pendent on the assigned frequencies of I and II because most of these cancel out. It is interesting to note that most of the calculated isotope effect is temperature independent.

For a number of reactions involving carbonium ion-like transition states it has been shown that k_H/k_D is substantially greater than unity for both α- and β-deuterium substitution.[9,15-17] Values, ranging from 1.05 to 1.3 *per isotopic substitution* have been reported. The small isotope effect found in the present case (about 1.015 per substitution) along with the ability of a substrate-like model to reproduce the effect militates strongly against any large degree of carbonium ion character in the transition state. If the small excess of observed effect over that predicted is real, however, it may be due to a slight degree of carbonium ion character in the transition state.

Experimental

The preparation of I and II have been described previously.[3,10] Rate constants were measured as before.[3]

Acknowledgment.—The authors are pleased to acknowledge the financial support of the National Science Foundation and the Air Force Office of Scientific Research.

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[16] K. B. Wiberg, *ibid.*, **55**, 713 (1955).

[17] V. J. Shiner and S. Cross, THIS JOURNAL, **79**, 3599 (1957).

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE UNIVERSITY, AMES, IOWA]

Reactions of Monohaloörganosilanes and Magnesium in Tetrahydrofuran

BY WALTER STEUDEL AND HENRY GILMAN

RECEIVED JUNE 8, 1960

Monohaloörganosilanes react with magnesium in tetrahydrofuran to give essentially two classes of compounds. Products of tetrahydrofuran ring cleavage are obtained when no aromatic groups are linked to the silicon atom, whereas aryl-containing halosilanes form the corresponding disilanes. By the latter reaction, a new class of disilanes of the general formula PhRHSiSiHRPh has become readily available. The preparation of 1,1,2,2-tetraphenyldisilane, 1,2-dimethyl-1,2-diphenyldisilane and 1,2-diethyl-1,2-diphenyldisilane is described.

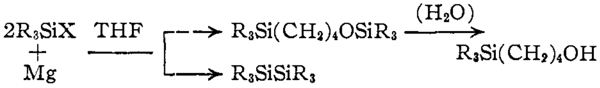
Reactions of halosilanes with magnesium have been of special interest because of the possible formation of silyl Grignard reagents with silicon directly linked to magnesium. No such reagent has been isolated; however, the intermediate formation of such compounds has been proposed by several workers.[1-3]

Emé1eus, Maddock and Reid[1] suggested the formation of an unstable Grignard compound SiH_3MgI from the reaction of iodosilane with magnesium in diisoamyl ether to account for the formation of monosilane and hydrogen. No disilane could be detected in their experiments. An analogous reaction between bromosilane and magnesium is reported by Van Artsdalen and Gravis.[2] Eaborn[3] reported possible formation of a transient Grignard reagent from triethyliodosilane and magnesium in ether.

Recently, strong evidence for the triphenylsilyl Grignard reagent has been shown by work of Selin and West.[4] Triphenylchlorosilane was coupled by cyclohexylmagnesium bromide and other Grignard reagents in tetrahydrofuran to give good yields of hexaphenyldisilane. Trimethylchlorosilane, under the same conditions, gave no reaction, but 1,1,1-trimethyl-2,2,2-triphenyldisilane was obtained when a mixture of trimethylchlorosilane and triphenylchlorosilane was treated with the Grignard reagent. The authors state that "apparently aromatic groups on silicon are necessary for the stabilization of the silyl Grignard reagent, just as they appear necessary for the formation of organosilylalkali compounds."[5] In this Laboratory, the direct coupling of triphenylchlorosilane by magnesium in diethyl ether proved to be unsuccessful,[6] but was eventually achieved by the use of tetrahydrofuran as the solvent.[7]

Anderson and Sprung[8] investigated the reaction of trimethylchlorosilane with magnesium in tetrahydrofuran in the presence of ethyl iodide or magnesium iodide and found that 4-trimethylsilylbutoxytrimethylsilane and 3-butenoxytrimethylsilane are formed as products of the cleavage of tetrahydrofuran. They propose a mechanism which involves the cleavage of the tetrahydrofuran ring by magnesium iodide in the presence of magnesium.

