Tetrahedron Vol. 49, No 1, pp. 235-242, 1993
Printed in Great Britain

0040-4020/93 $5.00+.00
© 1993 Pergamon Press Ltd

α-Arylation *vs.* α-Arylhydrazonylation of Alkyl Aryl Ketones with Arylazo *tert*-Butyl Sulfides

Carlo Dell'Erba, Marino Novi, Giovanni Petrillo* and Cinzia Tavani

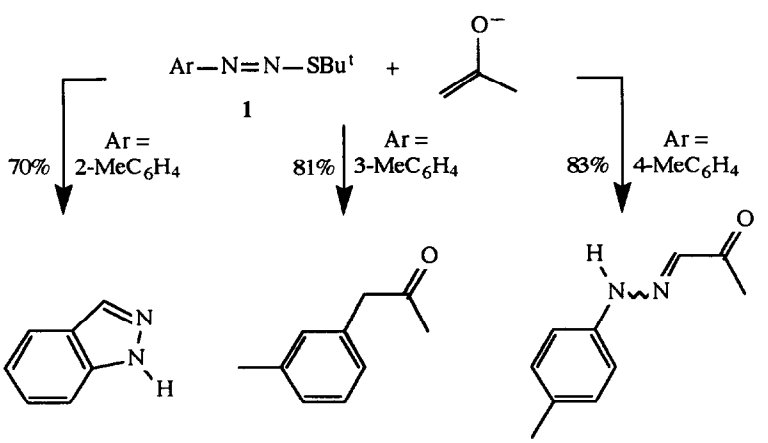
Istituto di Chimica Organica dell'Università, C.N.R. Centro di Studio per la Chimica dei Composti Cicloalifatici ed Aromatici, Corso Europa 26, I-16132 Genova, Italy

(*Received in UK 29 September* 1992)

Abstract. *Potassium enolates of alkyl aryl ketones react selectively in DMSO with phenylazo* ***1a*** *and 4-methylphenylazo tert-butyl sulfide* ***1b*** *undergoing respectively effective α-phenylation via $S_{RN}1$ and α-(4-methylphenyl)hydrazonylation via elimination-addition.*

Within the framework of an ongoing exploitation of azosulfides **1** as convenient reagents in $S_{RN}1$ arylations at carbon,[1-4] we have recently reported that, at variance with previous observations on the behaviour of **1** towards cyanide,[1] aryloxides[2] or 2,4-pentanedionate,[3] the α-arylation of the ketone enolates of acetone or pinacolone is not limited by the need for electronwithdrawing substituents in Ar.[4] Furthermore, the results obtained with the latter enolates reveal that, when suitable alkyl substituents are present in *ortho* or *para* position with respect to -N=N-SBu^t, different processes (leading to products which maintain the two nitrogens of **1**) effectively compete with, if not completely overcome, the $S_{RN}1$ arylation reaction.[4] The examples reported in Scheme 1 show a spectacular dependence of the main reaction outcome on the position of a methyl group in the aromatic ring of **1**. Thus, intramolecular cyclization to 1*H*-indazoles, α-arylation and α-arylhydrazonylation appear to be appealing routes open to the synthetic applications of azosulfides **1**.

Scheme 1

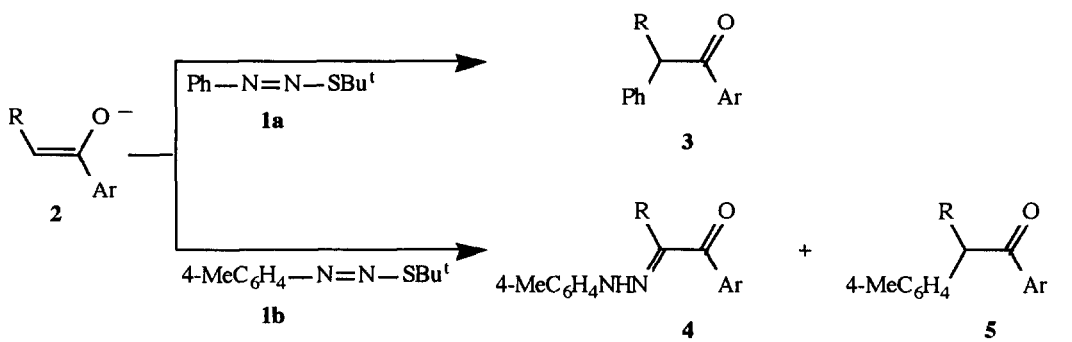


As a first development the observed almost quantitative phenylation of acetophenone [4] has led us to better investigate the applicability of our system in particular to alkyl aryl ketones. As a matter of fact, in the panorama of the available routes to α-arylketones,[5] the $S_{RN}1$ direct arylation by haloarenes, although fairly well suited as far as dialkyl ketones are concerned, when applied to alkyl aryl ketones is reportedly of more limited use,[6] due to the need for aryl halides characterised by favourable reduction potentials or for harsh experimental conditions. Accordingly the work herein also aimed at a better definition of the potentialities of azosulfides *vs.* haloarenes as reagents in $S_{RN}1$ processes. A further point of interest was, on the other hand, to ascertain whether the competitive formation of α-hydrazonylated products would also hold for such particular case.

