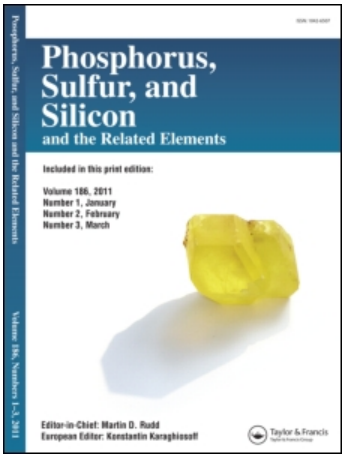

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REACTIONS OF N-(*p*-CHLOROSULFONYLPHENYL)MALEIMIDE

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REACTIONS OF N-(*p*-CHLOROSULFONYLPHENYL)MALEIMIDE

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N-Phenylmaleimide reacted with chlorosulfonic acid to give an excellent yield of the sulfonyl chloride (1), which with dimethylamine or aniline (2 equivs.) afforded the corresponding sulfonamides (2,3). However, use of more dimethylamine (4 equivs.) caused opening of the imido ring and addition to the double bond to yield the dimethylamide (12). Similar reaction with diethylamine in methanol resulted in nucleophilic ring-opening by the solvent leading to the methyl ester (13). Analogous reactions with morpholine, pyrrolidine and piperidine (3 equivs.) proceeded with addition and substitution to give 7–9. N-(*p*-chlorosulfonylphenyl)-3,4-dichloromaleimide (15) reacted with amines with substitution of both the 3- and sulfonyl chlorine atoms to give the sulfonamides (16–21).

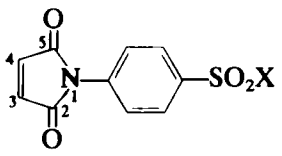
3-Chloro-4-phenoxy-N-phenylmaleimide reacted with chlorosulfonic acid to give the *bis*-sulfonyl chloride (22); condensation with dimethylamine caused displacement of the 4-(*p*-chlorosulfonylphenoxy) group to give 16. The various reactions are discussed and the structures of the products confirmed by microanalytical and spectroscopic data. The results of preliminary biological screening against 4 fungi and 2 enzymes are included.

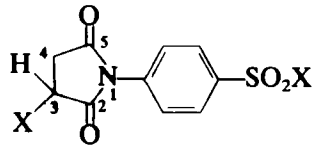
INTRODUCTION

Previous workers[1–3] have demonstrated that N-arylmaleimides are fungicidal against a wide spectrum of phytopathogenic fungi and damping of diseases. In addition, sulfonyl derivatives have well-established antibacterial[4] and antifungal properties;[5] consequently we decided to synthesise some sulfonyl maleimides as candidate fungicides.

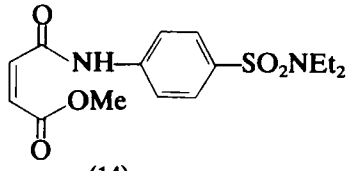
N-Phenylmaleimide was obtained in good yield (77%) by reaction of maleic anhydride with aniline and subsequent dehydration of N-phenylmaleamic acid by treatment with hot acetic anhydride-sodium acetate as previously described.[6] Refluxing maleic anhydride and aniline in glacial acetic acid gave a very poor yield (10%) of N-phenylmaleimide together with acetanilide and N-phenylmaleamic acid in agreement with other workers.[7] The failure was surprising, since this procedure works well for N-phenylphthalimide.[8] N-Phenylmaleimide was heated with chlorosulfonic acid (6 equivs.) at 80° to give an excellent yield (83%) of the sulfonyl chloride (1). Reaction of (1) with aqueous dimethylamine or aniline (2 equivs.) in methanol at room temperature resulted in selective nucleophilic substitution of the chlorine atom to give the sulfonamides (2,3) (Scheme 1). Subsequent condensation of 3 with trichloromethylsulfenyl chloride gave 4; this derivative is of special interest as a potential fungicide.[9]

The structure of the dimethylamide (2) was supported by the IR spectrum which exhibited the two carbonyl symmetric and antisymmetric stretching absorptions (1780, 1720 cm^{-1}) known[10a] to be characteristic of cyclic imides. The

