Maleimido and Dichloromaleimidobenzenesulphonyl Derivatives

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Abstract

N-Aryl- and N-aryl α,α'-dichloromaleimides, with chlorosulphonic acid gave the sulphonyl chlorides, which reacted with amines to give the corresponding sulphonamides. With the α,α'-dichloromaleimidosulphonyl chlorides one of the α-chlorine atoms was also substituted.

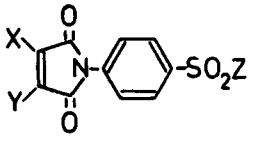
Several N-arylmaleimides are fungicidal,[1,2] and their chlorosulphonation was examined to discover more effective fungicides, since many sulphonyl derivatives show activity.[3]

N-Phenyl- and N-phenyldichloro-maleimides with chlorosulphonic acid (6 mols) at 40° (45 min and 6 min respectively) gave the corresponding p-maleimidobenzene-sulphonyl chlorides (1 and 2) which were converted to the amides (3-11) (Table 1) by condensation with amines in methanol at room temperature. The anilide (4), with perchloromethylmercapta n, afforded the trichloromethylthio derivative (5). In contrast, reaction with morpholine, piperidine and pyrrolidine (2 mols) gave the succinimides (12-14) (Table 2). With morpholine (1 mol) and triethylamine (1 mol) compound (1) gave a mixture of (6) and (12). The reaction of (1) with excess of dimethylamine (4 mols) in methanol (50°) afforded the ring-opened product probably (15)

$$Me_2NCOCH^{a}(NMe_2)CH_2^{b}CONHC_6H_4SO_2NMe_2$$
(15)

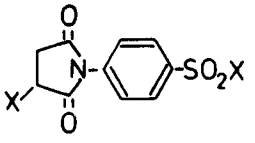
The structure is supported by the pmr spectrum (DMSO-d_6) δ : 10.00, s, 1H (NH), 8.00-7.70, m, 4H (ArH), 4.00-3.70, m, 1H (Ha), 3.20-2.80, m, 8H (H^b, $CONMe_2$), 2.60, s, 6H (SO_2NMe_2).

Table 1. p-Maleimido and Dichloromaleimidobenzenesulphonyl Derivatives.



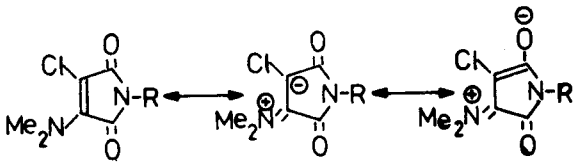
Compd. No.	X	Y	Z	mp °C	Yield (%)
1	H	H	Cl	139-40 lit.[4] 138-9	85
2	Cl	Cl	Cl	186-7	80
3	H	H	NMe_2	134-5	53
4	H	H	NHPh	190-1	65
5	H	H	$N(SCCl_3)Ph$	166-7	70
6	H	H	morpholino	189-90	50
7	Cl	NMe_2	NMe_2	205-6	75
8	Cl	morpholino	morpholino	149-50	80
9	Cl	pyrrolidino	pyrrolidino	170-1	85
10	Cl	NHPh	NHPh	190-1	80
11	Cl	NHC_6H_4Cl-p	NHC_6H_4Cl-p	206-7	75

Table 2. p-Succinimidobenzenesulphonyl Derivatives



Compd. No.	X	mp °C	Yield (%)
12	morpholino	254-5	85
13	piperidino	208-9	90
14	pyrrolidino	177-8	90

The chloride (2) was similarly reacted with amines (2 mols) in methanol at room temperature to give the amides (7-11), and in each case one chlorine atom was substituted but no attack on the second chlorine was observed. With excess dimethylamine (7 mols) in methanol (50°), only the amide (7) was isolated:



(R=$C_6H_4SO_2NMe_2$-p)

The absence of ring opening may be due to resonance, since the canonical structures (7a, 7b) would enhance the stability of the imido ring[5].

All products were characterized by microanalysis (CHN), pmr, ms and ir spectroscopy and their purity was checked by t.l.c.

References

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