The general usefulness of tetrahydrofuran as a solvent for the preparation of organometallic compounds gave the impetus to this investigation of the behavior of various monohaloörganosilanes toward magnesium in this solvent. Under the conditions employed there are two courses the reaction may follow



$$\begin{matrix} 2R_3SiX \\ + \\ Mg \end{matrix} \xrightarrow{THF} \begin{cases} R_3Si(CH_2)_4OSiR_3 \xrightarrow{(H_2O)} R_3Si(CH_2)_4OH \\ R_3SiSiR_3 \end{cases}$$

One of these leads to the formation of products from the cleavage of tetrahydrofuran to give, on hydrolysis, 4-organosilyl-substituted 1-butanols as the main products. This mode of reaction was always observed when the organohalosilane did not

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[1] H. J. Emé1eus, A. G. Maddock and C. Reid, *J. Chem. Soc.*, 353 (1941).

[2] E. R. Van Artsdalen and J. Gavis, THIS JOURNAL, **74**, 3196 (1952).

[3] C. Eaborn, *J. Chem. Soc.*, 2755 (1949).

[4] T. G. Selin and R. West, *Tetrahedron*, **5**, 97 (1959).

[5] H. Gilman and T. C. Wu, THIS JOURNAL, **73**, 4031 (1951).

[6] H. Gilman and T. C. Wu, *J. Org. Chem.*, **18**, 753 (1953).

[7] M. V. George, D. J. Peterson and H. Gilman, THIS JOURNAL, **82**, 403 (1960).

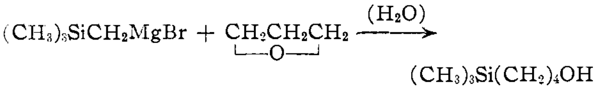
[8] R. P. Anderson and M. M. Sprung, WADC Technical Report 59-61, 47 (1959).

contain an aromatic group linked to silicon. The other process leads to the formation of disilanes. This coupling reaction occurs when at least one of the organic substituents of silicon is phenyl.

There is a considerable difference in the reaction times necessary for the two modes of reaction: the coupling reaction is completed in approximately one day, whereas the rate of the tetrahydrofuran cleavage reaction depends on the amount of iodine used to catalyze the process. The reaction may be completed in 7 hours in the presence of sufficient iodine, but it may take as long as one week when a small amount of iodine is used as in the coupling reactions.

Trimethylchlorosilane, when refluxed one week with tetrahydrofuran, magnesium and a few drops of ethyl iodide, gave on hydrolysis 4-hydroxybutyltrimethylsilane in a 40% yield. A corresponding amount of 4-trimethylsiloxybutyltrimethylsilane was obtained when the reaction mixture was worked up anhydrously. No 3-butenoxytrimethylsilane was isolated in this reaction. In a reaction carried out over a period of 24 hours with a relatively large amount of ethyl iodide, Anderson and Sprung[8] obtained the 3-butenoxy compound in 23% yield. Hexamethyldisilane could not be detected in any of these reactions.

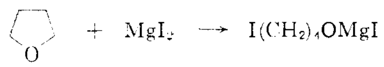
Speier[9] has previously reported the synthesis of 4-hydroxybutyltrimethylsilane by treating 4-chlorobutoxytrimethylsilane with active metals, such as lithium, sodium or magnesium. In order to prepare a sample for comparative purposes, we carried out a reaction between trimethylsilylmethylmagnesium bromide and trimethylene oxide. The 4-hydroxybutyl derivative was obtained in 50% yield.



$$(CH_3)_3SiCH_2MgBr + CH_2CH_2CH_2\ (\text{—O—}) \xrightarrow{(H_2O)} (CH_3)_3Si(CH_2)_4OH$$

Ether cleavage is also observed when tetrahydropyran is substituted for tetrahydrofuran. However, the reaction is slower, and only 40% of the trimethylchlorosilane had reacted after refluxing it with tetrahydropyran, magnesium and a few drops of ethyl iodide for one week. A 6.5% yield of 5-hydroxypentyltrimethylsilane was obtained.

