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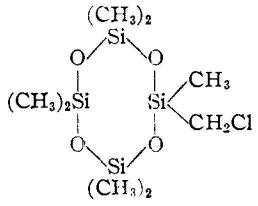
The Hydrolytic Cleavage of Methyl and Chloromethyl Siloxanes

BY R. H. KRIEBLE AND J. R. ELLIOTT

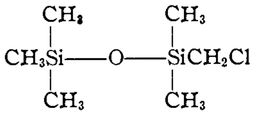
The hydrolytic cleavage of chloromethyl siloxanes by the action of alkali solutions to form chloromethanes has been described recently[1] in connection with the proof of structure of certain isomeric chloromethyl chlorosilanes. Methyl siloxanes have now been found to undergo Si–C cleavage under drastic treatment with alkali solutions to form methane. The nature of the siloxane products obtained in the cleavage of chloromethyl groups and the restrictions imposed by the cleavage on metathetical reactions involving chloromethyl siloxanes and alkaline agents are also reported.

For the study of the unsubstituted methyl cleavage three methyl siloxanes differing in the number of oxygens attached to the silicon were selected, namely, hexamethyldisiloxane $[(CH_3)_3Si]_2O$, a dimethyl silicone polymer $[(CH_3)_2SiO]_n$, and a monomethyl silicone polymer $[CH_3SiO_{3/2}]_n$. Monomethyl silicones are completely soluble in dilute aqueous sodium hydroxide solution, dimethyl silicone less readily and to a limited extent, and hexamethyldisiloxane practically not at all. At 100° in aqueous sodium hydroxide solution none of the methyl siloxanes undergo hydrolytic cleavage at an appreciable rate. In a rocking autoclave at 200°, however, all undergo cleavage with the formation of sodium silicate and methane. While the rate of cleavage of methyl siloxanes decreases with decreasing number of oxygens attached to silicon, the difference may not be significant owing to their marked differences in solubility.

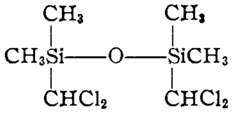
For the study of chloromethyl cleavage, heptamethylchloromethylcyclotetrasiloxane (I), pentamethylchloromethyldisiloxane (II) and tetramethyl-1,3-bis-dichloromethyldisiloxane (III) were selected as representative materials.



I



II



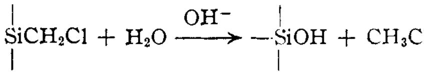
III

I was prepared in good yield by the chlorination of octamethylcyclotetrasiloxane[2] in the presence of ultraviolet light. Direct chlorination of hexamethyl disiloxane to yield II resulted in the formation of an aqueous phase indicating the reversal of the hydrolysis reaction of trimethylchlorosilane by the by-product hydrochloric acid.

$$2(CH_3)_3SiCl + H_2O \rightleftarrows [(CH_3)_3Si]_2O + HCl$$

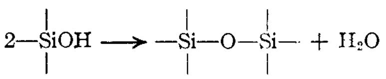
II was therefore prepared by the cohydrolysis of dimethylchloromethylchlorosilane and trimethylchlorosilane.[1] III was prepared by the hydrolysis of dimethyldichloromethylchlorosilane.[1] The isolation of a considerable yield of the intermediate silanol indicates a stabilizing influence of the substituent chlorine atoms on this compound.

No detectable hydrolysis occurred when I was refluxed with water or aqueous dioxane (single phase). With a hot solution of potassium hydroxide in *n*-butanol, however, methyl chloride and an infusible, insoluble polymer were produced. It was anticipated that the fission of methyl chloride would occur with the simultaneous formation of a silanol.



$$\overset{|}{\underset{|}{\text{Si}}}CH_2Cl + H_2O \xrightarrow{OH^-} -\overset{|}{\underset{|}{\text{Si}}}OH + CH_3Cl$$

The silanols so formed could condense to yield siloxane linkages.



$$2{-}\overset{|}{\underset{|}{\text{Si}}}OH \longrightarrow -\overset{|}{\underset{|}{\text{Si}}}-O-\overset{|}{\underset{|}{\text{Si}}}- + H_2O$$

If these reactions proceeded with the exclusion of all others, I would thus yield bis-(heptamethylcyclotetrasiloxanyl) oxide. The gel actually obtained was apparently a cross-linked polymer formed by rearrangement of siloxane linkages in the system under the reaction conditions. The cleavage of the chloromethyl group of I yields a silicon bearing three oxygens. Such silicones are potential points for cross-linking if the siloxane ring is opened.

