Reactions of Organic Anions. Part 180.[1] Orientation of the Carbanion Attack of Chloromethyl *p*-Tolyl Sulphone on 1-Cyanonaphthalene Derivatives†

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The carbanion of chloromethyl *p*-tolyl sulphone reacts with cyanonaphthalene derivatives to give bis-annulated products and/or S_NAr products and/or products of nucleophilic substitution of hydrogen depending on the structure of the substrates and on reaction conditions. The orientation of the initial carbanion attack is discussed.

In an earlier paper[2] we reported that carbanion of chloromethyl *p*-tolyl sulphone (**1**) reacts with 1-cyanonaphthalene (**2**) to give the bis-annulated product **5**, whereas its reaction with 1-nitronaphthalene (**6**) proceeded as vicarious nucleophilic substitution of hydrogen (VNS).[3,4]

This dramatic difference in the course of the reaction of the carbanion with electrophilic naphthalene derivatives **2** and **6** was rationalized in terms of the distribution of the negative charge in the anionic σ-adducts, which are intermediates in both of these processes.[2] Similar observations have been made in the reaction of **1** with some electrophilic heterocycles such as quinoxalines or naphthyridines.[5] In some instances it has even been possible to control the course of the reaction (annulation *versus* VNS) by varying the conditions.[6]

Results and Discussion

From general considerations it is accepted that the annulation of **2** proceeds *via* addition of the carbanion at C-4 to give a σ-adduct, which reacts further along the intramolecular S_N2 substitution pathway. The [3,4]-monoannulated intermediate produced (**4a**) is an active Michael acceptor, which consequently reacts rapidly with a second carbanion to give final product **5** (Scheme 1). An alternative pathway, namely initial addition of the carbanion at C-2 followed by formation of the [1,2]-monoannulated product **4b** and subsequent [3,4]-annulation was rejected since the former cannot behave as an electrophilic alkene.

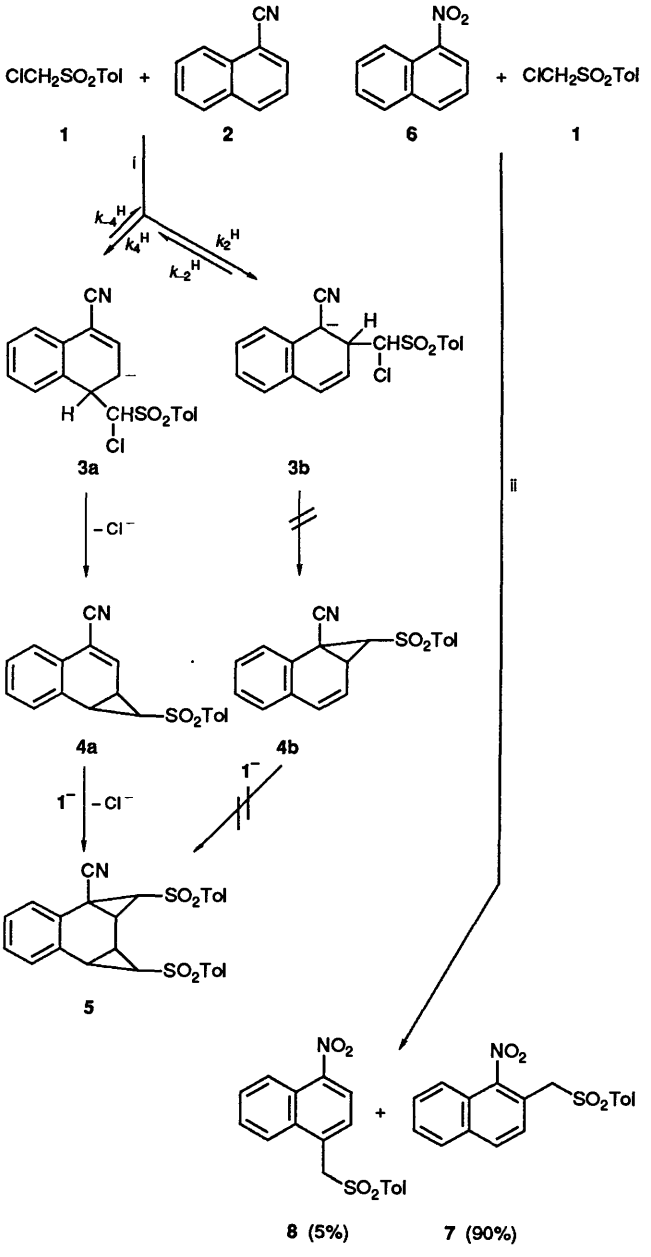
This reaction mode is not consistent with the orientation of the VNS reaction of **1** with 1-nitronaphthalene which proceeds predominantly at C-2. The following question must therefore be answered: why does the carbanion of **1** react with 1-cyanonaphthalene at C-4, whereas the corresponding reaction with 1-nitronaphthalene takes place at C-2?[7]

There could be two reasons for this difference: (*i*) that the modes of the nucleophilic attachment of the carbanion to **2** and **6** are different (it occurs at C-4 of **2** and preferentially at C-2 of **6**), and (*ii*) that there is, in fact, no substantial difference betweeen **2** and **6** in this respect; that in both cases the addition proceeds initially at C-2, but in the case of **2** this adduct does not undergo the cyclisation, whereas that at C-4 does.

