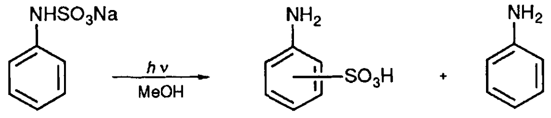
The Photochemistry of *para*-Substituted Phenylsulphamates—Photo-Fries Rearrangements

John M. Lally and William J. Spillane *
Department of Chemistry, University College, Galway, Ireland

The photolysis (254 nm) of a series of *para*-substituted phenylsulphamates, $XC_6H_4NHSO_3Na$ [X=H (**1a**), CH_3 (**1b**), F (**1c**), Cl (**1d**), Br (**1e**) and NO_2 (**1f**)] in degassed methanolic solutions has been examined. For **1a** and **1b** photo-Fries type rearrangements to sulphonic acids and photodegradation to anilines have been observed. The halogenosulphamates **1c**–**1e** do not rearrange but degrade to anilines and are photosolvolysed to *p*-methoxyphenylsulphamic acid. No notable spectral changes took place during the irradiation of **1f** over a relatively long period. Substrate concentration studies, radical scavenging and sensitization and quenching experiments on **1b** indicate that, as previously found for **1a**, its photolysis involves an intramolecular radical mechanism with the participation of two triplet states.

The photo-Fries rearrangement[1] has been extensively investigated and has been found to be fairly general for many aromatic systems including aryl esters,[2] ethers,[3] sulphonanilides,[4] sulphonates,[5] carbamates,[6] carbonates,[7] cinnamates,[8] sulphenanilides,[9] amides and anilides,[10] succinates,[11] ketones[12] and some heterocyclic systems.[13] There are only a few reports of photo-Fries type rearrangements involving N–S compounds[4,9] and recently we communicated details of the photolysis of the sodium salt of phenylsulphamic acid (**1a**) which yielded the isomeric anilinesulphonic acids **2**–**4** and aniline **5** (Scheme 1).[14]



1a

2 *ortho*
3 *meta*
4 *para*

5

Scheme 1

The involvement of an intramolecular radical rearrangement in the photolysis of **1a** was supported by the absence of a concentration effect and by the lowering of the yields of **2**–**4** when radical scavengers were present. Sensitization experiments and the construction of Stern–Volmer plots for product formation indicated that the rearrangement proceeds *via* a triplet state (T_1) and that aniline formation proceeds through two triplet states.

The formation of **3** in the rearrangement of **1a** is of note since *meta*-substitution has only been reported[1a,b,15] in a few cases in the photo-Fries rearrangement and in two of these cases[1b,15b] structural considerations result in the *meta* rearrangement being sterically enforced.

The type of substituent (electron attracting or electron repelling) and the position of the substituent relative to the reactive site have been shown to influence the mode of photochemical reaction in aryl compounds.[16] As a further extension of our studies and in order to explore the scope and generality of light-induced rearrangement, a number of *para*-substituted phenylsulphamates were irradiated at 254 nm. In this present paper, we discuss the photochemical reactions of the sodium salts of *para*-methyl-(**1b**), fluoro-(**1c**), chloro-(**1d**), bromo-(**1e**) and nitro-(**1f**) substituted phenylsulphamates.

Results and Discussion

The spectral data for **1a**–**f** are presented in Table 1. As a first approximation it may be inferred that electronically excited states in **1a** and (**1b**–**e**) are the same since the shapes of their UV absorption spectra are similar. Generally *para* substitution results in a bathochromic shift with a corresponding increase in the extinction coefficient. The shift to longer wavelength by **1b** may be attributed to the strong hyperconjugative effect of the methyl group. The more available the non-bonding electrons of the halogen groups are for interaction with the π-system of the aromatic ring, the greater the shift will be. Thus the shifts for the halogens are in the order of increasing electronegativity: Br > Cl > F. A substantial bathochromic shift results on *para*-substitution with a nitro group and this may be attributed to a strong resonance effect.

