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Behaviour of Arylazo *tert*-Butyl Sulfides with Ketone Enolates. Competition between $S_{RN}1$ α-Arylation and Azocoupling Reactions.

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Abstract. (*Z*)-Arylazo *tert*-butyl sulfides **1a-i** react, in DMSO and at room temperature, with potassium acetone enolate to give good yields of 1-aryl-2-propanones via spontaneous $S_{RN}1$ dark reactions. α-Phenylation of pinacolone and acetophenone enolates by **1a** likewise occurs in excellent yields. In agreement with the involvement of an electron-transfer catalyzed chain process, the reaction of the 4-bromo derivative **1n** with pinacolone enolate gives mainly the bis-substitution product **13**. With azosulfides **1j-m** the arylation pathway competes with a base-induced thiol elimination eventually leading, depending on the structure of the azosulfide, to indazoles **8** or **11** and/or to 2-oxopropanal arylhydrazones **9**, **10** or **12**.

α-Arylated ketones are important target molecules and, in particular, key intermediates in the synthesis of a variety of biologically interesting compounds. Consistently, a wide range of approaches has been developed for their synthesis. Besides methods involving arylation of ß-diketones or ß-ketoesters[1] (followed, respectively, by deacylation or dealkoxycarbonylation[2-5] of the resulting α-arylated products) and direct arylation of ketones with triphenylbismuth carbonate[6] or diaryliodonium salts,[7] a good deal of procedures are based on the acylation of benzylic organometallic compounds.[8] Alternative strategies include the reaction of arylboranes or arylcopper reagents with ketones, or their equivalents, possessing a leaving group such as halogen in α-position [9, 10] or an α,ß-epoxy bridge.[11]

As far as direct arylation of ketone enolates is concerned, reported procedures are based on their reactions with unactivated halogenoarenes via transition-metal catalyzed substitutions[12] or through electron-transfer induced $S_{RN}1$ processes.[13-23] Some drawbacks to the former method come from the requirement of special reagents, of drastic reaction conditions or of multistep operations. Presently, even if with some limitations, the most promising method for the arylation of ketone enolates thus appears to be the $S_{RN}1$ approach as evidenced, *inter alia*, by the large number of papers in the field of the homo- and heterocyclic aromatic series.

In this line and on the basis of our previous studies,[1a, 24-29] it was envisaged that, also as an alternative to the use of halogenoarenes, arylazo sulfides, easily available from the corresponding arylamines, might be in turn convenient $S_{RN}1$-arylating agents for ketone enolates. The easy participation of such compounds in $S_{RN}1$ processes (steps 1-4)

has been well evidenced, in fact, by the effective arylations of both sulfur[24, 25, 28] and carbon centered nucleophiles.[1a, 26-29]

$$\text{Ar-N=N-SR} + e^- \longrightarrow \underset{1^{-\bullet}}{\text{Ar-N=N-SR}^{-\bullet}} \quad (1)$$

$$\underset{1 : R = Bu^t}{1^{-\bullet}} \longrightarrow \text{Ar}^{\bullet} + N_2 + RS^- \quad (2)$$

$$\text{Ar}^{\bullet} + Nu^- \longrightarrow \text{Ar-Nu}^{-\bullet} \quad (3)$$

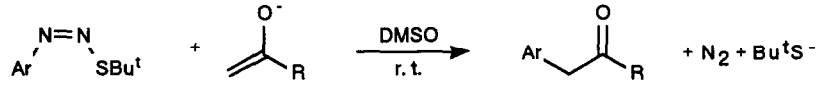
$$\text{Ar-Nu}^{-\bullet} + 1 \longrightarrow \text{Ar-Nu} + 1^{-\bullet} \quad (4)$$

We now report on the results of an investigation in which (*Z*)-arylazo *tert*-butyl sulfides **1a-n** were employed in reactions with the enolates of acetone (**2**), pinacolone (**3**) or acetophenone (**4**).

Results and Discussion

The reactions of (*Z*)-arylazo *tert*-butyl sulfides **1a-i** with 10 molar equivs. of potassium acetone enolate, prepared *in situ* from equimolar amounts of the ketone and Bu^tOK, gave rise, in DMSO and at room temperature (Scheme 1 and Table), to a fast disappearance of the substrate and to formation of 1-aryl-2-propanones **5a-i** in good yields. Similarly high yields of the corresponding arylated ketones were obtained from the reactions of **1a** with either pinacolone **3** or acetophenone enolate **4**. Under the same conditions, conversely, arylated ketones were obtained in yields ranging between trace amounts and 42% when substrates **1j-m** were reacted with acetone enolate. Actually, as sketched in Scheme 2, in the main products the nitrogen present in the azosulfide was retained and, depending on the structure of the substrate, either indazoles **8**, **11** or 2-oxopropanal arylhydrazones **9**, **10** or **12** were obtained.

Scheme 1



1 **2** : R = Me; **3** : R = Bu^t; **4** : R = Ph → **5** : R = Me; **6** : R = Bu^t; **7** : R = Ph

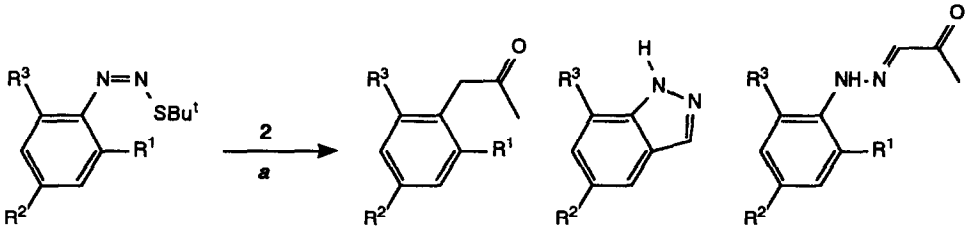
	Ar =		Ar =		Ar =		Ar =
a :	C_6H_5	**e** :	4-$Bu^tC_6H_4$	**i** :	4-$PhCOC_6H_4$	**m** :	2,4,6-$Me_3C_6H_2$
b :	1-naphthyl	**f** :	3-$MeOC_6H_4$	**j** :	2-MeC_6H_4	**n** :	4-BrC_6H_4
c :	2-naphthyl	**g** :	4-$MeOC_6H_4$	**k** :	4-MeC_6H_4		
d :	3-MeC_6H_4	**h** :	3-$PhCOC_6H_4$	**l** :	4-$Bu^iC_6H_4$		

