Competition between Carbon, Nitrogen, and Oxygen Nucleophilic Centres for Sulphur(VI) Attack in *NN*′-Disubstituted Sulphamides

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Reactions of five kinds, namely (i) the hydrolysis of substituted sulphamides to sulphamic acids, (ii) the hydrolysis of the substituted sulphamic acids to arylamine sulphates, (iii) the trans-sulphonation reactions of the sulphamic acids, (iv) the trans-sulphamoylation reactions of the substituted sulphamides, and (v) the amine interchange processes of the *NN*′-disubstituted sulphamides all appear to show certain common critical characteristics. Electron donation to the reaction site, the hexavalent sulphur atom, hinders all these processes, whereas electron withdrawal facilitates them. Because of this consistency we regard the key process around which this present work was constructed (the trans-sulphamoylation reaction) as being best interpreted in terms of direct nucleophilic attack at sulphur(VI) in the protonated sulphamide, most probably by the *para*-aryl carbon site in the aromatic nucleophilic substrate.

SOME years ago we reported [1,2] a new aromatic rearrangement which involved the intermolecular transfer of a sulphamoyl function (trans-sulphamoylation; path A, Scheme 1) from *NN*′-diarylsulphamides (1). This reaction was mechanistically interesting and also constituted a new route to substituted sulphonamides (2).[3] As a preliminary to a full mechanistic investigation, we have examined various processes which might or do compete with the rearrangement reaction.

EXPERIMENTAL

M.p.s were determined with an Electrothermal apparatus. Microanalyses were performed either by Drs. Weiler and Strauss, Oxford, or by Mrs. K. M. Duggan in this Department.

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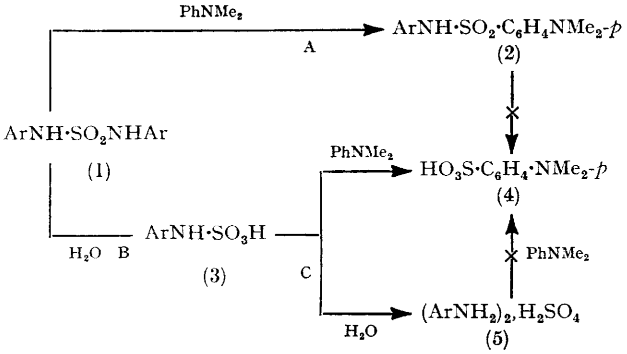
The three *NN'*-diarylsulphamides (1a—c) were prepared (*ca.* 30% yields) either by the reaction of sulphamide in dry pyridine with the appropriate arylamine[4] [for compounds (1a and b)] or by the reaction of sulphuryl chloride in dry pyridine with *p*-nitroaniline.[5] M.p.s agreed with the reported values,[4-6] and satisfactory analytical data (C, H, N, S) were obtained for samples dried (P_2O_5; 1 mmHg; 75°) for 48 h. The other *NN'*-disubstituted sulphamides (see Table 2) were prepared by standard methods and had the reported m.p.s.[7-9] Samples dried (P_2O_5; 20 mmHg; 78°) for 24 h gave satisfactory analytical data (C, H, N, S). Despite extensive drying these three sulphamides as bulk samples still retained occluded water.



a; Ar = Ph: b; Ar = *p*-MeO·C_6H_4: c; Ar = *p*-NO_2·C_6H_4

SCHEME 1

In the runs involving diarylsulphamides sealed glass ampoules were used for runs at 85°; runs at 196° were performed in a flask fitted with an air condenser with precautions taken to protect the mixture from moisture. The amine exchange runs were carried out in sealed glass ampoules.

Product Syntheses.—p-*Dimethylaminobenzenesulphonic acid derivatives.* *p*-Dimethylaminobenzenesulphonic acid, m.p. 265—267°, was prepared by the reaction of sulphuric acid with dimethylaniline,[10] or preferably by a modified Vilsmeier–Haack reaction.[11] The *S*-benzylthiouronium derivative had m.p. 203—204°. The sodium salt was mixed to a paste with 1·1 equiv. of phosphorus pentachloride, and an excess of aniline was then added. The mixture was diluted with an excess of ether and extracted with 10% sodium hydroxide. Acidification of the basic extracts yielded *p*-dimethylaminobenzenesulphonanilide (30%), m.p. 175—176° (lit.,[12] 176°). The *p*-nitro-analogue (2c), prepared similarly (25%), had m.p. 193—194°. n-Butylammonium and cyclohexylammonium sulphonates and the alkylammonium alkylsulphamates were prepared as described elsewhere.[13]

Rearrangement Studies.—(A) *With the diarylsulphamides* (1) *and dimethylaniline.* These were performed under anhydrous conditions, first with *NN'*-diphenylsulphamide as model compound, then with the three arylsulphamides and dimethylaniline in the presence of measured amounts of water. We shall illustrate the reactions concerned with compound (1a).

