Tetrahedron Vol 47, No 2, pp 333-342, 1991
Printed in Great Britain

0040-4020/91 $3 00+00
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ARYLATION OF POTASSIUM 2,4-PENTANEDIONATE VIA $S_{RN}1$ ON DIAZOSULFIDES

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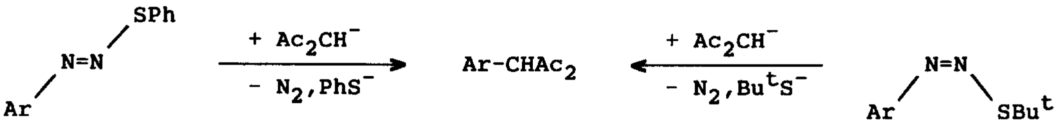
(*Received in UK* 18 *September* 1990)

Summary: Potassium 2,4-pentanedionate reacts with diazosulfides (E)-1 and (Z)-2 in DMSO to give 3-aryl-2,4-pentanediones 3 via an $S_{RN}1$ process. Advantages and drawbacks of such new access to 3 are reported together with relevant mechanistic implications.

The large number of investigations concerning the arylation of active methylene compounds mirror the importance that the relevant arylated products have as synthetic targets. Consistently, a survey of current arylation methods offers a wide panorama including: a) S_NAr or aryne substitutions respectively on activated[1] and unactivated[2] haloarenes; b) Pd-catalyzed substitutions on halobenzenes;[3] c) copper-catalyzed substitutions of the halogen of o-halogenoarenecarboxylic acids;[4] d) arylations employing either diaryliodonium salts[5,6] or organolead[7,8] and organobismuth[7,9] reagents; e) reactions via cyclopentadienyliron complexes of chloroarenes;[10] f) homolytic substitution of aromatic hydrocarbons induced by either Mn(III),[11] Ce(IV),[12] or anodic oxidation[13] of β-dicarbonyl compounds; g) free-radical chain arylation of 2,4-pentanedione by action of reducing metal salts on arenediazonium tetrafluoroborates;[14] h) $S_{RN}1$ reactions of enolates with haloarenes.[15-18] As regards their general applicability, however, each of the above methods appears to suffer from some practical disadvantages and/or limitations.

As an alternative to the existing methodology it was envisaged, on the basis of our previous studies,[19-23] that diazosulfides (Ar-N=N-SR), readily accessible from the corresponding arylamines, might serve as convenient substrates for the $S_{RN}1$ arylation of active methylene compounds. In this line, we report herein on the synthesis of some 3-aryl-2,4-pentanediones 3 by reaction of (E)-arylazo phenyl sulfides (E)-1 and (Z)-arylazo tert-butyl sulfides (Z)-2 with potassium 2,4-pentanedionate in DMSO.[24]



(E)-1a-c,g,k

3a-n

(Z)-2b-n

1-3	Ar	1-3	Ar
a	$4\text{-}NO_2C_6H_4$	h	$3\text{-}CNC_6H_4$
b	$4\text{-}CNC_6H_4$	i	$3\text{-}PhCOC_6H_4$
c	$4\text{-}PhCOC_6H_4$	j	$2\text{-}NO_2C_6H_4$
d	$4\text{-}MeCOC_6H_4$	k	$2\text{-}CNC_6H_4$
e	$4\text{-}BrC_6H_4$	l	C_6H_5
f	$4\text{-}MeOC_6H_4$	m	2-naphthyl
g	$3\text{-}NO_2C_6H_4$	n	3-pyridyl

Results and Discussion

The data reported in the Table show that the reaction of a tenfold excess of potassium 2,4-pentanedionate (generated _in situ_ by addition of the diketone to an equimolar amount of commercial potassium _tert_-butoxide) with diazosulfides (E)-1 and (Z)-2 in DMSO gives variable yields of the arylation products 3.

