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1-PHENYLAZO-1-ALKENES[1]

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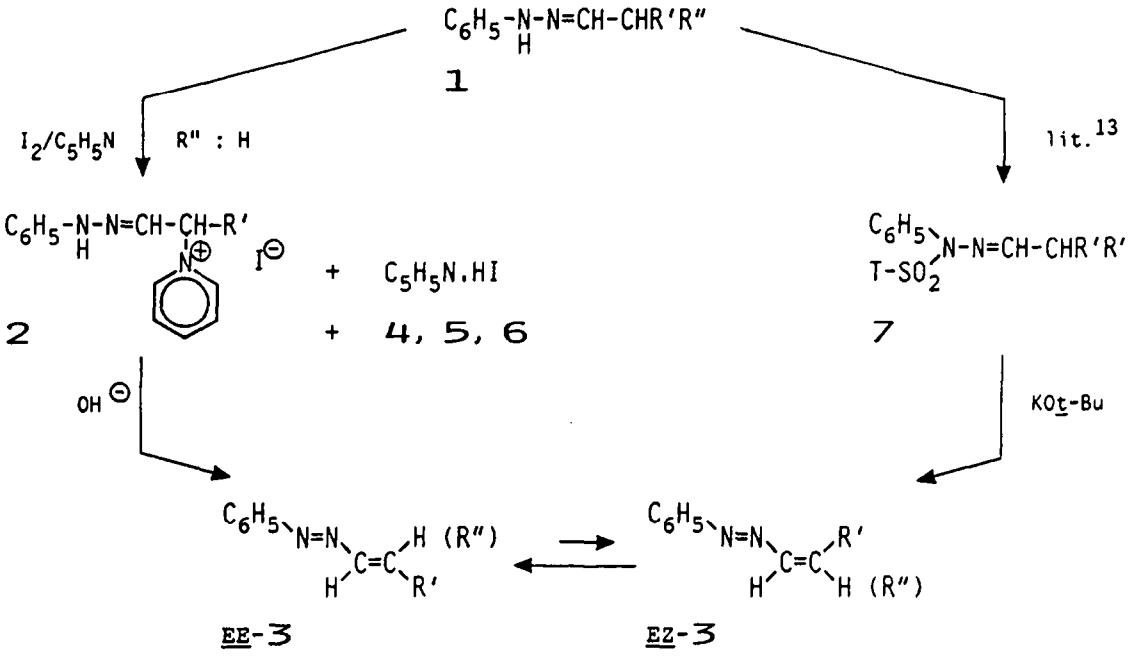
Abstract - Aliphatic aldehyde phenylhydrazones **1** were converted into 1-phenylazo-1-alkenes **3** either by the reaction with I_2 and pyridine followed by base induced 1,4-elimination of pyridine.HI (Method A), or *via* N-(4-methylbenzenesulfonyl)-N-phenylhydrazones **7** which undergo 1,4-elimination of *p*-toluenesulfinic acid upon treatment with KOt-Bu (Method B). Both procedures yield mixtures of configurational isomers of the phenylazo-alkenes *EE*- and *EZ*-**3b-3e**; Method B is giving rise to a kinetically controlled isomer mixture (*EZ*-**3** predominant), which equilibrates to the thermodynamic ratio (*EE*-**3** predominant) as afforded by Method A.

Among the various strategies pursued for the synthesis of conjugated azoalkenes, several procedures have in common the 1,4-elimination of suitably substituted hydrazones. Phenylhydrazones of aliphatic and araliphatic ketones upon reaction with iodine in pyridine are converted into α-pyridiniumalkanone phenylhydrazone iodides; the subsequent base induced 1,4-elimination of pyridinium iodide provides a practicable access to many phenylazo-alkenes.[3] Extending the scope of this method, the reaction of iodine and pyridine is now applied to aldehyde phenylhydrazones **1** in order to prepare 1-phenylazo-1-alkenes **3**.[4] An entirely different approach has been reported:[5] the Wittig reaction of arylazomethylenetriphenylphosphorane with certain aldehydes was employed for the synthesis of some 2-substituted 1-arylazo-ethenes.

Syntheses and Reactions.

