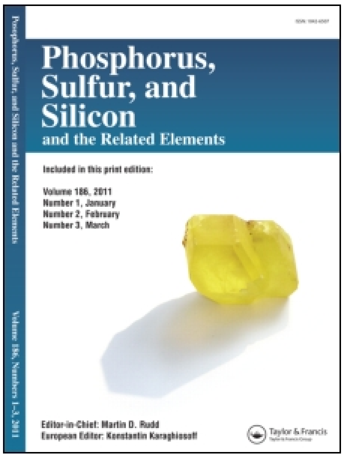

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SOME SULFONYL DERIVATIVES OF CAMPHOR, N-PHENYLSUCCINIMIDE, 2-AMINOPHENOL AND SUBSTITUTED BENZOIC ACIDS

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SOME SULFONYL DERIVATIVES OF CAMPHOR, N-PHENYLSUCCINIMIDE, 2-AMINOPHENOL AND SUBSTITUTED BENZOIC ACIDS

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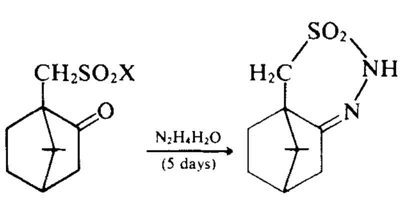
Camphor-10-sulfonyl chloride (**1**) reacts with hydrazine to give the hydrazide (**2**), if the reaction is prolonged the benzothiadiazine dioxide (**3**) is obtained. *p*-Succinimidobenzenesulfonyl chloride (**9**) with hydrazine (1 mol.) gave the hydrazide (**10**), but with excess hydrazine the amide ring was opened to give the bis-hydrazide (**13**). Anisamide (**23**) was converted to the chloride (**24**) and the dimethylamide (**25**) and acetone hydrazone (**26**). Reaction of the hydrazide with anisaldehyde gave the 4,4′-dimethoxybenzalazine (**27**). 2-Acetoxyacetanilide (**28**) with chlorosulfonic acid afforded a mixture of 4-acetamido-3-hydroxy- and 3-acetamido-4-hydroxy-benzenesulfonyl chlorides (**29**,**30**). Chlorosulfonation of 4-acetoxyacetanilide gave the sulfonyl chloride, but with 3-acetoxyacetanilide no pure product was isolated.

INTRODUCTION

The work reported here is a continuation of our program on the synthesis and reactivity of sulfonyl derivatives as candidate pesticides.[1-3]

DISCUSSION

Previous efforts[4] to convert camphor-10-sulfonyl chloride (**1**) (Scheme 1) to the hydrazide (**2**) gave the hexahydrobenzothiadiazine-3,3-dioxide (**3**). Further examination of reaction of the chloride (**1**) with hydrazine showed that with hydrazine (2 mols.) in ethanol at −10° (3h) or in benzene at room temperature (1h) the chlo-



(**3**)

X = Cl (**1**); $NHNH_2$ (**2**); $NHN{=}C(CH_3)_2$ (**4**); $NHN{=}CHC_6H_4NO_2$-*p* (**5**); N_3 (**6**); N = $P(C_6H_5)_3$ (**7**); NHC_6H_5 (**8**)

SCHEME 1

TABLE I

Camphor-10-Sulfonyl Derivatives

No	Yield (%)	M.p., °C	Formula	Found (%) C	Found (%) H	Found (%) N	Found (%) S	Required (%) C	Required (%) H	Required (%) N	Required (%) S	R_F	Lit. m.p. and Ref.
1	97	65–67										0.53[a]	65–67[4]
2	35	80–82	$C_{10}H_{19}N_2O_3S$	48.4	7.5	11.5	13.0	48.6	7.7	11.3	12.95	0.30	
3	72	182–184	$C_{10}H_{16}N_2O_2S$	52.4	6.8	12.2	—	52.6	7.05	12.3	—	0.80[b]	186–188[4]
4	82	119–121	$C_{13}H_{23}N_2O_3S$	54.4	7.8	9.6	10.9	54.35	8.0	9.75	11.15	—	
5	78	142–144	$C_{17}H_{22}N_3O_5S$	53.6	5.6	11.1	—	53.7	5.8	11.05	—	—	
7	26	215–218	$C_{28}H_{31}NO_3PS$	68.2	6.1	2.8	—	68.3	6.1	3.0	—	—	
8	70	119–122	$C_{16}H_{22}NO_3S$	62.1	6.8	4.7	10.6	62.3	7.1	4.5	10.4	0.68	

[a] EtOH—H_2O 1:2. [b] MeOH.