Table 1 UV spectral data—substituent variation[a]

Compound	X[b]	λ_{S_1}/nm	λ_{S_2}/nm	$\varepsilon_{S_1} \times 10^{-3}$ $dm^3 mol^{-1} cm^{-1}$ (log ε)	$\varepsilon_{S_2} \times 10^{-3}$ $dm^3 mol^{-1} cm^{-1}$ (log ε)
1a	H	274	228	0.832 (2.92)	8.34 (3.92)
1b	CH_3	277	230	0.897 (2.95)	9.37 (3.97)
1c	F	277	230	1.05 (3.02)	7.15 (3.85)
1d	Cl	281	236	1.06 (3.02)	13.0 (4.11)
1e	Br	284	239	1.02 (3.01)	14.2 (4.15)
1f	NO_2	340	220	10.4 (4.02)	5.8 (3.76)

[a] The solvent was water. [b] Refers to *para*-substitution in p-$XC_6H_4NHSO_3Na$.

The photoreactivities of **1b**–**f** were initially checked by measuring the change in their UV spectra with irradiation time. With the exception of the *p*-nitro compound **1f** the spectral changes appeared to be quantitative from the isosbestic points. The spectral changes for **1b** are shown in Fig. 1 and for comparison the changes for **1a** are displayed in Fig. 2. Fig. 3 shows the changes for **1c**, **1d** and **1e**. Fig. 4 displays the change for compound **1f**.

Irradiation of **1b**.—A methanolic solution of the *p*-methyl compound **1b** was irradiated for 1 min in a Rayonet photoreactor at 254 nm and the products were analysed by reversed-phase HPLC. The results are given in Table 2 together with those obtained from the irradiation of **1a** for comparison. Compound **1b** undergoes photorearrangement to 4-methylaniline-3-sulphonic acid (**6**) and 4-methylaniline (**7**) is also formed (Scheme 2). Compound **7** may form by a photohydro-

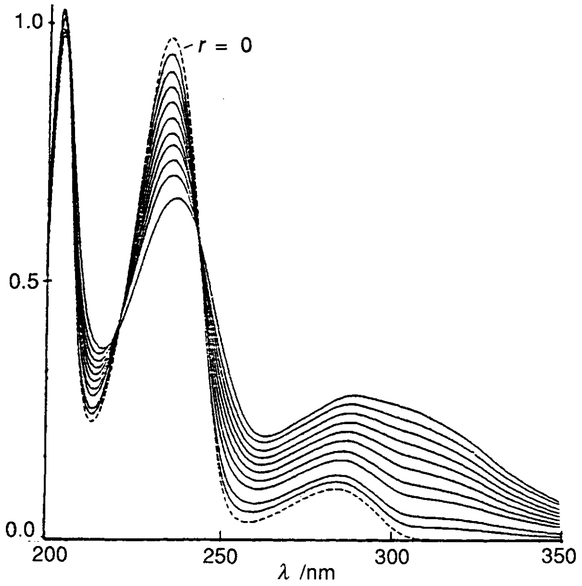


Fig. 1 Spectral change of sodium *p*-methylphenylsulphamate (**1b**) in methanol (degassed) with irradiation time of 1 min

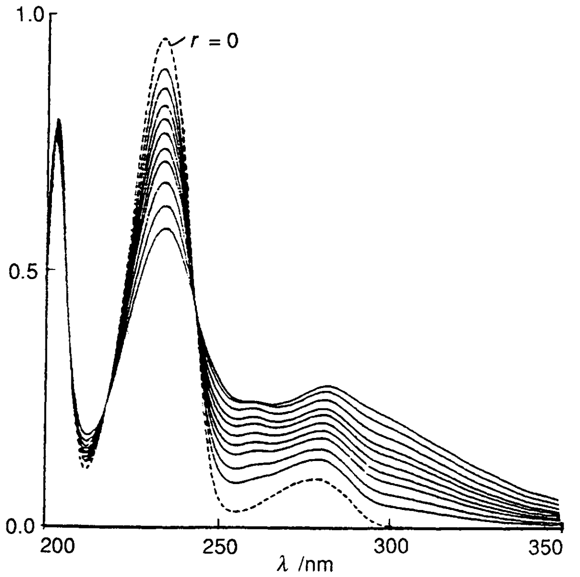


Fig. 2 Spectral change of sodium phenylsulphamate (**1a**) in methanol (degassed) with irradiation time of 1 min

Table 2 Photolysis of compounds **1a** and **1b** at 254 nm

Compound[a]	Conversion (%)	Amine (%)	*ortho* (%)	*meta* (%)	*para* (%)
1a	7.0	27.0 (**5**)[b]	22.2 (**2**)	5.1 (**3**)	39.4 (**4**)
1b	8.7	54.1 (**7**)	41.2 (**6**)	—	—