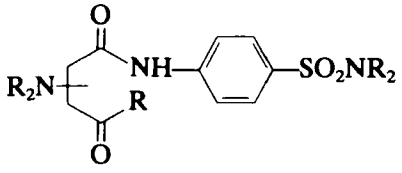




X	X
(1) Cl	(7) C_4H_8NO
(2) NMe_2	(8) C_4H_9N
(3) NHPh	(9) $C_5H_{11}N$
(4) $N(SCCl_3)Ph$	(10) NMe_2
(5) C_4H_8NO	(11) NEt_2
(6) NEt_2	



(14)



R	R′
(12) Me	NMe_2
(13) Et	OMe

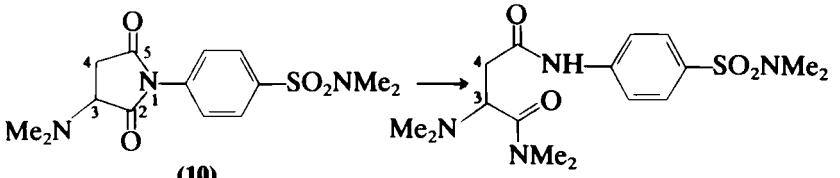
SCHEME 1

PMR spectrum confirmed *p*-sulfonation because the aromatic protons resonated as a multiplet (δ8.00–7.70) with the AA′BB′ pattern, and the aliphatic-aromatic proton ratio was 2:1. The mass spectrum showed the molecular ion (M^+, 280) with fragment ions at 236 and 172 corresponding to successive loss of the dimethylamine and sulfonyl moieties respectively; the ion at 119 (PhNCO) appears to be a characteristic feature of the molecular spectra of N-phenylimides.[11]

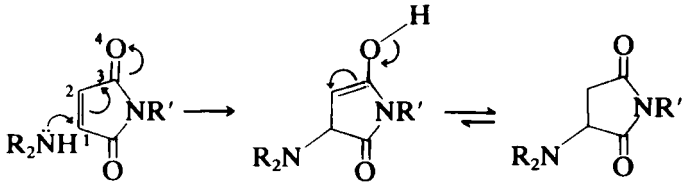
The sulfonyl chloride (1) reacted with morpholine (2 equivs.) in methanol to give equal amounts of the maleimide (5) and the succinimide (7). Separation was achieved by column chromatography on silica gel and elution with ethyl acetate-acetone (6:1).

The chloride (1) reacted with larger amounts (3 equivs.) of pyrrolidine or piperidine in methanol by substitution of the chlorine atom and addition to the maleimide double bond leading to high yields of the succinimides (8,9). The structures were supported by IR spectra (2 carbonyl absorptions at 1780,

1710 cm^{-1}) and the PMR spectra showing aliphatic-aromatic proton ratios of 9:2 and 11:2 respectively. Surprisingly repetition using less amine (2 equivs.) afforded lower yields of the same products (8,9), indicating that the rate of addition to the $\alpha\beta$-double bond was comparable to the rate of nucleophilic substitution. Reaction of (1) with an equimolar amount of pyrrolidine in presence of triethylamine gave a low yield of 8; selective nucleophilic substitution of the chlorine atom was not observed. On the other hand, morpholine with a lower nucleophilicity leads to some substitution to form the maleimide (5) and aniline, a much poorer nucleophile, only yields (3). In contrast, when the chloride was treated with a larger quantity (3–4 equivs.) of aqueous dimethylamine in methanol nucleophilic ring opening by methanol and addition of the amine to the double bond occurred to give the N,N-dimethylsuccinamide (12). Repetition of the experiment using acetonitrile as solvent gave a mixture of the succinimide (10; 70%) and the dimethylsuccinamide (12; 30%), separated by column chromatography. The IR spectrum of (10) showed two carbonyl absorptions (1780, 1725 cm^{-1}), whereas in (12) the carbonyl absorptions appeared at appreciably lower frequency (1690, 1625 cm^{-1}) in agreement with values observed for *sec.* and *tert.* amides.[10(b)] Comparison of the PMR spectra showed that compound (12) contained the NH group (δ10.0) and 6 additional methyl protons (δ3.0) corresponding to the dimethylamide group. The dimethylamino group may be attached to either the 3- or 4-carbon atom. TLC in various solvent systems showed only one spot indicating that 12 is not a mixture of isomers. It is possible that the inductive effect (−I) of the dimethylamino group may lead to preferential nucleophilic ring opening at the adjacent carbonyl carbon atom forming the 3-dimethylamino derivative (12a):



