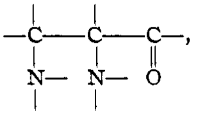

$-\underset{\underset{|}{N-}}{\overset{|}{C}}-\underset{\underset{|}{N-}}{\overset{|}{C}}-\underset{O}{\overset{}{\underset{\|}{C}}}-$, have been found to add Grignard reagents to give varying amounts of the expected tertiary carbinol.

LINCOLN, NEBRASKA RECEIVED SEPTEMBER 3, 1940

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

The Mechanism of Ketone Formation from trans Indene Glycol and Halohydrins

BY C. M. SUTER AND H. BAYARD MILNE

It was reported by Bartlett and co-workers[1] that refluxing *cis*-1,2-dimethylcyclohexanediol-1,2 with 20% sulfuric acid gave 2,2-dimethylcyclohexanone whereas the *trans* isomer undergoes conversion to 1-acetyl-1-methylcyclopentane.[2]

Similarly, *cis*-1,2-dimethylcyclopentanediol-1,2 gave the dimethylcyclopentanone and the *trans* compound a resinous material, presumably from the intermediate diene. It was pointed out[1] that in these pinacolic rearrangements the group that migrates is closest to that face of the adjacent carbon atom which is opposite the hydroxyl being replaced, and hence the reaction probably occurs with Walden inversion. More recently it has been shown by Meerwein[3] that if the *cis*-dimethylcyclohexanediol is heated with 2% sulfuric acid at 150–160°, a 70% yield of 1-methyl-1-acetylcyclopentane results and that an appreciable amount of dimethylcyclopentanone can be obtained from the *trans* cyclopentanediol. Furthermore Criegee and Plate[4] have reported that both the *cis* and *trans* diphenylacenaphthenediols readily rearrange to the ketone in the presence of an acid catalyst. These results raise the question as to how generally applicable is the Walden inversion mechanism of pinacolic rearrangement and suggest further investigations on the behavior of a variety of cyclic glycols.

It has been known for some time[5] that both *cis* and *trans* indene glycols upon boiling with dilute acid yield 2-indanone. A clue to the mechanism whereby *trans* indene glycol rearranges was found in the observation of Hermans[6] that the *cis* and *trans* glycols are interconvertible in dilute acid solution. This suggested that the *trans* glycol did not go directly to the ketone but was first isomerized to the *cis* compound which in turn underwent rearrangement. The adequacy of this mechanism has been verified by studying the kinetics of ketone formation from the two glycols in acid solution. By plotting the rates of ketone formation for the two glycols (Figs. 1, 2) it at once became evident that the *trans* glycol yielded little or no ketone and that interconversion of the glycols was rapid compared with the rate of ketone formation. Reaction mixtures containing initially either glycol soon reached a steady state where the rates of ketone formation were the same. Both glycols were isolated from a typical reaction mixture when the starting material was the *trans* isomer, confirming the data on reaction rates.

The theoretical relationship between the concentrations of the two glycols and the ketone may be derived readily, assuming all reactions are first order where the hydrogen ion activity is constant.

$$\textit{trans}\text{ glycol} \underset{k_2}{\overset{k_1}{\rightleftarrows}} \textit{cis}\text{ glycol} \xrightarrow{k'} \text{ketone}$$

Let x, z and y be the concentrations of *cis* and *trans* glycols and ketone, respectively; the sum of these is the constant a. Then

$$\mathrm{d}x/\mathrm{d}t = k_1z - k_2x - k'x$$
$$\mathrm{d}y/\mathrm{d}t = k'x$$
$$\frac{\mathrm{d}^2y}{\mathrm{d}t^2} - k'\frac{\mathrm{d}x}{\mathrm{d}t} = 0 \text{ and}$$
$$\mathrm{d}z/\mathrm{d}t = k_2x - k_1z$$

Solving for y

$$\frac{\mathrm{d}^2y}{\mathrm{d}t^2} + (k_1 + k_2 + k')\frac{\mathrm{d}y}{\mathrm{d}t} + k'k_1y = k'k_1a \text{ or}$$
$$y = c_1e^{rt} + c_2e^{st} + a \tag{1}$$[7]

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[1] Bartlett and Pöckel, THIS JOURNAL, **59**, 820 (1937); Bartlett and Bavley, *ibid.*, **60**, 2416 (1938).

[2] Nametkin and Delektorsky, *Ber.*, **57**, 583 (1924).

[3] Meerwein, *Ann.*, **542**, 123 (1939).

