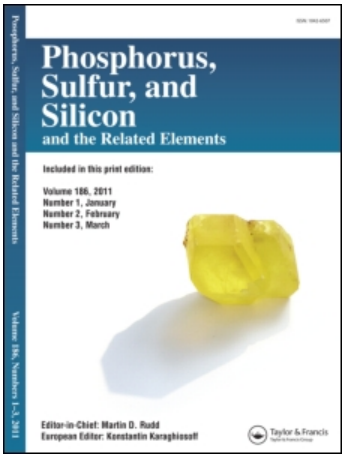

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DL CAMPHOR 3-SULFONIC ACID AND OTHER KETO α-SULFONIC ACIDS

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DL CAMPHOR 3-SULFONIC ACID AND OTHER KETO α-SULFONIC ACIDS

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Sulfur trioxide-dioxan reagent has been used to convert acetophenone, 4-t-butylcyclohexanone, DL camphor and menthone to the α-sulfonic acids (**3**, **5**, **2** and **12**). Attempts to convert **3**, **5** and **12** to the corresponding sulfonyl chlorides were unsuccessful. However, camphor-3-sulfonyl chloride (**6**) was obtained, and was characterized as the amides (**7–10**) and the *N*-phenylhydrazide (**11**). With chlorosulfonic acid, **3** afforded the 2ω-disulfonyl chloride (**4**). The mechanism of α-sulfonation is briefly discussed together with the spectral data and results of preliminary biological screening

INTRODUCTION

The work described in this paper forms part of our general program on the chemistry and biological activity of organic sulfonyl derivatives.[1–3] In particular, it extends previous studies of camphor-10-sulfonyl derivatives.[4,5]

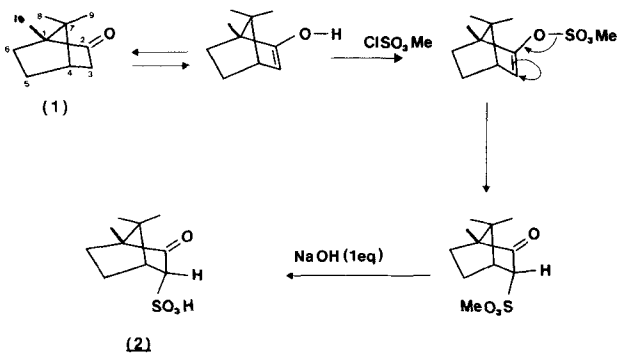
Camphor is known[6–8] to form three different sulfonic acids depending on the reagents used. Acetyl sulfonate yields the 10-sulfonic acid; chlorosulfonic or fuming sulfuric acid the 8-sulfonic acid; and methyl chlorosulfonate followed by hydrolysis the 3-sulfonic acid. The 10-acid has been extensively studied and the position of sulfonation has been confirmed by X-ray crystallography.[9–10] The 8-acid has been studied both by X-ray crystallography[11] and by two dimensional NMR[12]: both techniques indicate that sulfonation occurs on the *gem*-methyl group remote from the carbonyl group. The formation of the 8- and 10-acids is considered[13–15] to involve Wagner and Nemetkin rearrangements of the derived carbocations formed in the acidic media.

In contrast, comparatively little work has been reported on camphor-3-sulfonic acid and derivatives.

DISCUSSION

Camphor (**1**) is reported[16,17] to react with methyl chlorosulfonate, under essentially neutral conditions, to give the 3-sulfonic acid (**2**); this precludes involvement of carbocations and the reaction almost certainly goes *via* the enolic form of camphor (Scheme 1):

Camphor is known[18] to react readily with bromine, presumably by a similar mechanism, to give 3-bromocamphor. X-ray studies showed[11] that the bromine atom is in the *endo*-configuration which suggested that in **2**, the sulfonic acid



(1) (2)

SCHEME 1

group is also *endo* and this assignment was supported by NMR spectroscopy.[19] Camphor-3-sulfonic acid (**2**) has always previously been obtained using methyl chlorosulfonate as the sulfonating reagent; however it is well-established[20] that sulfur trioxide-dioxan complex is an excellent general reagent for the α-sulfonation of ketones. We prepared the sulfur trioxide-dioxan reagent as previously described[21] and successfully used it for the sulfonation of acetophenone (cf. Ref. 22) to give the ω-sulfonate (**3**) (Scheme 2). **3** with hot excess chlorosulfonic acid afforded the disulfonyl chloride (**4**), identical to the compound previously reported by Suter and Weston.[23] The reagent similarly converted 4-t-butylcyclohexanone into the 2-sulfonate (**5**).