Taking into account that the substantial double bond character of C_1–C_2 bond in the naphthalene ring is responsible for the higher rate of nucleophilic addition at C-2 in compound **6** one would expect similar situation for **2**, thus favouring hypothesis (*ii*).

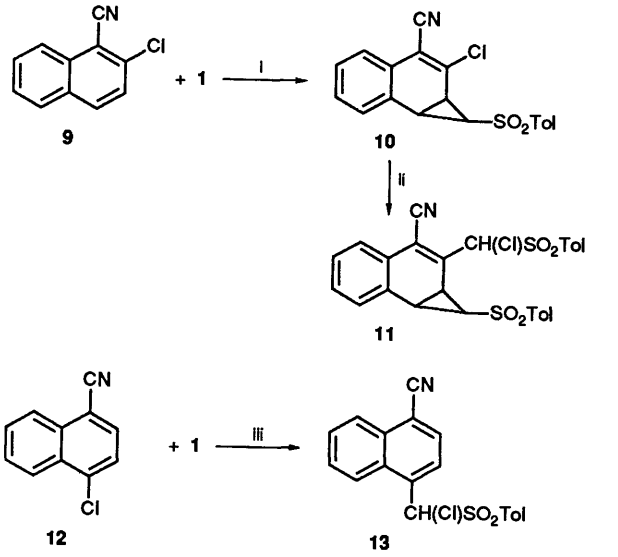
Some of our early observations of the reaction of **1** with 2-chloro-1-cyano- (**9**) and 4-chloro-1-cyanonaphthalene (**12**) also favour the second option (Scheme 2).

2-Chloro-1-cyanonaphthalene (**9**) reacts with **1** faster than does the 4-chloro isomer to give **11** apparently *via* an initial



Scheme 1 *Reagents:* i, Bu^{t}OK–DMSO; ii, NaOH–DMSO

† This paper was submitted to mark the 150th anniversary of the Chemical Society/Royal Society of Chemistry.



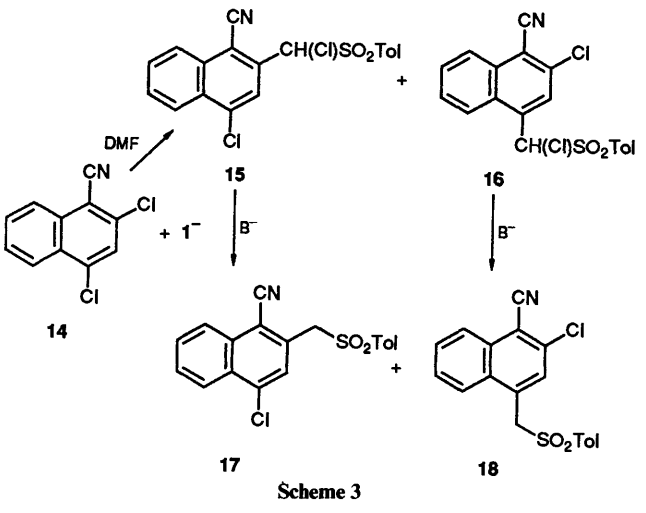
Scheme 2 *Reagents:* i, Bu^{t}OK–DMF, −40 °C; ii, 1^-; iii, Bu^{t}OK–DMSO, 20 °C

addition at C-4, [3,4]-annulation and vinylic nucleophilic substitution of 2-Cl. The reverse order of events is not possible, because the eventual product of an S_NAr reaction of 2-Cl is a strong C–H acid which, in the reaction mixture, should exist in the form of a carbanion, inactive towards nucleophilic addition. The reaction of **1** with **12** was substantially slower and gave only the product of an S_NAr reaction at 4-Cl (**13**), which did not react further, thus confirming the mechanism proposed above. Since, as a rule, nucleophiles add to electrophilic arenes faster at positions occupied by hydrogen than by halogen, the conversion **12** ⟶ **13** should be preceded by the addition of 1^- to **12** at C-2 to give a σ_2^H-adduct, which does not react further. Owing to the reversibility of the addition, **13**, (*via* a σ_4^{Cl}-adduct) is finally produced. On this basis one can conclude that cyclisation of the σ_2^H-adduct is a much slower process than cyclization of the σ_4^H-adduct formed *via* addition of 1^- to **9**. This reasoning, although supporting hypothesis (*ii*) cannot be considered as direct proof.