[a] 0.01 mol dm^{-3} **1a** or **1b** in MeOH and 1 min irradiation time. Percentages are based on consumed material. [b] The numbers in parentheses refer to the structures Nos. in the scheme.

lysis-type reaction in each solvent since the methanol and ethylene glycol used, though Analar or HPLC grade, were not thoroughly dried but capture of a hydrogen atom by an anilinyl radical is consistent with the higher proportion of the product (Table 4, see later) in the presence of a potential H-atom donor, butanethiol. A mass balance of >93% was obtained in each solvent indicating a clean reaction. The 4-methyl group blocks migration to the *para* position causing a subsequent increase in

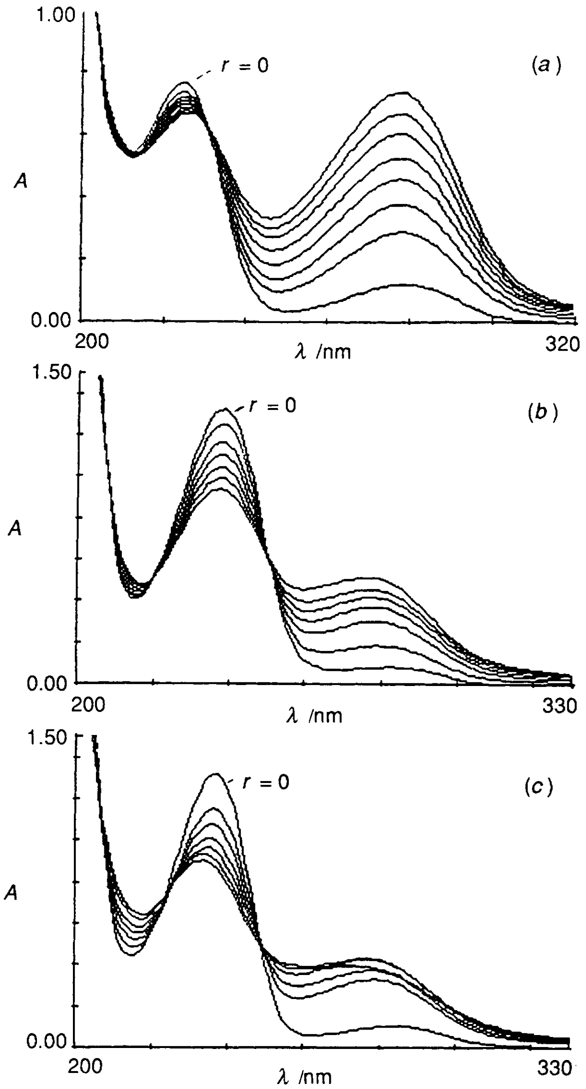


Fig. 3 Spectral changes of degassed methanolic solutions of sodium *p*-fluoro- (*a*), *p*-chloro- (*b*) and *p*-bromo- (*c*) phenylsulphamates. Total irradiation time for each compound *ca.* 42 s.

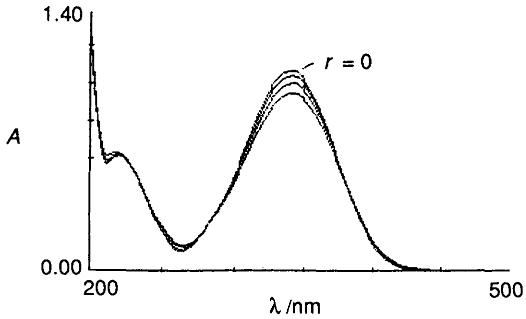
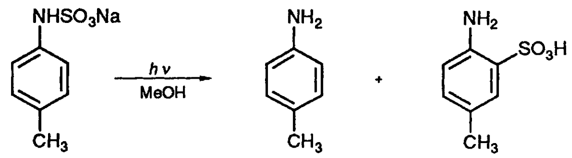


Fig. 4 Spectral change of methanolic solution of sodium *p*-nitrophenylsulphamate (**1f**) with irradiation. Total irradiation time *ca.* 10 min.



