Tetrahedron Vol. 46, No. 23, pp. 7977-7990, 1990
Printed in Great Britain

0040-4020/90 $3.00+.00
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$S_{RN}1$ C-ARYLATION OF POTASSIUM ARYLOXIDES BY ARYLAZO PHENYL OR *TERT*-BUTYL SULFIDES IN DMSO

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(*Received in UK* 1 *August* 1990)

Summary: Aryloxide ions ($Ar'O^-$) behave as C-nucleophiles towards diazosulfides (ArN=NSR; R = Ph, Bu^t) leading to unsymmetrical hydroxybiaryls (ArAr'OH) *via* C-C coupling. The reaction is particularly suited for the synthesis of terms which contain electron-withdrawing groups on the Ar moiety. The $S_{RN}1$ mechanism is proposed on the grounds of experimental evidences.

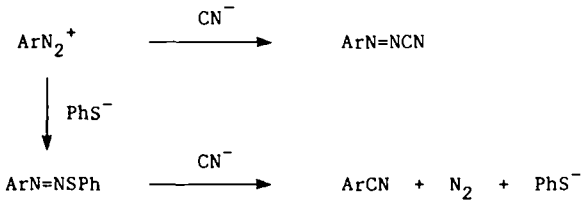
We have recently been concerned with new synthetic approaches from arenediazonium salts through their preliminary conversion into the covalent diazosulfides ArN=NSAr' (**1**) either generated *in situ*[1-3] or isolated.[3,4] The treatment of **1** with a number of nucleophiles under argon in DMSO triggers electron-transfer processes which involve an $S_{RN}1$ propagation cycle, eventually leading to the substitution products **2**:

$$\underset{\mathbf{1}}{ArN{=}NSAr'} + Nu^- \xrightarrow{DMSO} \underset{\mathbf{2}}{ArNu} + N_2 + Ar'S^-$$

The advantages of such reactions have been enlighted. Both sulfur ($Ar'S^-$)[1,3] and carbon (CN^-)[3,4] nucleophiles have been positively tested; in the latter case, the employment of S-phenyl diazosulfides (**1**, Ar' = Ph) prevents the formation of diazocyanides ArN=NCN, the classical azo-coupling process of diazonium salts[5] being thus replaced by a synthetically useful C-C coupling leading to aromatic nitriles (Scheme 1).

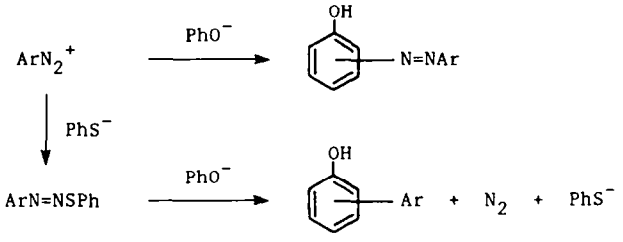
More recently we reported a preliminary account on the application of a similar strategy with nucleophiles such as aryloxide ions,[6] whose well-known coupling with diazonium salts invariably affords azo compounds *via* N-C bond formation (Scheme 2). Conversely, the treatment of DMSO solutions of S-phenyl diazosulfides (**1**, Ar' = Ph) with

Scheme 1



the same nucleophiles involves an effective arylation *via* C-C bond formation, eventually leading to hydroxybiaryls (Scheme 2).[6]

Scheme 2



ortho + *para* isomers

Herein, besides more extensive data relevant to the reaction between potassium aryloxides and S-phenyl diazosulfides, the application of the reaction to the analogous S-*tert*-butyl diazosulfides is reported, which enables to better define scope and limitations as well as to reach mechanistic conclusions.

Results and Discussion

Results are collected in Tables 1 and 2, where experiments are identified so as to attribute like numbers or letters to like Ar moieties or nucleophiles respectively. The use of potassium salts of aryloxides rather than the initially employed[6] tetrabutylammonium salts, besides easier isolation and handling has been essentially suggested by the practical advantage provided by the possibility of generating the nucleophile *in situ* from equimolar amounts of phenol and potassium *tert*-butoxide without appreciably affecting reaction times or yields. Accordingly, most experiments in the Tables conform to such methodology.

Synthetic aspects

From the available literature on the reactivity of diazosulfides, it is herein relevant to recall that, in acetone, a number of S-phenyl derivatives (**1**, Ar' = Ph) have

Table 1. Reactions between arylazo phenyl sulfides (ArN=NSPh) and potassium aryloxides ($Ar'O^-K^+$) in DMSO.[a,b]

Entry	Ar	Ar'	t	*ortho*-arylation	*para*-arylation
1a	$4\text{-}CNC_6H_4$	C_6H_5	60 min	49%[c]	23%[c]
1b	"	$4\text{-}MeC_6H_4$	90 min	64%	10%[d]
1b'	"	"[e]	3 h	40%	3%[d]
1c[f]	"	$2,6\text{-}Bu^t{}_2C_6H_3$[g]	4 h		58%
1d	"	2-naphthyl[g]	3 h	70%[h]	
1e	"	$4\text{-}NO_2C_6H_4$	24 h[i]	51%	
2b	$3\text{-}CNC_6H_4$	$4\text{-}MeC_6H_4$	45 min	65%	10%[d]
4b	$4\text{-}NO_2C_6H_4$	"	30 min	70%	10%[d]
5b	$3\text{-}NO_2C_6H_4$	"	50 min	70%	12%[d]
6b	$2\text{-}NO_2C_6H_4$	"	50 min	52%	

