

simply a mixture of III and IV but is possibly a mixture of 1,3-dichlorocyclohexanes contaminated with small amounts of III and IV. Analysis of V gave the following results.

Anal. Calcd. for $C_6H_{10}Cl_2$ (153.0): C, 47.1; H, 6.6. Found: C, 46.9; H, 6.5.

Treatment of II with 12 *N* hydrochloric acid, as described above, gave a mixture of dichlorocyclohexanes in 88% yield. Of this product 25% was subsequently isolated as IV and the remainder as a mixture of III and V.

When I was heated with 12 *N* hydrochloric acid at 105° for three hours only 15% of the total dichlorocyclohexane fraction was recovered as crystalline IV in contrast to the 25% yield obtained when the time of heating was five hours.

cis-1,4-Dibromocyclohexane (VI) and *trans*-1,4-Dibromocyclohexane (VII).—I, 18.1 g., was heated under refluxing conditions with 60 ml. of 48% hydrobromic acid for two hours. In the absence of any separation of a solid phase,⁴ the products were isolated as described above for the dichlorocyclohexanes. Distillation gave 16.3 g. of a fraction b.p. 100–104° (13 mm.) and 6 g. of a high boiling residue. Storage of the distillate at 0° gave 4.7 g. (11%) of VII, m.p. 110–112°, after one recrystallization from 60–70° ligroin, lit.^{4,8} m.p. 112°, and 11.6 g. of a liquid. Analysis of VII gave the following results.

Anal. Calcd. for $C_6H_{10}Br_2$ (242.0): C, 29.8; H, 4.2. Found: C, 29.8; H, 4.3.

Further fractionation of the liquid through a 20-plate column gave a major portion consisting of a number of fractions, b.p. 104–105° (13 mm.), and a final fraction, b.p. 105–107° (13 mm.). From the latter fraction, after storage at 0°, there was obtained 0.5 g. of VI, m.p. 45–47.5°, lit.⁸ m.p. 48°. Elementary analysis¹² and an examination of the infrared spectrum of VI indicated that the product isolated was contaminated with a small amount of material of lesser halogen content.

Although the various fractions comprising the major portion of the distillate exhibited very similar infrared spectra, elementary analysis clearly indicated that this material was not a pure compound but a mixture of components of varying halogen content. Attempts to resolve this mixture were unsuccessful.

Infrared Spectra.—The infrared spectra given in Fig. 1 were determined with a Baird infrared spectrophotometer using either liquid films (0.001") or 25% solutions in carbon disulfide (0.1 mm. cell thickness).

(12) Found: C, 30.9; H, 4.3.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, STANFORD UNIVERSITY]

The Preparation and Properties of Triphenylsulfonium Polyhalides¹

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Triphenylsulfonium tribromide, triiodide and dichlorobromide have been prepared by the action of the appropriate halogen on triphenylsulfonium bromide in aqueous solution. Triphenylsulfonium chloride and iodide are also described for the first time. Triphenylsulfonium pentabromide and probably higher polybromides were obtained by action of bromine vapor on triphenylsulfonium bromide or tribromide. The ultraviolet and infrared absorption spectra of these substances have been examined in an attempt to deduce structural information about them. Electrolysis of triphenylsulfonium salts has been found to result in decomposition of the triphenylsulfonium cation to diphenyl sulfide and polymeric materials.

In contrast to the more widely known trisubstituted sulfonium halides, trisubstituted sulfonium polyhalides have received only limited investigation. Steinkopf and Müller² report the preparation of phenyldimethylsulfonium triiodide by action of methyl iodide on diphenyl disulfide, and Werner³ has prepared trimethylsulfonium tetrachloroiodide by the action of chlorine on trimethylsulfonium iodide. Treatment of the latter compound with sodium hydroxide produced trimethylsulfonium dichloroiodide. We became interested in a more detailed study of such polyhalides by way of electrolysis experiments described briefly below. The present investigation is concerned with the preparation of triphenylsulfonium (TPS) polyhalides and an attempt to obtain structural information concerning them.