The nucleophilic addition of amines to the $\alpha\beta$-unsaturated double bond of maleimides is known[12] to proceed *via* the conjugative (1,4-) addition mechanism:



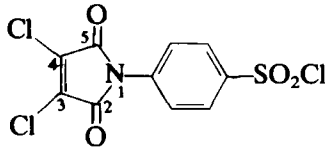
The sulfonyl chloride (1) was treated with anhydrous diethylamine under various conditions:

With the amine (3–4 equivs.) in acetonitrile the only product was the succinimide (11), no ring opening occurred possibly due to the low solubility of

the product in this solvent. Repetition of the experiment using less amine (2 equivs.) gave a mixture of (11; 20%) and the maleimide (6; 80%).

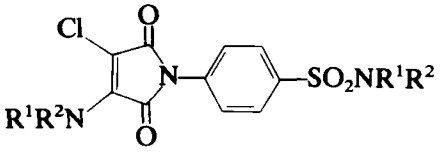
Treatment with the amine (3–4 equivs.) in methanol afforded only the methylsuccinamate (13; 60%). Repetition with less amine (2 equivs.) gave a mixture of three compounds (14, 84%; 6, 13% and 11, 3%) which by recrystallization gave the methyl maleamate (14).

The results demonstrate that under these conditions, nucleophilic ring-opening by the solvent is favoured. When the experiment was performed in aqueous methanol, the same three compounds (6, 11, 14) were isolated but the yield of the maleamate was less (71%) probably because solvation of diethylamine by water molecules reduces the effectiveness of the base to promote methanolysis of the

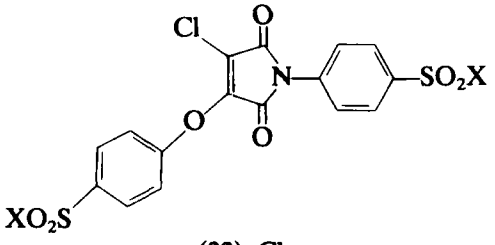


(15)

$3R^1R^2NH$



	R′	R^2
(16)	Me	Me
(17)	Et	Et
(18)	C_4H_8NO	C_4H_8NO
(19)	C_4H_9N	C_4H_9N
(20)	H	Ph
(21)	H	C_6H_4Cl-p



(22) Cl
(23) NMe_2

SCHEME 2

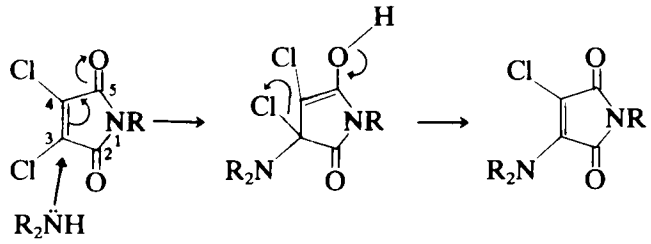
imido ring. The effect is clearly demonstrated in the reaction of (1) with dimethylamine (PK 10.73) in aqueous methanol when the dimethylsulfonamide (2) was isolated as the sole product without solvent participation. Similarly reactions with pyrrolidine (pKa 11.27) and piperidine (pKa 11.12) did not involve methanolysis which implies that the rate of nucleophilic attack by amines is faster than the competitive reaction with the methanol-base complex. In the case of diethylamine competitive attack by the latter becomes relatively more significant due to the larger steric size of the diethylamine molecule. The chloride (1) by reaction with hydrazine hydrate (2 equivs.) in methanol gave a water-soluble product; in contrast to the analogous reaction with N-(*p*-chlorosulfonylphenyl)-succinimide which gave both the mono- and bis-hydrazides.[13]

