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A Novel Approach to 1-Aryl-2-(*p*-tolylazo)alkenes from Alkyl Aryl Ketones

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Abstract: 1-Aryl-2-(*p*-tolylazo)alkenes were synthesized starting from alkyl aryl ketones in good overall yield. The employed three-step procedure involves: *i*) α-*p*-tolylhydrazonylation of ketone enolates with *tert*-butyl *p*-tolylazosulfide **1**; *ii*) selective reduction of the carbonyl function of the obtained α-*p*-tolylhydrazono ketones **3** with $NaBH_4$; *iii*) dehydration of the ensuing hydrazono alcohols **4** either in an Et_2O/dil. H_2SO_4 two-phase system or in pyridine/acetic anhydride.

In the course of our studies on the reactivity of arylazosulfides, we have recently reported their ability, when properly substituted, to behave as hydrazonylating agents.[1] In particular, *tert*-butyl *p*-tolylazo sulfide **1** reacts with the enolates of ketones to generally provide excellent yields of the corresponding α-*p*-tolylhydrazono derivatives.[1b,d] Extension of such a kind of reactivity to esters and amides has been conveniently performed.[1e] The interest of the above α-hydrazonylated carbonyl derivatives undoubtedly arises from the presence of two functionalities able to undergo a wide range of useful transformations.

In this perspective, as an example of synthetic exploitation of our hydrazonylation procedure, we report herein on the overall transformation of alkyl aryl ketones **2** into 1-aryl-2-(*p*-tolylazo)alkenes **5** *via* the selective reduction of the carbonyl function of **3** and the dehydration of the ensuing α-hydrazono alcohols **4** (Scheme 1).

RESULTS AND DISCUSSION

Azoalkenes (1,2-diaza-1,3-dienes) are compounds of noteworthy synthetic interest[2] since the conjugated heterodiene system, in which the azo group has an activating effect upon the olefinic double bond, is susceptible of attack at C(4) by a variety of nucleophiles, in addition and cycloaddition reactions.[3] Most literature syntheses[2a] of azoalkenes consist of a base-induced 1,4-elimination from the parent hydrazones bearing a good leaving group (*e.g.* Cl^-, Br^- or $RCOO^-$) on the carbon α to the C=N double bond. In this kind of approach to diazadienes the hydroxide ion, which is a well-recognized relatively poor leaving group, has found only scanty[2a] utilization.

Nonetheless, the availability[1b,d] of α-hydrazono ketones, *e.g.* **3**, easily envisageable precursors of the corresponding α-hydrazono alcohols **4**, surely makes the dehydration of the latter compounds an appealing final step to the target conjugated system. As a first trial of the overall ketone-to-azoalkene transformation we started from alkyl aryl ketones **2**: *i.e.* substrates bound to provide, along the planned synthetic sequence, an easily removable benzylic hydroxy group in **4** coupled with stabilization of the desired azoalkene **5** by π-electron conjugative interactions between the diene and the aromatic systems.

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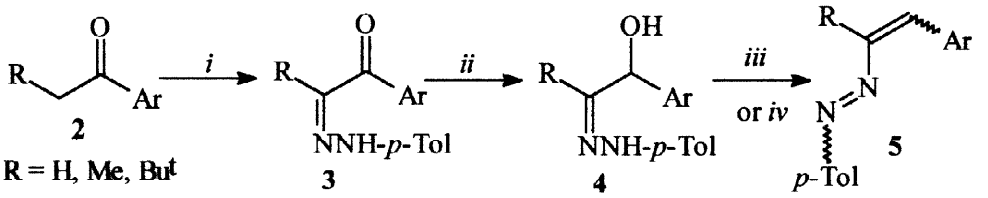
Scheme 1



i: DMSO/ButOK, 4-MeC$_6$H$_4$NNSBu^t (**1**), 25 °C. *ii*) MeOH/NaBH$_4$, 0 °C. *iii*) Et$_2$O/dil. H$_2$SO$_4$, 25 °C. *iv*) Pyridine/Ac$_2$O, 50 °C.

Table 1. α-Keto hydrazones **3a-n** from azosulfide **1** and the potassium salts of ketones **2a-n**.[a]

Entry	2	R	Ar	3	Yield %[b]
1	**2a**	H	Ph	**3a**	96[c]
2	**2b**	H	2-MeOPh	**3b**	68[c]
3	**2c**	H	3-MeOPh	**3c**	57[c]
4	**2d**	H	4-MeOPh	**3d**	98[c]
5	**2e**	H	2-Thienyl	**3e**	72[c]
6	**2f**	H	3-Thienyl	**3f**	98[c]
7	**2g**	H	2-Furyl	**3g**	85
8	**2h**	H	*N*-Me-2-Pyrrolyl	**3h**	98
9	**2i**	H	2-Pyridyl	**3i**	97
10	**2j**	H	3-Pyridyl	**3j**	48
11	**2k**	Me	Ph	**3k**	60[c,d]
12	**2l**	Me	4-MeOPh	**3l**	66[d]
13	**2m**	Bu^t	Ph	**3m**	45
14	**2n**	Bu^t	4-MeOPh	**3n**	52

a) **[Azosulfide]** = 0.065 M; the enolate (2-2.5 mol. equiv. *vs.* azosulfide) was generated *in situ* from equimolar amounts of **2** and *tert*-BuOK in DMSO; reaction times (1-2 h) were judged by the TLC disappearance of **1**. *b*) Yields are based on **1** and refer to isolated products. *c*) Duplicate experiment of ref. 1b. *d*) Obtained *via* a slight modification (see Experimental) of the standard procedure (ref. 1b).

The already described[1a,b] α-hydrazonylation method with *tert*-butyl *p*-tolylazo sulfide **1** was applied to ketones **2a-n** to furnish (Table 1) the corresponding α-hydrazono ketones **3a-n** in satisfactory to excellent yield.