1b **7** **6**

Scheme 2 No *meta* product formed

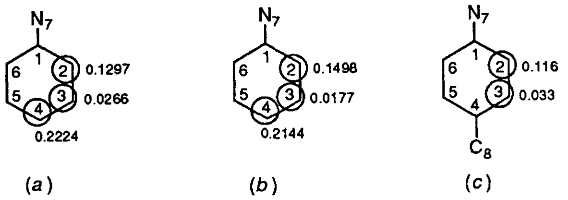


Fig. 5 Odd-electron densities of the anilinyl radical from (*a*) MINDO/3 and (*b*) Shizuka [see ref. 10(*b*)] and of (*c*) the 4-methylanilinyl radical from MINDO/3

Table 3 Effect of solvent on the photoreaction of **1b**[a]

Solvent	Conversion (%)	4-Methylaniline (%)	4-Methylaniline-3-sulphonic acid (%)
Water	9.7	58.9	37.5
Methanol	8.7	54.1	41.2
Ethylene glycol	9.6	58.3	35.4

[a] 1 min irradiation time; 0.01 mol dm^{-3} substrate. Percentages are based on consumed material.

Table 4 Effect of additives on the photoreaction of **1b**[a]

Additive	c/mol dm^{-3}	Conversion (%)	4-Methylaniline (%)	4-Methylaniline-3-sulphonic acid (%)
Butanethiol	0.002	10.5	77.7	19.0
Acetophenone	0.200	—[b]	—[b]	—[b]
Benzene	0.200	9.9	61.2	34.3
(*E*)-penta-1,3-diene	0.005	5.8	86.3	9.2
	0.001	7.7	74.1	19.5
None[c]		8.1	54.3	41.4

[a] In methanol and 1 min irradiation time; 0.01 mol dm^{-3} substrate. Percentages are based on consumed material. [b] Not detected. [c] Refers to direct irradiation, *i.e.* without additive.

the yields of *ortho* product and degradation product relative to that obtained from the parent **1a** due to the absence of the possibility of *para* migration. Surprisingly no *meta*-rearranged product formed in any of the solvents. Some *meta* product would be expected since an increase in electron density at the position *meta* to the amino group would be expected due to the electron-donating 4-methyl group. Following Shizuka,[10b] who successfully correlated the *ortho*:*para* ratio of rearranged products from the photo-Fries rearrangement of acetanilide with the calculated semiempirical odd π-electron densities of the anilinyl radical, we calculated odd π-electron densities for each position of the anilinyl and the 4-methylanilinyl radicals using a MINDO/3 method[17] (Fig. 5).[17] The MINDO/3 results for the anilinyl radical compare favourably with those of Shizuka. Interestingly, the π-electron densities for the anilinyl radical from MINDO/3 correlate very accurately the substitution pattern that we have observed when compound **1a** is photolysed. The experimentally observed (Table 2) ratio of *ortho*, *meta* and *para* for **1a** is 4.3:1:7.7 and from MINDO/3 this is given as 4.8:1:8.3. Shizuku's calculations give 8.3:1:12. For the 4-methylanilinyl radical there is an increase (compared with the anilinyl radical) in electron density at the *meta* position (to the amino group) and a decrease at the *ortho* position. This is as expected from the introduction of the 4-methyl substituent. The reason for the absence of 4-methylaniline-3-sulphonic acid in the photolysis products of **1b** is unclear.

The effect of the initial concentration of **1b** on the product distribution was examined over a range of concentrations (0.001–0.05 mol dm^{-3}) in water and as with compound **1a**[14] little change was found in the proportion of **6** to **7** formed at the varying concentrations. This indicates the involvement of a solvent cage and suggests that the reaction is intramolecular.[6a] Suprisingly, change of solvent here had little effect on the product distribution (Table 3).

Effect of Additives on **1b**.—The effect of a number of additives on the photoreaction was studied (Table 4). A clean reaction was evident since in each case >95% of the starting material was accounted for as **6** and **7**. As with **1a**[14] the yield of rearrangement products is considerably lowered in the presence of the radical scavenger butanethiol with a corresponding increase in the yield of 4-methylaniline suggesting participation of a radical process in the photorearrangement. Sensitization with acetophenone proved unsuccessful* but benzene did prove effective in yielding the same photoproducts as those in the direct irradiation indicating triplet-state involvement. To see if this was the case the effect of adding (*E*)-penta-1,3-diene was examined at two concentrations. The increase in the ratio of 4-methylaniline to 4-methylaniline-3-sulphonic acid with increasing concentration of diene suggests the participation of two excited states.† Therefore by analogy with the results obtained from quenching studies on the photoreaction of **1a**,[14] it seems reasonable to conclude that these excited states are again two triplet states—a long-lived state, T_1, leading to 4-methylaniline-3-sulphonic acid and 4-methylaniline, and a short-lived state, T_2, leading to 4-methylaniline only.