3,4-Dichloro-N-phenylmaleimide, prepared previously described,[14] was heated with chlorosulfonic acid (6 equivs.) at 45° to yield the sulfonyl chloride (15) (80%). The chloride (15) was characterized by reaction with amines (3 equivs.) to give the amides (16–21) (Scheme 2). The IR spectra showed two carbonyl absorptions (1780, 1730 cm^{-1}) indicating that the imido ring was present. The dimethylamide (16) had an additional band at 1670 cm^{-1} arising from conjugation of the dimethylamino and the carbonyl groups as shown in the resonance structures (16a, 16b).

(16) **(16a)** **(16b)**

(R = p-Me$_2$NSO$_2$C$_6$H$_4$)

The structure of (16) was supported by the PMR spectra which showed an aliphatic/aromatic proton ratio of 3:1 with the aromatic protons resonating as a multiplet (δ8.00–7.50) with the AA'BB' pattern. The substitution of the α-chlorine atom by the amine probably occurs *via* the addition-elimination (AE) mechanism:



The initial step is a conjugate addition analogous to that previously observed in the reaction of N-arylmaleimides with amines. Treatment of the chloride (15) with a large excess (6–7 equivs.) of dimethylamine or diethylamine in boiling methanol (3 hr) gave the identical amides (16, 17). The 4-chlorine atom appeared to be resistant to nucleophilic attack probably due to the contribution of the

resonance structures (16a, 16b), while the stability of the imido ring may be associated with steric factors.[15]

3,4-Dichloro-N-phenylmaleimide reacted with phenol-triethylamine to yield the 4-phenoxy derivative.[11] The latter on treatment with chlorosulfonic acid (12 equivs.) at room temperature gave the *bis*-sulfonyl chloride (22) (Scheme 2). It was interesting that subsequent reaction of 22 with dimethylamine (4 equivs.) in methanol did not yield the expected bis-dimethylamide (23); the dimethylsulfamoylphenoxy group was displaced by the dimethylamino group yielding the succinimide (16), the product was identical to that previously obtained by direct reaction of dimethylamine with the sulfonyl chloride (1). The structure was supported by the PMR spectrum (aliphatic-aromatic proton ratio 3:1) and the mass spectrum (M^+, 415) (Table I).

TABLE I

Physical data for the imido derivatives

Compd no.	Yield (%)	M.p. (°C)	Molecular formula	Microanalysis Found (Calc.) % C	H	N	MS (M^+)
1	83	139–140	$C_{10}H_6ClNO_4S$	44.0 (44.2)	2.3 (2.2)	5.3 (5.1)	273*
2	53	134–135	$C_{12}H_{12}N_2O_4S$	51.2 (51.4)	4.5 (4.3)	9.9 (10.0)	280
3	65	190–191	$C_{16}H_{12}N_2O_4S$	58.2 (58.5)	3.6 (3.65)	8.3 (8.5)	328
4	70	166–167	$C_{17}H_{11}Cl_3N_2O_4S_2$	43.0 (42.7)	2.3 (2.3)	5.8 (5.9)	482*
5	50	189–190	$C_{14}H_{14}N_2O_5S$	52.0 (52.2)	4.2 (4.3)	8.6 (8.7)	322
6	80	199–200	$C_{14}H_{16}N_2O_4S$	54.4 (54.5)	5.0 (5.2)	9.3 (9.1)	308
7	50	255	$C_{18}H_{23}N_3O_6S$	52.7 (52.8)	5.7 (5.6)	10.2 (10.3)	409
8	90	177–178	$C_{18}H_{22}N_3O_4S$	57.0 (57.4)	6.1 (5.9)	11.0 (11.2)	376
9	85	208–209	$C_{20}H_{26}N_3O_4S$	59.3 (59.4)	6.6 (6.4)	10.3 (10.4)	404
10	70	184–185	$C_{14}H_{19}N_3O_4S$	51.5 (51.7)	5.7 (5.8)	12.7 (12.9)	325
11	82	119–120	$C_{18}H_{27}N_3O_4S$	56.5 (56.7)	7.0 (7.1)	10.8 (11.0)	381
12	65	228	$C_{16}H_{26}N_4O_4S$	51.7 (51.9)	6.9 (7.0)	15.4 (15.1)	370
13	53	96–97	$C_{19}H_{31}N_3O_5S$	55.0 (55.2)	7.4 (7.5)	9.9 (10.2)	413

