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# CYANOALKOXYSILANES

KURT C. FRISCH[1] AND MILTON WOLF[2]

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The susceptibility of the Si—O linkage in alkoxysilanes towards hydrolysis is well known (1). The hydrolysis of alkoxysilanes makes these derivatives suitable as intermediates for the formation of silanols and siloxanediols (2–5).

Tertiary alkoxysilanes, *e.g.* tertiary butoxysilanes, on the other hand show remarkable stability, particularly in neutral or basic media (6, 7). Similarly, the tertiary alkoxy linkage in tertiary alkoxyaminosilanes is resistant to hydrolysis as no noticeable cleavage of the Si—O bond occurs in the following reaction (6, 8):

$$(\textit{tert}\text{-RO})_2\text{Si}(\text{NH}_2)_2 + 2\ \text{H}_2\text{O} \rightarrow (\textit{tert}\text{-RO})_2\text{Si}(\text{OH})_2 + 2\ \text{NH}_3$$

In the present investigation tertiary alkoxysilanes were prepared in which one of the alkyl groups was replaced by a cyano group in order to promote greater interchain attraction. The cyanoalkoxysilanes were prepared by reaction of acetone cyanohydrin with methylchlorosilanes in the presence of pyridine as hydrohalogen acceptor. With trimethylchlorosilane the reaction proceeded as follows:

$$(\text{CH}_3)_3\text{SiCl} + (\text{CH}_3)_2\text{C}(\text{CN})\text{OH} \rightarrow \underset{\text{I}}{(\text{CH}_3)_3\text{Si—O—C}(\text{CH}_3)_2\text{CN}}$$

Dimethyldichlorosilane yielded the corresponding difunctional compound:

$$(\text{CH}_3)_2\text{SiCl}_2 + 2\,(\text{CH}_3)_2\text{C}(\text{OH})\text{CN} \rightarrow \underset{\text{II}}{\text{NC}(\text{CH}_3)_2\text{C—O—Si}(\text{CH}_3)_2\text{—O—C}(\text{CH}_3)_2\text{CN}}$$

A dichlorosilane was prepared by reaction of acetone cyanohydrin with an excess of methyltrichlorosilane:

$$\text{CH}_3\text{SiCl}_3 + (\text{CH}_3)_2\text{C}(\text{OH})\text{CN} \rightarrow \underset{\text{III}}{\text{NC}(\text{CH}_3)_2\text{C—O—Si}(\text{CH}_3)\text{Cl}_2}$$

Dilution is of considerable importance in this reaction since the dichlorosilane (III) can be obtained in very good yields using a threefold excess of methyltrichlorosilane as well as an ample supply of solvent (benzene). If the ratio of methyltrichlorosilane to acetone cyanohydrin is 2:1 and less solvent is used, the main reaction is as follows:

$$\text{CH}_3\text{SiCl}_3 + 2\ (\text{CH}_3)_2\text{C}(\text{OH})\text{CN} \rightarrow [\text{NC}(\text{CH}_3)_2\text{C—O}]_2\text{—Si}(\text{CH}_3)\text{Cl}$$

The dichloro- (III) and the monochloro-silane (IV) were converted into the acetoxy derivatives. 2-Cyano-2-propoxymethyldiacetoxysilane (V) was hy-

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[1] Present address: E. F. Houghton & Co., Philadelphia 33, Penna.

[2] Present address: Bristol Laboratories Inc., Syracuse 1, N. Y.

drolyzed to give the corresponding silanediol (VI):

$$NC(CH_3)_2C{-}O{-}Si(CH_3)Cl_2 + 2\,Ac_2O \rightarrow$$

$$\underset{V}{NC(CH_3)_2C{-}O{-}Si(CH_3)(OAc)_2} \xrightarrow{H_2O} \underset{VI}{NC(CH_3)_2C{-}O{-}Si(CH_3)(\,OH)}$$

Under analogous conditions bis(2-cyano-2-propoxy)methylacetoxysilane (VII) hydrolyzed to yield the silanol (VIII):

$$[NC(CH_3)_2{-}C{-}O]_2{-}Si(CH_3)(OAc) \xrightarrow{H_2O} \underset{VIII}{[NC(CH_3)_2{-}C{-}O]_2{-}Si(CH_3)(OH)}$$

