

4. An explanation is advanced for the formation of *n*-pentadecane- γ -keto- α, α' -dicarboxylic acid from chaulmoogric acid.

5. Power suggested that the formula of chaulmoogric acid was 1-(α -carboxy-*n*-dodecyl)- Δ^4 -cyclopentene in equilibrium with a tautomeric bicyclopentane derivative. In view of the facts mentioned above it may be concluded that chaulmoogric acid does not exist in a tautomeric state and is merely 1-(α -carboxy-*n*-dodecyl)- Δ^4 -cyclopentene.

6. By analogous reasoning, the structure of hydnocarpic acid is 1-(α -carboxy-*n*-decyl)- Δ^4 -cyclopentene.

URBANA, ILLINOIS

REACTIONS OF COMPOUNDS OF TRIPHENYLMETHYL AND TRIPHENYLSILICYL IN LIQUID AMMONIA

BY CHARLES A. KRAUS AND RAPHAEL ROSEN

RECEIVED MAY 13, 1925

PUBLISHED NOVEMBER 5, 1925

While triphenylmethyl and other similar groups have been the subject of extensive investigation, our knowledge of the chemical properties of these groups is still very limited. The present investigation was undertaken for the purpose of securing further information regarding the chemistry of the triphenylmethyl and triphenylsilicyl groups.

Metallic Derivatives of Triphenylmethyl

Schlenk and Marcus¹ obtained a sodium derivative of triphenylmethyl by reduction of the chloride with sodium in the presence of mercury in ether. Kraus and Kawamura² have obtained the sodium and potassium compounds by the reduction of the halides with metals in liquid ammonia as well as by the direct action of the alkali metals on triphenylmethane in the same solvent.

Properties.—The alkali-metal derivatives of triphenylmethyl are true salts. They are readily hydrolyzable and oxidizable, readily soluble in liquid ammonia and appreciably, though much less, soluble in various organic solvents, such as toluene.

Schlenk and Marcus³ have shown that solutions of sodium triphenylmethyl in ether conduct the electric current to some extent, the conductance increasing with increasing concentration.

In the present investigation, solutions of sodium and potassium triphenylmethyl for conductance measurements were prepared in liquid ammonia by the action of the free metals on triphenylmethane. For the sodium and potassium salts at 0.05 and 0.08 *N*, the equivalent con-

¹ Schlenk and Marcus, *Ber.*, **47**, 1664 (1914).

² Kraus and Kawamura, *THIS JOURNAL*, **45**, 2756 (1923).

³ Ref. 1, p. 1678. For the equivalent conductance they found 4.8×10^{-2} at a dilution of 26.62 liters per mole.

ductance was found to be 64 and 32, respectively. Triphenylmethane does not conduct appreciably in liquid ammonia. It is evident that the sodium and potassium triphenylmethyl compounds are true salts and that they undergo normal ionization in liquid ammonia.⁴

Oxidation of Sodium and Potassium Triphenylmethyl.—According to Schlenk and Marcus,¹ sodium triphenylmethyl is oxidized to sodium peroxide and triphenylmethyl peroxide in ether. In the dry state the potassium salt is spontaneously inflammable in air. In liquid-ammonia solution the sodium and potassium salts are readily oxidized by means of molecular oxygen. The product of oxidation is precipitated as the reaction proceeds, while the characteristic red color of the salt disappears. When the oxidation product is allowed to come to room temperature, it is at first very readily soluble in ether, the alkali-metal peroxide being left behind. The ether solution is faintly yellow. After some time, a white compound crystallizes which was shown to be triphenylmethyl peroxide, m. p. 178°; this turns orange on melting and is soluble in carbon disulfide and insoluble in benzene and water. However, the ether-soluble compound, obtained when the reaction mixture is allowed to warm to room temperature, is not the initial product of oxidation, as will be shown below.

When oxidation is carried out in liquid ammonia, two atoms of oxygen are absorbed per molecule of sodium or potassium salt. This was established by carrying out the reaction in closed tubes and weighing the contents before and after oxidation. The volume of oxygen absorbed was also measured in several experiments and found to check with the observed weights. Table I gives the results of several experiments with sodium and potassium triphenylmethyl.