(i) *Anhydrous conditions.* (a) *At* 85° *for* 0·5 *h.* Compound (1a) (2 g, 0·008 mol) and dimethylaniline (10 ml, 0·078 mol) were heated together at 85° for 0·5 h. The solution was kept at room temperature overnight but no solid material separated. Addition of ether (*ca.* 100 ml) did not cause precipitation. The ethereal solution was extracted with 0·5N-sodium hydroxide (2 × 30 ml) and the combined extracts were acidified with 10% hydrochloric acid to yield starting material (1·86 g, 93%), m.p. 109—110° (from ethanol). In a similar reaction allowed to proceed for 26 h 92% of starting material was recovered.

(b) *At* 196° *for* 2 *h.* The same amounts as in run (a) were used. When the mixture was left at room temperature overnight, compound (2a) (1·62 g, 73%), m.p. 175—176° (from ethanol), separated out. The dimethylaniline mother liquor was treated with ether (*ca.* 100 ml) and extracted with 0·5N-sodium hydroxide (2 × 30 ml). Acidification of the combined extracts afforded starting material (1a) (23%).

(ii) *In the presence of water.* (a) *At* 85° *for* 0·5 *h.* Compound (1a) (2 g, 0·008 mol), water (0·144 g, 0·008 mol), and dimethylaniline (10 ml, 0·078 mol) were heated together at 85° for 0·5 h. The mixture, which contained a white precipitate, was cooled to 0° and maintained at this temperature overnight. The solid material was filtered off and washed with ether to leave aniline sulphate (0·68 g, 30%) m.p. >300°; picrate, m.p. 183—185°. Work-up of the filtrate as before afforded starting material (65%).

(b) *At* 85° *for* 26 *h.* The same amounts as in run (ii) (a) were used. After 12 h at 0°, a solid separated out. This was filtered off and washed free of dimethylaniline with ether (50 ml). The ethereal washings were added to the dimethylaniline mother liquor. The material was leached with hot ethanol (30 ml), leaving aniline sulphate (1·16 g, 50%). Concentration of the ethanolic solution yielded *p*-dimethylaminobenzenesulphonic acid (4) (0·08 g), m.p. 265—270°. On addition of ether (50 ml) to the dimethylaniline mother liquor a further quantity (0·035 g) of this sulphonic acid was precipitated. Starting material (0·72 g, 36%) was recovered from the ethereal solution.

(c) *At* 196° *for* 2 *h.* The same amounts as run (ii) (a) were used. Compound (4) (1·56 g, 97%) separated out overnight.

The reactions of compound (1b) parallel those just described and are summarised in Table 1. Only with compound (1c) were differences observed. We will illustrate this with one run—the data from all the runs are again summarised in Table 1.

Reaction of the nitro-compound (1c). Compound (1c) (2 g, 0·0059 mol), water (0·106 g, 0·0059 mol), and dimethylaniline (10 ml, 0·078 mol) were heated together at 196° for 2 h and then kept at room temperature overnight. The gummy material deposited was filtered off and washed with ether (100 ml). The ethereal washings were added to the mother liquor (liquor A). The gummy material was extracted with hot water (30 ml) (residue A) and the aqueous extract was concentrated to yield the sulphonic acid (4) (87%). Residue A was dissolved in 0·5N-sodium hydroxide. Acidification of this solution with 10% hydrochloric acid

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precipitated the sulphonamide (2c), m.p. 192—194°. Liquor A was washed with cold water, dried (Na_2SO_4), and evaporated to give *p*-nitroaniline. Addition of light petroleum (100 ml) to the dimethylaniline mother liquor gave more but not all of the *p*-nitroaniline (*p*-nitroaniline is slightly soluble in light petroleum). No efforts further to those described were made to isolate all the *p*-nitroaniline liberated.