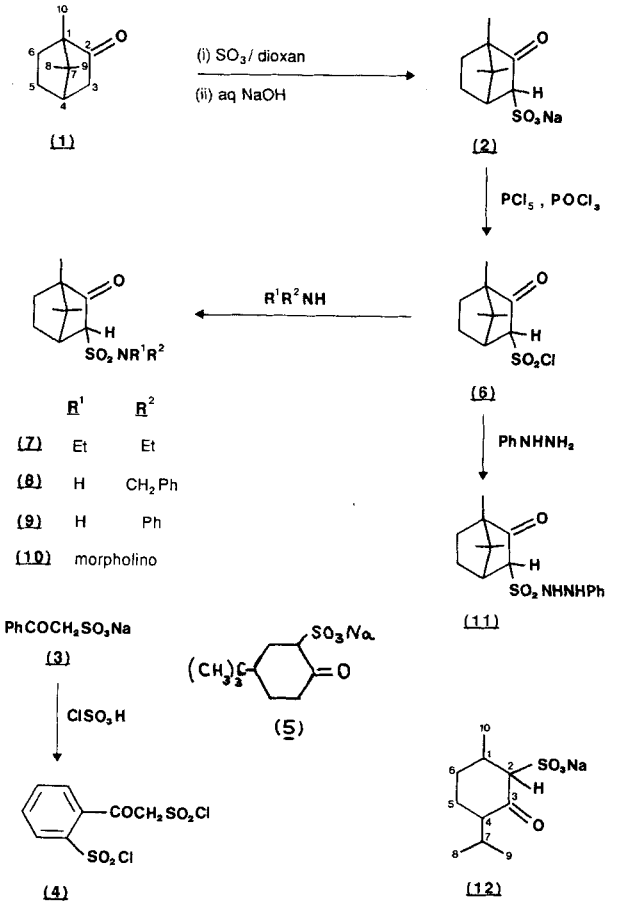
We found that DL camphor (**1**) reacted with sulfur trioxide-dioxan reagent followed by neutralisation (NaOH) to give sodium camphor-3-sulfonate (**2**), which was characterized as the S-benzylisothiouronium salt. **2** by fusion with phosphorus pentachloride gave a low yield (26%) of the sulfonyl chloride (**6**). Subsequent condensation of **6** with diethylamine, benzylamine, aniline, morpholine and phenylhydrazine afforded moderate yields (40–66%) of the amides (**7–10**) and the hydrazide (**11**).

On the other hand, the attempts to obtain camphor-3-sulfonyl azide or hydrazide by treatment of **6** with sodium azide in aqueous acetone or hydrazine hydrate only resulted in camphor-3-sulfonic acid.

The failure is a reflection of the special sensitivity of camphor-3-sulfonyl chloride (**6**) towards base-catalysed hydrolysis. The sulfonic acid is stabilized, cf, the sulfonyl chloride (**6**), by intramolecular (O—H · · · O) hydrogen bonding involving the adjacent carbonyl group (Figure 1).

This argument also explains the failure to convert the keto-sulfonic acids (**3**, **5** and **12**) into the corresponding sulfonyl chlorides. With camphor-8- and 10-sulfonic acids, the formation of the sulfonyl chlorides was much easier because now intramolecular hydrogen-bonding in the acids is not favoured since it involves 8- and 7-membered ring intermediates.

The IR spectra showed the normal absorption bands associated with the N—H, C=O and SO_2 groups.[24] In the proton NMR spectra of the camphor-3-sulfonyl derivatives, the resonance due to the C-3 hydrogen atom moved downfield (δ 4.0 ppm) as a result of the attached electron–withdrawing sulfonyl group. The



SCHEME 2

deshielding influence of the sulfonyl group was also observed in the ^{13}C NMR spectra where the carbon-3 resonance shifted downfield (δ 67 ppm). The 9- and 10-methyl resonances are considered to appear at a slightly lower field than the 8-methyl group due to their closer proximity to the carbonyl group. The MS of the majority of the compounds showed the molecular ions (M^+), although the hydrazide (**11**) suffered extensive decomposition in agreement with previous results.[25]

The compounds described have been examined for biocidal activity against insects, weeds and fungi; there was no insecticidal or herbicidal activity, but several showed antifungal properties.

