denser portion of the Friedrich's condenser. Filtered compressed air was bubbled through the inlet tube A at the rate of about 3–5 drops per second. The air outlet tube B was connected by means of "Tygon" tubing to an auxiliary vertical water condenser D which prevented the loss of water vapor from the heated solution. The dithiol emulsion undergoing oxidation was kept at constant elevated temperatures by refluxing vapors which were returned by condenser E. Liquids of suitable boiling points which were used as constant temperature baths were methylene chloride, 42°; acetone, 56°; ethanol (absolute), 78.4°; isopropyl acetate, 88.5°. Filtered compressed air was bubbled through the emulsions at a rate of between three to five drops per second for seven days. At the end of this time, the polymers were isolated by pouring the latex into about 1500 ml. of rapidly stirred methanol. The precipitated polymers were extracted with chloroform from a Soxhlet extractor whereupon most of the polymers went completely into solution (except some of IIIa prepared at 80° and above). The volume of chloroform solution was reduced to about 50 ml. and an equal volume of low boiling petroleum ether (b.p. 30–60°) was added to thin the viscosity and allow for better reprecipitation into about 1500 ml. of rapidly stirred methanol. The precipitated polymer was collected and dried in a vacuum oven at 60° for 24 hr.

a. *Polydisulfide of 1,3-Di-(2-mercaptoethyl)-tetramethyldisiloxane* (I). Analytical values for sulfur content of the soluble polydisulfides IIIa tended to be low in sulfur. Discrepancies became wider at the higher temperatures of formation.

b. *Polydisulfide of 1,3-Di-(3-mercaptopropyl)-tetramethyldisiloxane.* All the polydisulfides IIIb were completely soluble in chloroform. No variation was shown in analytical composition among polymers prepared over the temperature range investigated.

Preparation of Polypolysulfides. IIIa: To a solution of 6.0 g. (0.024 base mol.) of the polydisulfide of 1,3-di-(2-mercaptoethyl)-tetramethyldisiloxane (η = 0.428) in 100 ml. of chloroform was added a solution of 3.0 g. (0.094 g.-atom) of sulfur dissolved in carbon disulfide. The solvents were removed and the residue was maintained at 150–160° for 4 hr. (Note: Invariably hydrogen sulfide fumes were evolved to a greater or lesser degree as shown by lead acetate paper.) At the end of this time a high vacuum was applied for an additional hour to sublime out unreacted sulfur. On cooling the melt a solid dark brown rubbery polymer, 7.3 g. (95%), was obtained which was incompletely soluble in chloroform. The soluble portion (~10%) had an inherent viscosity of 0.145 (0.5% in chloroform).

Anal. Calcd. for $(C_8H_{20}OSi_2S_{3.49})x$: C, 31.99; H, 6.78; Si, 18.71; S, 37.26. Found: C, 29.73; H, 6.04; Si, 19.80; S, 36.27.

IIIb: In an analogous manner, 9.0 g. (0.032 base mol.) of the polydisulfide from 1,3-di-(3-mercaptopropyl)-tetramethyldisiloxane (η = 0.627) was heated with 2.383 g. (0.075 g.-atom) of sulfur at 150–155° for 4 hr. followed by high vacuum for an additional hour. The polymer, 11.23 g. (93%), when cool was a dark rubbery solid, incompletely soluble in chloroform. The soluble portion had an inherent viscosity of 0.153 (0.5% in chloroform).

Anal. Calcd. for $(C_{10}H_{24}OSi_2S_{3.66})x$: C, 35.97; H, 7.25; Si, 16.83; S, 35.16. Found: C, 34.57; H, 7.00; Si, 17.89; S, 34.44.

URBANA, ILLINOIS

[CONTRIBUTION FROM THE GENERAL ELECTRIC COMPANY RESEARCH LABORATORY]

Alkylation of β-Cyanoethyltrichlorosilane and Preparation of β-Cyanoethyl(methyl)polysiloxanes

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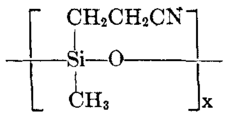
Received August 3, 1959

The reaction of equimolar amounts of β-cyanoethyltrichlorosilane, methylmagnesium bromide, and pyridine produced a mixture of the mono-, di-, and tri-methylated compounds. With methylzinc iodide (methyl iodide + zinc–copper couple) only β-cyanoethyltrimethylsilane was obtained, while dimethylcadmium gave only β-cyanoethyl(methyl)dichlorosilane. Hydrolysis of the dichlorosilane yielded β-cyanoethyl(methyl)polysiloxane oils. These oils do not undergo appreciable silicon-carbon cleavage either with bases or acids, in contrast to the α-cyano substituted polysiloxanes.