A mechanism for the cleavage of tetrahydrofuran by dimethyldichlorosilane, magnesium and magnesium iodide has been proposed.[8] Applied to our reactions with trimethylchlorosilane it may be formulated as



$$I(CH_2)_4OMgI + Mg + 2ClSi(CH_3)_3 \longrightarrow (CH_3)_3Si(CH_2)_4OSi(CH_3)_3 + MgI_2 + MgCl_2$$

There seems to be no evidence to attribute the ether cleavage to a trialkylsilyl Grignard reagent.

In contrast, there is strong evidence (but no definite proof as yet) that silylmagnesium halides are involved in the synthesis of disilanes from aryl-containing monohaloörganosilanes with magnesium in tetrahydrofuran. These organosilylmagnesium halides may be formed directly by the reaction of the halosilane with magnesium, or indirectly by interaction of the halosilane and preformed organomagnesium halide. This latter proposal is essentially similar to that suggested earlier by Selin and West.[4]

The difference between the ether cleavage reaction and the coupling reaction is clearly shown in the following experiment. When a mixture of trimethylchlorosilane (0.9 mole) and triphenylchlorosilane (0.1 mole) reacted with magnesium in tetrahydrofuran, three products were obtained: 4-hydroxybutyltrimethylsilane in a 49% yield, 1,1,1-trimethyl-2,2,2-triphenyldisilane in a 24% yield (based on triphenylchlorosilane) and hexaphenyldisilane in a 12% yield. Here again, no hexamethyldisilane could be detected, although both of the other possible coupling products were present.

The direct coupling of triphenylchlorosilane by magnesium to give hexaphenyldisilane in good yield has already been mentioned.[7]

By the same coupling reaction, other symmetrical disilanes can be prepared. Thus, 1,1,2,2-tetraphenyl-1,2-dimethyldisilane was obtained from methyldiphenylchlorosilane in a 6.5% yield.

In these reactions of trisubstituted chlorosilanes, unidentified products containing hydroxyl groups and boiling over a wide temperature range are formed to a large extent. The yields of disilanes are considerably lower than from the reaction with sodium in boiling xylene[10] which remains the method of choice for the preparation of hexasubstituted disilanes.

However, the results are different when disubstituted halosilanes with one silicon–hydrogen bond are submitted to coupling reactions. The reaction of diphenylchlorosilane and sodium in boiling xylene gives a low yield of 1,1,2,2-tetraphenyldisilane (10%).[11] The same product is formed by the action of lithium on diphenylchlorosilane in tetrahydrofuran, but it is quickly transformed into diphenylsilyllithium and subsequent products.[12] Under special conditions a 5% yield of the disilanes can be isolated.[11] However, when diphenylchlorosilane in tetrahydrofuran was refluxed for 24 hours with magnesium, 1,1,2,2-tetraphenyldisilane was obtained in a 65% yield. This compound was converted to a known derivative, 1,2-di-*p*-tolyl-1,1,2,2-tetraphenyldisilane, by treatment with *p*-tolyllithium.

Diphenylbromosilane gave 1,1,2,2-tetraphenyldisilane in a similarly good yield (53%). The bromosilane, however, reacted considerably faster than the chlorosilane, and the reaction was completed in 12 hours.

From methylphenylchlorosilane, there was obtained 1,2-dimethyl-1,2-diphenyldisilane in 56% yield, and 1,2-diethyl-1,2-diphenyldisilane was formed in 39% yield from ethylphenylchlorosilane.

This new class of symmetrical disilanes of the general formula PhRHSiSiHRPh, where R may be aryl or alkyl, is thus readily available from the corresponding halosilanes. These silicon–hydro-

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(9) J. L. Speier, THIS JOURNAL, **74**, 1003 (1952).

(10) H. Gilman and G. E. Dunn, *ibid.*, **73**, 5077 (1951).

(11) W. Steudel and H. Gilman, unpublished studies.