Since we could observe directly neither the C-2 σ-adduct of **2**, nor the products of its transformation, we have investigated the reaction of 2,4-dichloro-1-cyanonaphthalene (**14**) in order to compare the rates of addition at C-2 and C-4. It is reasonable to assume that ratios of the rates of addition at C-2 and C-4 in **2** and **14** should be similar *i.e.* $k_2^H/k_4^H \approx k_2^{Cl}/k_4^{Cl}$. Taking into account that σ^{Cl}-adducts rapidly lose Cl^- to give S_NAr products the ratio of the yields of these products should reflect k_2^H/k_4^H to a good approximation.

Synthesis of 2,4-dichloro-1-naphthonitrile (**14**) proved somewhat troublesome. Eventually it was obtained from 2,4-dichloro-1-naphthol,[8] which was converted into a phosphorus derivative with PBr_5 and then pyrolysed[9] to 1-bromo-2,4-dichloronaphthalene. The bromine was then selectively converted into the nitrile in an exchange reaction with cuprous cyanide.[10]

When the reaction of **14** with 1^- (dimethylformamide, 20 °C) was carried out for 16 h, two isomeric products were isolated namely, **17** (28%) and **18** (16%), evidently formed by dehalogenation of the initial S_NAr products at C-2 and C-4. Because of a poor material balance (42%) the final ratio C-2/C-4 = 1.6 was obviously an artifact seemingly caused by differences in stability of the corresponding anions of the initial products in the reaction mixture. When the reaction was carried out for 0.5 h, products **15** (14%) and **17** (2%) were isolated along with unchanged **14** (59%). Neither compound **16** nor **18** could be detected in the remaining reaction mixture (Scheme 3).



Scheme 3

The identification of the corresponding isomers **17** and **18**, *i.e.* the determination of position of the $-CH_2Ts$ in the naphthalene ring was made based upon Nuclear Overhauser Effect (NOE) measurements. Upon irradiation of the CH_2 signal, a large enhancement (10%) of the 5-H signal of the minor isomer was observed, thereby proving that CH_2Ts group occupies position 4, while in the second product there was no enhancement of the 5-H signal (isomer **17**).

As expected in the reaction of **1** with **14**, substitution of 2-Cl was mainly observed. Our hypothesis that the nucleophilic attachment to the 1-cyanonaphthalene derivatives proceeds initially at C-2 is supported by additional evidence arising from the reaction of **1** with 4-chloro-1-naphthonitrile (**12**) carried out in the presence of an excess of base under milder conditions (Bu^{t}OK–DMF, −30 to −20 °C, 2 h). Contrary to the previously described reaction in dimethyl sulphoxide (DMSO) (Bu^{t}OK–DMSO, 20 °C, 0.5 h) which gave **13**, product **15** was obtained, apparently *via* oxidation of the initially formed σ_2^H-adduct.

$$12 + 1 \xrightarrow{i} 15$$

Scheme 4 *Reagents:* i, Bu^{t}OK–DMF, −30 to −20 °C, 2 h

We are thus provided with unambiguous evidence that the carbanion of **1** adds to 1-cyanonaphthalene in a fast reaction at position 2, but the initially formed, unstable σ_2^H-adduct **3b** does not react *via* the intramolecular S_N2 pathway, so **4b** is not produced. Since the formation of **3b** is a reversibly process and is not followed by further conversion, the isomeric σ-adduct **3a** is subsequently formed *via* a slower addition of 1^- to **2** at position 4. In contrast with **3b**, **3a** is transformed into **4a** *via* an intramolecular S_N2 process and finally into **5** (Scheme 1). Thus, a new question is raised: is there any specific hindrance to the intramolecular S_N2 process in **3b**, which is not present in **3a**, such that only the latter forms the annulation product **4a**, while **3a** and **3b** are in equilibrium, or is this simply a case of kinetic *versus* thermodynamic control? That is to say whereas $k_2^H > k_4^H$, the dissociation rates $k_{-2}^H \gg k_{-4}^H$, therefore $K_2^H < K_4^H$. Thus, upon equilibration the system contains practically exclusively **3a**, which in a relatively slow S_N2 reaction forms **4a** and finally **5**.

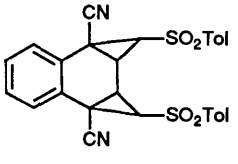
Although the relationship between the kinetic and thermodynamic control of the formation of the isomeric σ-adducts from 1-nitronaphthalene was not investigated, our observation of the VNS hydroxylation with alkyl hydroperoxide anion[11] strongly supports the latter hypothesis. For example, 1-nitronaphthalene (**6**) can be selectively hydroxylated with Bu^{t}OOH at position 2 or 4, the orientation being controlled by the rate of the elimination.