Many of the properties of the alkylpolysiloxanes, for example, their abnormally low boiling points and viscosity-temperature coefficients, are due to the low barrier to rotation about the Si—O bond and the consequent very low intermolecular forces in these molecules.[1] These properties can be altered significantly by the introduction of polar substituents into the hydrocarbon groups attached to the silicon atoms of the siloxane chains. The cyano group is among the more polar of these substituents and it has been shown that cyanomethyl groups attached to silicon bring about a large increase in the intermolecular forces, as measured by the activation energies for viscous flow and entropies of vaporization of a number of model silanes and siloxanes.[2] The cyanomethyl group, however, is readily cleaved from silicon by water, particularly in the presence of either acid or base.

$$\equiv SiCH_2CN + H_2O \longrightarrow \equiv SiOH + CH_3CN$$

This type of hydrolytic cleavage is characteristic of organosilicon compounds with electron-withdrawing groups on the carbon atom adjacent to silicon. It would be expected that compounds having a nitrile group on the β carbon would have approximately the same polar characteristics as the α substituted compounds, but might be more resistant to silicon-carbon cleavage. To test this hypothesis a β-cyanoethyl substituted polysiloxane,



$$\left[-\underset{CH_3}{\overset{CH_2CH_2CN}{Si}}-O- \right]_x$$

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[1] E. G. Rochow, *Chemistry of the Silicones*, 2nd edition, p. 115, John Wiley and Sons, New York, N. Y. (1951).

[2] M. Prober, *J. Am. Chem. Soc.*, **77**, 3224 (1955).

has been prepared and its properties examined.[3]

Alkylation of β-cyanoethyltrichlorosilane. For the purposes of this investigation an organosilicon compound having two hydrolyzable groups attached to silicon was required. It was anticipated that the reaction of methylmagnesium bromide with β-cyanoethyltrichlorosilane, which can readily be obtained by the addition of trichlorosilane to acrylonitrile,[4-7] would provide a convenient preparation of β-cyanoethyl(methyl)dichlorosilane.[8] It was found that recovery of the nitriles was facilitated and the yields improved when the reaction was carried out in the presence of one mole of a tertiary amine for each mole of methylmagnesium bromide. The recovery of β-cyanoethyl compounds from the reaction in ether of equimolar amounts of Grignard reagent, pyridine, and β-cyanoethyltrichlorosilane was 61%. Only 60% of this was the monomethyl compound, however, the remainder being made up of unreacted β-cyanoethyltrichlorosilane (16%), β-cyanoethyldimethylchlorosilane (21%) and β-cyanoethyltrimethylsilane (3%).

Although the Grignard reagent may be used for the preparation of β-cyanoethyl(methyl)dichlorosilane, the tendency toward replacement of more than one of the chlorine atoms reduces the yield and gives a mixture of products from which the monomethyl compound can be separated only with difficulty. Organozinc reagents show an even greater tendency to polymethylation; the only products isolated from the reaction of equimolar amounts of methyl iodide and β-cyanoethyltrichlorosilane in the presence of a zinc-copper couple were β-cyanoethyltrimethylsilane (33%, based on methyl iodide) and unreacted starting material.

By far the best reagent found for the monomethylation of β-cyanoethyltrichlorosilane was dimethylcadmium. Pure dimethylcadmium reacted smoothly with the chlorosilane in refluxing toluene, depositing yellow plates of methylcadmium chloride which were replaced as the reaction proceeded by a fine white precipitate of cadmium chloride. The reaction of one mole of the chlorosilane with an equivalent amount (0.5 mole) of dimethylcadmium gave a 90% yield of β-cyanoethyl(methyl)dichlorosilane. Even when a two-fold excess of dimethylcadmium was used the monomethylated compound was the major product. The high yields and ease of separation of the product more than compensate for the additional step involved in the preparation of the cadmium reagent.

