When the chloroform was removed, the remaining oil crystallized upon cooling and amounted to 3.1 g. (84%) of crude 3-nitrobenzonitrile, m.p. 90–105° and 117–118° after several recrystallizations from aqueous methanol. An authentic sample of nitrile was prepared by nitrating benzonitrile and, when purified, melted 117–118°, reported[13] 117–118°. Mixed melting points showed no depression.

(b) **2-Nitrobenzonitrile and 4-Nitrobenzonitrile.**—These procedures were exactly the same as described for 3-nitrobenzonitrile. Thus 2-nitrobenzoyl chloride and 2-nitrobenzamide yielded 2.1 g. (57%) of 2-nitrobenzonitrile, m.p. 95–105° (crude) and 109–110° (pure), reported[14] 110°; while 4-nitrobenzoyl chloride and 4-nitrobenzamide gave 3.1 g. (84%) of nitrile, m.p. 135–138° (crude) and 148–149° (pure), reported[15] 147.5–148.5°.

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[13] F. Beilstein and A. Kulhberg, *Ann.*, **146**, 336 (1868).

[14] A. Reissert, *Ber.*, **30**, 1039 (1897).

[15] M. T. Bogert and L. E. Wise, THIS JOURNAL, **32**, 1495 (1910).

MADISON, WISCONSIN RECEIVED MAY 21, 1951

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, DUKE UNIVERSITY]

Cleavage of Benzyl-, Diphenylmethyl- and Triphenylmethyltrimethylsilanes by Potassium Amide and Certain Other Bases[1]

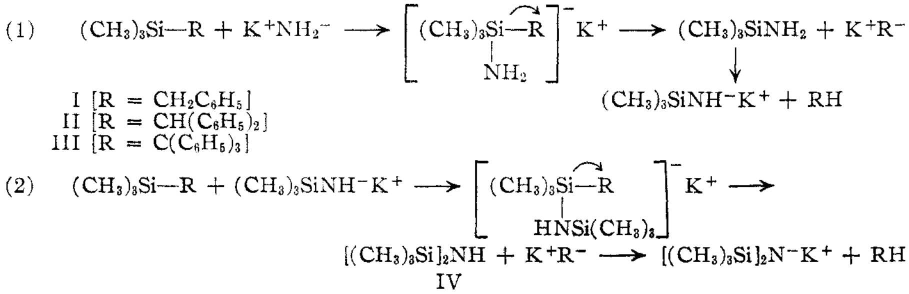
BY CHARLES R. HAUSER AND CHARLES R. HANCE

The benzyl, diphenylmethyl and triphenylmethyl groups in appropriately tetrasubstituted hydrocarbon silanes have been cleaved from silicon by potassium amide in liquid ammonia and by sodium ethoxide in refluxing ethanol. However, such cleavages were not effected by certain other basic reagents. The influence of the metallic cation and the medium was studied. Some new syntheses are described.

Although various silanols and siloxanes have been cleaved by bases to form hydrocarbons along with silicon derivatives,[2] allyltrimethylsilane has apparently been the only tetrasubstituted hydrocarbon silane cleaved previously by a base. This hydrocarbon silane was cleaved by long refluxing with methanolic potassium hydroxide to form propylene and trimethylmethoxysilane.[3] Indeed, Gilman and co-workers[2c] have shown that such hydrocarbon silanes as tetraphenylsilane and trimethylphenylsilane fail to undergo cleavage with butyl lithium in refluxing ether.

We have found that three hydrocarbon silanes, benzyltrimethylsilane (I), diphenylmethyltrimethylsilane (II) and triphenylmethyltrimethylsilane (III) are readily cleaved by potassium amide in liquid ammonia. None of the original silanes were recovered after one hour. Silane I gave toluene (77%) and silicon products which, on the basis of their physical properties, were hexamethyldisilazane (IV) (14%) and an azeotropic mixture (43%) of trimethylsilanol and hexamethyldisiloxane. The latter two compounds were formed presumably from IV during the working up process, such a hydrolysis having been reported previously.[4] Silanes II and III immediately produced red colored liquid ammonia solutions indicating the formation of the diphenylmethide and triphenylmethide ions.[5] On neutralization of the reaction mixtures with ammonium chloride, these silanes gave diphenylmethane (90%) and triphenylmethane (91%), respectively. No attempt was made to isolate the silicon products. In other experiments, the liquid ammonia was replaced by ether and Dry Ice added; silane II gave diphenylacetic acid (61%) and diphenylmethane (30%), and silane III gave triphenylacetic acid (20%) and triphenylmethane (72%).[6]

