpha{=}C_\beta$ bonds. The signals of the protons of the phenyl ring of III constitute an AB quartet with J_{AB} = 8.0 Hz, δ_A = 7.44 ppm, and δ_B = 7.10 ppm.

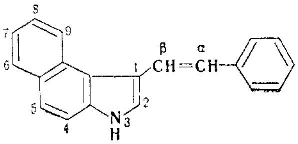
The PMR spectrum of a sample of I indicates the presence of two isomers, one of which is identical to Ia. The spin—spin coupling constant (SSCC) of the olefin protons of the second isomer is 12 Hz; this is characteristic for substituted stilbenes with a cis orientation of the olefin protons [3].

An examination of Eugon spherical atomic models shows that a planar structure of the molecule is excluded in this case. A cisoid orientation of the $C_2{=}C_3$ and $C_\alpha{=}C_\beta$ bonds with a dihedral angle between the planes of the phenyl and benzindole rings of close to 60° is possible; in this case one must take into account the possibility of ±30° rotation of the olefin fragment. This geometry explains the shift of the signal of the 2-H proton to strong field ($\Delta\delta$ = 0.42 ppm) under the influence of the π current of the phenyl ring. The shift to strong field of the signals of the olefin protons in isomer Ib as compared with Ia is in agreement with the noncoplanarity of the benzene and phenyl rings. The observed long-range SSCC $J_{2,\beta}$ = 0.8 Hz of isomer Ib also constitues evidence for the stability of this conformation.

An analysis of the PMR spectrum of a sample of IIa and Eugon spherical atomic models showed that it is the isomer with a trans orientation of the olefin protons in the planar molecule and a cisoid orientation of the exocyclic $C_\alpha{=}C_\beta$ bond relative to the $C_1{=}C_2$ bond ($J_{2,\beta}$=0.8 8 Hz), as in the α-acyl-β-([4,5]-benzindol-3-yl)ethylene molecule [4]. The PMR spectrum of a sample of II indicates the presence of two isomers, one of which is identical to IIa. The structure of the second isomer (IIb) is similar to that of nonplanar isomer Ib, viz., a cis orientation of the olefin protons and orientation of the phenyl ring at an acute angle relative to the plane of benzindole near the 2-H proton. This conclusion was drawn on the basis of SSCC $J_{\alpha,\beta}$ = 12.0 Hz and $J_{2,\beta}$ = 0.8 Hz and the considerable shift of strong field of the signals of the 2-H, α-H, and β-H protons.



I a,b



II a,b

EXPERIMENTAL

The PMR spectra of solutions of the compounds in d_6-DMSO were recorded with an HA-100 (Varian) spectrometer with hexamethyldisiloxane as the internal standard. The UV spectra of solutions in ethanol were obtained with a Specord spectrophotometer. The IR spectra of suspensions of the compounds in mineral oil were recorded with a UR-20 spectrometer.

TABLE 2. Parameters of the PMR Spectra

Compound	Chemical shifts of the protons, δ, ppm									SSCC, J, Hz			
	1-H	2-H	3-H	4-H	5-H	6-H	9-H	α-H	β-H	α, β	NH—H	4,5	2, β
Ia	12,15	7,69	—	8,05	7,52	8,30	7,85	7,13	7,48	15,8	2,5	8,6	—
Ib	11,97	7,17*	—	—	—	8,23	7,78	6,50	6,80	12,0	0,6*	8,0	0,8
IIa	—	7,67	11,65	7,53 cp		7,88	8,43	6,96	7,81	15,8	3,0	—	0,8
IIb	—	7,05*	11,43	7,50 cp		7,80	8,90	6,46	7,25	12,0	0,8*	—	0,8
III	12,12	7,66	—	8,05	7,49	—	—	7,05	7,39	16,4	2,6	8,2	—

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*The position and multiplicity of the signal were determined by double resonance.

α-Phenyl-β-(1H-benzo[g]indol-3-yl)ethylene (I). A 1.9-g (4.8 mmole) sample of benzyltriphenylphosphonium chloride was added to a solution of 0.19 g (4.84 mmole) of potassium in 10 ml of tert-butyl alcohol, and the mixture was stirred in a stream of nitrogen for 20 min. A 0.78 g (4.0 mmole) sample of 3-formyl-1H-benzo[g]indole was added at pH ∿ 7, and the mixture was stirred at room temperature until the reaction was complete according to TLC data (24 h). It was then poured into 100 ml of water, and the aqueous mixture was extracted with benzene. The benzene was removed by vacuum distillation, and the residue was separated by chromatography with a column with d = 2 cm, L 100/250 μ silica gel (50 g) as the adsorbent, and benzene as the eluent to give 0.33 g (30%) of a mixture of stereoisomers Ia and Ib. Isomers Ia and Ib were separated on plates (25 × 25 cm) with LL$_{254}$ 5/40 μ silica gel as the adsorbent and ether—petroleum ether (2:1) as the eluent.

α-Phenyl-β-(3H-benzo[e]indol-1-yl)ethylene (II). This compound was obtained as a mixture of stereoisomers IIa and IIb in 13% yield by a method similar to that used in the preparation of I.

α-(p-Tolyl)-β-(1H-benzo[g]indol-3-yl)ethylene (III). The reaction of 0.38 g (9.7 mmole) of potassium, 20 ml of tert-butyl alcohol, 4.0 (9.6 mmole) of p-methylbenzyltriphenylphosphonium chloride, and 0.78 g (4.0 mmole) of 3-formyl-1H-benzo[g]indole for 48 h by a method similar to that used in the preparation of I gave 0.28 g (20%) of ethylene III.

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