1,8-Dinitro-anthraquinone.—The dinitro acid described above was found to be difficult to condense but when it was heated for three hours to 150° with a 23% oleum containing boric acid the dinitro-anthraquinone was obtained; m. p., 310°.

Anal. Calcd.: N, 9.40. Found: 9.60.

Its melting point identifies it as 1,8-dinitro-anthraquinone which is said to melt at 312°. From this it is probable that both the nitro groups enter the benzyl-*o*-benzoic acid *ortho* to the —CH_2— but in separate rings.

Naphthalic Anhydride.—This anhydride was heated with benzene and aluminum chloride but no evidence of any condensation could be found. It was always recovered unchanged. It was heated with hydroquinone and sulfuric acid to 150–180° but no condensation took place.

Summary

Phthalic anhydride has been condensed with *m*-fluorotoluene, *o*- and *p*-fluoro- and *o*-chloro-ethylbenzenes, *m*-diethyl-, *m*-di-*iso*propyl- and cyclohexylbenzenes. The resulting *o*-benzoylbenzoic acids have been condensed to the corresponding substituted anthraquinones. *o*-Benzylbenzoic acid has been nitrated to the 2,2′-dinitro derivative which has been oxidized to *o*-(*o*-nitrobenzoyl)3-nitrobenzoic acid and this condensed to 1,8-dinitro-anthraquinone.

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CHEMISTRY OF THE TRIMETHYLTIN GROUP

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When a carbon atom is joined to three aryl groups, its remaining valence is strongly amphoteric and the group is capable of existing in the positive or negative or the neutral condition. The triphenylmethyl group is the most familiar example of this type of compound. It is known that many other elements, combined with alkyl or aryl groups, form similar compounds. The general group formula is $R_{n-1}M^{n}$, where R is a hydrocarbon group and M is an element of valence *n*. Groups of the type $R_{n-2}M^{n}$ are also known. These, however, will be discussed in a subsequent paper.

Groups of the type $R_{n-1}M^{n}$ often resemble the triphenylmethyl group very closely and exhibit amphoteric properties in a marked degree. While a number of these groups are known to exist,[1] their physical and chemical properties have not been studied extensively. The present investigation is intended to supply further data, particularly with regard to the chemical properties of the trimethyltin group. As has been pointed out elsewhere,[2]

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[1] Rügheimer, *Ann.*, **364**, 53 (1910). E. Krause, *Ber.*, **54**, 2060 (1921); **55**, 888 (1922). Schlenk, Renning and Racky, *Ber.*, **44**, 1178 (1911). Kraus, THIS JOURNAL, **35**, 1732 (1913). Midgley, Hochwalt and Calingaert, *ibid.*, **45**, 1821 (1923). Ladenburg, *Ann. Spl.*, **8**, 65 (1872).

[2] (a) Kraus, *Rec. trav. chim.*, **42**, 588 (1923); (b) THIS JOURNAL, **46**, 2196 (1924). (c) Kraus and Callis, *ibid.*, **45**, 2624 (1923). (d) Kraus and Greer, *ibid.*, **45**, 3078 (1923).

this group resembles the triphenylmethyl group and in certain respects, also, the methyl group or hydrogen.

The Free Trimethyltin Group

Preparation.—The free trimethyltin group may be obtained by the reduction of the trimethyltin halides with metallic sodium in liquid ammonia solution. The reaction proceeds quantitatively according to the equation

$$(CH_3)_3SnX + Na = NaX + (CH_3)_3Sn \qquad (1)$$

The bromide, which was preferably employed in this preparation, was made by brominating tetramethyltin.

The calculated amount of bromine (2 atoms of bromine per atom of tin) is allowed to drop slowly into tetramethyltin in a distilling flask, cooled to a temperature of about 10°. When the required amount of bromine has been introduced the mixture is allowed to come to room temperature and the product is purified by fractional distillation and crystallization. A small amount of dimethyltin dibromide is formed, while a corresponding amount of tetramethyltin remains unchanged. There is little loss of tin compound if the lower- and higher-boiling fractions are preserved and worked over. Trimethyltin bromide melts at 27° and boils at 165°. Its purity is readily recognized by the sharpness of its melting point.

