those for the other three tetrachlorides, yet the difference is greatest for that substance. In all cases the symmetry number would turn out greater than 12 (59 for CCl_4) if the results were used to calculate that quantity.

On the assumption that some more fundamental difficulty is not involved, it is possible that the differences found are to be ascribed to incomplete knowledge of the vibrational states of non-linear polyatomic molecules. Accordingly, great accuracy cannot, at present, be ascribed to the results of spectroscopic entropy calculations for polyatomic molecules in those cases where all of the necessary energy levels are not accurately known and correctly interpreted. For the approximate estimation of free energies[6] such entropies are, however, often of considerable value.

(6) Kassel, THIS JOURNAL, **55**, 1351 (1933).

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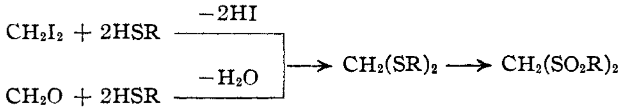
THE METHYLENE DISULFONES[1]

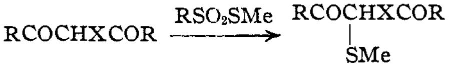
Sir:

These substances are of considerable interest as cogeners of Sulphonal. The general methods of preparation, outlined as early as 1877,[2] are expressed



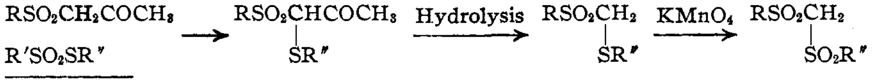
$$\left.\begin{array}{l}CH_2I_2 + 2HSR \xrightarrow{-2HI} \\ CH_2O + 2HSR \xrightarrow{-H_2O}\end{array}\right] \longrightarrow CH_2(SR)_2 \longrightarrow CH_2(SO_2R)_2$$

In the past month a simple modification of the former scheme was described by Stutz and Shriner which, by obviating the isolation of mercaptan, greatly reduces the offensive odor of the process. Unfortunately, the yields were not very good, and the methylene disulfides, though less volatile, have persistent and unpleasant odors. These drawbacks can be avoided completely by an extension of the work of Brooker and Smiles.[3] They showed



$$RCOCHXCOR \xrightarrow{RSO_2SMe} RCO\underset{\displaystyle SMe}{\underset{|}{C}}HXCOR$$

By applying this to sulfonyl ketones I developed a process (1931)[4] whereby disulfones were obtained with no obnoxious intermediate at all.



$$\begin{array}{l}RSO_2CH_2COCH_3\\ R'SO_2SR''\end{array} \longrightarrow RSO_2\underset{\displaystyle SR''}{\underset{|}{C}}HCOCH_3 \xrightarrow{\text{Hydrolysis}} RSO_2\underset{\displaystyle SR''}{\underset{|}{C}}H_2 \xrightarrow{KMnO_4} RSO_2\underset{\displaystyle SO_2R''}{\underset{|}{C}}H_2$$

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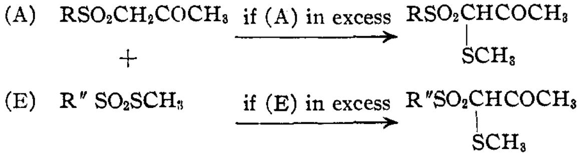
(1) Stutz and Shriner, THIS JOURNAL, **55**, 1242 (1933).

(2) Claesson, *J. prakt. Chem.*, **15**, 176 (1877).

(3) Brooker and Smiles, *J. Chem. Soc.*, 1723 (1926).

(4) D. T. Gibson, *ibid.*, 2637 (1931).

It is evident that this reaction possesses the additional advantage of applicability to the preparation of unsymmetrical[5] methylene disulfones, and in developing it to that end a most interesting type of radical exchange has been discovered[6]



$$\begin{array}{lcl} (A)\quad RSO_2CH_2COCH_3 & \xrightarrow{\text{if (A) in excess}} & RSO_2\underset{\displaystyle SCH_3}{\underset{|}{C}}HCOCH_3 \\ \quad + & & \\ (E)\quad R''SO_2SCH_3 & \xrightarrow{\text{if (E) in excess}} & R''SO_2\underset{\displaystyle SCH_3}{\underset{|}{C}}HCOCH_3 \end{array}$$

Results already obtained indicate that the exchange is $R''SO_2$ for RSO_2 (rather than R″ for R). Further, where R and R″ are both aryl (or both alkyl), the exchange of radicals is a mass action effect, but while alkyl sulfonylacetones are readily converted to aryl derivatives, the reverse has not been observed.

Obviously, if R = R″, the exchange phenomenon is not observed, and as methylene di-*n*-butyl disulfone now figures in the literature with two widely discrepant melting points,[7] I would suggest that the sulfonyl acetone route might be used to give an independent confirmation of one or the other value.

[5] Posner, *Ber.*, **36**, 200 (1903).

[6] *J. Chem. Soc.*, 1819 (1932); 306 (1933).

[7] Stutz and Shriner, Ref. 1, m. p. 96°; Whitner and Reid, THIS JOURNAL, **43**, 638 (1921), m. p. 182°.

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THE FRACTIONATION OF ISOTOPES BY ELECTROLYSIS

Sir:

In view of recent communications regarding the isotopic fractionation of the elements of water by electrolysis [Washburn and Urey, *Proc. Nat. Acad. Sci.*, **18**, 496 (1932); Lewis, THIS JOURNAL, **55**, 1297 (1933); Washburn, Smith and Frandsen, *J. Chem. Phys.*, **1**, 288 (1933)] it is of interest to record that in 1923 Dr. Malcolm M. Haring, working under my direction at Columbia University, achieved a slight fractionation of mercury by the same method. Electrolysis of an acid solution of mercurous nitrate, using a low voltage and low current density, gave mercury with a density only 0.999981 that of ordinary mercury. This value was the average of fourteen different electrolyses. Parallel experiments in which a high voltage and high current density were employed gave mercury with density unchanged.

The reduction in density, it will be seen, was only 19 parts per million, which represented three times the average deviation of the individual results. The greatest difficulty encountered in the whole investigation was