The formation of products 3 is believed[19-23] to occur via an $S_{RN}1$ process[30] involving an initial single-electron transfer [step (1)] from the pentanedionate anion to the substrate to form the corresponding radical anion ($1^{\bullet-}$ or $2^{\bullet-}$) which enters a typical $S_{RN}1$ propagation cycle [steps (2)-(4)]. It should be stressed that, though on the whole the RS-N=N- group behaves as leaving group, the most likely primary event of step (2) is the cleavage of the N-S bond to give a diazenyl radical precursor of the aryl radical.

$$\underset{(E)\text{-}1 \text{ or } (Z)\text{-}2}{\text{Ar-N=N-SR}} + Ac_2CH^- \rightleftharpoons 1^{\bullet-} \text{ (or } 2^{\bullet-}) + Ac_2CH^{\bullet} \qquad (1)$$

$$1^{\bullet-} \text{ (or } 2^{\bullet-}) \longrightarrow Ar^{\bullet} + N_2 + RS^- \qquad (2)$$

$$Ar^{\bullet} + Ac_2CH^- \longrightarrow \underset{3^{\bullet-}}{Ar\text{-}CHAc_2^{\bullet-}} \qquad (3)$$

$$3^{\bullet-} + \text{Ar-N=N-SR} \rightleftharpoons 3 + 1^{\bullet-} \text{ (or } 2^{\bullet-}) \qquad (4)$$

Table. Reactions of diazosulfides 1 and 2 with potassium 2,4-pentanedionate in DMSO [a]

Expt. no.	Diazosulfide	Conditions [b]	3a-n yield (%) [c,d]
1	(E)-1a	LL, 5 h	72
2	(E)-1b	LL, 0.5 h	60
3	(E)-1b	LL, 0.5 h [e]	46
4	(E)-1b	LL, 0.5 h [f]	39
5	(Z)-2b	I, 26 h	74 [g,d]
6	(Z)-2b	CPE, 0.43 F/mol	69 [h]
7	(E)-2b	CPE, 0.56 F/mol	73 [h]
8	(E)-1c	I, 1.5 h	48
9	(Z)-2c	I, 28 h	45 [i,d]
10	(Z)-2d	I, 27 h	64
11	(Z)-2e	I, 2.5 h	43 [j,d]
12	(Z)-2f	I, 15 h	9
13	(E)-1g	LL, 3.5 h + I, 1 h	71
14	(Z)-2g	I, 23 h	51 [k,d]
15	(Z)-2h	I, 5 h	84
16	(Z)-2i	I, 2.5 h	58 [l]
17	(Z)-2j	I, 3 h	74
18	(E)-1k	I, 0.75 h	67
19	(Z)-2k	I, 22 h	77
20	(Z)-2l	I, 6 h	7
21	(Z)-2m	I, 8 h	26
22	(Z)-2n	I, 17 h	60

[a] [Diazosulfide] = 0.065 M, $[Ac_2CH^-K^+]$ = 0.650 M, unless otherwise specified. [b] Experiments were carried out either at the laboratory light (LL), or under irradiation (I) by a sunlamp, or by constant potential electrolysis (CPE). [c] Yields refer to products isolated by column chromatography, unless differently stated. [d] In expts 5, 9, 11, 14, and 16 the unreacted substrate was found by ^{1}H NMR to be partially isomerized into the (E)-form. [e] $[Ac_2CH^-K^+]$ = 0.33 M. [f] $[Ac_2CH^-K^+]$ = 0.13 M. [g] 9% of unreacted substrate recovered. [h] Determined by ^{1}H NMR. [i] 25% of unreacted substrate recovered. [j] 23% of unreacted substrate recovered. [k] 21% of unreacted substrate recovered. [l] 12% of unreacted substrate recovered.

The results obtained show that while the reactions on diazosulfides (E)-1 are mostly spontaneous processes (although irradiation does increase the overall reaction rate), photostimulation by a sunlamp is needed to carry out experiments on diazosulfides (Z)-2. The differential reactivity of the two kinds of substrates is well evidenced when comparing expts 2 and 5 or, more closely, expts 8 and 9 which were carried out under similar (irradiation) conditions: the photo-induced reaction on (E)-1c goes to completion in 1.5 hr, while with (Z)-2c, after 28 hr 25% of unreacted substrate is recovered, which was partially isomerized into the more stable (E)-isomer.[31] In the light of the involvement of an $S_{RN}1$ mechanism, the lower reactivity of S-tert-butyl diazosulfides (Z)-2, which has been already observed in the reactions with aryloxides,[23] most likely is the result of a concomitance of factors: i) a more negative reduction potential of (Z)-2 with respect to the corresponding S-phenyl derivative (E)-1,[23] which negatively influences both the initiation step (1) and the propagation step (4); ii) a slower fragmentation of radical anions $2^{\bullet-}$ with respect to the corresponding $1^{\bullet-}$ in consequence of a presumable higher energy of the N-S bond. Actually, S-tert-butyl diazosulfides (Z)-2 generally show greater thermal stability than the corresponding (E)-1.[28,32] On a practical point of view, the greater stability of diazosulfides (Z)-2 represents an advantage because, in the first place, they are more easily purifiable e.g. by crystallization and/or chromatography and, in the second place, their use allows a better definition of the applicability range of the studied reactions without complications brought about by some instability of the substrate, which would affect the significance of the outcome.