TABLE 1

Reaction of *NN'*-diarylsulphamides with dimethylaniline in the absence and in the presence of water

Run no.*	X in (p-XC_6H_4·$NH)_2SO_2$	Reaction conditions Time (h)	Temp. (°C)	Sulphamide † recovery	Amine ‡	Sulphonic acid	Sulphonanilide
1	H	0·5	85	93			
2	H	26	85	92			
3	H	2	196	23			73
4	H	0·5	85	65	30		
5	H	26	85	36	50	7	
6	H	2	196			97	
7	MeO	0·5	85	85	15		
8	MeO	26	85	52	43	4 §	
9	MeO	2	196			97 §	
10	NO_2	0·5	85	56	38		
11	NO_2	26	85		55		24
12	NO_2	2	196		77 ¶	87 ¶	11

* Runs 1—3 were carried out in the absence of water with a dimethylaniline–sulphamide molar ratio of *ca.* 10 : 1. Runs 4—12 involved a dimethylaniline–sulphamide–water molar ratio of *ca.* 10 : 1 : 1. † Recovered sulphamide and the yields of products are expressed as %. ‡ Isolated as the sulphate in runs 4, 5, 7, and 8 and as the free base in runs 10—12. § Isolated as the anisidine salt. ¶ 77% Of the theoretical yield of *p*-nitroaniline was isolated; the total yield of sulphonic acid + rearrangement product is 100%.

TABLE 2

Sulphonation of aniline and *NN'*-dimethylaniline and attempted sulphonation of anisole with *NN'*-disubstituted sulphamides *

Run no.	R_2N in $(NR_2)_2SO_2$	Amount (g)	Substrate (10 ml)	Temp. (°C)	Time (h)	Sulphonation product (p-$R^1C_6H_4$·$SO_3^-R^{2+}$) R^1	R^2	Other material recovered $(NR_2)_2SO_2$	R^3NH·$SO_3^-R^{4+}$ R^3	R^4
1	Bu^{n}NH	0·5	$PhNH_2$	185	6	NH_2	NH_3Bu^n(88)			
2	Bu^{n}NH	0·5	$PhNMe_2$	195	6	NMe_2	NH_3Bu^n(87)			
3	C_4H_8NO	0·5	$PhNH_2$	185	6			(78)		
4	C_4H_8NO	0·5	$PhNMe_2$	195	6			(80)		
5	ChNH	0·5	$PhNH_2$	185	6	NH_2	NH_3Ch(80)			
6	ChNH	2·0	$PhNH_2$	185	6	NH_2	NH_3Ch(13) † [a]			
7	ChNH	1·0	$PhNH_2$	155	4			(42)	Ch	NH_3Ch(24)
8	ChNH	0·5	$PhNMe_2$	195	6	NMe_2	NH_3Ch(68)			
9	ChNH	2·0	$PhNMe_2$	195	6	NMe_2	NH_3Ch(37) † [b]			
10	ChNH	1·0	$PhNMe_2$	155	4	NMe_2	NH_3Ch(7)	(38)	Ch	NH_3Ch(40)
11	ChNH	2·0	PhOMe	155	12			(99)		
12	ChNH	2·0	PhOMe	185	4			(95)		

* Figures in parentheses are % yields. Ch = cyclohexyl. † Cyclohexylamine sulphate was also recovered: [a] 9%; [b] 11%.

(B) *With the other* NN'*-disubstituted sulphamides* (*Table* 2). A typical example is as follows (run 1). A mixture of *NN'*-di-n-butylsulphamide (0·5 g, 0·0024 mol) and aniline (10 ml) was maintained at 185° for 6 h and then left overnight at ambient temperature. The solution was treated with ether (10 ml); the white solid which separated gave n-butylammonium *p*-aminobenzenesulphonate (0·52 g, 88%), m.p. 174—175° (from ethanol); picrate, m.p. 151° (lit.,[14] 151°); *S*-benzylthiouronium derivative, m.p. 182° (lit.,[14] 182°).