In the reported reaction of **6** with the anion of chloromethyl *p*-tolyl sulphone ($\mathbf{1}^-$) the substitution occurred predominantly at C-2[3,4] (NaOH–DMSO, 20 °C; 2-isomer/4-isomer = 18, 95% yield[4]). On the basis of the reasoning presented in this paper, we therefore expected that the use of a weaker and less efficient base should influence the proportion in which the 4-isomer is formed. Indeed, when the reaction of **6** with $\mathbf{1}^-$ was carried out in such a way that the latter is in a low concentration thus acting both as a nucleophile and base, the ratio of 2-isomer/4-isomer was changed dramatically from 18 to 0.57, even though the total yield was still high (80%).

On the basis of the experiments discussed in this paper and by analogy to the case of VNS in **6** one can assume that the formation of the σ_2-adducts from 1-cyanonaphthalene derivatives is also a fast process, as in the case of 1-nitronaphthalene. Nevertheless, when their transformations are slow, due to the reversibility of the addition, they are converted into the more stable σ_4-adducts from which they are transformed into final products.

The greater difficulties encountered in the formation of a three-membered ring on the C_1–C_2 bond than on the C_3–C_4 can be ascribed to the lower negative-charge density on C-1 after addition to C-2 (this charge resides mainly on the nitrogen atom of the cyano group), than on C-3 upon addition to C-4. Addition to C-4 led to **3a**, which seems to be favourable (low energy), so the double bond between C-1 and C-2 is conjugated with a second aromatic ring. An electron pair localized mainly on C-3 causes an S_N2 reaction leading to the formation of the first cyclopropane ring.

However, when there is no other mode of transformation available, the formation of a cyclopropane ring on the C_1–C_2 bond is possible. This was shown in the reaction of $\mathbf{1}^-$ with naphthalene-1,4-dicarbonitrile **19** (which gave **20** in 33% yield). Additionally, because of the presence of the second cyano group, the negative charge in the corresponding adduct is efficiently delocalized, so the course of the reaction is partially shifted towards elimination leading to the VNS product **21** (26%). In naphthalene-1,2-dicarbonitrile (**22**) the formation of the VNS product **23** was observed exclusively (47%).



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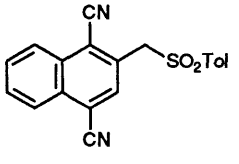

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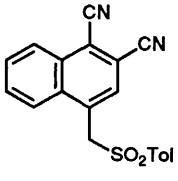

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Experimental

^{1}H NMR spectra were recorded with Varian EM-360 (60 MHz), Varian GEMINI-200 (200 MHz) and Bruker AM-500 (500 MHz) instruments with tetramethylsilane as an internal standard. Coupling constants *J* are expressed in hertz (Hz). IR spectra were measured with a Beckman IR 4240 spectrophotometer and mass spectra with a Finnigan 8200 spectrometer (electron impact method). Melting points are uncorrected. TLC analysis was carried out on foil plates coated with Merck 60F 254. Silica gel 100–200 and 230–400 mesh (Merck) was used for column chromatography. Starting materials were commercially available or were prepared according to procedures reported earlier: chloromethyl *p*-tolyl sulphone (**1**),[3] 1-naphthonitrile (**2**).[12]

2-Chloro-1-naphthonitrile (**9**).—This was prepared as follows. 2-Naphthylamine was acetylated[13] and the resulting *N*-acetyl derivative was brominated with Br_2 in CCl_4 solution as described for related compounds.[14] The resulting 1-bromo-2-acetamidonaphthalene was hydrolysed into 1-bromo-2-naphthylamine, which was transformed into 1-bromo-2-chloronaphthalene according to the known procedures[15] (diazotization was carried out in AcOH with H_2SO_4). Treatment of 1-bromo-2-chloronaphthalene with cuprous cyanide[10] yielded 2-chloro-1-naphthonitrile (**9**) (overall yield 30%), m.p. 88–89 °C (from ethanol) [Found: C, 69.6; H, 2.85; N, 7.3. Calc. for $C_{11}H_6ClN$ (*M* = 187.63) C, 70.42; H, 3.22; N, 7.47%]; δ_H(60 MHz; $CDCl_3$) 8.42–7.45 (m, ArH).

4-Chloro-1-naphthonitrile (**12**).—This was obtained from 1-methylnaphthalene *via* 4-chloro-1-naphthaldehyde.

4-Chloro-1-naphthaldehyde.—1-Methylnaphthalene was chlorinated,[16] and 4-chloro-1-methylnaphthalene was converted into the required naphthaldehyde according to procedures described for the transformation of methyl groups in aromatic systems[17] (61%), m.p. 68–71 °C (from hexane–$CHCl_3$) [Found: C, 69.3; H, 3.45. Calc. for $C_{11}H_7ClO$ (*M* = 190.63): C, 69.31; H, 3.70%]; δ_H(60 MHz; CCl_4) 9.98 (1 H, s, CHO), 9.15–8.81 (1 H, m, 2-H), 8.21–7.88 (1 H, m, 3-H) and 7.88–7.15 (4 H, m, ArH); *m/z* 192 (34%) and 190 (100), isotopic $M^{+\bullet}$), 191 (39), 189 (79), 164 (22), 163 (26), 162 (73), 161 (56), 155 (24), 127 (38), 126 (65), 125 (13), 99 (13), 87 (7), 81 (8), 77 (14), 75 (24), 74 (18), 63 (27), 51 (12) and 50 (12).