The selective reduction of the α-keto hydrazones **3** to the corresponding α-hydroxy hydrazones **4** (Table 2) has been performed in generally high yields with NaBH$_4$ in MeOH at 0 °C; significant amounts of the relevant hydrazino alcohol were never detected.

Interestingly enough, well in keeping with our expectation for an easy dehydration of **4**, the usual work-up of the final reduction mixture (see Experimental) brought about a spontaneous transformation of **4b** and **4d** into the corresponding diazadienes **5b** and **5d**: only a careful work-up in the cold allowed isolation of the two hydrazono alcohols. On the contrary, compounds **4g** and **4h** could never be isolated because of their ready dehydration to diazadienes **5g** and **5h** (Table 2, entries 7 and 8).

Table 2. β-Hydrazono alcohols **4** from α-ketohydrazones **3**.[a]

Entry	3	R	Ar	4	Yield%[b]
1	**3a**	H	Ph	**4a**	80
2	**3b**	H	2-MeOPh	**4b**	85
3	**3c**	H	3-MeOPh	**4c**	98
4	**3d**	H	4-MeOPh	**4d**	99
5	**3e**	H	2-Thienyl	**4e**	56
6	**3f**	H	3-Thienyl	**4f**	82
7	**3g**	H	2-Furyl	**4g**	*c*
8	**3h**	H	*N*-Me-2-Pyrrolyl	**4h**	*c*
9	**3i**	H	2-Pyridyl	**4i**	99[d]
10	**3j**	H	3-Pyridyl	**4j**	99[d]
11	**3k**	Me	Ph	**4k**	96
12	**3l**	Me	4-MeOPh	**4l**	92
13	**3m**	Bu^t	Ph	**4m**	99
14	**3n**	Bu^t	4-MeOPh	**4n**	97

a) [3] = 0.08 M in MeOH at 0 °C; $NaBH_4$ (generally 3 mol. equiv.) was added until the complete decoloration of the methanolic solution. Reaction times were around 1.5-2 h, the end of reaction being judged by both colour disappearance and TLC analysis. *b)* Unless otherwise stated yields refer to isolated, chromatographically pure products. *c)* Products **4g,h** could not be isolated as they readily dehydrate to **5g,h** respectively; the yields on the overall **3** to **5** transformation are 62% and 68%, respectively (see Table 3). *d)* Yields of crude material; given their instability on silica gel, compounds **4i,j** were used as such in the successive dehydration reaction.

The dehydration of the hydrazono alcohols **4a-f** was performed in a two-phase system of Et_2O/5% aq. sulphuric acid, the reaction being faster under sonication. The results collected in Table 3 show that in these mild acidic conditions **5a-f** are readily formed in good to high yields. On the other hand, the same two-phase acidic conditions proved uneffective with compounds **4k,m,n** and, as expected, **4i,j** which were recovered essentially unchanged.[4]

Unexpectedly, the hydrazono alcohol **4l** furnished 4-methoxybenzaldehyde (98% yield) together with variable amounts of a by-product to which, on the grounds of the ^{1}H-NMR spectrum,[5] could be tentatively assigned the structure of 3,6-dimethyl-1,4-bis(4-methylphenyl)-1,4-dihydrotetrazine. Formation of anisaldehydes, observed in traces even in the successful experiments of entries 2 and 3 (Table 3) formally requires scission of the C(OH)-C(=N) bond. Such bond breakage would result (Scheme 2) in the formation of a second fragment (an aldeyde *p*-tolylhydrazone) from which *e.g.* the by-product described above, isolated in the case of compound **4l**, could formally derive *via* oxidative dimerization.[7]

In this regard, it is noteworthy that in going from **4k** to **4l** the substitution of a hydrogen of the phenyl ring with a *p*-methoxy group induces a striking modification of reactivity under the same conditions. Actually, for **4k**, even after prolonged reaction times no product envisageably arising from C(OH)-C(=N) bond breakage, as for **4l**, is observed. This might suggest a fundamental role played by the methoxy substituent in favouring the process leading to formation of aldehydes from α-hydrazono alcohols in acidic conditions. However,

Table 3. Diazadienes **5** obtained by dehydration in acidic conditions of β-hydrazono alcohols **4**.[a]

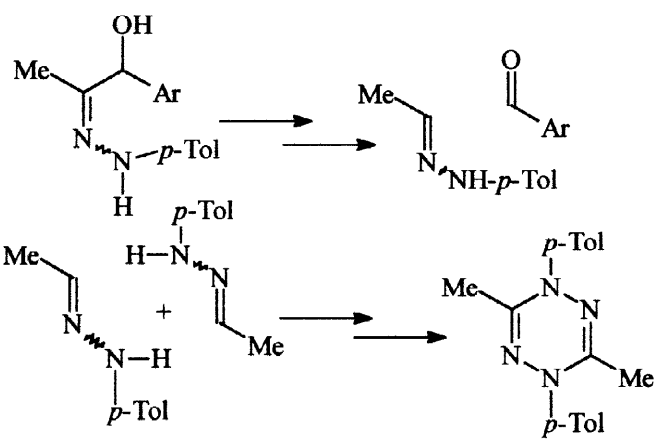
Entry	4	R	Ar	5	Yield%[b]
1	**4a**	H	Ph	**5a**	85
2	**4b**	H	2-MeOPh	**5b**	84
3	**4c**	H	3-MeOPh	**5c**	76
4	**4d**	H	4-MeOPh	**5d**	93
5	**4e**	H	2-Thienyl	**5e**	86
6	**4f**	H	3-Thienyl	**5f**	98
7	**4g**	H	2-Furyl	**5g**	62[c]
8	**4h**	H	*N*-Me-2-Pyrrolyl	**5h**	68[c]

a) [**4**] = 0.042M, H_2SO_4 5% was added (ml equiv. to the employed ml of solvent). The reaction mixture was kept in an ultra-sound bath. Reaction times were 1.5-3h and were judged by the TLC analysis. *b*) Yields refer to isolated products. *c*) Products **5g,h** were obtained directly from the crude reduction products **4g,h** respectively, which were not isolated.