Trimethyltin bromide, like the corresponding chloride,[2d] combines with one molecule of ammonia to form a comparatively stable, solid compound. For many purposes this compound is more conveniently manipulated than the original bromide. It is prepared by passing a stream of ammonia gas through a cold solution of the bromide in petroleum ether, and immediately thereafter filtering and removing adhering petroleum ether by means of a vacuum pump.

Anal. Subs., 0.0674: AgBr, 0.0487. Calcd. for $Sn(CH_3)_3Br.NH_3$: Br, 30.65. Found: 30.76.

When an ammonia solution of trimethyltin bromide or chloride is treated with metallic sodium, reaction takes place at once with the formation of a white precipitate and the disappearance of the color due to sodium. This precipitate is trimethyltin formed according to Equation 1. After addition of the equivalent amount of sodium, the ammonia is evaporated and warm water is added for the purpose of dissolving the inorganic salt present. The free group, which melts at 23°, separates as a heavy, oily liquid. After having been repeatedly washed, the water mixture is transferred to a separatory funnel and the free group is filtered through anhydrous sodium sulfate in an atmosphere of nitrogen. Water is not appreciably soluble in the compound and sodium sulfate is satisfactory as a drying agent.

Anal. Subs., 0.4176, 0.6318, 0.6298: SnO_2, 0.3845, 0.5841, 0.5779. Calcd. for $Sn(CH_3)_3$: Sn, 72.46. Found (Carius): 72.52, 72.70, 72.27.

Properties.—Above its melting point (23°) trimethyltin is a mobile liquid; b. p., 85–88° (45 mm.) (uncorr.). The recrystallized material boils at 182° (756 mm.) (corr.); d_{25}, 1.570. The liquid cannot be distilled in air since the hot vapors flash in the condenser. In an inert atmosphere some decomposition takes place at the boiling point.

The molecular weight of trimethyltin was determined in benzene at its boiling point by the Beckmann method. The results are given in Table I.

At lower concentrations, the molecular weight corresponds fairly closely to that of the free group; 171.1 as against 163.8 calculated. As the concentration increases,

TABLE I

MOLECULAR WEIGHT OF TRIMETHYLTIN IN BENZENE AT THE BOILING POINT

Solvent G.	Solute G.	Moles of solute per liter of solvent	Δt °C.	Apparent mol. wt.
27.82	0.0659	0.0072	0.037	171
15.13	.0804	.0162	.066	215
27.82	.2853	.0313	.116	236
16.21	.3114	.0587	.208	246
15.13	.3419	.0693	.221	272
15.28	.4024	.0805	.247	284
27.82	.5912	.0648	.179	316
16.21	.7404	.1395	.363	335
15.28	.7428	.1484	.369	352

the molecular weight increases, ultimately reaching a value a little higher than that required for a bimolecular compound of the trimethyltin group. These results are in accord with those obtained by Rügheimer[1] with trimethyltin under corresponding conditions.[3]

Reactions.—With sodium in liquid ammonia, trimethyltin reacts as follows: $Sn(CH_3)_3 + Na = (CH_3)_3SnNa$. Trimethyltin is not very soluble in liquid ammonia and the reaction is slow unless the compound is present in a finely divided state. Reaction proceeds fairly promptly when the liquid is dropped into a solution of sodium. The reaction, however, is much more rapid when sodium is added to the compound, as it is originally precipitated by reduction from its halides. To 0.133 g. of sodium was added 0.917 g. of $Sn(CH_3)_3$. The blue color due to sodium was discharged and a light yellow solution resulted. These proportions correspond to 1.03 atoms of sodium per atom of tin. The slight excess of sodium is doubtless due to oxidation of the metal in the course of weighing.

In the absence of oxidizing agents, trimethyltin remains unchanged indefinitely. When the compound is left in contact with air for a short time a white solid is precipitated. Oxidation is best carried out by pouring the compound onto a watch glass and leaving it covered with a filter paper for some days. Under these conditions complete conversion takes place. The oxidation product is insoluble in water and organic solvents. Treated with concd. hydrobromic acid it gives a readily soluble compound which was identified as trimethyltin bromide. With sulfuric acid, the oxidation product yields colorless prisms whose properties correspond with those of the sulfate.[4] Apparently oxidation takes place according to the equation, $2Sn(CH_3)_3 + {}^1/_2O_2 = (CH_3)_3SnOSn(CH_3)_3$.