TABLE I
OXIDATION OF SODIUM TRIPHENYLMETHYL

No.	(C ₆ H ₅) ₃ CCl	Metal	Gain found G.	Gain calcd. G.	O ₂ obs. Cc.	O ₂ calcd. Cc.
1	0.8822	0.1420	0.0973	0.0988	72.0	69.2
2	.8212	.1320	.0892	.0918	64.0	64.2

OXIDATION OF POTASSIUM TRIPHENYLMETHYL

1	1.9088	0.5376	0.2236	0.2200
2	1.5716	.4422	.1790	.1810

As may be seen, the weight as well as the volume of oxygen absorbed corresponds with that calculated on the assumption that one molecule of oxygen combines with one molecule of the alkali-metal salt.

While the product of the reaction, after warming to room temperature,

⁴ Schlenk and Marcus attribute the increasing equivalent conductance of these salts in ether to complex formation. This behavior, however, is common to all salts dissolved in solvents of low dielectric constant, and cannot well be ascribed to the formation of complex ions without further data.

consists of sodium peroxide and an oxide of triphenylmethyl which is soluble in ether, the compound initially precipitated from liquid ammonia appears to contain alkali metal in combination with the organic group. The nature of this compound has not as yet been determined. That potassium peroxide was not present in the initial compound was shown by a study of the oxidation of this product. Potassium peroxide is readily oxidized to the tetroxide, K_2O_4 , in liquid-ammonia solution.⁵ When the original potassium salt is oxidized, only one molecule of oxygen is absorbed even though the process of oxidation be continued for hours. When this product is allowed to come to room temperature for some time and then again subjected to oxidation in liquid ammonia, further quantities of oxygen are absorbed. This is shown by the following experiments in which oxidation was continued for six hours.

No.	$(C_6H_5)_3CCl$	K	Gain in wt., g.	Calcd. gain in O
1	0.5635	0.1580	0.0734	0.0646
2	.5608	.1575	.0645	.0645

In the course of the weighings the products of oxidation remained at room temperature for several hours. Ammonia was then recondensed and the process of oxidation renewed. At the end of several hours, No. 1 was found to have further absorbed 0.0118 g. and No. 2, 0.0355 g. of oxygen. To form potassium tetroxide, 0.0322 g. of oxygen is required. Expt. 2 is in excellent agreement with this value. No. 1 is somewhat low, the total excess of oxygen at the end of the final oxidation amounting to 0.0206 g. The oxidation of potassium peroxide to the tetroxide does not always proceed smoothly and this may be the cause of the discrepancy. In any case, potassium peroxide was not present in the initial product, while the subsequent absorption of oxygen indicates its presence later.

Ammonolysis of Sodium and Potassium Triphenylmethyl.—The triphenylmethyl salts may be looked upon as being formed by the action of an ammonio base on triphenylmethane according to the equation— $(C_6H_5)_3CH + KNH_2 = (C_6H_5)_3CK + NH_3$. When triphenylmethane is treated with potassium amide in liquid ammonia, reaction takes place immediately as is shown by the intense red color of the resulting solution. That this reaction goes practically to completion was shown by oxidizing the final product. After converting 0.3380 g. of potassium to the amide, 2.1132 g. of triphenylmethane was added and the reaction product then oxidized; 205 cc. of oxygen (747 mm., 18°) as absorbed, or 189 cc. under standard conditions. This is equivalent to 0.2700 g. of oxygen as compared with 0.2766 g. calculated for the oxidation of the salt to potassium and triphenylmethyl peroxides.

It was to be expected that triphenylmethane would prove to be an exceedingly weak acid in liquid ammonia. It follows, then, that solutions

⁵ Earl F. Whyte, observations to appear later in THIS JOURNAL.

of the sodium and potassium salts should exhibit an appreciable hydrolysis (ammonolysis). Yet the amount of hydrolysis cannot be large, since triphenylmethane is only slightly soluble in liquid ammonia and solutions of the sodium and potassium salts give no indication of the presence of free triphenylmethane. Kraus and Kawamura² have observed that, although the potassium salt which separates from solution on evaporation of ammonia, is entirely stable, the sodium salt undergoes a change, slowly at room temperature and more rapidly at higher temperatures, whereby the characteristic red color disappears. The corresponding calcium salt is converted rapidly even at liquid-ammonia temperatures. Schlenk and Ochs⁶ have found that when an ethereal solution of the sodium salt is treated with ammonia at ordinary temperature, hydrolysis occurs with the formation of triphenylmethane and sodium amide.