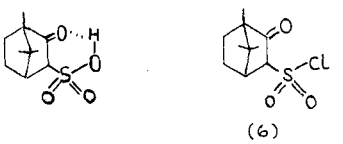


FIGURE 1

The preliminary fungicide screen was carried out at 100 ppm against grey mould on lettuce, vine downy mildew, potato late blight, wheat rust, apple and barley powdery mildew and rice blast. Compounds **7**, **10** and **11** were active; **7** and **10** against powdery mildew and **11** against rice blast fungus.

EXPERIMENTAL

Elemental analyses were carried out by ICI plc (Pharmaceuticals Division, Alderley Park, Cheshire, England). Melting points were determined using a Gallenkamp electric apparatus and are uncorrected. IR spectra were measured as Nujol mulls on a Unicam SP 1000 spectrophotometer. NMR spectra were recorded on a Bruker WP 80 spectrometer using TMS as internal standard, an asterisk indicates signals that are removed by D_2O treatment. TLC was performed using Camlab Polygram silica gel plates sensitized to UV 254 nm.

Preparation of sulfur trioxide-dioxan complex[21]

Sulfur trioxide was distilled from 65% oleum into dry ethylene dichloride (180 ml) contained in a weighed flask cooled in an ice-water bath. An equimolar amount of dioxan (purified by refluxing with sodium) was gradually added to the stirred sulfur trioxide solution in an ice-salt bath so that the internal temperature is kept <5°C (addition takes ca. $4\frac{1}{2}$ hours).

Sodium acetophenone ω-sulfonate (**3**)

Acetophenone (24 g, 0.2 mol) was gradually added to sulfur trioxide-dioxan complex (0.2 mol) so that the temperature of the mixture is maintained <35°C. After addition had been completed (ca. 1 hour), the mixture was stirred for 2 hours and poured into water (300 ml). The aqueous layer was separated and neutralized to pH7 with aqueous sodium hydroxide, and was evaporated to dryness. The solid residue was extracted with boiling 60% aqueous ethanol (70 ml); the extract on cooling gave (**3**) as colourless crystals (31 g, 70%) mp 270°C. (Found: C, 42.3; H, 3.1; S, 14.3. $C_8H_7O_4S.Na\frac{1}{4}H_2O$ requires C, 42.4; H, 3.1; S, 14.1%. IR ν_{max} 1680 (C=O), 1600 (ArC=C) cm^{-1}.
NMR (MeOH-d_4) δ: 8.1–7.4 (m, 5H, ArH), 4.5(s, 2H, CH_2SO_2).

The sodium salt (**3**) was characterized by reaction with an aqueous solution of S-benzylisothiouronium chloride to give the S-benzylisothiouronium salt (80%), mp 130–132° (lit.[22] 152°C). (Found: C, 51.8; H, 4.9; N, 7.7. $C_{16}H_{18}N_2O_4S_2\frac{1}{4}H_2O$ requires C, 51.8; H, 4.9; N, 7.6%). IR ν_{max} 3370, 3330, 3150 (NH), 1660(C=O), 1600 (ArC=C), 1360, 1180 (SO_2) cm^{-1}.

MS no M^+(366), 166, 124, 105, 91, 65, 45.

2-Chlorosulfonylacetophenone-ω-Sulfonyl Chloride (**4**)

Sodium acetophenone-ω-sulfonate (**3**) (5 g, 0.002 mol) was added portionwise to chlorosulfonic acid (13.1 g, 0.01 mol) with swirling; the mixture was heated on the steam bath for $1\frac{1}{2}$ hours. The solution was poured onto crushed ice to give a white precipitate which was washed with water and ether to give **4** (1.3 g, 20%) mp 196–197°C (lit.[23] 194–195°C). TLC (EtOAc-cyclohexane 1:1) one spot R_F 0.38.

4 (0.5 g, 0.0016 mol) was stirred with aniline (0.6 g, 0.0064 mol) in ether (20 ml) for 2 hours. Evaporation gave a yellow gum which by trituration with water and ether gave the dianilide derivative (0.5 g, 70%) mp 210–212°C (lit.[23] 209–210°C). (Found: C, 55.9; H, 4.2; N, 6.6. $C_{20}H_{18}N_2O_5S_2$ requires C, 55.8; H, 4.2; N, 6.5%).