4-Chloro-1-naphthonitrile (**12**).—The aldehyde obtained above was transformed into the cyano derivative[18] (**12**) (95%), m.p. 89–90 °C (from hexane–$CHCl_3$) [Found: C, 71.2; H, 3.0; N, 7.3. Calc. for $C_{11}H_6ClN$ (*M* = 187.63): C, 70.42; H, 3.22; N, 7.47%); δ_H(60 MHz; $CDCl_3$) 8.53–8.13 (2 H, m, 2- and 3-H) and 8.02–7.47 (4 H, m, ArH).

1-Bromo-2,4-dichloronaphthalene.—1-Naphthol was chlorinated to give *2,4-dichloro-1-naphthol*[8] (96% yield), and the hydroxy group was then converted into a bromo substituent according to method described in literature.[9] Some modifications were made: commercial PBr_5 was used and hydroxy compound was used in a twofold instead of a fourfold excess. The product was purified by column chromatography (eluent: hexane) (yield 95%), m.p. 97–98 °C (from hexane) [Found: C, 42.95; H, 1.64. Calc. for $C_{10}H_5BrCl_2$ (*M* – 275.96): C, 43.52; H, 1.83%]; δ(60 MHz; $CDCl_3$) 8.37–8.00 (2 H, m, 5- and 8-H) and 7.78–7.37 (3 H, m, 3-, 6- and 7-H); *m/z* 278 (43%), 276 (100), 274 (60, isotopic $M^{+\bullet}$), 232 (14), 230 (15), 197 (24), 195 (38), 162 (22), 160 (70), 125 (31), 123 (12), 99 (14), 98 (16), 81 (13), 80 (31), 75 (15), 74 (14) and 62 (13).

2,4-Dichloro-1-naphthonitrile (**14**).—1-Bromo-2,4-dichloronaphthalene was transformed into (**14**) according to a known procedure.[10] 58% of the starting compound was recovered. The yield based on the consumed starting material was 90%, m.p. 118–120 °C (from hexane–$CHCl_3$) (Found: C, 59.3; H, 2.15; N, 6.35. $C_{11}H_5NCl_2$ (*M* = 222.07) requires C, 59.49; H, 2.27; N, 6.31%); ν_{max}($CHCl_3$)/cm^{-1} 2235 (CN); δ_H(500 MHz; CCl_4) 8.32 (1 H, d, *J* = 8.45, 8-H), 8.21 (1 H, dd, *J* = 8.34 and 0.60, 5-H), 7.89–7.77 (2 H, m, 6- and 7-H) and 7.77 (1 H, s, 3-H); *m/z* 225 (11%), 223 (65), 221 (100, isotopic $M^{+\bullet}$), 187 (13), 186 (12) and 151 (9).

Naphthalene-1,4-dicarbonitrile (**19**).—This was prepared from 1-methylnaphthalene as follows. Bromination in position 4,[14] transformation the methyl group into a cyano group[17,18] followed by bromine exchange with CuCN.[10,19] The total yield was 28%, m.p. 203–205 °C (from ethanol) (lit.,[20] 208 °C).

Naphthalene-1,2-dicarbonitrile (**22**). This was prepared from 2-methylnaphthalene according to procedures described for related compounds as follows: bromination in position 1,[14] and then the sequence of the reactions described above for naphthalene-1,4-dicarbonitrile. The total yield was 22%, m.p. 186 °C (from ethanol) (lit.,[21] 190 °C).

Reaction Procedures.—(*a*) Bu^{t}OK–DMF *system.*—To a stirred solution of Bu^{t}OK (380 mg, 3.4 mmol) in DMF (7 cm^3) cooled to −30 to −40 °C was added dropwise a solution of chloromethyl *p*-tolyl sulphone (**1**) (440 mg, 2.15 mmol) and the appropriate naphthonitrile (1.0 mmol) in DMF (3 cm^3) over 5 min. The reaction was continued at this temperature, and then poured into dilute aqueous HCl (3%; 100 cm^3). The precipitate formed was extracted with $CHCl_3$ (2 × 20 cm^3) and the combined organic layers were washed with water (40 cm^3) and dried ($MgSO_4$). Products were isolated by column chromatography and purified by recrystallization to give: **11** (from **9**, yield 62%; T_{react} = −40 °C, t_{react} = 20 min; eluent $CHCl_3$–acetone 20:1); **15** (from **12**, yield 10%, t_{react} = 2 h; Bu^{t}OK (500 mg, 4.46 mmol) and chloromethyl *p*-tolyl sulphone (220 mg, 1.08 mmol) were used, the reaction was carried out in 5 cm^3 of DMF at −30 to −20 °C; eluent hexane–$CHCl_3$ 2:1); **20** (33%) and **21** (26%) (from **19**; T_{react} = −35 °C, t_{react} = 20 min; eluent $CHCl_3$–acetone 20:1); **23** (from **22**, 47%; T_{react} = −30 °C, t_{react} = 10 min; eluent $CHCl_3$).