It appears that triphenylmethane is an acid of such strength that a small amount of hydrolysis occurs in liquid-ammonia solutions of the sodium and potassium salts. Since sodium amide is a much weaker base than potassium amide, hydrolysis should be more pronounced in the case of the sodium than in that of the potassium salt while, in the case of the calcium salt, hydrolysis might be expected to be complete.

Experiments were carried out to determine whether the salts crystallized from liquid-ammonia solution with ammonia of crystallization. This was done by preparing the salts in a weighed tube and determining the gain in weight after evaporation of the solvent ammonia. It was found that the potassium salt crystallizes from solution, ammonia-free, while the sodium salt crystallizes with one molecule of ammonia at liquid-ammonia temperature. This salt is stable at that temperature and the ammonia must therefore be present in combination with the salt.

The results obtained with sodium triphenylmethyl are given below.

No.	(C ₆ H ₅) ₃ CCl	Na	Gain in wt. found, g.	Calcd. for 1 mol. eq. of NH ₃
1	2.6368	0.4358	0.1643	0.1618
2	0.8637	.1429	.0542	.0530

The weight of ammonia absorbed corresponds closely with that required for one molecule of ammonia per molecule of salt. The color of the compound is lost at higher temperatures without change of weight. From the product of this reaction, triphenylmethane was extracted and was characterized by its melting point and solubility, while the presence of sodium amide was indicated by the evolution of ammonia on treatment with water.

With potassium triphenylmethyl the following results were obtained.

No.	(C ₆ H ₅) ₃ CCl	K	Gain in wt. found, g.	Calcd. for 1 mol. eq. of NH ₃
1	0.5593	0.1576	0.0086	0.0343
2	.4993	.1406	.0029	.0306

⁶ Schlenk and Ochs, *Ber.*, **49**, 614 (1916).

The results clearly indicate that the potassium salt contains no ammonia. The red color characteristic of the compound is retained at 100° under a high vacuum. No triphenylmethane could be extracted from the residue. The stability of the potassium salt at high temperatures is due to the absence of ammonia. When ammonia gas is passed over this salt at 100°, potassium amide and triphenylmethane are formed, as in the case of the sodium salt.

With calcium the following results were obtained.

No.	(C ₆ H ₅) ₃ CCl	Ca	Gain in wt. found, g.	Calcd. for	
				1 mol. eq. of NH ₃	2 mol. eq. of NH ₃
1	1.3467	0.1939	0.1412	0.0826	0.1652
2	2.6033	.3756	.2637	.1597	.3197
3	1.2596	.1812	.1112	.0773	.1540

The weight of the contents of the tube at the end of the reaction indicates the presence of ammonia or nitrogen. In the case of Expts. 1 and 2, the process of evacuation at 100° was continued only for a short time and the gain in weight corresponds nearly with the presence of two molecules of ammonia per atom of calcium. In the case of Expt. 3, the tube was exhausted for a longer period at 100° and the weight is much below that calculated for two molecules of ammonia. In all probability the calcium amide originally formed was converted to calcium nitride or some other de-ammonation product.

There can be little doubt that sodium triphenylmethyl ammonolyzes by interaction with the ammonia originally present in the compound as ammonia of crystallization. The stability of the potassium salt is primarily due to the absence of ammonia from the compound originally precipitated.

The reaction between triphenylmethane and the alkali metal amides is a reversible one. The salts being strongly colored, triphenylmethane serves as a very sensitive indicator of the Ostwald type in liquid ammonia. In pure liquid ammonia or in the presence of ammonium salts (acids), it yields a colorless solution while, in the presence of soluble bases, even at very low concentrations, the deep red color of the alkali-metal salt appears. Even potassium hydroxide, whose solubility in ammonia is exceedingly low, imparts a distinct color to a solution of triphenylmethane. When oxygen is passed through this solution, the color is discharged, due to oxidation of the potassium salt. When the solution is allowed to stand, the color reappears. This process may be repeated a number of times or until the concentration of water reaches such a value that the solution gives a neutral reaction.

Reactions of Triphenylmethyl Chloride

Addition Compounds.—The triphenylmethyl halides conduct the electric current with considerable facility when dissolved in liquid am-

monia.⁷ It is known that these compounds likewise conduct the current in sulfur dioxide⁸ while in nitrobenzene they yield solutions of low conducting power.^{8b} Measurements with the fused chloride showed that it does not conduct the current. These properties of triphenylmethyl chloride closely resemble those of trimethyltin chloride. It has been shown that the electrolytic properties of the latter compound are due to the formation of a complex cation by interaction of the trimethyltin group with the solvent.⁹ It was to be expected, therefore, that triphenylmethyl chloride would combine with ammonia and the amines to form compounds having salt-like properties.