The reaction of acetaldehyde phenylhydrazone (**1a**) in pyridine solution with iodine produced a mixture of water-soluble salts (Scheme 1). Pyridinium iodide was extracted with cold ethanol, thus permitting the isolation of crystalline 1-[2-(2-phenylhydrazono)ethyl]pyridinium iodide (**2a**) from the residue. The aqueous solution of the pyridinium salt **2a** was treated with sodium hydroxide, the resultant phenylazo-ethene (**3a**) was extracted with ether and isolated as a yellow oil.

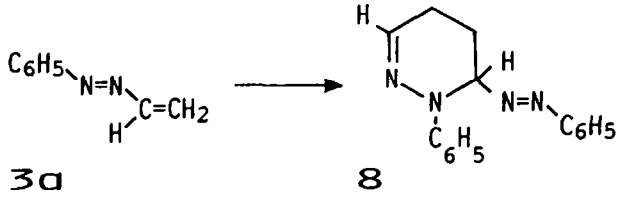
Scheme 1:



R', R" see Table 1; T : 4-$CH_3C_6H_4$

Phenylazo-ethene (**3a**) gradually underwent cyclodimerization; the only regioisomer formed was 1-phenyl-6-phenylazo-1,4,5,6-tetrahydropyridazine (**8**) (Scheme 2). The regioselectivity of this hetero Diels-Alder reaction parallels that of the dimerization of α,β-unsaturated carbonyl compounds (e.g. acrolein,[6] 1-phenyl-2-propen-1-one[7]) and of 2-phenylazo-1-alkenes[8] (these heterodienes have in common a terminal methylene group).

Scheme 2:



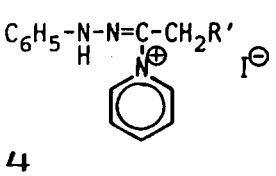
The reaction of the homologous aldehyde phenylhydrazones **1b-1g** (all having an α-methylene group) with iodine and pyridine gave rise to a complex mixture (Scheme 1): The conversion of propionaldehyde phenylhydrazone (**1b**) yielded the following products: Beside pyridinium iodide and the desired 1-[2-(2-phenyl-

Table 1: 1-Phenylazo-1-alkenes **3**

			Method A[a] (1->[2]->3)				Method B[a] (7->3)			
3	R'	R"	temp., time	purif. (b,c)	yield [%][d]	ratio *EE*:*EZ*[e]	solv[b] temp	purif. (b,c)	yield [%]	ratio *EE*:*EZ*
a	H	H	(a)		38	-	B, 12°C	SiO_2, P/E 9:1	51	-
b	CH_3	H	r.t., 20 h	(f)	33[g]	73:27	E, -60°C	SiO_2, P/E 2:1	43	5:95
							T, -20°C	SiO_2, P/E 2:1	68	15:85
c	CH_3CH_2	H	40°C,	Al_2O_3, P/E 8:2	21	85:15	E, -50°C	Al_2O_3, P/E	35	35:65
d	$(CH_3)_2CH$	H	r.t., 14 h	SiO_2, P/E 9:1	34	90:10	E, -35°C	Al_2O_3, P/E 8:2	49	37:63
e	*n*-C_5H_{11}	H	50°C, 2 h	SiO_2, P/E 9:1	26	85:15	E, -55°C	Al_2O_3, P/E 8:2	46	40:60
f	C_6H_5	H	0°C, 2 h	(h)	57	100:0	E, -60°C	(h)	65	100:0
g	$C_6H_5CH_2$	H	50°C, 1.5 h	SiO_2, B	23[i]	100:0				
h	CH_3	CH_3					E, -55°C	Al_2O_3, P/E 8:2	23	-

(a) For the detailed procedure see Experimental.
(b) Solvents: B benzene, E diethyl ether, P petroleum ether, T toluene.
(c) Column chromatography, see Experimental.
(d) Overall yields are calculated for the actual conversion of **1** into **3**.
(e) The isomer ratio was determined by ^1H nmr immediately after work-up.
(f) Kugelrohr distillation at 60°C, 5 Pa.
(g) **1b** (24%) was recovered, and in addition, **6b** (27%) was isolated.[9]
(h) M.p. 114-117°C (hexane); lit.[5] 111°C.
(i) Within a few days **3g** completely isomerized into cinnamaldehyde phenylhydrazone (**9g**) (identical with authentic sample[10]).