(*b*) Bu^{t}OK–DMSO *system.* To a stirred solution of chloromethyl *p*-tolyl sulphone (440 mg, 2.15 mmol) and the appropriate naphthonitrile (1.0 mmol) in DMSO (4 cm^3) was added dropwise a solution of Bu^{t}OK (500 mg, 4.46 mmol) in DMSO (6 cm^3) over 5 min at room temperature. The reaction mixture was treated as in the preceding procedure to give: **5** (from **2**, 48%; t_{react} = 5 min; the product was isolated by recrystallization from ethanol); **13** (from **12**, 18%; t_{react} = 30 min; eluent $CHCl_3$).

(*c*) *Reaction of* 2,4-*dichloro*-1-*naphthonitrile* (**14**) *with chloromethyl* p-*tolylsulphone* (**1**). To a stirred solution of chloromethyl *p*-tolyl sulphone (420 mg, 2.05 mmol) in DMF (7.5 cm^3) cooled to −40 °C was added Bu^{t}OK (230 mg, 2.05 mmol). After 15 min, a solution of 2,4-dichloro-1-naphthonitrile (222 mg, 1.0 mmol) in DMF (2.5 ml) was added dropwise over 1 min. The mixture was allowed to warm to room temperature and the reaction was continued with stirring overnight and then treated as in procedure (*a*). Crude products were isolated by column chromatography (hexane–AcOEt 5:1) and purified by recrystallization to give **17** (92 mg, 26%) and **18** (58 mg, 16%).

When the reaction was carried out 0.5 h at room temperature 2,4-dichloro-1-naphthonitrile (**14**) (130 mg, 59%) was recovered, and the C-2 chlorine S_NAr product, **15** (53 mg, 14%) and product **17** (7 mg, 2%) were isolated.

1,2-*Bis*(p-*tolylsulphonyl*)-1,1a,1b,2,2a,6b-*hexahydrodicyclopropa*[a,c]*naphthalene*-1-*carbonitrile* (**5**).—M.p. 244–246 °C (from ethanol) [Found: C, 65.9; H, 4.55; N, 3.25. $C_{27}H_{23}NO_4S_2$ (*M* = 489.60) requires C, 66.24; H, 4.74; N, 2.86%] ν_{max}(KBr)/cm^{-1} 2250 (CN); δ_H(300 MHz; $CDCl_3$) 7.90 (2 H, d, *J* = 8.24, 2 H of H-Tol), 7.80 (2 H, d, *J* = 8.55, 2 H of H-Tol'), 7.44–7.38 and 7.24–7.15 (8 H, 2 × m, ArH), 3.17 (1 H, d, *J* = 6.4, 10-H), 2.85 (1 H, d, *J* = 6.4, 2-H), 2.83–2.77 and 2.72–2.67 (3 H, 2 × m, 3-, 4- and 9-H) and 2.50 and 2.48 (6 H, 2 × s, 2 × CH_3); δ_C(75 MHz; $CDCl_3$) 145.8 and 145.3 ($C_6H_5CH_3$ and $C_6H_5CH_3$), 136.6 and 135.8 Tol-C-SO_2 × 2), 130.33, 130.27, 128.06 and 127.61 (Tol-C × 4), 130.33, 129.40, 128.71 and 128.56 (C-5, C-6, C-7 and C-8), 129.0 and 125.1 (C-4a and C-8a), 116.5 (CN), 53.3 (C-10, $^1J_{CH}$ = 176), 48.3 (C-9, $^1J_{CH}$ = 176), 26.7 (C-2, $^1J_{CH}$ = 170), 21.7 (2 × CH_3, $^1J_{CH}$ = 127), 21.2 ($^1J_{CH}$ = 172) and 20.6 ($^1J_{CH}$ = 172) (C-3 and C-4) and 20.5 (C-1); *m*/*z* 489 ($M^{+\bullet}$, 2%), 334 (100), 271 (27), 254 (18), 194 (23), 179 (40), 178 (31), 155 (35), 151 (21), 139 (60), 91 (55) and 44 (17).