(12) H. Gilman and W. Steudel, *Chemistry & Industry*, 1084 (1959).

gen bonds are very reactive and make the compounds useful as intermediates in the synthesis of types with one or more silicon–silicon bonds. Thus, 1,2-dichloro derivatives can be formed by the reaction with chlorine,[11] or organic groups may be directly introduced by the use of organolithium reagents.[13]

Experimental

All reactions were carried out under an atmosphere of dry, oxygen-free nitrogen in oven-dried glassware. Magnesium turnings (Mallinckrodt, "for Grignard reactions") were dried in an oven before use. The chlorosilanes, if not stated otherwise, were purchased from Dow Corning Corp. in a purified grade. Tetrahydrofuran and tetrahydropyran were refluxed over sodium wire followed by distillations from lithium aluminum hydride immediately before use.

Trimethylchlorosilane, Magnesium and Tetrahydrofuran.—A mixture of 109 g. (1 mole) of trimethylchlorosilane, 12.2 g. (0.5 g. atom) of magnesium, 150 ml. (1.8 moles) of tetrahydrofuran and 5 drops of ethyl iodide was refluxed with stirring for 175 hours. Titration of an aliquot with standardized sodium hydroxide-solution indicated that 94% of the chlorosilane had reacted. Water was added to the mixture, and the organic products were extracted with ether. Upon drying and removal of the ether, there was obtained by distillation 29.0 g. (40%) of 4-hydroxybutyltrimethylsilane, b.p. 179–180°, n^{20}_D 1.4338, d^{20}_{20} 0.837 (lit.[9] values: b.p. 96° (25 mm.), n^{25}_D 1.4315, d^{25}_4 0.830).

In another experiment the products were worked up anhydrously. The main product was 4-trimethylsilylbutoxytrimethylsilane, b.p. 82° (12 mm.), n^{20}_D 1.4188 (lit.[9] values: b.p. 94° (24 mm.), n^{25}_D 1.4166). This compound could be converted readily into 4-hydroxybutyltrimethylsilane by hydrolysis with dilute acid.

Two experiments were carried out according to the procedure of Anderson and Sprung[8] using 4 ml. of ethyl iodide per mole of trimethylchlorosilane and an equivalent amount of anhydrous magnesium iodide, respectively. In both runs, the reaction was completed in 7 hours and work-up gave 4-hydroxybutyltrimethylsilane in yields of 28 and 31%.

4-Hydroxybutyltrimethylsilane from Trimethylsilylmethylmagnesium Bromide and Trimethylene Oxide.—A solution of trimethylsilylmethylmagnesium bromide, prepared from 38.4 g. (0.23 mole) of bromomethyltrimethylsilane, 5.6 g. (0.23 g. at.) of magnesium and 150 ml. of ether, was treated with 4.9 g. (0.084 mole) of trimethylene oxide in 20 ml. of ether. The mixture was refluxed for 1 hour and then 150 ml. of dry benzene was added. The ether was carefully removed by distillation through a short Vigreux column and the resulting benzene solution was refluxed for 4 hours. Hydrolysis was effected with dilute acid and the mixture was worked up in the usual manner. The products were distilled to give 6.12 g. (50%) of 4-hydroxybutyltrimethylsilane, b.p. 40–41° (0.5 mm.), n^{20}_D 1.4348. The infrared spectra of this compound and of the compound prepared by tetrahydrofuran cleavage were identical.

Trimethylchlorosilane, Magnesium and Tetrahydropyran.—A mixture of 52.2 g. (0.481 mole) of trimethylchlorosilane, 5.8 g. (0.24 g. atom) of magnesium, 100 ml. (0.98 mole) of tetrahydropyran and 5 drops of ethyl iodide was refluxed with stirring. After 168 hours, 40% of the chlorosilane had reacted. The mixture was hydrolyzed and worked up as previously described to give 2.5 g. (6.5%) of 5-hydroxypentyltrimethylsilane, b.p. 91–92° (12 mm.), n^{20}_D 1.4358, d^{20}_{20} 0.968 (lit.[9] values: b.p. 110° (25 mm.), n^{25}_D 1.4358, d^{25}_4 0.841).