The structure of 2-cyano-2-propoxytrimethylsilane (I) was established by reaction with methylmagnesium iodide and hydrolysis of the imine (IX) by refluxing with hydrochloric acid. The resulting hydroxyketone, 2-hydroxy-2-methylbutanone-3 (X) was identified by means of its 2,4-dinitrophenylhydrazone:

$$\underset{I}{(CH_3)_3Si{-}O{-}C(CH_3)_2CN} + CH_3MgI \rightarrow \underset{IX}{(CH_3)_3Si{-}O{-}C(CH_3)_2C({=}NH)(CH_3)}$$

$$\xrightarrow{aq.\,HCl} (CH_3)_3SiOH + \underset{X}{(CH_3)_2C(OH)COCH_3}$$

The stability of the Si—O linkage in the above described cyanoalkoxysilanes towards hydrolysis in neutral, acid, and alkaline media was determined. No cleavage occurred in water while slow hydrolysis took place in 5% aqueous hydrochloric acid and 5% aqueous sodium hydroxide solution over a period of 16 hours at room temperature.

## EXPERIMENTAL

All yields are based on the amount of acetone cyanohydrin used.

*2-Cyano-2-propoxytrimethylsilane* (I). A solution of 54.3 g. (0.5 mole) of trimethylchlorosilane in 50 cc. of dry benzene was added dropwise with stirring to a solution of 42.6 g. (0.5 mole) of acetone cyanohydrin and 39.6 g. (0.5 mole) of anhydrous pyridine in 100 cc. of dry benzene. The reaction mixture was cooled with an ice bath (0–5°). The addition of the chlorosilane solution required a period of one hour. After the addition was completed a copious precipitate of pyridine hydrochloride had formed. The reaction mixture was allowed to stand at room temperature overnight. The pyridine hydrochloride was filtered off and washed with benzene. The benzene was then removed from the filtrate by distillation and the residual, light yellow oil was fractionally distilled.

The product, a colorless liquid, distilled at 145.5–147°. The yield was 74.9 g. corresponding to 95.3%; $n_D^{20}$ 1.4022; $d_4^{20}$ 0.857; $M_R$ (Calc'd), 44.81; $M_R$ (Found), 44.7.

*Anal.* Calc'd for $C_7H_{15}NOSi$: Si, 17.9; N, 8.9.

Found: Si, 18.0; N, 8.9.

*Bis(2-cyano-2-propoxy)-dimethylsilane* (II). The same procedure was used for the preparation of this compound as described for 2-cyano-2-propoxytrimethylsilane.

The product distilled as a colorless liquid, b.p. 124–126° at 21 mm.; $n_D^{20}$ 1.4174; $d_4^{20}$ 0.9644; $M_R$ (Calc'd), 59.34; $M_R$ (Found), 59.06. The yield was 80.5 g. (93.9%).

*Anal.* Calc'd for $C_{10}H_{18}N_2O_2Si$: Si, 12.4; N, 12.4.

Found: Si, 12.6; N, 12.5.

*2-Cyano-2-propoxymethyldichlorosilane* (III). A solution of 85 g. (1 mole) of acetone cyanohydrin and 79 g. (1 mole) of dry pyridine in 200 cc. of benzene was added slowly to a solution of 448.5 g. (3 moles) of methyltrichlorosilane in 300 cc. of benzene. The mixture was well stirred and kept at 0–5° with an ice-bath. Afterwards the mixture was allowed to stir at room temperature for 2½ hours. The white precipitate of pyridine hydrochloride was filtered and washed with benzene. The solvent was removed from the filtrate by distillation and the residual liquid was vacuum-distilled.

The product, a colorless liquid distilled at 70–71° at 15 mm.; $n_D^{23}$ 1.4210; $d_4^{23}$ 1.137; $M_R$ (Calc'd), 44.07; $M_R$ (Found), 44.22. The yield was 148 g. (75%).

*Anal.* Calc'd for $C_5H_9Cl_2NOSi$: Si, 14.1; N, 7.1.
Found: Si, 14.1; N, 7.4.

*2-Cyano-2-propoxymethyldiacetoxysilane* (V). The acetoxy derivative was prepared by refluxing a mixture of the above dichlorosilane with an equivalent amount of acetic anhydride for 2 hours. A few drops of a triethanolamine solution in acetic anhydride was added to catalyze the reaction. The product distilled at 130–132° at 14 mm. as a colorless liquid.