TLC (EtOAc-cyclohexane 1:1) one spot R_F 0.78.

IR ν_{max} 3300 (NH), 1700 (C=O), 1600 (ArC=C), 1350, 1160 (SO_2) cm^{-1}.

Sodium 4-t-butylcyclohexanone-2-sulfonate (**5**)

4-t-Butylcyclohexanone (30.8 g, 0.02 mol) was reacted with sulfur trioxide-dioxan complex (0.02 mol) as previously described.

Neutralization with aqueous sodium hydroxide afforded **5** (38.4 g, 75%) m.p. 145–147°C (Found: 44.9; H, 7.0. $C_{10}H_{17}O_4S{\cdot}Na\frac{1}{2}H_2O$ requires C, 45.2; H, 6.8%). IR ν_{max} 1720 (C=O), 1360, 1160 (SO_2) cm^{-1}. **5** was characterized as the S-benzylisothiuronium salt needles (70%) m.p. 165–166°C. (Found: C, 53.6; H, 6.9; N, 7.2. $C_{18}H_{28}N_2O_4S_2$ requires C, 54.0; H, 7.0; N, 7.0%). IR ν_{max} 3350, 3150 (NH), 1715 (C=O), 1380, 1180 (SO_2) cm^{-1}. NMR (DMSO-d_6) δ: 9.1* (s, 2H, NH_2), 7.9* (s, 2H, NH_2) 7.50–7.20 (m, 5H, ArH), 4.45 (s, 2H, $PhCH_2$), 2.5–1.45 (m, 8H, cyclohexyl H), 0.85 (s, 9H, Me).

DL Sodium Camphor-3-sulfonate (**2**)

A solution of camphor (1) (30.4 g, 0.2 mol) in dichloromethane (50 ml) was added dropwise to freshly prepared sulfur trioxide-dioxan complex (0.2 mol) with stirring so that the temperature was maintained <35°C. The mixture was then stirred for 4 hours and poured into water (300 ml); the aqueous layer was separated and neutralized to pH7 with 5M aqueous sodium hydroxide. The solution was evaporated under reduced pressure; the solid residue was extracted with boiling 60% aqueous ethanol (3 × 80 ml). Cooling gave the sodium sulfonate (**2**) (37 g, 73%), m.p. 250°C (decomp.) (Found: C, 44.6; H; 5.6; S, 12.8. $C_{10}H_{15}O_4SNa.\frac{1}{2}H_2O$ requires C, 45.8; H, 6.1; S, 12,2%). IR ν_{max} 1750 (C=O), 1380, 1180 (SO_2) cm^{-1}. The sulfonate (**2**) was characterized by formation of the S-benzylisothiouronium salt (80%), m.p. 175–177°C. (Found: C, 53.6; H, 6.5; N, 7.0; S, 16.1, $C_{18}H_{26}N_2O_4S_2$. H_2O requires C, 53.7; H, 6.6; N, 7.0; S, 15.9%). TLC (EtOH) one spot R_F 0.9. IR ν_{max} 3360 (NH), 1730 (C=O), 1370, 1180 (SO_2), 1600 (ArC=C) cm^{-1}.

NMR ($CDCl_3$): δ9.05* (s, 2H, SO_3NH_2), 7.85* (s, 2H, NH_2-C), 7.35–7.25 (m, 5H, ArH), 4.45 (s, 2H, CH_2Ph), 3.95 (d, 1H, C-3H, J 5.5 Hz), 2.5–1.6 (m, 5H, cyclohexyl H), 0.95 (s, 3H, 10-Me), 0.85 (s, 3H, 9-Me), 0.75 (s, 3H, 8-Me) ^{13} CNMR ($CDCl_3$)δ: 211.7 (C-2), 171 (C(NH_2-S), 133.6–128.4 (5ArC), 69.7(C-3), 59.5(C-1), C-4(47.5), 45.6(C-7), 35.8(S-CH_2), 30.5(C-5) 21.1(C-6), 19.6(C-10), 18.7(C-9), 9.9(C-8).