Anal. Subs., 0.2114, 0.2039: SnO_2, 0.1877, 0.1804. Calcd. for $[(CH_3)_3Sn]_2O$: Sn, 69.10. Found (Carius): 69.71, 69.69.

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[3] It is of interest to note that Ladenburg[1] prepared triethyltin by reduction of triethyltin iodide with metallic sodium. His determinations of the vapor density of this compound correspond to the formula $[(C_2H_5)Sn]_2$. On reducing $(CH_3)_3SnI$ with metallic sodium he obtained only $(CH_3)_4Sn$.

[4] Hiortdahl, *Compt. rend.*, **88**, 584. Cahours, *Ann.*, **114**, 378 (1860).

It might be expected that sulfur would react with the free group in a manner similar to oxygen. A weighed quantity of trimethyltin was dissolved in benzene and an equivalent quantity of sulfur (likewise dissolved in benzene) added. After several days the solution was filtered and the benzene evaporated. In case the reaction is incomplete, crystals of sulfur separate in this process.

Trimethyltin Sulfide.—$[(CH_3)_3Sn]_2S$, is a light yellow oil with a sharp, unpleasant odor; d_{25}, 1.649; b. p., 233.5–235.5° (759 mm.) (corr.). It forms almost colorless leaflets; m. p., 6° (corr.). Slight decomposition occurs on distillation at ordinary pressures. The compound is insoluble in water but readily soluble in organic solvents and acids (nitric acid precipitates sulfur) with evolution of hydrogen sulfide. When the liquid is left exposed to air, a precipitate is slowly formed, presumably due to oxidation.

Anal. Subs., 0.5014, 0.4833: SnO_2, 0.4213, 0.4091.

Subs., 0.5014: $BaSO_4$, 0.3495. Calcd. for $[(CH_3)_3Sn]_2S$: Sn, 66.01; S, 8.92. Found: Sn, 66.34, 66.67; S, 9.57.

Trimethyltin reacts readily with the halogens at room temperature. In benzene solution, 0.3397 g. combined with 0.2556 g. of iodine. This corresponds to a ratio of 1 atom of iodine per atom of tin. On evaporating the benzene, there was left behind a liquid which was identified as trimethyltin iodide.

In some of the earlier preparations, trimethyltin was extracted with ether and the ether solution dried with calcium chloride. This operation was carried on in air, since the oxidation of the compound under these conditions is not rapid. It was found that reaction apparently occurred between trimethyltin and calcium chloride, since trimethyltin chloride was formed, as indicated by its characteristic odor. Further investigation showed that a reaction occurs between calcium chloride and trimethyltin dissolved in organic solvents in the presence of dry air. As much as 40% of the compound was converted to chloride, while a certain amount of calcium carbonate was found to be present in the calcium chloride at the end of the reaction. In the absence of air, however, no reaction was observable between calcium chloride and trimethyltin. This reaction was not studied further.

Reactions were also found to occur between trimethyltin and other metallic halides. With mercuric chloride in ether, a rapid reaction occurs with the formation of trimethyltin chloride and mercury. Apparently, trimethyltin is sufficiently electropositive to reduce mercury from its chloride.

Sodium-Trimethyltin

Preparation.—As already noted, sodium-trimethyltin is formed by the action of sodium on trimethyltin in liquid ammonia. The same compound is formed when a trimethyltin halide is reduced by means of metallic sodium in liquid ammonia, reaction taking place in two stages as follows.

$$(CH_3)_3SnX + Na = NaX + (CH_3)_3Sn;\ (CH_3)_3Sn + Na = NaSn(CH_3)_3 \qquad (2)$$

To 1.447 g. of trimethyltin chloride was added 0.343 g. of sodium. This yielded a clear yellow solution, and further addition of sodium yielded a permanent blue solution. The ratio of the reaction constituents corresponds to 2.03 atoms of sodium per molecule of the chloride in accordance with the above equations.

