Pergamon

Tetrahedron 54 (1998) 6147–6158

TETRAHEDRON

# Reactions of Chloromethyl Aryl Sulfones Carbanions with Anthraquinone Derivatives

**Mieczysław Mąkosza,* Shamil Nizamov and Zofia Urbańczyk-Lipkowska**

Institute of Organic Chemistry, Polish Academy of Sciences, Kasprzaka 44/52, 01-224 Warsaw, Poland

Received 23 February 1998; revised 31 March 1998; accepted 2 April 1998

***Abstract:*** Carbanions of chloromethyl phenyl sulfone and chloromethyl *p*-tolyl sulfone react with anthraquinone containing electrondonating substituents in two major ways: vicarious nucleophilic substitution (VNS) of hydrogen and addition to the carbonyl group. The reaction course depends on electrondonating effects of these substituents - strong electron donors promote the VNS reaction.



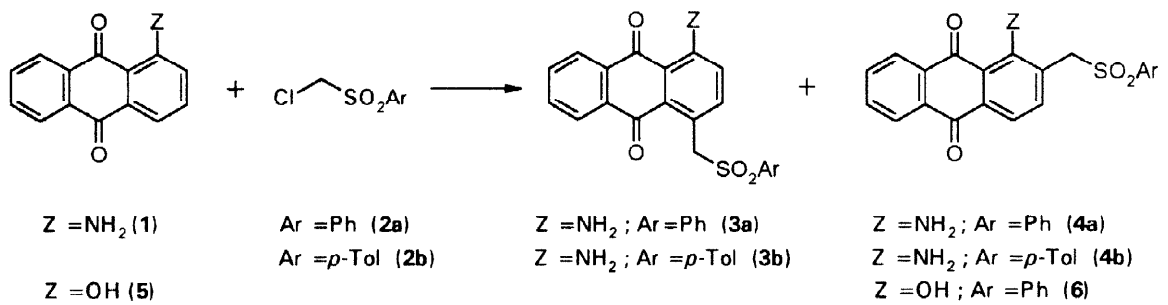
*Keywords*: anthraquinones, carbanions, *N*-oxides, vicarious nucleophilic substitution, X-ray crystal structure.

Vicarious nucleophilic substitution (VNS) of hydrogen is a general reaction between electrophilic arenes mainly nitroarenes and nucleophiles containing leaving groups at nucleophilic centres such as α-halocarbanions, alkylhydroperoxides, 4-amino-1,2,4-triazoles, sulfenamides etc[1-4]. In this process functionalized carbon substituents, hydroxy and aminogroups can be directly introduced into the aromatic ring. A variety of electrophilic arenes: carbo and heterocyclic nitroarenes, heterocycles being electrophilic due to their electronic structure such as 1,2,4-triazine or pteridine and also nonbenzonoid electrophilic arenes: tropilium cation, azulene etc undertake this reaction[5-9]. A similar process, although of limited scope can occur in electrophilic alkenes[10]. Due to the know electrophilic character of anthraquinone it appeared that the VNS reaction should occur with this arene. Thus simple synthesis of functionally substituted anthraquinones would be possible. There is one known reported example of the intermolecular VNS reaction in anthraquinone molecule – 5-hydroxyquinizarin was

0040-4020/98/$19.00 
*PII:* S0040-4020(98)00307-X

alkylated in position 2 with anion of 4-nitromethyl-5-methyl dihydro-2(3H)-furanone. In this process the nitro group acted as the leaving group[11]. An interesting example of intramolecular VNS reaction in the anthraquinone ring, a key step in the synthesis of aklavinone precursor was also reported. The reaction consisted of the Michael addition of $PhSCH_2CN$ to 1-hydroxy-8-methoxy-2-(1'-oxo-2'-pentenyl)anthraquinone followed with ring closure and β-elimination of PhSH[12-13].

Our first attempts at the VNS reaction of 9,10-anthraquinone and 1-chloro-9,10-anthraquinone with the carbanion of chloromethyl *p*-tolyl sulfone (**2b**) in DMSO in the presence of *t*-BuOK failed. On the other hand 1-amino-9,10-anthraquinone (**1**) which contains a strongly electrondonating substituent reacted with the carbanions of chloromethyl aryl sulfones **2a** and **2b** according to the VNS pathway giving two isomeric products of substitution of hydrogen in position 4 and 2 (Scheme 1) with yield 40 and 16% for **2a**, 23 and 8% for **2b** correspondingly.




Z =$NH_2$ (1)
Z =OH (5)

Ar =Ph (2a)
Ar =*p*-Tol (2b)

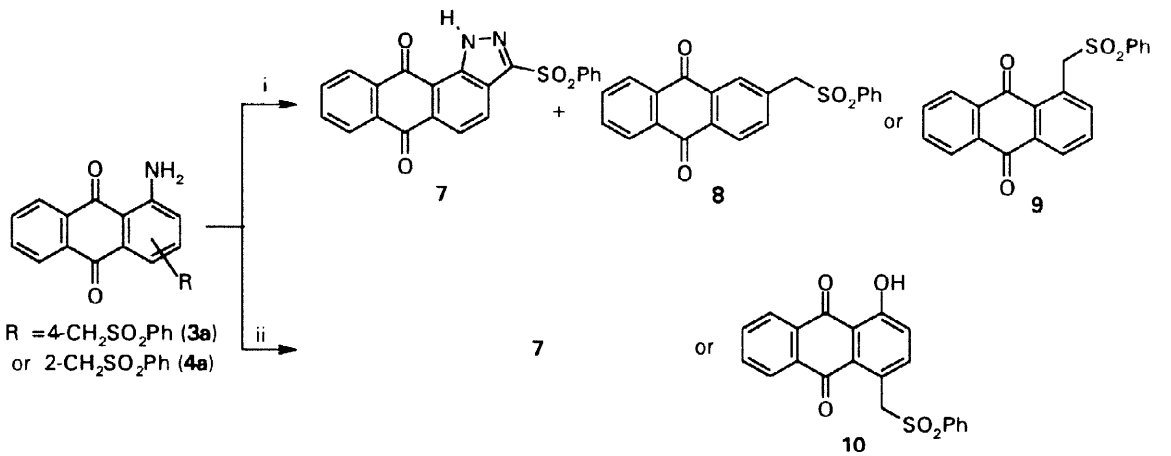
Z =$NH_2$ ; Ar=Ph (3a)
Z =$NH_2$ ; Ar =*p*-Tol (3b)