TABLE I (*Cont'd*)

Compd no.	Yield (%)	M.p. (°C)	Molecular formula	Microanalysis Found (Calc.) % C	H	N	MS (M^+)
14	84	124–125	$C_{15}H_{20}N_2O_5S$	52.6 (52.9)	5.9 (5.9)	8.0 (8.2)	340
15	81	186–187	$C_{10}H_4Cl_3NO_4S$	31.3 (31.5)	1.0 (1.05)	3.8 (3.7)	385*
16	76	205–206	$C_{14}H_{16}ClN_3O_4S$	47.0 (47.0)	4.5 (4.5)	11.5 (11.7)	359*
17	80	131–132	$C_{18}H_{24}ClN_3O_4S$	52.0 (52.2)	5.8 (5.8)	10.1 (10.2)	415*
18	78	149–150	$C_{18}H_{20}ClN_3O_6S$	48.6 (48.9)	4.7 (4.5)	9.4 (9.5)	443*
19	85	170	$C_{18}H_{20}ClN_3O_4S$	52.6 (52.7)	5.0 (4.9)	10.1 (10.3)	411*
20	80	190–191	$C_{22}H_{16}ClN_3O_4S$	58.0 (58.2)	3.6 (3.5)	9.2 (9.3)	455*
21	75	206–207	$C_{22}H_{14}Cl_3N_3O_4S$	50.6 (50.5)	2.7 (2.7)	8.1 (8.0)	527*
22	85	201	$C_{16}H_8Cl_3NO_7S_2$	38.5 (38.7)	1.7 (1.6)	2.7 (2.8)	501*

* Appears as an ion cluster, highest molecular mass ion is quoted.

Selected compounds at 100 ppm were screened using the *in vitro* agar plate technique[16] against the following fungi: *Trichoderma viride, Aspergillus niger, Fusarium culmorum* and *Absidia glauca.* The most fungicidal compound was the trichloromethylthio derivative (4) which was six times more active than N-phenylmaleimide.

The sulfonylmaleimides (2–3, 5–6) were appreciably more active than the parent compounds indicating that sulfonation enhances fungitoxicity. The maleimides were more active than the succinimides (7–8); consequently the maleimido double bond appears to be a beneficial structural feature. The trichloromethylthio compound (4) was also the most active at 100 ppm in tests against the enzymes α-glucosidase and β-galactosidase.

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EXPERIMENTAL

NMR spectra were recorded on a Bruker WP 80 spectrometer using tetramethylsilane as internal standard, signals indicated by an asterisk were removed by treatment with D_2O. IR spectra were measured as Nujol mulls using a Unicam SP 1000 spectrophotometer. Mass spectra were recorded with a VG Micromas V15 spectrometer operating at 60 eV. TLC was carried out on Camlab Polygram silica gel plates sensitized to UV 254 nm. Melting points were determined with a Gallenkamp electric apparatus and are uncorrected.

N-(p-chlorosulfonylphenyl)maleimide (1)

N-Phenylmaleimide (17.3 g, 0.1 mol) was gradually added to chlorosulfonic acid (70 g, 0.6 mol) at 0°C with swirling. The mixture was heated at 45–50°C for 1 hour, cooled to room temperature and poured onto ice (150 g). The precipitate was filtered off and dried to give the chloride (22.4 g) as a cream powder, m.p. 139–140°C (lit.[17] 138–139°C). A portion of the solid was recrystallized from petroleum ether (60–80°C), to give the analytical sample of (1). IR ν_{max} 1780, 1720 (C=O), 1600(ArC=C), 1340, 1160 (SO_2) cm^{-1}, MS: 273, 271 (M^+), 236 (M—Cl), 172 (M—SO_2Cl).

