The use of 200 cc. of ethylene dichloride instead of the carbon disulfide in the above preparation allows better stirring. The yield of product in this case was 44 g.

Semicarbazone of (I).—This was prepared by heating on a steam-bath under reflux for three hours a mixture of 4.7 g. of (I), 25 cc. of ethanol, 15 cc. of water, 7 g. of sodium acetate and 5.5 g. of semicarbazide hydrochloride. The product was allowed to stand several days at 5° and the white crystalline deposit filtered off. It was recrystallized three times from water to a constant melting point of 194–195° and dried *in vacuo* at 100° for analysis.

Anal. Calcd. for $C_{15}H_{26}O_2N_4$: C, 61.22; H, 8.84; N, 19.04. Found: C, 61.55; H, 9.27; N, 19.00.

A mixed melting point with the semicarbazone of 2-cyclohexenylcyclohexanone of m. p. 195–196° showed a 15° depression.

Oxime of (I).—This was prepared by heating on a steam-bath under reflux for three hours a mixture of 2 g. of (I), 30 cc. of ethanol, 30 cc. of water, 3.3 g. of sodium acetate and 1.7 g. of hydroxylamine sulfate. Since the product did not crystalline on cooling, the solution was evaporated to dryness *in vacuo* and extracted with ether. Upon evaporation of the ether extract a soft mass was obtained which solidified when rubbed with 20 cc. of petroleum ether. The solid material was recrystallized from nitromethane and then from petroleum ether (b. p. 90–100°) to form white crystals, m. p. 163–164°.

Anal. Calcd. for $C_{14}H_{24}O_2N_2$: C, 66.66; H, 9.52; N, 11.11. Found: C, 66.53; H, 9.66; N, 10.85.

(I) **Condensation of Acetonitrile with 2-Cyclohexenylcyclohexanone.**—To a stirred suspension of 89.5 g. of powdered, sublimed, anhydrous aluminum chloride in 150 g. of ethylene dichloride, there was added dropwise a mixture of 27.5 g. of acetonitrile and 118 g. of 2-cyclohexenylcyclohexanone[2] while cooling the reaction mixture to 20–30°. After stirring for twenty-one hours at room temperature the mixture was added to chipped ice and the oil layer separated, washed with water and dried *in vacuo*. The residual oil (109 g.) was distilled under reduced pressure and the fraction boiling at 175–225° (0.5–1 mm.) was collected; yield 17 g. It was recrystallized from petroleum ether (b. p. 90–100°) and formed white crystals, m. p. 140–141°, which gave no depression in melting point with the product (I) obtained from cyclohexanone and acetonitrile.

Hydrolysis of (I).—A mixture of 1000 g. of 10% sulfuric acid and 179 g. (I), prepared from cyclohexanone and acetonitrile was blown with steam for five hours and the distillate (3500 cc.) collected. The oil layer was separated from the distillate and the aqueous layer extracted with ether. The combined oil and ether extract upon distillation *in vacuo* at 10 mm. yielded 52 g. of 2-cyclohexenylcyclohexanone, b. p. 133–136° (10 mm.), identified by its semicarbazone, m. p. 194–195°, and by its mixed melting point with an authentic sample of the semicarbazone of 2-cyclohexenylcyclohexanone of m. p. 195–196° with which it gave no significant depression.

(II) **Condensation of Cyclohexanone with Benzonitrile.**—The procedure given for (I) above was followed, using 133.5 g. of anhydrous aluminum chloride, 300 cc. of ethylene dichloride, 103 g. of benzonitrile and 196 g. of cyclohexanone. The crude product was a brown oil weighing 264 g. Upon extraction with hot petroleum ether (b. p. 90–100°) a light brown powder (82 g.) was left behind as a residue. This was recrystallized several times with considerable loss from petroleum ether and finally from ethylcyclohexane to a constant m. p. 120–121°.

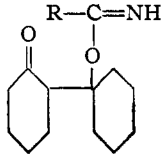
Anal. Calcd. for $C_{19}H_{25}O_2N$: C, 76.25; H, 8.36; N, 4.68. Found: C, 76.74; H, 8.58; N, 4.66.

(III) **Condensation of Propionitrile with Cyclohexanone.**—The procedure given for (I) above was applied to a mixture of 133.5 g. of anhydrous aluminum chloride, 200 cc. of ethylene dichloride, 55 g. of propionitrile and 196 g. of cyclohexanone. The crude product was a brown oil (154 g.) which gradually crystallized in part after several days standing. The sticky crystalline product was spread out on porous tile which absorbed the oily impurity leaving about 80 g. of pinkish crystals. This material was recrystallized from petroleum ether (b. p. 90–100°) to a constant m. p. 92–93°; yield 60 g.

Anal. Calcd. for $C_{15}H_{25}O_2N$: C, 71.71; H, 9.96; N, 5.68. Found: C, 71.88; H, 10.18; N, 5.55.