[4] Criegee and Plate, *Ber.*, **72B**, 178 (1939).

[5] Böeseken and van Loon, *Proc. Acad. Sci. Amsterdam*, **20**, 1186 (1918).

[6] Hermans, *Z. physik. Chem.*, **113**, 337 (1924).

[7] An expression similar to (1) was developed by Esson [*Phil. Trans.*, **156**, 220 (1866)] to account for the rate of oxidation of oxalic acid by permanganate. In this, however, it was assumed that a substance was converted into a final product by two paths; one of these was a one-step and the other a two-step process. None of the three changes was considered to be reversible. Esson's mechanism for the oxalic acid oxidation is therefore not closely related chemically to the indene glycol behavior although the same type of exponential equation describes both phenomena.

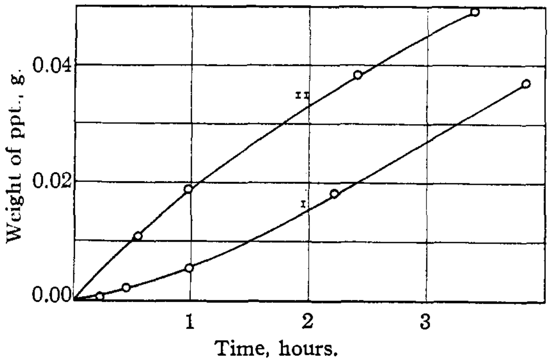

Fig. 1.—Conversion of indene glycols to 2-indanone (as dinitrophenylhydrazone) in 0.98 *N* H_2SO_4: I, ketone from *trans*-glycol; II, ketone from *cis*-glycol.

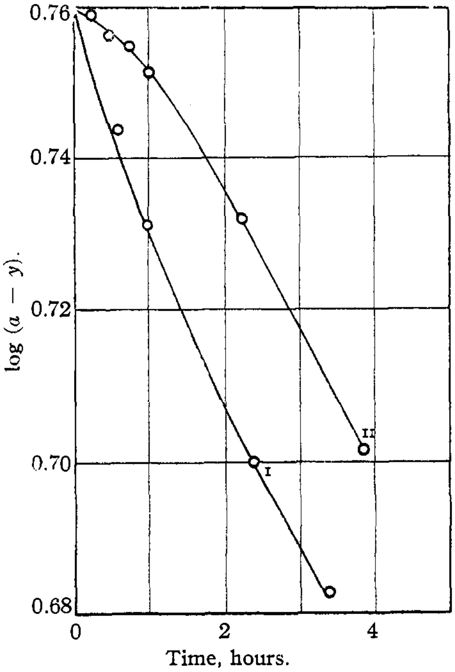

Fig. 2.—Ketone formation from *cis*-(I) and *trans*-(II) indene glycols in 0.98 *N* H_2SO_4.

If the initial value of x is b, then

$$c_1 = \frac{k'b + as}{r - s} \text{ and } c_2 = \frac{k'b + ar}{s - r}$$

where

$$r = \frac{-(k_1 + k_2 + k') - \sqrt{(k_1 + k_2 + k')^2 - 4k_1k'}}{2}$$

$$s = \frac{-(k_1 + k_2 + k') + \sqrt{(k_1 + k_2 + k')^2 - 4k_1k'}}{2}$$

The values of x and z may be expressed by similar equations. For the special case where the starting material is the *trans* glycol, $b = 0$ and $c_1 = as/(r - s)$, $c_2 = ar/(s - r)$. Where the starting material is the *cis* glycol, $b = a$ and

$$c_1 = \frac{a(k' + s)}{r - s} \text{ and } c_2 = \frac{a(k' + r)}{s - r}$$

Equation (1) may be somewhat simplified when the *trans* glycol is the initial material

$$a - y = \frac{ar}{r - s}e^{st} - \frac{as}{r - s}e^{rt}$$

$$\frac{a - y}{a} = \frac{r}{r - s}e^{st}\left[1 - \frac{s}{r}e^{(r - s)t}\right] \text{ or}$$

$$\ln\frac{a - y}{a} = \ln\frac{r}{r - s} + st + \ln\left[1 - \frac{s}{r}e^{(r - s)t}\right] \qquad (2)$$