N-(p-chlorosulfonylphenyl)-3,4-dichloromaleimide (15)

3,4-Dichloro-N-phenylmaleimide (0.1 mol) was similarly reacted with chlorosulfonic acid (0.6 mol) at 45°C for 10 minutes to give 15. TLC (EtOAc-cyclohexane 1:2) showed one spot, R_F 0.53. IR ν_{max} 1780, 1730 1670 (C=O), 1600 (ArC=C), 1340, 1160 (SO_2) cm^{-1}.

3-Chloro-4-(chlorosulfonylphenoxy)-N-(p-chlorosulfonylphenyl)maleimide (22)

Chlorosulfonic acid (23.3 g, 0.2 mol) was added gradually to 3-chloro-4-phenoxy-N-phenylmaleimide (5 g, 0.017 mol) at room temperature. After 12 hours, the solution was poured onto crushed ice and the precipitate filtered off with suction. The solid was washed with water and recrystallized from petroleum ether (60–80°) to give 22 (7 g). TLC (EtOAc-cyclohexane 1:2) showed one spot, R_F 0.47. IR ν_{max} 1725, 1650 (C=O), 1600 (ArC=C), 1340, 1160 (SO_2) cm^{-1}. Repetition of the reaction at 80° or 45° gave a solid m.p. 170–177°C; TLC showed 4 spots, R_F 0.60, 0.47, 0.35, 0.21.

General procedure for reaction of the sulfonyl chloride (1) with amines

The amine (0.02 mol) was gradually added to a solution of (1) (0.01 mol) in methanol (25 ml) at 0°C. The mixture was left at room temperature for 2 hours and was added to ice-water (50 ml). The precipitate was filtered off with suction, washed with water (2 × 25 ml) and dried. The product was purified by recrystallization from methanol to give the sulfonamides (2–3, 5–6) (Scheme 1). Repetition using larger amounts (0.03 mol) of morpholine, pyrrolidine or piperidine gave the succinimides (7–9) (Table 1). However, reaction of (1) (0.01 mol) with dimethylamine (0.03 mol) in acetonitrile gave a product (3 g), m.p. 176–179°C. TLC (EtOAc-MeOH 3:1) showed 2 spots R_F 0.70, 0.30. Chromatography on silica gel (30 g) and elution with ethyl acetate-petroleum ether (60–80) (1:2) gave the 3-dimethylaminosuccinimide (10, 70%) and the N,N-dimethylsuccinamide (12, 30%).

Compound 10

IR ν_{max} 1780, 1720 (C=O), 1600 (ArC=C), 1340, 1160 (SO_2) cm^{-1}; PMR ($CDCl_3$) δ 8.0–7.4 (m, 4H, ArH), 4.10–3.80 (dd, 1H, 3-H), 3.10–2.80 (m, 2H, 4-H), 2.70 (s, 6H, SO_2NMe_2), 2.40 (s, 6H, NMe_2).

Compound 12

Ir ν_{max} 3200, 3280 (NH), 1690 (CONH), 1625 (CONMe_2), 1600 (ArC=C), 1340, 1160 (SO_2) cm^{-1}; PMR (DMSO-d_6) δ10.0* (s, 1H, NH), 7.80 (s, 4H, ArH), 4.20–4.05 (dd, 1H, 3-H), 3.05 (s, 6H, $CONMe_2$), 2.90–2.45 (m, 2H, 4-H), 2.65 (s, 6H, SO_2NMe_2), 2.35 (s, 6H, NMe_2).