Hydrolysis of II with aqueous alkali also yielded methyl chloride. If no rearrangement of siloxane linkages occurred under the reaction conditions, decamethyltetrasiloxane would be the product after condensation of the silanols first formed.

$$(CH_3)_3SiOSi(CH_3)_2CH_2Cl + H_2O \xrightarrow{NaOH} [(CH_3)_3SiOSi(CH_3)_2]_2O + 2CH_3Cl$$

Hexamethyldisiloxane, octamethyltrisiloxane and dodecamethylpentasiloxane were isolated from the product in addition to the expected decamethyltetrasiloxane. Such products can only be explained on the basis of rearrangement of siloxane linkages.

Compound III evolved methylene chloride on treatment with alcoholic potassium hydroxide at reduced pressure. No attempt was made to isolate the siloxane products.

Silicon–carbon cleavage in chloromethylsilox-

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[1] Krieble and Elliott, THIS JOURNAL, **67**, 1810 (1945).

[2] Patnode and Wilcock, THIS JOURNAL, **68**, 358 (1946).

anes is competitive with carbon–chloride hydrolysis. Comparative hydrolyses of compounds I and III were made in a 10% potassium hydroxide solution in moist butanol. The duration of each run was fifteen minutes. The results are shown in Table I. The greater ease of cleavage of a dichloromethyl group over a chloromethyl group is evident.

Table I

Alkaline Hydrolysis of Chloromethylsiloxanes

Compound, -siloxane	Temp., °C.	Yield, chloromethane, %	Yield, chloride ion, %	Total reacted, %
Heptamethylchloromethylcyclotetra- (1)	110	42	46	88
Tetramethyl-1,3-bis (dichloromethyl)-di-	45	78	1.5	80

Fission of chloromethyl groups occurs in the presence of even such weak bases as alcoholic ammonia. Thus hexamethyldisiloxane and octamethyltrisiloxane (indicating both silicon–carbon cleavage and siloxane rearrangement) were isolated from the reaction product of II with alcoholic ammonia at room temperature. I refluxed with aqueous alcoholic sodium cyanide gave an infusible, insoluble gel.

The fission reaction therefore imposes serious limitations on replacement reactions of the chlorine in chloromethyl siloxanes by other groups through the use of alkaline reagents.

Experimental

Cleavage of Methylsiloxanes.—Three polysiloxanes containing three, two and one methyl groups per silicon, respectively, were each contacted in a 3-liter autoclave with a solution of 60 g. of sodium hydroxide in 500 g. of water. After charging the reactants the autoclave was flushed with nitrogen to remove air after which it was closed and heated rapidly. On reaching 200° shaking was started and the temperature was maintained at this value until a constant pressure was obtained. The autoclave was then allowed to cool to 30°. A sample of the residual gas was bled into a low temperature Podbielniak column for analysis and the remainder exhausted through a wet test meter. Distillational analysis of the residual gases from each of the polymers showed the presence of only methane and nitrogen. The results are summarized in Table II.

Table II

Siloxane	Moles monomeric units	Time at 200° to reach constant press., hr.	Final press., mm.	Vol. gas at S. T. P., liters	% Yield methane
$[(CH_3)_3SiO_{1/2}]_2$	0.5	8	465	25.4	76
$[(CH_3)_2SiO]_n$	0.5	5	400	17.3	77
$[(CH_3)SiO_{3/2}]_n$	1.0	2	420	20[a]	89

[a] Calculated from 120 p. s. i. residual pressure in autoclave at room temp.