It was obvious from inspection of the data on ketone formation that k_1 and k_2 did not differ greatly in value while k' was perhaps one-tenth as large as these. Under these circumstances the last term of equation (2) becomes negligible for values of t greater than two hours and hence r and s were determinable from data on the rate of formation of 2-indanone from the *trans* glycol The value of k' was found by determining the initial rate of ketone formation from the pure *cis* glycol. Knowing the values of r, s and k' it was possible to evaluate k_1 and k_2. From a typical experiment in 0.98 *N* sulfuric acid at 86° $s = -0.044$, $r = -1.29$, $k_1 = 0.69$, $k_2 = 0.55$ and $k' = 0.081$. Here time is expressed in hours and $\log_e$ has been used. The curves of equation (1) using the above constants agree satisfactorily with the observed data. The agreement is just as good when the *cis* glycol is the starting material as for the *trans* isomer. This strongly supports the hypothesis that the *trans* glycol is first isomerized to the *cis* compound which then undergoes rearrangement. There is as yet no evidence to indicate at which carbon atom inversion occurs in the interconversion of the glycols but it is probable that only the carbon adjacent to the benzene ring is involved. An analogous inversion occurs in the action of acid upon *l*-ephedrine.[8]

In earlier experiments it had been observed[9] that the rate constant for the decomposition of *cis* indene chlorohydrin to 1-indanone slowly decreased with time. There was then no satisfactory explanation for this. Likewise it had been found that *trans* indene bromohydrin[10] and chlorohydrin[9] were converted into 1-indanone when heated in acid solution. These observations suggested that the *cis* and *trans* halohydrins are, like the glycols, interconvertible in acid solution and that ketone formation from the *trans* isomer is preceded by isomerization.

The solubility of the halohydrins in water is

[8] Emde, *Helv. Chim. Acta*, **12**, 365 (1929); Emde and Spaenhauer, *ibid.*, **13**, 3 (1930).

[9] Suter and Lutz, This Journal, **60**, 1360 (1938).

[10] Porter and Suter, *ibid.*, **57**, 2023 (1935).

somewhat low for satisfactory reaction rate measurements; for *trans* indene bromohydrin this is 0.43 g./100 ml. of solution at 86°. In one preliminary experiment, a 0.172 *N* solution of sulfuric acid, maintained at 86°, was kept saturated with the indene bromohydrin by stirring with excess of the solid. At suitable intervals samples of the solution were withdrawn and the extent of ketone formation determined. The rate of ketone formation increased over a period of several hours and the increase was much greater than could be accounted for by the effect of the increased acid concentration (due to the accumulation of hydrogen bromide in the solution) on the bromohydrin. In subsequent similar experiments the same general trend was shown but the results were somewhat erratic. Thereafter the behavior of the halohydrins was studied without having any excess solid present and most of the reactions were run in 20% (by volume) dioxane.

A comparison of the rates of formation of hydrogen bromide and ketone from the bromohydrin under various conditions gave interesting results. In initially neutral aqueous solution at 86° after 1080 minutes, 50% of the bromine was precipitated by silver nitrate while the ketone formed amounted to only 6% of this. When the solution was 0.1 *N* in sulfuric acid at the start the ketone formation rose to 44% of the ionic bromine produced and 58% of the bromine had been hydrolyzed. In further experiments in 20% dioxane the rate of bromide ion formation was found to be approximately one-half that for aqueous solutions. Starting in a neutral solution, the rate of bromide ion formation corresponded to a first order reaction with $k_{Br^-} = 1.4 \times 10^{-4}$. In a solvent made from dioxane (20%) and 0.128 *N* sulfuric acid the average rate of bromide ion formation increased to $k_{Br^-} = 2.0 \times 10^{-4}$, but the "constant" increased with time and a strong odor of 2-indanone was observed. Analysis for the ketone in another run showed that its rate of formation also increased with time, the first order k_k changing from 1.27×10^{-5} at 1254 minutes to 1.75×10^{-5} at 3872 minutes. The formation of ketone thus occurs less than one-tenth as rapidly as bromide ion. The difference in k_{Br^-} and k_k here was much greater than for aqueous solutions. In strongly acid solutions the rate of bromide ion formation increased but not in proportion to the acidity. The increase in k_{Br^-} with time still occurred. In a solvent made from dioxane and 1.14 *N* sulfuric acid $k_{Br^-} = 4.4 \times 10^{-4}$ and for a similar solvent made from 4.48 *N* acid it increased to 6.56×10^{-4}. In these solutions the rate of ketone formation approached that of the bromide ion and became more closely first order with respect to the bromohydrin. For the solution made from the 4.48 *N* acid $k_k = 5.5 \pm 0.2 \times 10^{-4}$. Under such conditions the ketone is chiefly 1-indanone.