[a][ArN=NSPh] 0.07-0.09M; if not otherwise stated $Ar'O^-K^+$ (10 molar equivalents with respect to substrate) was generated *in situ* from equimolar amounts of Ar'OH and $Bu^tO^-K^+$. [b]Yields refer to products isolated by column chromatography, unless differently specified. ArSPh by-products were always isolated, generally within 15-25% yield. [c]Determined by HPLC. [d]4-Aryl-4-methyl-2,5-cyclohexadienone (**3**). [e]Two molar equivalents with respect to substrate. [f]Data from ref. 6. [g]The isolated potassium salt was employed. [h]1-(4-Cyanophenyl)-2-naphthol. [i]Under irradiation by a sunlamp.

been shown[7] to quantitatively couple with β-naphthol in the presence of H_2O, MeOH, or MeCOOH, to afford α-arylazo derivatives. The outcome was attributed to the formation of free diazonium cations, catalyzed by acids or anyway favoured by the polarity of the medium: accordingly, any reactivity was completely suppressed in neat acetone.[7]

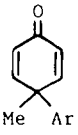
It is therefore noticeable that in the system herein the main reaction pathway is always represented by arylation at the ring-carbons of the nucleophile which are conjugated with the ionized hydroxylic function. According to our expectations azo-coupling derivatives are not observed but in trace amounts, occasionally formed most likely because of adventitious water in the medium: as a matter of fact, the addition of a 10% volume of water to the reaction mixture of run 1c of Table 1 drastically reduces the rate to furnish, after 18 h, only a 24% yield of *para*-arylated product together with a 40% yield of the azo-coupling derivative 4-[(4-cyanophenyl)azo]-2,6-di-*tert*-butylphenol.

Table 2. Photostimulated reactions between arylazo *tert*-butyl sulfides ($ArN{=}NSBu^t$) and potassium aryloxides ($Ar'O^-K^+$) in DMSO.[a,b]

Entry	Ar	Ar'	t	*ortho*-arylation	*para*-arylation
1a	$4\text{-}CNC_6H_4$	C_6H_5	40 min	42%[c]	20%[c]
1b	"	$4\text{-}MeC_6H_4$	45 min	63%	[d,e]
1b'	"	"[f]	40 min	69%	8%[e]
1c	"	$2,6\text{-}Bu^t{}_2C_6H_3$[f]	5 h		64%
1d	"	2-naphthyl	35 min	65%[g]	
1e	"	$4\text{-}NO_2C_6H_4$	80 h	35%[h]	
1f	"	$4\text{-}CF_3C_6H_4$	45 min	66%	
1g	"	$4\text{-}BrC_6H_4$	60 min	56%	
1h	"	$4\text{-}MeOC_6H_4$	2 h	76%	
2b	$3\text{-}CNC_6H_4$	$4\text{-}MeC_6H_4$	2 h	61%	10%[e]
7b	$4\text{-}PhCOC_6H_4$	"	2.5 h	54%	
8b	$3\text{-}PhCOC_6H_4$	"	3.5 h	53%	
9b	C_6H_5	"[f]	75 min	23%	
9h	"	$4\text{-}MeOC_6H_4$	90 min	49%	
10b	$4\text{-}MeOC_6H_4$	$4\text{-}MeC_6H_4$	24 h	21%	
11b	$4\text{-}BrC_6H_4$	"	3 h	33%	
12b	3-pyridyl	"	75 min	58%	
13b	2-naphthyl	"	2 h	28%	

[a] $[ArN{=}NSBu^t]$ 0.07M; if not otherwise stated $Ar'O^-K^+$ (10 molar equivalents with respect to substrate) was generated *in situ* from equimolar amounts of Ar'OH and $Bu^tO^-K^+$. [b] Yields refer to products isolated by column chromatography, unless differently specified. $ArSBu^t$ by-products were always isolated, generally within 10-25% yield. [c] Determined by HPLC. [d] Detected (TLC) but not quantified. [e] 4-Aryl-4-methyl-2,5-cyclohexadienone (**3**). [f] The isolated potassium salt was employed. [g] 1-(4-Cyanophenyl)-2-naphthol. [h] Partially isomerized[8] substrate (27%) also recovered.