Trimethylchlorosilane and Triphenylchlorosilane.—A mixture of 97.7 g. (0.9 mole) of trimethylchlorosilane, 29.5 g. (0.1 mole) of triphenylchlorosilane, 12.2 g. (0.5 g. atom) of magnesium, 150 ml. (1.8 moles) of tetrahydrofuran and 5 drops of ethyl iodide was stirred and refluxed. Titration indicated that 98% of the chlorosilanes had reacted after 160 hours. Water was added and the insoluble material was filtered to give some unreacted magnesium and 3.2 g. (12%) of hexaphenyldisilane, m.p. 366–370°, after purification. The ether extract of the filtrate was dried and distilled. There were obtained 39.3 g. (49%) of 4-hydroxybutyltrimethylsilane and 7.93 g. (24%, based on triphenylchlorosilane) of 1,1,1-trimethyl-2,2,2-triphenyldisilane, b.p. 218–220° (11 mm.), m.p. 105–108°. A portion of the latter material was recrystallized from methanol to give colorless crystals, m.p. 108–109°. A mixed melting point with an authentic specimen showed no depression.

1,2-Dimethyl-1,1,2,2-tetraphenyldisilane.—A mixture of 46.6 g. (0.2 mole) of methyldiphenylchlorosilane, 4.9 g. (0.2 g. atom) of magnesium, 100 ml. of tetrahydrofuran and 20 drops of ethyl iodide was stirred and refluxed for 24 hours. The mixture was then added to dilute acid. The organic layer was separated and dried. Upon removal of the solvents the residue crystallized partially to give 2.6 g. (6.6%) of 1,2-dimethyl-1,1,2,2-tetraphenyldisilane. Upon recrystallization from petroleum ether (b.p. 60–70°) the compound melted at 141–143°. A mixed melting point with an authentic sample showed no depression. Distillation of the liquid products gave unidentified oils which distilled over a range from 90 to 225° (0.1 mm.). The infrared spectra showed the presence of hydroxyl groups.

1,1,2,2-Tetraphenyldisilane. From Diphenylchlorosilane.—A mixture of 46.3 g. (0.212 mole) of diphenylchlorosilane, 2.9 g. (0.12 g. atom) of magnesium, 100 ml. of tetrahydrofuran and 3 drops of ethyl iodide was refluxed with stirring. The solution turned dark brown after a few minutes, and later a dark precipitate of magnesium chloride separated. After 24 hours, as ascertained by titration of aliquots, the reaction was completed. The mixture was poured into dilute acid. The organic material was extracted with ether, the organic layer was dried and the ether was removed. The remainder crystallized partially to yield 32.1 g. of crude product, melting over the range 66–78°. Recrystallization from petroleum ether (b.p. 60–70°) gave 25.1 g. (65%) of 1,1,2,2-tetraphenyldisilane, m.p. 79–80°.

Anal. Calcd. for $C_{24}H_{22}Si_2$: C, 78.64; H, 6.06; Si, 15.31. Found: C, 78.42; H, 6.11; Si, 15.1.

A solution containing 1.1 g. (0.08 mole) of this compound, 0.011 mole of *p*-tolyllithium and 35 ml. of ether was stirred 18 hours at room temperature. Upon hydrolysis there was obtained from the organic layer 1.08 g. (66%) of 1,2-di-*p*-tolyl-1,1,2,2-tetraphenyldisilane, m.p. 251–253°, which was shown to be identical with an authentic specimen[14] by a mixed melting point determination and by comparison of the infrared spectra.

In a second preparation of 1,1,2,2-tetraphenyldisilane under the conditions described above, 60 hours was required to complete the reaction, and a 58% yield of pure material was obtained. When the reaction mixture was worked up by distillation, the main fraction distilled at 180–210° (0.5 mm.) with partial decomposition. From this fraction, a 22% yield of the disilane could be obtained.

In other runs, small amounts of ethylene chloride, benzyl chloride, diphenyldichlorosilane and bromobenzene, respectively, were added to the reaction mixture in order to catalyze the reaction (no ethyl iodide was added). In no instance could reaction be observed. However, anhydrous magnesium iodide, prepared by the reaction of iodine with magnesium in the tetrahydrofuran prior to the addition of the diphenylchlorosilane, was found to be as effective as ethyl iodide. A slow reaction was also brought about by the addition of 10 drops of ethyl bromide; after 24 hours, only 50% of the diphenylchlorosilane had reacted. It should be noted that in all other cases the reaction started immediately upon addition of ethyl iodide.