hydrazono)propyl]pyridinium iodide (**2b**), also the isomeric 1-[1-(2-phenylhydrazono)-propyl]pyridinium iodide (**4b**) and its oxidation product 1-phenyl-3-ethyl-1,2,4-triazolo[4,3-a]pyridinium iodide (**5b**), and 1,5-diphenyl-3-ethylformazane (**6b**)[9] were isolated.[4,11]



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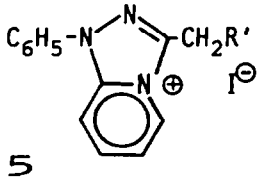

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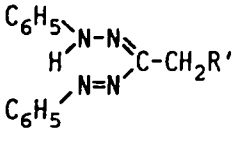

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R' see Table 1.

The side-reaction of aldehyde phenylhydrazones **1** leading to the salts **4** parallels the conversion of ketone arylhydrazones with bromine in pyridine into N-(arylazo-alkyl)pyridinium bromides[2,12] which are not capable of undergoing tautomerization. The bicyclic salt **5b** arises from subsequent oxidation of the pyridinium salt **4b** with iodine, as has been proved separately.[4,11] The conversion of aldehyde phenylhydrazones **1** into formazanes **6** is indicative of phenyldiazonium ion (presumably derived from phenyldiazenium ion: owing to some water present, it may be generated from the conceivable N-(phenylazo-alkyl)-pyridinium precursor of **4**,[2] *vide-supra*): accordingly, addition of 2-naphthol afforded 1-phenylazo-2-naphthol.

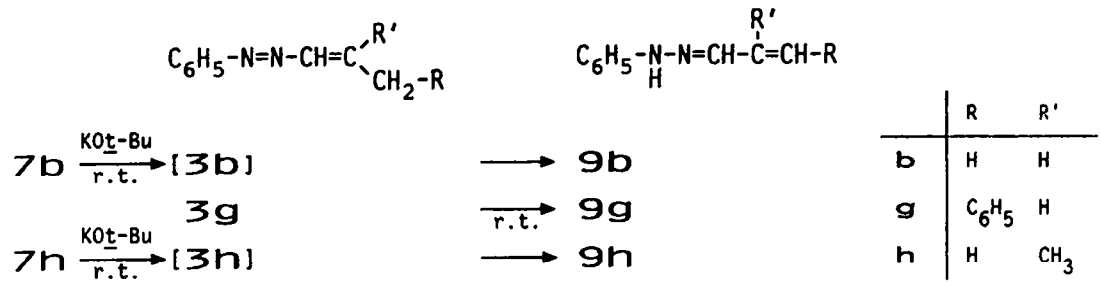
For the preparation of the 1-phenylazo-1-alkenes **3b-3g**, the isolation of the precursory pyridinium salts **2** is not required (Method A). The mixture of products resulting from the reaction of phenylhydrazones **1** with iodine and pyridine was extracted with petroleum ether in order to remove unchanged starting material **1** and the formazane **6** formed. The fraction left behind containing the salts **2**, **4**, **5**, and pyridinium iodide was treated with aqueous sodium bicarbonate solution; the colored products **3** were extracted with petroleum ether; purification (cf. Table 1) furnished the yellow or orange oils *EE*- and *EZ*-**3b-3e**, *EE*-**3g**, and crystalline *EE*-**3f**.

The competitive reactions of aldehyde phenylhydrazones **1** with iodine and pyridine provided unsatisfactory yields of 1-phenylazo-1-alkenes **3**. This led to pursue an alternative approach: Tosylation of aldehyde phenylhydrazones forming N-(4-methylbenzenesulfonyl)-N-phenylhydrazones[13] followed by base induced 1,4-elimination of *p*-toluenesulfinic acid brings about the conversion into phenylazo-alkenes; so far, this reaction has found only scattered application (the bases used were sodium isopropoxide[14] and lithium hydride[15]).