A number of experiments were carried out with *cis* and *trans* indene chlorohydrins in which the rate of chloride ion formation was determined. These are summarized in Fig. 3. The rate has its lowest value with the *trans* isomer in neutral solution and the highest value with the *cis* isomer under the same conditions. With increasing acid concentration the rates for the two isomers approach each other until in the solutions made from dioxane and 4.48 *N* sulfuric acid they are nearly identical.

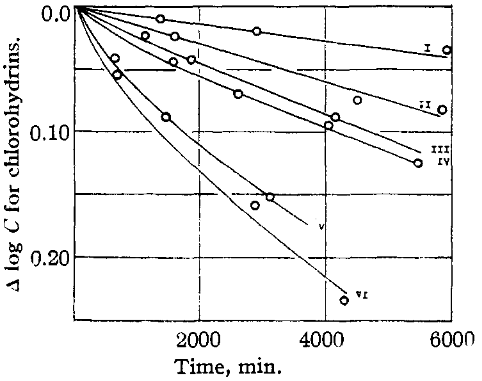

Fig. 3.—Rates of chloride ion formation in 20% dioxane: I, *trans* isomer, neutral solution; II, *trans* isomer, 0.100 *N* H_2SO_4; III, *trans* isomer, 3.78 *N* H_2SO_4; IV, *cis* isomer, 3.78 *N* H_2SO_4; V, *cis* isomer, 0.100 *N* H_2SO_4; VI, *cis* isomer, neutral solution.

It is evident from these results that the behavior of the indene halohydrins on hydrolysis is complex. The results obtained are qualitatively explained by assuming that the *trans* compounds hydrolyze to either *cis* or *trans* indene glycol. The glycols are in equilibrium as already observed and the *cis* glycol is responsible for the 2-indanone appearing in slightly acidic solutions. Occurring simultaneously with this set of reactions is the interconversion of the *cis* and *trans* halohydrins; the *cis* chlorohydrin decomposes directly to 1-indanone as shown in earlier work.[9] The *cis* bromohydrin has not become available for investigation but it has been observed that the filtrate from the reaction mixture in which the *trans* isomer is prepared by the action of hypobromous acid on indene gives a strong test for 1-indanone. Apparently the small per cent. of the *cis* bromohydrin produced is lost rapidly by ketone formation.

Experimental

Preparation of Materials.—A particularly convenient method of preparing indene bromohydrin[10,11] involves the use of an emulsifying agent. In a 5-liter 3-necked flask fitted with an efficient stirrer and a dropping funnel was placed 2 liters of water, 30 g. of "Dreft" and 116 g. of indene. After the indene was completely emulsified with the temperature of the mixture at 70°, a saturated solution of bromine in aqueous sodium bromide was added in the usual manner until a slight yellow color persisted. The stirrer was stopped and the solid indene bromohydrin settled out. After decanting the supernatant liquid the residue was filtered by suction which gave 204 g. (94%) of colorless product, m. p. 126–127°. The oily impurities were retained in the liquid.

In the preparation of *trans* indene glycol from the bromohydrin[10] a small amount of the *cis* glycol also was recovered. Pure *cis* glycol was prepared by permanganate oxidation of indene according to the procedure of Hermans.[6] The *cis* and *trans* indene chlorohydrins had been prepared earlier.[9]

Rate Determinations on Indene Glycols.—A weighed sample (0.7 to 0.9 g.) of the indene glycol was dissolved in 128.6 ml. of the standard acid in a reaction vessel surrounded by the vapor of boiling trichloroethylene (86 ± 0.2°). About one minute was required to dissolve the glycol. At suitable intervals samples of the solution were pipetted into 40 ml. of 0.4% 2,4-dinitrophenylhydrazine reagent,[12] heated on the steam-bath for five minutes and filtered through a Gooch crucible. The precipitate was washed with 15 ml. of cold water and dried in a vacuum oven at 50–60° (25 mm.). The results of typical experiments are shown in Figs. 1 and 2.

The 2,4-dinitrophenylhydrazone of 2-indanone is insoluble in water and even in absolute alcohol the solubility is very slight. Difficulty was encountered in drying the precipitate as it decomposes readily when heated above 100°. Even at 50° and 25 mm. an occasional sample would show darkening. By employing known amounts of 2-indanone it was shown that the darkening was accompanied by approximately a 5% increase in weight above the theoretical value, indicating air oxidation. Another source of error in the determination of ketone was due to the precipitation being carried out in hot acid solution where conversion of glycol to ketone would continue. However, by making each precipitation in exactly the same manner consistent results were obtained.