Besides the above practical advantages, the fact that, at variance of the S-phenyl analogues, diazosulfides (Z)-2 do not react spontaneously with potassium 2,4-pentanedionate allows to attain further evidences for the mechanism of the studied reactions. In fact, besides the catalytic effect of light, the $S_{RN}1$ character of the system herein could be confirmed by electrochemical experiments carried out on both (Z)- and (E)-2b [this last kind of diazosulfide was studied because a more or less advanced (Z)-2 to (E)-2 isomerization was always observed in the course of the studied reactions]. The cyclovoltammetric analysis of the two substrates above showed a sharp decrease in the height of their irreversible reduction peak by addition of increasing amounts of potassium 2,4-pentanedionate. Such behaviour is indicative[33] of an electrocatalytic process well in agreement with the expectation of a chain process consecutive to the formation of the substrate radical anion at the cathode surface. On a more quantitative basis the results of preparative electrolyses (expts 6 and 7), carried out at the potential of the first reduction wave of the substrate on either (Z)-2b or (E)-2b and in the presence of a tenfold excess of potassium 2,4-pentanedionate, showed the formation of the arylation product 3b in yields comparable to those obtained (expt. 5) in the photostimulated reaction on (Z)-2b. This last outcome together with the values of 0.43 and 0.56 electrons per molecule, obtained by chronocoulometry of the same experiments, leaves little doubts about the intervention of a chain process in the system herein.

Further analysis of the data reported in the Table shows that, in agreement with previous results on the $S_{RN}1$ reactivity of the same diazosulfides with carbon nucleophiles[20,22,23] and of halobenzenes with monoanions of β-dicarbonyl compounds,[15,17,34-38] the yields of arylation products are satisfactory provided that an electronwithdrawing substituent is present in the Ar of (E)-1 and (Z)-2. Thus diazosulfides (Z)-2f and (Z)-2l gave only trace amounts of the corresponding α-arylated-β-dicarbonyl derivatives, whose yields slightly improve in the case of the 2-naphthyl derivative (Z)-2m and become again satisfactory with the 3-pyridyl analogue (Z)-2n. As a matter of fact, the initial use of enolates of β-dicarbonyl compounds in $S_{RN}1$ reactions was disappointing as the monoanions from malonic esters,[34-37] acetoacetic esters,[34,36,37] and β-diketones[34,36-38] all failed to react with phenyl radicals and even[34] with the more electrophilic 2-quinolyl radicals. Later on, the influence of either a cyano[15,17,18] or a benzoyl[17] group in the aryl moiety of haloarenes in facilitating $S_{RN}1$ reactions with monoanions of active methylene compounds has been evidenced; such favourable effect has been attributed[15] a) to a faster aryl radical/nucleophile coupling due to an increased electrophilicity of Ar• and b) to a more favoured electron-transfer from the radical anion of the substitution product to the substrate. In the system herein, as the propagation step (4) should be thermodinamically and kinetically favoured in all cases,[39] the meagre yield of arylation product observed with (Z)-2f, (Z)-2l, and (Z)-2m has to be attributed to the relatively lower electrophilicity of the aryl radicals involved in the relevant $S_{RN}1$ propagation cycles. Most likely, in such cases the key step (3) is so slow that competitive pathways for the aryl radicals can overcome the substitution-product-forming coupling with the nucleophile. In previous papers,[20-23] we have often underlined that in $S_{RN}1$ reactions on diazosulfides main competing paths for aryl radicals are: a) hydrogen atom transfer from the medium or electron transfer from whichever reducing species present (followed by protonation of the ensuing aryl anion) to give eventually the reduction product ArH; b) coupling with the thiolate anion formed by fragmentation of the diazosulfide radical anion [step (2)], which, in the present cases, would lead to formation of aryl phenyl (4) or tert-butyl sulfides (5) via competing $S_{RN}1$ propagation cycles. In all the experiments reported in the Table, reduction products ArH together with 5-30% of sulfides 4 or 5 were consistently detected (TLC and/or ^{1}H NMR) in the reaction mixtures. Accordingly, in order to limit, as far as possible, the intervention of undesired secondary paths, all the studied reactions were carried out using an excess of potassium 2,4-pentanedionate; expts. 2, 3, and 4 confirm that when the concentration of the nucleophile is decreased the yield of arylation product 3b drops to lower values.