	I.r. Data (ν_{max}, cm^{-1})	Ms. Data
2	3200 (NH), 1740 (CO), 1380, 1170 (SO_2)	246 (M^+), 215 (M—$NHNH_2$), 150 (M—SO_2NHNH_2), 120
3	3215 (NH), 1735 (CO), 1385, 1175 (SO_2)	228 (M^+), 163 (M—SO_2), 121
4	3200 (NH), 1740 (CO), 1380, 1170 (SO_2)	287 (M^+), 217, 199, 151, 123, 121
5	3210 (NH), 1740 (CO), 1595 (arom C=C), 1385, 1170 (SO_2)	No M^+ ion at 380, 217, 152, 123
7	1740 (CO), 1600 (arom C=C), 1360, 1160 (SO_2)	492 (M^+), 216 (M—$NP(C_6H_5)_3$), 152, 121
8	3220 (NH), 1740 (CO), 1600 (arom C=C), 1380, 1160 (SO_2)	308 (M^+), 216 (M—NHC_6H_5), 152, 121

ride was recovered. However with more hydrazine (4 mols.) in ethanol at 0° (2h), the hydrazide (**2**) was isolated and was characterized as the hydrazones (**4–5**) (Table I). If the reaction of the chloride (**1**) with hydrazine in ethanol is prolonged (5 days), the thiadiazine dioxide (**3**) was obtained as previously reported.[4]

This was also obtained by heating the hydrazide (**2**) indicating that formation from the chloride (**1**) is a two stage process:

$$(\mathbf{1}) \rightarrow (\mathbf{2}) \rightarrow (\mathbf{3})$$

Camphor-10-sulfonyl azide (**6**) failed to react with norbornene in boiling tetrahydrofuran (8h); although with triphenylphosphine reaction occurred to give the phosphinimine (**7**).

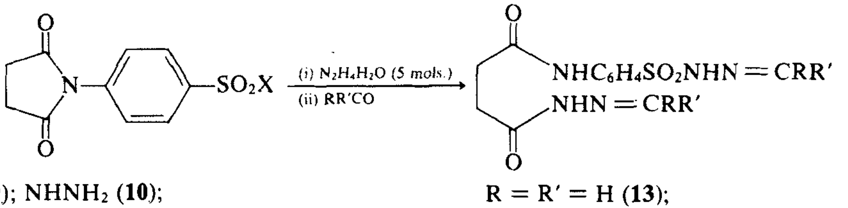
The chloride (**1**) reacted with aniline to give the *N*-phenylsulfonamide (**8**) which was resistant to hydrazine (4 mols.) in boiling methanol (8h). The lack of reactivity of the carbonyl group is probably a consequence of steric hindrance and N—H . . . O hydrogen bonding.

In previous work,[5] *p*-succinimidobenzenesulfonyl chloride (**9**) (Scheme 2) was reacted with hydrazine to give the bis-hydrazide (**13**) formed by cleavage of the imide ring.

The bis-hydrazide was formed when excess hydrazine (2 or 5 mols.) was used, and was converted to the hydrazones (**14–17**). The nucleophilic cleavage of the imide ring would be favored by the presence of the electron-withdrawing phenylsulfonyl group in (**9**) (cf. Refs. 6–7). With less hydrazine (1 mol.), the hydrazide (**10**), was obtained (Table II) this is of interest in view of the known fungicidal activity of imides.[8–9] The azide[5] (**18**) reacted with triphenylphosphine and norbornene to give the derivatives (**19,20**) (cf. Ref. 10); but reaction with boiling dimethyl sulfoxide (8h) gave a black tar. With dimethylamine and *p*-nitroaniline (2 mols.) the chloride (**9**) gave the amides (**21,22**) with no ring opening in contrast to the reaction with hydrazine (2 mols.).