It was found that triphenylmethyl chloride combines readily with one molecule of pyridine to form a white crystalline compound; m. p., 173–174°. This compound is readily soluble in hot alcohol and pyridine and insoluble in carbon disulfide and benzene.

Anal. Subs., 0.142, 0.2310. Calcd. for 1 and 2 molecules of pyridine: Cl, 9.92, 8.12. Found: 9.65, 9.71.

The chloride combines with aniline to form a white compound, m. p. 189–190°, soluble in pyridine and insoluble in ether, petroleum ether, benzene and carbon disulfide.

Anal. Subs., 0.2575, 0.1687. Calcd. for 1 and 2 molecules of aniline: Cl, 9.54, 7.63. Found: 8.61, 8.52.

Aniline in the compound was also determined directly by conversion to the hydrochloride and weighing.

Anal. Subs., 0.4238: aniline hydrochloride, 0.1244. Calcd. for 1 molecule of aniline: 0.1477.

Ammonolysis of Triphenylmethyl Chloride.—It might be expected that triphenylmethyl chloride would combine with one molecule of ammonia to form compounds similar to those just described. It was found, however, that when the chloride is treated with ammonia, two molecules of ammonia are concerned in the reaction. Ammonia was condensed on the chloride in a weighed tube and the mixture stirred for four or five hours. In a second experiment the compound was finely pulverized before being treated with ammonia. The following results were obtained.

No.	Wt. of compd., g.	Gain in weight, g.		
		Found	Calcd. for 1 NH ₃	2NH ₃
1	0.5713	0.0594	0.0350	0.0700
2	.9094	.1084	.0545	.1090

The gain in weight is a little under that required for two molecules of ammonia per molecule of the compound. A weighed quantity of triphenylmethyl chloride was dissolved in 15 cc. of absolute ether and ammonia

⁷ Kraus, unpublished observations.

⁸ (a) Walden, *Ber.*, **35**, 2020 (1902). (b) Gomberg, *Ber.*, **35**, 2405 (1902).

⁹ Kraus and Callis, *THIS JOURNAL*, **45**, 2630 (1923); Kraus and Greer, *ibid.*, **45**, 2946, 3078 (1923).

passed through for five or six hours. No precipitate appeared. When the ammonia was driven off, however, a white precipitate was formed (ammonium chloride) and upon evaporation of the ether and subsequent evacuation of the reaction tube, the final weight indicated the presence of two molecules of ammonia in the reaction product.

Anal. Subs. (chloride), 0.7855: gain in weight, 0.0956. Calcd. for 2NH_3 : 0.0964.

Since ammonium chloride is not appreciably soluble in ether and since no precipitate was formed until the ether mixture was heated for the purpose of driving off the ammonia, it appears probable that a complex compound is initially formed which is soluble in the ether-ammonia mixture and which, when heated, ammonolyzes with the precipitation of ammonium chloride. The reaction may be represented by the equation: $(\text{C}_6\text{H}_5)_3\text{CCl} + 2\text{NH}_3 = (\text{C}_6\text{H}_5)_3\text{CNH}_2 + \text{NH}_4\text{Cl}$. On extraction of the final product with ether, triphenylmethylamine was obtained while ammonium chloride was left behind as residue. The amine was identified by its melting point, 103° , and by its reactions, while ammonium chloride was identified by its tendency to sublime and its solubility in water.

When triphenylmethyl chloride is dissolved in liquid ammonia, hydrolysis takes place to a slight extent. This is indicated by the fact that when a small quantity of potassium is added to ammonia which has stood in contact with triphenylmethyl chloride for some time, reaction takes place with the evolution of hydrogen, while the solution remains colorless. Triphenylmethyl chloride is very difficultly soluble in ammonia while ammonium chloride is readily soluble. When larger quantities of potassium are added to ammonia in the presence of triphenylmethyl chloride, only a small amount of hydrogen is evolved, showing that, for the most part, the reaction takes place directly between the metal and triphenylmethyl chloride.