Table. Reactions of diazosulfides **1a-1l** with potassium ketone enolates **2, 3** or **4** in DMSO[a]

Substr.	Enolate	React. time (min)[b]	$ArCH_2COR$ yield (%)[c]
1a	**2**	100	**5a**: 75
1a	**3**	120	**6a**: 80
1a	**4**	90	**7a**: 95
1b	**2**	60	**5b**: 75
1c	**2**	30	**5c**: 76
1d	**2**	90	**5d**: 81
1e	**2**	90	**5e**: 86
1f	**2**	90	**5f**: 79
1g	**2**	90	**5g**: 69
1h	**2**	40[d]	**5h**: 44
1i	**2**	45	**5l**: 78

[a] Experiments were carried out under argon in the laboratory light and at room temperature; [azosulfide] = 0.065 M; potassium ketone enolates (10 mol. equiv. with respect to substrate) were generated *in situ* from equimolar amounts of ketone and Bu^tOK. [b] The end of the reaction was approximately determined following the disappearance of the azosulfide by TLC. [c] Yields refer to products isolated by column chromatography; $ArSBu^t$ and ArH by-products were detected in all cases but not quantified, unless otherwise stated. [d] Benzophenone (36%) was also isolated.

Scheme 2



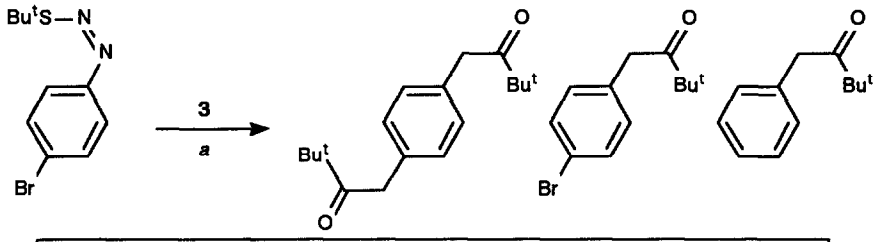
1j	R^1 = Me; R^2 = R^3 = H	**5j**: 10%	**8** : 70%	
1k	R^2 = Me; R^1 = R^3 = H	**5k**: tr.[b]		**9** : 83%
1l	R^2 = Bu^i; R^1 = R^3 = H	**5l**: 42%		**10** : 44%
1m	R^1 = R^2 = R^3 = Me	**5m**: 30%	**11** : 50%	**12** : 15%

[a] See footnotes *a-c* of the Table; reaction time : **1j** (90 min.), **1k** (40 min.), **1l** (30 min), **1m** (120 min.) [b]Detected by ^1H NMR in mixed chromatographic fractions.

With pinacolone enolate the 4-bromo-substituted azosulfide **1n** chiefly underwent (Scheme 3) substitution of both the *tert*-butylthioazo group and bromine to product **13** besides mono-substitution to **6n**; trace amounts of the debromination product **6a** were also detected in the reaction mixture.

Rationalization of the apparently discrepant reactivity of azosulfides **1a-n** with ketone enolates can be achieved when considering, in the studied reactions, the conceivable involvement of two processes: an electron-transfer catalyzed and a base-induced pathway which will be hereinafter discussed separately.

Scheme 3



1n	13 : 49%	6n : 10%	6a : tr [b]

[a] See footnotes *a-c* of the Table; reaction time: 90 min. [b] Detected by ^{1}H NMR in mixed chromatographic fractions.

Electron-transfer Catalyzed Pathway

As far as the α-arylation of ketones is concerned, on the grounds of the acquired knowledge on the behaviour of azosulfides with nucleophiles in DMSO,[1a, 24-29] we believe that the process herein represents a likely candidate for the occurence of the $S_{RN}1$ mechanism (steps 1-4; Nu^- = ketone enolate) triggered (step 1) by a spontaneous electron transfer from the enolate to the substrate. Such spontaneous initiation of the chain reaction is not surprising in view of the marked electron-donor properties of ketone enolates and of the favourable reduction potentials of arylazo *tert*-butyl sulfides.[30] As a matter of fact, unlike other nucleophiles commonly employed in $S_{RN}1$ processes, dark reactions with ketone enolates are observed not only with electron-poor azahetaryl halides (such as pyridazine and pyrazine[31] or quinoxaline and quinazoline[17] derivatives) but even with the less easily reducible iodobenzene.[15, 19, 20, 32]

In agreement with the intervention of an $S_{RN}1$ process in the studied reactions, besides the detection, in all our experiments, of ArH and ArSBu^t as typical by-products,[1a, 29] are also the results obtained with the 4-bromo-substituted azosulfide **1n** (Scheme 3).[33] The occurence of bis-substitution in substrates with two leaving groups is, in fact, commonly regarded as a conclusive test for the $S_{RN}1$ process[35] and has been repeatedly observed in the reactions of dihalogenoarenes with ketone enolates[18, 34, 36, 37] as well as in those of halogeno-substituted azosulfides with both S-[24b, 25, 28] and C-nucleophiles.[26b, 28] With reference to the $S_{RN}1$ propagation cycle represented by steps 2, 3 and 4 with Ar = 4-BrC_6H_4 and Nu = CH_2COBu^t, on the grounds of the acquired knowledge on such processes, the observed behaviour of azosulfide **1n** can thus be well explained: the radical anion intermediate 4-$BrC_6N_4CH_2COBu^t$ $^{-\bullet}$ formed in step 3 can either (step 4) transfer its odd electron (to give **6n**) or lose bromide ion originating the radical $Bu^tCOCH_2C_6H_4$ $^\bullet$. The latter, in turn, can competitively undergo either coupling with the enolate (to give the bis-