Properties.—Sodium-trimethyltin is readily soluble in liquid ammonia to which it imparts a pale yellow color. It is very reactive toward electronegative elements or compounds containing such elements. A solution of this compound in liquid ammonia, therefore, is an important synthetic reagent, since it makes it possible to transfer the trimethyltin group to other compounds by simple metathetic reaction. These reactions often proceed quantitatively.

When a solution of sodium-trimethyltin in ammonia is evaporated, a light yellow compound crystallizes. This compound is unstable even at room temperature and decomposes readily at higher temperatures. At liquid-ammonia temperatures the compound contains no ammonia, as is shown by the following data: 0.530 g. of trimethyltin chloride was treated with 0.130 g. of sodium, a total weight of 0.660 g. of reacting materials. On completion of the reaction and removal of the ammonia, the contents of the reaction tube were found to weigh 0.653 g. This is in accord with Equations 2.

Above room temperatures the salt breaks down rapidly and at 75° forms a metallic mirror on the walls of the containing tube. This material is evidently an alloy of sodium and tin, since it reacts violently with water. Attempts were made to study the gaseous products of decomposition but the results obtained were not consistent. Large quantities of hydrocarbon gases were evolved which were probably contaminated with some tetramethyltin. The density of several samples of the gas yielded the values 28.37 and 44.0 for the mean molecular weight of the gaseous mixture.

Reactions.—With a trimethyltin halide, the sodium salt reacts immediately with the formation of trimethyltin according to the equation: $NaSn(CH_3)_3 + (CH_3)_3SnX = NaX + 2(CH_3)_3Sn$. The reaction product was characterized by its melting point and other properties.

As already mentioned, the trimethyltin group is in many respects similar to the alkyl group. The sodium salt, therefore, resembles the sodium alkyls. When the salt is treated with an organic halide, the corresponding metal halide is formed, while the group unites with the organic residue according to the equation: $RX + NaSn(CH_3)_3 = NaX + RSn(CH_3)_3$. This reaction takes place when the affinity between the trimethyltin group and the carbon residue is marked. Otherwise, free trimethyltin may be precipitated from solution.

The sodium salt, in liquid ammonia solution, was treated with *p*-dichlorobenzene. This compound is not appreciably soluble in liquid ammonia. The reaction was therefore facilitated by the addition of ether to the reaction mixture. Under these conditions, a white solid is precipitated, while the ether solution turns red. The reaction does not proceed quantitatively and a certain amount of the original dichlorobenzene was found present in the final reaction product. After the residue had been washed with alcohol, it was finally recrystallized from benzene from which it separated in the form of small, colorless needles; m. p., 123–124° (corr.). The compound was shown to be free from halogen. By nitric acid it is decomposed with ignition. It reacts readily with iodine in benzene solution, giving trimethyltin iodide and *p*-di-iodobenzene; m. p., 126.5–128.5°.

Anal. Subs., 0.3509, 0.3028: SnO_2, 0.2642, 0.2271. Calcd. for $C_6H_4[Sn(CH_3)_3]_2$: Sn, 58.82. Found: 59.33, 59.07.

Its molecular weight was determined in benzene with the results shown in Table II.

TABLE II

MOLECULAR WEIGHT OF $C_6H_4[Sn(CH_3)_3]_2$ IN BENZENE

Wt. of compound, g.	0.2805	0.3930	0.4704
Δ*t*, °C.	.113	.136	.175
Mol. wt.	362	422	393
Calcd. mol. wt. of $C_6H_4[Sn(CH_3)_3]_2$	403.6		Av. 392

Evidently reaction takes place as follows: $2Sn(CH_3)_3Na + C_6H_4Cl_2 = C_6H_4[Sn(CH_3)_3]_2 + 2NaCl$.

An attempt was made to substitute the trimethyltin group for chlorine in ethylene chloride by treating the latter compound with sodium-trimethyltin in liquid ammonia. A hydrocarbon gas was given off while at the same time free trimethyltin and sodium chloride were formed. Presumably, reaction takes place as follows: $2Sn(CH_3)_3Na + CH_2Cl.CH_2Cl = 2(CH_3)_3Sn + CH_2{:}CH_2 + 2NaCl$.

