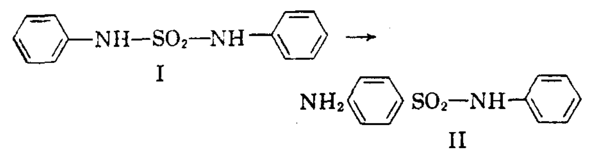
Communications TO THE EDITOR

A New Aromatic Rearrangement.[1] The Migration of Substituted Sulfamyl Groups

Sir:

When aniline and sulfamide are allowed to react in a 1:1 ratio at 150° for six hours without solvent, they form sulfanilanilide (II) in 24% yield and not 1,3-diphenylsulfamide (I).[2] When sulfamide is heated at 150° for three hours in a large excess of aniline, I is the major product (60%), even though small quantities (1–5%) of II are detected. By further heating of I in aniline solution in the presence of catalysts such as ammonium, anilinium, or triethylammonium hydrochlorides, it can be converted into II, thus



When I is heated for three hours at 150° in an excess of *N*,*N*-dimethylaniline, 4-dimethylaminobenzenesulfonanilide is formed in 26% yield. Its formation results from the transfer of a phenylsulfamyl group from I to the amine, and it suggests the rearrangements of I are *intermolecular.*

Some further transfer experiments in *N*,*N*-dimethylaniline (for three-hour periods and without catalyst) resulted in the migration (from the appropriate sulfamide) of a *p*-tolylsulfamyl group in 43% yield and a 2-pyridylsulfamyl entity quantitatively. With 1-phenylsulfamide, both phenylsulfamyl and sulfamyl moieties substituted the amine solvent to the respective extents of 3 and 12%. Sulfamide under these conditions yielded largely ammonium imidodisulfamide, but some (5%) 4-dimethylaminobenzenesulfonamide was obtained. Both 1,3-diphenyl-1,3-dimethylsulfamide and 1-phenyl-3,3-dimethylsulfamide failed to react. The transfer of sulfamyl functions to a phenolic ether was attempted. Thus I was refluxed in anisole (at 150° for three hours) in the presence of aniline hydrochloride. However no attack of solvent was detected; II was formed in 10% yield and 75% of I was recovered.

A solution of 1,3-di(2′-pyridyl)sulfamide (III) in an excess of aniline was refluxed for three hours. On work-up, a 1.5% yield of II was isolated together with a 45% yield of I. No pyridyl substituted sulfonamide could be detected. Amide exchange processes thus occur readily, and when exchange is complete, rearrangement of the product begins. This reaction of III in aniline was repeated with an equimolar quantity of aniline hydrochloride present. While I was then obtained in diminished yield (2%) the yield of II increased to 22%, and again no pyridyl substituted sulfonamide resulted. Even in a solvent, the exchange process dominated. A solution of III and equimolar quantities of aniline and aniline hydrochloride in an excess of phenetole was refluxed for three hours. On work-up, the sole product isolated was II in 32% yield. A solution of I in an excess of *N*-methylaniline was refluxed (at 193°) for seventeen hours. The possible exchange product does not rearrange. A 35% yield of 4-*N*-methylaminobenzenesulfonanilide resulted. Apparently where steric hindrance is offered to exchange, transfer reactions can be observed.

The yields of products mentioned above represent yields of purified materials. In general, the substances concerned correspond to greater than 90% of the total materials isolated. A side reaction occurring in all the reactions examined despite precautions adopted to maintain dry reaction systems was hydrolysis of the substituted sulfamides to salts of the corresponding sulfamic acids.

We feel that these rearrangements involve sulfamylonium ions ($(RNHSO_2)^+$), and the evidence at hand suggests that these are much more readily liberated from sulfamides than are sulfonylonium ions[3] from sulfonamides undergoing rearrangement.

This work was supported in part by the Office of Naval Research.

RESEARCH AND DEVELOPMENT DEPARTMENT
PENNSALT CHEMICALS CORP.
WYNDMOOR, PA.

FRANCIS L. SCOTT[4]
CHARLES W. SCHAUMANN
JAMES P. KING

Received October 4, 1960

---

[1] When we had completed this work, we discovered that Vollmann, Geilenkirchen, and Hamann, of I.G. Farbenindustrie, Uerdingen, had noticed 1,3-diphenylsulfamide could be converted into sulfanilanilide. This has never been published and is not abstracted in the P.B. Abstracts. It is mentioned in P.B. Report 103,755 from the 1944 Zetko Exchange of Information.

[2] The reaction of aniline and sulfamide to yield I has been described by A. Paquin, *Angew. Chem.*, **A60**, 316 (1948); K. Hamann, German Patent **869,065**: 2nd March, 1953; and A. V. Kirsanov, *Zhur. Obshchei Khim.*, **23**, 223 (1953).

[3] See S. Searles and S. Nukina, *Chem. Revs.*, 59, 1077 (1959). We are indebted to Prof. Searles for a copy of this article prior to its publication.

[4] To whom correspondence is to be addressed, at University College, Cork, Ireland.