Summary

Cyclohexanone condenses in the presence of aluminum chloride with nitriles R–CN to yield crystalline compounds which appear to be iminoethers of the aldol of cyclohexanone having the general formula



Philadelphia, Pa. Received September 11, 1947

---

[2] Hückel, Neunhoffer, Gerche and Frank, *Ann.*, **477**, 119 (1930).

[Contribution from the School of Chemistry and Physics of The Pennsylvania State College]

A New Synthesis of Organosilicon Compounds[1]

By F. W. Pietrusza,[2] L. H. Sommer and F. C. Whitmore

In a previous communication[3] we reported the preparation of *n*-octyltrichlorosilane in almost quantitative yield from the reaction of 1-octene with trichlorosilane in the presence of a small amount (7 mole %) of diacetyl peroxide. The use of a weak ultraviolet source as the catalyst gave a 24% yield.

$$RCH{=}CH_2 + SiHCl \xrightarrow[\text{or U. V. L.}]{(CH_3COO)_2} RCH_2CH_2SiCl_3 \quad (1)$$

In extension of these results, the present paper reports that this new synthesis[4] is generally applicable to the addition of $SiHCl_3$ to olefins of varied structure, *i. e.*, $RCH{=}CH_2$, $RCH{=}CHR$, $R_2C{=}$

---

[1] Paper XV in a series on organosilicon compounds. See This Journal, **70**, 445 (1948), for XIV.

[2] This paper comprises part of the subject matter of a thesis submitted by E. W. Pietrusza in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the Graduate School of The Pennsylvania State College. Allied Chemical and Dye Corporation Fellow 1945–1947.

[3] Sommer, Pietrusza and Whitmore, This Journal, **69**, 188 (1947).

[4] An excellent treatment of other syntheses of organosilicon compounds is given in Rochow, "Introduction to the Chemistry of the Silicones," John Wiley and Sons, New York, N. Y., 1946, pp. 18–30.

TABLE I

ADDITION OF TRICHLOROSILANE TO OLEFINS

Olefin[k]	Cat.	Reaction Temp., °C.	Reaction Time, hr.	Product[h]	B. p. °C.	Mm.	$n^{20}D$	Anal. % Cl[f] Calcd.	Anal. % Cl[f] Found	Yield, %
1-Octene	A[a]	50–63	9	$CH_3(CH_2)_5CH_2CH_2SiCl_3$	231–232	(731)	1.4480	43.0	43.0	99.0
1-Octene[j]	L[b]	44–74	40	$CH_3(CH_2)_5CH_2CH_2SiCl_3$	232	(727)	1.4480	43.0	42.8	47.0
2-Octene	A	50–62	18	$C_8H_{17}SiCl_3$	222–223	(721)	1.4532	43.0	42.8	99.0
2-Methyl-1-heptene	A	49–58	25	$CH_3(CH_2)_5CH(CH_3)CH_2SiCl_3$	221–222	(736)	1.4500	43.0	42.8	70.0
2-Methyl-2-butene	A	41–45	20	$C_5H_{11}SiCl_3$	163–167	(729)	1.445	51.9	51.8	24.6
2-Methyl-2-butene[j]	L	42–52	45	$C_5H_{11}SiCl_3$	164–165	(736)	1.4503	51.9	52.1	64.0
2-Methyl-1-propene[j]	L	25–30	135	$CH_3CH(CH_3)CH_2SiCl_3$	145–146	(730)	....	55.6	53.3	5.0
2,3-Dimethyl-2-butene	A	45–53	23	$CH_3CH(CH_3)C(CH_3)_2SiCl_3$[i]	186–187	(728)	1.4631	48.6	48.3	59.3
2,4,4-Trimethyl-1-pentene	A	49–50	15	$C_8H_{17}SiCl_3$	207–208	(721)	1.4478	43.0	42.8	9.1
2,4,4-Trimethyl-2-pentene	A	49–52	42	$C_8H_{17}SiCl_3$	219–220	(731)	1.4667	43.0	42.7	9.3
1,1-Dineopentylethylene	A	50–60	27	$C_{12}H_{25}SiCl_3$	260–275	(739)	1.4581	35.2	31.2	1.6
Allyl chloride	A	43–47	27	$C_3H_6SiCl_4$	165–166	(721)	1.451	50.2[g]	50.5	20.4
Allyl chloride	L	41–43[d]	45	$C_3H_6SiCl_4$	165–180	(726)	....	50.2	51.3	8.4

[a] Diacetyl peroxide, 3.8 mole%, based on olefin used. [b] Ultraviolet light applied externally. [c] Reaction was performed in a Vycor flask. (1-Octene when placed in a Pyrex flask and exposed to ultraviolet light for seventy-two hours gave a 24.3% yield of product, and when placed in a quartz flask and exposed to ultraviolet light for twenty-four hours gave a 31% yield of product.) [d] Quartz flask. [e] Pyrex glass, sealed ampule. [f] Values were obtained by treating a weighed sample with excess standard base and back-titrating with standard acid. [g] In this case, only the chlorines attached to silicon are neutralized by 0.1 *N* base. See Sommer, Dorfman, Goldberg and Whitmore, THIS JOURNAL, 68, 488 (1946). [h] Empirical formulas are given when the mode of addition of $SiHCl_3$ is uncertain. [i] F. p. 15–16°. [j] 0.2 mole. [k] 0.33 mole.