Z =$NH_2$ ; Ar =Ph (4a)
Z =$NH_2$ ; Ar =*p*-Tol (4b)
Z =OH ; Ar =Ph (6)

**Scheme 1**

The reaction with both of these sulfones **2a** and **2b** proceeded preferentially at position 4, ratio 2- : 4- substitution was 1:2,5 and 1:2,9 correspondingly. Also 1-hydroxy-9,10-anthraquinone (**5**) entered the VNS reaction with **2a** giving a single product of the VNS in position 2, yield 20% whereas 52% of the substrate was recovered. Since spectral analysis (NMR and IR) was insufficiently diagnostic to determine the site of the substitution in 1-amino-9,10-anthraquinone, structures of products **3a** and **4a** were unambiguously established by way of chemical transformations (Scheme 2).

Diazotation of the amino group in the minor product (**4a**) followed by reduction of the diazonium salt with phosphinic acid gave 2-phenylsulfonylmethyl-9,10-anthraquinone (**8**) in which the position of the substituent was established on the basis of $^1H$ NMR, namely coupling constants 1H-3H(1,9Hz), 1H-4H(0,5Hz) and 3H-4H(8,0Hz). Moreover during the diazotation-reduction process partial cyclization of the diazonium salt, resulting in the formation of the anthraquinono pyrazole derivative (**7**) took place.




Reagents: (i) 1. $H_2SO_4$, $NaNO_2/H_2O$; 2. $H_3PO_2$ (ii) 1. $H_2SO_4$, $NaNO_2/H_2O$; 2. $H_2O$

## Scheme 2

The cyclization was the only reaction giving **7** in yield 97%, when the diazonium salt was not treated with the reducing agent. The formation of the anthraquinono pyrazole derivative confirms location of the sulfonylmethyl substituent *ortho* to the amino group. Since **4a** was identified as the VNS product in position 2, **3a** should contain the substituent in position 4.

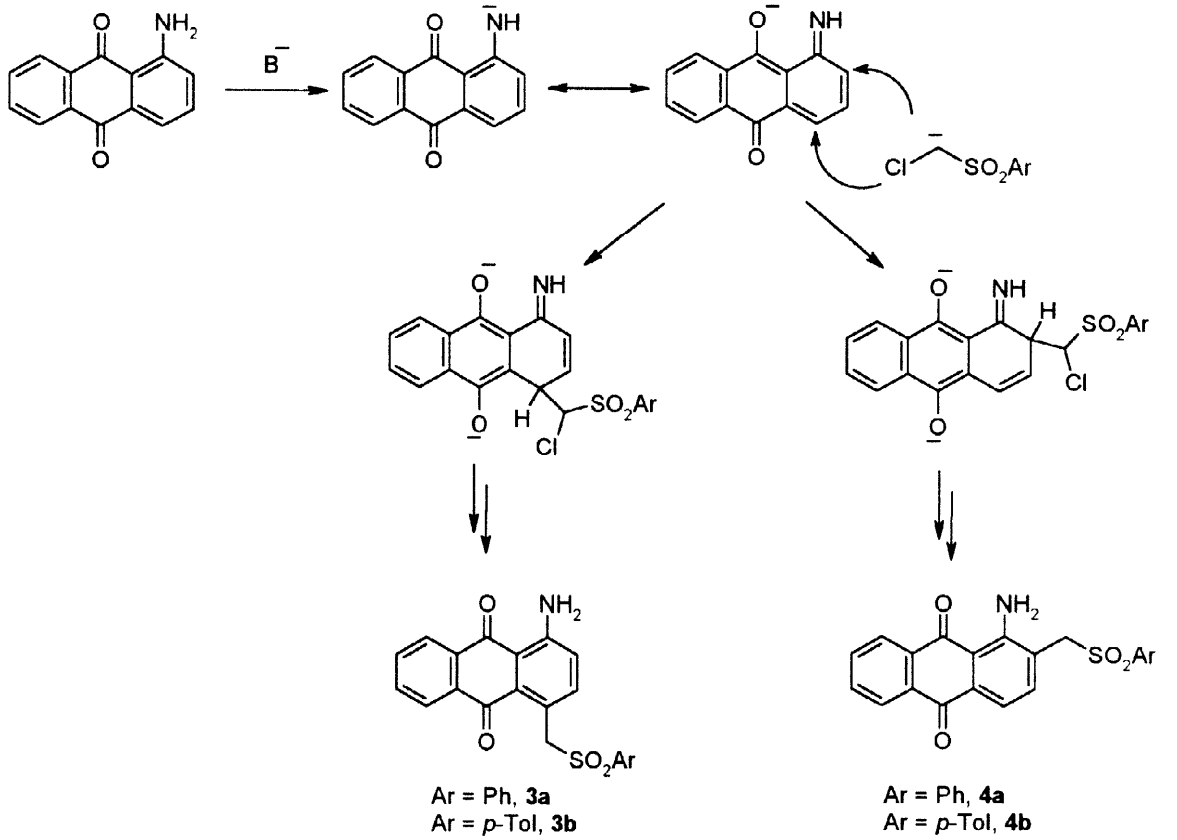
The VNS product in 1-hydroxy-9,10-anthraquinone was identified in a similar way. Diazotation of **3a** followed by hydrolysis resulted in the formation of 1-hydroxy-4-phenylsulfonylmethyl-9,10-anthraquinone (**10**). This product was not identical to the product of VNS in 1-hydroxy-9,10-anthraquinone (**6**) hence the latter should contain phenylsulfonylmethyl substituent in position 2. Moreover in $^1H$ NMR spectrum of **6** $^1H,^1H$ coupling constants of aromatic region were very similar to that of **4a** and **4b** (Table1).