Anyway, on a strictly synthetic point of view the overall procedure reported herein for the arylation of 2,4-pentanedione is an useful alternative to other methods[1-18] due to its simplicity, to the mild conditions required, and to the possibility of utilizing readily available arylamines as starting materials. On this regard, the method herein can be considered complementary to the already cited[14] arylation of 2,4-pentanedione by action of reducing metal salts on arenediazonium tetrafluoroborates. To our experience, in fact, starting from an arylamine, the isolation of the diazonium tetrafluoroborate salt or of the corresponding diazosulfide (E)-1 or (Z)-2 proceeds with comparable yields. Thus, any difference in the yields of 3 between the two methods is bounded to the successive arylation reactions, which proceed with different chain mechanisms. Comparison of the yields of 3a, 3d, 3i, and 3j obtained herein with those (38-45%) reported[14] for the same terms suggests that in the presence of electronwithdrawing substituents the synthetic approach to 3 via diazosulfides is preferable. On the contrary, for 3f and 3l, because of the different reaction chain mechanism involved in the metal-catalyzed arylation with arenediazonium tetrafluoroborates, the reported[14] yields of 32% for 3f and of 48% for 3l represent a substantial improvement with respect to the meagre yields of the method herein.

This study is being extended to the $S_{RN}1$ arylation of other active hydrogen compounds.

Experimental

M p s were taken on a Büchi 535 melting point apparatus and are uncorrected ^{1}H NMR spectra were recorded (Me_4Si as internal standard) on either of the following Varian instruments EM360A, FT 80, Gemini 200

New compounds (italicized) gave satisfactory elemental analyses

Materials Petroleum ether and benzine refer to the fractions with b p 30–50 °C and 80–100 °C, respectively Dimethyl sulfoxide (Fluka AG) was used as received after storage over molecular sieves (4Å) Potassium *tert*–butoxide (Aldrich, 97%) was used without further purification 2,4–Pentanedione (Aldrich) was distilled under reduced pressure and stored over molecular sieves (4Å)

Substrates Diazosulfides **(E)–1** and **(Z)–2**, synthesized[25] in more than 80% yield from commercially available arylamines, were isolated and purified as previously reported [23] Physical and spectroscopic data relevant to (E)–arylazo phenyl sulfides **1a**, **1b**, and **1g** as well as to (Z)–arylazo *tert*–butyl sulfides **2b**, **2c**, **2e**, **2f**, **2h**, **2i**, and **2l–2n** have been reported in a previous paper [23]

(E)–(4–Benzoylphenyl)azo phenyl sulfide **1c** m p 71 3–72 0 °C (petroleum ether), ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7 45–7 60 (5H, m), 7 60–7 76 (4H, m), 7 77–7 84 (2H, m), and 7 85–7 92 (2H, half part of AA′BB′, *J* 8 8 Hz)

(E)–(2–Cyanophenyl)azo phenyl sulfide **1k** m p 44 8–45 7 °C (petroleum ether), ^{1}H NMR (CD_3COCD_3, 80 MHz) δ 7 46–7 60 (5H, m), 7 66–7 79 (3H, m), and 7 86–7 97 (1H, m)

(Z)–(4–Acetylphenyl)azo tert–butyl sulfide **2d** m p 47 4–47 8 °C (petroleum ether); ^{1}H NMR ($CDCl_3$, 80 MHz) δ 1 60 (9H, s), 2 62 (3H, s), 7 10 and 8 07 (2H each, AA′BB′, *J* 8 6 Hz)

(Z)–(3–Nitrophenyl)azo tert–butyl sulfide **2g** m p 40 0–40 5 °C (petroleum ether), ^{1}H NMR ($CDCl_3$, 80 MHz) δ 1 62 (9H,s), 7 39 (1H, m), 7 68 (1H, app t), 7 94 (1H, app t), and 8 21 (1H, m)

(Z)–(2–Nitrophenyl)azo tert–butyl sulfide **2j** m p 57 7–58 3 °C (petroleum ether), ^{1}H NMR ($CDCl_3$, 80 MHz) δ 1 62 (9H, s), 6 97 (1H, dd, *J* 7 60 and 1 60 Hz), 7 35–7 85 (2H, m), and 8 22 (1H, dd, *J* 8 0 and 1 50 Hz)