In general a TPS polyhalide resulted by action of an aqueous solution of a halogen on a TPS halide. Thus TPS tribromide was produced in good yield by treating an aqueous solution of TPS bromide⁴ with bromine water. TPS triiodide resulted when TPS bromide reacted with an iodine-potassium iodide solution. An attempt was made to prepare TPS trichloride by action of chlorine water on TPS bromide in the presence of a large excess of

chloride ion. The product, however, proved to be TPS dichlorobromide. Accordingly, TPS chloride was prepared by neutralization of TPS hydroxide solution⁴ with hydrochloric acid. The action of chlorine water on aqueous TPS chloride, however, produced no insoluble trichloride. When TPS chloride was treated with bromine water, TPS dichlorobromide rather than TPS dibromochloride was formed.

The physical properties of the TPS polyhalides are in marked contrast to those of the simple TPS halides. The latter are white, high-melting solids which, with the exception of the iodide, are highly water soluble and insoluble in most organic solvents. The polyhalides are relatively low-melting solids, virtually insoluble in water, but soluble in dilute alkali and in many typical organic solvents. The colors of the TPS polyhalides vary with the halogen present; the dichlorobromide is cream-yellow, the tribromide bright orange, and the triiodide red-purple.

Both TPS bromide and tribromide show the interesting property of being deliquescent with respect to bromine. When either salt is exposed to bromine vapor the latter is absorbed until the salt dissolves into a red liquid. When this is exposed to air bromine is lost rapidly, crystallization occurs, and the material finally reverts to TPS tribromide. When the loss of bromine from the red liquid was followed quantitatively (Fig. 1) it was found that the weight loss reached a plateau

(1) Presented before the Division of Organic Chemistry, 121st National Meeting, American Chemical Society, Milwaukee, Wis., Spring, 1952.

(2) W. Steinkopf and S. Müller, *Ber.*, **56**, 1926 (1923).

(3) E. A. Werner, *J. Chem. Soc.*, **89**, 1625 (1906).

(4) B. S. Wildi, S. W. Taylor and H. A. Potratz, *THIS JOURNAL*, **73**, 1965 (1951).

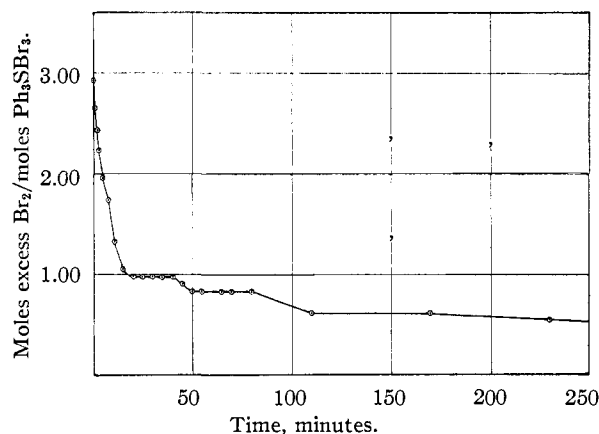
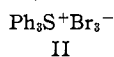
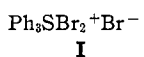


Fig. 1.—Bromine loss from a mixture of triphenylsulfonium tribromide and bromine.

at a value corresponding to one mole excess bromine. The red solid at this point corresponded analytically to TPS pentabromide. It seems probable here that the above red liquid consists of a mixture of higher TPS polybromides. The other alternative that TPS tribromide merely absorbs bromine and dissolves in it is less likely in that TPS tribromide is insoluble in solvents such as carbon tetrachloride which, like bromine, have no dipole moment.

The avidity of TPS bromide for bromine was further demonstrated in a competition experiment with cesium tribromide, a typical inorganic trihalide. The latter was placed in one end and TPS bromide in the other end of a sealed glass tube. On warming for several days the cesium tribromide was completely converted to cesium bromide, and the TPS bromide to TPS tribromide.

While the structure of trihalide ions is understood,⁵ an interesting structural question arises in connection with the present sulfonium trihalides. Since sulfur may be able to expand its octet⁶ it is conceivable that the present TPS trihalides may have the extra halogen coordinated in the cation (I) rather than as usual in the anion (II).



We have attempted to gain information on this point by examination of the ultraviolet and infrared absorption spectra of the TPS trihalides.

Attempts were made to determine the ultraviolet absorption spectra of the TPS trihalides in chloroform. Except for the dichlorobromide, however, such chloroform solutions did not obey Beer's law on dilution. This may have been due either to dissociation of the trihalides into halide and halogen, or to association effects described below. TPS bromide itself also did not obey Beer's law in chloroform solution. This may perhaps be due to the association of the ion pairs into higher aggregates in solvents of low dielectric constant, in the fashion described by Kraus⁷ for tetraalkylammonium salts in benzene solution.