These results, although only qualitative, demonstrate a surprising difference in the effect of substitution of methyl for chlorine in β-cyanoethyltrichlorosilane (and presumably other polychlorosilanes) on reactivity towards organometallic reagents of different metals. β-Cyanoethyl(methyl)dichlorosilane reacts much less readily with dimethylcadmium than does β-cyanoethyltrichlorosilane, while the reverse is true with the organozinc reagent; methyl substitution appears to have relatively little effect on reactivity toward the Grignard reagent.

β-Cyanoethyl(methyl)polysiloxanes. Hydrolysis of β-cyanoethyl(methyl)dichlorosilane by stirring an ether solution with ice yielded β-cyanoethyl(methyl)polysiloxane as a viscous oil, which was insoluble in diethyl ether, ethanol, toluene, and other hydrocarbon solvents, but was readily soluble in dimethylformamide. This solubility behavior, which is the reverse of that observed with dimethylpolysiloxanes, indicates that the intermolecular forces were substantially increased, as expected, by the incorporation of the polar β-cyanoethyl group. This is supported by the relatively high activation energy for viscous flow of the cyanoethyl oil (6.9 Kcal. as compared with 3.8 Kcal. for linear dimethylpolysiloxanes.)[9]

Hydrolysis of β-cyanoethyl(methyl)dimethoxysilane with water[10] did not yield the expected β-cyanoethyl(methyl)silanediol. A solid product, m.p. 60–70° was obtained, apparently a mixture of siloxanediols, $HO[Si(CH_3)(CH_2CH_2CN)O]_NH$, which had a silanol content of 9.3%, corresponding to an average value of $n = 3$.

Hydrolytic stability of β-cyanoethyl(methyl)polysiloxane. The stability of the silicon-carbon bond in the β-cyanoethyl(methyl)polysiloxane oil toward hydrolytic cleavage was tested by refluxing samples of the oil for 24 hr. with 5% sodium hydroxide and sulfuric acid solutions. The solutions were acidified with sulfuric acid, diluted to 200 ml. with water, distilled, and the first 100 ml. of distillate was titrated for propionic acid, which would be formed if the silicon-carbon bond were cleaved either before or after hydrolysis of the nitrile group. For comparison, equivalent samples of propionitrile were treated under the same conditions. There was no detectable silicon-carbon cleavage in the sample of the oil which was refluxed with acid. A very small

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(3) The preparation of a polysiloxane of this type by the hydrolysis of β-cyanoethyl(methyl)dichlorosilane was recently reported, but no properties were given.

(4) M. Prober and G. D. Cooper, Fr. Patent 1,116,726 (1956).

(5) S. Nozakura and S. Konotsune, *Bull. Chem. Soc. Japan*, **29**, 322, 326 (1956).

(6) R. A. Pike and D. L. Bailey, Abstracts of the 134th meeting of the American Chemical Society, 49P, September 1958.

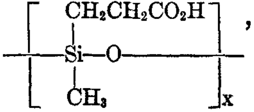
(7) J. C. Saam and J. L. Speier, *J. Org. Chem.*, **24**, 427 (1959).

(8) In a paper which appeared after our work was completed the preparation of this compound in low yields by the pyridine-catalyzed addition of methyldichlorosilane to acrylonitrile was reported. [A. D. Petrov and V. M. Vdovin, *Isvest. Akad. Nauk. SSSR, Otdel. Khim. Nauk.*, **1957**, 1490]. More recently its preparation in 22% yield *via* the Grignard reaction was also reported (ref. 7).

(9) Ref. 1, p. 113.

(10) S. W. Kantor, *J. Am. Chem. Soc.*, **76**, 2712 (1953).

amount of cleavage (less than 0.10%) occurred in the sample which was refluxed with base, but it is not known whether this represents cleavage of the nitrile or of the amide or acid formed on hydrolysis. A comparable α-cyano substituted compound, cyanomethylheptamethylcyclotetrasiloxane, was completely cleaved by refluxing for 24 hr. with 5% sodium hydroxide solution, and 38% cleaved with 5% hydrochloric acid.[2]

β-Carboxyethyl(methyl)polysiloxanes. Hydrolysis of β-cyanoethyl(methyl)polysiloxane by warming with 96% sulfuric acid yielded β-carboxyethyl-(methyl)polysiloxane,  $\left[-\overset{CH_2CH_2CO_2H}{\underset{CH_3}{Si}}-O-\right]_x$, a colorless, extremely viscous oil, readily soluble in dilute sodium hydroxide solution.