Treatment of N-phenyl-N-tosylhydrazones **7**[13] with potassium *t*-butoxide afforded 1-phenylazo-1-alkenes **3** in moderate yields (Method B, cf. Scheme 1; Table 1). The reaction could not be brought to completion, and invariably, some starting material **7** was recovered despite of prolonged reaction times. Low reaction temperatures (-60 to -20°C) are imperative in order to prevent base catalyzed tautomerization to α,β-unsaturated aldehyde phenylhydrazones: For example, the reaction of **7h** with potassium *t*-butoxide at room temperature afforded methacrolein phenylhydrazone (**9h**),[10] and likewise, **7b** yielded acrolein phenylhydrazone (**9b**)[11] (Scheme 3). Without base catalyst, pure 3-phenyl-1-phenylazo-1-propene (**3g**) isomerized within a few days yielding cinnamaldehyde phenylhydrazone (**9g**)[10].

Moreover, a nonnucleophilic base is required to induce the elimination reaction converting **7** into **3**. Otherwise, nucleophilic addition of the base to the hydrazone C=N double bond followed by 1,2-elimination of *p*-toluenesulfinic acid occurs as a competing reaction affording different products.[11]

Scheme 3:



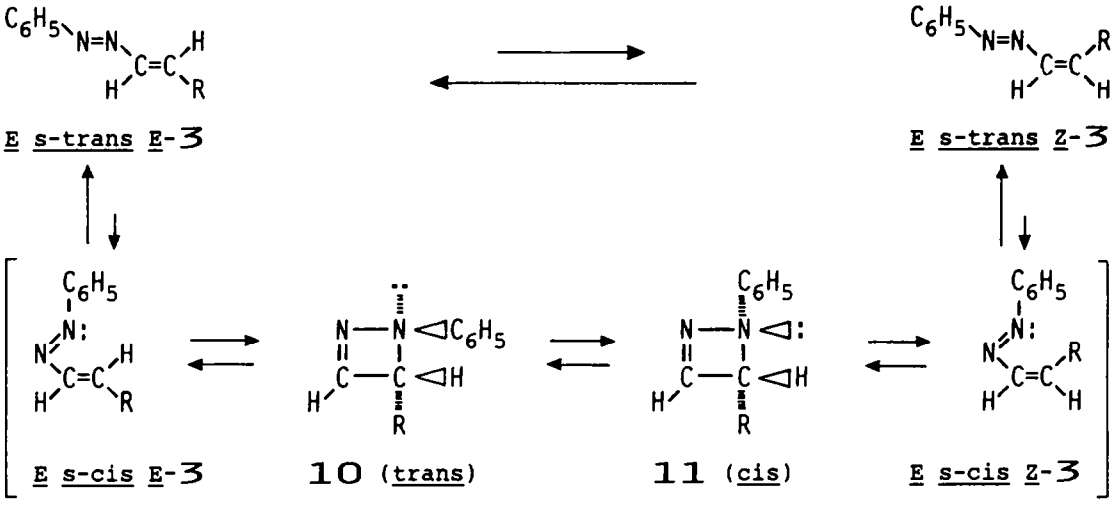
The α-substitution of phenylhydrazones by iodine and pyridine (Method A) is restricted to α-methyl- and α-methylene groups.[3] On the other hand, the alternative approach (Method B) offers the advantage of converting phenylhydrazones with an α-methine group *via* N-phenyl-N-tosylhydrazones into phenylazo-alkenes: Thus, 1-phenylazo-2-methyl-1-propene (**3h**) is accessible from the hydrazone **7h**.

Both synthetic routes (Methods A and B) furnish mixtures composed of the two configurational isomers of monoalkyl-substituted phenylazo-alkenes *EE*- and *EZ*-**3b-3e** (Table 1). Invariably, an excess of the *EE*-**3** isomers is produced by Method A, the isomer ratio as determined by ^{1}H nmr (Table 2) remaining constant at room temperature. In sharp contrast to this, the product mixture obtained from the N-phenyl-N-tosylhydrazones **7** (Method B) consists predominantly of the *EZ*-**3** isomers (with the exception of *EE*-**3f** and *EE*-**3g** being the only isomers formed by both procedures). Obviously, Method B provides kinetically controlled products, the isomer ratio of the resultant mixture changes and gradually approaches the thermodynamic equilibrium ratio as furnished directly by Method A.