(5) N. V. Sidgwick, "The Chemical Elements and their Compounds," Vol. II, Oxford University Press, London, 1950, p. 1192 ff.

(6) R. H. Eastman and R. M. Wagner, *THIS JOURNAL*, **71**, 4089 (1949). Earlier references given here.

(7) D. T. Copenhafer and C. A. Kraus, *ibid.*, **73**, 4557 (1951).

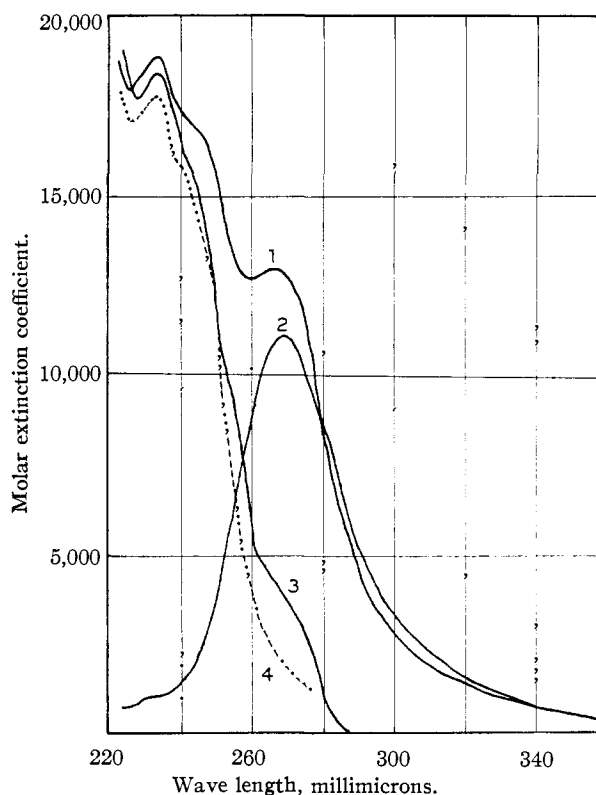
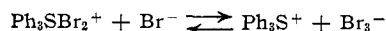


Fig. 2.—Ultraviolet absorption spectra of triphenylsulfonium bromide, triphenylsulfonium tribromide and lithium tribromide: 1, TPS tribromide; 2, lithium tribromide; 3, TPS bromide; 4, $\epsilon_1 - \epsilon_2$.

In a 9:1 by volume methanol-water solution TPS tribromide again disobeyed Beer's law. Here deviations must have been due to dissociation of the tribromide ion, however, since (a) TPS bromide shows a satisfactory absorption spectrum in 95% ethanol,⁴ and (b) the deviations were eliminated when the solvent contained excess bromide ion. In Fig. 2 the spectra of TPS tribromide, lithium tribromide and TPS bromide are shown in dilute methanol containing excess bromide. It is seen that the difference in the molar extinction coefficients for the first two salts is very nearly equal to the molar extinction coefficient of TPS bromide at the wave lengths in question. Curve 2 for lithium tribromide is practically identical with the spectrum reported for tetrabutylammonium tribromide in ethylene chloride solution.⁸ These facts are in accord with II as the structure of TPS tribromide. They do not rigorously exclude I, however, since similar results might be noted with I in the presence of excess bromide ion, *i.e.*



The infrared absorption spectra of TPS trihalides were examined in the region 8-15 μ in mineral oil suspension (Fig. 3). It is seen that, while the shorter wave length regions of the spectra are reasonably similar, considerable differences in fine structure are evident at longer wave lengths. Since cesium tribromide showed no discrete ab-

(8) R. E. Buckles, A. I. Popov, W. F. Zelezny and R. J. Smith, *ibid.*, **73**, 4526 (1951).