**Table 1.** $^1H,^1H$ (*ortho*) coupling constants (Hz) of 2H,3H,4H aromatic protons for disubstituted anthraquinones.

| | 3a | 3b | 4a | 4b | 6 | 10 |
|---|---|---|---|---|---|---|
| 2H-3H | 8,7 | 8,7 | -- | -- | -- | 8,8 |
| 3H-4H | -- | -- | 7,7 | 7,7 | 7,7 | -- |

Thus the intermolecular VNS reaction in the anthraquinone containing strongly electrondonating substituents does occur. Apparently conjugation of these substituents with one of the carbonyl groups as shown in Scheme 3 using resonance structures -

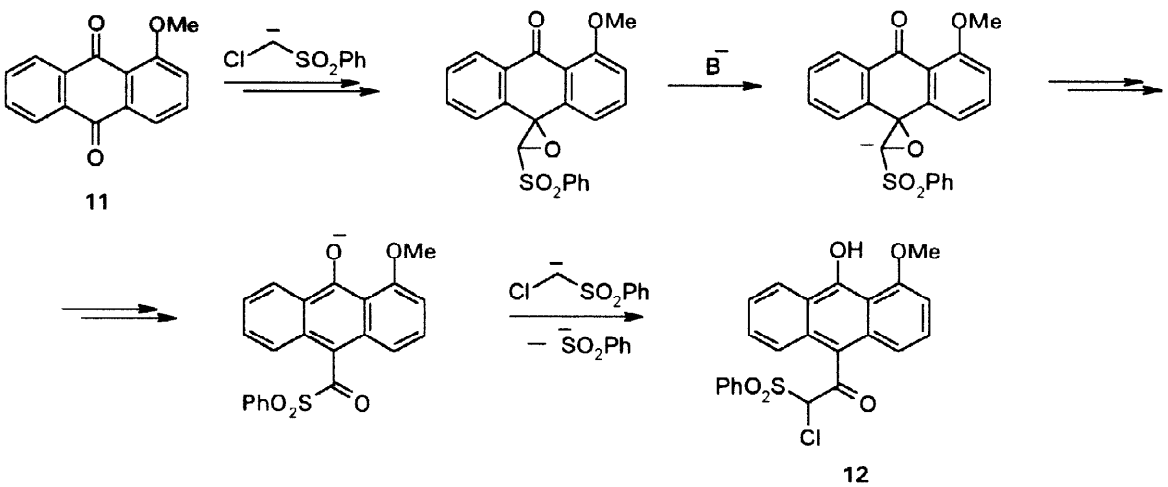
destroys the aromatic character of the ring thus rendering it more sensitive to nucleophilic attack. Such peculiar phenomena that electrondonating substituents can activate electrophilic aromatic ring towards nucleophilic attack were reported for other systems[14].




**Scheme 3**

The reaction of 1-methoxy-9,10-anthraquinone with chloromethyl phenyl sulfone carbanion proceeds *via* a different pathway - addition to the carbonyl group. When this reaction was carried out in the presence of KOH in DMSO a complicated mixture of products was formed which were not separated and identified. On the other hand when an equimolar mixture of the reactants in DMSO was treated with *t*-BuOK, hydroxyantracene derivative (**12**) was isolated in yield of 17%. Since the molecular formula indicated stoichiometry 1:2, the reaction was carried out using two-fold excess of the sulfone giving **12** in 61% yield. The structure of compound **12** was elucidated on the basis of NMR, mass spectra and X-ray analysis. Its $^{1}H$ NMR spectrum contains signals of 12 protons in the aromatic region, moreover one signal of the phenolic proton at 10,9 ppm was also present. In the $^{13}C$ NMR spectrum only one signal of carbon atom

of carbonyl group (191,0 ppm) was observed. The structure of **12** was definitely established by X-ray crystallography as is shown in Figure 1. Formation of **12** can be rationalised by speculative mechanistic pathway as shown in Scheme 4.




**Scheme 4**

The difference in the reaction course between the carbanion of **2a** and 1-OMe and 1-OH anthraquinones is apparently due to much less efficient conjugation of MeO than $O^-$ substituents with the quinone moiety. In the latter case the aromatic character of the ring is lost so it is more susceptible to nucleophilic addition whereas the reaction of carbanion with 1-methoxy-9,10-anthraquinone proceeds at the carbonyl group. Some examples of nucleophilic addition of carbanions to the carbonyl group of anthraquinone are reported[15,16,20].

Attempts at the reaction of chloromethyl phenyl sulfone carbanion with 1- and 2-*N,N*-dimethylamino-9,10-anthraquinone resulted in formation of complicated mixtures of products which were not separated nor the isolated products identified. During these processes we have observed additional formation of adducts of DMSO carbanion to 2-*N,N*-dimethylamino-9,10-anthraquinone.