surprisingly enough, the *para*-methoxy derivative **4n**, where a *tert*-butyl replaces the methyl group bonded to the hydrazonylated carbon of **4l**, is recovered unchanged when treated for prolonged times with Et_2O/dil. H_2SO_4. Thus, the concomitant presence of a methyl at the hydrazonylated carbon and of a *p*-methoxy substituent in the aromatic moiety turns out to be essential in making **4l** particularly prone to a fragmentation process (Scheme 2) whose real mechanism is at the moment unclear, even if the differential behaviour of **4l** and **4n** would suggest the involvement of the enehydrazine tautomer of **4l** as precursor. A particularly intriguing aspect still lacking a convincing rationalization is represented by the failure to detect the formation of appreciable amounts of **5n** from the *p*-methoxy derivative **4n**: such an outcome clearly contrasts with the favourable effect that strong electron-donating aryl moieties seem to exert on the acid-catalized **4** to **5** transformation (*cf.* previous findings on the easy dehydration of **4b,d,g,h**).

The dehydration of the hydrazono alcohols **4i-n** to the corresponding diazadienes **5i-n** could be realized in acetic anhydride/pyridine,[2b] a process which involves an acetylation of the hydroxy group followed by a base-induced 1,4-elimination of AcOH. In our system, the temperature was maintained below 50 °C in order to

Scheme 2



minimize undesired decomposition reactions. The results obtained, collected in Table 4, are satisfactory for entries 9, 10, 13 and 14, while not well-identified competitive pathways again appear to prevail in the case of **4k** and **4l** (entries 11 and 12).[8]

Finally, as regards the stereochemistry of the isolated diazadienes, compounds **5a-j** are diastereomerically pure, presumably *(E,E)*-isomers. Actually, their ^{1}H-NMR spectra show in every case coupling constants for the ethylenic protons ($J \sim 13.5$ Hz) which are typical for an *(E)*-geometry around the C=C double bond;[10] on the other hand it is likely that the N=N group too assumes an *(E)*-configuration, as *(Z)*-isomers are known to be unstable and to readily transform into *(E)*-isomers.[11] As reported in the Experimental part, furthermore, the ^{1}H-NMR spectra show the presence of two stereoisomers for **5k,l**, while a single stereoisomer was observed in the case of **5m,n**: no experimental evidence is at hand to unequivocally attribute configuration in these last cases.

Table 4. Diazadienes **5** obtained by reaction of the corresponding hydrazonoalcohols **4** with Ac_2O in pyridine.[a]

Entry	4	R	Ar	5	Yield%[b]
9	**4i**	H	2-Pyridyl	**5i**	66
10	**4j**	H	3-Pyridyl	**5j**	71
11	**4k**	Me	Ph	**5k**	30
12	**4l**	Me	4-MeOPh	**5l**	25
13	**4m**	Bu^t	Ph	**5m**	75
14	**4n**	Bu^t	4-MeOPh	**5n**	79

a) [**4**] = 0.5 M in pyridine; Ac_2O: 10 mol. equiv.; reaction temperature: 50 °C; reaction times: 0.5-1h, as judged by TLC analysis. *b)* Yields refer to isolated products.

EXPERIMENTAL

Melting points were determined on a Büchi 535 apparatus and are uncorrected. ^{1}H-NMR and ^{13}C-NMR spectra were taken on a Varian Gemini 200 spectrometer in $CDCl_3$ solution (unless otherwise stated); TMS was used as internal standard and chemical shifts are reported as δ values (ppm).

Materials

Petroleum ether and light petroleum refer to the fractions with bp 40-60 °C and 80-100 °C, respectively. Dimethylsulfoxide (DMSO) was used as received after storage over molecular sieves (4 Å). Column (or preparative plate) chromatographies were performed on silica gel using petroleum ether and gradients (or appropriate mixtures) with CH_2Cl_2, Et_2O or AcOEt as eluants, the solvents being distilled before use. Potassium *tert*-butoxide, 4-methylaniline, 2-, 3- and 4-methoxyacetophenone, 4-methoxypropiophenone, 2- and 3-acetylthiophene, 2-acetylfuran, 2-acetyl-*N*-methylpyrrole, 2- and 3-acetylpyridine were commercial products used as received. Acetophenone and propiophenone were commercial products distilled before use and stored over molecular sieves (4 Å). 3,3-Dimethylbutyrophenone[12] and 3,3-dimethyl(*p*-methoxy)-butyrophenone[13] were prepared according to the Friedel-Crafts reaction by using commercial *tert*-butylacetyl chloride.

(*Z*)-*tert*-Butyl *p*-tolylazo sulfide **1** was prepared from commercial 4-methylaniline, as previously reported.[1a]

***α-Ketohydrazones* 3a-n**

Compounds **3a-f, k** have been previously described;[1b] hydrazones **3g-j** and **3l-n** were prepared according to the method already described;[1b] yields of **3k** and **3l** were improved *vs.* the standard procedure (49% and 54% respectively) by very slow addition of further 1.2 mol. equiv. of *tert*-BuOK (dissolved in DMSO) to the reaction mixture, after the addition of **1**. Compounds were obtained usually as *(E)* stereoisomers, which undergo isomerization to the *(Z)* form in $CDCl_3$ solution; DMSO-d_6 solutions show a single isomer, probably the *(Z)* form.