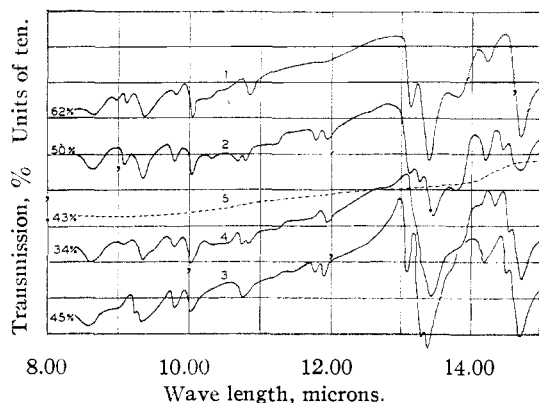


Fig. 3.—Infrared absorption spectra of triphenylsulfonium polyhalides: 1, dichlorobromide; 2, tribromide; 3, penta-bromide; 4, triiodide; 5, cesium tribromide.

sorption in this region, the spectra in Fig. 3 must be due to the TPS cation only. The observed spectral differences may then be due to one of two causes: (a) each cation absorbing is different, *i.e.*, the cation structures correspond to I, or (b) the nature of the transparent anion alters the spectrum of the absorbing cation. To decide between these possibilities the infrared spectra of the simple TPS halides were examined (Fig. 4). Here too, spectral differences may be noted at longer wave lengths. While these observations are in accord with structure II and cause (b) above, structure I is still not excluded. Although our experimental attempts to differentiate between I and II have thus been ambiguous, it seems safer at present to assume structure II as correct by analogy with the known inorganic trihalides, and our previous discussion is predicted on this assumption.

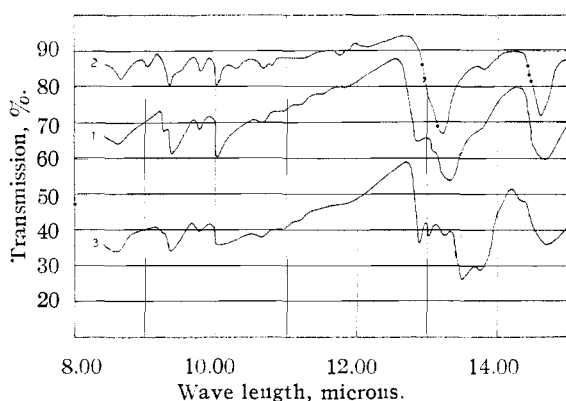


Fig. 4.—Infrared absorption spectra of triphenylsulfonium halides: 1, chloride; 2, bromide; 3, iodide.

Trisubstituted sulfonium salts have never been investigated electrolytically. Such experiments seemed desirable, since they might provide evidence for a cathodically produced triarylsulfur radical, $\text{Ar}_3\text{S}^\cdot$, or a hexaaryl disulfide, $\text{Ar}_3\text{S}-\text{SAr}_3$, species having, respectively, a nonet and decet of electrons about sulfur.

Electrolysis of aqueous solutions of TPS bromide produced oxygen and TPS tribromide at the anode and hydrogen and diphenyl sulfide at the cathode. Since the copious anodic formation of TPS tri-

bromide obscured the more interesting cathode process, attention was turned to the electrolysis of TPS nitrate, where the only anode product was oxygen. At the cathode hydrogen, diphenyl sulfide and an alkali-soluble tar were noted. Thus if the radical $\text{Ph}_3\text{S}^\cdot$ were produced at the cathode, it appears unstable with respect to Ph_2S and Ph^\cdot . The latter radical may have reacted with water to form polymeric phenolic products, explaining the alkali-soluble tar obtained.

Experimental

Triphenylsulfonium Bromide.—This was prepared by the action of phenylmagnesium bromide on diphenyl sulfoxide after the procedure of Wildi, Taylor and Potratz.⁴ The purified product had m.p. 292.5° (Fisher block). The authors report m.p. 285–286°, taken presumably in a capillary tube.

Triphenylsulfonium Nitrate.—This was prepared by the action of one equivalent of silver nitrate on triphenylsulfonium bromide. The physical properties were in agreement with those reported by Wildi, Taylor and Potratz.⁴

Triphenylsulfonium Chloride.—Triphenylsulfonium bromide (3.0 g.) was dissolved in water (100 ml.) and the solution treated with silver oxide (10 g.) and glass beads. The mixture was stirred (Hershberg stirrer) in the dark overnight, when a filtered portion was found bromide free on acidification with nitric acid and treatment with silver nitrate solution. The bulk was accordingly filtered (Celite), and the cake rinsed well with water. The undiluted filtrate had pH 12.6. The filtrate and washings were acidified with a slight excess of hydrochloric acid. The clear solution was evaporated to dryness *in vacuo* at 100° and the residue dissolved in chloroform. The solution was filtered through Norit and evaporated, leaving 2.36 g. (90%) of white solid. This was recrystallized by dissolving in 5 ml. of hot chloroform and adding 40 ml. of boiling acetone; 1.70 g., m.p. 297–298° (Fisher block). The material was quite hygroscopic.