Preparation of Heptamethylchloromethylcyclotetrasiloxane, I.—A 1-liter, 4-necked flask, cooled by an ice-bath was fitted with a mechanical oil-sealed stirrer, a gas inlet tube extending to the bottom of the flask, a reflux condenser leading to a hydrogen chloride scrubber containing water, and a G. E. 4-watt germicidal lamp inserted through the central neck; 741 g. (2.50 moles) of octamethylcyclotetrasiloxane (m. p. 17.0°) was placed in the flask and the system was swept with dry nitrogen for ten minutes. The lamp was started and a stream of dry chlorine was introduced. Reaction began immediately. The stream of chlorine was adjusted to maintain the temperature of the reactants at 25–40°. After forty minutes the flask was again swept with nitrogen. Titration of the hydrogen chloride scrubber showed the presence of 0.74 mole of hydrochloric acid; the gain in weight of the reaction products was 26 g., equivalent to 0.75 g. atom of chlorine. The product was washed twice with water, clarified with fuller's earth and distilled at reduced pressure. After removing unchanged starting material, 167 g. (0.51 mole) of heptamethylchloromethylcyclotetrasiloxane, I, b. p. 127° (50 mm.), b. p. 214° (760 mm.), m. p. −1°, $n^{20}D$ 1.4158, d^{20}_4 1.0444 was collected.

Anal. Calcd. for $C_8H_{23}ClO_4Si_4$: Cl, 10.7; $R^{20}D$,[3] 79.54. Found: Cl, 10.2; $R^{20}D$, 79.47.

Chlorination of Hexamethyldisiloxane.—Three moles (486 g.) of hexamethyldisiloxane was placed in the apparatus described above. After sweeping with nitrogen a relatively slow stream of chlorine was passed into the reactants for four hours. A heavy, water miscible, second phase weighing 39 g. and containing 0.42 equivalent of acid had formed. This corresponds approximately to a saturated solution of hydrochloric acid (23°). By difference the lower phase contained 23.4 g. (1.3 moles) of water. By titration with aqueous alkali the upper phase was found to contain 2.5 equivalents of chlorine attached to silicon. In order to check the reversibility of the hydrolysis reaction of chlorosilanes, anhydrous hydrogen chloride was bubbled through hexamethyldisiloxane. Within a few minutes an aqueous hydrochloric acid phase separated.

Preparation of Dimethyldichloromethylsilanol and Tetramethyl - 1,3 - bis - dichloromethyldisiloxane.—Fifty grams of dimethyldichloromethylchlorosilane was hydrolyzed by pouring into a slurry of excess ice in several volumes of ether. The final temperature was below 0°. The organic phase was separated immediately, washed four times with water and distilled in a fractionating column of 20 theoretical plates. After removing the ether the pressure was reduced to 40 mm. and 20 cc. of distillate was obtained at 89°. This distillate turned cloudy on standing at room temperature for thirty minutes and a substantial aqueous phase separated. It was redistilled and by immediate analysis for chlorine by sodium peroxide fusion was shown to be dimethyldichloromethylsilanol.

Anal. Calcd. for $C_3H_8OCl_2Si$: Cl, 44.6. Found: Cl, 44.7.

Another fraction, containing most of the remainder of the product, was collected in the range 149–150° (40 mm.). This material was identified as tetramethyl-1,3-bis-dichloromethyldisiloxane, $n^{20}D$ 1.4660, d^{20}_4 1.2213.

Anal. Calcd. for $C_6H_{14}OCl_4Si_2$: Cl, 47.3; $R^{20}D$, 68.3.[3] Found: Cl, 46.8; $R^{20}D$, 68.0.

Hydrolysis of Heptamethylchloromethylcyclotetrasiloxane (I).—A 1-cc. portion of I was refluxed with 5 cc. of water for four hours and another with 5 cc. of water plus 15 cc. of neutral dioxane for four hours (single phase). In each case the product was neutral to methyl orange attesting to the lack of hydrolysis of the chlorine.