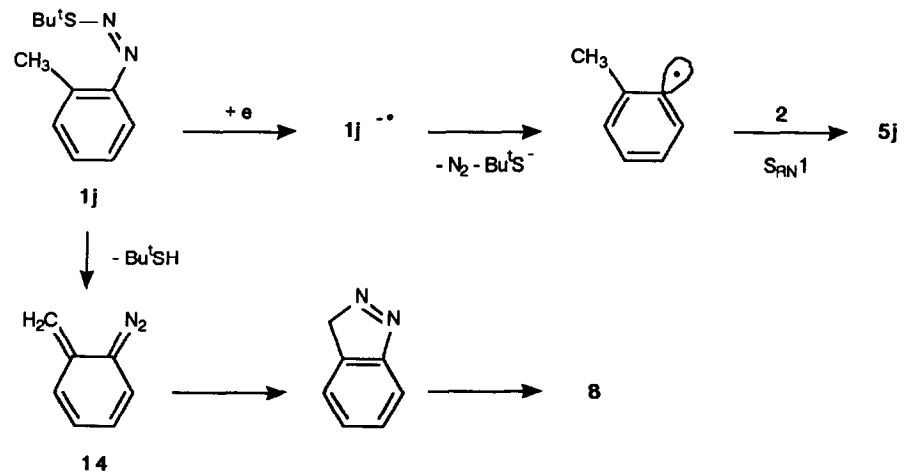
substitution product **13** via a new $S_{RN}1$ cycle) or reduction to the corresponding anion which by successive protonation eventually furnishes **6a**.

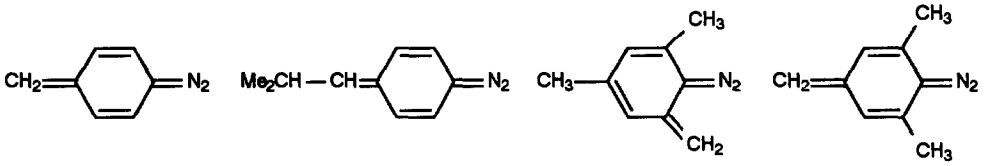
As a final observation on the electron-transfer catalyzed reactions of arylazo *tert*-butyl sulfides, the results of the reaction between **1a** and acetophenone enolate have to be stressed as the almost quantitative yield of deoxybenzoin **7a** obtained under mild conditions and with no need of photostimulation further evidences the good electron-accepting properties of **1a** which make it a very convenient substrate for $S_{RN}1$ processes. It is well known, in fact, that in the reactions with enolates of aralkyl ketones the presence of an easily reducible substrate is required for an effective initiation and propagation of $S_{RN}1$ processes as evidenced by: (i) the lack of reactivity of bromobenzene[23, 38] and 2-bromopyridine;[36] (ii) the intense and long irradiation required by the very slow reactions with iodobenzene[16, 23] and 2-chloroquinoline;[39] (iii) the favourable electronic effect of the acetyl group in the reactions of 2- and 4-bromoacetophenone;[23] (iv) the successful reactions with good electron-accepting pyrimidine,[40] pyrazine,[31] purine[21] and indole[22] halogenoderivatives.

Base-induced Pathway

As previously mentioned the behaviour of azosulfides **1j-m** with the enolate of acetone somehow differentiates from that of the other substrates examined. To explain the competitive formation of products **8-12** it is significative to point out that the 3-Me- (**1d**), the 4-Bu^t- (**1e**) and even the 3-MeO- (**1f**) and 4-MeO-substituted (**1g**) substrates exclusively give α-arylation products through electron-transfer catalyzed reactions. The reduction potentials of **1d-g** presumably are not substantially less negative than those of **1j-m** and therefore the latter azosulfides should participate in electron-transfer induced reactions as effectively as the former compounds. To interpret the results obtained with azosulfides **1j-m**, one needs to realize that all these substrates, at variance of **1d-g**, have as common feature the presence of benzylic hydrogens whose intrinsic acidity is enhanced by an electron-accepting azothiogroup in 2- or 4-position. It is therefore envisageable that the enolate ion, besides as electron donor, can act as base towards these substrates inducing a *tert*-butanethiol elimination from the azosulfide which, as shown in Scheme 4 for the case of **1j**, leads to alkylidene diazocyclohexadiene intermediates in a way which recalls the base-induced elimination from the intermediates of diazo group transfer reactions.[41, 42]

Scheme 4





15 **16** **17** **18**

The formation of **14**, **15** and **16** from **1j**, **1k** and **1l** respectively as well as that of **17** and **18** from **1m**, in a base-induced pathway competitive with the electron-transfer catalyzed $S_{RN}1$ arylation, gives a rationale to the isolation of the products reported in Scheme 2. As a matter of fact, 2-methylene diazoderivatives **14** or **17** are expected [43a, 44] to undergo fast intramolecular azo coupling to indazoles **8** or **11**, while the 4-alkylidene analogues **15**, **16** and **18**, by coupling with the excess acetone enolate, would eventually give 2-oxopropanal arylhydrazones **9**, **10** or **12**. Such a kind of coupling of diazoderivatives with nucleophiles is not unprecedented.[43b]

In support to the above hypothesis, an independent experiment showed the formation of indazole **8** in yield similar to that reported in Scheme 2 by treatment of **1j** with one molar equivalent of Bu^tOK in DMSO at room temperature.

At the light of the proposed mechanisms, moreover, the different product distribution observed (Scheme 2) can be rationalized on the grounds of a different balance between the two competing pathways. Thus, the fact that, in going from **1k** to **1l**, the yield of arylhydrazone decreases in favour of the arylation product can be explained by the lower acidity of the benzylic protons in the isobutyl group of **1l**. Finally, it is noticeable that a relatively high yield of α-arylation is obtained with **1m**, although the presence of three ionizable methyl groups should statistically favour the base-induced pathway. It is likely that in **1m** some steric inhibition to conjugation of the azothiogroup with the aromatic ring decreases the methyl hydrogen acidity while increases the nucleofugacity of the distorted azothio group in the competing electron-transfer catalyzed process.