Furthermore, a remarkable regioselectivity with respect to the aryloxide anion leaves no place whatsoever to the arylation of either *meta* carbons or of the oxygen of the ionized hydroxylic group (to eventually form diaryl ethers). More in detail, as to the competition between *ortho*- and *para*-arylation, an essentially statistical factor seems to play when both positions are originally unsubstituted (Table 1, entry 1a). Thus, the somewhat higher *ortho* to *para* ratio (46:14) reported in the previous communication[6] can possibly be ascribed to a differential counter-ion effect played by the tetrabutylammonium with respect to the potassium cation. Surprisingly enough, the competition between the two ring positions is not completely eluded when engaging the *para* position by means of methyl substitution, and cyclohexadienone derivatives **3**, although in low yields, are isolated with potassium *p*-chresolate (Table 1,



3

entries 1b,b', 2b, 4b, 5b, and Table 2, entries 1b,b' and 2b).

Yields of arylation products reported in Table 1 and relevant to reactions carried out on S-phenyl diazosulfides (**1**, Ar' = Ph) are always satisfactory; however, only terms containing strongly electron-withdrawing groups have been tested, as otherwise the decreasing substrate stability would have affected the significance of the outcome, independently of the intrinsic limitations of the reaction itself. In this respect S-*tert*-butyl diazosulfides (ArN=NSBu^t) are of much help, as they are generally more stable than the corresponding S-phenyl derivatives. Thus, although, at variance with the latter, their reactions require photostimulation, S-*tert*-butyl diazosulfides allow a better definition of the substrate applicability range to our reaction, and data in Table 2 also pertain to this aspect: it actually results that the absence of electron-withdrawing groups on the aromatic ring effectively hampers the arylation process (see entries 9b, 10b, 11b, and 13b) although yields rise again to more satisfactory figures when the basic strength of the aryloxide is increased (cf. entries 9b and 9h). The importance of the presence of an electron-poor aromatic ring in the substrate in positively affecting the yield of arylation products is further confirmed by the outcome relevant to the 3-pyridylazo sulfide (entry 12b).

On the other hand, satisfactorily enough, our system proves fairly versatile as far as the aryloxide is concerned (Table 2, entries 1a-h), although in the case of *para*-nitrophenoxide prolonged times still leave appreciable amounts of unreacted, partially isomerized,[8] substrate (entry 1e). It is noteworthy, at this regard, that the reaction of the same aryloxide with the corresponding (4-cyanophenyl)azo phenyl sulfide (Table 1,

entry 1e) only occurs under photostimulation, at variance with all other runs on S-phenyl diazosulfides.

Mechanistic aspects

On the grounds of the acquired knowledge on the behaviour of diazosulfides with either sulfur- or carbon-nucleophiles in DMSO,[1-4] the arylations herein represent likely candidates for the occurrence of the $S_{RN}1$ mechanism,[12] *i.e.* an electron-transfer chain process involving aryl radicals and radical anions whose incidence in synthesis has been boosted in the last few years. In particular, a number of recent reports show that aryloxide ions do act as carbon nucleophiles, within $S_{RN}1$ propagation cycles, towards aryl radicals generated from aromatic haloderivatives either photochemically[13,14] or electrochemically.[15] It is noteworthy that, very much like the results herein, *i*) no O-arylation to form diaryl ethers has been detected, well in line with the recognized unreactivity of oxygen nucleophiles in aromatic $S_{RN}1$ processes,[12] and *ii*) the yields of arylation products have been found particularly satisfactory in the presence of electron-withdrawing substituents on the haloarene.[16]

Besides the outlined synthetic advantages, the use of *tert*-butyl diazosulfides as substrates reveals to be particularly useful with respect to the possibility of applying electrochemical recognition tests for the $S_{RN}1$ mechanism[18] because, at variance with the S-phenyl derivatives, they do not react at appreciable rates by simply mixing with the nucleophile in the daylight at room temperature. Thus, a cyclovoltammetric analysis on *tert*-butyl (4-cyanophenyl)azo sulfide qualitatively evidences the onset of an electrocatalytic process by addition of increasing amounts of *p*-chresolate through the sharp decrease of the irreversible reduction wave of the substrate. On a more quantitative basis, an electrolysis of the same substrate at a controlled potential corresponding to its first reduction wave and in the presence of 22 equivalents of *p*-chresolate leads to a 59% yield of *ortho*-arylated product (together with traces of the relevant cyclohexadienone derivative **3**), in good agreement with the analogous photostimulated reaction (entry 1b of Table 2); a very low current consumption (0.16 F/mol) definitely indicates the occurrence of an efficient chain process.

Thus, as exemplified on the representative *p*-chresolate, the propagation steps depicted in Scheme 3 can be confidently proposed for the chain reaction herein, which is most likely triggered by an initial electron transfer from the aryloxide to substrate. The key chain-carrying step is the coupling of the aryl radical (deriving from the fragmentation of the substrate radical anion, possibly through a discrete diazenyl radical) with the effective nucleophilic site of the reactant, *i.e.* a conjugatively activated ring-carbon *ortho* or *para* with respect to the ionized hydroxy group. An electron transfer to substrate (step *c* or *c'*) from the so-formed radical anion (which could be envisaged as a ketyl) completes the propagation cycle, followed by rearomatization (when possible) of the resulting cyclohexadienone *via* deprotonation in the basic medium (step *d*).[19] The feasibility of step *c'* has been experimentally tested on the isolated

Scheme 3

R = Ph, Bu^t
Ar' = 4-MeC_6H_4

4-(4-cyanophenyl)-4-methyl-2,5-cyclohexadienone (**3**, Ar = 4-CNC_6H_4): an E_{pc} value of -2.04V (*vs.* $Ag/AgNO_3$ 0.01M in DMSO) seems to guarantee a fast electron transfer to the corresponding S-*tert*-butyl (E_{pc} = -1.45V) or S-phenyl (E_{pc} = -1.23V[4b]) diazosulfides, and confidently suggests an analogous favourable situation as far as step c is concerned. Both statistical and sterical factors most likely contribute to the meagre yields of cyclohexadienones **3** throughout.

