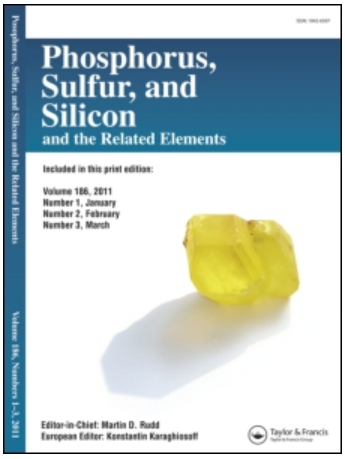

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SOME DERIVATIVES OF 3-AMIDO-4-METHYLBENZENESULFONYL CHLORIDE

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SOME DERIVATIVES OF 3-AMIDO-4-METHYLBENZENESULFONYL CHLORIDE

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3-Amido-4-methylbenzenesulfonyl chloride (**2**) has been converted to the phenylhydrazide (**3**), hydrazide (**4**), 13 hydrazones (**5**) and a sulfonylpyrazole (**6**). The azide (**8**) was also prepared and it reacted with triphenylphosphine to give the iminophosphorane (**9**). The n.m.r. spectra of the hydrazones are discussed with special reference to the resonances of the SO_2NH and N=CH groups and these are correlated with the Hammett σ constants of the substituents. The i.r. and m.s. data of the compounds are also briefly discussed.

INTRODUCTION

A wide range of aromatic sulfonyl derivatives, especially azides, hydrazides and hydrazones have been synthesised[1–6] as potential pesticides. Previous work has demonstrated fungicidal activity in sulfonamides,[7] sulfonohydrazides,[8] and nematical properties in sulfonyl azides.[8] In continuation of this programme, the current paper describes the preparation of 3-amido-4-methylbenzene-sulfonyl derivatives.

DISCUSSION

o-Toluamide (**1**) (Scheme) on treatment with only 3 mols. of chlorosulfonic acid gave the sulfonyl chloride (**2**) in excellent yield. This indicates that the amido group, unlike the carboxylic acid group, does not condense with chlorosulfonic acid (see Ref. 9).

Subsequent reaction with phenylhydrazine gave the phenylhydrazide (**3**), and with hydrazine the hydrazide (**4**) was obtained which condensed with a range of carbonyl compounds to give the corresponding hydrazones (**5a–5m**). The reaction of the hydrazide (**4**) with acetylacetone gave the pyrazole (**6**). The mass spectrum of this compound showed loss of sulfur dioxide, which agrees with our previous observations[10] and is a similar process to the pyrolysis of alkyl sulfones.[11]

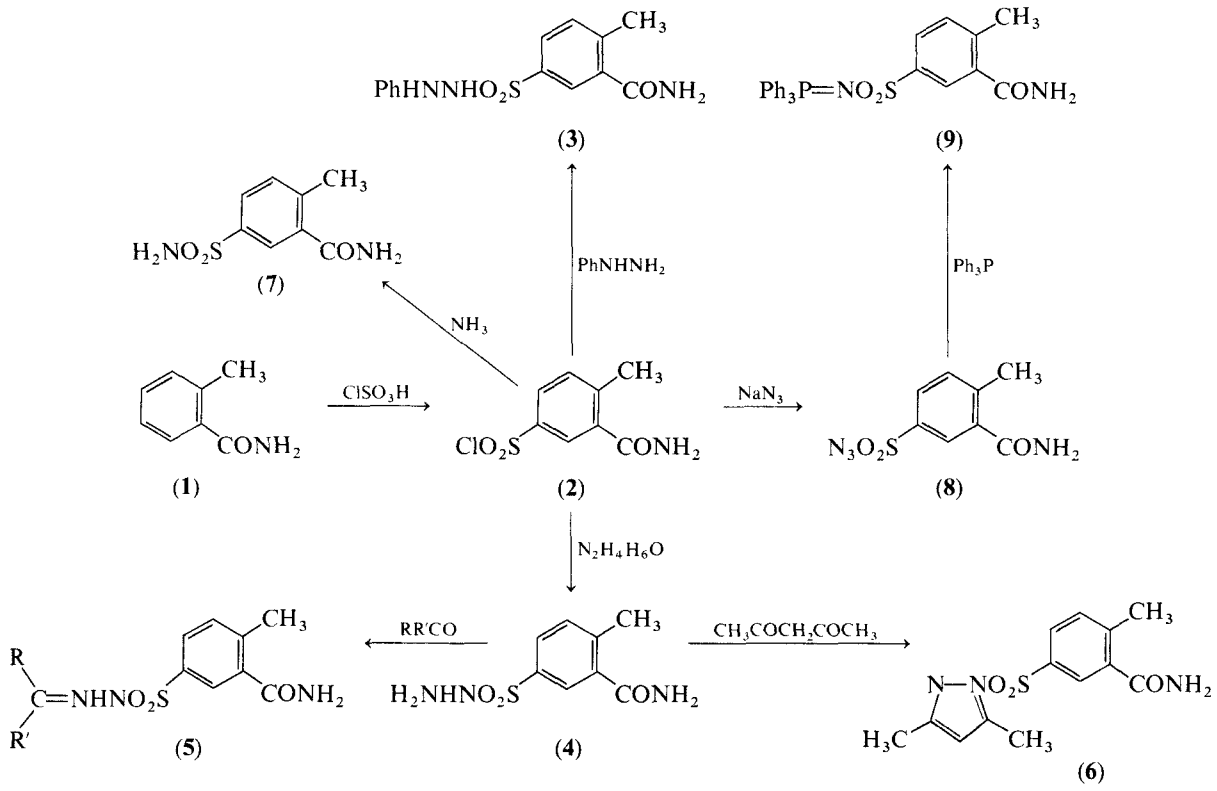
The reaction of the sulfonyl chloride (**2**) with ammonia gave the amide (**7**), and with sodium azide the azide (**8**). Sulfonyl azides generally undergo 1,4-dipolar additions with alkenes such as norbornene and cyclohexene;[8] however, the azide (**8**) was unreactive to both norbornene and cyclohexene even after prolonged boiling (48h) in ether (cf. Ref. 6). On the other hand, the azide (**8**) did react with triphenylphosphine to give the iminophosphorane (**9**).