These cleavages appear to involve displacements on silicon (through the expansion of its octet) as represented by equations (1) and (2). In (1) the amide ion displaces the benzyl, diphenylmethyl or triphenylmethyl group (R) as an anion and, in (2), the anion of the trimethylaminosilane, which is formed in (1), displaces more of the hydrocarbon anion to form the disilazane (IV). The latter is probably converted by the alkyl anion (R^-) or by the amide ion to its anion. In the somewhat similar reaction of triethylsilane with potassium amide, Kraus and Nelson[7] obtained, in addition to hydrogen, the anion of hexaethyldisilazane (also called ditriethylsilicylamine).



$$(1)\quad (CH_3)_3Si—R + K^+NH_2^- \longrightarrow \left[\begin{array}{c}(CH_3)_3Si—R\\ |\\ NH_2\end{array}\right]^- K^+ \longrightarrow \begin{array}{c}(CH_3)_3SiNH_2 + K^+R^-\\ \downarrow\\ (CH_3)_3SiNH^-K^+ + RH\end{array}$$

I [R = $CH_2C_6H_5$]
II [R = $CH(C_6H_5)_2$]
III [R = $C(C_6H_5)_3$]

$$(2)\quad (CH_3)_3Si—R + (CH_3)_3SiNH^-K^+ \longrightarrow \left[\begin{array}{c}(CH_3)_3Si—R\\ |\\ HNSi(CH_3)_3\end{array}\right]^- K^+ \longrightarrow$$

$$\underset{\text{IV}}{[(CH_3)_3Si]_2NH} + K^+R^- \longrightarrow [(CH_3)_3Si]_2N^-K^+ + RH$$

In agreement with these equations, 11 mole per cent. of potassium amide gave with silane I twice this amount (22%) of toluene and 21% of the disilazane (IV) which was isolated as the azeotrope

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[1] The work was carried out under Contract N7onr-455 with the Office of Naval Research.

[2] See especially (a) G. Martin and F. S. Kipping, *J. Chem. Soc.*, **95**, 302 (1909); (b) R. H. Krieble and J. R. Elliot, THIS JOURNAL, **68**, 2291 (1946); and (c) H. Gilman, R. A. Benkeser and G. E. Dunn, *ibid.*, **72**, 1689 (1950).

[3] L. H. Sommer, L. J. Tyler and F. C. Whitmore, *ibid.*, **70**, 2872 (1948).

[4] R. O. Sauer and R. H. Hasek, *ibid.*, **68**, 241 (1946).

[5] Although silane II has a benzohydrilic hydrogen that might be ionized by the amide ion to produce a colored anion, silane III has no such active hydrogen and the color is undoubtedly due to the triphenylmethide ion formed on cleavage.

[6] This relatively low yield of triphenylacetic acid is rather surprising since the triphenylmethide ion has been carbonated in high yield under somewhat similar conditions. See R. Levine, E. Baumgarten and C. R. Hauser, THIS JOURNAL, **66**, 1230 (1944).

[7] C. A. Kraus and W. K. Nelson, *ibid.*, **56**, 195 (1934).

of the silanol and siloxane. Most (69%) of the original silane was recovered. Similarly, 35 mole per cent. of potassium amide produced with silane II almost twice this amount (62%) of diphenylmethane, 38% of the original silane being recovered.

Silanes I, II and III were found to be cleaved fairly readily by the more weakly basic sodium ethoxide in refluxing ethanol. Silanes II and III were cleaved completely by this reagent within four hours yielding diphenylmethane (87%) and triphenylmethane (97%), respectively. Silane I, however, was only partially cleaved after five hours, 58% of the silane being recovered. It was also found that refluxing alcoholic potassium hydroxide effected the complete cleavage of silane III within four hours. Silane I was partially cleaved by this reagent after seven hours, 39% of the silane being recovered.