N-Acetylanthranilic acid did not react with chlorosulfonic acid (5 or 7 mols.) at 65–85°; at higher temperatures (120–130°) extensive decomposition occurred. The failure may be due to steric hindrance by the bulky *ortho*-carboxylic acid group inhibiting mesomeric activation of the aromatic ring by the acetamido group.

p-Hydroxybenzoic acid with chlorosulfonic acid (5 mols.) also failed to give the 3-sulfonyl chloride (cf. Ref. 3). Chlorosulfonation of anisamide (**23**) was successful (Scheme 3). The chloride (**24**) was characterized as the derivatives (**25,26**) (Table III); with anisaldehyde the hydrazide gave the azine (**27**) (cf. Ref. 11).



X = Cl (**9**); $NHNH_2$ (**10**);
$NHN{=}C(CH_3)_2$ (**11**); $NHN{=}CHC_6H_5$ (**12**);
N_3 (**18**); $N = P(C_6H_5)_3$ (**19**);

(**20**); $N(CH_3)_2$ (**21**);

$NHC_6H_4NO_2$-*p* (**22**)

R = R' = H (**13**);
R = H, R' = *p*-$NO_2C_6H_4$ (**14**);
R = H, R' = C_6H_5 (**15**);
R = H, R' = *p*-ClC_6H_4 (**16**);
R = H, R' = *p*-HOC_6H_4 (**17**);

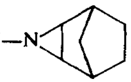
SCHEME 2

TABLE II

p-Succinimidobenzenesulfonyl Derivatives

No	Yield (%)	M.p., °C	Formula	Found (%) C	H	N	S	Required (%) C	H	N	S	R_F	Lit. m.p. and Ref.
9	63	196–198										0.58	195–198[5,13]
10	68	121	$C_{10}H_{11}N_3O_4S$	44.8	4.5	15.4	11.7	44.6	4.1	15.6	11.9	0.53	
11	70	116	$C_{13}H_{15}N_3O_4S$	50.3	5.1	13.8	—	50.5	4.85	13.6	—	0.42[a]	
12	65	145–148	$C_{17}H_{15}N_3O_4S$	56.9	4.1	11.5	—	57.1	4.2	11.75	—	0.40[a]	
13	60	165–166										0.37	169[5]
14	82	204–206	$C_{24}H_{21}N_7O_8S$	50.5	3.8	17.0	—	50.8	3.7	17.3	—		
15	66	214–216	$C_{24}H_{23}N_5O_4S$	60.2	4.8	14.4	—	60.4	4.8	14.7			
16	85	195	$C_{24}H_{21}Cl_2N_5O_4S$	52.5	4.0	12.9	—	52.7	3.8	12.8	—		
17	86	192	$C_{24}H_{23}N_5O_6S$	56.8	4.8	13.8	—	56.6	4.5	13.75	—		
18	80	140–142										0.47	142[5]
19	76	205	$C_{28}H_{23}N_2O_4PS$	65.2	4.2	5.2	6.0	65.4	4.5	5.4	6.2	0.38	
20	82	150	$C_{17}H_{18}N_2O_4S$	58.6	5.2	8.2	9.4	58.9	5.2	8.1	9.25	0.41	
21	90	202–204	$C_{12}H_{14}N_2O_4S$	51.0	5.0	9.8	—	51.1	5.0	9.9	—	0.27	
22	82	230–232	$C_{16}H_{13}N_3O_6S$	51.3	3.7	11.0	8.4	51.2	3.5	11.2	8.5		

[a] EtOAc—light petroleum (60–80°) 4:1

	I.r. Data (ν_{max}, cm^{-1})	Ms. Data
9	1710 (CO), 1590 (arom C=C), 1350, 1180 (SO_2)	273 (M^+), 238 (M—Cl), 174 (M—SO_2Cl), 132
10	3300 (NH), 1680 (CO), 1600 (arom C=C), 1350, 1170 (SO_2)	269 (M^+), 238 (M—$NHNH_2$), 174 (M—SO_2NHNH_2), 86
12	3250 (NH), 1685 (CO), 1595 (arom C=C),1360, 1165 (SO_2)	357 (M^+), 245
13	3300 (NH), 1700, 1680 (CO), 1600 (arom C=C), 1360, 1160 (SO_2)	
18	2140 (N_3), 1710 (CO), 1600 (arom C=C), 1350, 1170 (SO_2)	280 (M^+), 238 (M—N_3), 174 (M—SO_2N_3), 132
19	1720 (CO), 1595 (arom C=C), 1330, 1170 (SO_2)	
20	1715 (CO), 1600 (arom C=C), 1330, 1170 (SO_2)	346 (M^+), 238 (M—N ), 174, 132

N.m.r. Data (δ, p.p.m.)