(Z)–(2–Cyanophenyl)azo tert–butyl sulfide **2k** yellow oil, ^{1}H NMR ($CDCl_3$, 200 MHz) δ 1 63 (9H, s), 7 07–7,15 (1H, m), 7 38–7 54 (1H, m), and 7 63–7 82 (2H, m)

(E)–(4–Cyanophenyl)azo *tert*–butyl sulfide **2b** a pure sample was obtained by refluxing a CCl_4 solution of the (Z)–isomer The isomerization[40] was followed by ^{1}H NMR (60 MHz) on aliquots of the solution taken at different times After completion of the isomerization, the solution was concentrated under reduced pressure and chromatographed on a silica gel column[40] eluting first with petroleum ether and then with petroleum ether–dichloromethane mixtures of gradually increasing polarity Diazosulfide **(E)–2b** had m p 103 6–104 7 °C (MeOH) (lit ,[27] m p 104–106 °C)

No pure sample of other diazosulfides **(E)–2** was prepared, however, in most cases, it was possible to follow by ^{1}H NMR the (Z) to (E) isomerization, without appreciable decomposition, by recording spectra at variuos times of $CDCl_3$ solutions of the parent isolated (Z)–isomer stored in the NMR tubes at room temperature and in the dark ^{1}H NMR ($CDCl_3$, 80 MHz) data **(E)–2c**, δ 1 66 (9H, s) and 7 50–7 90 (9H, m), **(E)–2d**, δ 1 65 (9H, s), 2 62 (3H, s), 7 59 and 8 03 (2H each, AA′BB′, *J* 8 7 Hz), **(E)–2e**, δ 1 62 (9H, s) and 7 40–7 50 (4H, m), **(E)–2f**, δ 1 61 (9H, s), 3 82 (3H, s), 6 91 and 7 55 (2H each, AA′BB′, *J* 9 2 Hz), **(E)–2g**, δ 1 67 (9H, s), 7 63 (1H, app t), 7 91 (1H, m), 8 23 (1H, m), and 8 34 (1H, m), **(E)–2i**, δ 1 63 (9H, s) and 7 4–7 9 (9H, m), **(E)–2k**, δ 1 65 (9H, s), 7 38–7 54 (2H,m), 7 57–7 68 (1H, m), **(E)–2m**, δ 1 66 (9H, s), 7 27–7 72 (4H, m), 7 73–7 96 (2H, m), and 8 62–8 83 (1H m)

Reactions of Diazosulfides with Potassium 2,4–Pentanedionate The experiments were performed under argon by addition of a DMSO solution of substrate (2 mmol in 12 ml) to a magnetically stirred solution of potassium 2,4–pentanedionate, prepared *in situ* by dropping the β–diketone (20 mmol) into a cooled solution of potassium *tert*–butoxide (20 mmol) in 18 ml of DMSO When needed, irradiation was performed with a 300W Osram sunlamp placed ca

15 cm from the reaction flask (Pyrex), an appropriately positioned fan served to maintain the reaction temperature around 25 °C The end of reaction was judged by ceasing of nitrogen evolution and/or TLC analysis. Usual work-up involved pouring of the reaction mixture into ice/3% HCl followed by extraction with ether and washing of the combined extracts with brine In the case of the experiment on **(Z)-2n** the reaction mixture was diluted with water and the pH adjusted to neutrality with 3% HCl After drying of the ether extracts (Na_2SO_4) the solvent and the excess 2,4-pentanedione was distilled off in a rotary evaporator (60 °C, 5-10 mmHg) Column chromatography on silica gel of the residue (petroleum ether and petroleum ether-dichloromethane mixtures of gradually increasing polarity as eluant) gave pure 3-aryl-2,4-pentanediones **3** in variable yields (see Table)

3-Aryl-2,4-pentanediones **3** ^{1}H NMR analysis revealed that in $CDCl_3$ solution all the isolated compounds **3** exist only as enol tautomers [41]

3-(4-Nitrophenyl)-2,4-pentanedione **3a** m p 119 8-121 0 °C (EtOH) (lit ,[14] m p 119 °C)

3-(4-Cyanophenyl)-2,4-pentanedione **3b** m p 146 7-147 6 °C (benzine) (lit ,[15] m p 145-150 °C)

3-(4-Benzoylphenyl)-2,4-pentanedione **3c** m p 126 9-127 2 °C (benzine) (lit ,[17] m p 131 °C)

3-(4-Acetylphenyl)-2,4-pentanedione **3d** m p 97 4-98 1 °C (petroleum ether) (lit ,[14] 98 °C)