In the n.m.r. spectra of the aromatic aldehyde sulfonohydrazones (**5c–5m**), special attention was focused on the SO_2NH and N=CH proton resonances. The resonance signal at low field (δ10.88–11.85), which disappeared on D_2O treatment, can be assigned to the SO_2NH proton. The values are in general agreement with those noted[10] for pyridine-3-sulfonohydrazones, and probably arise from the combined effects of the π-system, the electron-withdrawing sulfonyl group, and some interaction with the solvent. The chemical shifts of the SO_2NH proton were investigated using the Hammett equation. There is a satisfactory correlation between the change in chemical shift, $\Delta\delta$, resulting from *meta*- and *para*-substitution, and the Hammett σ constant,[12] for which the regression line is given by Eq. (1):

$$\Delta\delta = 0.76\sigma - 0.08 \quad (1)$$

(correlation coefficient, r, 0.957; standard deviation, s, 0.08). The N=CH proton signal was more difficult to assign as it occurred in the region of the aromatic proton resonances, and varied between δ7.37–7.97. The variation in chemical shift correlated less well with the Hammett σ constant (r, 0.783; s, −0.15), and the regression line is given by Eq. (2):

$$\delta = 0.40\sigma - 0.15 \quad (2)$$



(**a**) R = R′ = Me
(**b**) R, R′ = $(CH_2)_5$
(**c**) R = H, R′ = Ph
(**d**) R = H, R′ = *p*-HOC_6H_4
(**e**) R = H, R′ = *p*-$NO_2C_6H_4$
(**f**) R = H, R′ = *p*-ClC_6H_4
(**g**) R = H, R′ = *p*-BrC_6H_4
(**h**) R = H, R′ = *o*-$NO_2C_6H_4$
(**i**) R = H, R′ = *m*-$NO_2C_6H_4$
(**j**) R = H, R′ = *m*-ClC_6H_4
(**k**) R = H, R′ = *m*-BrC_6H_4
(**l**) R = H, R′ = *m*-MeC_6H_4
(**m**) R = H, R′ = PhCh=CH

Scheme

The slope of the line indicated by Eq. (1) is greater than that represented by Eq. (2), which reflects the relative sensitivities of the SO_2NH and N=CH protons to substituent effects.