MS: no M^+ (398), 354, 138, 120, 91, 83, 64, 48

DL Camphor-3-Sulfonyl Chloride (**6**)

Sodium DL camphor-3-sulfonate (**2**) (10 g, 0.039 mol) was mixed with phosphorus pentachloride (16.4 g; 0.078 mol) at at room temperature. The mixture was heated in an oil bath at 120°C for 1 hour (after which period hydrogen chloride evolution ceased). The solution was poured onto crushed ice; the semi-solid precipitate collected, washed with ice-water, and dried over P_2O_5 for 24 hours to give **6** (2.6 g, 26%), m.p. 45–48°C.

TLC (EtOAc-cyclohexane 1:1) one spot R_F 0.90. Sodium fusion test positive for Cl and S. IR ν_{max} 1760 (C=O), 1360, 1170 (SO_2) cm^{-1}.

MS: 250 (M^+), 151 (camphor), 123, 107, 95, 83, 65, 55, 48.

DL Camphor-3-N,N-diethylsulfonamide (**7**)

Diethylamine (0.58 g, 0.008 mol) in THF (10 ml) was added dropwise to a stirred solution of camphor-3-sulfonyl chloride (**6**) (1 g, 0.004 mol). The suspension was stirred for 6 hours, the solid was filtered off and the filtrate evaporated under reduced pressure. The oily residue was extracted with ether (100 ml); the extract was washed with 1 M hydrochloric acid (1 × 20 ml), H_2O (2 × 20 ml) dried (Na_2SO_4) and evaporated to give **7** as an oil (0.45 g, 40%). TLC (ethyl acetate-cyclohexane 1:1) one spot R_F 0.73. $n_D^{20} = 1.4980$. Beilstein test negative. (Found: C, 58.2; H, 8.6; N, 4.6. $C_{14}H_{25}NO_3S$ requires C 58.5; H, 8.7; N, 4.9%). IR ν_{max} 1760 (C=O), 1380, 1140 (SO_2) cm^{-1}.

MS: 287 (M^+), 272 (M-Me), 258(M-Et), 244, 220, 205, 151 (camphor), 137, 123, 109, 95, 91, 72, 58.

DL Camphor-3-N-benzylsulfonamide (**8**)

A mixture of camphor-3-sulfonyl chloride (**6**) (1 g, 0.004 mol) and benzylamine (0.9 g, 0.008 mol) in THF (15 ml) was stirred at room temperature for 6 hours. A similar work up procedure to 7 above afforded **8** (0.65 g, 51%), m.p. 120–121°C. TLC (EtOAc-petroleum ether 1:1) one spot R_F 0.84. (Found: C, 63.2; H, 7.0; N, 3.7. $C_{17}H_{23}NO_3S$ requires C 63.5; H, 7.2; N, 3.4%).

IR ν_{max} 3330 (NH), 1750 (C=O), 1610 (ArC=C), 1330, 1445 (SO_2) cm^{-1}. NMR ($CDCl_3$) δ: 7.65–7.05 (m, 5H, ArH), 5.2* (s, 1H, NH), 4.35 (d, 2H, CH_2Ph, J 8.0 Hz), 3.6 (d, 1H, C-3H, J 5.2 Hz), 2.55–1.4 (m, 5H, cyclohexyl H), 1.0 (s, 3H, 10-Me), 0.95 (s, 3H, 9-Me), 0.65 (s, 3H, 8-Me). ^{13}CNMR ($CDCl_3$)δ: 209 (C-2), 136–128 (Ar-C), 70(C-3), 59(C-1), 47.5 (CH_2-NH), 46(C-4), 45 (C-7), 30(C-5), 21(C-6), 19(C-10), 18(C-9), 9(C-8). MS: 320 (M-1), 257 (M-SO_2), 205, 151 (camphor), 124, 106, 91, 77, 69, 55, 51.

DL Camphor-3-N-phenylsulfonamide (**9**)

A mixture of camphor-3-sulfonyl chloride (**6**) (1 g, 0.004 mol) and aniline (0.89, 0.008 mol) in THF (25 ml) was stirred at room temperature for 18 hours. The usual procedure afforded **9** (0.72 g, 59%), m.p. 169–170°C. TLC (EtOAc-cyclohexane 1:1) one spot R_F 0.33. (Found: C, 62.6; H, 7.1; N, 4.5, $C_{16}H_{21}NO_3S$ requires C, 62.5; H, 6.8; N, 4.6%). IR ν_{max} 3260 (NH), 1745 (C=O), 1600 (ArC=C), 1345, 1150 (SO_2) cm^{-1}.

