been discontinued, there will be no further meetings of the Committee on Grants-in-Aid.

A limited fund is still available, however, for the making of grants in the medical sciences only. The next meeting of the Council's Division of Medical Sciences for the awarding of grants will be held in November, 1936. Applications should be addressed to the Secretary, Division of Medical Sciences, National Research Council, 2101 Constitution Avenue, Washington, D. C. Applications to be considered at the November meeting must be on file on or before October 1, 1936.

Frank R. Lillie,
Chairman, National Research Council

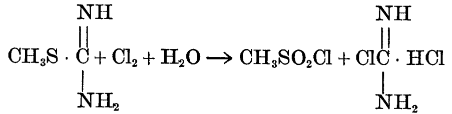
SPECIAL ARTICLES

THIOUREA AS A KEY REAGENT FOR THE PREPARATION OF ALIPHATIC SULPHONYL CHLORIDES AND BROMIDES[1]

A class of organic compounds which has not received its proper share of attention by organic chemists is that comprising the aliphatic sulphonyl halides, ($R\cdot SO_2Cl$ and $R\cdot SO_2Br$) and their derivatives. They represent one of the forgotten groups in our rapid development of the chemistry of aliphatic compounds. The introduction of the sulphonic acid radical ($—SO_2OH$) into aliphatic compounds by direct treatment with sulphuric acid is extremely limited in its application and is not of practical utility. The method of synthesis which has proven most serviceable is one involving direct replacement of a halogen atom in an aliphatic compound with the sulphonic acid group by interaction with sodium sulphite. The standard procedure for conversion of sulphonic acids into their corresponding halides is by treatment with the required phosphorus halide (PCl_5 or PBr_5). In many cases, however, this method is not practical, and furthermore the use of phosphorus halides has serious objections in both industrial and laboratory operations.

Professor Karrer in the revised edition[2] of his well-known book, "Lehrbuch der Organischen Chemie," introduces the chapter on sulphonic acids as follows: "In der aliphatischen Reihe spielen Sulfonsauren eine untergeordnete Rolle (s.d.); sie sind für allgemeinere Verwendbarkeit zu schwer zugänglich."

The authors desire to report in this preliminary note that aliphatic sulphonyl chlorides and bromides can be prepared with ease without the use of phosphorus halides in any form. In place of the common phosphorus halides used in organic synthesis for preparing such halides the authors substitute thiourea. Starting with this cheap sulphur reagent and an aliphatic halide or alcohol we have developed a method of synthesis which makes the sulphonyl halides available in any quantity desired. The reaction applied, for example, for the synthesis of methyl sulphonyl chloride II is expressed below:



$$CH_3S\cdot\underset{\underset{NH_2}{|}}{\overset{\overset{NH}{\|}}{C}} + Cl_2 + H_2O \rightarrow CH_3SO_2Cl + Cl\underset{\underset{NH_2}{|}}{\overset{\overset{NH}{\|}}{C}}\cdot HCl$$

I. II. III.

The s-methylisothiourea I, which is obtained in quantitative yield in the form of its sulphate by interaction of dimethyl sulphate with thiourea, reacts with nascent chlorine in cold aqueous solution to form the sulphonyl chloride II in a yield of 76 per cent. of theory. Marvel, Helfrick and Belsley[3] report that the yield of this same sulphonyl chloride II when prepared by treatment of the sodium salt of methyl sulphonic acid (CH_3SO_2ONa) with phosphorus pentachloride is 21–27 per cent. of theory. If bromine is substituted for chlorine in the authors' process an excellent yield of methyl sulphonyl bromide (CH_3SO_2Br) is obtained. A paper describing this new method of preparing aliphatic sulphonyl halides has been presented by the authors for publication in a future number of the *Journal of the American Chemical Society*.

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James M. Sprague

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[1] From the Sterling Chemistry Laboratory of Yale University, New Haven, Connecticut.

[2] "Lehrbuch der Organischen Chemie," Vierte Auflage, Georg Thieme, Verlag, Leipzig (1936).

[3] *Jour. Amer. Chem. Soc.*, 51: 1272, 1929.

BAR DUPLICATION

In connection with the article "Bar as a Duplication,"[1] published in the February 28 issue of Science, and signed by C. B. Bridges in Pasadena on February 21, the attention of American readers is called to the fact that essentially the same findings and interpretation as here given by Bridges had already been set forth by the undersigned in co-authorship with Prokofyeva and Kossikov in a preliminary article without figures, entitled "Unequal Crossing over in the Bar Mutant as a Result of Duplication of a Minute Chromosome Section."[2] This article was sent in on December 15, 1935, to the bi-monthly journal, *Comptes Rendus of the Academy of Sciences of the USSR*, and was published in the second number of that journal for 1936, issued on January 25. This issue probably did not

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[1] C. B. Bridges, Science, 83: 210–211, 1936.

[2] H. J. Muller, A. A. Prokofyeva-Belgovskaya and K. V. Kossikov, *C.R. Acad. Sci. USSR.*, 2: 78, 1936.