EXPERIMENTAL

β-Cyanoethyltrichlorosilane was prepared by the addition of trichlorosilane to acrylonitrile.[4] *β-Cyanoethyltrimethoxysilane* was prepared in 83% yield by the reaction of the chlorosilane with methanol and pyridine in benzene; b.p. 112–113°/17 mm., n_D^{20} 1.4142.

Anal. Calcd. for $C_6H_{13}O_3NSi$: C, 41.1; H, 7.5. Found: C, 41.4; H, 7.4.

Reaction of β-cyanoethyltrichlorosilane with methylmagnesium bromide and pyridine. Methylmagnesium bromide (3.0 mol.) in 1.5 l. of diethyl ether was added over a 3-hr. period to a stirrred solution of 565 g. (3.0 mol.) of β-cyanoethyltrichlorosilane and 273 g. (3.0 mol.) of pyridine in 2 l. of ether. After completing the addition the mixture was refluxed for 1.5 hr. and then stirred overnight at room temperature. The mixture was filtered and the filtrate was distilled. There was obtained 409 g. of crude chlorosilanes boiling at 78–80°/4.5 mm. A 90% aliquot of this material was converted to the ethoxy compounds for easier separation. Rectification of the product yielded 5.3 g. (0.04 mol.) of β-cyanoethyltrimethylsilane, b.p. 77–80°/30 mm., 55.4 g. (0.35 mol.) of β-cyanoethyldimethylethoxysilane (I), b.p. 106–108°/30 mm., 187.2 g. (1.00 mol.) of β-cyanoethyl(methyl)diethoxysilane (II), b.p. 123–125°/30 mm., and 57.2 g. (0.26 mol.) of β-cyanoethyltriethoxysilane, b.p. 135–137°/29 mm.

Anal. Calcd. for (I): Si, 15.0. Found: Si, 15.0. Calcd. for (II): Si, 17.9. Found: Si, 18.4.

When the reaction was carried out under the same conditions, but in the absence of pyridine, filtration of the reaction mixture was very difficult and the filtrate consisted of two phases, one of which was an extremely viscous oil, presumably a complex of the cyano compounds with the magnesium halide produced in the reaction. The yield of β-cyanoethyl(methyl)dichlorosilane was only 14%.

In another experiment 4.4 mol. of methylmagnesium bromide in 1 l. of ether was added over a 3-hr. period to a solution of 377 g. (2.0 mol.) of β-cyanoethyltrichlorosilane and 348 g. (4.4 mol.) of pyridine. The mixture was stirred for 3 hr. and then filtered and the filtrate was distilled. There was obtained 58 g. (0.46 mol.) of β-cyanoethyltrimethylsilane, b.p. 92–93°/46 mm., and 87 g. (0.59 mol.) of β-cyanoethyldimethylchlorosilane, b.p. 119–120°/42 mm., n_D^{20} 1.4442.

Anal. Calcd. for $C_5H_{10}NClSi$: Cl, 24.0. Found: Cl, 24.4.

Reaction of β-cyanoethyltrichlorosilane with dimethylcadmium. A solution of 131 g. (0.92 mol.) of dimethylcadmium, prepared by the method of Krause,[11] and 320 g. (1.7 mol.) of β-cyanoethyltrichlorosilane in 600 ml. of toluene was refluxed under nitrogen. A precipitate of yellow plates began to form after about 30 min. and was replaced as the reaction proceeded by a fine white precipitate of cadmium chloride. After 9 hr. the solution was filtered and the filtrate distilled, yielding 288 g. (90%) of β-cyanoethyl(methyl)dichlorosilane, b.p. 87°/7 mm., n_D^{20} 1.4568–1.4574. Rectification of 530 g. of this material in a 100-plate column yielded 500 g. of material having b.p. 128.5°/50 mm., n_D^{20} 1.4571, d_4^{20} 1.2015; lit.[6] n_D^{22} 1.4560, d_4^{25} 1.206.