Besides the electrochemical tests, support to the $S_{RN}1$ mechanism is provided by the detection, in all our experiments, of sulfides ArSR (R = Ph, Bu^t) as by-products. Their rationalization is rather straightforward when recalling that RS^- ions, herein generated by the fragmentation step a of Scheme 3, are efficient nucleophiles in $S_{RN}1$ processes, and can therefore successfully compete with the 'external' nucleophile for the aryl radical: the coupling eventually leads, through an alternative propagation cycle,[4b] to the sulfide. As expected, the competitivity of the sulfur nucleophile becomes less effective when increasing the aryloxide to substrate molar ratio (cf. entries 1b' and 1b of Table 1, where the amount of aryloxide was increased from 2 to 10 mol. equiv., which also yield 41% and 22% of sulfide respectively) and accordingly all the preparative runs herein have been carried out with a tenfold excess of nucleophile.

It is noteworthy that, although the occurrence of bis-substitution, commonly regarded as a conclusive test for the $S_{RN}1$ process,[12] has been already observed in reactions involving diazosulfides with both S-[1b,2,3] and C-nucleophiles,[3,4b] we were herein unable to detect appreciable amounts of products deriving from the concomitant replacement of both $-N{=}N-SBu^t$ and an additional $S_{RN}1$ leaving group such as a bromine atom on either the aryl moiety of the diazosulfide (entry 11b) or on the aryloxide (entry 1g); the occurrence of bis-substitution is obviously dependent on the nature of the radical anion of the primary substitution product and on the consequent competitivity of the fragmentation of the C-Br bond (eventually leading to bis-substitution) with respect to the electron transfer to substrate (step c of Scheme 3), the latter process being evidently more favoured herein.

It should finally be mentioned that overall reduction products (ArH) have been often detected and in some instances isolated in variable amounts, most likely originating from well-recognized[12] $S_{RN}1$ termination processes on aryl radicals such as H-atom abstraction from the medium or reduction to aryl anions followed by protonation.

Experimental

M.p.s were taken on a Büchi 535 melting point apparatus and are uncorrected. ^1H NMR spectra ($CDCl_3$ or CD_3COCD_3) were recorded on a Varian FT 80 (or a Varian GEMINI 200 when specified) instrument (Me_4Si as internal standard). IR spectra (neat or nujol mull) were recorded on a Perkin-Elmer 881 Infrared Spectrophotometer. HPLC was performed by means of a Hewlett-Packard HP 1090 instrument on a Supelcosil LC-18-DB (25 cm x 4.6 mm ID) reverse-phase column; gradient elution with H_2O/MeOH mixtures was employed.

New compounds (italicized) gave satisfactory elemental analyses, with a few specified exceptions for which analytical samples could not be obtained: however, spectral data were always in full agreement with the proposed structures.

For their characterization substrates or products are listed, within different classes, according to their molecular formula.

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. Phenols were all commercial samples used as received with the exception of *p*-chresol, which was distilled before use. Potassium phenoxides for runs 1c,d of Table 1 and 1b',c and 9b of Table 2 were prepared from equimolar amounts of potassium *tert*-butoxide and of the appropriate phenol in MeOH by reduced-pressure evaporation of the solvent followed by repeated washing of the salt with cyclohexane and finally with anhydrous Et_2O.

Substrates. - Both S-phenyl [as *(E)*-isomers[9,70]] and S-*tert*-butyl [as *(Z)*-isomers[8-11]] diazosulfides were prepared in higher than 80% yield from commercial-grade arylamines according to a reported procedure.[7] Crude products were obtained by either filtration and carefull washing with cold MeOH or by extraction into Et_2O. For their characterization diazosulfides were purified by flash-chromatography (silica gel; hexane or hexane-dichloromethane mixtures as eluant) and/or crystallization from an appropriate solvent in the cold; crude or at most chromatographed samples were used throughout for the arylation reactions, given their satisfactory degree of purity.

S-Phenyl diazosulfides (ArN=NSPh).

(E)-(2-Nitrophenyl)azo phenyl sulfide ($C_{12}H_9N_3O_2S$): m.p. 57-58°C (toluene/petroleum ether);[21] ^{1}H NMR ($CDCl_3$): δ 7.3-7.9 (m).

(E)-(3-Nitrophenyl)azo phenyl sulfide ($C_{12}H_9N_3O_2S$): m.p. 48.0-49.3°C (petroleum ether) (lit.:[7] 48°C).