2-Furyl [(4-methylphenyl)hydrazono]methyl ketone **3g**: mp 158.2-159.2 °C (EtOH/H_2O); ^{1}H-NMR: 2.33 (3H, s), 6.59 (1H, dd, *J* 1.8 and 3.6 Hz), 7.15 and 7.22 (2H each, AA'BB', *J* 8.8 Hz), 7.27 (1H, d, *J* 3.6 Hz), 7.55 (1H, s), 7.65 (1H, d, *J* 1.8 Hz), 14.25 (1H, br s). Found: C, 68.3; H, 5.4; N, 12.1% ($C_{13}H_{12}N_2O_2$ requires C, 68.4; H, 5.3; N, 12.3%).

2-N-Methylpyrrolyl [(4-methylphenyl)hydrazono]methyl ketone **3h**: mp 138.2-139.0 °C (EtOH); ^{1}H-NMR: 2.31 (3H, s), 4.01 (3H, s), 6.19 (1H, dd, *J* 2.5 and 4.2 Hz), 6.85 (1H, app. t), 7.04 (1H, dd, *J* 1.7 and 4.2 Hz), 7.12 and 7.17 (2H each, AA'BB', *J* 9.0 Hz), 7.45 (1H, s), 14.03 (1H, br s). Found: C, 69.8; H, 6.3; N, 17.5% ($C_{14}H_{15}N_3O$ requires C, 69.7; H, 6.3; N, 17.4%).

2-Pyridyl [(4-methylphenyl)hydrazono]methyl ketone **3i**: mp 147.6-149.2 °C (EtOH); ^{1}H-NMR: 2.34 (3H, s), 7.17 and 7.28 (2H each, AA'BB', *J* 8.5 Hz), 7.46 (1H, ddd, *J* 1.3, 4.7 and 7.7 Hz), 7.88 (1H, app. td, *J* 1.7 and 7.7 Hz), 8.14 (1H, dt, *J* 7.7 Hz), 8.38 (1H, s), 8.73 (1H, dm, *J* 4.7 Hz), 14.54 (1H, br s). Found: C, 70.4; H, 5.6; N, 17.6% ($C_{14}H_{13}N_3O$ requires C, 70.3; H, 5.5; N, 17.6%).

3-Pyridyl [(4-methylphenyl)hydrazono]methyl ketone **3j**: mp 131.8-132.4 °C (taken up with petroleum ether); ^{1}H-NMR: 2.35 (3H, s), 7.18 and 7.28 (2H each, AA'BB', *J* 8.5 Hz), 7.45 (1H, ddd, *J* 0.8, 4.8 and 8.0 Hz), 7.69 (1H, s), 8.26 (1H, dm, *J* 8.0 Hz), 8.79 (1H, dd, *J* 1.7 and 4.8 Hz), 9.22 (1H, dd, *J* 0.8 and 2.2 Hz), 14.58 (1H, br s). Found: C, 70.3; H, 5.6; N, 17.5% ($C_{14}H_{13}N_3O$ requires C, 70.3; H, 5.5; N, 17.6%).

4-Methoxyphenyl 1-[(4-methylphenyl)hydrazono]ethyl ketone **3l**: mp 174.6-176.0 °C (EtOH); ^{1}H-NMR: 2.19 (3H, s), 2.30 (3H, s), 3.89 (3H, s), 6.95 (2H, AA' of AA'BB', *J* 7.0 Hz), 7.02 and 7.11 (2H each, AA'BB', *J* 8.6 Hz), 7.83 (1H, br s), 8.04 (2H, BB' of AA'BB', *J* 7.0 Hz). Found: C, 72.2; H, 6.4; N, 10.0% ($C_{17}H_{18}N_2O_2$ requires C, 72.3; H, 6.4; N, 9.9%).

Phenyl 1-[(4-methylphenyl)hydrazono]-2,2-dimethylethyl ketone **3m**: mp 68.1-68.6 °C (EtOH/H_2O); ^{1}H-NMR: 1.25 (9H, s), 2.25 (3H, s), 6.83 and 7.01 (2H each, AA'BB', *J* 8.4 Hz), 6.93 (1H, br s), 7.49 (2H, m), 7.63 (1H, m), 7.89 (2H, m). Found: C, 77.6; H, 7.6; N, 9.5% ($C_{19}H_{22}N_2O$ requires C, 77.5; H, 7.5; N, 9.5%).

4-Methoxyphenyl 1-[(4-methylphenyl)hydrazono]-2,2-dimethylethyl ketone **3n**: mp 73.3-74.3 °C (petroleum ether); ^{1}H-NMR: 1.25 (9H, s), 2.25 (3H, s), 3.87 (3H, s), 6.83 (2H, half AA'BB', *J* 8.5 Hz), 6.90 (1H, br s), 6.98 (4H, m), 7.85 (2H, half AA'BB', *J* 9.0 Hz). Found: C, 73.9; H, 7.4; N, 8.7% ($C_{20}H_{24}N_2O_2$ requires C, 74.1; H, 7.5; N, 8.6%).

***Reduction of α-ketohydrazones* 3a-n**

In an Erlenmeyer flask, the α-ketohydrazone was dissolved in MeOH (1 mmol in 12-20 ml, according to the hydrazone solubility) and $NaBH_4$ (3 mol. equiv.) was added (in small portions every 30 min) under magnetic stirring keeping the temperature at 0 °C by an external ice bath. The reaction was followed by TLC and at the end poured into saturated NH_4Cl solution/ice and extracted with diethyl ether. The combined organic layers were washed with water and dried (Na_2SO_4). The solvent was evaporated to give a residue

which was taken-up with petroleum ether and filtered. The obtained products are generally pure enough for the successive dehydration reaction. Whenever possible, analytical samples were obtained by crystallization.