Interestingly, adduct of DMSO carbanion addition to the carbonyl group of 2-*N,N*-dimethylamino-9,10-anthraquinone (**14**) was obtained in good yield (85%), when KOH was added to a solution of **13** in DMSO. The product was formed as a mixture of diastereoisomers which was oxidized to the single product - sulfone containing *N,N*-dimethylaminooxide substituent (Scheme 5). Introduction of two oxygen atoms was established by elemental analysis. The structure of **15** co-crystallized with one molecule of MeOH was established by X-ray crystallography (see Figure 2). Both geometry and involvement of the O5 atom as an acceptor in the two strong hydrogen bonds indicate

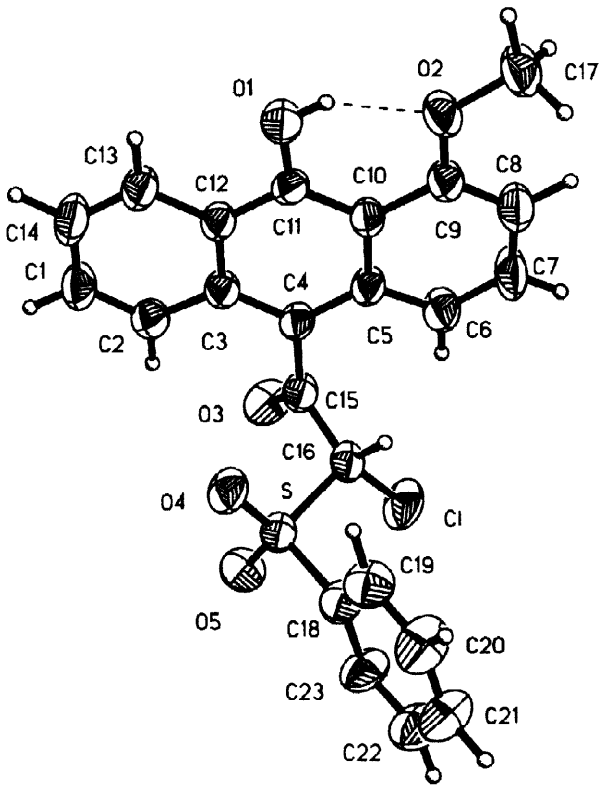



**Figure 1**. ORTEP diagram of the molecule of compound **12** with an intramolecular hydrogen bond. Thermal ellipsoids shown at 50 % probability level.

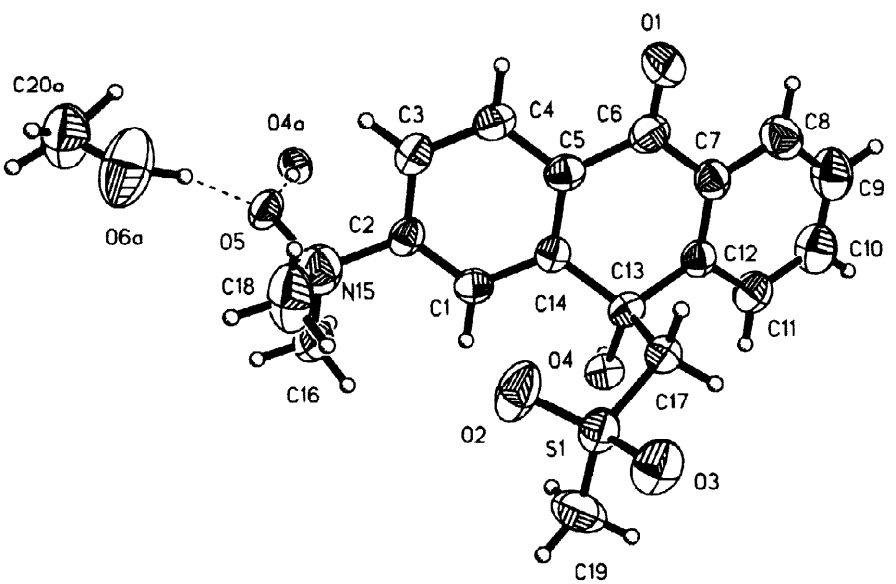
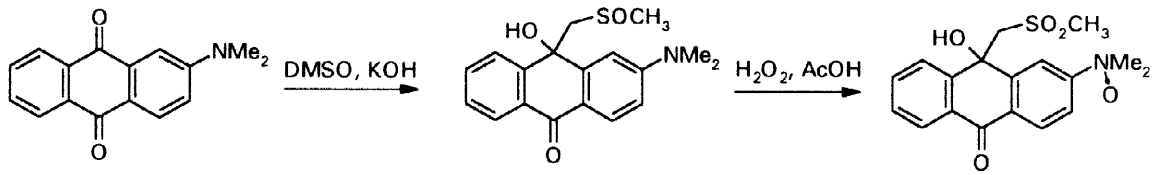



**Figure 2**. ORTEP diagram of the molecule of compound **15** with O5 atom involved in two intermolecular hydrogen bonds. Thermal ellipsoids shown at 50 % probability level.

that **15** is in fact N-oxide. Its spectral characteristics are consistent with this structure. Addition of DMSO carbanion to the carbonyl group of some ketones were described in the literature[17-19]. Moreover, a similar example of the addition of the DMSO carbanion to 1-*N,N*-dimethylamino-9,10-anthraquinone was reported recently[20].




13 14 15

**Scheme 5**

## EXPERIMENTAL SECTION

All melting points are uncorrected. $^{1}H$ and $^{13}C$ NMR spectra were obtained on a Varian Gemini (200 MHz) or Bruker AMX (500 MHz) instruments; chemical shifts are reported in ppm downfield from TMS as internal standard; coupling constants *J* are given in Hertz. Infrared (IR) absorption spectra were recorded on Acculab 1 Beckman spectrometer in KBr disks. Mass spectra were recorded on AMD 604 Interctra spectrometer. All reactions were carried out under argon atmosphere unless otherwise noted in glassware that was oven-dried. Silica gel Merck 60 (230-400 mesh ASTM) was used for column chromotography. The following starting materials were prepared according to the published procedures: chloromethyl phenyl (and *p*-tolyl) sulfone (**2a** and **2b**)[21], 1-hydroxy-9,10-anthraquinone (**5**)[22], 1-methoxy-9,10-anthraquinone (**11**)[23]. 2-*N,N*-dimethylamino-9,10-anthraquinone (**13**) was prepared from 2-amino-9,10-anthraquinone *via* the Leuckart reaction at 120 °C, yield 71%[24], m.p. 185-186 °C (ref[25]: m.p. 188-189 °C). Other reagents were commercially available.