2-[*Chloro*(p-*tolylsulphonyl*)*methyl*]-1-*tolylsulphonyl*-1a,7b-*dihydro*-1H-*cyclopropa*[a]*naphthalene*-3-*carbonitrile* (**11**).—M.p. 230–231 °C (from ethanol) [Found: C, 61.95; H, 4.0; N, 2.65. $C_{27}H_{22}ClNO_4S_2$ (*M* = 524.05) requires C, 61.88, H, 4.23; N, 2.67%]; ν_{max}($CHCl_3$)/cm^{-1} 2220 (CN); δ_H(200 MHz; $CDCl_3$) 7.87–7.30 (12 H, m, ArH), 5.82 [1 H, s, CH(Cl)Ts], 3.64–3.56, 3.35–3.27 and 1.85–1.75 (3 H, 3 × m, cyclopropyl-H) and 2.46 (6 H, s, 2 × CH_3); *m*/*z* 370 (39%), 369 (24), 368 (100, $M^{+\bullet}$ − SO_2Tol), 213 (31), 178 (20), 139 (13), 91 (19), 71 (14), 57 (17) and 43 (16).

4-[*Chloro*(p-*tolylsulphonyl*)*methyl*]-1-*naphthonitrile* (**13**).—M.p. 173–174 °C (from ethanol) [Found: C, 63.7; H, 3.85; N, 3.7; Cl, 9.69. $C_{19}H_{14}ClNO_2S$ (*M* = 355.84) requires C, 64.13; H, 3.97; N, 3.94; Cl, 9.96%]; ν_{max}($CHCl_3$)/cm^{-1} 2230 (CN); δ_H(60 MHz; $CDCl_3$) 8.40–7.25 (10 H, m, ArH), 6.58 [1 H, s, CH(Cl)Ts] and 2.45 (3 H, s, CH_3); *m*/*z* 355 ($M^{+\bullet}$, 3%), 202 (32), 201 (15), 200 (100), 166 (13), 164 (16), 140 (6), 139 (6), 91 (11), 65 (9), 57 (5) and 43 (4).

4-*Chloro*-2-[*chloro*(p-*tolylsulphonyl*)*methyl*]*naphthonitrile* (**15**).—M.p. 190–191 °C (from hexane–$CHCl_3$); ν_{max}($CHCl_3$)/cm^{-1} 2240 (CN); δ_H(200 MHz; $CDCl_3$) 8.43–8.37 and 8.32–8.23 (2 H, 2 × m, 5- and 8-H), 8.02 (1 H, s, 3-H), 7.89–7.78 (4 H, m, 6-, 7-H and 2 × Tol-H), 7.39 (2 H, d, *J* = 8.0, 2 × Tol-H), 6.25 [1 H, s, CH(Cl)Ts] and 2.49 (3 H, s, CH_3); *m*/*z* 393 (7%), 391 (34), 389 (40, isotopic $M^{+\bullet}$), 355 (9), 290 (16), 254 (17), 253 (13), 238 (11), 236 (66), 234 (100), 200 (9), 174 (4), 164 (19), 155 (3), 139 (6), 91 (10) and 65 (8) (Found: M^+, 389.0044. Calc. for $C_{19}H_{13}Cl_2NO_2S$; *M*, 389.0044) (Found: *m*/*z*, 233.9877. Calc. for $C_{12}H_6Cl_2N$; $M^{+\bullet}$ − SO_2Tol, 233.9877).

4-*Chloro*-2-(p-*tolylsulphonylmethyl*)-1-*naphthonitrile* (**17**).—M.p. 219–220 °C (from hexane–$CHCl_3$) (Found: C, 63.05; H, 4.1; N, 3.6; Cl, 10.15. $C_{19}H_{14}ClNO_2S$ (*M* = 355.84) requires C, 64.13; H, 3.97; N, 3.94; Cl, 9.96%); ν_{max}($CHCl_3$)/cm^{-1} 2230 (CN); δ_H[500 MHz; $CDCl_3$–$(CD_3)_2SO$ 5:1] 8.37–8.32 (1 H, m, 8-H), 8.18–8.13 (1 H, m, 5-H), 7.85–7.78 (2 H, m, 6- and 7-H), 7.65 (1 H, s, 3-H), 7.63 and 7.34 (AA'XX', Tol-H), 4.81 (2 H, s, CH_2), 2.46 (3 H, s, CH_3); NOE effect: CH_2 (4.81 ppm) was irradiated: 3-H (5.82%), 5-H (0.02%) and 8-H (0.13%); *m*/*z* 357 (4%) and 355 (12, isotopic $M^{+\bullet}$), 202 (33), 200 (100), 174 (4), 165 (8), 164 (14), 155 (3), 149 (4), 140 (4), 139 (4), 138 (5), 123 (3), 111 (5), 97 (8), 91 (13), 83 (6), 65 (6), 59 (11), 57 (16), 43 (10) (Found: M^+, 355.0424. Calc. for $C_{19}H_{14}ClNO_2S$: *M*, 355.0434).