Cleavages of this type depend not only on the strength of the basic anion but apparently also on the metallic cation and on the medium. In Table I are summarized the results obtained with silane III which was studied more extensively than the others. It can be seen from this table that sodium amide in liquid ammonia was as effective as potassium amide, whereas lithium amide brought about little if any cleavage under similar conditions. Moreover, potassium amide was effective in ether suspension, but sodium amide[8] and lithium amide were not. However, no differences were observed with lithium ethoxide, sodium ethoxide and potassium hydroxide all three of which were effective in refluxing ethanol. Diethylaminomagnesium bromide, ethylmagnesium bromide and butyl lithium in refluxing ether and sodium phenyl in benzene at 45° all failed to effect the cleavage of silane III.[9] Although the insolubility of the reagent in the medium might be an important factor in certain cases, these failures appear to be due mainly to the lack of sufficient dissociation of the organometallic compounds.[10]

TABLE I

REACTION OF TRIPHENYLMETHYLTRIMETHYLSILANE (III) WITH BASIC REAGENTS (EXCESS)

Reagent	Medium (reflux temp.)	Time, hr.	$(C_6H_5)_3CH$ yield, %
Potassium amide	Liq. ammonia	1	91
Sodium amide	Liq. ammonia	1	92
Lithium amide	Liq. ammonia	1	1–5
Potassium amide	Ether	4	30–40[a]
Sodium amide	Ether	5	None
Lithium amide	Ether	2	None
Sodium ethoxide	Ethanol	4	97
Lithium ethoxide	Ethanol	4	97
Potassium hydroxide	Ethanol	4	97
Diethylaminomagnesium bromide	Ether	7	None
Ethylmagnesium bromide	Ether	7	None
Butyllithium	Ether	6	None
Sodium phenyl	Benzene (45°)	2	None

[a] Isolated mostly as triphenylacetic acid (see experimental).

Experimental

Benzyltrimethylsilane (I).—This compound was prepared by a modification of the method of Gilman and Marshall.[11] To a stirred solution of 2.0 moles of benzylmagnesium chloride in 1300 ml. of anhydrous diethyl ether was added 103.5 g. (0.95 mole) of trimethylchlorosilane (b.p. 56–57°) in 500 ml. of ether. After 56 hours the mixture was saturated with carbon dioxide gas and hydrolyzed with 400 ml. of ice-cold 3 *N* hydrochloric acid. The ether phase was washed with 10% sodium carbonate (until free from phenylacetic acid), dried over Drierite and the solvent distilled. The residue was taken up in petroleum ether (b.p. 30–60°) and the solution washed successively with cold concentrated sulfuric acid, 10% sodium bicarbonate and finally water. After drying over Drierite and removing the solvent, the residue was distilled yielding 143 g. (91%) of (I), b.p. 95° at 34 mm.; $n^{25}D$ 1.4910. On redistillation at atmospheric pressure the product boiled at 190° (uncor.); $n^{25}D$ 1.4909 (reported b.p. 191.1–191.3 (cor.); $n^{24.7}D$ 1.4909).[12]

Diphenylmethyltrimethylsilane (II).—A suspension of potassium diphenylmethide in 500 ml. of ether, prepared from 49.0 g. (0.29 mole) of diphenylmethane (m.p. 24–25°) and 11.35 g. (0.29 g. atom) of potassium (through the amide),[13] was purged of ammonia by refluxing the ether and passing in nitrogen until the exit gases were neutral to litmus. To the stirred red suspension was added 31.4 g. (0.29 mole) of trimethylchlorosilane in 100 ml. of ether, the color changing almost immediately to pale orange. The mixture was stirred for 2 hours and allowed to stand overnight. The mixture was poured into 150 ml. of ice-water. The ether phase was washed with 50 ml. of 10% sodium bicarbonate, dried over Drierite, and the solvent distilled. The white solid residue was washed twice with cold 95% ethanol leaving 41.5 g. (60%) of (II), m.p. 73–75°. A sample recrystallized from ethyl ether melted at 74.5–75.5°, and boiled at 135° at 4 mm.