The base-induced 1,4-elimination of *p*-toluenesulfinic acid from the phenyltosylhydrazones **7** (Method B) is related to the Shapiro reaction:[16] The base-catalyzed decomposition of tosylhydrazones has been reported to afford an abnormally high *Z/E* ratio of the olefins formed,[17] and parallels the observed preference of the formation of *Z*-olefins **3** from **7**.

Like other phenylazo-alkenes,[18,19] the *EE*- and *EZ*-1-phenylazo-1-alkenes **3b-3e** are interconvertible at r.t., the olefinic double bond undergoing an unusually facile and apparently uncatalyzed isomerization. The following tentative rationalization is offered (Scheme 4): A clear preference of the s-*trans* conformation at the central single bond of the heterodiene system of both *EE*- and *EZ*-**3** is inferred by the extinction coefficients of the π-π*-absorption[18,20] (Table 3). However, some equilibrium concentration of the s-*cis* conformer has to be considered; the s-*cis* conformers of both *EE*- and *EZ*-**3** feature the geometric prerequisite for an electrocyclization reaction:

Scheme 4:



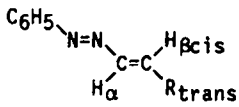
By analogy to the well documented butadiene - cyclobutene interconversion,[21] a conrotatory ring-closure of the heterodienes *EE*- and *EZ*-**3** is conceived to form the intermediate diazetine derivatives[22] **10** and **11**, with *trans*- and *cis*-oriented alkyl- and N-phenyl-substituents, respectively. Unlike cyclobutenes, the diazetines **10** and **11** may equilibrate owing to inversion at the pyramidal nitrogen atom. Conrotatory ring-opening in a manner providing the energetically favoured *E*-configuration of the azo group, eventually gives rise to the azo-alkenes *EE*-and *EZ*-**3**, the respective olefinic configuration reflecting the stereochemistry of the cyclic valence isomers **10** and **11**.

Structure.

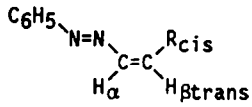
^{1}H nmr: The phenylazo-1-alkenes **3** display clearly discernible signals (Table 2): Apart from phenyl resonances, the signal at lowest field due to the effect of the geminal phenylazo substituent is assigned to the olefinic proton Hα at C-1.[23] Both olefinic protons Hβ at C-2 resonate at higher field, Hβ_{trans} being the most shielded olefinic proton.

The assignment of *EE*- and *EZ*-**3** is mainly based on the typical coupling constants across the olefinic bond $^3J_{cis}$ = 7.5-9.5 Hz, $^3J_{trans}$ = 14-15 Hz, and also $^4J_{cis} \leq 1$ Hz, $^4J_{trans} \cong 2$ Hz. The configurational isomers *EE*- and *EZ*-**3** show significant trends of proton shifts: The chemical shift of Hα is marginally affected by an alkyl group at C-2. With reference to **3a**, alkyl substitution at C-2 entails deshielding of Hβ, Hβ_{cis} being significantly stronger affected than Hβ_{trans}. The olefinic configuration is also reflected by the allylic proton shifts, the protons at C-3 of R_{cis} resonating at lower field.

Table 2: ^1H nmr Data of 1-Phenylazo-1-alkenes **3**.(a,b)