11 9.86, s, 1H (NH); 7.8–7.6, m, 4H (4ArH); 2.1, d, 4H (2XCH_2); 1.81, s, 6H (2XCH_3).

21 8.0–7.15, m, 4H (4ArH); 2.80, d, 4H (2XCH_2); 2.15, s, 6H (2XCH_3)

TABLE III

5-Amido-2-Methoxybenzenesulfonyl Derivatives

No	Yield (%)	M.p., °C	Formula	Found (%)				Required (%)				R_F	Lit. m.p. and Ref.
				C	H	N	S	C	H	N	S		
24	68	134	$C_8H_8ClNO_4S$	38.3	3.4	5.7	12.7	38.5	3.2	5.6	12.8	0.62	
25	70	189–191	$C_{10}H_{14}N_2O_4S$	46.6	5.5	10.9	12.2	46.5	5.4	10.85	12.4	0.58	
26	34	195	$C_{11}H_{15}N_3O_4S$	46.2	5.0	14.6	—	46.3	5.3	14.7	—	0.59	
27	10	166–169										—	168[14]

I.r. Data (ν_{max}, cm^{-1}) N.m.r. Data (δ, p.p.m.)

25 3420, 3170 (NH), 1680 (CO), 1320, 1135 (SO_2) 258 (M^+), 242 ($M-NH_2$), 214, 194

N.m.r. Data (δ, p.p.m.)

24 8.40*, s, 2H ($CONH_2$); 8.2, d, 1H (Ar-6H); 7.91, d, 1H (Ar-4H); 7.32, d, 1H (Ar-3H); 2.70, s, 3H (OCH_3)

25 8.65*, s, 2H ($CONH_2$), 8.33, d, 1H (Ar-6H); 7.95, d, 1H (Ar-4H); 7.30, d, 1H (Ar-3H); 3.0, s, 6H ($N(CH_3)_2$; 2.72, s, 3H (OCH_3).

26 8.85*, s, 3H (CO, NH_2, SO_2NH); 8.55, d, 1H (Ar-6H); 8.10, d, 1H (Ar-4H); 7.30, d, 1H (Ar-3H); 3.50, s, 3H (OCH_3); 1.80, s, 6H ($N{=}C(CH_3)_2$.

27 8.64, s, 2H ($2XN{=}CH$); 7.83–7.05, m, 8H (8 ArH); 3.82, s, 6H ($2XOCH_3$).

TABLE IV

4-Acetamido-3-Hydroxybenzenesulfonyl Derivatives

No	Yield (%)	M.p., °C	Formula	Found (%)				Required (%)				R_F
				C	H	N	S	C	H	N	S	
31	90	176	$C_{14}H_{15}N_3O_4S$ $1H_2O$	49.6	5.0	11.9		49.9	4.8	12.4		0.67[a]
32	72	209	$C_{14}H_{14}N_2O_4S$	55.0	4.9	9.4	10.6	54.9	4.6	9.2	10.5	0.71[a]
33	46	176–177	$C_8H_8N_4O_4S$	37.6	3.1	22.0	12.3	37.5	3.1	21.9	12.5	0.58[a]

I.r. Data (ν_{max}, cm^{-1}) Ms. Data

31 3450 (OH), 3250 (NH), 1660 (CO), 1600 ($C{=}C$), 1340, 1170 (SO_2) 321 (M^+)

32 3450 (OH), 3250 (NH), 1660 (CO), 1595 ($C{=}C$), 1390, 1160 (SO_2) 306 (M^+)

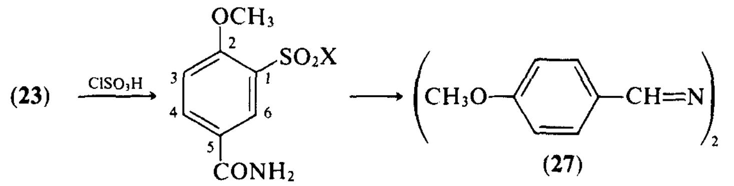
33 3460 (OH), 3300 (NH), 1660 (CO), 1600 ($C{=}C$), 1380, 1170 (SO_2) 256 (M^+), 214 ($M-CH_2CO$), 172, 108

N.m.r. Data (δ, p.p.m.)