Anal.[14] Calcd. for $C_{16}H_{20}Si$: C, 79.90; H, 8.39. Found: C, 80.22; H, 8.61.

Triphenylmethyltrimethylsilane (III).—A suspension of potassium triphenylmethide in 500 ml. of ether, prepared from 68.5 g. (0.28 mole) of triphenylmethane (m.p. 92–93°) and 11.8 g. (0.30 g. atom) of potassium amide,[6] was purged of ammonia as described above in the preparation of (II). To the stirred red suspension was added 32.3 g. (0.297 mole) of trimethylchlorosilane in 100 ml. of ether, the red color being discharged within one hour. After standing overnight the mixture was worked up as described for (II) to give a semi-solid residue which was filtered with suction. The solid (37 g., m.p. 155–162°) was recrystallized several times from benzene to give 25.1 g. (28%) of pure (III) melting at 169.5–170.5°.

Anal.[14] Calcd. for $C_{22}H_{24}Si$: C, 83.49; H, 7.64. Found: C, 83.37; H, 7.43.

Cleavages by Alkali Amides (A) Cleavage of Silane I.—To approximately 250 ml. of anhydrous liquid ammonia (distilled from sodium) contained in a 500-ml. three-necked, round-bottomed flask fitted with a Dry Ice condenser, a glass stirrer (sealed by lubricated rubber tubing) and a dropping funnel was added 14.8 g. (0.38 g. atom) of clean potassium. The metal was converted (presumably quantitatively) to potassium amide by stirring with a trace of powdered rusty iron. To the stirred solution of the amide (0.38

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(8) Similarly, silane I failed to be cleaved by sodium amide in ether, 90% of the silane being recovered.

(9) Similarly, silane II failed to react when refluxed for seven hours with butyllithium in ether. In contrast to this Gilman and co-workers (ref. 2c) have found that trimethyl-9-fluorenylsilane, which presumably has a more active hydrogen than silane II, undergoes metallation with this reagent; the lithium derivative, on carbonation, formed a carboxylic acid which readily underwent cleavage.

(10) As Gilman and co-workers have already pointed out, the silicon carbon bond in certain compounds may be cleaved by butyllithium. Thus, the phenyl group of triphenylsilanol and hexaphenyldisiloxane is cleaved by this reagent (ref. 2c). It seems possible that this cleavage occurs because the lithium of the reagent may coördinate with the oxygen of the silane and thereby allow the reaction to proceed within a coördination complex; such a coördination is not possible with hydrocarbon silanes.

(11) H. Gilman and F. J. Marshall, THIS JOURNAL, **71**, 2066 (1949).

(12) Kraus and von Grosse, "Die Chemie der metallorganischen Verbindungen," Gebruder Borntraeger, Berlin, 1937, p. 263, Table 41.

(13) R. S. Yost and C. R. Hauser, THIS JOURNAL, **69**, 2325 (1947).

(14) Analyses by Clark Microanalytical Laboratory, Urbana, Ill.

mole) was added 50.8 g. (0.308 mole) of silane I in 50 ml. of ether and the stirring continued for one hour. The Dry Ice condenser was replaced by a water condenser and the liquid ammonia evaporated as rapidly as possible on the steam-bath, ether being added to maintain the volume at 300 ml. The resulting ether suspension was decomposed with carbon dioxide gas followed by water. The ether phase was washed with 10% sodium bicarbonate, followed by water and dried over Drierite. After removing part of the solvent on the steam-bath, the solution (about 250 ml.) was fractionated through a 90-cm. glass helices packed column to give: (1) 10.8 g., b.p. 89–90°, $n^{20.5}_D$ 1.3840; (2) 4.0 g., b.p. 90–109°, n^{20}_D 1.4450; (3) 17.6 g., b.p. 109–110°, n^{20}_D 1.4938; (4) 2.0 g., b.p. 110–120°; and (5) 3.4 g., b.p. 126–130°, $n^{20.5}_D$ 1.4096. Fraction (1) was identified as an azeotrope of trimethylsilanol and hexamethyldisiloxane (reported b.p. 90.4–90.6°, n^{20}_D 1.3800)[15]; yield 43%. On treatment with sulfuric acid the mixture was converted entirely to hexamethyldisiloxane boiling at 100°. Fraction (3) was identified as toluene (66%) by oxidation to benzoic acid (m.p. and mixed m.p. 121.5–122.0°). The yield of toluene is raised to 77% if fractions (2) and (4) are interpolated. Fraction (5) appeared to be hexamethyldisilazane (14%) (reported b.p. 126.2°, n^{20}_D 1.4078).[15] A qualitative nitrogen test was positive. None of the original silane was recovered.