Anal. Calcd. for $C_4H_7NCl_2Si$: C, 28.6; H, 4.2; Cl, 42.2; mol. refr., 38.46.[12] Found: C, 28.7; H, 4.3; Cl, 42.4; mol. refr., 38.12.

In one experiment the reaction mixture was filtered after 1 hr. and the precipitate was washed with toluene and dried in vacuum. It consisted of large, slightly yellow plates, which turned purple very rapidly upon exposure to air. Hydrolysis of a sample in dilute sulfuric acid yielded 75% of the amount of methane calculated for methylcadmium chloride.

A solution of 89 g. (0.625 mol.) of dimethylcadmium and 113 g. (0.6 mol.) of β-cyanoethyltrichlorosilane in 400 ml. of benzene was refluxed for 12 hr. Fractional distillation of the filtrate yielded 69 g. (69% of β-cyanoethyl(methyl)dichlorosilane, b.p. 104.5/17 mm., n_D^{20} 1.4568, along with 22 g. (21%) of β-cyanoethyltrichlorosilane, b.p. 95°/17 mm.

β-Cyanoethyl(methyl)dimethoxysilane was prepared by the reaction of the β-cyanoethyl(methyl)dichlorosilane with methanol and pyridine in benzene; b.p. 89–90°/8 mm., n_D^{20} 1.4192, d_4^{20} 0.9862.

Anal. Calcd. for $C_6H_{13}O_2NSi$: C, 45.3; H, 8.2; mol. refr., 40.72. Found: C, 45.6; H, 8.1; mol. refr., 40.80.

β-Cyanoethyl(methyl)diacetoxysilane was prepared by the reaction of the chloro compound with acetic anhydride: b.p. 133°/5 mm., n_D^{20} 1.4326, d_4^{20} 1.1193.

Anal. Calcd. for $C_8H_{13}O_4NSi$: C, 44.6; H, 6.1; mol. refr., 49.98. Found: C, 44.3; H, 6.3; mol. refr., 49.93.

β-Cyanoethyl(methyl)polysiloxane. A solution of 47 g. of β-cyanoethyl(methyl)dichlorosilane in 350 ml. of diethyl ether was stirred for 2 hr. with 50 g. of ice. The oil layer was separated from the three-phase system, dried over sodium sulfate and then heated for 1.5 hr. at 175° and 1.5 mm. pressure. The only volatile product was a small amount of water. Before heating the oil had a moderately strong silanol absorption band at 2.89 microns, which was almost completely absent after heating. The colorless, viscous oil, presumably a mixture of cyclic and linear silanol chain-stopped polysiloxanes, weighed 26 g. (85% of theoretical). It was insoluble in ether, ethanol, hexane, and toluene, but was readily soluble in dimethylformamide.

Anal. Calcd. for $(C_4H_7ONSi)_x$: C, 42.5; H, 6.2; N, 12.4. Found: C, 41.5; H, 5.9; N, 12.3.

A solution of 10 g. of the oil in 20 ml. of 96% sulfuric acid was warmed for 1 hr. on a steam bath and then poured into 100 ml. of water. The oil which separated upon standing was washed thoroughly with water and then was heated for 1 hr. at 150°, yielding β-carboxyethyl(methyl)polysiloxane as a stiff gum, readily soluble in 10% sodium hydroxide solution.

Sample	Moles Propionic Acid in Distillate
Cyanoethyl oil + 5% sodium hydroxide	5×10^{-6}
Propionitrile + 5% sodium hydroxide	1.1×10^{-2}
Cyanoethyl oil + 5% sulfuric acid	0
Propionitrile + 5% sulfuric acid	1.2×10^{-3}

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(11) E. Krause, *Ber.*, 50, 1813 (1917).

(12) Molar refractions were calculated from the bond refraction values of E. L. Warrick, *J. Am. Chem. Soc.*, 68, 2455 (1946). The value for the C≡N bond was taken as 4.73 ml., which is the average of values obtained for eight compounds in this laboratory.

Anal. Calcd. for $(C_4H_8O_3Si)_x$: C, 36.3; H, 6.1; neut. equiv., 132. Found: C, 33.9; H, 6.2; neut. equiv., 130.

