was obtained from beta-octanol and *p*-toluenesulfinyl chloride. Starting with a dextro-beta-octanol, $[\alpha]^{20}_{5893}$ +9.48° homogeneous, $[\alpha]^{20}_{4359}$ +22.40° in ethanol (c = 4.992), Kenyon and his co-workers obtained, through this series of reactions, a levo-beta-octyl thiocyanate, $[\alpha]^{20}_{5893}$ −71.41° homogeneous, $[\alpha]^{20}_{5893}$ −64.68° in ethanol (c = 5.010), $n^{17°}_{\mathrm{D}}$ 1.4651, $d^{20°}_{4}$ 0.795.

In the series of reactions used by the writers a dextrorotatory octanol yielded a dextrorotatory thiocyanate, while in the procedure used by Kenyon a levo-octyl thiocyanate was obtained from a dextrorotatory octanol. Since an asymmetric carbon atom is involved in both series of reactions, the difference in the results may be explained by the occurrence or absence of the Walden inversion.

The refractive index of the thiocyanate prepared by the writers agrees with that reported by Kenyon and his co-workers, indicating that the compounds are of the same degree of chemical purity. The density of the writers' compound, however, was 0.919, whereas Kenyon reported 0.795.

The molecular refraction of beta-octyl thiocyanate, calculated from the revised values of Eisenlohr for the atomic refractions[2] and employing 13.21 for the thiocyanate radical, is 51.09. The observed molecular refraction for the writers' compound, obtained with the Lorentz–Lorenz formula, is 51.31, whereas with the values for refractive index and density reported by Kenyon 59.31 is obtained.

These results indicate that the value for the density found by the writers is closer to the true value than is that found by Kenyon, *et al.* Since the specific refraction (homogeneous) is dependent on the density, this value is also subject to revision.

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[2] Landolt–Börnstein, "Physikalisch-chemische Tabellen," Aufl. 5, Bd. 2, Julius Springer, Berlin, 1923, p. 985.

DIVISION OF INSECTICIDE INVESTIGATIONS
BUREAU OF ENTOMOLOGY AND PLANT QUARANTINE
U. S. DEPARTMENT OF AGRICULTURE
WASHINGTON, D. C.
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A Stopcock Substitute

BY WALTER C. SCHUMB AND H. IRVING CRANE

In the course of a certain investigation in this Laboratory it was found necessary to devise a means of interrupting the flow of a benzene solution. A stopcock could not be used, since the ordinary organic stopcock lubricants are readily attacked by benzene, and the reactivity of the solute toward moisture or reactive hydrogen made the use of certain other types of lubricant, such as phosphoric acid, out of the question. The device shown in the diagram is an adaptation of Stock's stopcock for gases [*Ber.*, **58,** 2058 (1925)].

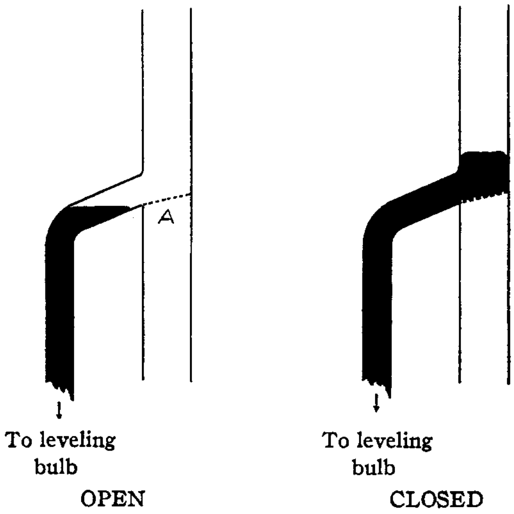

Fig. 1.

The device, constructed of Pyrex glass, consists essentially of a fritted glass plate (A) (80 mesh), so placed that mercury can be flowed over it at will by means of a suitable leveling bulb.

Obviously the device is applicable to any liquid of not too high viscosity, which does not attack mercury. The high surface tension of mercury prevents any of it passing through the fritted plate.

RESEARCH LABORATORY OF INORGANIC CHEMISTRY
MASSACHUSETTS INSTITUTE OF TECHNOLOGY
CAMBRIDGE, MASS.
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The Rearrangement of Alkyl Aryl Thioethers

BY WENDELL H. TAYLOR

In a recent study of the reaction between aromatic mercaptals and formaldehyde, the author[1] postulated a rearrangement of formaldehyde diaryl mercaptals involving the migration of the —CH_2 group from sulfur to the benzene nucleus, with regeneration of the —SH groups. Such a change would be essentially similar to the rearrangement of the alkyl aryl thioethers and it was therefore of interest to investigate such thioether rearrangements under conditions comparable to those under which the analogous oxygen com-

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[1] W. H. Taylor, THIS JOURNAL, **57**, 1065 (1935).

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 found[3] 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 reported[4] 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 $—CH_2—S—R$ to $R(CH_2—)SH$ was definitely established.

For assistance with a part of the experimental work the author wishes to thank Messrs. W. A. Bastedo, Jr., and R. W. Storer.

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 $Pb(SC_6H_4CH_3)_2$: Pb, 43.4; calcd. for $Pb(S{\cdot}C_6H_3{\cdot}C_3H_5{\cdot}CH_3)_2$: 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 $Pb(SC_6H_5)_2$: Pb, 48.7; calcd. for $Pb(SC_6H_4C_4H_9)_2$: Pb, 38.5. This would correspond to a mixture of the two mercaptides containing 69% of the lead salt of *s*-butyl thiophenol.

FRICK CHEMICAL LABORATORY
PRINCETON, N. J.
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[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).

The Spinning Top Ultracentrifuge and the Sedimentation of Small Molecules

BY J. W. WILLIAMS AND C. C. WATSON

In recent articles McBain and O'Sullivan[1] 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

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