2-*Chloro*-4-(p-*tolylsulphonylmethyl*)-1-*naphthonitrile* (**18**).—M.p. 227–228 °C (from hexane–$CHCl_3$) (Found: C, 63.8; H, 3.45; N, 3.75; Cl, 10.0; S, 8.55. $C_{19}H_{14}ClNO_2S$ (*M* = 355.84) requires C, 64.13; H, 3.97; N, 3.94; Cl, 9.96; S, 9.01%); ν_{max}($CHCl_3$)/cm^{-1} 2225 (CN), δ_H[500 MHz; $CDCl_3$–$(CD_3)_2SO$ 10:1] 8.20 (1 H, d, *J* = 8.4, 8-H), 7.96 (1 H, d, *J* = 8.5, 5-H), 7.75–7.70 (1 H, m, 6-H), 7.62–7.57 (1 H, m, 7-H), 7.56 and 7.27 (4 H, 2 × d, *J* = 8.1, Tol-H), 7.31 (1 H, s, 3-H), 4.83 (2 H, s, CH_2) and 2.43 (3 H, s, CH_3); NOE effect: CH_2 (4.83 ppm) was irradiated: 3-H (6.76%), 5-H (10.01%) and 8-H (0.15%); *m*/*z* 357 (4%) and 355 (12%) (isotopic $M^{+\bullet}$), 202 (32), 200 (100), 174 (6), 165 (8), 164 (13), 155 (3), 139 (3), 138 (3), 123 (3), 111 (5), 97 (8), 91 (10), 83 (9), 71 (10), 69 (10), 57 (17), 55 (8) and 43 (10).

1,2-*Bis*(*tolylsulphonyl*)-1,1a,1b,2,2a,6b-*hexahydrodicyclopropa*[a,c]*naphthalene*-2a,6b-*dicarbonitrile* (**20**).—M.p. 297–300 °C (from ethanol) (Found: C, 65.3; H, 4.15; N, 5.0; S, 12.4. $C_{28}H_{22}N_2O_4S_2$ (M = 514.61) requires C, 65.35; H, 4.31; N, 5.44; S, 12.46%); $\nu_{max}(CHCl_3)/cm^{-1}$ 2240 (CN); δ_H(200 MHz; $CDCl_3$) 8.40–7.25 (12 H, m, H-Ar), 3.40–3.30 and 3.03–2.93 (4 H, AA'XX', 2-, 3-, 9- and 10-H) and 2.50 (6 H, s, 2 × CH_3); *m*/*z* 514 ($M^{+\bullet}$, 3%), 359 (20), 295 (91), 280 (22), 268 (25), 253 (10), 219 (17), 204 (14), 203 (16), 191 (16), 155 (26), 139 (66), 91 (100), 69 (18), 65 (24), 57 (18) and 43 (19).

2-(p-*Tolylsulphonylmethyl*)*naphthalene*-1,4-*dicarbonitrile* (**21**).—M.p. 244–245 °C (from ethanol) [Found: C, 69.1; H, 3.8; N, 8.05; S, 9.05. $C_{20}H_{14}N_2O_2S$ (M = 346.40) requires C, 69.35; H, 4.07; N, 8.09; S, 9.26%]; $\nu_{max}(CHCl_3)/cm^{-1}$ 2225 (CN); δ_H(200 MHz; $CDCl_3$) 8.45–7.20 (8 H, m, ArH), 8.03 (1 H, s, 3-H), 4.72 (2 H, s, CH_2) and 2.43 (3 H, s, CH_3); *m*/*z* 346 ($M^{+\bullet}$, 12%), 192 (15), 191 (100), 164 (14), 155 (40), 91 (37) and 65 (13).

4-(p-*Tolylsulphonylmethyl*)*naphthalene*-1,2-*dicarbonitrile* (**23**).—M.p. 255–257 °C (from ethanol) (Found: C, 68.65; H, 4.0; N, 8.3; S, 8.95. $C_{20}H_{14}N_2O_2S$ (M = 346.40) requires C, 69.35; H, 4.07; N, 8.09; S, 9.26%); ν_{max}(KBr)/cm^{-1} 2220 (CN); δ_H(200 MHz; $CDCl_3$) 8.45–7.30 (9 H, m, ArH), 4.83 (2 H, s, CH_2) and 2.45 (3 H, s, CH_3); *m*/*z* 346 ($M^{+\bullet}$, 13%), 192 (17), 191 (100), 165 (16), 164 (17), 155 (41), 91 (37), 65 (15), 44 (19) and 28 (15).

Reaction of 1-*Nitronaphthalene* (**6**) *with the Anion of Chloromethyl* p-*Tolyl Sulphone* (**1**).—The carbanion of chloromethyl *p*-tolyl sulphone (2.2 mmol) was prepared in DMF (7 cm^3) as in procedure (*c*) and was then added dropwise over 2 min to a solution of 1-nitronaphthalene (173 mg, 1.0 mmol) in DMF (3 cm^3). The reaction was continued at room temperature for 1.5 h and treated as in procedure (*c*) to give **7** (29%) and **8** (51%).

Acknowledgements

This work was supported by a grant CPBP 01.13, from the Polish Academy of Sciences.

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Paper 1/00387I
Received 28*th January* 1991
Accepted 22*nd March* 1991