(E)-(4-Nitrophenyl)azo phenyl sulfide ($C_{12}H_9N_3O_2S$): m.p. 95.2-96.8°C (benzine) (lit.:[22] 96-97°C).

(E)-(3-Cyanophenyl)azo phenyl sulfide ($C_{13}H_9N_3S$): m.p. 70-71°C; ^{1}H NMR (CD_3COCD_3): δ 7.5-8.0 (m); IR: 2223 cm^{-1} (CN).

(E)-(4-Cyanophenyl)azo phenyl sulfide ($C_{13}H_9N_3S$): m.p. 110.7-111.0°C; ^{1}H NMR (CD_3COCD_3): δ 7.3-7.8 (m).

S-*tert*-Butyl diazosulfides (ArN=NSBu^t).

(Z)-tert-Butyl 3-pyridylazo sulfide ($C_9H_{13}N_3S$): m.p. 22-23°C; ^{1}H NMR ($CDCl_3$, 200 MHz): δ 1.62 (9H, s), 7.41-7.43 (2H, m), 8.40-8.41 (1H, m), 8.58-8.62 (1H, m).

(Z)-(4-Bromophenyl)azo tert-butyl sulfide ($C_{10}H_{13}BrN_2S$): red oil; ^{1}H NMR ($CDCl_3$): δ 1.59 (9H, s), 6.97 and 7.57 (2H each, AA'BB', *J* 8.7 Hz); analytical sample not available.

(Z)-*tert*-Butyl phenylazo sulfide ($C_{10}H_{14}N_2S$): m.p. 48-49°C (MeOH) (lit.:[9] 48°C).

(Z)-tert-Butyl (3-cyanophenyl)azo sulfide ($C_{11}H_{13}N_3S$): yellow oil; ^{1}H NMR ($CDCl_3$): δ 1.61 (9H, s), 7.17-7.41 (2H, m), 7.56-7.64 (2H, m); IR 2223 cm^{-1} (CN).

(Z)-tert-Butyl (4-cyanophenyl)azo sulfide ($C_{11}H_{13}N_3S$): m.p. 69.1-70.1°C (petroleum ether); ^{1}H NMR ($CDCl_3$, 200 MHz): δ 1.61 (9H, s), 7.13 and 7.77 (2H each, AA'BB', *J* 8.7 Hz), in agreement with a reported spectrum;[11] IR: 2228 cm^{-1} (CN).

(Z)-tert-Butyl (4-methoxyphenyl)azo sulfide ($C_{11}H_{16}N_2OS$): yellow oil; ^{1}H NMR ($CDCl_3$): δ 1.59 (9H, s), 3.82 (3H, s), 6.95 and 7.25 (2H each, AA'BB', *J* 9.2 Hz); analytical sample not available.

(Z)-tert-Butyl 2-naphthylazo sulfide ($C_{14}H_{16}N_2S$): m.p. 54.6-55.2°C (petroleum ether); ^{1}H NMR ($CDCl_3$): δ 1.60 (9H, s), 7.26 (1H, dd, *J* 1.9 and 8.7 Hz), 7.41-7.55 (3H, m), 7.73-7.97 (3H, m).

(Z)-(3-Benzoylphenyl)azo tert-butyl sulfide ($C_{17}H_{18}N_2OS$): m.p. 74.1-74.5°C (petroleum ether); ^{1}H NMR ($CDCl_3$): δ 1.60 (9H, s), 7.3-7.9 (9H, m).

(Z)-(4-Benzoylphenyl)azo tert-butyl sulfide ($C_{17}H_{18}N_2OS$): m.p. 91.0-91.9°C (toluene/petroleum ether); ^{1}H NMR ($CDCl_3$): δ 1.62 (9H, s), 7.14 and 7.93 (2H each, AA'BB', *J* 8.5 Hz), 7.5-7.8 (5H, m); IR: 1662 cm^{-1} (CO).

Reactions of diazosulfides with aryloxides. - The experiments were carried out under argon, the apparatus being deaerated using five freeze-pump-thaw cycles. Reactions were started by dropping a DMSO solution of substrate into a double volume of a magnetically stirred solution of the nucleophile (prepared *in situ* from equimolar amounts of the appropriate phenol and potassium *tert*-butoxide, unless the isolated potassium aryloxide was used). The initial substrate concentration was 0.07—0.09M in the case of S-phenyl diazosulfides, 0.07M in the case of S-*tert*-butyl diazosulfides. Irradiation was performed with a 300W Osram sunlamp placed *ca.* 15 cm from the reaction vessel (Pyrex flask) and an appropriately positioned fan served to maintain the reaction temperature around 25°C. The end of reaction was judged by ceasing of gas evolution and/or TLC analysis. Usual workup involved dilution with 3-5% HCl (5-6 vol.) and 4-fold extraction with Et_2O, followed by washing of the combined extracts with brine. In the case of the reaction on the S-*tert*-butyl 3-pyridyl sulfide, after dilution with brine the pH of the aqueous layer was adjusted to neutrality. The organic layer was dried (Na_2SO_4) and the solvent removed under reduced pressure at room temperature. Column chromatography on silica gel (hexane, hexane-dichloromethane, or hexane-ethyl acetate mixtures as eluant) yielded pure products. For runs analyzed by HPLC the residue from solvent evaporation was dissolved in MeOH.