EE-3



EZ-3

3	R_{cis}	R_{trans}	Solv.	Hα	$H\beta_{cis}$	$H\beta_{trans}$	R_{cis}	R_{trans}
a	H	H	C(c)	7.21	6.14	5.82	H	H
			B(c)	7.38	6.13	5.52	H	H
			Δ(d)	-0.17	0.01	0.30	-	-
b *EE*	H	CH_3	C	7.16	6.79	-	H	2.00
			B	7.32	6.72	-	H	1.60
			Δ	-0.16	0.07	-	-	0.40
b *EZ*	CH_3	H	C	7.04	-	6.22	2.23	H
			B	7.23	-	5.83	2.11	H
			Δ	-0.19	-	0.41	0.12	
c *EE*	H	CH_2CH_3	C	7.17	6.80	-	H	2.38, 1.17
			B	7.37	6.82	-	H	2.00, 0.80
			Δ	-0.20	-0.02	-	-	0.38, 0.37
c *EZ*	CH_2CH_3	H	C	7.03	-	6.10	2.85, 1.18	H
			B	7.22	-	5.83	2.77, 0.97	H
			Δ	-0.19		0.27	0.08, 0.21	-
d *EE*	H	$CH(CH_3)_2$	C	7.12	6.73	-	H	2 57, 1.15
			B	7.37	6.85	-	H	2.23, 0.90
			Δ	-0.25	-0.12	-	-	0.34, 0.25
d *EZ*	$CH(CH_3)_2$	H	C	6.97	-	5.90	3.73, 1.18	H
			B	7.20	-	5.71	3.88, 1.04	H
			Δ	-0.23	-	0.19	-0.15, 0.14	-
e *EE*	H	$CH_2C_4H_9$	B	7.41	6.84	-	H	2.3-1.8 1.5-0.6
e *EZ*	$CH_2C_4H_9$	H	B	7.28	-	5.88	2.9-2.6 1.7-0.6	H
f *EE*	H	C_6H_5	B	8.18	7.70	-	H	6.8-6.3
g *EE*	H	$CH_2C_6H_5$	B	7.26	(e)	-	H	3.23, 7.2-6.9
h	CH_3	CH_3	C	7.07	-	-	2.32	2.00
			B	7.25	-	-	2.16	1.66
			Δ	-0.18	-	-	0.16	0.34

(a) C_6H_5-N=N-CH=: δ(CCl_4): 7.8-7.5 (m, 2H, H_o); 7.4-6.6 (m, 4H, H_m, H_p, Hα). δ(C_6D_6): 8.0-7.7 (m, 2H, H_o), 7.5-6.6 (m, 4H, H_m, H_p, Hα).

(b) Olefinic coupling (Hα, Hβ): $^3J_{cis}$: 7.5-9.5 Hz; $^3J_{trans}$: 14-15 Hz.
Allylic coupling (Hα, HC-3): $^4J_{cis} \leq 1$ Hz; $^4J_{trans} \cong 2$ Hz.
Vicinal coupling (Hβ, HC-3): $^3J = 7.5$ Hz.

(c) Solvents: B benzene; C CCl_4.

(d) Δ = δ(CCl_4) - δ(C_6D_6).

(e) Submerged under aromatic signals.

The shift difference is largest between R_{cis} and R_{trans} methine of *EE*- and *EZ*-**3d**, in line with results of earlier studies on similar systems.[25]

The use of C_6D_6 as solvent exerts significant effects in different directions as the solvent shift differences $\Delta = \delta(CCl_4) - \delta(C_6D_6)$ of olefinic and allylic protons reveal: $H\alpha$ experiences a downfield shift (negative Δ) by an average of 0.2 ppm irrespective of the olefinic configuration; the protons *cis* to the phenylazo group, i.e. $H\beta_{cis}$ and the protons at C-3 of R_{cis} are only slightly affected (increasing branching at C-3 enhances deshielding), but $H\beta_{trans}$ and the protons at C-3 of R_{trans} are significantly shifted to lower field (positive Δ). These characteristic solvent shifts agree well with results on related double-bonded systems.[25] Moreover, they are useful in structural assignments, for instance, they permit configurational assignments of systems lacking olefinic coupling constants, e.g. **3h**.

Table 3: Uv-vis Spectra of 1-Phenylazo-1-alkenes **3**.

				λ_{max} [nm] (log ε) (ethanol)		
3	R'	R"	*EE*:*EZ*(a)	K-band	π-π^*	n-π^*
a	H	H	-	227 (3.92)	295 (4.09)	417 (2.57)
b	CH_3	H	5:95	229 (4.02)	303 (4.24)	427 (2.47)
c	CH_3CH_2	H	85:15	229 (4.04)	303 (4.32)	423 (2.53)
c	CH_3CH_2	H	35:65	230 (4.09)	305 (4.35)	426 (2.56)
d	$(CH_3)_2CH$	H	90:10	229 (3.96)	300 (4.16)	419 (2.55)
d	$(CH_3)_2CH$	H	37:63	230 (4.06)	305 (4.32)	420 (2.52)
e	$CH_3(CH_2)_4$	H	85:15	231 (4.19)	302 (4.30)	420 (2.45)
e	$CH_3(CH_2)_4$	H	40:60	230 (3.98)	306 (4.27)	425 (2.45)
h	CH_3	CH_3	-	231 (4.06)	313 (4.37)	423 (2.63)

(a) The isomer ratio was determined by ^1H nmr.