A solution of 1.32 cc. (0.0042 mole) of I, 5.0 cc. of a 10% solution of potassium hydroxide in *n*-butanol, and 0.2 cc. of water was placed in a small fractionating column, the pressure equalizer line of which was connected to a small trap of about 2-cc. volume immersed in liquid air. After fifteen minutes of refluxing the trap was connected to a mercury filled gas buret. After deaerating the sample the liquid air-bath was removed and the material allowed to vaporize into the buret. Forty-four cc. of gas at 23° and 753 mm. (0.0018 mole) was obtained. The gas was completely condensed in a 2-cc. bulb immersed in a melting slush of carbon tetrachloride (−22°) at 950 mm. pressure and completely volatilized therefrom at 670 mm., confirming that the gas was methyl chloride. The potassium chloride precipitated in the reaction mixture was dissolved

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[3] Sauer, This Journal, 68, 954 (1946).

by adding water and shaking. After removing the organic phase the aqueous phase was found to contain 0.00192 equivalent of chloride ion by Volhard titration. Thus the cleavage reaction proceeded to the extent of 42% and the competitive carbon–chlorine hydrolysis, 46%. The organic phase, containing suspended gel particles, was left in an oven at 100° for four hours to remove volatile solvent. The residue was an infusible gel, insoluble in ether and benzene.

Treatment of Heptamethylchloromethylcyclotetrasiloxane (I) with Sodium Cyanide.—A solution of 16.5 g. (0.050 mole) of I, 3.0 g. (0.060 mole) of sodium cyanide, 6.0 cc. of water and 25.0 cc. of 95% ethanol was boiled under reflux. In about forty-five minutes gel began to form in the flask. After four hours the aqueous phase was decanted and the gel boiled with water to extract salt. The formation of a gel could occur only as a result of silicon-carbon cleavage accompanied by siloxane rearrangement to yield a cross-linked polymer. The aqueous phase and the wash water were combined and acidified with acetic acid. Cyanide ions were removed by adding excess nickelous nitrate and filtering. Titration with 0.1 *N* silver nitrate showed the presence of 0.0133 equivalent of chloride ion.

Hydrolysis of Pentamethylchloromethyldisiloxane (II).—A mixture of 98 g. (0.50 mole) of II, 34 g. (0.60 mole) of potassium hydroxide, 200 cc. of 95% ethanol, and 25 cc. of water was refluxed for six and one-half hours. Some potassium chloride precipitated, indicating that not all the chlorine escaped as methyl chloride. After washing with water, the product (54.5 g.) was distilled in a small fractionating column. Four major fractions were obtained: (A) 7 g. hexamethyldisiloxane, b. p. 99.6°, $n^{20}_{\rm D}$ 1.3771; (B) 13 g. octamethyltrisiloxane,[2] b. p. 152°, $n^{20}_{\rm D}$ 1.3858, D^{20}_4 0.8213; (C) 7 g. decamethyltetrasiloxane,[2] b. p. 192°, $n^{20}_{\rm D}$ 1.3901; and (D) 3.5 g. dodecamethylpentasiloxane,[2] b. p. 227°, $n^{20}_{\rm D}$ 1.3932.

Anal. Calcd. for (B), $C_8H_{24}O_2Si_3$: C, 40.63; H, 10.23; Si, 35.61. Found: C, 40.83; H, 10.57, 10.13; Si, 35.52, 35.68. Calcd. for (C), $C_{10}H_{30}O_3Si_4$: C, 38.67; H, 9.74. Found: C, 39.14, 39.10; H, 9.94, 9.78. Calcd. for (D). $C_{12}H_{36}O_4Si_5$: C, 37.46; H, 9.43. Found: C, 37.33, 38.11; H, 9.43, 9.59.

Ammonolysis of Pentamethylchloromethyldisiloxane (II).—A mixture of 50 g. of II, 200 g. absolute ethanol and 48 g. of anhydrous ammonia was allowed to stand in the dark at room temperature for one month, after which the product was decanted from the copious precipitate of ammonium chloride and poured into a large amount of water. The oil phase was collected and fractionally distilled in a small column. The first fraction boiled *ca.* 100° and after redistillation gave 2 g. of hexamethyldisiloxane, b. p. 100.5°, $n^{20}_{\rm D}$ 1.3782. Another constant boiling distillate was collected at 145°, $n^{20}_{\rm D}$ 1.3845. This material was found to be octamethyltrisiloxane.

Anal. Calcd. for $C_8H_{24}O_2Si_3$: C, 40.63; H, 10.23. Found: C, 41.01, 40.51; H, 10.17, 10.21.

The remaining material had an ammoniacal odor and fractional distillation yielded no pure compounds. The complex nature of the products is understandable in view of the silicon–carbon cleavage and siloxane rearrangement which has evidently occurred.