Concluding Remarks

On a synthetic point of view, the $S_{RN}1$ reactions of (*Z*)-arylazo *tert*-butyl sulfides represent a promising strategy for the direct arylation of ketone enolates. The spontaneous initiation of the chain process and the excellent yield of deoxybenzoin in the reaction of **1a** with acetophenone enolate suggest that the method herein may be particularly exploitable for α-arylations of aralkyl ketones and, consistently, researches are in progress in order to evaluate its applicability in synthesis. Limitations to the present arylation reactions arise from the employment of alkyl-substituted azosulfides with acidic benzylic hydrogens. On the other hand, the formation of compounds such as the reported indazoles and arylhydrazones indicates the possible development of the reactivity of azosulfides along interesting lines.

Experimental

Melting points were determined on a Buchi 535 apparatus and are uncorrected. The ^1H NMR spectra were recorded with either a Varian FT80 or Gemini 200 spectrometer. Tetramethylsilane was used as internal standard and chemical shifts are reported as δ values (p.p.m.). IR spectra (neat or nujol mull) were recorded on a Perkin-Elmer 881 Infrared Spectrophotometer.

Materials.

Petroleum ether and light petroleum refer to the fractions with b.p. 40-60 °C and 80-100 °C, respectively. Dimethylsulfoxide (Fluka) was used as received after storage over molecular sieves (4 Å). Potassium *tert*-butoxide (Aldrich, 97%) was employed without further purification. Arylamines, used for the synthesis of azosulfides **1**, were all commercially available but for 4-isobutylaniline which was sinthesized through a reported procedure.[45] Acetone, pinacolone and acetophenone were commercial products used as received after storage over molecular sieves (4 Å).

***(Z)-Arylazo tert-Butyl Sulfides* 1a-n.**

These substrates were synthesized,[46] isolated and purified[29] as reported. Physical and spectroscopic data relevant to compounds **1c**, **1g**, **1h**, **1i** and **1n** have been reported in a previous paper.[29] Physical data of **1a** and **1m** matched literature values.[47]

(Z)-1-Naphthylazo tert-butyl sulfide **1b**: yellow oil; (Found: C, 68.7; H, 6.5; N, 11.4. $C_{14}H_{16}N_2S$ requires: C, 68.8; H, 6.6; N, 11.5%); ^{1}H NMR ($CDCl_3$, 80 MHz) δ 1.57 (9H, s), 7.05 (1H, d, *J* 7.2 Hz), 7.47 (3H, m) and 7.80 (3H, m).

(Z)-(3-Methylphenyl)azo tert-butyl sulfide **1d**: yellow oil; (Found: C, 63.2; H, 7.8; N, 13.5. $C_{11}H_{16}N_2S$ requires: C, 63.4; H, 7.7; N, 13.4%); ^{1}H NMR ($CDCl_3$, 200 MHz) δ 1.60 (9H, s), 2.40 (3H, s), 6.89 (2H, m), 7.14 (1H, m) and 7.34 (1H, m).

(Z)-(4-tert-butylphenyl)azo tert-butyl sulfide **1e**: m.p. 61.2-62.0 °C (petroleum ether); (Found: C, 67.4; H, 8.9; N, 11.0. $C_{14}H_{22}N_2S$ requires: C, 67.1; H, 8.9; N, 11.2%); ^{1}H NMR ($CDCl_3$, 200 MHz) δ 1.35 (9H, s), 1.60 (9H, s), 7.11 and 7.49 (2H each, AA'BB' system, *J* 8.7 Hz).

(Z)-(3-Methoxyphenyl)azo tert-butyl sulfide **1f**: yellow oil; (Found: C, 59.5; H, 7.4; N, 12.3. $C_{11}H_{16}N_2OS$ requires: C, 58.9; H, 7.2; N, 12.5%); ^{1}H NMR ($CDCl_3$, 200 MHz) δ 1.60 (9H, s), 3.82 (3H, s), 6.66 (2H, m), 6.86 (1H, m) and 7.37 (1H, m).

(Z)-(2-Methylphenyl)azo tert-butyl sulfide **1j**: orange oil; (Found: C, 63.0; H, 7.6; N, 13.3. $C_{11}H_{16}N_2S$ requires: C, 63.4; H, 7.7; N, 13.4%); ^{1}H NMR ($CDCl_3$, 200 MHz) δ 1.60 (9H, s), 2.13 (3H,s), 6.79 (1H, m) and 7.26 (3H, s).

(Z)-(4-Methylphenyl)azo tert-butyl sulfide **1k**: yellow oil; (Found: C, 63.5; H, 7.8; N, 13.6. $C_{11}H_{16}N_2S$ requires: C, 63.4; H, 7.7; N, 13.4%); ^{1}H NMR ($CDCl_3$, 80 MHz) δ 1.59 (9H, s), 2.38 (3H, s), 7.03 and 7.28 (2H each, AA'BB' system, *J* 8.5 Hz).

(Z)-(4-Isobutylphenyl)azo tert-butyl sulfide **1l**: orange oil; (Found: C, 67.0; H, 8.9; N, 11.3. $C_{14}H_{22}N_2S$ requires: C, 67.1; H, 8.9; N, 11.2%); ^{1}H NMR ($CDCl_3$, 80 MHz) δ 0.92 (6H, d, *J* 6.6 Hz), 1.60 (9H, s), 1.89 (1H, m), 2.50 (2H, d, *J* 7.3 Hz), 7.07 and 7.24 (2H each, AA'BB' system, *J* 8.4 Hz).

Reactions of Azosulfides with Potassium Ketone Enolates.