An attempt was also made to combine the trimethyltin group with the triethyl-lead group. Triethyl-lead chloride was prepared by treating tetraethyl-lead with hydrogen chloride in petroleum ether. The crystals that separated were washed with ether, filtered off and dried. Analysis yielded 10.56% of chlorine as against 10.72% calculated. When the triethyl-lead chloride was introduced into an ammonia solution of sodium-trimethyltin, a precipitate was formed which quickly turned gray. A similar result was obtained when trimethyl-lead chloride was employed in place of the corresponding ethyl compound. Apparently the compounds formed are unstable.

Sodium-trimethyltin in liquid ammonia was also treated with triphenylmethyl chloride. Reaction did not take place readily but when the triphenylmethyl chloride was added in ethereal solution, reaction occurred. A mixture of compounds resulted, the nature of which was not determined.

When sodium-trimethyltin is treated with a triethyltin halide, immediate reaction occurs with the precipitation of a compound which is liquid at liquid-ammonia temperature. Apparently reaction takes place as follows.

$$(CH_3)_3SnNa + Sn(C_2H_5)_3I = NaI + (CH_3)_3Sn{-}Sn(C_2H_5)_3 \qquad (3)$$

At higher concentrations, and particularly at lower temperatures, the trimethyltin group is bimolecular.[5] It seems, therefore, that when the sodium salt of the trimethyltin group is treated with a triethyltin halide, a compound is formed between the two groups. As stated, the mixture is liquid at liquid-ammonia temperatures, and since an equimolecular mixture of the two free groups precipitates a solid phase in the neighborhood of —5°, it follows that in the product of Reaction 3 the two groups are combined;[6] d_{20}, 1.431; b. p., 235° (748 mm.).

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[5] R. H. Bullard, *Dissertation*, Brown University, **1925**.

[6] S. B. E. Towne, *Thesis*, Clark University, **1924**.

Anal. Subs., 0.1849, 0.2306: SnO_2, 0.1554, 0.1937. Calcd. for $(CH_3)_3Sn.Sn(C_2H_5)_3$: Sn, 63.27. Found: 66.33, 66.16.

Subs. (benzene soln.), 0.3645: I_2 absorbed, 0.2601. Calcd. $[(CH_3)_3Sn.Sn(C_2H_5)_3 + I_2 = (CH_3)_3SnI + (C_2H_5)_3SnI]$: 0.2504.

Action of Sodium on Tetramethyltin

A preliminary experiment showed that sodium reacts readily with tetramethyltin in liquid ammonia with the formation of a light yellow solution and the evolution of a considerable quantity of combustible gas, while a precipitate is formed at the same time. Approximately 2 atoms of sodium are required per molecule of tetramethyltin. It was inferred that reaction takes place as follows.

$$(CH_3)_4Sn + Na + NH_3 = NaSn(CH_3)_3 + NaNH_2 + CH_4 \qquad (4)$$

In order to establish the precise nature of this reaction, a weighed quantity of tetramethyltin was sealed in a small, thin-walled glass bulb which was crushed under a solution containing a known weight of sodium. Reaction took place immediately with the evolution of a large quantity of gas which was collected over water. The volume and the density of this gas were determined after it had been dried. At the end of the reaction the solution was still slightly blue and the color was discharged on the addition of 0.011 g. of ammonium chloride. Numerically, 1.591 g. of tetramethyltin was added to 0.410 g. of sodium. The ammonium chloride added was equivalent to 0.005 g. of sodium, leaving 0.405 g. of sodium, which reacted with tetramethyltin. This corresponds to 1.98 atoms of sodium per molecule of tetramethyltin. At 748 mm. pressure, the gas evolved occupied a volume of 225 cc. at 22°, corresponding to 199.4 cc. N. T. P. This volume is equivalent to 0.0892 mole of gas as against 0.0890 mole of tetramethyltin. Evidently one mole of gas is evolved per mole of tetramethyltin.

The density of the gas was determined by weighing a known volume of the gas at definite temperature and pressure, and its mean molecular weight calculated from these data; 353 cc. of gas (24.7°, 150 mm.) weighed 0.0662 g. This corresponds to a mean molecular weight of 23.2. It was anticipated that the gas evolved would prove to be methane, but the observed molecular weight was much above the expected value. It was thought that the discrepancy might be due to the presence of tetramethyltin, vapors of which were carried over with the escaping gases during the reaction. The somewhat low value of sodium, 1.98, further indicated that this might be the case. Accordingly, the gases escaping from the reaction mixture were passed through a concentrated solution of sodium in liquid ammonia before they were collected. A determination of the mean molecular weight under these conditions yielded the value 17.47.