Results and Discussion

Results of the reactions of the phenyl- **1a** and of the 4-methylphenyl-azosulfide **1b** with the enolates **2a-h** of alkyl aryl ketones are summarized in Scheme 2 and Tables 1 and 2. It is immediately apparent that, as observed for the enolate of acetone,[4] a *p*-methyl group governs the main reaction pathway, its presence leaving to the α-arylation at best a secondary role. Once this dicothomic behaviour is acknowledged,our hopes for an effective α-phenylation of aralkyl ketones have surely met with success. Actually, with aryl methyl ketones yields remain more than satisfactory throughout, an exception being represented by the 3-thienylderivative (expt. 6), where the reaction is accompanied by substantial amounts of tarry material possibly deriving from decomposition of the thiophene moiety. The comparison of experiments 7 and 8 with 1 measures the negative influence of branching at the α-carbon of the enolate: on going from the enolate **2a** (acetophenone) to either **2g** (propiophenone) or **2h** (butyrophenone) the decrease in yield of **3** is significant, though achievement of

Scheme 2



Compounds **2-5**					
	R =	Ar =		R =	Ar =
a	H	Ph	**e**	H	2-thienyl
b	H	2-$MeOC_6H_4$	**f**	H	3-thienyl
c	H	3-$MeOC_6H_4$	**g**	Me	Ph
d	H	4-$MeOC_6H_4$	**h**	Et	Ph

Table 1. Reactions between Phenylazo *tert*-Butyl Sulfide **1a** and Enolates **2a-h.** [a]

Expt.	Reaction time (min) [b]	Product	Yield (%) [c]	Expt.	Reaction time (min) [b]	Product	Yield (%) [c]
1	60	**3a**	95[d]	6	80	**3f**	48
2	120	**3b**	58 (71[e])	7	60	**3g**	60
3	60	**3c**	76			**8**	10
4	100	**3d**	77	8	90	**3h**	52
5	60	**3e**	66			**9**	16

a) Conditions argon, r t , 10 mol equiv of enolate with respect to azosulfide, [azosulfide] = 0 065 M The enolate was generated *in situ* from equimolar amounts of the relevant ketone and Bu^{t}OK prior to the addition of **1a**. b) The reported time refers in all cases but one (expt 2) to completion of the reaction, as judged by the TLC disappearance of the azosulfide c) Yields of isolated products d) From ref 4 e) Yield based on the reacted **1a**