**General procedure for the reaction of chloromethyl aryl sulfones with 1-amino-9,10-anthraquinone.** To a stirred solution of potassium *tert*-butoxide (392 mg, 3,5 mmol) and 1-amino-9,10-anthraquinone (223 mg, 1 mmol) in DMSO (8 mL) a solution of sulfone **2a** or **2b** (1 mmol) in DMSO (2 mL) was added dropwise at 18-20 °C during 3-4 min. The reaction mixture was stirred for 1 hour, poured into 5% aq HCl (200 mL) and the solid product was filtered. After separation by column chromotography (methylene chloride/hexane - 2:1 to 10:1 eluent) products **3a** and **4a** or **3b** and **4b** were obtained.

**1-Amino-4-phenylsulfonylmethyl-9,10-anthraquinone (3a).** Recrystallized from ethyl acetate/methylene chloride, dark red solid (yield 149 mg, 40%), m.p. 248-251 °C. $^1$H NMR (200 MHz, $CDCl_3$) δ: 8.21-8.14(m, 1H), 7.94-7.87(m, 1H), 7.77-7.60(m, 4H), 7.44(d, 1H, *J*=8.7), 7.40-7.27(m, 3H), 6.96(d, 1H, *J*=8.7), 5.29(s, 2H); IR $\nu_{max}$: 3449, 3332, 1663, 1642, 1618, 1305, 1148 cm$^{-1}$. Anal. calcd for $C_{21}H_{15}NSO_4$: C 66.83, H 4.01, N 3.71, S 8.50. Found: C 66.75, H 3.82, N 3.86, S 8.54.

**1-Amino-2-phenylsulfonylmethyl-9,10-anthraquinone (4a).** Recrystallized from ethyl acetate/chloroform, orange solid (yield 59 mg, 16%) m.p. 292-295 °C(dec.). $^1$H NMR (200 MHz, $CDCl_3$) δ: 8.37-8.22(m, 2H), 7.88-7.51(m, 7H), 7.49(d, 1H, *J*=7.7), 6.94(d, 1H, *J*=7.7), 4,47(s, 2H); IR $\nu_{max}$: 3458, 3452, 3295, 1661, 1560, 1304, 1291, 1149 cm$^{-1}$. Anal. calcd for $C_{21}H_{15}NSO_4$: C 66.83, H 4.01, N 3.71, S 8.50. Found: C 66.75, H 3.71, N 3.86, S 8.53.

**1-Amino-4-(*p*-tolylsulfonylmethyl)-9,10-anthraquinone (3b).** Recrystallized from EtOH, purple crystals (yield 89 mg, 23%), m.p. 206-208 °C. $^1$H NMR (200 MHz, $CDCl_3$) δ: 8.19-8.13(m, 1H), 7.88-7.81(m, 1H), 7.76-7.60(m, 2H), 7.56-7.48(m, 2H), 7.44(d, 1H, *J*=8.7), 7.12-7.02(m, 2H), 6.95(d, 1H, *J*=8.7), 5.26(s, 2H), 2.14(s, 3H); IR $\nu_{max}$: 3450, 3328, 1641, 1612, 1298, 1272, 1150 cm$^{-1}$. Anal. calcd for $C_{22}H_{17}NSO_4$: C 67.50, H 4.38, N 3.58, S 8.19. Found: C 67.51, H 4.46, N 3.46, S 8.14.

**1-Amino-2-(*p*-tolylsulfonylmethyl)-9,10-anthraquinone (4b).** Recrystallized from EtOH, orange solid (yield 30 mg, 8%), m.p. 252-254 °C. $^1$H NMR (200 MHz, $CDCl_3$) δ: 8.37-8.20(m, 2H), 7.86-7.62(m, 4H), 7.47(d, 1H, *J*=7.7), 7.36-7. 26(m, 2H), 6.92(d, 1H, *J*=7.7), 4.44(s, 2H), 2.45(s, 3H); IR $\nu_{max}$: 3454, 3452, 1660, 1615, 1303, 1282, 1146 cm$^{-1}$. Anal. calcd for $C_{22}H_{17}NSO_4$: C 67.50, H 4.38, N 3.58, S 8.19. Found: C 67.53, H 4.10, N 3.40, S 8.24.

**1-Hydroxy-2-phenylsulfonylmethyl-9,10-anthraquinone (6).** A solution of 1-hydroxy-9,10-anthraquinone (224 mg, 1 mmol) and chloromethyl phenyl sulfone (191 mg, 1 mmol) in DMSO (15 mL) was added dropwise to preformed anion $NaCH_2SOCH_3$ (3,5 eq) in DMSO (3 mL) during 10-12 min at 20 °C. The stirring was continued for 1h under this conditions. The reaction mixture was poured into 5% aq HCl (200 mL), the solid was filtered and dried in air. After purification by column chromotography (methylene chloride/hexane - 5/1 to methylene chloride eluent) product **6** was obtained (yield 74 mg, 20%). Recrystallization from ethanol gave a yellow solid, m.p. 198-200 °C. $^1$H NMR (200 MHz, $CDCl_3$) δ: 12.73(s, 1H), 8.35-8.21(m, 2H), 7.83(d, 1H, *J*=7.7), 7.89-7.71(m, 4H), 7.67-7.56(m, 1H), 7.47(d, 1H, *J*=7.7), 7.52-7.36(m, 2H), 4.59(s, 2H); IR $\nu_{max}$: 1673, 1632, 1434, 1305, 1295, 1256, 1150 cm$^{-1}$. HRMS(EI): $M^+$ 378.05687; calc. for $C_{21}H_{14}SO_5$: 378.05619.