The above hydrolytic reaction is reversible. When ammonium chloride is added to a solution of triphenylmethylamine in liquid ammonia and this in turn is treated with metallic potassium, potassium triphenylmethyl is formed as is indicated by the red color of the solution and by the absence of any evolution of hydrogen. The potassium salt so formed may be oxidized to the peroxide. The following are the data for such oxidation: 0.0959 g. of triphenylmethylamine was treated with 0.0198 g. of ammonium chloride which formed 0.1031 g. of triphenylmethyl chloride; to this was added 0.0298 g. of potassium; oxygen was passed through the reaction mixture until the characteristic color of the solution disappeared; on weighing, it was found that 0.0141 g. of oxygen had been absorbed, as compared with 0.0102 g. calculated for triphenylmethyl peroxide and potassium peroxide.

Action of Potassium on Triphenylmethylamine.—The organic amines are very weak acids which react slowly with the alkali metals with evolu-

tion of hydrogen and more readily with potassium amide with the formation of the corresponding ammonio salts of the amine.¹⁰ Triphenylmethylamine does not react with potassium amide, indicating that its acidic properties are extremely weak. On treatment of triphenylmethylamine with metallic potassium in liquid-ammonia solution, potassium amide and potassium triphenylmethyl are formed according to the equation $(C_6H_5)_3CNH_2 + 2K = (C_6H_5)_3CK + KNH_2$. The potassium amide was not identified but the formation of potassium triphenylmethyl was evident from the characteristic color of the resulting solution. A similar reaction was obtained with sodium.

Reactions of Triphenylsilicly Chloride

Schlenk, Renning and Racky prepared free triphenylsilicly by reduction of the chloride with metallic sodium in xylene.¹¹ In view of the similarity of silicon and carbon compounds, it was thought that sodium triphenylsilicly might be prepared by reaction of the halide of this group with metallic sodium in liquid-ammonia solution. This compound, if obtainable, would be of great value in the synthesis of other organic silicon compounds.

Triphenylsilicly was prepared according to the method of Dilthey and Eduardoff.¹² The silicly was halogenated according to the following procedure. Dry hydrogen chloride is passed through a solution of triphenylsilicly in absolute ether in an Erlenmeyer flask. The ether is gradually carried away by the stream of hydrogen chloride and crystals of triphenylsilicly chloride are gradually precipitated in comparatively pure form. The reaction is complete at the end of about three hours. The product is filtered off, washed with absolute ether and recrystallized from dry petroleum ether. Traces of the ether are removed with a vacuum pump. The filtrate is concentrated and further quantities of the chloride are obtained. A yield of approximately 90% of crude material was obtained in this way. Analysis of the chloride yielded the following results.

No.	$(C_6H_5)_3SiCl$, g.	$AgCl$, g.	SiO_2 , g.	Cl, %	Si, %
1	0.2002	0.0976	0.0406	9.58	12.06
2	.1737	.0848	.0340	9.48	12.08
				Calcd. 9.59	12.02

Reduction in Liquid Ammonia.—Triphenylsilicly chloride is only slightly soluble in liquid ammonia and reaction between this compound and sodium, therefore, takes place in the presence of an excess of sodium. Apparently the linkage of the phenyl groups with silicon is not stable in the presence of strong reducing agents. As much as from 5 to 6 atomic

¹⁰ White, Morrison and Anderson, *THIS JOURNAL*, **46**, 967 (1924). Compare also White, *ibid.*, **45**, 784 (1923).

¹¹ Schlenk, Renning and Racky, *Ber.*, **44**, 1178 (1911).

¹² Dilthey and Eduardoff, *Ber.*, **37**, 1139 (1904).

equivalents of sodium are used up when the chloride is treated with an excess of sodium. The properties of the resulting product depend upon the amount of alkali metal employed. Using about 4 atoms of sodium per molecule of compound, the reaction product was readily oxidizable while with an excess of sodium the product was comparatively inert. Definite compounds could not be isolated from the reaction mixture.

Ammonolysis of Triphenylsiliclyl Chloride.—The reaction between sodium and this chloride is complicated owing to the fact that the chloride ammonolyzes in liquid ammonia.

Subs., $[(C_6H_5)_3SiCl]$, 0.3114, 0.2584: gain when treated with liquid ammonia for some hours 0.0369, 0.0296. Calcd. for 2 mols. of NH_3 : 0.0391, 0.0325.