The experiments were performed, under argon and at room temperature, by addition of a DMSO solution of azosulfide (2 mmol in 12 ml) to a magnetically stirred solution of potassium enolates **2**, **3** or **4**, prepared *in situ* by dropping the corresponding ketone (20 mmol) into a cold solution of Bu^tOK (20 mmol) in 18 ml of DMSO. After addition of the substrate, the reactions were kept under magnetic stirring for the time reported (see Table and Schemes 2 and 3), the end of reaction being judged following by TLC the disappearance of the substrate. Usual work-up invoived pouring of the reaction mixture into ice/3% HCl followed by extraction with ether and washing of the combined extracts (Na_2SO_4), the solvent and the excess ketone being distilled off in a rotary evaporator under reduced pressure. Column chromatography on silica gel of the residue (eluants: light petroleum and gradients with CH_2Cl_2 or AcOEt) allowed separation of the products reported.

α-Arylated Ketones.

Most products were identified on the basis of their ^{1}H NMR spectrum and, when liquid, characterized through the corresponding 2,4-dinitrophenylhydrazone (2,4-DNPH).

1-Phenyl-2-propanone **5a** gave ^{1}H NMR in agreement with that reported;[48] 2,4-DNPH: m.p. 151.2-152.0 °C (lit.,[49] m.p. 151 °C).

1-(1-Naphthyl)-2-propanone **5b**: ^{1}H NMR ($CDCl_3$, 80 MHz) δ 2.07 (3H,s), 4.06 (2H, s), 7.43 (4H, m) and 7.80 (3H, m); 2,4-DNPH: m.p. 173.2-174.5 °C (EtOH-AcOEt) (lit.,[50] m.p. 174-176 °C).

1-(2-Naphthyl)-2-propanone **5c**: ^{1}H NMR ($CDCl_3$, 80 MHz) δ 2.14 (3H, s), 3.81 (2H, s), 7.36 (3H, m) and 7.73 (4H, m); 2,4-DNPH: m.p. 170-171 °C (EtOH-AcOEt) (lit.,[51] m.p. 172.5-173 °C).

1-(3-Methylphenyl)-2-propanone **5d**: ^{1}H NMR ($CDCl_3$, 200 MHz) δ 2.13 (3H, s), 2.33 (3H, s), 3.64 (2H, s), 7.03 (3H, m) and 7.22 (1H, m); *2,4-DNPH*: m.p. 84.9-86 °C (EtOH); (Found: C, 58.2; H, 4.9; N, 17.2. $C_{16}H_{16}N_4O_4$ requires: C, 58.5; H, 4.9; N, 17.1%); ^{1}H NMR ($CDCl_3$, 200 MHz) δ 1.99 (3H, s), 2.35 (3H, s), 3.69 (2H, s), 7.16 (4H, m), 8.03 (1H, d, *J* 9.6 Hz), 8.34 (1H, dd, *J* 2.6 and 9.6 Hz), 9.14 (1H, d, *J* 2.6 Hz) and 11.07 (1H, br s).

1-(4-tert-Butylphenyl)-2-propanone **5e**: ^{1}H NMR ($CDCl_3$, 200 MHz) δ 1.31 (9H, s), 2.14 (3H, s), 3.65 (2H, s), 7.13 and 7.35 (2H each, AA'BB' system, *J* 8.3 Hz). *2,4-DNPH* : m.p. 153.0-153.5 °C (EtOH); (Found: C, 61.8; H, 6.0; N,

15.3. $C_{19}H_{22}N_4O_4$ requires: C, 61.6; H, 6.0; N, 15.1%); ^{1}H NMR ($CDCl_3$, 200 MHz) δ 1.32 (9H, s), 2.00 (3H, s), 3.69 (2H, s), 7.18 and 7.36 (2H each, AA'BB' system, *J* 8.2 Hz), 8.03 (1H, d, *J* 9.6 Hz), 8.33 (1H, dd, *J* 2.6 and 9.6 Hz), 9.14 (1H, d, *J* 2.6 Hz) and 11.06 (1H, br s).

1-(3-Methoxyphenyl)-2-propanone **5f**: ^{1}H NMR ($CDCl_3$, 200 MHz) δ 2.14 (3H, s), 3.65 (2H, s), 3.79 (3H, s), 6.79 (3H, m) and 7.24 (1H, m); *2,4-DNPH*: m.p. 109.3-110.1 °C (EtOH); (Found: C, 55.6; H, 4.7; N, 16.5. $C_{16}H_{16}N_4O_5$ requires: C, 55.8; H, 4.7; N, 16.3%); ^{1}H NMR ($CDCl_3$, 200 MHz) δ 2.00 (3H, s), 3.70 (2H, s), 3.81 (3H, s), 6.83 (3H, m), 7.27 (1H, m), 8.02 (1H, d, *J* 9.6 Hz), 8.33 (1H, dd, *J* 2.6 and 9.6 Hz), 9.14 (1H, d, *J* 2.6 Hz) and 11.06 (1H, br s).

1-(4-Methoxyphenyl)-2-propanone **5g**: ^{1}H NMR ($CDCl_3$, 80 MHz) δ 2.09 (3H, s), 3.59 (2H, s), 3.74 (3H, s), 6.82 and 7.09 (2H each, AA'BB' system, *J* 8.7 Hz); 2,4-DNPH: m.p. 102.0-103.4 °C (lit.,[52] m.p. 104-105 °C).

1-(3-Benzoylphenyl)-2-propanone **5h** showed IR and ^{1}H NMR spectra in agreement with those reported.[2]

1-(4-Benzoylphenyl)-2-propanone **5i**: ^{1}H NMR ($CDCl_3$, 80 MHz) δ 2.21 (3H, s), 3.80 (2H, s), 7.31 (2H, AA' of AA'BB' system, *J* 8.1 Hz), 7.54 (3H, m) and 7.79 (4H, m); *2,4-DNPH*: m.p. 139.0-140.0 °C (EtOH); (Found: C, 62.5; H, 4.2; N, 13.0. $C_{22}H_{18}N_4O_5$ requires: C, 63.1; H, 4.3; N, 13.4%); ^{1}H NMR ($CDCl_3$, 80 MHz) δ 2.04 (3H, s), 3.82 (2H, s), 7.44 (5H, m), 7.80 (4H, m), 7.98 (1H, d, *J* 9.6 Hz), 8.34 (1H, dd, *J* 2.5 and 9.6 Hz), 9.13 (1H, d, *J* 2.5 Hz) and 11.09 (1H, br s).