Hydrolysis of Tetramethyl-1,3-bis-dichloromethyldisiloxane, III.—Six grams (0.020 mole) of III was added carefully to 50 cc. of a 10% solution of potassium hydroxide in *n*-butanol and 2 cc. of water at 0° contained in the pot of a small fractionating column, the pressure equalizer line of which was connected to a vacuum system through a small trap cooled with Dry Ice–acetone. The pressure was reduced to 25 mm. On mixing the pot contents an exothermic reaction occurred and spontaneous boiling began immediately. After heating under reflux (45°) for fifteen minutes the reaction product was poured into an excess of water and analyzed for chloride ion as described for I. Only 0.00058 equivalent was formed. The trap contents were transferred to a Podbielniak column and distilled at reduced pressure. The yield of methylene chloride, b. p. 195 mm. 6.5°, was 0.311 mole. Thus the cleavage reaction proceeded to 78% of the theoretical and the competitive carbon–chlorine hydrolysis, 1.5%.

Discussion

The cleavage reaction in the methyl and chloromethyl siloxanes is in many respects formally analogous to the cleavage step in the haloform reaction. The cleaving system may be represented in a general way by $X_3C\text{-}AY_3$ in which A is the atom which acquires the hydroxyl and may be either carbon or silicon. C-A cleavage, when A is carbon, usually occurs only when all three X positions are occupied by halogen or similar electronegative groups, and at least two of the valences to Y's are occupied by oxygen.[4] The cleavage reaction is always in competition with hydrolysis of the C–X bond. With a lesser degree of halogen substitution on the X-bearing carbon, this hydrolysis predominates. When A is silicon, however, cleavage competes successfully with hydrolysis even when only one of the X's is halogen and when only one of the Y's is oxygen. Furthermore, it proceeds readily under moderate conditions of alkalinity and temperature. A trend toward greater ease of cleavage with increasing chlorine substitution in the X positions is evident. The difference between carbon and silicon in the cleavage reaction appears to be a matter of rate rather than free energy change since, for example, according to the data of Parks and Huffman,[5] even the cleavage of acetone to acetic acid and methane is favored by a free energy change of about 10 kcal.

It is reasonable to assume that the reaction in each case is of the nucleophilic type, hydroxyl ion substituting at a positive center for the group which most readily dissociates from the center as a negative ion. This ion immediately acquires a proton from water to give a molecule and a new hydroxyl ion. Placing electronegative substituents in the Y positions increases the positive charge on A and renders it more susceptible to nucleophilic attack. Electronegative substituents at X on the other hand should increase the positive charge on C much more than on A. Since in the cleavage reaction hydroxyl reacts at A in preference to C, the explanation of the effect of substituents at C must now be looked for in their influence in determining the extent to which the X_3C group will dissociate from A in relation to the extent to which the Y groups will dissociate when A is attacked by hydroxyl ion.

An explanation for the increase in reactivity when carbon is replaced by silicon may be sought in the fact that silicon is markedly less electronegative than carbon.[6] Therefore, when a carbon atom at A is replaced by a silicon atom, A becomes a more positive center and hence is more suscep-

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(4) Fuson and Bull, *Chem. Rev.*, **15**, 275 (1934).

(5) Parks and Huffman, "The Free Energies of Some Organic Compounds," Chemical Catalog Co., Reinhold Publ. Corp., New York, N. Y., 1932.

(6) Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1939, p. 64.

tible to attack by hydroxyl ion. The silicon system should thus attain a reactivity corresponding to the carbon analog when it has a lesser degree of electronegative substitution in the Y positions.

When A is attacked by hydroxyl, that group of the four groups attached to A (3 Y's and one CX_3) which has the strongest attraction for electrons should be the one to dissociate. In an unsubstituted methyl siloxane, therefore, the dissociating group should be siloxy in preference to methyl. However, the resulting silanols may readily recondense under the reaction conditions. Silanol formation, however, will account for the extensive rearrangement of the siloxane system which is always observed to occur simultaneously with the cleavage reaction. Placing electronegative substituents in the X positions should increase the ratio of CX_3 dissociation to Y dissociation. Since the former is irreversible, it may appear as the only observable reaction.