From the resulting mixture, after ammonolysis of the chloride, colorless triphenylsiliclylamine was isolated by extraction with petroleum ether; m. p., 55–56°. Ammonium chloride was identified as a second product of hydrolysis in ammonia.

The specific conductance of triphenylsiliclyl chloride in the fused condition was found to be 2.2×10^{-6} reciprocal ohms.

Anal. Subs., 0.2255, 0.2508: SiO_2 , 0.0504, 0.0556. Calcd. for $(C_6H_5)_3SiNH_2$: Si, 10.16. Found: 10.49, 10.40.

Summary

1. Sodium and potassium triphenylmethyl are salts, exhibiting normal ionization in liquid ammonia.

2. Triphenylmethyl peroxide and sodium or potassium peroxide are obtained as final products after oxidation of the corresponding salts in liquid ammonia. There is evidence indicating the existence of intermediate products.

3. Sodium and potassium triphenylmethyl are formed by the action of the corresponding amides on triphenylmethane in liquid ammonia. The reaction is reversible and hydrolysis of the salts is obtained under suitable conditions. The potassium salt crystallizes free from ammonia, and the sodium salt with 1 molecule of ammonia. Triphenylmethane is a sensitive indicator in liquid ammonia, being red in alkaline and colorless in acid solution.

4. Triphenylmethyl chloride is slightly hydrolyzed in liquid ammonia. The reaction is reversible and triphenylmethyl chloride is formed by the action of ammonium chloride on triphenylmethylamine. Triphenylmethyl chloride is hydrolyzed to the amine and ammonium chloride on evaporating an ammonia solution of the compound and on treating the compound with ammonia vapor at higher temperatures. Triphenylmethyl chloride forms addition compounds with pyridine and aniline.

5. Triphenylmethylamine does not react with potassium amide. With metallic potassium it yields potassium triphenylmethyl and potassium amide.

6. The phenyl linkage is broken down when triphenylsilyl chloride is reduced with metallic sodium in liquid ammonia. Triphenylsilyl chloride hydrolyzes in liquid ammonia with the formation of triphenylsilylamine and ammonium chloride.

BROWN UNIVERSITY
PROVIDENCE, RHODE ISLAND

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF BRITISH COLUMBIA]

THE CATALYTIC PREPARATION OF ETHER FROM ALCOHOL BY MEANS OF ALUMINUM OXIDE

BY R. H. CLARK, W. E. GRAHAM AND A. G. WINTER

RECEIVED MAY 15, 1925

PUBLISHED NOVEMBER 5, 1925

Introduction

Considerable work has been done on the dehydration of alcohol in the gaseous phase by means of solid catalysts, and of all catalysts alumina now appears to be the most efficient. The optimum temperature recommended by Senderens¹ for the production of ether by this means is 250°; above this temperature increasing amounts of ethylene are formed. Pure ether is also dehydrated to ethylene at temperatures above 250°. Senderens reports his best yield of ether from a catalyst prepared by precipitating aluminum hydroxide from sodium aluminate with sulfuric acid. He considers this form of alumina better than that obtained by precipitating the hydroxide from aluminum salts by ammonia. Senderens does not give any detailed information about the preparation of the catalyst, nor about the yields obtained.

Mailhe and de Godon² report a 71% yield of ether at 190°, using anhydrous aluminum sulfate as catalyst.

Pease and Yung³ obtained a 60% yield of ether at 250° with alumina prepared from aluminum nitrate and ammonia. Ipatiew⁴ obtained an appreciable amount of alcohol from equimolecular quantities of ether and water, thereby showing the reaction to be reversible.

It is generally considered that the nature of the surface of the catalyst plays a considerable part in the activation of the reaction. The idea that the spacing of atoms or molecules is a factor in catalytic reactions at surfaces has been considered by Langmuir.⁵ Further experimental evidence of this has been given by Adkins,⁶ for reactions similar to that

¹ Senderens, *Ann. chim. phys.*, [8] **25**, 505 (1912).

² Mailhe and de Godon, *Bull. soc. chim.*, **25**, 565 (1916).

³ Pease and Yung, *THIS JOURNAL*, **46**, 390 (1924).

⁴ Ipatiew, *Ber.*, **37**, 2986 (1904).

⁵ Langmuir, *Trans. Faraday Soc.*, **17**, 617 (1922).

⁶ Adkins, *THIS JOURNAL*, **44**, 385, 2175 (1922); **45**, 809 (1923); **46**, 130 (1924).