1-(2-Methylphenyl)-2-propanone **5j**: ^{1}H NMR ($CDCl_3$, 200 MHz) δ 2.13 (3H, s), 2.24 (3H, s), 3.70 (2H, s) and 7.17 (4H, m); 2,4-DNPH: m.p. 140.5-141.3 °C (EtOH) (lit.,[53] m.p. 145 °C).

1-(4-Isobutylphenyl)-2-propanone **5l**: ^{1}H NMR ($CDCl_3$, 80 MHz) δ 0.89 (6H, d, *J* 6.5 Hz), 1.84 (1H, m), 2.13 (3H, s), 2.45 (2H, d, *J* 7.1 Hz), 3.65 (2H, s) and 7.10 (4H, br s); *2,4-DNPH* : m.p.142.0-143.0 °C (EtOH); (Found: C, 61.7; H, 6.0; N, 15.4. $C_{19}H_{22}N_4O_4$ requires: C, 61.6; H, 6.0; N, 15.1%); ^{1}H NMR ($CDCl_3$, 80 MHz) δ 0.89 (6H, d, *J* 6.4 Hz), 1.99 (4H in all, overlapped s and m), 2.46 (2H, d, *J* 7.1 Hz), 3.69 (2H, s), 7.13 (4H, br s), 7.99 (1H, d, *J* 9.5 Hz), 8.32 (1H, dd, *J* 2.5 and 9.5 Hz), 9.14 (1H, d, *J* 2.5 Hz) and 11.05 (1H, br s).

1-(2,4,6-Trimethylphenyl)-2-propanone **5m**: ^{1}H NMR ($CDCl_3$, 200 MHz) δ 2.13 (3H, s), 2.20 (6H, s), 2.26 (3H, s), 3.72 (2H, s) and 6.87 (2H, s); *2,4-DNPH* : m.p. 161.0-162.3 (EtOH), (Found: C, 60.2; H, 5.6; N, 15.5. $C_{18}H_{20}N_4O_4$ requires: C, 60.7; H, 5.7; N, 15.7%); ^{1}H NMR ($CDCl_3$, 200 MHz) δ 1.99 (3H, s), 2.29 (9H, s), 3.78 (2H, s), 6.90 (2H, s), 7.78 (1H, d, *J* 9.6 Hz), 8.27 (1H, dd, *J* 2.6 and 9.6 Hz), 9.12 (1H, d, *J* 2.6 Hz) and 11.06 (1H, br s).

3,3-Dimethyl-1-phenyl-2-butanone **6a** showed IR and ^{1}H NMR spectra in agreement with those reported.[38]

1-(4-Bromophenyl)-3,3-dimethyl-2-butanone **6n**: m.p. 58.6-59.1 °C (petroleum ether); (Found: C, 56.4; H, 5.8. $C_{12}H_{15}BrO$ requires: C, 56.5; H, 5.9%); ^{1}H NMR ($CDCl_3$, 200 MHz) δ 1.20 (9H, s), 3.75 (2H, s), 7.04 and 7.43 (2H each, AA'BB' system, *J* 8.3 Hz).

Deoxybenzoin **7a**: m.p. 52.5-54.0 °C (MeOH) (lit.,[54] m.p. 55-56) showed ^{1}H NMR spectrum in agreement with that reported.[10]

1,4-Bis(3,3-dimethyl-2-oxobutyl)benzene **13**: m.p. 105.0-105.8 °C (EtOH) (lit.,[34] m.p. 101-101.5 °C) showed ^{1}H NMR spectrum in agreement with that reported.[34]

Indazoles

Indazole **8** was identified by comparison (^{1}H NMR and mixed m.p.) with a commercial authentic sample.

5,7-Dimethylindazole **11**: m.p. 132.6-133.6 °C (light petroleum) (lit.,[55] m.p. 133-134 °C); ^{1}H NMR ($CDCl_3$, 200 MHz) δ 2.43 (3H, s), 2.53 (3H, s), 7.02 (1H, s), 7.37 (1H, s), 8.00 (1H, s) and 10.16 (1H, br s).

2-Oxopropanal Arylhydrazones

2-Oxopropanal (4-methylphenyl)hydrazone **9**: m.p. 114.3-115.3 °C (EtOH-H_2O) (lit.,[56] m.p. 114-115 °C); ^{1}H NMR ($CDCl_3$, 200 MHz) δ 2.32 (3H, s), 2.44 (3H, s), 7.07 (2H, AA' of AA'BB', *J* 8.7 Hz), 7.14 (3H, m) and 8.38 (1H, br s).

2-Oxopropanal (4-isobutylphenyl)hydrazone **10**: m.p. 89.5-90.5 °C (EtOH-H_2O); (Found: C, 71.5; H, 8.2; N, 12.8. $C_{13}H_{18}N_2O$ requires: C, 71.5; H, 8.3; N, 12.8%); ^{1}H NMR ($CDCl_3$, 200 MHz) δ 0.90 (6H, d, *J* 6.6 Hz), 1.83 (1H,m), 2.44 [5H in all, overlapped s and d (*J* 7.2 Hz)], 7.10 (4H, s), 7.15 (1H, m) and 8.40 (1H, br s).

2-Oxopropanal (2,4,6-trimethylphenyl)hydrazone **12**: m.p. 157.6-158.5 °C (EtOH-H_2O); (Found: C, 70.3; H, 7.7; N, 13.6. $C_{12}H_{16}N_2O$ requires: C, 70.5; H, 7.9; N, 13.7%); ^{1}H NMR ($CDCl_3$, 200 MHz) δ 2.19 (6H, s), 2.28 (3H, s), 2.34 (3H, s), 6.70 (1H, br s), 6.91 (2H, s) and 7.66 (1H, br s).