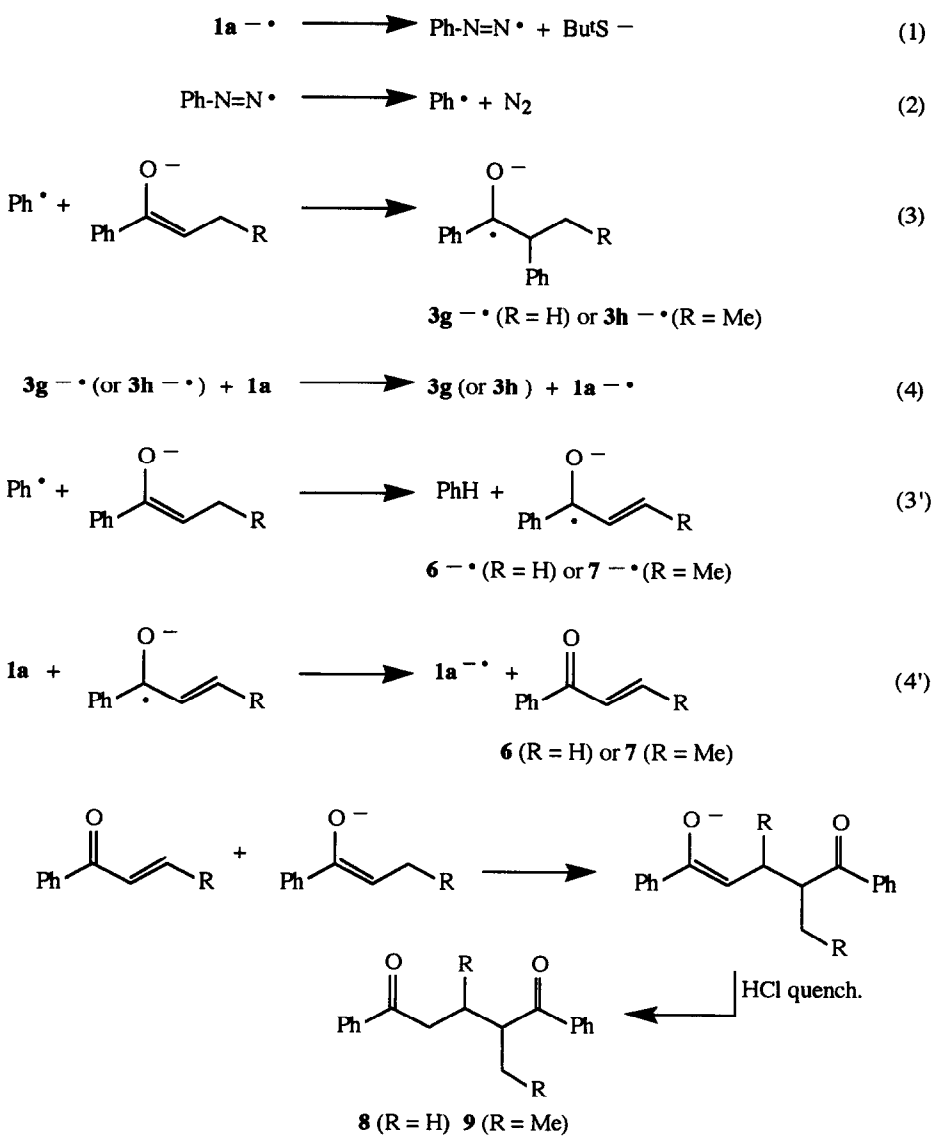
Table 2. Reactions between 4-Methylphenylazo *tert*-Butyl Sulfide **1b** and Enolates **2a-h.** [a]

Expt.	Reaction time (min) [b]	Product	Yield (%) [c]	Expt.	Reaction time (min) [b]	Product	Yield (%) [c]
9	60	**4a**	90	14	60	**4f**	89
10	60	**4b**	95	15	75	**4g**	47
11	60	**4c**	57			**5g**	36
		5c	29	16	60	**4h**	52
12	60	**4d**	92			**5h**	24
13	60	**4e**	72[d]				
		5e	18[d]				

a) Conditions argon, r t , 5 mol equiv of enolate with respect to azosulfide, [azosulfide] = 0 065 M The enolate was generated *in situ* from equimolar amounts of the relevant ketone and Bu^{t}OK prior to the addition of **1b** b) The reported time refers in all cases to completion of the reaction, as judged by the TLC disappearance of the azosulfide c) Yields of isolated products, unless otherwise specified d) ^{1}H NMR yields on the crude product mixture

acceptable α-phenylation is not precluded. According to the involvement, in the studied reactions, of an $S_{RN}1$ process (whose propagation cycle is exemplified by steps 1-4 of Scheme 3 for **2g** and **2h**) such reduction in the yield of the desired α-arylated product can be justified by the intervention of a side reaction of β-hydrogen abstraction from the α-branched enolates (step 3') by the same phenyl radical intermediate of the concurrent $S_{RN}1$ process.[7-13] This event leads to relatively stable radical anions (**6** $^{-\bullet}$ or **7** $^{-\bullet}$) and triggers an alternative propagation cycle (steps 1, 2, 3' and 4') completed by an electron transfer to **1a** (step 4') with formation of α,β-unsaturated ketones (**6** or **7**). This sequence finds definite support in the isolation of 2-methyl-1,5-diphenyl- **8** (10%) and 2-ethyl-3-methyl-1,5-diphenyl-1,5-pentanedione **9** (16%) respectively in experiments 7 and 8, readily rationalizable (Scheme 3) *via* a Michael addition of the corresponding enolate precursors to **6** and **7**.