*Anal.* Calc'd for $C_9H_{15}NO_5Si$: Si, 11.4. Found: Si, 11.6.

*2-Cyano-2-propoxymethyldisilanol* (VI). The above acetoxy derivative (V) was hydrolyzed in a saturated salt solution. The mixture was extracted with ether, washed with water, and the ether extract dried over sodium sulfate. The solvent was evaporated and the last traces of acetic acid were removed by a vacuum distillation at room temperature. The product was a colorless liquid which could not be distilled without decomposition.

*Anal.* Calc'd for $C_5H_{11}NO_3Si$: Si, 17.4; M. W., 161.
Found: Si, 16.1; M. W., 165.

*Bis(2-cyano-2-propoxy)methylchlorosilane* (IV). This compound was prepared in an analogous manner to that of 2-cyano-2-propoxymethyldichlorosilane. The product distilled as a colorless liquid, b.p. 96–97° at 0.2 mm. The yield was 44 g. (25%).

*Anal.* Calc'd for $C_9H_{15}ClN_2O_2Si$: Si, 11.4; N, 11.4.
Found: Si, 11.6; N, 11.8.

*Bis(2-cyano-2-propoxy)methylacetoxysilane* (VII). The acetoxy derivative was a colorless liquid, distilling at 100° at 0.07 mm.

*Anal.* Calc'd for $C_{11}H_{18}N_2O_4Si$: Si, 10.4. Found: Si, 11.0.

*Bis(2-cyano-2-propoxy)methylsilanol* (VIII). The hydrolysis of bis(2-cyano-2-propoxy)-methylacetoxysilane (VII) was carried out in an analogous manner to that of 2-cyano-2-propoxymethyldiacetoxysilane (V). The product was a colorless liquid.

*Anal.* Calc'd for $C_9H_{16}O_3Si$: Si, 12.3; M. W., 228.
Found: Si, 11.9; M. W., 225.

*Structure proof of 2-cyano-2-propoxytrimethylsilane* (I). Methylmagnesium iodide was prepared from 7.95 g. (0.056 mole) of methyl iodide, 1.46 g. (0.60 g.) of magnesium turnings, and 50 cc. of ether.

A solution of 8.62 g. (0.055 mole) of 2-cyano-2-propoxytrimethylsilane in 50 cc. of ether was added dropwise to the above Grignard solution over a period of 30 minutes. Heat was evolved on addition of the nitrile and an oil separated in the reaction mixture.

The mixture was then hydrolyzed by addition of 50 cc. of conc'd HCl and 100 cc. of water, followed by refluxing for a period of one hour. The ether was removed and the aqueous solution was neutralized and saturated with sodium chloride. The reaction mixture was continuously extracted with ether for 48 hours. The solvent was then removed and the residual material fractionally distilled. The product, 2-hydroxy-2-methyl butanone-3 (X), distilled as a colorless liquid; b.p. 96–100° at 149–150 mm. Constants were: $n_D^{25.5}$ 1.4095 (lit. b.p. 139–141°, $n_D^{20}$ 1.4155).

*The 2,4-dinitrophenylhydrazone* derivative of the above hydroxyketone was prepared. Recrystallized from water it melted at 138–139°, the same value as obtained by Aston and Greenberg (9) for this compound.

*Stability tests with 2-cyano-2-propoxytrimethylsilane.* This silane was recovered unchanged from water. Stirring in a 5% NaOH solution for 16 hours at room temperature caused slow hydrolysis. About 55% of the material was recovered unchanged. Using a 5% HCl solution under the same conditions, only about 40% of the product was recovered.

These experiments indicated therefore that slow hydrolysis had taken place in acid and alkaline media on prolonged stirring at room temperature.

## SUMMARY

1. Cyanoalkoxysilanes were prepared in excellent yields from acetone cyanohydrin and methylchlorosilanes.
2. Cyanoalkoxychlorosilanes were converted into the corresponding acetoxy derivatives and the latter hydrolyzed to the silanols.
3. A proof of structure was carried out on 2-cyano-2-propoxytrimethylsilane.
4. Tests were carried out to determine the stability of 2-cyano-2-propoxytrimethylsilane in neutral, acid, and alkaline media.

PITTSFIELD, MASS.

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