The remaining data are summarised in Table 2. Products from runs 2, 5, and 8 were worked up as just described. In runs 3, 4, 11, and 12 unchanged sulphamide was recovered in large quantities; material from these runs was worked up by a similar method. Products from runs 6 and 9 were worked up by an analogous procedure. Overnight at room temperature, cyclohexylammonium sulphate [benzoyl derivative, m.p. 148–149° (lit.,[14] 147°)] separated out in both runs. Addition of ether (10 ml) to the mother liquor yielded the cyclohexylammonium salt of *p*-aminobenzenesulphonic acid, m.p. 256—257° (run 6) or *p*-dimethylaminobenzenesulphonic acid, m.p. 246—248° (run 9). Attempted chromatographic separation of the remaining material in run 9 on an alumina column yielded only tars, which were not resolved on attempted crystallisation from ethanol–ether or n-pentane. In run 6, the ethereal mother liquor was extracted with 0·5N-sodium hydroxide (2 × 30 ml); acidification of the extracts with 10% hydrochloric acid did not yield a solid product. The ethereal solution was washed with water (2 × 30 ml) and dried (Na_2SO_4), and the ether was evaporated off. The aniline solution remaining was passed through a column of alumina and eluted with chloroform. A considerable quantity of a tar was obtained which was not resolved on attempted crystallisation from ethanol–ether or n-pentane.

Material from runs 7 and 10 was worked up in the same manner. In run 7, the cooled solution was kept at room temperature overnight and ether (20 ml) was added. Fractional crystallisation from ethanol–ether of the material (0·86 g) which separated gave dicyclohexylsulphamide (0·42 g, 42%) and cyclohexylammonium cyclohexylsulpha-

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[14] 'Organic Reagents for Organic Analysis,' Hopkin and Williams, Chadwell Heath, 1956.

mate (0·26 g, 24%). However in run 10, a small quantity of cyclohexylammonium *p*-dimethylaminobenzenesulphonate (0·08 g, 7%), m.p. 247°, was isolated.

Attempted Sulphonation of Aniline with n-Butylammonium Sulphate.—n-Butylammonium sulphate (1 g, 0·0041 mol) and aniline (10 ml) were heated at 184° for 24 h. The sulphate, which remained largely undissolved, was recovered quantitatively by filtration of the cooled mixture.

Amine Exchange Runs.—*Run* 1. Compound (1a) (1 g, 0·004 mol) and n-butylamine (10 ml) were heated at 75° for 24 h. After 24 h at room temperature, *NN'*-di-n-butylsulphamide (0·45 g) had separated out. The mother liquor was evaporated to half bulk and water (10 ml) was added, whereupon more dibutylsulphamide (0·35 g), separated out. The combined solid fractions (0·8 g, 96%) were recrystallised (from 95% ethanol) to yield a sample of m.p. 125°.

Run 2. Compound (1a) (1 g, 0·004 mol) and cyclohexylamine (10 ml) were heated at 75° for 24 h. After 14 h at room temperature no solid had separated. The amine was evaporated off under reduced pressure at 60—70° to leave 3—4 ml of solution. Water (10 ml) was added and dicyclohexylsulphamide (1·05 g, 100%) precipitated out.

Run 3. Compound (1a) (1 g, 0·004 mol) and morpholine (10 ml) were heated together at 75° for 24 h. After 24 h at room temperature, a solid had separated out. Addition of ether (150 ml) to the solution precipitated compound (1a) (0·54 g). The filtered solution was extracted with 0·5N-sodium hydroxide (2 × 30 ml) and the combined extracts were acidified with 10% hydrochloric acid to yield more starting material (1a) (0·4 g). Material from run 4 was worked up similarly.

RESULTS AND DISCUSSION

We have used as a ' base-line ' in the present studies the interaction of compound (1a) with dimethylaniline. By careful exclusion of water, the key rearrangement process, namely, trans-sulphamoylation (path A, Scheme 1) was examined without interference. It proved a slow reaction, no rearrangement being detected after 26 h at 85°.

In runs carried out at 85° for 0·5 h in the presence of water (Table 1) all three diarylsulphamides showed the same kind of behaviour, *i.e.* partial hydrolysis to the corresponding alkylammonium sulphates (5) (path C, Scheme 1), with no evidence of any other process. We have established elsewhere [15] that such hydrolyses in aqueous media are acid-catalysed and in fact have found that compound (1a), after being refluxed for several h in 0·05N-sodium hydroxide, can be recovered in 92% yield.[16]

In the longer runs at 85° with added water, alkylammonium sulphate formation was again observed, the reactivity pattern being similar to that displayed in the shorter runs. However, two new reactions became visible; these reactions, while not substantial in terms of yield, were nevertheless keys to the kind of competitive behaviour compounds (1) may display. With two of the materials, (1a and b), small quantities (7 and 4%, respectively) of compound (4) were isolated. With compound (1c) the reaction was not entirely clean (some gums being formed), but none of compound (4) was isolated; instead 24% of the rearrangement product, the substituted sulphonamide (2c) was obtained.

