

pounds isomerize, and comparable also to the conditions of the above-mentioned mercaptal reaction.

The rearrangement of two allyl aryl thioethers has previously been reported,² both, however, involving "pyrolysis" of the compounds at their rather high boiling points (215–264°) in the absence of solvents or rearranging agents. The present communication reports briefly on the rearrangement of allyl *p*-tolyl sulfide, *s*-butyl *p*-tolyl sulfide and *s*-butyl phenyl sulfide in the presence of zinc chloride–acetic acid reagent which has been found³ a satisfactory rearranging medium for the oxygen ethers at temperatures as low as 112°.

In the three cases studied the thioether underwent partial rearrangement to one or more alkyl-substituted thiophenols, obtained finally by precipitation as lead mercaptides. Simultaneously a scission of the thioether molecule appeared to take place, fairly large amounts of allene and butylene being evolved. This is in sharp contrast to the non-production of unsaturated gases reported⁴ in thioether and oxygen ether pyrolysis, but corresponds exactly to the observations of Sprung and Wallis. The presence of thiophenol and *p*-thiocresol as the other scission products was indicated by the high percentage of lead found by analysis of the total lead mercaptide precipitate, and by interpolation an approximate ratio of rearrangement product to decomposition product was obtained. Although a part of the thiophenols set free in the reaction suffered oxidation to disulfides and could not be weighed as lead mercaptides, thereby rendering an accurate estimate of the extent of the rearrangement impossible, the isomerization of $-\text{CH}_2-\text{S}-\text{R}$ to $\text{R}(\text{CH}_2-)\text{SH}$ was definitely established.

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Experimental

The thioethers were prepared in good yields by heating the appropriate alkyl bromide for twenty-four hours at 110–120° with the sodium salt of thiophenol or *p*-thiocresol. Allyl *p*-tolyl sulfide had the properties described by Hurd; *s*-butyl phenyl sulfide, b. p. 104–105° (25 mm.); *s*-butyl *p*-tolyl sulfide b. p. 135–138° (22 mm.). All were colorless liquids of not unpleasant odor, giving no reaction with alcoholic lead acetate solution. The zinc chloride–

acetic acid reagent contained 10 g. of fused zinc chloride in 26 cc. of solution.

In a typical experiment 20–30 cc. of the zinc chloride solution was heated for three hours at 135–150° in a flask provided with a dropping funnel and connected *via* a reflux condenser to a gas buret. After the air thus had been displaced partially, 2.5–10 g. of the thioether was run in and the heating continued for twenty-four hours more, by which time the evolution of gas had practically ceased. By passing steam into the reaction flask all remaining gas was easily driven over into the buret, the contents of which were tested from time to time during the reaction period. The heavy, brownish product which remained in the flask was extracted with ether, and the portion of this which then dissolved in warm 95% alcohol was treated immediately with a saturated alcoholic solution of lead acetate. The precipitate of lead mercaptides was filtered off, washed, dried and analyzed for lead by the usual method of gentle ignition followed by treatment with nitric and sulfuric acids to give lead sulfate.

In the rearrangement of allyl *p*-tolyl sulfide, the volume of gaseous product having the properties of allene—odor, inflammability with luminous flame, reaction with bromine water and with mercuric chloride, inertness toward ammoniacal silver nitrate—amounted to 30–60 cc. per gram of thioether originally taken, the yield decreasing as the reaction temperature was raised from 135 to 150°. The orange lead mercaptide precipitate, presumably a mixture of the lead salts of *p*-thiocresol and 2-allyl-4-methyl thiophenol, gave on analysis 40.2–40.8% Pb. Calcd. for $\text{Pb}(\text{SC}_6\text{H}_4\text{CH}_3)_2$: Pb, 43.4; calcd. for $\text{Pb}(\text{S}-\text{C}_6\text{H}_5\text{C}_2\text{H}_5\text{CH}_3)_2$: Pb, 38.9. The value obtained by analysis would correspond to a mixed mercaptide precipitate containing from 57.5–71% of the lead salt of 2-allyl-4-methyl thiophenol.

In the case of the butyl aryl ethers similar results were obtained. The gaseous product had the properties of butylene but was produced in smaller quantity—from 25–37 cc./g. of the butyl phenyl sulfide, and from 10–15 cc./g. of the butyl *p*-tolyl sulfide. Only in the case of the former was a quantitative analysis of the mercaptide precipitate made. The heavy yellow powder was found to contain 41.8% Pb. Calcd. for $\text{Pb}(\text{SC}_6\text{H}_5)_2$: Pb, 48.7; calcd. for $\text{Pb}(\text{SC}_6\text{H}_4\text{C}_2\text{H}_5)_2$: Pb, 38.5. This would correspond to a mixture of the two mercaptides containing 69% of the lead salt of *s*-butyl thiophenol.