In chloromethylsiloxanes, the relative selectivity of the cleavage reaction over C–Cl hydrolysis may also be interpreted as a result of the polarity of the C–Si bond, hydroxyl reacting more readily with the more positive center.

The ease of cleavage of the trimethylsilylmethyl group from mercury in the Kharasch criterion of electronegativity, found by Whitmore and Sommer,[7] can be explained on this basis; silicon, in the role of an electron source, making the carbon more negative, and hence more susceptible to electrophilic attack by hydrogen chloride.

Acknowledgments.—We are indebted to Mr. L. B. Bronk for the microelementary and chloride analyses and to Dr. L. V. McCarty for the Podbielniak distillation.

Summary

1. The chlorination of octamethylcyclotetrasiloxane and hexamethyldisiloxane is described.

2. The preparation and properties of heptamethylchloromethylcyclotetrasiloxane, dimethyldichloromethylsilanol and tetramethyl-1,3-bis-dichloromethyldisiloxane are reported.

3. The hydrolytic cleavage of methyl and chloromethyl groups attached to silicon by alkaline reagents has been demonstrated.

4. The hydrolytic cleavage is accompanied by rearrangement of siloxane linkages.

5. A mechanism for the alkali catalyzed hydrolytic cleavage is proposed.

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[7] Whitmore and Sommer, THIS JOURNAL, **68**, 481 (1946).

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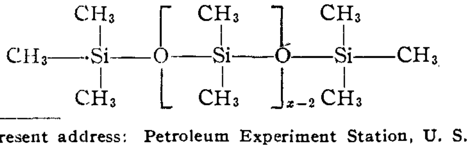
Equilibria between Linear and Cyclic Polymers in Methylpolysiloxanes

BY DONALD W. SCOTT[1]

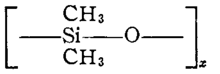
The equilibrium molecular size distributions in methylpolysiloxane systems have been studied by Wilcock.[2] He found that not only linear and branched species, but also cyclic species, were present in the "equilibrated" polymers, and that the molecular size distributions observed experimentally showed significant deviations from the theoretical distributions for systems consisting only of linear and branched species. In the present work, additional data were obtained for the molecular size distributions in equilibrium methylpolysiloxane systems containing monofunctional and difunctional units, and the theory of the molecular size distributions in these systems was extended to include cyclic as well as linear species.

The linear methylpolysiloxanes[3] have the general formula



$$CH_3-\underset{CH_3}{\overset{CH_3}{Si}}-\left[O-\underset{CH_3}{\overset{CH_3}{Si}}-\right]_{x-2}O-\underset{CH_3}{\overset{CH_3}{Si}}-CH_3$$

and the cyclic methylpolysiloxanes[3,4] have the general formula



$$\left[-\underset{CH_3}{\overset{CH_3}{Si}}-O-\right]_x$$

where x is the number of silicon atoms in the molecule. For brevity, these compounds will be designated by $MD_{x-2}M$ and D_x, respectively, M denoting the monofunctional or chain terminating unit $(CH_3)_3SiO_{1/2}$ and D denoting the difunctional unit $(CH_3)_2SiO$.[5,6]

This paper reports the molecular size distributions found for two equilibrium methylpolysiloxane mixtures, the first prepared by equilibration without any diluent, in which case mostly linear compounds were present at equilibrium, and the second prepared by equilibration in dilute solution in an inert solvent (carbon tetrachloride), in which case the equilibrium was shifted more in favor of the cyclic compounds. The experimental methods were similar to those used by Wilcock.[2] Mixtures of appropriate composition were "equilibrated" with a suitable catalyst (sulfuric acid or

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[1] Present address: Petroleum Experiment Station, U. S. Bureau of Mines, Bartlesville, Okla.

[2] Wilcock, paper presented at the 110th meeting of the American Chemical Society, Chicago, Ill., Sept., 1946.

[3] Patnode and Wilcock, THIS JOURNAL, **68**, 358 (1946).

[4] Hunter, Hyde, Warrick and Fletcher, *ibid.*, **68**, 667 (1946).

[5] Hurd, *ibid.*, **68**, 364 (1946).

[6] Wilcock, *ibid.*, **68**, 691 (1946).