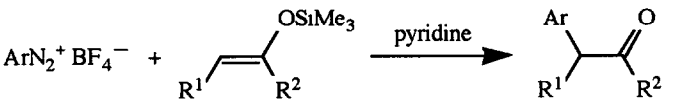
Scheme 3



Altogether the results herein allow two considerations of general character relevant to the employment of azosulfides **1** as convenient synthons of aryl cations. First of all, the successful α-phenylation of alkyl aryl ketones once more restates the advantages (mild conditions with no need for photostimulation) that, thanks to their particularly favourable reduction potentials, azosulfides may offer with respect to alternative possible reagents in $S_{RN}1$ arylations.[5b,6] Secondly, for a comparison with the use of the parent arenediazonium salts to the same target, the recent report[14] on the α-arylation of ketones of Scheme 4 should be mentioned, where an

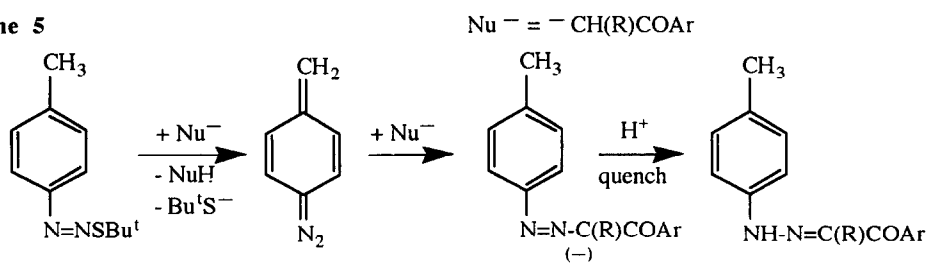
operatively less appealing isolation of the relevant trimethylsilyl enol ethers is necessary. It is worth stressing, moreover, that the latter method, at variance with that employing azosulfides as arylating agents,[4] does not appear[14] to be effective with enolates of dialkyl ketones.

Scheme 4



As far as the behaviour of the *p*-tolylazosulfide **1b** is concerned, its hydrazonylating capability (Table 2) has been already justified[4] on the grounds of a base-catalyzed *tert*-butanethiol elimination followed by nucleophilic attack of the enolate (Scheme 5). In agreement with such mechanism and as for the analogous reactions with acetone enolate (Scheme 1),[4] the essential role played by the position of the methyl group *para* to the electronwithdrawing azothio function is well evidenced by the not-tabulated result of the reaction of 3-methylphenylazo *tert*-butyl sulfide with the enolate **2a** where the $S_{RN}1$ arylation to 3-methylbenzyl phenyl ketone **10** is virtually quantitative (96%). Of course, the latter process, induced by the behaviour of the enolates as electron donors (*i.e.* chain initiators through the formation of the azosulfide radical anion) instead of as bases, is also operative in the reactions on **1b**, leading to variable amounts of α-*p*-tolylation of the ketone enolates. Consistently, the results collected in Table 2 show that the yields of **4** are more than satisfactory but for some cases (expt. 11, 15 and 16) where the α-arylation process proves to be particularly competitive. It must be remarked that, although the overall stoicheiometry of the hydrazonylation should require two equivalents of enolate, the employment of excess base (5 mol. equiv. with respect to **1b**) generally leads to somewhat better yields. On the other hand, the unreacted ketone can be most often easily recovered by fractional distillation of the crude residue (see Experimental) and in just one case (expt. 9) the use of two equivalents of base brought about a semplification of the procedure allowing to collect **4a** (85%) by filtration after acidic quenching. Finally, in the one case tested (enolate **2g**) the base to azosulfide molar ratio did not significantly affect the relative yields of **4** and **5** [49% and 28% (by ^{1}H NMR) respectively, with two equivalents of **2g**, as compared to expt. 15].

Scheme 5



Besides to the effectiveness of azosulfides in the α-arylation of ketone enolates, the α-arylhydrazonylation of the same nucleophiles (which can be selectively obtained in the presence of *para*-benzylic hydrogens in **1**) is, in turn, a non trivial result. This is because the classical azo-coupling with arenediazonium salts is sometimes complicated, in particular with methyl ketones,[15] by the difficulty of isolating the resulting hydrazonoketones,

which are readily transformed, in the reaction conditions, into formazanes *via* an overall bis-substitution process. Thus, although azo-coupling at tertiary positions can be somewhat more effectively achieved,[16] α-arylhydrazonylated ketones are generally synthesized through an azocoupling process exploiting the presence on the α-carbon of a second electronwithdrawing group (*e.g.* CHO, COMe) which is successively removed in the basic medium (Japp-Klingemann reaction).[15a,17,18] It is noteworthy that, to this end, *via* preliminary formylation of **2g** and **2h**, compounds **4g** and **4h** have been obtained in 68% and 62% overall yield respectively,[17b] with an obviously far more complex and time-comsuming procedure. It should be furthermore reminded that 2-oxohydrazones are not easily obtained by condensation of 1,2-diketones with hydrazine derivatives.[19]

Experimental

The ketones were commercial products used as received after storage over molecular sieves (4 Å). Petroleum ether and light petroleum refer to the fractions with bp 40-60 °C and 80-100 °C respectively.