The hydrazono alcohols **4b** and **4d** could be isolated through concentration of the ether extracts, under vacuum and at *ca.* 10 °C, to a small volume, followed by insolubilization of the products with petroleum ether at 0 °C. Evaporation to dryness at room temperature gives substantial dehydration of **4b** and **4d** to the corresponding azoalkenes **5b** and **5d**. Consistently, from the reduction of 2-furyl- **3g** and 2-*N*-methylpyrrolyl [(4-methylphenyl)hydrazono]methyl ketone **3h** the corresponding β-hydrazonoalcohols **4g** and **4h** could not be isolated because the latter compounds spontaneously dehydrate to diazadienes **5g** and **5h** during the work-up of the reaction.

1-Phenyl-2-[(4-methylphenyl)hydrazono]ethanol **4a**: mp 106.5-107.5 °C (Et_2O/petroleum ether); ^{1}H-NMR (DMSO-d_6): 2.18 (3H, s), 5.16 (1H, dd, *J* 4.3 and 6.8 Hz), 5.77 (1H, d, *J* 4.3 Hz), 6.81 and 6.98 (2H each, AA'BB', *J* 8.4 Hz), 7.10 (1H, d, *J* 6.8 Hz), 7.31 (5H, m), 9.70 (1H, br s). Found: C, 74.9; H, 6.7; N, 11.6% ($C_{15}H_{16}N_2O$ requires C, 75.0; H, 6.7; N, 11.7%).

1-(2-Methoxyphenyl)-2-[(4-methylphenyl)hydrazono]ethanol **4b**: yellow oil used as crude material for the successive dehydration reaction; ^{1}H-NMR (DMSO-d_6): two stereoisomers **A** and **B** are present (54:46 molar ratio): 2.17 [3H (**B**), s], 2.19 [3H (**A**), s], 3.77 [3H (**B**), s], 3.82 [3H (**A**), s], 5.45 [2H (**B**), m], 5.82 [1H (**A**), app. t, *J* 5.3 Hz], 5.91 [1H (**A**), d, *J* 5.3 Hz], 6.33 [1H (**A**), d, *J* 5.3 Hz], 6.78 [2H (**A**), AA' of AA'BB', *J* 8.5 Hz], 6.97 [4H (**A**) + 6H (**B**), m], 7.16 [1H (**B**), d, *J* 6.3 Hz], 7.32 [1H (**A**) + 1H (**B**), m], 7.44 [1H (**B**), dd, *J* 7.6 Hz], 7.49 [1H (**A**), d, *J* 7.8 Hz], 9.19 [1H (**A**), br s], 9.62 [1H (**B**), br s].

1-(3-Methoxyphenyl)-2-[(4-methylphenyl)hydrazono]ethanol **4c**: mp 89.0-90.0 °C (Et_2O/petroleum ether); ^{1}H-NMR (DMSO-d_6): 2.18 (3H, s), 3.74 (3H, s), 5.12 (1H, dd, *J* 4.4 and 6.8 Hz) 5.77 (1H, d, *J* 4.4 Hz), 6.90 [7H in all, partly overlapped AA'BB' (*J* 8.2 Hz) and m], 7.09 (1H, d, *J* 6.8 Hz), 7.26 (1H, app. t), 9.70 (1H, br s). Found: C, 70.9; H, 6.8; N, 10.5% ($C_{16}H_{18}N_2O_2$ requires C, 71.1; H, 6.7; N, 10.4%).

1-(4-Methoxyphenyl)-2-[(4-methylphenyl)hydrazono]ethanol **4d**: mp 110-115 °C (Et_2O/petroleum ether); ^{1}H-NMR (DMSO-d_6): two stereoisomers **A** and **B** are present (70:30 molar ratio): 2.18 [3H (**A**) + 3H (**B**), s], 3.73 [3H (**A**) + 3H (**B**), s], 5.09 [1H (**A**), dd, *J* 4.4 and 6.8 Hz], 5.67 [1H (**A**) + 1H (**B**), m], 5.86 [1H (**B**), d, *J* 4.7 Hz], 6.43 [1H (**B**), d, *J* 6.3 Hz], 6.81 [2H (**A**), AA' of AA'BB', *J* 8.5 Hz], 6.94 [4H (**A**) + 6H (**B**), m], 7.08 [1H (**A**), d, *J* 6.8 Hz], 7.28 [2H (**A**), BB' of AA'BB', *J* 8.5 Hz], 7.36 [2H (**B**), half AA'BB', *J* 8.8 Hz], 9.39 [1H (**B**), br s], 9.66 [1H (**A**), br s]. Found: C, 70.9; H, 6.6; N, 10.2% ($C_{16}H_{18}N_2O_2$ requires C, 71.1; H, 6.7; N, 10.4%).

1-(2-Thienyl)-2-[(4-methylphenyl)hydrazono]ethanol **4e**: mp 93.2-94.0 °C (toluene/petroleum ether); ^{1}H-NMR: 2.28 (3H, s), 3.53 (1H, d, *J* 4.0 Hz), 5.65 (1H, app.t), 6.93 (2H, AA' of AA'BB', *J* 8.5 Hz), 7.01 (1H, dd, *J* 3.5 and 4.9 Hz), 7.08 (3H, m), 7.19 (1H, d, *J* 4.0 Hz), 7.31 (1H, dd, *J* 1.3 and 4.9 Hz), 7.43 (1H, br s). Found: C, 63.0; H, 5.8; N, 11.1% ($C_{13}H_{14}N_2OS$ requires C, 63.4; H, 5.7; N, 11.4%).