When 33.4 g. (0.203 mole) of silane I was allowed to react with only 0.022 mole of potassium amide under similar conditions, there was isolated 3.7 g. (21%) of azeotrope, b.p. 85–105°; 4.2 g. (22%) of toluene, b.p. 108–120°; and 23 g. (69%) of silane I, b.p. 180–189°.

(B) **Cleavage of Silane II.**—To 0.06 mole of potassium amide, prepared in 200 ml. of liquid ammonia as described above (300-ml. flask), was added 4.5 g. (0.019 mole) of silane II in 40 ml. of ether. After stirring one hour the mixture was acidified with excess solid ammonium chloride (4 g.) and the ammonia replaced by ether. The ether suspension was filtered and the solvent distilled from the filtrate. Distillation of the residue yielded 2.84 g. (90%) of diphenylmethane, b.p. 262–265°. None of the original silane was recovered.

In another experiment 4.70 g. (0.02 mole) of silane II was allowed to react with 0.06 mole of potassium amide in ammonia for one hour. The ammonia was replaced by ether and the mixture carbonated with excess powdered Dry Ice. After standing several hours the mixture was poured into 100 ml. of water. The ether phase was extracted with two 50-ml. portions of 10% sodium carbonate and 50 ml. of water, dried over Drierite and the solvent distilled leaving 1.0 g. (30%) of diphenylmethane, b.p. 260–265°. The aqueous extracts were combined, washed with 40 ml. of ether, and acidified with hydrochloric acid yielding diphenylacetic acid, m.p. and mixed m.p. 144–146°; yield 2.5 g. (61%).

When 5.40 g. (0.0225 mole) of silane II was allowed to react with only 0.008 mole of potassium amide (made from 0.33 g. of potassium) and the mixture carbonated, there was obtained 2.34 g. (62%) of diphenylmethane, b.p. 259–265°; 2.05 g. (38%) of silane II (m.p. 72–75°) being recovered. No diphenylacetic acid was isolated.

(C) **Cleavage of Silane III.**—This silane (3.37 g., 0.01 mole) was allowed to react with 0.027 mole of potassium amide in liquid ammonia and, after one hour, the mixture was acidified with ammonium chloride as described for silane II. On removal of the solvent from the ether solution, there was obtained 2.30 g. (91%) of triphenylmethane (m.p. and mixed m.p. 91.5–93°). None of the original silane was recovered.

When 7.73 g. (0.025 mole) of silane III and 0.10 mole of potassium amide were allowed to react and the mixture carbonated as described for silane II, there was isolated 1.40 g. (20%) of triphenylacetic acid (m.p. and mixed m.p. 263–265°), and 4.29 g. (72%) of triphenylmethane (m.p. 91.5–93.5°).

In another experiment the last traces of ammonia were removed from an ether suspension of 0.05 mole of potassium amide by refluxing the mixture for 40 hours and passing in nitrogen. To the ammonia free suspension was added 2.0 g. (0.006 mole) of silane III. After ten minutes at room temperature the color of the mixture became red (indicating the formation of triphenylmethide ion) and ammonia began to be evolved (as indicated by a test with moist litmus at the upper end of the condenser). After four hours the mixture was carbonated with powdered Dry Ice and the products worked up as described for silane II. There was isolated 0.57 g. (31%) of phenylacetic acid, m.p. and mixed m.p. 262–264°, and material (1.40 g.) melting at 145–159°, which, judging from mixed melting point determinations with silane III and triphenylmethane, consisted of 80–90% of recovered silane III and 10–20% of the hydrocarbon.