Anal. Calcd. for $\text{C}_{18}\text{H}_{15}\text{SCl}$: Cl, 11.86. Found: Cl, 11.61.

Triphenylsulfonium Iodide.—Triphenylsulfonium bromide (0.50 g.) was dissolved in water (10 ml.) and treated with a solution of potassium iodide (4 g.) in water (15 ml.). A white precipitate immediately formed, was filtered, washed, and air-dried; 0.44 g. (78%), m.p. 244° (Fisher block). The material was recrystallized twice by dissolving in *ca.* 1 ml. of chloroform and adding 5 ml. of boiling acetone; m.p. 250° (Fisher block).

Anal. Calcd. for $\text{C}_{18}\text{H}_{15}\text{SI}$: C, 55.41; H, 3.88. Found: C, 55.09, 55.18; H, 3.92, 3.94.

Triphenylsulfonium Tribromide.—Triphenylsulfonium bromide (0.50 g.) was dissolved in water (10 ml.) and treated with an excess of bromine water. The colloidal precipitate formed was quickly coagulated by shaking after addition of a little sodium chloride. The orange solid was filtered, rinsed with water, and dried. It weighed 0.54 g. (74%) and had m.p. 124.5–125°. It was recrystallized from ethanol (12 ml.) to give shining orange needles, m.p. 125–126°.

Anal. Calcd. for $\text{C}_{18}\text{H}_{15}\text{SBr}_3$: C, 43.00; H, 3.01; S, 6.37; Br, 47.64. Found: C, 42.68, 42.82; H, 3.00, 3.03; S, 6.15; Br, 47.74.

Triphenylsulfonium Triiodide.—Triphenylsulfonium bromide (0.50 g.) was treated with 30 ml. of 0.1 N I_2 -KI solution. A black precipitate immediately formed and coagulated. It was filtered, rinsed with water, and dried; 1.05 g. (110%), m.p. 97–98°. Three recrystallizations from a mixture of acetone and ethanol gave the pure, constant-melting product, permanganate colored prisms, m.p. 137.5–138°.

Anal. Calcd. for $\text{C}_{18}\text{H}_{15}\text{SI}_3$: C, 33.58; H, 2.35; S, 4.97; I, 59.10. Found: C, 33.54, 33.60; H, 2.46, 2.50; S, 4.94; I, 58.66.

Triphenylsulfonium Dichlorobromide.—Triphenylsulfonium bromide (1.00 g.) and sodium chloride (3 g.) were dissolved in water (10 ml.) and the solution treated with 50 ml. of freshly saturated chlorinic water. A pale yellow col-

loidal precipitate immediately formed, which quickly coagulated on shaking. This was filtered, washed well with water, and air-dried; 0.95 g. (78%), m.p. 125–125.5°. Attempts were made to recrystallize this from ethanol and from mixtures of acetone and 2-propanol, but it quickly attacked these solvents. Attempts to crystallize from water resulted in decomposition of the material in the hot solution. The material was accordingly analyzed without purification.

Anal. Calcd. for $C_{18}H_{15}SBrCl_2$: Cl, 52.20; H, 3.65; S, 7.74; total halogen, 36.40. Found: C, 51.99, 52.08; H, 3.59, 3.59; S, 7.50; total halogen, 36.80.

Attempted Formation of Triphenylsulfonium Trichloride.

—Triphenylsulfonium chloride (0.25 g.) was dissolved in water (5 ml.) and sodium chloride (1 g.) added. The addition of freshly saturated chlorine water, however, gave no precipitate, indicating that the trichloride does not form under the conditions for formation of the other trihalides. When bromine water was added to the clear solution, however, a pale yellow precipitate formed. This was filtered, rinsed, and dried. It had m.p. 125.5–126° and showed no mixed m.p. depression (125–125.5°) with authentic triphenylsulfonium dichlorobromide.