31 10.85*, s, 1H (SO_2NH); 9.40, 9.28*, 2H (CON*H*, OH); 8.50, d, 1H(H_A); 7.54–6.64, m, 8H (C_6H_5, Ar-5H, -6H, N*H* Ph); 2.20, s, 3H ($COCH_3$).

33 1140, 1H (CONH); 9.38*, s, 1H(OH); 8.50, d, 1H (H_A); 7.60, dd, 1H (Ar-6H); 7.25, d, 1H(Ar-5H); 2.18, s, 3H ($COCH_3$).

*These signals were removed after shaking with D_2O.

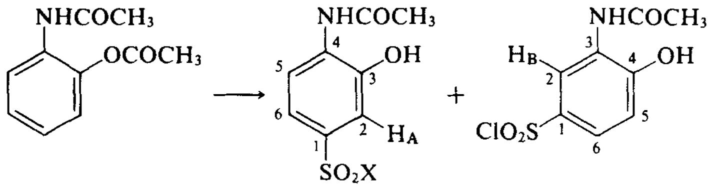


(27)

X = Cl (**24**); $N(CH_3)_2$ (**25**); $NHN{=}C(CH_3)_2$ (**26**)

SCHEME 3

2-Acetoxyacetanilide (**28**) with chlorosulfonic acid gave the sulfonyl chlorides (**29**,**30**) (Scheme 4); the i.r. spectrum showed that *O*-deacetylation had occurred, supported by a positive test with ferric chloride, and the fact that chlorosulfonation of 2-hydroxyacetanilide afforded the same products (cf. Ref. 3). The n.m.r. spectrum indicated that a mixture of the chlorides (**29**) and (**30**) was formed, mainly (**29**). The spectrum showed two doublets and a doublet of doublets with splittings of 7 and 2 Hz from the ABC systems. Calculation of the empirical shifts of the protons H_A and H_B using reference data[12] suggests that proton H_B is deshielded by approximately 0.6 ppm as cf. proton H_A. The observed shifts of the lowest field resonances are 9.05 ppm (minor component) and 8.45 ppm (major component). The fact that the chloride (**29**) is the major component indicates that the dominant directive influence is due to the acetamido rather than the hydroxy group which can be explained in terms of "out of plane" hydrogen bonding between the NH and CO groups.



(**28**) (**29**) (**30**)

X = Cl (**29**); $NHNHC_6H_5$ (**31**); NHC_6H_5 (**32**); N_3 (**33**)

SCHEME 4

The chloride (**29**) was characterized by preparation of the phenylhydrazide (**31**), anilide (**32**), and azide (**33**) (Table IV).

Reaction of 3-acetoxyacetanilide with chlorosulfonic acid (5 mols.) at 60–80° afforded black tars. 4-Acetoxyacetanilide by similar treatment gave 5-acetamido-2-hydroxybenzenesulfonyl chloride; but attempts to form derivatives with aniline, phenylhydrazine and dimethylamine were unsuccessful.

EXPERIMENTAL

I.r. spectra were recorded as Nujol mulls using a Perkin-Elmer 237 spectrophotometer. N.m.r. spectra were measured with a Varian HA 100 spectrometer using tetramethylsilane as internal standard and in deutrodimethylsulfoxide. Mass spectra were determined with an AEI MS9 spectrometer at 70 eV. Microanalyses by Butterworth Microanalytical Consultancy Limited, Teddington, England and I.C.I. Limited, Pharmaceuticals Division, Alderley Park, Cheshire, England. T.l.c. was carried out on silica gel G plates developed with iodine vapor using ethyl acetate-cyclohexane (2:1) except where otherwise stated.