From Diphenylbromosilane.—Diphenylbromosilane was prepared according to a procedure used for the preparation of phenylbromosilane[15] by passing anhydrous hydrogen bromide through a solution of 92 g. (0.5 mole) of diphenylsilane in 60 ml. of ether for 2 days. The ether was removed and the reaction products were distilled under reduced pressure. There were obtained 49 g. of unreacted diphenylsilane and 51 g. (39%) of diphenylbromosilane, b.p. 102° (0.5 mm.).

Anal. Calcd. for $C_{12}H_{11}Br$: Br, 30.4; Si, 10.67. Found: Br, 30.4; Si, 10.58.

A mixture of 26.3 g. (0.1 mole) of diphenylbromosilane, 2.9 g. (0.12 g. atom) of magnesium, 25 ml. of tetrahydrofuran and 2 drops of ethyl iodide was stirred and refluxed as described in the above reactions. The reaction was com-

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[13] H. Gilman and E. A. Zuech, THIS JOURNAL, **81**, 5925 (1959).

[14] H. Gilman and T. C. Wu, *ibid.*, **75**, 3762 (1953).

[15] M. C. Harvey, W. H. Nebergall and J. S. Peake, *ibid.*, **79**, 1437 (1957).

pleted in 12 hours, and work-up yielded 9.7 g. (53%) of pure 1,1,2,2-tetraphenyldisilane.

1,2-Dimethyl-1,2-diphenyldisilane.—A mixture of 31.3 g. (0.2 mole) of methylphenylchlorosilane, 4.9 g. (0.2 g. atom) of magnesium, 100 ml. of tetrahydrofuran and 5 drops of ethyl iodide was refluxed with stirring. The reaction was completed in 33 hours. Dry pentane (100 ml.) was added and the mixture was filtered through a glass filter. The solid was washed with an additional 20 ml. of pentane, and the filtrate was fractionated to give 13.6 g. (56%) of 1,2-dimethyl-1,2-diphenyldisilane, b.p. 81–83° (0.003 mm.), $n^{20}{}_D$ 1.5769, $d^{20}{}_{20}$ 0.980.

Anal. Calcd. for $C_{14}H_{18}Si_2$: C, 69.3; H, 7.49; *MR*, 82.0. Found: C, 69.01; H, 7.31; *MR*, 82.0.

1,2-Diethyl-1,2-diphenyldisilane.—A mixture of 25.2 g. (0.148 mole) of ethylphenylchlorosilane, 3.6 g. (0.15 g. atom) of magnesium, 75 ml. of tetrahydrofuran and 3 drops of ethyl iodide was refluxed and stirred for 65 hours. The reaction products were worked up as before. There was obtained 7.75 g. (39%) of 1,2-diethyl-1,2-diphenyldisilane, b.p. 110–111° (0.1 mm.), $n^{20}{}_D$ 1.5656, $d^{20}{}_{20}$ 0.969.

Anal. Calcd. for $C_{16}H_{22}Si_2$: Si, 20.7; *MR*, 91.2. Found: Si, 20.4; *MR*, 91.0.

Acknowledgments.—This research was supported by the United States Air Force under Contract 33 (616)-6127 monitored by Materials Laboratory, Directorate of Laboratories, Wright Air Development Center, Wright–Patterson AFB, Ohio. The authors are grateful to E. A. Zuech for assistance. Infrared analyses were obtained through the courtesy of the Institute for Atomic Research, Iowa State University, and special acknowledgment is made to Dr. V. A. Fassel, Mr. R. Kniseley and Miss E. Conrad for the spectra.

[CONTRIBUTION NO. 620 FROM THE CENTRAL RESEARCH DEPARTMENT, EXPERIMENTAL STATION, E. I. DU PONT DE NEMOURS AND CO., WILMINGTON 98, DEL.]