Anal. Calcd. for $C_{18}H_{15}SBrCl_2$: C, 52.20; H, 3.65. Found: C, 51.88, 52.04; H, 3.80, 3.89.

Action of Bromine Vapor on Triphenylsulfonium Bromide.

—Triphenylsulfonium bromide was placed on an open watch glass. Bromine was placed on a second open glass adjacent to the first, and the two samples were covered with a larger watch glass. Immediately the triphenylsulfonium bromide darkened, and within a few minutes had been converted into a deep red liquid. This was removed from contact with bromine vapor and scratched. Rapid crystallization occurred, and the powder gradually changed from deep orange-red to light orange. The sample was recrystallized from ethanol giving orange platelets of triphenylsulfonium tribromide, m.p. 124–125°.

Triphenylsulfonium Pentabromide.—Triphenylsulfonium tribromide (0.45 g.) was placed on a tared watch glass and exposed to bromine vapor as described above. In a short time it had reverted to a red liquid. The watch glass was removed and weighed. The liquid was stirred and scratched, reweighing at measured time intervals. After crystallization had occurred the solid was spread thinly over the surface of the watch glass to provide maximum exposure. The sample lost weight rapidly at first, then reached a plateau of "constant" weight. This weight corresponded to one molar equivalent of excess bromine. On further exposure to air the red-orange solid gradually became light orange, and the sample weight slowly approached the starting weight of 0.45 g. The data in this experiment are presented graphically in Fig. 1. A sample of the red-orange solid obtained during the weight-loss plateau was removed and sealed up prior to analysis. It has m.p. 68.5–70° in a sealed capillary. Its infrared spectrum is shown in Fig. 2.

Anal. Calcd. for $C_{18}H_{15}SBr_5$: Br, 60.30. Found: Br, 59.98.

In another experiment 0.50 g. of TPS tribromide was exposed to bromine vapor as described above until the red puddle appeared to have increased to about constant weight (about 2.5 hours.). The sample at this point weighed 2.35 g., corresponding to a mole ratio $Br_2/TPS Br_2$ of 11.5.

Action of Bromine Vapor on Triphenylsulfonium Nitrate.

—TPS Nitrate (0.30 g.) was exposed to bromine vapor as above, when it gradually absorbed bromine and dissolved into a red puddle. The latter was exposed to air. It lost bromine and finally crystallized to a tacky solid, m.p. 50–58°, weighing 0.38 g. This was recrystallized twice from 2-propanol to give light orange platelets, m.p. 123–124°, mixed m.p. with TPS tribromide 124–125°.

Competition of Cesium Bromide and Triphenylsulfonium Bromide for Bromine.—Cesium tribromide was prepared by the action of 1.5 equivalents of bromine water on an aqueous solution of cesium bromide. The orange cesium tribromide (0.20 g.) was placed in one end of a sealed glass tube, and white triphenylsulfonium bromide (0.20 g., 1.08 equiv.) placed in the other end. On standing for several days part of the cesium tribromide had turned white and part of the triphenylsulfonium bromide had turned orange. The sealed tube was placed before a heat lamp for several more days, when the cesium tribromide had become com-

pletely white cesium bromide, and the triphenylsulfonium bromide had been converted to the orange tribromide. The tube was opened. The triphenylsulfonium tribromide showed the theoretically correct weight and had m.p. 124–125°.

Ultraviolet Absorption Spectra.—Attempts to determine the ultraviolet absorption spectra of triphenylsulfonium trihalides in chloroform solution were hampered by the fact that the solution did not obey Beer's law on dilution. Thus at 450 $m\mu$ triphenylsulfonium triiodide had a molar extinction coefficient of 2030 in 10^{-3} solution and 500 in 10^{-4} M solution. A similar discrepancy with dilution was noted for the tribromide at 350 $m\mu$. The trichloride, however, obeyed Beer's law adequately on dilution. Triphenylsulfonium bromide was also found not to obey Beer's law in chloroform. Thus at 310 $m\mu$ its molar extinction coefficient was 1025 in 10^{-3} and 320 in 10^{-4} M solution. The spectra curves accordingly are not shown.

In 9:1 methanol-water solution triphenylsulfonium tribromide also showed deviations from Beer's law on dilution. These deviations were eliminated, however, if the methanol-water solvent was 10^{-1} M in lithium bromide.