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The Spinning Top Ultracentrifuge and the Sedimentation of Small Molecules

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In recent articles McBain and O'Sullivan¹ have discussed their development of the air-driven spinning top as transparent ultracentrifuge. As we read these reports we cannot escape the feeling that a certain pronouncement in them requires further analysis. In the "Communication" a

(2) Hurd and Greengard, *THIS JOURNAL*, **52**, 3356 (1930).

(3) Sprung and Wallis, *ibid.*, **56**, 1715 (1934).

(4) Hurd and Webb, *ibid.*, **58**, 943 (1936).

(1) McBain and O'Sullivan, *THIS JOURNAL*, **57**, 780, 2631 (1935).

"fortunate accident" is mentioned which made it possible "to observe the sedimentation velocity of a boundary in aqueous solution of mercuric chloride: $s = 0.891 \times 10^{-13}$ cm./sec./dyne; theory = 0.890×10^{-13} ." Later, in the definitive article, McBain and O'Sullivan make the claim that they have recorded for the first time the sedimentation velocity of an ordinary molecule (mercuric chloride), this as a footnote to the statements "For sedimentation equilibrium of ordinary molecules, powers ranging from 100,000 to 1,000,000 times gravity are essential. Still higher powers will be required for observing their sedimentation velocity."

It has seemed worth while to examine this extremely important claim, which is made more striking because of the remarkable agreement between theory and observation (about 0.1%) which is reported. Such examination is extremely difficult because definite information is lacking as regards the speed at which the rotor was turning, how the position of the boundary was observed and located at the ends of the several intervals of time during the centrifuging, how the distances from the center of the cell were measured, how the absence of convection effects was proved, what was the concentration of the solution and the temperature of the cell used in the experiment, how long the centrifuging was continued, etc. However, by making calculations which involve the dimensions of the apparatus, the rotor speeds, and strengths of the materials of construction mentioned in other parts of the longer article, it is concluded that their sedimentation power was not over 350,000 times gravity. For a molecule of weight and density of mercuric chloride in water at ordinary temperatures, one may calculate that the actual sedimentation rate with such centrifugal force would be of the order of 1 mm. per hour.

With the apparatus as described and with the assumption of technique and evaluation of the data according to the methods developed by Svedberg, it is highly improbable that such a rate could be measured with the precision claimed. Also, a serious difficulty is that the back diffusion would so blur the boundary that the distance of travel of the latter in any ordinary interval of time would be hard to estimate. Experiments of Pedersen² made in the Svedberg laboratory may be cited in this connection. Working with

aqueous solutions of mercuric chloride and at 350,000 times gravity, this investigator was able to establish equilibrium in a cell with liquid column about 5 mm. in height after something like seven hours of centrifuging. However, no mention is made by Pedersen of the observations of the velocity of the sedimentation.

Actually, in view of the very careful Pedersen experiments and several statements contained in the article in question, there may be some doubt that a true sedimentation velocity was observed. In addition to the two sentences quoted above, McBain and O'Sullivan define an ultracentrifuge as being "any centrifuge of low or high power in which convection does not occur, and in which it is possible to measure any redistribution of the contents." Again in referring to the behavior of a rotor which is described as having several advantages (speed, uniformity of temperature, strength) over the one in which the experiment in question took place, there is the statement "With the driving air arbitrarily thermostated to within $\pm 0.02^\circ$ and the room temperature controlled, the same rotor will sometimes sediment molecules as small as purified egg albumin (molecular weight about 35,000)."

It is a matter of some surprise to find the theoretical sedimentation velocity constant for mercuric chloride molecules in aqueous medium expressed to three significant figures when no temperature is specified. The value of the constant varies considerably with temperature because the viscosity of the solvent is involved. The variation amounts to approximately 2% per degree in aqueous solution at ordinary centrifuge temperatures. For mercuric chloride the theoretical sedimentation constant expressed to two significant figures is 0.73 at 20° , 0.82 at 25° and 0.89 at 30° . The temperature of the cell during the experiment was not determined with precision.

Since the records of the experiment and the calculation for the corresponding theoretical specific sedimentation velocity for mercuric chloride are so incomplete, we are impelled to suggest that a further account of the work be presented before it can be given serious consideration as the first measurement of the sedimentation velocity of an ordinary molecule.

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(2) Pedersen, *Z. physik. Chem.*, **A170**, 53 (1934).