Hydroxybiaryls. Liquid terms were further confirmed by reaction with 1-naphthylisocyanate or 4-nitrobenzoyl chloride and characterization of the resulting urethane or 4-nitrobenzoate respectively.

4-Methyl-2-(3-pyridyl)phenol ($C_{12}H_{11}NO$): m.p. 122.5-123.5°C (toluene/petroleum ether); ^{1}H NMR ($CDCl_3$, 200 MHz): δ 2.32 (3H, s), 6.9-7.1 (3H, m), 7.3-7.4 (1H, m), 7.9-8.0 (1H, m), 8.5 (1H, m), 8.81 (1H, br. s);[23] IR: 3000 cm^{-1} (OH).

4-Bromo-2-(4-cyanophenyl)phenol ($C_{13}H_8BrNO$): m.p. 172.5-173.1°C (benzine); ^{1}H NMR ($CDCl_3$, 200 MHz): δ 5.23 (1H, br. s), 6.83-6.87 (1H, m), 7.36-7.40 (2H, m), 7.63 and 7.76 (2H each, AA'BB', *J* 8.9 Hz); IR: 2231 cm^{-1} (CN), 3364 cm^{-1} (OH).

2-(4-Cyanophenyl)-4-nitrophenol ($C_{13}H_8N_2O_3$): m.p. 258.8-259.6°C (toluene); ^{1}H NMR (CD_3COCD_3, 200 MHz): δ 7.25 (1H, d, *J* 8.9 Hz), 7.90 (4H, app. s), 8.2-8.3 (2H, m);[23] IR: 2228 cm^{-1} (CN), 3322 cm^{-1} (OH).

2-(4-Cyanophenyl)phenol ($C_{13}H_9NO$): m.p. 113.5-114.0°C (toluene); ^{1}H NMR (CD_3COCD_3): δ 6.9-7.4 (4H, m), 7.79 (4H, app. s), 8.67 (1H, br. s); IR: 2231 cm^{-1} (CN), 3365 cm^{-1} (OH).

4-(4-Cyanophenyl)phenol ($C_{13}H_9NO$): m.p. 198.5-199.0°C (toluene) (lit.:[24] 193-194°C); ^{1}H NMR (CD_3COCD_3): δ 6.97 and 7.61 (2H each, AA'BB', *J* 8.8 Hz), 7.79 (4H, app. s);[23] IR: 2228 cm^{-1} (CN), 3377 cm^{-1} (OH).

2-(4-Bromophenyl)-4-methylphenol ($C_{13}H_{11}BrO$): oil; ^{1}H NMR ($CDCl_3$): δ 2.30 (3H, s), 4.98 (1H, br. s), 6.8-7.0 (3H, m), 7.34 and 7.59 (2H each, AA'BB', *J* 8.6 Hz). The *urethane* from the reaction with 1-naphthylisocyanate had m.p. 187.3-188.1°C (EtOH); ^{1}H NMR ($CDCl_3$): δ 2.39 (3H, s), 7.2-7.9 (14H, m); IR: 1710 cm^{-1} (CO), 3251 cm^{-1} (NH).

4-Methyl-2-(2-nitrophenyl)phenol ($C_{13}H_{11}NO_3$): m.p. 132.1-133.3°C (benzine); ^{1}H NMR ($CDCl_3$): δ 2.32 (3H, s), 4.87 (1H, br. s), 6.7-8.0 (7H, m).

4-Methyl-2-(3-nitrophenyl)phenol ($C_{13}H_{11}NO_3$): m.p. 123.0-124.5°C (benzine); ^{1}H NMR ($CDCl_3$): δ 2.33 (3H, s), 4.93 (1H, br. s), 6.8-8.4 (7H, m); IR: 3503 cm^{-1} (OH).

4-Methyl-2-(4-nitrophenyl)phenol ($C_{13}H_{11}NO_3$): m.p. 117.5-119.0°C (benzine); ^{1}H NMR ($CDCl_3$): δ 2.33 (3H, s), 4.96 (1H, br. s), 6.9-7.1 (3H, m), 7.70 and 8.29 (2H each, AA'BB', *J* 8.9 Hz); IR: 3494 cm^{-1} (OH).

4-Methyl-2-phenylphenol ($C_{13}H_{12}O$): m.p. 65.6-67.0°C (petroleum ether) (lit.:[25] 67-68°C).

4-Methoxy-2-phenylphenol ($C_{13}H_{12}O_2$): oil; ^{1}H NMR ($CDCl_3$): δ 3.77 (3H, s), 4.97 (1H, br. s), 6.7-7.9 (3H, m), 7.44 (5H, m); IR: 3411 cm^{-1} (OH). The *urethane* from the reaction with 1-naphthylisocyanate had m.p. 132.0-132.8°C (toluene/petroleum ether); ^{1}H NMR ($CDCl_3$): δ 3.83 (3H, s), 6.9-7.9 (15H, m); IR: 1750 cm^{-1} (CO), 3419 cm^{-1} (NH).