1-(3-Thienyl)-2-[(4-methylphenyl)hydrazono]ethanol **4f**: mp 97.4-98.4 °C (petroleum ether); ^{1}H-NMR (DMSO-d_6): 2.18 (3H, s), 5.20 (1H, dd, *J* 4.7 and 6.8 Hz), 5.72 (1H, d, *J* 4.7 Hz), 6.81 and 6.98 (2H each, AA'BB', *J* 8.4 Hz), 7.07 (1H, dd, *J* 1.2 and 5.0 Hz), 7.14 (1H, d, *J* 6.8 Hz), 7.36 (1H, d, *J* 3.0 Hz), 7.51 (1H, dd, *J* 3.0 and 5.0 Hz), 9.72 (1H, br s). Found: C, 63.1; H, 5.6; N, 11.1% ($C_{13}H_{14}N_2OS$ requires C, 63.4; H, 5.7; N, 11.4%).

1-(2-Pyridyl)-2-[(4-methylphenyl)hydrazono]ethanol **4i**: yellow oil isolated as crude material, which slowly decomposes in the air; ^{1}H-NMR: 2.27 (3H, s), 4.90 (1H, br s), 5.43 (1H, d, *J* 5.2 Hz), 6.91 and 7.06 (2H each, AA'BB', *J* 8.4 Hz), 7.10 (1H, d, *J* 5.2 Hz), 7.24 (1H, m), 7.46 [2H in all, partly overlapped d (*J* 7.7 Hz) and br s], 7.71 (1H, td, *J* 1.7 and 7.7 Hz), 8.56 (1H, app. d, *J* 4.8 Hz).

1-(3-Pyridyl)-2-[(4-methylphenyl)hydrazono]ethanol **4j**: red oil isolated as crude material, which slowly decomposes in the air; ^{1}H-NMR: 2.28 (3H, s), 3.10 (1H, br s), 5.46 (1H, d, *J* 4.0 Hz), 6.89 and 7.06 (2H each, AA'BB', *J* 8.4 Hz), 7.13 (1H, d, *J* 4.0 Hz), 7.35 (1H, m), 7.75 [2H in all, partly overlapped d (*J* 8.3 Hz) and br s], 8.6 (2H in all, 2 partly overlapped br s).

1-Phenyl-2-[(4-methylphenyl)hydrazono]propanol **4k**: mp 101.3-102.3 °C (light petroleum); ^{1}H-NMR: 1.71 (3H, s), 2.30 (3H, s), 4.63 (1H, d, *J* 3.7 Hz), 5.17 (1H, d, *J* 3.7 Hz), 7.01 [3H in all, partly overlapped AA' of AA'BB' (*J* 8.1 Hz) and br s], 7.11 (2H, BB' of AA'BB', *J* 8.1 Hz), 7.35 (5H, m). Found: C, 75.2; H, 7.1; N, 10.7% ($C_{16}H_{18}N_2O$ requires C, 75.6; H, 7.1; N, 11.0%).

1-(4-Methoxyphenyl)-2-[(4-methylphenyl)hydrazono]propanol **4l**: mp 123.8-124.2 °C (light petroleum); ^{1}H-NMR: 1.67 (3H, s), 2.29 (3H, s), 3.79 (3H, s), 4.67 (1H, br s), 5.11 (1H, s), 6.87 (2H, AA' of AA'BB', *J* 8.8 Hz), 7.00 [3H in all, partly overlapped AA' of AA'BB' (*J* 8.5 Hz) and br s], 7.09 (2H, BB' of AA'BB', *J* 8.5 Hz), 7.26 (2H, BB' of AA'BB', *J* 8.8 Hz). Found: C, 71.6; H, 7.3; N, 10.0% ($C_{17}H_{20}N_2O_2$ requires C, 71.8; H, 7.1; N, 9.9%).

1-Phenyl-2-[(4-methylphenyl)hydrazono]-3,3-dimethylbutanol **4m**: mp 82.8-83.5 °C (petroleum ether); ^{1}H-NMR: 1.23 (9H, s), 2.24 (3H, s), 2.53 (1H, d, *J* 3.8 Hz), 5.66 (1H, d, *J* 3.8 Hz), 6.82 and 6.99 (2H each, AA'BB', *J* 8.4 Hz), 7.39 (5H, m), 8.63 (1H, br s). Found: C, 76.8; H, 8.4; N, 9.7% ($C_{19}H_{24}N_2O$ requires C, 77.0; H, 8.2; N, 9.5%).

1-(4-Methoxyphenyl)-2-[(4-methylphenyl)hydrazono]-3,3-dimethylbutanol **4n**: yellow oil; ^{1}H-NMR (DMSO-d_6): 1.12 (9H, s), 2.17 (3H, s), 3.72 (3H, s), 5.55 (1H, d, *J* 3.7 Hz), 6.47 (1H, d, *J* 3.7 Hz), 6.79 (2H, AA' of AA'BB', *J* 8.4 Hz), 6.88 (2H, AA' of AA'BB', *J* 8.8 Hz), 6.96 (2H, BB' of AA'BB', *J* 8.4 Hz), 7.27 (2H, BB' of AA'BB', *J* 8.8 Hz), 9.58 (1H, br s). Found: C, 73.9; H, 8.2; N, 8.5% ($C_{20}H_{26}N_2O_2$ requires C, 73.6; H, 8.0; N, 8.6%).

1-Aryl-2-(p-tolylazo)alkenes 5a-n

The hydrazono alcohol (**4a-f**) was dissolved in a one-neck flask in diethyl ether (1 mmol in 24 ml) and 24 ml of 5% aq. H_2SO_4 were added; the flask was maintained in an ultra-sound bath at room temperature and the end of the reaction (1.5-3h) was judged by TLC disappearance of the substrate. From the final reaction mixture the organic layer was separated and the aqueous one extracted with diethyl ether. The combined organic layers were washed with saturated $NaHCO_3$ solution, dried (Na_2SO_4), filtered and evaporated under vacuum. The residue was then purified by column cromatography and/or crystallization.