**3-Phenylsulfonyl-anthraquinono[2,1-d]-1H-pyrazole (7).** To a stirred solution of **4a** (3,0 mg, 0,008 mmol) in 96% $H_2SO_4$ (0,3 mL) a solution of sodium nitrite (1,0 mg, 0,015 mmol) in $H_2O$ (1 drop) was added at 0 °C. After 15 min the cooling bath was removed, the reaction mixture was diluted with $H_2O$ (6 mL) and heated on the boiling water bath for 4h. After cooling, the reaction mixture was extracted with $CH_2Cl_2$, the extract dried with $MgSO_4$ and the solvent evaporated. The product was purified by flash chromatography (methylene chloride/ether - 10/1 eluent) to give **7** as a yellow crystalline product (yield 3,0 mg, 97%), m.p. 335-337 °C. $^1$H NMR (200 MHz, DMSO-$d_6$) δ: 8.58 (d, 1H, *J*=8.5), 8.26-8.18 (m, 2H), 8.17 (d, 1H, *J*=8.5), 8.13-8.05 (m, 2H), 8.01-7.90 (m, 2H), 7.79-7.61 (m, 3H); IR $\nu_{max}$: 3305, 1668, 1651, 1587, 1350, 1330, 1307, 1286, 1156, 1147, 1080, 996 cm$^{-1}$. HRMS(EI): $M^+$ 388.05191; calcd for $C_{21}H_{12}N_2SO_4$: 388.05178.

**2-Phenylsulfonylmethyl-9,10-anthraquinone (8).** To a stirred solution of **4a** (19 mg, 0,05 mmol) in 96% $H_2SO_4$ (0,5mL) a solution of sodium nitrite (5 mg, 0,07 mmol) in $H_2O$ (2 drops) was added at 0 °C. After 15 min 0,6M $H_3PO_2$ (4 mL) was added and the cooling bath removed. The reaction mixture was allowed to warm to room temperature, stirred for an additional 4h and extracted with $CH_2Cl_2$. The organic extract dried with anhydrous $MgSO_4$ and the solvent evaporated. The residue was purified by passing through a short silicagel column (methylene chloride to methylene chloride/ether - 10/1 eluent) to give **7** (yield 5 mg, 28%) and **8** (yield 8 mg, 41%). Recrystallization from ethyl acetate/hexane give **8** as pale yellow crystals, m.p. 212-214 °C. $^1$H NMR (200 MHz, $CDCl_3$) δ: 8.36-8.27 (m, 2H), 8.27 (dd, 1H, *J*=8.0; 0.5), 7.95 (dd, 1H, *J*=1.9; 0.5), 7.87-7.78 (m, 2H), 7.75-7.61 (m, 3H), 7.66 (dd, 1H, *J*=1.9; 8.0), 7.56-7.45 (m, 2H), 4.50 (s, 2H); IR $\nu_{max}$: 1673, 1663, 1318, 1311, 1298, 1156 cm$^{-1}$. HRMS(EI): $M^+$ 362.06107; calcd for $C_{21}H_{14}SO_4$: 362.06128.

**1-Phenylsulfonylmethyl-9,10-anthraquinone (9).** From **3a** (38 mg, 0,1mmol) according to the procedure used for **8** compound **9** was obtained (yield 35 mg, 96%) as pale yellow crystals, m.p. 242-243 °C. $^1$H NMR (200 MHz, $CDCl_3$) δ: 8.42(dd, 1H, *J*=6.7;2.6), 8.27-8.17(m, 1H), 8.11-8.01(m, 1H), 7.82-7.68(m, 6H), 7.49-7.32(m, 3H), 5.45(s, 2H); IR $\nu_{max}$: 1669, 1308, 1143 cm$^{-1}$. HRMS(EI): $M^+$ 368.06107; calcd for $C_{21}H_{14}SO_4$: 368.06128.

**1-Hydroxy-4-phenylsulfonylmethyl-9,10-anthraquinone (10).** From **3a** (38 mg, 0,1 mmol) in 96% $H_2SO_4$ (1mL) and solution of sodium nitrite (7 mg, 0,1 mmol) in $H_2O$ (3 drops) according to the procedure used for **7**, compound **10** was obtained (yield 16 mg, 42%) as a dark yellow solid, m.p. 230-232 °C (hexane/ethyl acetate). $^1$H NMR (200 MHz, $CDCl_3$) δ: 13.28 (s, 1H), 8.28-8.18 (m, 1H), 8.07-7.98 (m, 1H), 7.83-7.69 (m, 4H), 7.61 (d, 1H, *J*=8.8), 7.47-7.33 (m, 3H), 7.30 (d, 1H, *J*=8.8), 5.33 (s, 2H); IR $\nu_{max}$: 1642,

1592, 1306, 1300, 1285, 1252, 1149 $cm^{-1}$. HRMS(EI): $M^+$ 378.05614; calcd for $C_{21}H_{14}SO_5$: 378.05619.