NMR ($CDCl_3$)δ: 7.5–7.2 (m, 5H, ArH), 7.15* (s, 1H, NH), 3.85 (d, 1H, C-3H, J 5.2 Hz), 2.5–1.65 (m, 5H, cyclohexyl H), 1.0 (s, 3H, 10-Me), 0.95 (s, 3H, 9-Me), 0.70 (s, 3H, 8-Me).

^{13}CNMR ($CDCl_3$)δ: 209 (C-2), 136–126 (ArC), 66(C-3), 59 (C-1), 47 (C-4), 46 (C-7), 30 (C-6), 22(C-5), 19.5 (C-10), 18.5 (C-9), 10 (C-8).

MS: 307 (M^+), 151 (camphor), 123, 107, 93 (aniline), 83, 69, 55.

DL Camphor-3-sulfonylmorpholidate (**10**)

Camphor-3-sulfonyl chloride (**6**) (1 g, 0.004 mol) was stirred with morpholine (0.7 g, 0.008 mol) in THF (30 ml) for 16 hours. Evaporation under reduced pressure and extraction with ether (100 ml) afforded **10** as a yellow oil (0.8 g, 66%). TLC (EtOAc; cyclohexane 1:5) one spot R_F 0.40. (Found: C, 55.5; H, 7.8; N, 4.7 $C_{14}H_{23}NO_4S$ requires C, 55.8; H, 7.6; N, 4.6%).

MS: 301 (M^+), 215 (M-morpholino), 151 (camphor), 107, 86 (morpholine), 69, 55.

DL Camphor-3-N-phenylsulfonohydrazide (**11**)

A solution of freshly redistilled phenylhydrazine (0.86 g, 0.008 mol) in THF (8 ml) was added dropwise to a stirred solution of camphor-3-sulfonyl chloride (**6**) (1 g, 0.004 mol) in THF (20 ml). The mixture was stirred overnight to give **11** (0.52 g, 48%), m.p. 107–109°C. Beilstein test was negative. TLC (cyclohexane: EtOAc 3:2) one spot R_F 0.6. (Found: C 59.4; H, 6.8; N, 8.5, $C_{16}H_{22}N_2O_3S$ requires C, 59.6; H, 6.8; N, 8.7%). IR ν_{max} 3340, 3300 (NH), 1745 (C=O), 1605 (ArC=C), 1330, 1155 (SO_2) cm^{-1}.

NMR ($CDCl_3$)δ: 7.5–6.9 (m, 5H, ArH), 6.5* (s, 2H, NH), 4.2 (d, 1H, C-3H, J 5.2 Hz), 3.6–1.8 (m, 5H, cyclohexyl H), 1.05 (s, 3H, 10-Me), 1.0 (s, 3H, 9-Me), 0.8 (s, 3H, 8-Me).

MS (electron impact) no M^+ (322), 152 (camphor), 109, 95, 91, 77, 44, 64, 51.

MS (chemical ionization) showed the $M^+ + 1$ ion (323).

Sodium Menthone-2-sulfonate (**12**)

Menthone (25.3 g, 0.16 mol) was added dropwise to stirred freshly prepared sulfur trioxide reagent (0.16 mol) so that the temperature was kept <35°C. The mixture was stirred at room temperature for 3 hours and poured onto water (250 ml). The aqueous layer was neutralized with aqueous sodium hydroxide and the solution evaporated to dryness. The white residue was extracted with boiling 75% aqueous ethanol (2 × 50 ml) to give **12** (30.2 g, 74%) m.p. 125°C (decomp).

The sodium sulfonate (**12**) was characterized by formation of the S-benzylisothiouronium salt (72%), m.p. 138–140°C. TLC (EtOH) one spot R_F 0.60. (Found: C, 53.8; H, 7.1; N, 7.0, S, 15.8. $C_{18}H_{28}N_2O_4S_2$ requires C, 54.0; H, 7.0; N, 7.0; S, 16.0%). NMR ($CDCl_3$) δ: 8.8* (s, 4H, NH), 7.4–7.0 (m, 5H, ArH), 4.25 (s, 2H, CH_2Ph), 3.90 (d, 1H, C-2H), 2.6–1.8 (m, 6H, cyclohexyl H), 1.9 (s, 9H, Me).

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