In the dimethylaniline reaction liquor initially two nucleophiles can compete for attack at the hexavalent sulphur site in compounds (1), these nucleophiles being water and the dimethylaniline itself (either N or C centres). With the most electrophilic of the sulphamides (1c) the dimethylaniline (predominant in quantity though clearly not in reactivity, at 85°) attacks sulphur *prior to* any hydrolysis [under the experimental conditions compounds (2) are not converted into the acid (4)], and compound (2c) can be isolated. With the less electrophilically active (and therefore more selective) sulphamides (1a and b), attack of water occurs exclusively and the corresponding arylsulphamic acids (3a and b) are formed as intermediates. We regard the formation of the sulphonic acid (4) as attesting to the presence of such sulphamic acids (3) as intermediates. The appropriate sulphamic acid then undergoes competitive attack *vis-à-vis* water and dimethylaniline.* In the runs concerned the water attack is again predominant, yielding the arylamine salts (5). However, compounds (3) possess more reactive sulphur centres than compounds (1) and so attack by dimethylaniline to yield the sulphonic acid (4) occurs.

In the high temperature runs, in the presence of water, these trends are reflected in a different way. First, no sulphate formation was observed; therefore the ready low-temperature hydrolysis of the sulphamic acid system (3) is completely dominated by the reaction with the higher activation energy, namely trans-sulphonation, to yield compound (4). Only with the most electrophilic sulphamide (1c) was this tendency resisted to any extent, its rearrangement reaction [to yield (2c)] remaining a competitor [though minor (11%)] to the hydrolysis–sulphonation process (B) which takes place to the extent of 87%.

Because of the common pattern of reactivity displayed in three diverse reactions, namely (i) hydrolysis of compounds (1) to arylammonium sulphates (5), (ii) hydrolyses (and trans-sulphonations) of the sulphamic acids (3), and (iii) (to a lesser extent) the trans-sulphamoylation reaction [(1) $\longrightarrow$ (2)] we consider that all three occur by nucleophilic attack at sulphur, a process which we have unequivocally demonstrated in the first two instances.[15,18]

The sequence given in Scheme 2 outlines some of the mechanistic options. There are three paths available for the generation of a sulphamoylating species from the protonated sulphamide (6): (*a*) dissociation to a sulphamoylium ion (7), which will most probably be ' solvated '

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* In our initial report on these results [17] the pattern of behaviour recorded here was also reported. However, the earlier details differed somewhat from the present, inasmuch as we were not then aware of the tenacity with which diarylsulphamides can retain quantities of moisture. Therefore the sulphamide–water ratios given were not accurate.

[15] W. J. Spillane, J. A. Barry, and F. L. Scott, *J.C.S. Perkin II*, submitted for publication.

[16] F. L. Scott, unpublished data.

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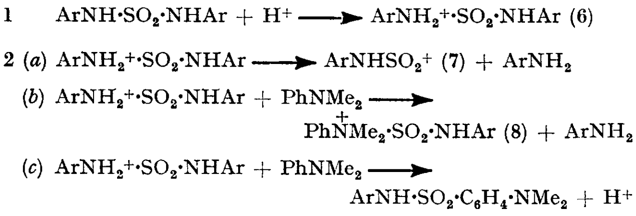
as the tertiary amine salt (8); (*b*) nucleophilic displacement by the tertiary amine (at N) to yield the salt (8), and (*c*) direct attack on an aromatic ring by (6) to yield the sulphonamide (2), the ultimate sulphamoylation product. The possibility of direct aromatic attack on the ion (6) is supported by, for example, (i) a direct equivalent trans-nitrosation shown recently to be involved in the Fischer–Hepp reaction[19] and by (ii) our radiochemical studies with [^{35}S]-labelled 1-naphthylsulphamic acid, wherein nuclear sulphonation without [^{35}S]-exchange with non-labelled sulphuric acid in the medium was reported.[20]



1 $ArNH\cdot SO_2\cdot NHAr + H^+ \longrightarrow ArNH_2^{+}\cdot SO_2\cdot NHAr$ (6)

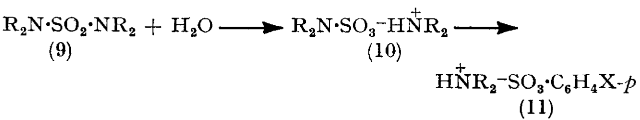
2 (*a*) $ArNH_2^{+}\cdot SO_2\cdot NHAr \longrightarrow ArNHSO_2^{+}$ (7) $+ ArNH_2$