**[9-Hydroxy-1-methoxy-anthryl-(10)]-phenylsulfonylchloromethyl ketone (12).** To a stirred solution of *t*-BuOK (224 mg, 2 mmol) and 1-methoxy-9,10-anthraquinone (119 mg, 0.5 mmol) in DMSO (5mL) a solution of chloromethyl phenyl sulfone (200 mg, 1.05 mmol) in DMSO (1 mL) was added dropwise at 18 °C. The reaction mixture was stirred at 20 °C for 1h and poured into 5% HCl. The precipitate was filtered and purified *via* column chromathography (silicagel was washed with AcOH before used, hexane/methylene chloride/ether - 3/1/0,1 eluent). Yield 135 mg (61%), m.p. 206-207 °C (methylene chloride). $^1H$ NMR (500 MHz, $CDCl_3$) δ: 10.90(s, 1H), 8.49(m, 1H), 7.95(m, 1H), 7.90-7.87 (m, 2H), 7.71-7.58 (m, 3H), 7.52-7.40(m, 4H), 6.75(m, 1H), 6.09 (s, 1H), 4.16(s, 3H); $^{13}C$ NMR (500 MHz, $CDCl_3$) δ: 191.0, 157.2, 156.5, 135.6, 134.6, 132.3, 131.2, 130.3(2C), 129.7, 128.8(2C), 128.3, 124.3, 123.7, 123.5, 121.4, 119.9, 118.2, 109.6, 102.1, 75.7, 56.5; IR $\nu_{max}$: 3272, 1676, 1619, 1575, 1558, 1450, 1334, 1282, 1249, 1225, 1172, 1155, 1130, 1084, 761 $cm^{-1}$; HRMS (EI): $M^+$ 440,04870, calcd for $C_{23}H_{17}ClSO_5$: 440,04843. Anal. calcd for $C_{23}H_{17}ClSO_5$: C 62,65; H 3,89; Cl 8.04; S 7,27. Found: C 62,41; H 3,98; Cl 8.21; S 7,19.

**2-*N,N*-dimethylamino-9-hydroxy-9-methylsulfinylmethyl-10-anthrone (14a,b).** To a stirred solution of 2-*N,N*-dimethylamino-9,10-anthraquinone (251 mg, 1 mmol) in DMSO (20 mL) powdered potassium hydroxide (560 mg, 10 mmol) was added at once at 20 °C. The reaction mixture was stirred at 20 °C for 1h and poured into cold 5% HCl. The product was extracted with methylene chloride, the extract was washed with water and dried over anh. $MgSO_4$. The solvent was evaporated and the residue was purified *via* flash chromatography (methylene chloride to methylene chloride/acetone - 1/1 eluent). Yield of a mixture of diastereoisomers (**14a,b**) 280mg (85%), m.p. 190-191 °C(dec.). Recrystallization from methylene chloride gave one diastereoisomer **14a**, m.p. 202-203 °C(dec.). $^1H$ NMR (500 MHz, $CDCl_3$) δ: 8.22(m, 1H), 8.09(d, 1H, *J*=8.8 Hz), 8.05(m, 1H), 7.66(m, 1H), 7.51(m, 1H), 7.23(d, 1H, *J*=2.6 Hz), 6.73(dd, 1H, *J*=8.8, 2.6 Hz), 5.84(s, 1H), 3.25(d, 1H, *J*=13.1 Hz), 3.15(s, 6H), 2.80(d, 1H, *J*=13.1 Hz), 2.45(s, 3H); $^{13}C$ NMR (500 MHz, $CDCl_3$) δ: 181.7, 153.9, 148.9, 144.3, 132.2, 131.3, 130.1, 128.6, 127.4, 125.8, 118.5, 11.5, 106.9, 73.3, 69.3, 40.2, 39.2; IR $\nu_{max}$: 3182, 1659, 1600, 1576, 1372, 1322, 1003 $cm^{-1}$. EI MS: $M^+$ 329. Anal. calcd for $C_{18}H_{19}NSO_3$: C 65,63; H 5,81; N 4,25; S 9,74. Found: C 65,87; H 6,03; N 4,18; S 9,68.

**2-*N,N*-dimethylamino-9-hydroxy-9-methylsulfonylmethyl-10-anthrone *N*-oxide (15).** To a stirred solution of **14a,b** (329mg, 1mmol) in AcOH (6 mL) 30% $H_2O_2$ (680 mg, 20mmol) was added at 90 °C. The reaction mixture was stirred at 90 °C for 0,5h. The solvent was removed *in vacuo* and the residue was purified by flash chromathography

(methylene chloride/methanol - 3/1 to 1/1 eluent). Recrystallization from methylene chloride/ether gave **15**, yield 294mg(81%), m.p. 145-147 °C(dec.). For X-ray analysis **15** was recrystallized from hexane/methylene chloride/ether/methanol - 3/3/1/0.5, p.dec. 134 °C.

$^1$H NMR (500 MHz, $CDCl_3$) δ: 10,09(vbr, 1H), 8,34-8,30(m, 2H), 8,15-8,12(m, 1H), 7,85-7,80(m, 1H), 7,67-7,62(m, 2H), 7,03-6,98(m, 1H), 3,67(s, 3H), 3,49(d, 1H, *J*=15,1Hz), 3,31(s, 3H), 3,13(d, 1H, *J*=15,1Hz), 2,77(s, 3H); $^{13}$C NMR (500 MHz, $CDCl_3$) δ: 181.7, 155.5, 146.8, 146.5, 134.3, 130.8, 130.5, 129.1, 128.3, 127.5, 126.3, 119.3, 119.0, 69.6, 69.5, 63.3, 60.5, 43.9; IR $\nu_{max}$: 3423, 3449, 2920, 1664, 1602, 1310, 1133 $cm^{-1}$. LSIMS(HR): $(M+H)^+$ 362,10622; calcd for $C_{18}H_{20}NSO_5$: 362,10664.