Uv-vis: The 1-phenylazo-1-alkenes **3** exhibit three absorption maxima in this range (Table 3). As has been found for 2-phenylazo-1-alkenes,[18,20] both the wavelength of the π-π^* excitation and the intensity of the n-π^* absorption provide evidence of the *E*-configuration of the azo group of **3**.

The λ_{max} of the π-π^* absorption is affected both by the number of alkyl-substituents attached to the olefinic bond at C-2 of **3**, and by the position relative to the phenylazo group: With reference to phenylazo-ethene **3a**, each additional alkyl group at C-2 causes a bathochromic shift by 5-8 nm (*EE*-**3**) or 8-11 nm (*EZ*-**3**). These incremental values for β-alkyl substituents in phenylazo-alkenes (complementing the wavelength increments evaluated for α-alkyl- and α,β-dialkyl-substituents[18,20]) range intermediate between those reported for alkylated conjugated dienes (5 nm) and enones (12 nm).[26]

EXPERIMENTAL

The aldehyde phenylhydrazones **1** (prepared following standard procedures) were distilled or recrystallized before use; the N-(4-methylbenzenesulfonyl)-N-phenylhydrazones **7** are available as described in a published procedure.[13] Column chromatography was carried out on silica (Kieselgel 0.05-0.2 mm, Macherey a Nagel) or alumina (Aluminiumoxid 60, 0.063-0.2 mm, Merck) after deactivation by addition of 10% H_2O. Petroleum ether refers to the fraction within the boiling range 40-60°C. Solvents were evaporated using a rotary evaporator Vapsilator (Chemophor) at ca 20 mbar. Analytical tlc sheets were coated with silica gel (0.25 mm, Sil G UV254, Macherey & Nagel). Melting points (m.p.) were determined on a Kofler hot stage microscope (Reichert). The spectroscopic data have been obtained with the following instruments: Beckman AccuLab 4 (ir), Gilford Spectrophotometer 250 (uv-vis), JEOL C-60-HL and JNM-PMX 60 (^{1}H nmr at 60 MHZ).

1-[2-(2-Phenylhydrazono)ethyl]pyridinium iodide (**2a**): To a stirred solution of acetaldehyde phenylhydrazone (**1a**) (2.35 g, 17.5 mmol) in pyridine (15 mL) under nitrogen was added finely powdered I_2 (5 g, 19.7 mmol) causing a rise in temperature to 50-60°C. After continued stirring for 12 h, the dark precipitate formed was filtered off and washed with ice cold ethanol (3 x 5 mL) to yield pale yellow crystals **2a** (2.63 g, 44%); m.p. (dec.) 146-149°C (methanol/water 1:1). ^{1}H nmr (DMSO-d_6): d 5.53 (2H, d, J = 4.5 Hz, =CH-CH_2); 6.5-7.3 (5H, m, C_6H_5); 7.43 (1H, t, J = 4.5 Hz, =C*H*-CH$_2$); 8.0-9.2 (5H, m, $C_5H_5N^+$-); 10.3 (1H, s broad, NH, exchangeable with D_2O). Ir (KBr): 3190 (NH); 1630 cm^{-1} (C=N). Anal. Calcd. for $C_{13}H_{14}IN_3$ (339.18): C, 46.04; H, 4.16; N, 12.39. Found: C, 46.35; H, 4.29; N, 12.45.

Phenylazo-ethene (**3a**): A solution of **2a** (0.60 g, 1.77 mmol) in water (30 mL) was placed in a separatory funnel. After addition of ether (30 mL) and *N* NaOH (5 mL) the mixture was thoroughly shaken. The yellow ether phase was separated, and the aqueous phase was extracted with ether (2 x 30 mL). The combined organic phases were washed with water (3 x 30 mL) and dried ($MgSO_4$). The solvent was slowly evaporated at 0°C to avoid losses of the product **3a** due to its tendency to codistill with the solvent. The oily residue was kept under high vacuum at 0°C for several hours to give the pure (by tlc and ^{1}H nmr) yellow oil **3a** (0.20 g, 86%).