(*b*) $ArNH_2^{+}\cdot SO_2\cdot NHAr + PhNMe_2 \longrightarrow Ph\overset{+}{N}Me_2\cdot SO_2\cdot NHAr$ (8) $+ ArNH_2$

(*c*) $ArNH_2^{+}\cdot SO_2\cdot NHAr + PhNMe_2 \longrightarrow ArNH\cdot SO_2\cdot C_6H_4\cdot NMe_2 + H^+$

SCHEME 2

Alkylsulphamoylium ions (of type $R_2NSO_2^{+}$) have been suggested as intermediates in the solvolyses of dialkylsulphamoyl chlorides, particularly in the presence of mercury(II) perchlorate.[21] Similarly, their conjugate bases, the alkylsulphonylamines, $RNSO_2$, have recently been invoked as intermediates in several reactions.[22] Because of the apparent tendency of alkyl groups to promote, or at least stabilise, such scissions we next extended our sulphamide study to some other *NN'*-disubstituted sulphamides (9) (Scheme 3). We used three such compounds, *NN'*-di-n-butyl- and *NN'*-dicyclohexyl-sulphamides and *NN'*-sulphuryldimorpholine and three substrates, aniline, dimethylaniline, and anisole. The morpholine derivative proved unreactive towards aniline and dimethylaniline (Table 2). Similarly anisole was unaffected by *NN'*-dicyclohexylsulphamide.



$R_2N\cdot SO_2\cdot NR_2 + H_2O \longrightarrow R_2N\cdot SO_3^{-}H\overset{+}{N}R_2 \longrightarrow H\overset{+}{N}R_2{}^{-}SO_3\cdot C_6H_4X\text{-}p$

(9) (10) (11)

SCHEME 3

With dimethylaniline, *NN'*-di-n-butylsulphamide (6 h; 185°) yielded the corresponding *p*-substituted sulphonic acid, as its butylammonium salt (11; $X = NMe_2$, $R_2N = BuNH$), by a reaction akin to those discussed earlier with the diarylsulphamides except that in the alkyl case no extra water had to be added to produce the intermediary sulphamic acid (10). Clearly despite our care in drying and general precautions taken to exclude water and to dry the reagents, enough water was present to induce reaction. With aniline as substrate (a reaction we could not attempt with the substituted diphenylsulphamides because of ready amine interchange) no amine interchange was detected, the material obtained again being the trans-sulphonation product (11; $X = NH_2$, $R_2N = BuNH$).

We explored the processes operating in the alkylsulphamide case in more detail by use of *NN'*-dicyclohexylsulphamide (9; $R_2N = C_6H_{11}NH$) as model reagent. Apart from obtaining sulphonic acids in runs 5 and 8, we obtained substantial amounts of the cyclohexylammonium salt of cyclohexylsulphamic acid (10; $R_2N = C_6H_{11}NH$) in two runs at 155°.

In these latter reactions therefore we have evidence to substantiate our hypothesis (path B, Scheme 1) that sulphamic acids are intermediates in these amine-induced cleavages of sulphamides (water being available). The sulphonic acid (11; $X = NMe_2$, $R_2N = C_6H_{11}NH$) was the sole product isolated under more forcing conditions (196°; 6 h), as expected.

These results can be rationalised along with the arylsulphamide results discussed earlier. First, the sulphamides involved are clearly less electrophilic than the diaryl cases and so no rearrangements (or even amine exchanges) are observed. This again argues against sulphamoylium species of the type $RNHSO_2^{+}$ or $RNSO_2$ being involved. Secondly, as expected, these compounds are less prone to the other reactions also, being hydrolysed and sulphonated more slowly.

As we have mentioned, these latter sulphamides did not undergo amine exchanges of the type $(RNH)_2SO_2 + R'NH_2 \rightleftharpoons (R'NH)_2SO_2 + RNH_2$ with arylamines, whereas diarylsulphamides themselves exchange readily with other more basic arylamine functions. We checked to see whether the reverse reaction, exchange of aryl for alkyl functions in sulphamides, could occur. Maintaining compound (1a) in excess of n-butylamine or cyclohexylamine for 24 h at 75° gave quantitatively the corresponding *NN'*-dialkylsulphamide. With morpholine as reaction medium and again with compound (1a) as substrate no such exchange occurred.

[2/689 *Received*, 23*rd March*, 1972]

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