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References and Notes

1 (a) Dell'Erba, C.; Novi, M.; Petrillo, G.; Tavani, C.; Bellandi, P. *Tetrahedron* **1991**, *47*, 333; (b) pertinent references cited therein.
2 Sugai, S.; Ikawa, H.; Okazaki, T.; Akaboshi, S.; Ikegami, S. *Chem. Lett.* **1982**, 597.
3 Beugelmans, R.; Bois-Choussy, M.; Boudet, B. *Tetrahedron* **1982**, *38*, 3479.
4 Krapcho, D. *Synthesis* **1982**, 893.
5 March, J. *Advanced Organic Chemistry*, 3rd Ed., Wiley, New York, 1985, p. 566.
6 Barton, D.H.R.; Lester, D.J.; Motherwell, W.B.; Barros Papoula, M.T. *J. Chem. Soc., Chem. Commun.* **1980**, 246. Barton, D.H.R.; Barros Papoula, M.T.; Guilhem, J.; Motherwell, W.B.; Pascard, C.; Tran Huu Dau, E. *J. Chem. Soc., Chem. Commun.* **1984**, 732.
7 Moriarty, R.M.; Vaid, R.K. *Synthesis* **1990**, 431.
8 Negishi, E.; Chiu, K.; Yosida, T. *J. Org. Chem.* **1975**, *40*, 1676. Milstein, D.; Stille, J.K. *J. Am. Chem. Soc.* **1978**, *100*, 3636; *J. Org. Chem.* **1979**, *44*, 1613. Labadie, J.W.; Stille, J.K. *J. Am. Chem. Soc.* **1983**, *105*, 6129. Labadie, J.W.; Tueting, D.; Stille, J.K. *J. Org. Chem.* **1983**, *48*, 4634. D'Incan, E.; Sibille, S.; Perichon, J. *Tetrahedron Lett.* **1986**, *27*, 4175. Prasad, J.S.; Liebeskind, L.S. *Tetrahedron Lett.* **1987**, *28*, 1857. Creary, X. *J. Org. Chem.* **1987**, *52*, 5026. Babudri, F.; Fiandanese, V.; Musio, R.; Naso, F.; Sciacovelli, O.; Scilimati, A. *Synthesis* **1991**, 225.
9 Hussey, A.S.; Herr, R.R. *J. Org. Chem.* **1959**, *24*, 843. Brown, H.C.; Nambu, H.; Rogic, M.M. *J. Am. Chem. Soc.* **1969**, *91*, 6852. Sacks, C.E.; Fuchs, P.L. *J. Am. Chem. Soc.* **1975**, *97*, 7372. Sakurai, H.; Shirahata, A.; Araki, Y.; Hosomi, A. *Tetrahedron Lett.* **1980**, *21*, 2325. Lei,X.; Doubleday, C.; Turro, N.J. *Tetrahedron Lett.* **1986**, *27*, 4671.
10 Rathke, M.W.; Vogiazoglou, D. *J. Org. Chem.* **1987**, *52*, 3697.
11 Wender, P.A.; Erhardt, J.M.; Letendre, L.J. *J. Am. Chem. Soc.* **1981**, *103*, 2114. Marino, J.P.; Jaén, J.C. *J. Am. Chem. Soc.* **1982**, *104*, 3165.
12 Semmelhack, M.F.; Stauffer, R.D.; Rogerson, T.D. *Tetrahedron Lett.* **1973**, 4519. Hegedus, L.S.; Stiverson, R.K. *J. Am. Chem. Soc.* **1974**, *96*, 3250. Semmelhack, M.F.; Chong, B.P.; Stauffer, R.D.; Rogerson, T.D.; Chong, A.; Jones, R.D. *J. Am. Chem. Soc.* **1975**, *97*, 2507. Fauvarque, J.F.; Jutand, A. *J. Organometal. Chem.* **1979**, *177*, 273. Kosugi, M.; Suzuki, M.; Hagiwara, I.; Goto, K.; Saitoh, K.; Migita, T. *Chem. Lett.* **1982**, 939. Kuwajima, I.; Urabe, H. *J. Am. Chem. Soc.* **1982**, *104*, 6831. Negishi, E.; Akiyoshi, K. *Chem. Lett.* **1987**, 1007. Nair, V.; Turner, G.A.; Chamberlain, S.D. *J. Am. Chem. Soc.* **1987**, *109*, 7223.
13 Rossi, R.A.; de Rossi, R.H. *Aromatic Substitution by the $S_{RN}1$ Mechanism*, ACS Monograph 178, American Chemical Society, Washington, D.C., 1983, pp. 13-36.
14 Scamehorn, R.G.; Bunnett, J.F.; *J. Org. Chem.* **1977**, *42*, 1457. Galli, C.; Bunnett, J.F. *J. Am. Chem. Soc.* **1979**, *101*, 6137. Bunnett, J.F.; Galli, C. *J. Chem. Soc., Perkin Trans. 1* **1985**, 2515. Bunnett, J.F.; Mitchel, E.; Galli, C. *Tetrahedron* **1985**, *41*, 4119. Dillender, S.C. Jr.; Greenwood, T.D.; Hendi, M.S.; Wolfe, J.F. *J. Org. Chem.* **1986**, *51*, 1184. Usui, S.; Fukazawa, Y. *Tetrahedron Lett.* **1987**, *28*, 91. Estel, L.; Marsais, F.; Queguiner, G. *J. Org. Chem.* **1988**, *53*, 2740.
15 Scamehorn, R.G.; Bunnett, J.F. *J. Org. Chem.* **1979**, *44*, 2604.
16 Semmelhack, M.F.; Bargar, T. *J. Am. Chem. Soc.* **1980**, *102*, 7765.
17 Carver, D.R.; Hubbard, J.S.; Wolfe, J.F. *J. Org. Chem.* **1982**, *47*, 1036.
18 Carver, D.R.; Greenwood, T.D.; Hubbard, J.S.; Komin, A.P.; Sachdeva, Y.P.; Wolfe, J.F. *J. Org. Chem.* **1983**, *48*, 1180.
19 Galli, C.; Bunnett, J.F. *J. Org. Chem.* **1984**, *49*, 3041.
20 Scamehorn, R.G.; Hardacre, J.M.; Lukanich, J.M.; Sharpe, L.R. *J. Org. Chem.* **1984**, *49*, 4881.
21 Nair, V.; Chamberlain, S.D. *J. Am. Chem. Soc.* **1985**, *107*, 2183; *J. Org. Chem.* **1985**, *50*, 5069.
22 Beugelmans, R.; Bois-Choussy, M. *Heterocycles* **1987**, *26*, 1863.
23 Beugelmans, R.; Bois-Choussy, M.; Tang, Q. *J. Org. Chem.* **1987**, *52*, 3880.
24 (a) Petrillo, G.; Novi, M.; Garbarino, G.; Dell'Erba, C. *Tetrahedron Lett.* **1985**, *26*, 6365.; (b) *Tetrahedron* **1986**, *42*, 4007.
25 Novi, M.; Petrillo, G.; Sartirana, M.L. *Tetrahedron Lett.* **1986**, *27*, 6129.
26 (a) Novi, M.; Petrillo, G.; Dell'Erba, C. *Tetrahedron Lett.* **1987**, *28*, 1345; (b) Petrillo, G.; Novi, M.; Garbarino, G.; Dell'Erba, C. *Tetrahedron* **1987**, *43*, 4625.
27 Petrillo, G.; Novi, M.; Dell'Erba, C. *Tetrahedron Lett.* **1989**, *30*, 6911.
28 Novi, M.; Garbarino, G.; Petrillo, G.; Dell'Erba, C. *Tetrahedron* **1990**, *46*, 2205.
29 Petrillo, G.; Novi, M.; Dell'Erba, C.; Tavani, C.; Berta, G. *Tetrahedron* **1990**, *46*, 7977.
30 Electrochemical studies are planned in order to determine standard reduction potentials (E^0) of arylazo *tert*-butyl sulfides. Anyway, several hints[1a,29] indicate that the substitution, in an aromatic substrate, of the good electronwithdrawing Bu^tSNN- for the more commonly used $S_{RN}1$ leaving group iodine, brings about a marked shift of the E^0 value toward less negative potentials (*i.e.* it renders the substrate a better electron-acceptor). The results herein in the reaction of **1a** with acetophenone enolate **4** further substantiate this assumption (see text further on).
31 Carver, D.R.; Komin, A.P.; Hubbard, J.S.; Wolfe, J.F. *J. Org. Chem.* **1981**, *46*, 294.
32 Scamehorn, R.G.; Bunnett, J.F. *J. Org. Chem.* **1977**, *42*, 1449.