Ketone Formation from Indene Bromohydrin.—A typical experiment in aqueous dioxane solution will be described. A mixture of 25 ml. of pure dioxane and 100 ml. of 0.128 *N* sulfuric acid was heated to 86° in the vapor of refluxing trichloroethylene. In this was dissolved 1.7516 g. of *trans* indene bromohydrin. At convenient intervals 25 ml. samples were withdrawn and titrated for bromide ion with 0.1 *N* silver nitrate. The results are given in Table I.

TABLE I

HYDROLYSIS OF INDENE BROMOHYDRIN

Time, min.	0.1 *N* $AgNO_3$, ml.	$k \times 10^4$ ($\log_{10}$)
286	1.46	1.53
1296	6.84	2.06
1548	8.24	2.16
1949	9.61	2.20

The values of *k* are about 2% low since the expansion of the solution on heating has not been allowed for. A similar run using 2.1813 g. of bromohydrin in which the ketone formed was precipitated with dinitrophenylhydrazine is summarized in Table II. The dinitrophenylhydrazone melted at 200° while pure 2-indanone dinitrophenylhydrazone melts at 202°.

TABLE II

KETONE FORMATION FROM INDENE BROMOHYDRIN

Time, min.	Wt. ppt., mg.	$k \times 10^5$ ($\log_{10}$)
1254	18.7	1.27
1772	32.3	1.67
2732	79.1	2.33[a]
3872	83.6	1.75

[a] This sample darkened on heating and hence probably increased in weight during drying.

cis **Indene Chlorohydrin from the** ***trans*** **Isomer.**—One gram of *cis* indene chlorohydrin (m. p. 110–111°) was dissolved in a mixture of 25 ml. of dioxane and 100 ml. of 4.48 *N* sulfuric acid and heated at 86° for twelve hours. The solution was cooled and filtered and the solid crystallized from benzene. The first fraction melted at 109° and the second at 118°. This last fraction after another benzene treatment gave 0.25 g. of crystals, m. p. 124°. *trans* Indene chlorohydrin melts at 124°.

Hydrolysis of ***cis*** **and** ***trans*** **Indene Chlorohydrins.**—A weighed quantity of the *cis* or *trans* chlorohydrin was added to a solvent heated to 86° that had been made by mixing 25 ml. of dioxane with 100 ml. of distilled water or standard sulfuric acid. At suitable intervals, 25-ml. samples of solution were withdrawn and titrated with 0.1 *N* silver nitrate. The results are shown in Fig. 3, where $\Delta \log c$ is plotted against the time in minutes, *c* being the concentration of chlorohydrin.

Summary

Rate determinations on the conversion of *cis* and *trans* indene glycols to 2-indanone in aqueous solutions support the hypothesis that ketone formation occurs only through the *cis* glycol, the *trans* glycol undergoing isomerization before the ketone is formed. Furthermore, the *cis* glycol was isolated from a typical reaction mixture where the *trans* isomer was the starting material.

The conversion of the *trans* indene halohydrins in acid solutions to 1-indanone probably occurs through a similar isomerization, although here

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(11) Pope and Read, *J. Chem. Soc.*, **99**, 2071 (1911); **101**, 760 (1912).

(12) Shriner and Fuson, "Identification of Organic Compounds," John Wiley and Sons, New York, N. Y., 1935, p. 38.

the simultaneous formation of an indene glycol and consequently some 2-indanone makes a quantitative interpretation of the results difficult.

EVANSTON, ILLINOIS RECEIVED SEPTEMBER 28, 1940

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY AND PHYSICS OF THE PENNSYLVANIA STATE COLLEGE]

The Preparation and Properties of Certain Trifluoromethyl Compounds[1]

BY J. H. SIMONS, R. L. BOND AND R. E. MCARTHUR

Although compounds containing the trifluoromethyl radical are of considerable interest and have important uses, the number of them that are known is relatively small. Only a few methods of synthesis are available, and these are usually specific in nature, so that any one of them is capable of use in producing only a limited number of compounds. Many of the trifluoromethyl compounds that have been reported are prepared from benzotrifluoride. This is produced from benzotrichloride by either the Swarts[1a] reaction or by the action of hydrogen fluoride.[2] As the trifluoromethyl group is both stable and unreactive, many aromatic derivatives of benzotrifluoride can be and have been made. By the oxidation of one of these, aminobenzotrifluoride, Swarts[3] obtained trifluoroacetic acid. With this acid as the starting material and the use of known methods of organic chemistry, he prepared a considerable number of other compounds that can be considered as derivatives of trifluoroacetic acid, such as the amide, cyanide, esters, etc. By electrolysis[4] of the acid in aqueous solution he obtained hexafluoroethane.