Irradiation of **1c**, **1d** *and* **1e**.—In Table 5 are presented the results obtained from the photolyses of methanolic solutions of the *para*-halogeno-substituted phenylsulphamates (Scheme 3). The dramatic drop in pH observed after just one minute of irradiation time and the high yield of photosolovlysis product, 4-methoxyphenylsulphamic acid **8** point to substantial carbon–halogen bond cleavage. Photorearrangement of **8** is unlikely since it would absorb only a fraction of the incident light at less than 10% conversions. High yields of 4-chloro- and 4-bromoaniline were obtained but only a trace of 4-fluoroaniline was detected. This is a result of thermal nitrogen–sulphur bond cleavage at the low final pH values[18] reached on irradiation of **1d** and **1e**. However the final pH value reached for **1c** is less acidic at 4.0 and hence little cleavage of the N–S bond occurs. In these irradiations no phenylsulphamic acid (**1a**), which would arise from homolytic cleavage of the carbon–halogen bond followed by hydrogen abstraction from the solvent was detected. It is unlikely that there were any rearrangement products formed since no other peaks were detected on the HPLC chromatogram except for traces of 4-methoxyaniline arising from thermal cleavage at low pH of the nitrogen–sulphur bond in **8**.

These results are not surprising. Photolysis of aryl halides is well known to lead to the homolytic fission of the carbon–halogen bond in non-polar solvents,[19] but in aqueous or

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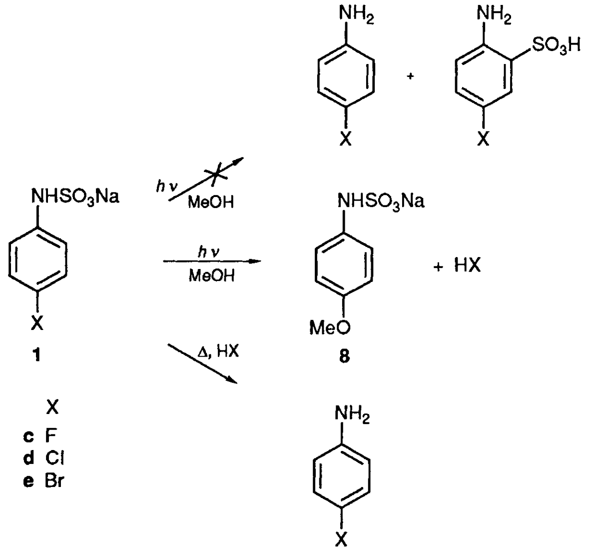
* A referee has pointed out that the absence of reaction in acetophenone may be due to the fact that its concentration was so high that substrate absorption was swamped. The concentration of sensitizers was chosen in such a way that >93% of the incident light was absorbed.

† A second referee has suggested that the 1,3-diene might be increasing the yield of anilines/toluidines by acting as a source of hydrogen atoms. This is unlikely because in unpublished studies on **1a** when biacetyl was substituted for the diene, a curve which was almost identical with that reported[14] for aniline formation in the presence of the diene in the photoreaction of **1a** was obtained.

Table 5 Irradiation of *p*-halogenated phenylsulphamates[a]

Compound	Conversion (%)	*p*-$MeOC_6H_4NHSO_3Na$ (%)	*p*-$XC_6H_4NH_2$ (%)	Initial pH	Final pH
1c	14.7	93.2	<1	7.5	4.0
1d	32.8	54.0	35.5	7.8	1.5
1e	18.9	44.4	40.2	8.4	2.2

[a] 0.01 mol dm^{-3} in methanol and irradiation time of 1 min. Percentages are based on consumed material.