3-(4-Bromophenyl)-2,4-pentanedione **3e** m p 112 9-113 3 °C (petroleum ether), ^{1}H NMR, δ 1 89 (6H, s), 2 64 (3H, s), 7 31 and 8 00 (2H each, AA′BB′, *J* 8 2 Hz), and 16 71 (1H, s)

3-(4-Methoxyphenyl)-2,4-pentanedione **3f** m p 68 5-69 5 °C (petroleum ether) (lit ,[14] m p 70 °C)

3-(3-Nitrophenyl)-2,4-pentanedione **3g** m p 77 9-78 1 °C (benzine), ^{1}H NMR, δ 1 90 (6H, s), 7 53-7 65 (2H m), 8 05-8 32 (2H, m), and 16 76 (1H,s)

3-(3-Cyanophenyl)-2,4-pentanedione **3h** m p 108 0-109 3 °C (benzine) (lit ,[15] m p 108 °C)

3-(3-Benzoylphenyl)-2,4-pentanedione **3i** m p 90 3-90 8 °C (benzine) (lit ,[14] 104 °C), ^{1}H NMR, δ 1 92 (6H, s), 7 33-7 68 (6H, m), 7 68-7 90 (3H, m), and 16 70 (1H, s)

3-(2-Nitrophenyl)-2,4-pentanedione **3j** m p 68 1-69 1 °C (petroleum ether) (lit ,[14] m p 67 °C)

3-(2-Cyanophenyl)-2,4-pentanedione **3k** m p 92 8-94 0 °C (benzine) (lit ,[15] m p 92-94 °C)

3-Phenyl-2,4-pentanedione **3l** m p 55 0-56 0 °C (petroleum ether) (lit ,[14] m p 57 °C)

3-(2-Naphthyl)-2,4-pentanedione **3m** m p 88 9-89 9 °C (petroleum ether), ^{1}H NMR, δ 1 90 (6H, s), 7 20-7 95 (7H, m), and 16 73 (1H, s)

3-(3-Pyridyl)-2,4-pentanedione **3n** oil which easily solidifies on cooling in an ice-bath, ^{1}H NMR, δ 1 90 (6H, s), 7 30-7 60 (2H, m), 8 45-8 60 (2H, m), and 16 79 (1H, s)

Electrochemical determinations Cyclic voltammetry, constant potential electrolisis, and chronocoulometry were carried out using the same instrumentation and conditions described elsewhere [23]

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24 It is worth recalling that in the preparation of diazosulfides, by coupling of arenediazonium chlorides with thiols,[25,26] *the formation of (Z)–isomers is kinetically favoured* [27–29] *In the case of the S–phenyl derivatives*, however, the rate of (Z) to (E) isomerization is so high that it occurs almost completely during work–up of the reaction mixtures and only (E)–isomers are practically isolated [27–29] On the contrary, due to a much lower isomerization rate, S–*tert*–butyl diazosulfides can be obtained as pure (Z)–stereoisomers [27–29]

25 Sakla, A.B , Masoud, N K., Sawins, Z , Ebaid, W S *Helv Chim Acta* **1974**, *57*, 481

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31 Although stable as pure solids or oils, the (Z)-diazosulfides **2** slowly isomerize in solution to the more stable (E)-isomers [27-29]

32 van Zwet, H , Reiding, J , Kooyman, E C *Rec Trav Chim Pays-Bas* **1971**, *90*, 21

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39 As regards the propagation step (4′) of an $S_{RN}1$ cycle, the favourable effect of a phenylthioazo group (L = PhSNN-) on an otherwise thermodynamically disfavoured equilibrium (L = halogen) has been already evidenced in

$$\mathrm{ArNu}^{\cdot -} + \mathrm{ArL} \rightleftharpoons \mathrm{ArNu} + \mathrm{ArL}^{\cdot -} \qquad (4')$$

the reactions between diazosulfides (**E**)-**1** and cyanide ion [20] We confidently believe that the same favourable effect be in play also throughout the system herein for example, the peak reduction potential of **3b** (E_p -2 04 V, vs Ag/$AgNO_3$ 0 01 M in DMSO) was found, by cyclic voltammetry, to be more negative than that measured for (**Z**)-**2b** (E_p -1 45 V) in the same conditions

40 The (**E**)-**2** to (**Z**)-**2** isomerization is induced by light,[27-29] therefore to limit such possibility most operations were carried out in glassware wrapped in aluminium foil

41 Emsley, J , Freeman, N J , Bates, P A , Hursthouse, M B *J Chem Soc , Perkin Trans 1* **1988**, 297