Melting points were determined on a Büchi 535 apparatus and are uncorrected. Distillation of liquid samples was performed with a Kugelrohr apparatus, the quoted boiling points referring to the oven temperature. The ^{1}H NMR spectra were recorded with a Gemini 200 spectrometer; tetramethylsilane was used as internal standard and chemical shifts are reported as δ values (ppm).

The reaction products of Tables 1 and 2 were characterized by comparison of their physical constants with literature values, the ^{1}H NMR spectrum being in agreement with the proposed structure.

Reactions of Azosulfides with Potassium Ketone Enolates

The general procedure has been already described.[4] Usual work-up involved pouring of the reaction mixture into ice/3% HCl followed by extraction with ether, washing and drying (Na_2SO_4) of the combined extracts, and solvent evaporation under reduced pressure. Column chromatography on silica gel of the residue (eluants: petroleum ether and gradients with CH_2Cl_2) allowed separation of the reported products. It has been often possible to recover most of the excess starting ketone *via* fractional distillation (< 100 °C/1 mm Hg) of the residue prior to chromatography. In two instances (expt. 12 and 14) the hydrazonylated product precipitated after the acidic quenching and was most conveniently collected by filtration.

α-Arylation products

Benzyl phenyl ketone **3a**. mp 52.5-54.0 °C (MeOH) (lit.,[20] mp 55-56 °C).

Benzyl 2-methoxyphenyl ketone **3b**: bp 210 °C/1 mmHg (lit ,[21] bp 198-200 °C/0.05 mmHg); ^{1}H NMR ($CDCl_3$) δ 3.88 (3H, s), 4.29 (2H, s), 6 99 (2H, m), 7.24 (5H, m), 7.42 (1H, m), and 7.65 (1H, m).

Benzyl 3-methoxyphenyl ketone **3c**: bp 185 °C/5 mmHg (lit.,[22] bp 169-170 °C/13 mmHg); ^{1}H NMR ($CDCl_3$) δ 3.81 (3H, s), 4 25 (2H, s), 7.08 (1H, m), 7.30 (6H, m), 7.52 (1H, m), and 7 59 (1H, m).

Benzyl 4-methoxyphenyl ketone **3d**: mp 70.3-70.9 °C (light petroleum) (lit ,[23] mp 77 °C); ^{1}H NMR ($CDCl_3$) δ 3.86 (3H, s), 4 23 (2H, s), 6.93 and 8 00 (2H each, AA'BB', *J* 8.9 Hz), and 7 28 (5H, m).

Benzyl 2-thienyl ketone **3e**: mp 41.2-42.8 °C (EtOH) (lit.,[24] mp 50-51 °C), (Found· C, 71.1; H, 5 13. $C_{12}H_{10}OS$ requires. C, 71 3; H, 4 9%); ^{1}H NMR ($CDCl_3$) δ 4 19 (2H, s), 7 11 (1H, dd, *J* 3.8 and 4.9 Hz), 7.31 (5H, m), 7.63 (1H, dd, *J* 1 0 and 4.9 Hz), and 7.77 (1H, dd, *J* 1.0 and 3.8 Hz).

Benzyl 3-thienyl ketone **3f**: mp 90.5-92.0 °C (MeOH); (Found: C, 71.5, H, 4 8. $C_{12}H_{10}OS$ requires: C, 71.3, H, 4.9%); ^{1}H NMR ($CDCl_3$) δ 4 17 (2H, s), 7.29 (6H, m), 7 57 (1H, dd, *J* 1 3 and 5.1 Hz), and 8.09 (1H, dd, *J* 1.3 and 2 9 Hz).

Phenyl 1-phenylethyl ketone **3g**. mp 50 6-51 2 °C (EtOH) (lit.,[25] mp 50-52 °C).

Phenyl 1-phenylpropyl ketone **3h**: mp 53 0-54.0 °C (EtOH-H_2O) (lit.,[26] 57 °C).

3-Methoxyphenyl (4-methylphenyl)methyl ketone **5c** mp 74-75 °C (MeOH-H_2O); (Found· C, 77.9; H, 6 5. $C_{16}H_{16}O_2$ requires: C, 80.0; H, 6.7%); ^{1}H NMR ($CDCl_3$) δ 2 32 (3H, s), 3.84 (3H, s), 4 23 (2H, s), 7.13 (5H, m), 7.36 (1H, app t, *J* 7 9 Hz), 7.53 (1H, m), and 7.60 (1H, m).