1-Phenyl-6-phenylazo-1,4,5,6-tetrahydropyridazine (**8a**): 3a (0.53 g, 4 mmol) was stored without solvent at r.t. for 3 days; the resultant mixture was subjected to chromatography on silica (100 g) with ether/petroleum ether (1:9). The first

colored eluate contained starting material **3a** (0.08 g), the following fractions after evaporation of the solvent gave the pure (by tlc and ^{1}H nmr) yellow oil **8a** (0.31 g, 59%). ^{1}H nmr (CCl_4): δ 2.1-2.3 (4H, m, CH_2CH_2); 5.27 (1H, m, >CH-N=N); 6.77 (1H, m, -CH=N-N<); 6.5-7.7 (10H, m, 2 C_6H_5). Ir (CCl_4): 1620 (C=N); 1600, 1500 sh (C=C arom.); 1500, 1400 cm^{-1} sh (N=N). Uv-vis (*n*-hexane): λ_{max} [nm] (log ε) 270 (4.37) π-π*, 422 (2.50) n-π*.

Conversion of Aldehyde Phenylhydrazones **1** into 1-Phenylazo-1-alkenes **3**; (General Procedure) Method A: To a stirred solution of the aldehyde phenylhydrazones **1b-1g** (20 mmol) in pyridine (10 mL) under nitrogen is added dropwise within 15 min a solution of I_2 (5.08 g, 20 mmol) in pyridine (20 mL). Stirring is continued (cf. Table 1 for the individual conditions as temperature and reaction time) until all I_2 is consumed. The dark colored reaction mixture (with some precipitated pyridinium iodide) is distributed between water (40 mL) and petroleum ether (3 x 40 mL). The separated and combined organic phases contain unreacted starting material **1**, and in addition the formazane **6**. (**1b** and **6b** have been separated by chromatography on SiO_2, cf. Table 1). The aqueous phase is treated with $NaHCO_3$ (3.23 g, 40 mmol), warmed up to 50-60°C for 10 min, and subsequently extracted with petroleum ether (5 x 30 mL). (The aqueous phase contains the salts **4** and **5** as indicated by tlc and R_f-matching with authentic samples[11]). The combined organic extracts are washed with 0.5 *N* HCl (10 mL) with water (3 x 30 mL), and dried ($MgSO_4$). After evaporation of the solvent, the residual yellow or orange oil **3** is purified (cf. Table 1).

1-Phenylazo-1-alkenes **3** from N-(4-methylbenzenesulfonyl)-N-phenylhydrazones **5**; (General Procedure) Method B: A freshly prepared solution of potassium (0.15 g, 3.8 mmol) in *t*-butyl alcohol (3 mL) is added dropwise to a vigorously stirred solution of **5** (3.4 mmol) in an organic solvent (10 mL) at low temperature (the reaction conditions are listed in Table 1). After 30 min, a saturated ice-cold NaCl solution (30 mL) is added, and the two phases are separated. The organic phase is washed with water until neutral, dried ($MgSO_4$) and evaporated. The residual yellow or orange oil is taken up with *n*-hexane (10 mL), whereupon the unchanged starting material **7** crystallizes and is recovered by filtration. The filtrate is worked-up as indicated in Table 1.

1-Phenylhydrazono-2-methyl-2-propene (**9h**): To a solution of **9h** (1.00 g, 3.16 mmol) in toluene (15 mL) was added a solution of potassium (0.15 g, 3.8 mmol) in *t*-butyl alcohol (20 mL). After stirring for 1.5 h at r.t., water (30 mL) was added. The organic layer was separated, repeatedly washed with water until neutral and dried ($MgSO_4$). Evaporation of the solvent afforded crystalline **9h** (0.45 g, 89%), m.p. 70-72.5°C (petroleum ether; lit.[10] m.p. 73-74°C). ^{1}H nmr

(CCl_4): δ 1.97 (3H, m, CH_3); 4.4 (1H, s broad, C=CH); 5.1 (1H, m, C=CH); 6.2-7.2 (6H, m, C_6H_5, N=CH); 7.5 (1H, s broad, NH). Ir (CCl_4): 3320 (NH); 1600, 1570, 1505, 1490 cm^{-1} (C=C arom. and olefinic, C=N).

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