Cyanocarbon Chemistry. XVII. Tricyanoethylene and Tricyanovinyl Chloride[1]

BY C. L. DICKINSON, D. W. WILEY AND B. C. MCKUSICK

RECEIVED JUNE 27, 1960

Tricyanoethylene, hitherto the only unknown cyanoethylene, has been synthesized. It is chemically similar to tetracyanoethylene, but it reacts less vigorously. Addition of chlorine to tricyanoethylene is in striking contrast to the chlorination of most olefinic compounds in that initial attack seems to be by Cl^- to give a carbanion rather than by Cl_2 to give a cation. The resultant dichloride has been converted to tricyanovinyl chloride, which has proved to be a more versatile tricyanovinylating reagent than tetracyanoethylene.

The novelty and great variety of the reactions that tetracyanoethylene undergoes[2] encouraged us to attempt the synthesis of tricyanoethylene, the only unknown member of the cyanoethylene family, in order to see to what extent its properties parallel those of tetracyanoethylene.

We have succeeded in preparing tricyanoethylene in 27% over-all yield by means of the five-step synthesis shown in Chart I. The first step is the reaction of ethyl cyanoacetate with glycolonitrile to give ethyl 2,3-dicyanopropionate.[3] The latter was converted to the corresponding amide, which was dehydrated to 1,1,2-tricyanoethane. This was readily brominated to 1-bromo-1,1,2-tricyanoethane, which was dehydrobrominated by triethylamine to give tricyanoethylene in excellent yield. The dehydrobromination is the most critical step in the synthesis; tricyanoethylene decomposes rapidly in the presence of bases, so that the use of even a slight excess of triethylamine will result in no product whatever being isolated. The best practice is to use 90 to 95% of the amount of triethylamine theoretically required.

CHART I

SYNTHESIS OF TRICYANOETHYLENE

$$NCCH_2OH + NaCH(CN)CO_2C_2H_5 \xrightarrow[55\%]{}$$

$$NCCH_2CH(CN)CO_2C_2H_5 \xrightarrow[74\%]{NH_3}$$

$$NCCH_2CH(CN)CONH_2 \xrightarrow[80\%]{POCl_3} NCCH_2CH(CN)_2$$

$$\xrightarrow[91\%]{Br_2/H_2O} NCCH_2CBr(CN)_2 \xrightarrow[91\%]{(C_2H_5)_3N} NCCH{=}C(CN)_2$$

Tricyanoethylene is a crystalline solid melting at 42°. It is much more sensitive to base than tetracyanoethylene, being readily resinified by even traces of base. It is considerably less stable than tetracyanoethylene, which can be stored at room temperature indefinitely provided moisture is excluded. Although a highly purified sample of tricyanoethylene can be stored at room temperature, a slightly impure sample must be stored at solid carbon dioxide temperature or it will decompose in less than a day. Tricyanoethylene therefore is intermediate in stability between tetracyanoethylene and vinylidene cyanide.[4]

Chemically, tricyanoethylene is similar to tetracyanoethylene, but it generally reacts less rapidly. Thus, like tetracyanoethylene,[5] tricyanoethylene forms a Diels–Alder adduct with anthracene, but at room temperature the reaction requires hours instead of minutes. The acid-catalyzed addition of ketones to tetracyanoethylene[5] has its parallel in the addition of acetone to tricyanoethylene to give 4,5,5-tricyano-2-pentanone (I). Like tetracyanoethylene,[6] tricyanoethylene condenses with aniline

[1] Paper XVI, see R. M. Scribner, G. N. Sausen and W. W. Prichard, *J. Org. Chem.*, **25**, 1440 (1960).

[2] Paper I, T. L. Cairns, R. A. Carboni, D. D. Coffman, V. A. Engelhardt, R. E. Heckert, E. L. Little, E. G. McGeer, B. C. McKusick, W. J. Middleton, R. M. Scribner, C. W. Theobald and H. E. Winberg, THIS JOURNAL, **80**, 2775 (1958).

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[5] W. J. Middleton, R. E. Heckert, E. L. Little and C. G. Krespan, *ibid.*, **80**, 2783 (1958).

[6] B. C. McKusick, R. E. Heckert, T. L. Cairns, D. D. Coffman and H. F. Mower, *ibid.*, **80**, 2806 (1958).