2-(4-Cyanophenyl)-4-(trifluoromethyl)phenol ($C_{14}H_8F_3NO$): m.p. 148.5-150.0°C (benzine); ^{1}H NMR ($CDCl_3$): δ 5.70 (1H, br. s), 7.03 (1H, d, *J* 9.1 Hz), 7.5-7.7 (2H, m), 7.65 and 7.78 (2H each, AA'BB', *J* 8.6 Hz); IR: 2240 cm^{-1} (CN), 3306 cm^{-1} (OH).

2-(3-Cyanophenyl)-4-methylphenol ($C_{14}H_{11}NO$): m.p. 140.0-141.2°C (toluene/petroleum ether); ^{1}H NMR ($CDCl_3$): δ 2.32 (3H, s), 4.97 (1H, br. s), 6.8-7.8 (7H, m); IR: 2241 cm^{-1} (CN), 3357 cm^{-1} (OH).

2-(4-Cyanophenyl)-4-methylphenol ($C_{14}H_{11}NO$): m.p. 162-163°C (toluene); ^{1}H NMR (CD_3COCD_3): δ 2.28 (3H, s), 6.8-7.2 (3H, m), 7.79 (4H, app. s), 8.43 (1H, br. s); IR: 2235 cm^{-1} (CN), 3347 cm^{-1} (OH).

2-(4-Cyanophenyl)-4-methoxyphenol ($C_{14}H_{11}NO_2$): m.p. 158.8-159.4°C (toluene); ^{1}H NMR (CD_3COCD_3): δ 3.78 (3H, s), 6.88-6.92 (3H, m), 7.81 (4H, app. s), 8.28 (1H, s); IR: 2236 cm^{-1} (CN), 3430 cm^{-1} (OH).

2-(4-Methoxyphenyl)-4-methylphenol ($C_{14}H_{14}O_2$): oil; ^{1}H NMR ($CDCl_3$): δ 2.29 (3H, s), 3.83 (3H, s), 5.13 (1H, br. s), 6.8-7.4 (7H, m); IR: 3419 cm^{-1} (OH). The *urethane* from the reaction with 1-naphthylisocyanate had m.p. 122.0-123.8°C; ^{1}H NMR (CD_3COCD_3): δ 2.37 (3H, s), 3.82 (3H, s), 6.9-8.0 (14H, m); IR: 1711 cm^{-1} (CO), 3274 cm^{-1} (NH).

1-(4-Cyanophenyl)-2-naphthol ($C_{17}H_{11}NO$): m.p. 189.4-190.1°C (toluene/petroleum ether); ^{1}H NMR ($CDCl_3$, 200 MHz): δ 5.01 (1H, br. s), 7.2-7.4 (4H, m), 7.58 (2H, BB' of AA'BB', *J* 8.5 Hz), 7.8-7.9 (4H, m overlapped with AA' of AA'BB', *J* 8.5 Hz); IR: 2241 cm^{-1} (CN), 3379 cm^{-1} (OH).

4-Methyl-2-(2-naphthyl)phenol ($C_{17}H_{14}O$): b.p. 170°C/0.2mm Hg; ^{1}H NMR ($CDCl_3$): δ 2.34 (3H, s), 5.13 (1H, s), 7.0-7.2 (3H, m), 7.5-7.6 (3H, m), 7.8-8.0 (4H, m).

2-(3-Benzoylphenyl)-4-methylphenol ($C_{20}H_{16}O_2$): glassy oil; ^{1}H NMR ($CDCl_3$): δ 2.27 (3H, s), 5.98 (1H, br. s), 6.8-7.1 (3H, m), 7.5-8.0 (9H, m). The *ester* from the reaction with 4-nitrobenzoyl chloride had m.p. 107.1-107.8°C (benzine); ^{1}H NMR ($CDCl_3$): δ 2.42 (3H, s), 7.2-8.0 (12H, m), 8.18 (4H, app. s); IR ($CHCl_3$): 1658, 1741 cm^{-1} (CO).

2-(4-Benzoylphenyl)-4-methylphenol ($C_{20}H_{16}O_2$): m.p. 144.5-145.9°C (benzine); ^{1}H NMR ($CDCl_3$): δ 2.30 (3H, s), 6.8-7.1 (3H, m), 7.4-7.9 (9H, m);[23] IR: 1640 cm^{-1} (CO), 3405 cm^{-1} (OH).

4-(4-Cyanophenyl)-2,6-di-tert-butylphenol ($C_{21}H_{25}NO$): m.p. 155.8-156.8°C (benzine); ^{1}H NMR (CD_3COCD_3): δ 1.50 (18H, s), 6.33 (1H, s), 7.51 (2H, s), 7.80 (4H, s); IR: 2225 cm^{-1} (CN), 3628 cm^{-1} (OH).