Reaction of (1) (0.01 mol) with diethylamine under various conditions

(a) The amine (0.02 mol) in methanol, as previously described, reacted to give a white powder (3.1 g). TLC (EtOAc-cyclohexane 1:1) showed 3 spots (R_F 0.50, 0.40, 0.16) attributed to the maleamate (14, 83%), the maleimide (6, 13%) and the succinimide (11, 3%). Recrystallization of the solid from ethanol afforded 14. IR ν_{max} 3270 (NH), 1725 (COOMe), 1690 (CONH), 1600 (ArC=C), 1350, 1160 (SO_2) cm^{-1}; PMR ($CDCl_3$) δ: 11.10* (s, 1H, NH), 7.80 (s, 4H, ArH), 6.50–6.10 (q, 2H, CH=CH), 3.80 (s, 3H, OMe), 3.4–3.0 (q, 4H, NCH_2), 1.3–1.0 (t, 6H, NCH_2CH_3).
(b) With the amine (0.2 mol) in acetonitrile (25 ml) at room temperature for 2 hours, the reaction gave the maleimide (6, 80%), which was isolated by column chromatography on silica gel using ethyl acetate-petroleum ether (60–80°) as eluant. PMR ($CDCl_3$) δ: 8.00–7.20 (m, 4H, ArH), 6.90 (s, 2H, CH=CH), 3.40–3.15 (q, 4H, N-CH_2), 1.30–1.00 (t, 6H, NCH_2CH_3). MS: 308 (M^+), 293 (M – Me), 236 (M—NEt_2), 172 (M—SO_2NEt_2), 144, 118 (C_6H_4NCO), 82, 57, 54.
(c) The amine (0.3 mols) in acetonitrile afforded the 2-diethylamino-succinimide (11). TLC (EtOAc-cyclohexane) showed one spot, R_F 0.16. IR ν_{max} 1780, 1715 (C=O), 1600 (ArC=C), 1340, 1160 cm^{-1}. PMR ($CDCl_3$) δ:8.00–7.40 (m, 4H, ArH), 4.30–4.10 (dd, 1H, 3-H), 3.40–2.50 (m, 10H, 4-H, N-CH_2), 1.20–1.10 (t, 12H, Me).
(d) The amine (0.3 mol) in methanol (25 ml) gave the methyl succinamate (13). IR ν_{max} 3280 (NH), 1740 (COOMe) 1700 (CONH), 1600 (ArC=C), 1340, 1180 (SO_2) cm^{-1}, PMR ($CDCl_3$) δ:9.65* (s, 1H, NH), 7.80–7.65 (m, 4H, ArH), 4.30–4.10 (dd, 1H, 3(4)-H), 3.85 (s, 3H, OMe), 3.40–2.20 (m, 10H, 4(3)-H, N-CH_2).

N-(p-N'-Trichloromethylthio N'-phenylsulfamoylphenyl)maleimide (4)

The sulfonyl anilide (3, 1.64 g) was stirred with trichloromethanesulfenyl chloride (3.72 g) in ether (50 ml) for 2 hours. The solvent was evaporated under reduced pressure and the solid residue was washed with water. Recrystallization from acetone gave 4. IR ν_{max} 1780, 1720 (C=O), 1600 (ArC=C), 1340, 1160 (SO_2) cm^{-1}.

General procedure for reaction of N-(p-chlorosulfonylphenyl)-3,4-dichloromaleimide (15) with amines

The sulfonyl chloride (15) (0.01 mol) was treated with the amine (0.03 mol) in methanol (25 ml) for 3 hours. The mixture was added to crushed ice (100 g) and the solid product recrystallized from methanol to give the 3-chloromaleimide sulfonamides (16–21) (Scheme 2). Compound 16: IR ν_{max} 1780, 1730, 1670 (C=O), 1600 (ArC=C), 1340, 1160 (SO_2) cm^{-1}. PMR ($CDCl_3$) \8.00–7.50 (m, 4H, ArH), 3.50 (s, 6H, NMe_2), 2.70 (s, 6H, SO_2NMe_2). MS: 359 (M^+), 315 (M—NMe_2), 251 (M—SO_2NMe_2), 207 (M—SO_2NMe_2, NMe_2), 118 (C_6H_4NCO), 89.

Reaction of (22) with dimethylamine

The sulfonyl chloride (22) was treated with dimethylamine (4 mol equivs.) in methanol to give 3-chloro-4-dimethylamino N-(*p*-dimethylsulfamoyl)phenyl maleimide (16). TLC (EtOAc-cyclohexane 1:1) showed one spot, R_F 0.22. PMR ($CDCl_3$) δ:8.00–7.50 (m, 4H, ArH), 3.50 (s, 6H, NMe_2), 2.70 (s, 6H, SO_2NMe_2).

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