Comparison of the ultraviolet spectra of the benzaldehyde and cinnamaldehyde hydrazone (**5c**, **5m**) showed the expected bathochromic shifts, ($\Delta\lambda_{max}$ 35 nm), and increase in the molar extinction coefficient ($\Delta\varepsilon$11900), resulting from the increased delocalisation in the cinnamaldehyde hydrazone (**5m**) as compared with the benzaldehyde derivative (**5c**). The infrared spectra of the hydrazones (**5a**–**5m**) showed the asymmetric and symmetric stretching frequencies of the SO_2 group at approximately 1370 and 1160 cm^{-1} respectively; the asymmetric frequency is appreciably higher than the previously reported value of 1325 cm^{-1} for aromatic sulfonohydrazides and hydrazones.[13] The mass spectra of the hydrazide and hydrazones showed a fragmentation pattern in general agreement with that previously proposed.[14]

EXPERIMENTAL

I.r. spectra were determined as Nujol mulls using a Perkin Elmer 157 spectrophotometer. N.m.r. spectra were measured with a Varian HA 100 spectrometer using tetramethylsilane as internal standard and deuterodimethylsulfoxide-deuterochloro-

form as solvent. Mass spectra were obtained with a VG Micromass 16F spectrometer at 70 eV. Melting points were determined with a Kofler hot-stage apparatus and are uncorrected. Microanalyses were carried out by the Butterworth Microanalytical Consultancy, Teddington, England.

3-Amido-4-methylbenzenesulfonyl chloride (**2**)

o-Toluamide (**1**) (4 g) was heated with chlorosulfonic acid (10.5 g; 3 mol. equivs.) at 70° for 2h. The dark brown solution was stirred with crushed ice (100 g) for $\frac{1}{2}$ h to give the *sulfonyl chloride* as a cream powder (6.9 g, 98%) m.p. 136–139°. (Found: C, 41.0; H, 3.6; N, 6.2. $C_8H_8ClNO_3S$ requires C, 41.15; H, 3.4; N, 6.0%). ν_{max} 3500, 3300 (NH), 1370, 1175 (SO_2) cm^{-1}. N.m.r. δ 8.10–7.20 m (5H, 3ArH, $CONH_2$), 2.44s (3H, CH_3). Ms showed the molecular ion (M^+, 233) and fragment ions at 217 (M—NH_2), 198 (M—Cl), 134 (M—SO_2Cl), 118 (M—SO_2Cl—NH_2), 90 (M—SO_2Cl—$CONH_2$).

3-Amido-4-methylbenzenesulfono-N-phenylhydrazide (**3**)

The sulfonyl chloride (**1**) (1g) was reacted with phenylhydrazine (0.88g; 2 mol. equivs.) in ethanol (20 ml) at room temperature for 2 h. to give the *phenylhydrazide* (1.2 g, 98%), m.p. 166°. (Found: C, 55.0; H, 4.9; N, 14.0. $C_{14}H_{15}N_3O_3S$ requires C, 55.1; H, 4.9; N, 13.8%). ν_{max} 3450, 3360 (NH_2) 3280 (NH), 1675 (CO), 1380, 1160 (SO_2) cm^{-1}. M.s. did not show the molecular ion (M^+, 305), but gave fragment ions at 198 (M—PhNHNH), 183 (M—PhNHNH—CH_3), 134 (M—PhNHNHSO$_2$), 77 (C_6H_5).

3-Amido-4-methylbenzenesulfonohydrazide (**4**)

The sulfonyl chloride (**1**) (3 g) was reacted with hydrazine hydrate (20 ml of 98%) at 0° for $\frac{1}{4}$ h and then at room temperature for $\frac{1}{2}$ h. Addition of ice-water (200 ml) and recrystallization (EtOH) gave the *hydrazide* (1.8 g, 60%), m.p. 152–154°. (Found: C, 42.2; H, 4.9; N, 18.3. $C_8H_{11}N_3O_3S$ requires C, 41.9; H, 4.8; N, 18.3%). ν_{max} 3450, 3250 (NH), 1380, 1160 (SO_2) cm^{-1}. N.m.r. δ 8.24 s (1H, SO_2NH), 7.94–7.62 m (3 ArH), 7.36 d, (2 H, $NHNH_2$), 2.43 s (3 H, CH_3). The signals at δ 8.24 and 7.36 were removed by D_2O treatment. M.s. showed the molecular ion (M^+, 229) and fragment ions at 199 (M—NNH_2), 182, 166, 134.

3-Amido-4-methylbenzenesulfonohydrazones (*5a–5m*)

The hydrazide (**4**) was reacted with the appropriate carbonyl compound (1 mol. equiv.) in methanol at room temperature for 1 h. If no precipitate was observed, the solution was boiled under reflux for $\frac{1}{2}$ h. The precipitate was filtered off and washed with ice-water, methanol and ether to give the following hydrazones:

Acetone (**5a**) (82%), m.p. 171° (Found: C, 48.8; H, 5.7; N, 15.4 $C_{11}H_{15}N_3O_3S$ requires C, 49.1; H, 5.6; N, 15.6%). ν_{max} 3460, 3380, 3240 (NH), 1660 (CO), 1370, 1150 (SO_2) cm^{-1}. N.m.r. δ 9.96s (1H, SO_2NH), 7.94–7.30 m (3 ArH), 2.43 s (3H, CH_3), 1.77 d (6H, $=C(CH_3)_2$). Treatment with D_2O removed the signal at δ 9.96.