Similar experiments were carried out with silane III and excess sodium amide and lithium amide in liquid ammonia (one hour) and in ether (4–5 hours). The reactions in ether failed, 95–96% of silane III being recovered. In liquid ammonia the reaction with sodium amide gave the deep red color, characteristic of the triphenylmethide ion, and there was isolated a 92% yield of triphenylmethane, m.p. 89–93°. With lithium amide in liquid ammonia, however, only a slight pink color developed and there was recovered 92% of silane III, melting at 159–169°. This wide melting range indicated that the silane was contaminated with triphenylmethane to the extent of 1–5%.

Cleavage by Alkoxides and Hydroxides (A) Cleavage of Silane I.—To approximately 0.244 mole of sodium ethoxide in 100 ml. of absolute ethanol contained in a 200-ml. round-bottomed flask equipped with a 90-cm. glass helices packed fractionating column was added 17.3 g. (0.105 mole) of silane I. The solution was refluxed for five hours, 4.0 g. of material, b.p. 67–69°, $n^{20.5}_D$ 1.3738, being collected through the fractionating column. The column was operated at total reflux except when the reflux temperature dropped below 68°, then cuts were taken as long as the temperature remained constant. This material corresponds to an azeotrope of trimethylethoxysilane and ethanol (reported b.p. 66.4°, n^{20}_D 1.3729).[15] The undistilled mixture in the flask was cooled and neutralized with dilute hydrochloric acid (to phenolphthalein end-point). Water was added until no more organic liquid separated. The aqueous layer was discarded and the dried organic material distilled to give 10.0 g. (58%) of silane I, b.p. 189–190°.

In a similar manner, a solution of 15.3 g. (0.093 mole) of silane I and 0.2 mole of potassium hydroxide was refluxed for seven hours, 5.3 g. of azeotrope (b.p. 66–68°, $n^{20.5}_D$ 1.3756) being collected. There was recovered 6.0 g. (39%) of silane I, b.p. 187–189°.

(B) **Cleavage of Silanes II and III.**—To 0.04 mole of sodium ethoxide in 100 ml. of absolute ethanol in a 200-ml. round-bottomed flask equipped with an ordinary reflux condenser was added 3.6 g. (0.015 mole) of silane II and the solution refluxed for four hours. On neutralization of the solution with dilute hydrochloric acid, followed by addition of an equal volume of water, there was isolated 2.2 g. (87%) of diphenylmethane, b.p. 260–264°.

In a similar manner 3.9 g. (0.012 mole) of silane III was refluxed four hours with 0.048 mole of sodium ethoxide in 100 ml. of ethanol. There was obtained 2.90 g. (97%) of triphenylmethane, m.p. 91–92°. Essentially the same results were obtained in an analogous experiment with lithium ethoxide in ethanol.

Similarly 4.4 g. (0.014 mole) of silane III was cleaved by 0.032 mole of potassium hydroxide in 100 ml. of refluxing absolute ethanol in four hours, yielding 3.31 g. (97%) of triphenylmethane, m.p. 89–92°.

Attempted Cleavage of Silane III by Other Basic Reagents.—This silane was recovered (94–96%) after refluxing five to seven hours in ether solutions of excess diethylaminomagnesium bromide,[16] ethylmagnesium bromide and butyllithium[17] followed by decomposition with dilute hydrochloric acid.

Similarly silane III was recovered unchanged after refluxing six hours with excess butyllithium followed by carbonation with Dry Ice.

Silane III was also recovered (87%) after stirring two hours at 45° with excess sodium phenyl (prepared from sodium sand and chlorobenzene) in benzene, followed by carbonation (carbon dioxide gas). An alkaline extract of the reaction mixture gave, on acidification, benzoic acid (69%).

DURHAM, NORTH CAROLINA RECEIVED MAY 28, 1951

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[15] R. O. Sauer, THIS JOURNAL, **66**, 1707 (1944).

[16] C. R. Hauser and H. G. Walker, *ibid.*, **69**, 295 (1947).

[17] H. Gilman, E. A. Zoellner and W. M. Selby, *ibid.*, **54**, 1957 (1932).