**Table 2.** Crystal data and structure refinement for the compounds **12** and **15**.

| Identification code | **12** | **15** |
|---|---|---|
| Empirical formula | $C_{23}$ $H_{17}$ Cl $O_5$ S | $C_{19}$ $H_{23}$ $O_7$ S |
| Formula weight | 440.88 | 395.43 |
| Temperature (K) | 293(2) | 293(2) |
| Wavelength (Å) | | 1.54178 |
| Crystal system | Monoclinic | Monoclinic |
| Space group | P21/n | C2 |
| Unit cell dimensions (Å, °): | | |
| a | 8.342(1) | 17.922(2) |
| b | 10.197(2) | 8.4543(7) A |
| c | 23.779(3) | 14.0470(10) deg. |
| β | 93.82 | 117.39(9) |
| Volume ($Å^3$) | 2018.4 | 1889.8(3) |
| Z | 4 | 4 |
| $D_{calc}$ ($Mg\ m^{-3}$) | 1.451 | 1.390 |
| Absorption coeff ($mm^{-1}$) | 2.935 | 1.867 |
| F(000) | 912 | 836 |
| Crystal size (mm) | 0.14x0.14x0.07 | 0.07x0.14x0.07 |
| θ-range for data collection (°) | 3.73 to 72.82. | 3.54 to 62.92 |
| Index ranges | -10 ≤h ≤0, -12 ≤k ≤0, -29 ≤l ≤29 | -14 ≤h ≤19, -9 ≤k ≤9, -14 ≤l ≤15 |
| Reflections collected | 2576 | 2536 |
| Independent reflections | 2396 [R(int) = 0.2252] | 2443 [R(int) = 0.0185] |
| Refinement method | Full-matrix least-squares on $F^2$ | |
| Data / restraints / parameters | 2396 / 0 / 275 | 2443 / 1 / 265 |
| Goodness-of-fit on $F^2$ | 1.070 | 0.867 |
| Final R indices [I>2σ (I)] | R1 = 0.0750, wR2 = 0.1918 | R1 = 0.0472, wR2 = 0.1344 |
| R indices (all data) | R1 = 0.0826, wR2 = 0.2005 | R1 = 0.0478, wR2 = 0.1356 |
| Extinction coefficient | 0.0000(3) | 0.0004(2) |
| Largest diff. peak and hole ($e\ Å^{-3}$) | 0.467 and -0.707 | 0.409 and -0.260 |

Lists of the fractional coordinates and anisotropic temperature factors, bond lengths and bond angles have been deposited at the Cambridge Crystallographic Data Centre.

**X-Ray structure determination of compounds 12 and 15.** The crystals of **12** suitable for diffractometric measurements were obtained by recrystallization from

$CH_2Cl_2$ solution. Yellow crystals of **15** obtained from the mixture of solvents containing methanol turned orange on exposure to light and X-rays. Two experiments were taken for the same crystal: one, immediately after removing from the mother solution second, 24 hrs after the crystal turned orange. The same unit cell parameters and space groups were assigned in both experiments. For the second set of data however, least-squares refinement gave lower standard deviations and smaller temperature factors. Crystal data and details of data collection and structure refinement are collected in Table 2.

The structures were solved by direct methods[26] and refined by full-matrix least-squares[27]. The H-atoms were placed in idealised positions and refined riding on their parent atoms. The H-atom displacement parameters were assigned to be 1.2 $U_{eq}$ of the parent atom. The positions for the hydroxyl hydrogens were found from difference maps and refined.

## References

[1] Mąkosza M. and Winiarski J. Acc.Chem.Res. 1987;20:282.
[2] Katrizky AR, Laurenzo KS. J.Org.Chem. 1988;53:3978.
[3] Mąkosza M, Sienkiewicz K. J.Org.Chem. 1990;55:4979.
[4] Mąkosza M, Białecki M. J.Org.Chem. 1992;57:4784.
[5] Mąkosza M, Synthesis, 1991:103.
[6] Rykowski A, Mąkosza M. Liebigs Ann.Chem. 1988:627.
[7] Mąkosza M, Ostrowski S. J.prakt.chem. 1988;330:789.
[8] Ostrowski S, Mąkosza M. Liebigs Ann.Chem. 1989:95.
[9] Mąkosza M, Kuciak R, Wojciechowski K. Liebigs Ann. Chem. 1994:615.
[10] Mąkosza M, Kwast A. Tetrahedron, 1991;47:5001.
[11] Ashcroft AE, Davies DT, Sutherland JK. Tetrahedron, 1984;40:4579.
[12] Murphy RAJr, Cava MP. Tetrahedron Lett. 1984;25:803.
[13] Cava MP, Ahmed Z, Benfaremo N, Murphy RAJr, O'Mally GJ. Tetrahedron, 1984;40:4767.
[14] Gillies J, Ress CW. Tetrahedron Lett. 1996;37:4065
[15] Barton DHR, Jones DW. J.Chem.Soc. 1965:3563.
[16] Majnagashew IJ, Klimenko LS. Izv. Akademii Nauk, 1996:2710.
[17] Corey EJ, Chaykovsky M. J.Amer.Chem.Soc. 1965;87:1345.
[18] Corey EJ, Chaykovsky M. J.Org.Chem. 1963;28:254.
[19] Walling C, Bollyky L. J.Org.Chem. 1963;28:256.
[20] Arai S, Kato S, Hida M. Bull.Chem.Soc.Jpn. 1985:1458.
[21] Mąkosza M, Danikiewicz W, Wojciechowski K. Liebigs Ann.Chem. 1987:711
[22] Blankespoor RL, Smart RP, Batts ED, Kiste AA, Lew RE, Vander Vliet ME. J.Org.Chem. 1995;60:6852.
[23] Yamamoto G, Oki M. Bull.Chem.Soc.Jpn. 1981;54:473.
[24] Moller F, Schroter R. in: Hoyben-Weyl, Methoden der organischen chemie. Georg Tieme Verlag Stuttgart, 1957; V. 11/1:648.
[25] Allais A. Ann. de Chimie, 1947;739:777.
[26] Sheldrick GM. Acta Cryst. 1990;A46:467.
[27] Sheldrick GM. SHELXL93. Program for Refinement of Crystal Structures, 1993, University of Göttingen, Germany.