This value still being high, it was thought that the discrepancy was due to insufficient washing of the evolved gases. An apparatus was therefore devised whereby the evolved gases could be successively passed through a solution of sodium in liquid ammonia as often as desired. After the gas had been passed through a sodium solution 12 times, it was collected and freed from ammonia vapor and its density determined; 353 cc. of gas (26.4°, 446 mm.) weighed 0.1265 g. This corresponds to a mean molecular weight of 15.00 as against 16.03 for methane. It was inferred that the low value thus observed was due to the presence of a small amount of hydrogen formed by the interaction of sodium with the solvent in the washing solution. Accordingly, a quantity of the gas at known temperature and pressure was treated with palladium. After the temperature and pressure of the gas had been determined, the tube containing the palladium was heated until absorption of hydrogen took place, and thereafter brought to the original temperature. This process was repeated until no further change in pressure occurred. From the change in pressure due to absorption of hydrogen the percentage of hydrogen present in the mixture was calculated.

The original mixture at a pressure of 425.7 mm. yielded a final pressure of 397.5 mm., corresponding to an absorption of 28.2 mm. of hydrogen. This is equivalent to 6.6% of hydrogen in the mixture. The mean molecular weight of a mixture of 6.6% of hydrogen and 93.4% of methane is 15.07, which is in agreement with the determined value of 15.00.

The above reaction is of interest because of the light which it throws on the reduction process of organic halides by means of the alkali metals. In this reaction, hydrocarbons are formed together with various amino derivatives. Kraus and White[7] have already suggested that, in such reductions, sodium alkyl or aryl is formed, which ammonolyzes to hydrocarbon and amide. The reaction of the alkali metal amide on further addition of halide then leads to the formation of amines. In the reduction of tetramethyltin by means of metallic sodium, the original compound does not react with the amide and therefore permits the study of this phase of the reaction. In all likelihood, reaction takes place in two stages.

$$(CH_3)_4Sn + 2\ Na = NaSn(CH_3)_3 + NaCH_3 \quad (5)$$
$$NaCH_3 + NH_3 = CH_4 + NaNH_2 \quad (6)$$

Since sodium methyl, which is first formed, is a salt of an exceedingly weak acid, methane, hydrolysis (ammonolysis) occurs according to Reaction 6.

When sodium reacts with tetramethyltin a precipitate is invariably formed which is apparently sodium amide, whose solubility in liquid ammonia is low. When the reaction mixture is pumped free from ammonia and water is added, a violent reaction occurs and the presence of ammonia is readily detected. That sodium-trimethyltin is formed in the initial reaction was shown not only by the pale yellow color of the solution, but also by addition of ammonium chloride to the reaction mixture which resulted in the precipitation of droplets of $(CH_3)_3SnH$.[8]

Summary

1. Trimethyltin, $(CH_3)_3Sn$, has been prepared and its properties have been studied. At the boiling point of benzene, it is approximately monomolecular at low concentrations and bimolecular at high concentrations.

2. Free trimethyltin combines directly with sodium in liquid ammonia to form the compound $NaSn(CH_3)_3$. The properties of this compound and some of its reactions have been investigated. With oxygen, trimethyltin combines to form the oxide $[(CH_3)_3Sn]_2O$ and with sulfur the sulfide, $[(CH_3)_3Sn]_2S$. The compound *p*-$[(CH_3)_3Sn]_2C_6H_4$ has been prepared by the action of the corresponding chloride on sodium-trimethyltin.

3. The compound $(CH_3)_3Sn.Sn(C_2H_5)_3$ has been prepared.

4. Sodium reacts with tetramethyltin according to the equation: $Sn(CH_3)_4 + Na + NH_3 = (CH_3)_3SnNa + NaNH_2 + CH_4$.

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[7] Kraus and White, THIS JOURNAL, **45**, 777 (1923).

[8] Kraus and Greer, *ibid.*, **44**, 2629 (1922).