Cyclohexanone (**5b**) (92%), m.p. 175° (Found: C, 54.6; H, 5.9; N, 14.0. $C_{14}H_{19}N_3O_3S$ requires C, 54.4; H, 6.15; N, 13.6%). ν_{max} 3410, 3220 (NH), 1665 (CO), 1375, 1170 (SO_2) cm^{-1}.

Benzaldehyde (**5c**) (95%), m.p. 159° (Found: C, 56.6; H, 4.9; N, 13.5. $C_{15}H_{15}N_3O_3S$ requires C, 56.8; H, 4.7; N, 13.2%). ν_{max} 3500, 3380 (NH_2), 3200 (NH), 1660 (CO), 1370, 1165 (SO_2) cm^{-1}. N.m.r. δ 11.38 s (1H, SO_2NH), 8.20–7.20 m (8 ArH), 7.90 s (1H, N=CH), 2.40 s (3H, CH_3). The signal at δ 11.38 was removed by D_2O treatment. Ultraviolet spectrum: λ_{max} 275 nm ε_{max} 2300.

p-Hydroxybenzaldehyde (**5d**) (98%), yellow powder, m.p. 209°. (Found: C, 54.3; H, 4.8; N, 12.7. $C_{15}H_{15}N_3O_4S$ requires C, 54.1; H, 4.5; N, 12.6%). ν_{max} 3500 (OH), 3400, 3150 (NH), 1665 (CO), 1365, 1160 (SO_2) cm^{-1}. N.m.r. δ 10.88 s (1H, SO_2NH), 7.44–6.22 m (10H 7 ArH, OH, $CONH_2$) 7.37 s (1H, N=CH), 2.40 s (3H, CH_3). M.s. showed the molecular ion (M^+, 333) and fragment ions at 315 (M—H_2O), 198 (M—NHN=CH C_6H_4OH), 166, 150, 134, 122, 90.

p-Nitrobenzaldehyde (**5e**) (95%), m.p. 209–211° (decomp.) (Found: C, 49.9; H, 4.1; N, 15.6. $C_{15}H_{14}N_4O_5S$ requires C, 49.7; H, 3.9; N, 15.5%). N.m.r. δ 11.83 br s (1H, SO_2NH), 8.37–7.40 m (7 ArH), 7.95 s (1H, N=CH), 2.45 s (3H, CH_3).

p-Chlorobenzaldehyde (**5f**) (98%), m.p. 187–188°. (Found: C, 51.0; H, 4.7; N, 12.0. $C_{15}H_{14}ClN_3O_3S$ requires C, 51.2; H, 4.9; N, 11.95%). N.m.r. δ 11.40 s (1H, SO_2NH), 7.96–7.24 m (7 Ar H), 7.82 s (1H, N=CH), 2.41 s (3 H, CH_3).

p-Bromobenzaldehyde (**5g**) (79%), m.p. 188°. (Found: C, 45.6; H, 3.7; N, 10.9. $C_{15}H_{14}BrN_3O_3S$ requires C, 45.45; H, 3.5; N, 10.6%). N.m.r. δ 11.50 s (1H, SO_2NH), 7.90–7.20 m (7 ArH), 7.87 s (1H, N=CH), 2.37 s (3H, CH_3).

o-Nitrobenzaldehyde (**5h**) (95%), m.p. 194–196°. (Found: C, 49.8; H, 4.0; N, 15.7. $C_{15}H_{14}N_4O_5S$ requires C, 49.7; H, 3.9; N, 15.5%). ν_{max} 3400, 3225 (NH), 1650 (CO) 1365, 1160 (SO_2) cm^{-1}.

m-Nitrobenzaldehyde (**5i**) (97%), m.p. 184° (decomp.) (Found: C, 49.9; H, 4.1; N, 15.8. $C_{15}H_{14}N_4O_5S$ requires C, 49.7; H, 3.9; N, 15.5%). N.m.r. δ 11.85 s (1H, SO_2NH), 8.46–7.40 m (7 ArH), 8.01 s (1H, N=CH), 2.47 s (3 H, CH_3).

m-Chlorobenzaldehyde (**5j**) (90%), m.p. 168°. (Found: C, 51.0; H, 5.2; N, 12.1 $C_{15}H_{14}ClN_3O_3S$ requires C, 51.2, H, 4.9; N, 11.95%). N.m.r. δ 11.62 s (1H, SO_2NH), 8.0–7.20 m (7 ArH), 7.92 s (1 H, N=CH), 2.42 s (3 H, CH_3).