33 In view of expected $S_{RN}1$ reactivity and to limit possible polymerization, as reported to occur in the reactions of 1,4-dihalogenobenzenes with acetone enolate 2,[34] the reaction of **1n** was carried out with pinacolone enolate **3** and not with **2** as for the other substrates.
34 Alonso, R.A.; Rossi, R.A. *J. Org. Chem.* **1980**, *45*, 4760.
35 See ref. 13, pp. 205-212.
36 Komin, A.P.; Wolfe, J.F. *J. Org. Chem.* **1977**, *42*, 2481.
37 Bunnett, J.F.; Singh, P. *J. Org. Chem.* **1981**, *46*, 5022.
38 Bunnett, J.F.; Sundberg, J.E. *J. Org. Chem.* **1976**, *41*, 1702.
39 Hay, J.V.; Wolfe, J.F. *J. Am. Chem. Soc.* **1975**, *97*, 3702.
40 Oostveen, E.A.; Van der Plas, H.C. *Recl. Trav. Chim. Pays-Bas* **1979**, *98*, 441.
41 Hendrickson, J.B.; Wolf, W.A. *J. Org. Chem.* **1968**, *33*, 3610.
42 Regitz, M. *Synthesis* **1972**, 351; *Angew. Chem. Internat. Edn. Engl.* **1967**, *6*, 733.
43 Szele, I.; Zollinger, H. in *Topics in Current Chemistry*, Springer-Verlag, Berlin, **1983**, *112*, (a) p. 16; (b) pp. 6-8.
44 Bartsch, R.A.; Yang, I.-W. *J. Heterocycl. Chem.* **1984**, *21*, 1063 and references therein.
45 Stock, L.M.; Wasielewski, M.R. *J. Am. Chem. Soc.* **1977**, *99*, 50.
46 Sakla, A.B.; Masoud, N.K.; Sawiris, Z.; Ebaid, W.S. *Helv. Chim. Acta* **1974**, *57*, 481.
47 Van Zwet, H.; Kooyman, E.C. *Recl. Trav. Chim. Pays-Bas* **1967**, *86*, 993.
48 Pouchert, C.J.; Campbell, J.R. *The Aldrich Library of NMR Spectra*, Aldrich Chemical Co., Milwaukee, 1974, Vol. 6, 1A.
49 Hegedus, L.S.; Stiverson, R.K. *J. Am. Chem. Soc.* **1974**, *96*, 3250.
50 Campbell, N.; Anderson, W.; Gilmore, J. *J. Chem. Soc.* **1940**, 819.
51 Wilds, A.L.; Close, W.J.; Johnson, J.A. *J. Am. Chem. Soc.* **1946**, *68*, 89.
52 Huang, R.L. *J. Chem. Soc.* **1954**, 2539.
53 Konieczny, M.; Brobanski, B. *Roczniki Chem.* **1959**, *33*, 1027 (*Chem. Abstr.* **1960**, *54*, 6620c)
54 Allen, C.F.H.; Barker, W.E. *Organic Syntheses, Coll. Vol II* **1943**, 156.
55 Bamberger, E. *Justus Liebigs Ann. Chem.* **1899**, *305*, 308.
56 Richter, V.V.; Munzer, H. *Chem. Ber.* **1884**, *17*, 1929.