2-Thienyl (4-methylphenyl)methyl ketone **5e**: mp 84.0-86.0 °C; (Found: C, 71.4; H, 4.8. $C_{13}H_{12}OS$ requires: C, 72.2; H, 5.5%); ^{1}H NMR ($CDCl_3$) δ 2.31 (3H, s), 4.14 (2H, s), 7.11 [3H in all, AA' of AA'BB' (*J* 8.1 Hz) and dd (*J* 3.8 and 4.9 Hz) partially overlapped], 7.20 (2H, BB' of AA'BB', *J* 8.1 Hz), 7.61 (1H, dd, *J* 1.1 and 4.9 Hz), and 7.75 (1H, dd, *J* 1.1 and 3.8 Hz).

Phenyl 1-(4-methylphenyl)ethyl ketone **5g**: mp 42.7-43.0 °C (petroleum ether) (lit.,[27] mp 43-44 °C).

Phenyl 1-(4-methylphenyl)propyl ketone **5h**: mp 46.0-47.8 °C (petroleum ether) (lit.,[28] mp 54-55 °C); ^{1}H NMR ($CDCl_3$) δ 0.90 (3H, t, *J* 7.4 Hz), 1.86 (1H, dm, *J* 13.7 Hz) 2.19 (1H, dm, *J* 13.7 Hz), 2.28 (3H, s), 4.41 (1H, t, *J* 7.2 Hz), 7.09 and 7.19 (2H each, AA'BB', *J* 8.2 Hz), 7.43 (3H, m), and 7.96 (2H, m).

3-Methylbenzyl phenyl ketone **10**: bp 165 °C/1 mmHg (lit.,[29] bp 140-147 °C/1.7 mmHg); ^{1}H NMR ($CDCl_3$) δ 2.32 (3H, s), 4.23 (2H, s), 7.07 (3H, m), 7.20 (1H, m), 7.48 (3H, m), and 8.01 (2H, m).

Side products

2-Methyl-1,5-diphenyl-1,5-pentanedione **8**: oil, ^{1}H NMR ($CDCl_3$) δ 1.26 (3H, d, *J* 7.0 Hz), 1.95 (1H, m), 2.30 (1H, m), 3.00 (2H, m), 3.67 (1H, m), 7.44 (6H, m) and 7.97 (4H, m); such spectrum is in full agreement with that reported.[30]

2-Ethyl-3-methyl-1,5-diphenyl-1,5-pentanedione **9**: oil; (Found: C, 81.7; H, 7.6. $C_{20}H_{22}O_2$ requires: C, 81.6; H, 7.55%); two diastereomeric mixtures (**A** and **B**) were separated by chromatography on silica gel column. **A**: ^{1}H NMR ($CDCl_3$) δ 0.83 (3H, t, *J* 7.3 Hz), 0.94 (3H, d, *J* 6.6 Hz), 1.60 (1H, m), 1.92 (1H, m), 2.74 (2H, m), 3.18 (1H, dd, *J* 5.1 and 15.8 Hz), 3.52 (1H, m), 7.50 (6H, m) and 8.01 (4H, m); **B**: ^{1}H NMR ($CDCl_3$) δ 0.89 (3H, t, *J* 7.3 Hz), 1.06 (3H, d, *J* 6.6 Hz), 1.61 (1H, m), 1 93 (1H, m), 2.67 (2H, m), 3.10 (1H, dd, *J* 3.5 and 15.9 Hz), 3.51 (1H, m), 7.47 (6H, m), 7.83 (2H, m) and 7.94 (2H, m).

α-Arylhydrazonylation products.

Phenyl [(4-methylphenyl)hydrazono]methyl ketone **4a**: mp 115.8-117.8 °C (EtOH-H_2O) (lit.,[31] mp 122-123 °C); ^{1}H NMR ($CDCl_3$) δ 2.34 (3H, s), 7.21 (4H, AA'BB', *J* 8.5 Hz), 7.51 (3H, m), 7.70 (1H, s), 7.99 (2H, m), and 14.55 (1H, br s).

2-Methoxyphenyl [(4-methylphenyl)hydrazono]methyl ketone **4b**: mp 89.8-90.9 °C (light petroleum); (Found: C, 71.6; H, 5.8; N, 10.4 $C_{16}H_{16}N_2O_2$ requires: C, 71 6; H, 6.0; N, 10.5%); ^{1}H NMR ($CDCl_3$) δ 2.32 (3H, s), 3.93 (3H, s), 7.03 (2H, m), 7.14 and 7.23 (2H each, AA'BB', *J* 8 7 Hz), 7.48 (1H, m), 7.69 and 7.72 (2H in all, m and s overlapped), and 14 40 (1H, br s).