The spectra in Fig. 2 were taken in 9:1 methanol-water solution 10^{-1} M in lithium bromide, using a Beckman DU spectrophotometer. The lithium tribromide curve was obtained by dissolving the theoretical quantities of bromine and lithium bromide in the above solvent.

Infrared Absorption Spectra.—The infrared spectra shown in Figs. 3 and 4 were obtained using a Perkin-Elmer infrared spectrophotometer. The samples were prepared in mineral oil suspension after the procedure of Kuhn.⁹ The difference in per cent. absorption arises from the differing thicknesses of the various samples. The author is indebted to Prof. John H. Wise for these spectral determinations.

Electrolysis of Triphenylsulfonium Bromide in Water.—About one-tenth gram of the salt was dissolved in 10 ml. of water and the solution electrolyzed in a platinum crucible (anode) containing a platinum strip (cathode) suspended centrally. Several tenths of an ampere passed at twelve volts applied potential. The anode rapidly became coated with an orange solid which was scraped free, filtered, washed with water, and dried *in vacuo*; m.p. 123.5–124.5°. This showed no melting point depression (124–125°) when mixed with authentic triphenylsulfonium tribromide. As the electrolysis proceeded the solution became alkaline, and formation of the anode product ceased due to the fact that triphenylsulfonium tribromide is soluble in dilute alkali. In a separate electrolysis in which the fresh electrolyte contained phenolphthalein it was found that the alkalinity was produced rapidly at the cathode.

Electrolysis of Triphenylsulfonium Nitrate.—When the nitrate was electrolyzed as above alkalinity was produced at the cathode as indicated with phenolphthalein. This was neutralized by mixing, however. On prolonged electrolysis the bulk solution became acidic, in contrast to the bromide electrolysis. No insoluble anode product was noted, but a sweet-smelling oil floated to the surface in the cathode region. In addition hydrogen was produced at the cathode and oxygen at the anode in a 2:1 volume ratio, as indicated by the fact that the mixed electrode gases exploded on ignition. The cathode oil was also detected on re-examining the electrolysis of triphenylsulfonium bromide.

Four-tenths gram of the nitrate was dissolved in water (20 ml.) and electrolyzed at 12 volts for about five hours, cooling with tap water. C.P. benzene was kept over the electrolyte surface to pick up the cathode oil. A black, insoluble tarry substance was also formed at the cathode. This floated up to the benzene-water interface. It was filtered and found to be alkali-soluble. The benzene layer was dried over sodium sulfate, filtered, and evaporated to leave 0.17 g. of brown oil. This was redissolved in benzene and the solution extracted with 10% sodium hydroxide solution. The alkaline layer was acidified, extracted with benzene, and the extract washed and evaporated. There remained ca. 0.01 g. of dark solid with a faintly phenolic odor. This was partially soluble in water, and the solution produced a turbidity when treated with bromine water. The above alkali-washed benzene solution was dried, decolorized through Norit and evaporated to yield 0.12 g. of amber oil with a sweet odor. This was dissolved in a small amount of acetic acid, treated with excess 30% hydrogen per-

(9) L. P. Kuhn, *Anal. Chem.*, **22**, 276 (1950).

oxide, and warmed on the steam-bath for 1.5 hours. The cooled solution was thrown into water, when 0.10 g. (72%) of crude diphenyl sulfone, m.p. 122–123°, precipitated. The product after recrystallization from a chloroform-ligroin mixture had m.p. 127–128° and showed no m.p. depression (128–128.5°) when mixed with authentic diphenyl sulfone (of

m.p. 128–128.5°). Processing of the filtrate from the diphenyl sulfone produced only a negligible quantity of solid, m.p. 75–95°.

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A Suggestion on the Application of Hudson's Isorotation Rules¹

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When α -anomers of glycoses and glucose derivatives are lacking, calculations involving Hudson's isorotation rules have been made using the rotations of the known β -anomer and a related anomeric pair of glycoses. It is here suggested that the related anomeric pair employed in such calculations should be a pair whose aglycon bears the greatest structural similarity to the aglycon of the unknown α -anomer. To test this suggestion Hudson's rule calculations have been applied to all known pairs of substituted aromatic glycosides, and it is found that the proposed principle of aglycon similarity leads to the closest prediction of the optical properties of the α -anomers in over 97% of the cases. Bromination and nitration reactions have been applied to several acetylated aromatic glucosides in the phenyl and naphthyl series. The position of the substituent in each new product has been established by hydrolysis and characterization of the aglycon.