As reported in the previous paragraph, the hydrazono alcohols **4g,h** spontaneously dehydrate to **5g,h** during the work-up of the reduction reaction.

Diazadienes **5i-n** were obtained according to a method reported in literature.[2b] In a typical procedure, a solution of hydrazono alcohol (0.5 mmol) in dry pyridine (1 ml) was added of acetic anhydride (5 mmol) and gently warmed to 50 °C under magnetic stirring. At the end of the reaction (judged by TLC disappearance of the substrate, 15-60 min), the mixture was poured into cold water and extracted with diethyl ether. The ether extracts were washed with water, dried with Na_2SO_4, filtered and evaporated at reduced pressure. Pure products were generally obtained by column chromatography on silica gel.

1-(4-Methylphenylazo)-2-phenylethylene **5a**: mp 90.6-91.1 °C (EtOH); ^{1}H-NMR: 2.43 (3H, s), 7.28 (2H, m), 7.41 (3H, m), 7.67 [5H in all, partly overlapped AA'BB' (*J* 8.1 Hz) and d (*J* 13.5 Hz)], 7.98 (1H, d, *J* 13.5 Hz). Found: C, 80.8; H, 6.5; N, 12.2% ($C_{15}H_{14}N_2$ requires: C, 81.1; H, 6.4; N, 12.6%).

1-(4-Methylphenylazo)-2-(2-methoxyphenyl)ethylene **5b**: mp 86.2-87.0 °C (petroleum ether); ^{1}H-NMR: 2.41 (3H, s), 3.93 (3H, s), 6.98 (2H, m), 7.27 (2H, AA' of AA'BB', *J* 8.6 Hz), 7.35 (1H, m), 7.61 (1H, dd, *J* 1.5 and 7.7 Hz), 7.73 (2H, BB' of AA'BB', *J* 8.6 Hz) 7.96 (1H, d, *J* 13.7 Hz), 8.11 (1H, d, *J* 13.7 Hz). Found: C, 76.0; H, 6.6; N, 11.3% ($C_{16}H_{16}N_2O$ requires: C, 76.2; H, 6.4; N, 11.1%).

1-(4-Methylphenylazo)-2-(3-methoxyphenyl)ethylene **5c**: mp 50.4-50.7 °C (petroleum ether); ^{1}H-NMR: 2.42 (3H, s), 3.85 (3H, s), 6.93 (1H, dd, *J* 1.8 and 7.3 Hz), 7.14 (1H, app. d), 7.28 [5H in all, partly overlapped AA' of AA'BB' (*J* 8.4 Hz) and m], 7.65 (1H, d, *J* 13.9 Hz), 7.73 (2H, BB' of AA'BB', *J* 8.4 Hz), 7.97 (1H, d, *J* 13.9 Hz). Found: C, 76.2; H, 6.4; N, 11.1% ($C_{16}H_{16}N_2O$ requires: C, 76.2; H, 6.4; N, 11.1%).

1-(4-Methylphenylazo)-2-(4-methoxyphenyl)ethylene **5d**: mp 118.5-119.2 °C (EtOH); ^{1}H-NMR: 2.41 (3H, s), 3.85 (3H, s), 6.94 (2H, AA' of AA'BB', *J* 8.8 Hz), 7.27 (2H, AA' of AA'BB', *J* 8.3 Hz), 7.60 [3H in

all, partly overlapped BB' of AA'BB' (*J* 8.8 Hz) and d (*J* 13.2 Hz)], 7.71 (2H, BB' of AA'BB', *J* 8.3 Hz), 7.93 (1H, d, *J* 13.2 Hz). ^{13}C-NMR: 21.47, 55.38, 114.48, 122.48, 127.84, 129.51, 129.75, 140.94, 141.60, 145.14, 151.05, 160.86. Found: C, 76.5; H, 6.5; N, 11.0% ($C_{16}H_{16}N_2O$ requires: C, 76.2; H, 6.4; N, 11.1%).

1-(4-Methylphenylazo)-2-(2-thienyl)ethylene **5e**: mp 102.9-103.2 °C (light petroleum); ^{1}H-NMR: 2.42 (3H, s), 7.09 (1H, dd, *J* 3.8 and 5.0 Hz), 7.29 [3H in all, partly overlapped AA' of AA'BB' (*J* 8.4 Hz) and d (*J* 3.8 Hz)], 7.40 (1H, d, *J* 5.0 Hz), 7.70 and 7.83 [4H in all, partly overlapped BB' of AA'BB' (*J* 8.4 Hz) and AB (*J* 13.8 Hz)]. Found: C, 67.9; H, 5.3; N, 12.0% ($C_{13}H_{12}N_2S$ requires: C, 68.4; H, 5.3; N, 12.3%).

1-(4-Methylphenylazo)-2-(3-thienyl)ethylene **5f**: mp 111.2-112.5 °C (EtOH/H_2O); ^{1}H-NMR: 2.42 (3H, s), 7.28 (2H, AA' of AA'BB', *J* 8.1 Hz), 7.38 (2H, d, *J* 2.1 Hz), 7.55 (1H, t, *J* 2.1 Hz), 7.67 (1H, d, *J* 13.7 Hz), 7.73 (2H, BB' of AA'BB', *J* 8.1 Hz), 7.86 (1H, d, *J* 13.7 Hz). Found: C, 68.0; H, 5.5; N, 12.0% ($C_{13}H_{12}N_2S$ requires: C, 68.4; H, 5.3; N, 12.3%).