3-Methoxyphenyl [(4-methylphenyl)hydrazono]methyl ketone **4c**. mp 77.8-78 9 °C (EtOH); (Found: C, 71.9; H, 6.1; N, 10.3. $C_{16}H_{16}N_2O_2$ requires· C, 71.6; H, 6.0; N, 10.5%); ^{1}H NMR ($CDCl_3$) δ 2.33 (3H, s), 3.88 (3H, s), 7.11 and 7 16 [3H in all, BB' of AA'BB' (*J* 8.7 Hz) and m partially overlapped], 7.24 (2H, AA' of AA'BB', *J* 8 7 Hz), 7.39 (1H, app t, *J* 7.8 Hz), 7 51 (1H, m), 7.57 (1H, m), 7 67 (1H, s), and 14.53 (1H, br s)

4-Methoxyphenyl [(4-methylphenyl)hydrazono]methyl ketone **4d**: mp 122.6-124.6 °C (EtOH); (Found: C, 71.5, H, 6.2; N, 10.3. $C_{16}H_{16}N_2O_2$ requires: C, 71.6; H, 6.0; N, 10.5%); ^{1}H NMR ($CDCl_3$) δ 2.33 (3H, s), 3.89 (3H, s), 6.98 and 7.99 (2H each, AA'BB', *J* 9.0 Hz), 7.19 (4H, m), 7 67 (1H, s), and 14.48 (1H, br s).

2-Thienyl [(4-methylphenyl)hydrazono]methyl ketone **4e**: mp 115.8-117.6 °C (light petroleum); (Found: C, 63.7; H, 4.9; N, 11.3. $C_{13}H_{12}N_2OS$ requires: C, 63.9; H, 4 9; N, 11.5%); ^{1}H NMR ($CDCl_3$) δ 2.32 (3H, s), 7.17 (5H, m), 7.54 (1H, s), 7.76 (1H, dd, *J* 1.1 and 4.9 Hz), 7.79 (1H, dd, *J* 1.1 and 3 8 Hz), and 14.22 (1H, br s).

3-Thienyl [(4-methylphenyl)hydrazono]methyl ketone **4f**: mp 138.3-139.1 °C (EtOH); (Found: C, 63.7; H, 4.8; N, 11.2. $C_{13}H_{12}N_2OS$ requires. C, 63.9; H, 4.9; N, 11.5%); ^{1}H NMR ($CDCl_3$) δ 2.33 (3H, s), 7.18 (4H, AA'BB', J 8.7 Hz), 7.37 (1H, dd, *J* 2 9 and 5 1 Hz), 7 53 (1H, s), 7 61 (1H, dd, *J* 1.3 and 5.1 Hz), 8 12 (1H, dd, *J* 1.3 and 2.9 Hz), and 14.36 (1H, br s).

Phenyl 1-[(4-methylphenyl)hydrazono]ethyl ketone **4g**: mp 155.3-156.7 °C (EtOH) (lit.,[17b] mp 154-155 °C).

Phenyl 1-[(4-methylphenyl)hydrazono]propyl ketone **4h**: mp 132.8-134.1 °C (MeOH) (lit.,[26] 141-142 °C); (Found: C, 74.1; H, 6.5; N, 9.5 $C_{17}H_{18}N_2O$ requires C, 76.7, H, 6.8; N, 10 5%), ^{1}H NMR ($CDCl_3$) δ

1.19 (3H, t, *J* 7.7 Hz), 2.29 (3H, s), 2.73 (2H, q, *J* 7.7 Hz), 6.98 and 7.09 (2H each, AA'BB', *J* 8.4 Hz), 7.48 (3H, s), 7.94 (2H, m), and 8.05 (1H, br s).

AcknowledgementThe financial support by MURST (Roma) is gratefully acknowledged.We thank Miss S. Ghirardo for her skilful contribution.