Cyclohexadienones **3.**

4-Methyl-4-(3-nitrophenyl)-2,5-cyclohexadienone ($C_{13}H_{11}NO_3$): m.p. 95.6-96.7°C (benzine); ^{1}H NMR ($CDCl_3$): δ 1.77 (3H, s), 6.35 and 6.90 (2H each, AA'BB', *J* 10.0 Hz), 7.5-7.6 (2H, m), 8.1-8.2 (2H, m); IR: 1663 cm^{-1} (CO).

4-Methyl-4-(4-nitrophenyl)-2,5-cyclohexadienone ($C_{13}H_{11}NO_3$): m.p. 110.3-111.6°C (benzine); ^{1}H NMR ($CDCl_3$): δ 1.75 (3H, s), 6.34 and 6.89 (2H each, AA'BB', *J* 10.2 Hz), 7.49 and 8.21 (2H each, AA'BB', *J* 8.9 Hz); IR: 1664 cm^{-1} (CO).

4-(3-Cyanophenyl)-4-methyl-2,5-cyclohexadienone ($C_{14}H_{11}NO$): m.p. 136-140°C (benzine); ^{1}H NMR (CD_3COCD_3): δ 1.77 (3H, s), 6.25 and 7.11 (2H each, AA'BB', *J* 8.8 Hz), 7.7-7.8 (4H, m); IR: 1664 cm^{-1} (CO), 2230 cm^{-1} (CN); analytical sample not available.

4-(4-Cyanophenyl)-4-methyl-2,5-cyclohexadienone ($C_{14}H_{11}NO$): m.p. 185-187°C (toluene/petroleum ether); ^{1}H NMR (CD_3COCD_3): δ 1.76 (3H, s), 6.24 and 7.09 (2H each, AA'BB', *J* 10.2 Hz), 7.61 and 7.80 (2H each, AA'BB', *J* 8.8 Hz); IR: 1660 cm^{-1} (CO), 2229 cm^{-1} (CN).

Miscellaneous.

4-[(4-Cyanophenyl)azo]-2,6-di-tert-butylphenol ($C_{21}H_{25}N_3O$): m.p. 160.5-161.7°C (benzine); ^{1}H NMR ($CDCl_3$, 200 MHz): δ 1.51 (18H, s), 7.78 and 7.94 (2H each, AA'BB', *J* 8.8 Hz), 7.87 (2H, s); IR: 2220 cm^{-1} (CN), 3265 cm^{-1} (OH).

Aryl phenyl sulfides. 2-,[4b] 3-,[1b] 4-Nitrophenyl[1b] and 4-cyanophenyl[4b] phenyl sulfide were confirmed by comparison (undepressed mixed m.p.) with authentic samples. 3-Cyanophenyl phenyl sulfide was oxidized (H_2O_2/AcOH) and confirmed as sulfone[4b] by comparison (undepressed mixed m.p.) with an authentic sample.

Aryl *tert*-butyl sulfides. 3-Pyridyl,[26] 4-bromophenyl,[27] phenyl,[28] 4-methoxyphenyl,[29] and 2-naphthyl[30] *tert*-butyl sulfides were identified by comparison (^{1}H NMR and, for the last compound, mixed m. p.) with authentic samples from our laboratories.

tert-Butyl 3-cyanophenyl sulfide ($C_{11}H_{13}NS$) was oxidized (H_2O_2/AcOH) and characterized as *sulfone*: m.p. 123.7-125.0°C (benzine); ^{1}H NMR (CD_3COCD_3): δ 1.33 (9H, s), 7.9-8.2 (4H, m); IR: 1377 cm^{-1} (SO_2), 2232 cm^{-1} (CN).

tert-Butyl 4-cyanophenyl sulfide ($C_{11}H_{13}NS$): m.p. 56.3-56.9°C (petroleum ether); ^{1}H NMR ($CDCl_3$): δ 1.32 (9H, s), 7.61 (4H, app. s).

4-Benzoylphenyl tert-butyl sulfide ($C_{17}H_{18}OS$): m.p. 87.7-88.6°C (EtOH);[31] ^{1}H NMR ($CDCl_3$): δ 1.35 (9H, s), 7.50-7.60 (3H, m), 7.64 and 7.77 (2H each, AA'BB', *J* 8.6 Hz), 7.80-7.90 (2H, m).

Electrochemical determinations were conducted with an Amel Model 551 potentiostat equipped with the following Amel units: a Model 563 multipurpose unit, a Model 566 function generator, and a Model 863 x-y recorder. Experiments were carried out in DMSO/0.1M Bu_4NBF_4; working electrode: Pt-bead for CV, Pt-flag for CPE and chronocoulometry; reference electrode: Ag/$AgNO_3$ 0.01M in DMSO; sweep rate 100 mV/s.

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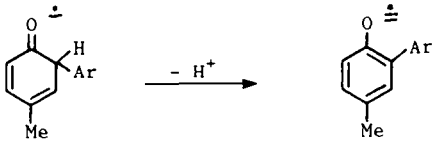

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