Camphor-10-Sulfonyl Triphenylphosphinimine (**7**)

The sulfonyl azide[4] (**6**) (1g) was refluxed with triphenylphosphine (1.02g) in tetrahydrofuran (15 ml) for 3h.

Reaction of p-*Succinimidobenzenesulfonyl chloride* (**9**) *with Hydrazine*

(a) *excess of hydrazine* The chloride (4g) was gradually added to a stirred solution of hydrazine hydrate (3.6g; 5 mols.) in ethanol (15 ml) at 0°. After 30 min. at room temperature, recrystallization (MeOH) gave the bis-hydrazide (**13**).

(b) *With less Hydrazine* (*1 mol.*) The chloride (**9**) (1g) dissolved in tetrahydrofuran (15 ml) was treated dropwise with hydrazine hydrate (0.2g of 98%; 1 mol.) and triethylamine (0.4g; 1 mol.) in tetrahydrofuran (10 ml) at 0°. After 3h at 0°, filtration and trituration (ice-water) gave the *hydrazide* (**10**). Sodium fusion test: N, $S(+)^{ve}$, $Cl(-)^{ve}$.

Reactions of the Azide (**18**)

(a) *With norbornene* The azide (1g) was refluxed with norbornene (0.35g; 1 mol.) in tetrahydrofuran (15 ml) for 4h to give the *aziridine* (**20**) (from aqueous acetone).

(b) *With triphenylphosphine* The azide (1g) was boiled with triphenylphosphine (0.95g; 1 mol.) in tetrahydrofuran (20 ml) for 6h to give the *phosphinimine* (**19**) (from methanol).

5-Amido-2-Methoxybenzenesulfonyl Chloride (**24**; X = Cl)

Anisamide (**23**) (10g) was heated with chlorosulfonic acid (23 ml; 3 mols.) at 65° for 4h. Addition of ice gave the *chloride*.

*Bis-*p-*methoxybenzalazine* (**27**)

5-Amido-2-methoxybenzenesulfonohydrazide (3.5g) was refluxed with anisaldehyde (1.1 mol.) in ethanol (30 ml) for 1h to give the azine.

4-Acetamido-3-Hydroxybenzenesulfonyl Chloride (**29**) *and 3-Acetamido-4-Hydroxybenzenesulfonyl chloride* (**30**)

2-Acetoxyacetanilide (**28**) (10g) in chloroform (20 ml) was heated with chlorosulfonic acid (5 mols.) at 50–60° for 2h. Treatment with ice and trituration with tetrahydrofuran gave the *chlorides* (**29,30**) (10.2g; 79%), m.p. 161–163°. N.m.r. ($(CD_3)_2SO$) δ: 13.43; s, 1H (NH); 9.66, s, 1H (OH); 9.05, d, 1H ($\overset{*}{H}_B$); 8.45, d, 1H (H_A); 7.85, dd, 1H (Ar-6$\overset{*}{H}$); 7.65, dd, 1H (Ar-6H); 7.45, d, 1H (Ar-5$\overset{*}{H}$); 7.20, d, 1H (Ar-5H); 2.37, s, 3H ($NHCOCH_3$). The signals at δ 13.43, 9.66 were removed by D_2O treatment and those due to minor component (**30**) are shown by asterisk. Ms. showed the molecular ion (M^+, 251, 249), and fragment ions at 209, 207.

The major chloride (**29**) was characterized as the derivatives: (**31–33**) (Table IV).

5-Acetamido-2-Hydroxybenzenesulfonyl Chloride

4-Acetoxyacetanilide (20g) was heated with chlorosulfonic acid (5 mols.) at 60–70° for 2h. Trituration with ice-water and light petroleum (60–80°) gave the *sulfonyl chloride* as a fawn powder (15g); m.p. 280°. (Found: C, 35.7; H, 4.0; N, 6.1. $C_8H_8ClNO_4S$. $1H_2O$ requires C, 35.9; H, 3.8; N, 5.7%). (Sodium fusion was $(+)^{ve}$ for N, Cl, S). Ms. showed the molecular ion (M^+, 251, 249 in ratio 1:3).

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