References and Notes

1. Novi, M.; Petrillo, G.; Dell'Erba, C. *Tetrahedron Lett.* **1987**, *28*, 1345. Petrillo, G.; Novi, M.; Garbarino, G.; Dell'Erba, C. *Tetrahedron* **1987**, *43*, 4625. Novi, M.; Garbarino, G.; Petrillo, G.; Dell'Erba, C. *Tetrahedron* **1990**, *46*, 2205.
2. Petrillo, G.; Novi, M.; Dell'Erba, C. *Tetrahedron Lett.* **1989**, *30*, 6911. Petrillo, G.; Novi, M.; Dell'Erba, C.; Tavani, C.; Berta, G. *Tetrahedron* **1990**, *46*, 7977. Petrillo, G.; Novi, M.; Dell'Erba, C.; Tavani, C. *Tetrahedron* **1991**, *47*, 9297.
3. Dell'Erba, C.; Novi, M.; Petrillo, G.; Tavani, C.; Bellandi, P. *Tetrahedron* **1991**, *47*, 333.
4. Dell'Erba, C.; Novi, M.; Petrillo, G.; Tavani, C. *Tetrahedron* **1992**, *48*, 325.
5. (a) See relevant literature cited in ref. 4. (b) Borosky, G.L.; Pierini, A.B.; Rossi, R.A. *J. Org. Chem.* **1992**, *57*, 247 and references therein.
6 (a) Norris, R.K. in *Comprehensive Organic Synthesis*, Semmelhack, M.F.; Ed., Pergamon Press: New York, 1991, vol. 4, pp. 463-466. (b) Rossi, R.A.; de Rossi, R.H. Aromatic Substitution by the SRN1 Mechanism, ACS Monograph 178, American Chemical Society: Washington, D.C., 1983.
7. Bunnett, J.F.; Sundberg, J.E. *Chem. Pharm. Bull.* **1975**, *23*, 2260.
8. Bunnett, J.F.; Sundberg, J.E. *J. Org. Chem.* **1976**, *41*, 1702.
9. Semmelhack, M.F.; Bargar, T.M. *J. Org. Chem.* **1977**, *42*, 1481.
10. Wolfe, J.F.; Moon, M.P.; Sleevi, M.C.; Bunnett, J.F.; Bard, R.R. *J. Org. Chem.* **1978**, *43*, 1019.
11. Semmelhack, M.F.; Bargar, T.M. *J. Am. Chem. Soc.* **1980**, *102*, 7765.
12. Beugelmans, R.; Bois-Choussy, M. *Synthesis* **1981**, 729.
13. Kornblum, N.; Cheng, S.I.; Kelly, W.J. *J. Org. Chem.* **1988**, *53*, 1830.
14. Sakakura, T.; Hara, M.; Tanaka, M. *J. Chem. Soc., Chem. Commun.* **1985**, 1545.
15. (a) Wulfman, D.S. in *The Chemistry of Diazonium and Diazo Groups*, Patai, S.; Ed., Wiley: New York, 1978, chapt. 8. (b) Parmerter, S.M. *Org. React.* **1959**, *10*, 1.
16. Garst, M.E.; Lukton, D. *Synth. Commun.* **1980**, *10*, 155.
17. (a) Phillips, R.R. *Org. React.* **1959**, *10*, 143. (b) Shvedov, V.I.; Alekseev, V.V.; Grinev, A.N. *Khim. Farm. Zh.* **1968**, *2*, 8 [*Chem. Abstr.* **1969**, *70*, 11469f].
18. The arylhydrazonylation of enol ethers *via* diazonium salts has also been reported: Seefelder, M.; Eilingsfeld, H. *Angew. Chem. Int. Ed. Engl.* **1963**, *2*, 484.
19. Attanasi, O.A.; Serra Zanetti, F. *Tetrahedron* **1992**, *48*, 2785 and references therein.
20. Allen, C.F.H.; Baer, W.E. *Org. Synth., Coll. Vol. II* **1943**, 156.
21. Farooq, M.O.; Rahman, W.; Ilyas, M.; Jehan, S. *Chem. Ber.* **1961**, *94*, 1996.
22. Cullen, D.L.; Black, P.S.; Meyer, E.F.; Ligthner, D.A.; Quistad, G.B.; Pak, C.S. *Tetrahedron* **1977**, *33*, 477.
23. Clerici, F.; Pocar, D.; Rozzi, A. *Tetrahedron* **1991**, *47*, 1937.
24. Jenkins, S.S. *J. Am. Chem. Soc.* **1932**, *54*, 1155.
25. McKenzie, A.; Roger, R. *J. Chem. Soc.* **1924**, *125*, 844.
26. Fiesselmann, H ; Ribka, J. *Chem. Ber.* **1956**, *89*, 27.
27. Curtin, D.Y.; Pollak, P.I. *J. Am. Chem. Soc.* **1951**, *73*, 992.
28. Roger, R.; Roberts, A.M. *J. Chem. Soc.* **1937**, 1753
29. Schwartz, L.H.; Landis, J.; Lazarus, S.B.; Stoldt, S.H. *J. Org. Chem.* **1972**, *37*, 1979.
30. Kiyooka, S.; Yamashita, T. *Chem. Lett.* **1987**, 1775.
31. Stierlin, R. *Chem. Ber.* **1888**, *21*, 2124.