In estimating the partial rotatory contribution, A , of the anomeric center in glycosides and related compounds by application of Hudson's isorotation rules,² precise calculations are frequently hampered by the unavailability of the required α -anomers. This difficulty has generally been circumvented by employing B values derived from a pair of related anomeric glycoside derivatives for calculating the desired A value. Thus Purves³ has calculated A values for a series of phenyl polyacetyl- D -thioglycosides and Hudson and co-workers⁴ A values for 2-naphthyl polyacetyl- D -glycosides, typical instances where the α -anomers are lacking, by using B values calculated on the basis of the corresponding anomeric polyacetyl- D -glucoses. Similarly, the specific rotations of unknown α -glycosides have been estimated² by appropriately combining the rotation of the known β -anomer with the rotations of a related anomeric pair of glycoses.

In principle, any anomeric pair of a related glycoside derivative might be employed in place of the glycoside itself to accomplish such calculations. Because of the approximate validity⁵ of the second isorotation rule, however, the figures calculated for unknown A values or specific rotations will vary widely depending on the nature of the second anomeric pair chosen for the calculations. The extent of such deviations can be seen in the tables.

While Professor Hudson has frequently emphasized the qualitative nature of the isorotation rules and while these have never led to an incorrect anomeric classification, it would nevertheless be desirable to have a guiding principle to ensure that predicted A values or predicted specific rotations be as accurate as possible. It is here suggested

that such a guiding principle be the following: In the application of the isorotation rules to the calculation of unknown specific rotations or A values, that anomeric pair should be selected for the calculation whose aglycon bears the greatest structural similarity to the aglycon of the unknown substance in question.

The validity of this proposition has been tested as follows. The rotations and A values of all known anomeric pairs of substituted aromatic glycosides have been tabulated. The rotations and A values of each α -anomer have then been assumed to be unknown, and have been calculated by combining the rotation of the β -anomer with the rotations of all known anomeric pairs of derivatives of the parent glycoside. The calculated values have then been compared with the known values to see which anomeric pair led to the closest prediction. The results of these calculations are presented in Tables II–V, with the closest prediction italicized in each case.

According to the proposed principle of aglycon similarity, the phenyl glycosides should be the most suitable pair on which to base predictions regarding optical properties of unknown substituted aryl glycosides. It is, of course, well known⁶ that aromatic glycosides show anomalously high B values, but the present principle of aglycon similarity as a basis for isorotation rule calculations does not appear to have been suggested explicitly in the past.

Examination of Tables II–V shows that the principle of aglycon similarity leads to the best prediction of A values and specific rotations in all but four out of 163 calculations. Occasionally the agreement between calculated and known values is striking. The principle appears to be least valid in the case of o -substituted aryl glycosides. Thus the properties of the o -tolyl glycosides seem in general better predicted on the basis of some anomeric pair other than the phenyl glycosides. Similarly, while the phenyl tetraacetyl- D -glucosides

(1) Presented before the Division of Sugar Chemistry, 121st National Meeting, American Chemical Society, Milwaukee, March, 1952.

(2) C. S. Hudson, *THIS JOURNAL*, **31**, 66 (1909).

(3) C. B. Purves, *ibid.*, **51**, 3619, 3627 (1929).

(4) W. T. Haskins, R. M. Hann and C. S. Hudson, *ibid.*, **69**, 1668 (1947).

(5) (a) W. W. Pigman and H. S. Isbell, *J. Research Natl. Bur. Standards*, **27**, 9 (1941); (b) W. W. Pigman, *ibid.*, **33**, 129 (1944); (c) E. M. Montgomery, N. K. Richtmyer and C. S. Hudson, *THIS JOURNAL*, **64**, 690 (1942); (d) C. D. Hurd and W. A. Bonner, *J. Org. Chem.*, **10**, 604 (1945).

(6) W. W. Pigman and R. M. Goepf, Jr., "Chemistry of the Carbohydrates," Academic Press, Inc., New York, N. Y., 1948, p. 80 ff.