Stability of β-cyanoethyl(methyl)polysiloxane oil to silicon-carbon cleavage. Two grams (0.018 equivalent) of the β-cyanoethyl oil was refluxed with 50 ml. of 5% sodium hydroxide solution. Ammonia was evolved and the polymer had completely dissolved within 0.5 hr. After 24 hr. the solution was acidified with sulfuric acid (no odor of hydrogen cyanide), diluted to 200 ml., distilled, and the first 100-ml. portion of the distillate was titrated for propionic acid. Another 2-g. portion was refluxed for 24 hr. with 50 ml. of 5% sulfuric acid, diluted, distilled, and titrated. For comparison, 1-g. (0.018 mol.) samples of propionitrile were treated in the same manner.

SCHENECTADY, N. Y.

[CONTRIBUTION FROM MATERIALS LABORATORY, WRIGHT AIR DEVELOPMENT CENTER]

Organosilicon Compounds. I. Synthesis of Some Long-Chain Tetraalkylsilanes[1]

HAROLD ROSENBERG, JAMES D. GROVES, AND CHRIST TAMBORSKI

Received September 10, 1958

The preparation of several series of unsymmetrical tetraalkylsilanes and one series of mixed symmetrical tetraalkylsilanes by the reaction of the appropriate *n*-alkylchlorosilane with *n*-alkyllithium compounds is described. Certain of the physical properties of the products are presented and discussed. Many of the silanes synthesized exhibit extremely wide liquidus range and may be considered representative of a new class of thermally stable fluids.

A number of symmetrical tetraalkylsilanes of the type R_4Si[2–10] have been reported since Friedel and Crafts[11] first prepared tetraethylsilane in 1863. In connection with a program to develop high-temperature fluids, however, it was of interest to investigate the synthesis and properties of unsymmetrical and mixed symmetrical tetraalkylsilanes of the type $RSiR'_3$ and $R_2SiR'_2$ to determine the structural requirements for optimum liquidus range. Compounds representative of these two types have been previously prepared by the reactions of the Grignard reagents with alkylchlorosilanes,[12–15] by alkyllithium compounds with trialkylsilanes[16] and alkyllithium compounds with alkylalkoxysilanes.[17]

$$4-n\ RMgX + R'_nSiCl_{4-n} \longrightarrow R_n'SiR\ 4-n + 4-n\ MgXCl$$

$$RLi + R'_3SiH \longrightarrow RSiR'_3 + LiH$$

$$4-n\ RLi + R'_nSiCl_{4-n} \longrightarrow R'_nSiR_{4-n} + 4-n\ LiCl$$

In an effort to extend the synthesis of both unsymmetrical ($RSiR'_3$) and mixed symmetrical ($R_2SiR'_2$) tetraalkylsilanes as classes, it was thought desirable to modify and combine the general methods of Bygden[12] and Gilman[16] in order to use the more reactive organolithium compounds (as compared to Grignard reagents) for obtaining increased yields with alkylchlorosilanes. Two series of long-chain tetraalkylsilanes of the type, $RSiR'_3$, and one series of the type, $R_2SiR'_2$, were thus prepared by the reaction of an appropriate *n*-alkylchlorosilane with various *n*-alkyllithium compounds.

$$n\text{-}C_{12}H_{25}SiCl_3 + 3\text{-}RLi \longrightarrow n\text{-}C_{12}H_{25}SiR_3 + 3LiCl$$

$$n\text{-}C_{18}H_{37}SiCl_3 + 3\text{-}RLi \longrightarrow n\text{-}C_{18}H_{37}SiR_3 + 3LiCl$$

$$(n\text{-}C_{12}H_{25})_2SiCl_2 + 2\text{-}RLi \longrightarrow (n\text{-}C_{12}H_{25})_2SiR_2 + 2LiCl$$

For the present study, *n*-dodecyl and *n*-octadecyl were chosen as typical examples of long-chain moieties while normal alkyl groups of from one to eighteen carbon atoms in length (with the exception of $n\text{-}C_{13}H_{27}$, $n\text{-}C_{15}H_{31}$, and $n\text{-}C_{17}H_{35}$) were selected for the other alkyl substituents.

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(1) Presented in part before the Division of Organic Chemistry at the 126th National Meeting, American Chemical Society, New York, N. Y., September 1954.

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