Other methods for preparing trifluoromethyl compounds are: the reaction of fluorine with carbon,[5] the reaction of fluorine with hydrocarbons or halogen derivatives of hydrocarbons,[6] the action of a carbon arc on carbon tetrafluoride or difluorodichloromethane,[7] and the reaction of mercurous or mercuric fluoride with polyhalogen derivatives of methane.[8] A patent disclosure[9] indicates the possible formation of trifluorochloromethane from the reaction of antimony fluoride with carbon tetrachloride. The Swarts reaction has been used to produce a few other trifluoromethyl compounds such as trifluorodimethyl ether.[10]

It was the purpose of this investigation to search for other methods of synthesis. A new one was found for the preparation of trifluorochloromethane. It was hoped that this compound would operate in the Grignard synthesis or one of its variations. Many such reactions were studied. Attempts were made to prepare trifluorobromo- and trifluoroiodomethane. New syntheses were found for the preparation of fluoroform. Studies were made of the reaction of fluorine with carbon tetrachloride and difluorodichloromethane, several reactions of iodine pentafluoride were performed, reactions in a carbon arc were studied, and the thermal decomposition of barium trifluoroacetate was investigated.

Experimental

Apparatus.—Parts of the apparatus used in this work have been described previously. These are the fluorine generator,[11] the low temperature distilling column,[12] the vapor density balance[13] and the magnetic stirrer reaction vessel.[14] Other special equipment was constructed for this work and some of it will be described in connection with its use.

The Reaction of Fluorine and Carbon Tetrachloride.—A reaction vessel made of copper was used. This carried a reflux condenser, from the top of which the gaseous products were obtained. The shaft of a mechanical stirrer extended through the reflux condenser and rotated in a lead bearing so designed that it could be tightened like a packing gland. The fluorine gas entered through a tube, the outlet of which was below the level of the liquid. An additional inlet tube was provided to supply carbon tetrachloride. The open end of this tube was above that of the fluorine tube so that it served as an indicator for the level of the liquid, and more liquid could be supplied before the

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[1] Portions of the material contained herein were included in a paper presented in the Symposium on Fluorine Chemistry at the meeting of the American Chemical Society in Detroit, Sept. 11, 1940.

[1a] Swarts, *Bull. sci. acad. roy. Belg.*, **35**, 375 (1898).

[2] Simons and Lewis, THIS JOURNAL, **60**, 492 (1938).

[3] Swarts, *Bull. sci. acad. roy. Belg.*, **8**, 343 (1922).

[4] Swarts, *ibid.*, **17**, 27 (1931).

[5] (a) Ruff and Keim, *Z. anorg. allgem. Chem.*, **192**, 249 (1930); (b) Simons and Block, THIS JOURNAL, **61**, 2962 (1939).

[6] (a) Fredenhagen and Cadenbach, *Ber.*, **67**, 928 (1934); (b) Calfee and Bigelow, THIS JOURNAL, **59**, 2072 (1937); (c) Calfee, Fukuhara and Bigelow, *ibid.*, **61**, 3552 (1939).

[7] (a) Ruff and Bretschneider, *Z. anorg. allgem. Chem.*, **210**, 173 (1933); (b) Thornton, Burg and Schlesinger, THIS JOURNAL, **55**, 3177 (1933).

[8] (a) Ruff, Bretschneider, Luchsinger and Miltschitzky, *Ber.*, **69**, 299 (1936); (b) Henne, THIS JOURNAL, **59**, 1200 (1937).

[9] Kinetics Chemicals, Inc., Brit. Pat. 391,168 (April 13, 1933).

[10] Booth and Burchfield, THIS JOURNAL, **57**, 2070 (1935).

[11] Simons, "Inorganic Syntheses," Vol. I, McGraw-Hill Book Company, Inc., New York, N. Y., 1939, p. 142.

[12] Simons, *Ind. Eng. Chem., Anal. Ed.*, **10**, 29 (1938).

[13] Simons, *ibid.*, **10**, 587 (1938).

[14] Simons, *ibid.*, **10**, 638 (1938).