1-(4-Methylphenylazo)-2-(2-furyl)ethylene **5g**: mp 112.0-113.2 °C (petroleum ether); ^{1}H-NMR: 2.41 (3H, s), 6.50 (1H, dd, *J* 1.7 and 3.4 Hz), 6.67 (1H, d, *J* 3.4 Hz), 7.26 (2H, AA' of AA'BB', *J* 8.2 Hz), 7.41 (1H, d, *J* 13.6 Hz), 7.52 (1H, d, *J* 1.7 Hz), 7.71 (2H, BB' of AA'BB', *J* 8.2 Hz), 7.90 (1H, d, *J* 13.6 Hz). Found: C, 73.5; H, 5.9; N, 13.5% ($C_{13}H_{12}N_2O$ requires: C, 73.6; H, 5.7; N, 13.2%).

1-(4-Methylphenylazo)-2-(2-N-methylpyrrolyl)ethylene **5h**: red solid which easily decomposes; ^{1}H-NMR: 2.40 (3H, s), 3.77 (3H, s), 6.25 (1H, m), 6.73 (1H, m), 6.81 (1H, m), 7.27 and 7.68 (2H each, AA'BB', *J* 8.5 Hz), 7.55 (1H, d, *J* 13.4 Hz), 7.91 (1H, d, *J* 13.4 Hz).

1-(4-Methylphenylazo)-2-(2-pyridyl)ethylene **5i**: mp 112.9-113.6 °C (petroleum ether); ^{1}H-NMR: 2.43 (3H, s), 7.28 (3H, m), 7.57 (1H, d, *J* 8.0 Hz), 7.74 (4H, m), 8.27 (1H, d, *J* 13.6 Hz), 8.69 (1H, br d, *J* 4.9 Hz). Found: C, 75.0; H, 6.2; N, 18.5% ($C_{14}H_{13}N_3$ requires: C, 75.3; H, 5.9; N, 18.8%).

1-(4-Methylphenylazo)-2-(3-pyridyl)ethylene **5j**: mp 116.3-117.2 °C (petroleum ether); ^{1}H-NMR: 2.44 (3H, s), 7.31 (2H, AA' of AA'BB', *J* 8.4 Hz), 7.42 (1H, m), 7.65 (1H, d, *J* 13.9 Hz), 7.75 (2H, BB' of AA'BB', *J* 8.4 Hz), 7.99 [2H in all, partly overlapped d (*J* 13.9 Hz) and m], 8.60 (1H, br d, *J* 4.8 Hz), 8.84 (1H, br s). Found: C, 75.2; H, 6.0; N, 19.0% ($C_{14}H_{13}N_3$ requires: C, 75.3; H, 5.9; N, 18.8%).

2-(4-Methylphenylazo)-1-phenylpropene **5k**: obtained as a mixture of stereoisomers **A** and **B** (73:27 molar ratio), which partially solidifies in the fridge; ^{1}H-NMR: 2.17 [3H (**B**), d, *J* 1.0 Hz], 2.28 [3H (**A**), d, *J* 1.0 Hz], 2.42 [3H (**A**) + 3H (**B**), s], 6.95 [1H (**B**), s], 7.51 [10 H (**A**) + 9H (**B**), m]. Found: C, 81.0; H, 6.9; N, 11.5% ($C_{16}H_{16}N_2$ requires: C, 81.3; H, 6.8; N, 11.9%).

2-(4-Methylphenylazo)-1-(4-methoxyphenyl)propene **5l**: obtained as a mixture of stereoisomers **A** and **B** (32:68 molar ratio), which partially solidifies in the fridge; ^{1}H-NMR: 2.15 [3H (**B**), s], 2.29 [3H (**A**), d, *J* 0.9 Hz], 2.42 [3H (**A**) + 3H (**B**), s], 3.85 [3H (**B**), s], 3.86 [3H (**A**), s], 6.92 [3H (**B**) in all, partly overlapped s and AA' of AA'BB' (*J* 8.5 Hz)], 6.98 [2H (**A**), AA' of AA'BB', *J* 9.0 Hz], 7.28 [2H (**A**) + 2H (**B**), m], 7.53 [2H (**A**), BB' of AA'BB', *J* 9.0 Hz], 7.60 [1H (**A**), s], 7.74 [2H (**A**) + 4H (**B**), m]. Found: C, 76.4; H, 7.0; N, 10.7% ($C_{17}H_{18}N_2O$ requires: C, 76.7; H, 6.8; N, 10.5%).

2-(4-Methylphenylazo)-1-phenyl-3,3-dimethylbutene **5m**: red oil; ^{1}H-NMR: 1.34 (9H, s), 2.42 (3H, s), 6.54 (1H, s), 7.23 (7H, m), 7.66 (2H, half AA'BB', *J* 8.3 Hz). Found: C, 81.8; H, 8.3; N, 9.8% ($C_{19}H_{22}N_2$ requires: C, 82.0; H, 8.0; N, 10.1%).

2-(4-Methylphenylazo)-1-(4-methoxyphenyl)-3,3-dimethylbutene **5n**: red oil; ^{1}H-NMR: 1.34 (9H, s), 2.42 (3H, s), 3.80 (3H, s), 6.64 (1H, s), 6.81 (2H, half AA'BB', *J* 8.8 Hz), 7.31 (4H, m), 7.67 (2H, half AA'BB', *J* 7.9 Hz). Found: C, 77.1; H, 8.2; N, 9.0% ($C_{20}H_{24}N_2O$ requires: C, 77.9; H, 7.8; N, 9.1%).

Other Compounds

Methoxybenzaldehydes were identified by comparison with commercial samples.

1-Hydroxy-1-phenylpropanone was identified by comparison with an authentic sample from our laboratories: yellow oil; ^{1}H-NMR: 2.08 (3H, s), 4.31 (1H, d, *J* 3.6 Hz), 5.10 (1H, d, *J* 3.6 Hz), 7.35 (5H, m).

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