m-Bromobenzaldehyde (**5k**) (80%), m.p. 170° (decomp.) (Found: C, 45.1; H, 3.3; N, 10.4 $C_{15}H_{14}BrN_3O_3S$ requires C, 45.45; H, 3.5; N, 10.6%). N.m.r. ($(CD_3)_2SO$) δ 11.63 s (1 H, SO_2NH), 8.20–7.10 m (7 ArH), 7.90 s (1 H, N=CH), 2.41 s (3 H, CH_3).

m-Tolualdehyde (**5l**) (78%), m.p. 164°. (Found: C, 58.2; H, 5.3; N, 12.8 $C_{16}H_{17}N_3O_3S$ requires: C, 58.0; H, 5.1; N, 12.7%). N.m.r. δ 11.38 s (1 H, SO_2NH), 8.0–7.1 m (7 ArH), 7.87 s (1 H, N=C*H*), 2.40 s (3 H, CH_3).

Cinnamaldehyde (**5m**) (87%), m.p. 174° (decomp.) (Found: C, 59.8; H, 5.3; N, 12.1. $C_{17}H_{17}N_3O_3S$ requires C, 59.5; H, 5.0; N, 12.2%). N.m.r. δ 11.37 s (1 H, SO_2NH), 8.02–7.26 m (8 ArH), 7.82 s (1 H, N=CH), 2.41 s (3 H, CH_3). Ultraviolet Spectrum: λ_{max} 310 nm, ε_{max} 14,200.

N-(3-Amido-4-methylbenzenesulfonyl) pyrazole (**6**)

The hydrazide (**4**) (2.29 g) was boiled under reflux with acetyl acetone (1 g; 1 mol. equiv.) in methanol (50 ml) for 2 h. Concentration under reduced pressure gave the *pyrazole* (1.5 g, 51%), m.p. 158°. (Found: C, 53.2; H, 5.2; N, 14.7. $C_{13}H_{15}N_3O_3S$ requires C, 53.2; H, 5.1; N, 14.3%). ν_{max} 3400, 3200 (NH), 1650 (CO), 1360, 1175 (SO_2) cm^{-1}. N.m.r. δ 8.04–7.40 m (5H, 3 ArH, $CONH_2$), 6.05 s (1 H, pyrazole=CH), 2.44 s (6 H, 2 × C—CH_3), 2.10 s (3 H, ArCH_3). M.s. showed the molecular ion (M^+, 293) and fragment ions at 229 (M—SO_2) 212, 199, 184, 168, 134, 118, 95.

3-Amido-4-methylbenzenesulfonyl Azide (**8**)

The sulfonyl chloride (**2**) (3.6 g) by reaction with sodium azide (1.86 g; 2 mol. equivs.) in aqueous methanol gave the *azide* as pale yellow plates (2.4 g, 69%), m.p. 170° (decomp.). (Found: C, 40.0; H, 3.2; N, 23.3. $C_8H_8N_4O_3S$ requires C, 40.0; H, 3.3; N, 23.3%). ν_{max} 3500, 3280 (NH), 1665 (CO), 2130 (N_3), 1370, 1170 (SO_2) cm^{-1}. M.s. gave the molecular ion (M^+, 240) and fragment ions at 198 (M—N_3), 134 (M—SO_2N_3), 118, 104, 90.

3-Amido-4-methylbenzenesulfonyl triphenyliminophosphorane (*9*)

The azide (**7**) (1.2 g) was treated with triphenylphosphine (1.3 g; 1 mol. equivs.) in ether (25 ml) at room temperature for 3 h. Filtration gave the *iminophosphorane* (9) (2.4 g, 99%), m.p. 77°. (Found C, 65.6; H, 4.9; N, 6.1. $C_{26}H_{23}N_2O_3PS$ requires C, 65.8; H, 4.85; N, 5.9%). ν_{max} 3450, 3250 (NH), 1370, 1160 (SO_2) cm^{-1}. Ms. showed the molecular ion (M^+, 474) and fragment ions at 410 (M—SO_2), 340 (SO_2N=PPh_3), 276, 198, 167, 134, 77.

3-Amido-4-methylbenzenesulfonamide (**7**)

(24% from EtOH), m.p. 185°. (Found: C, 45.1; H, 5.0; N, 12.9. $C_8H_{10}N_2O_3S$ requires C, 44.9; H, 4.7; N, 13.1%). N.m.r. δ 7.90–7.40 (3 ArH), 2.36 s (3 H, CH_3).

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