Scheme 3

alcoholic media a photosolvolysis reaction takes place.[19,20] The problem of competing photodehalogenation in photo-Fries reactions is not uncommon. Irradiation of halogeno-derivatives of *O*-benzoyloxyacetophenone gave results consistent with an initial cleavage of the carbon–halogen bond followed by rearrangement.[21] Shizuka[10b] in a study on the photo-Fries reaction of acetanilide found that rearrangement to the *para* position did not occur when it was occupied by a methyl or a chloro group; however 4-iodo and 4-bromo were displaced by the migrating acyl group. The latter was attributed to a predissociation of the C–Br and C–I bonds caused by irradiation. The fact that the chloro group was not displaced is somewhat surprising as Kobsa observed displacement of this on irradiation of 4-*tert*-butyl-2,6-dichlorophenyl acetate.[22]

Irradiation of **1f**.—Hardly any spectral change was observed upon irradiation at λ = 254 nm of a dilute solution of 4-nitrophenylsulphamate **1f** in methanol even after 10 min. This inertness could be attributed to an internal quenching mechanism caused by the atomic rearrangement of the nitro group (especially the oxygen atom) in the excited Franck–Condon state. This explanation was also put forward by Shizuka[10b] who obtained a similar result on irradiation of 4-nitroacetanilide which he also followed spectrophotometrically. In a study on the photo-Fries reaction of benzanilides, the inertness of 2-nitrobenzanilide and 2′-nitrobenzanilide has been attributed to a lowering of the excited-state energy by the nitro group.[10e] The deactivation of the aromatic ring and the occurrence of other competitive photochemical reactions of the nitro group, which aromatic nitro groups are known to undergo,[19,23] has been put forward to explain the great reluctance of nitro derivatives in photorearrangement in 4-nitro-substituted phenyl esters.[24] However this explanation does not merit serious consideration here as there is very little disappearance of starting material **1f**.

Experimental

The phenylsulphamates **1a–f** were synthesized as their sodium salts from the corresponding amines by reported methods[25,26] and gave satisfactory elemental analyses and a good sulphamate test.[18] UV spectra were recorded at room temperature using a Shimadzu UV-260 Spectrophotometer. A Pye-Unicam Model 290MK2 pH Meter was used for pH measurements.

Photolyses.—Irradiations were carried out in quartz tubes with a Rayonet Srinivassen-Griffen Photochemical RPR-100 Reactor equipped with 16 low-pressure mercury vapour lamps (254 nnm) mounted vertically round the inside wall of the chamber. Methanolic solutions of the phenylsulphamates (10 mmol dm^{-3}) were irradiated for 1 min in clear cylindrical quartz vessels (17.5 cm × 2 cm). The solutions were purged with helium prior to and during irradiation. Photolyses with various additives [*e.g.* (*E*)-penta-1,3-diene for quenching experiments] were performed in a similar manner. The irradiated mixtures were analysed directly by HPLC. In the irradiation of **1c–e** analysis was carried out immediately after irradiation in order to prevent thermal hydrolysis of the nitrogen–sulphur σ-bond at the low final pH values reached after only 1 min of irradiation.

UV Monitoring.—The phenylsulphamates **1a–f** were dissolved in methanol (HPLC grade) to make approximately 0.1 mmol dm^{-3} solutions which were flushed with helium. After the initial UV spectrum was taken, the 1 cm quartz cuvette containing the sample solution was then placed in the Rayonet irradiation chamber. The cuvette was withdrawn from the chamber at regular intervals and spectra were recorded.

HPLC Analysis.—Using a modification of a previously reported method[27] the irradiated solutions were analysed by ion-pair reversed-phase HPLC. A Spherisorb 10 ODS column (25 cm × 16 mm i.d.) and a mobile phase consisting of 20% v/v acetonitrile–water containing 0.003 mol dm^{-3} Na_2HPO_4 and 0.003 mol dm^{-3} tetrabutylammonium hydrogensulphate adjusted to pH 6.5, was used for all analyses. The flow rate was 2 cm^3 min^{-1} and detection was at 254 nm. The products were identified by comparison with authentic samples and external standard calibration curves were used for assaying the mixture of products of photolyses.

Acknowledgements

J. M. thanks the Department of Education (Irish Government) for a grant and University College Galway for a teaching fellowship during the period when this work was carried out. Dr. Fujio Kanetani (University of Hiroshima) is thanked for some authentic samples of sulphonic acids and Dr. J. M. Simmie of this department is thanked for the MINDO/3 calculations.

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Paper 1/00075F
Received 7*th January* 1991
Accepted 20*th February* 1991