CH_2, $R_2C{=}CHR$, $R_2C{=}CR_2$, where R is alkyl, and to allyl chloride.

Olefins having these structures give excellent yields of the alkyltrichlorosilane when R is a straight-chain group such as methyl, *n*-amyl, or *n*-hexyl. However, if R is a highly-branched group, such as *t*-butyl or neopentyl, with the branching close to the olefinic linkage, the yield is considerably reduced. The low yield of isobutyltrichlorosilane may possibly be due to the volatile nature of the olefin which in our case necessitated the use of a low reaction temperature.

Comparison experiments using peroxide and ultraviolet light as catalysts indicate that the former generally gives faster reaction. However, use of the latter with 2-methyl-2-butene gave a better yield of product.

It is of interest that the alkyltrichlorosilanes formed in these reactions are incapable of undergoing further reaction with olefins under the conditions used. This leads in most cases to a product of high purity. In this respect the present method compares favorably with the Grignard method and the direct method which generally give mixtures of alkylchlorosilanes.[4]

The synthesis of 1,1,2-trimethylpropyltrichlorosilane from 2,3-dimethyl-2-butene and trichlorosilane is of interest, since reported preparations of tertiary alkyl silicon compounds have previously been limited to the use of tertiary alkyl lithium compounds[5] which are somewhat difficult to prepare in good yield.

The results of a preliminary study of the reactions of 1-octene with silicon hydrides other than trichlorosilane indicate that the latter reacts far more readily. *n*-Propyldichlorosilane gave a low yield (6%) of impure product when diacetyl peroxide was used. Triethoxysilane gave no reaction using either catalyst. Triethylsilane gave no reaction using peroxide, and a low yield of impure product (3%) when light was used. Diethylsilane gave a fair yield of a product which appeared to be mainly the mono addition product, but which could not be purified because of the small amount of starting material used.

Silicon tetrachloride failed to react with 1-octene using either catalyst.

While no detailed proof is available for the formulation of the addition of trichlorosilane to olefins as a free-radical chain reaction,[3] such an assumption seems reasonable on the basis of the following points: (1) Extensive evidence for the decomposition of diacetyl peroxide and other peroxides into free radicals on heating is beyond question. (2) Catalysis by ultraviolet light is evidence for a free-radical mechanism. (3) The small amounts (3.8 mole %) of diacetyl peroxide used in the present syntheses leave little doubt that these are chain reactions.

Experimental

Trichlorosilane was prepared in excellent yield by passing dry hydrogen chloride over ferrosilicon.[6] The olefins used were synthesized and carefully purified by Dr. N. C. Cook of this laboratory, who kindly donated samples for this study. Crystalline diacetyl peroxide

---

(5) Tyler, Sommer and Whitmore, THIS JOURNAL, 69, 981 (1947)

(6) See Whitmore, Pietrusza and Sommer, *ibid.*, 69, 2108 (1947), for the procedure used and for references to earlier preparations.

was prepared by the method of Gambarjan as modified by Kharasch,[7] and dissolved in the olefin used. The peroxide content was determined by analysis.[8]

A detailed description of the procedure used in a typical trichlorosilane addition to an olefin is given. Essentially this same procedure was employed for the reactions given in Table I.

Olefin, Trichlorosilane and Diacetyl Peroxide.—1-Octene, 17.9 g., 0.16 mole, and trichlorosilane, b. p. 32°, 135.5 g., 1.0 mole, were placed in a three-necked flask with dropping funnel, thermometer, and a reflux condenser connected through a trap cooled in Dry Ice–acetone to a mercury seal 20 cm. in height. The system was swept with nitrogen for two hours, and the reaction mixture was heated to 45° under the slight extra pressure of the mercury. Crystalline diacetyl peroxide, 1.5 g., 0.013 mole, dissolved in 19.1 g., 0.17 mole, of 1-octene was then added during two hours. The mixture was heated at 50–63° for an additional nine hours.

After removal of excess trichlorosilane, the residue was distilled at reduced pressure and then redistilled at atmospheric pressure, giving 80.9 g. of clear colorless liquid, b. p. 231–232° at 728 mm., $n^{20}D$ 1.4480, 99% yield.

Anal. Calcd. for $C_8H_{17}SiCl_3$: Cl, 43.0. Found: Cl, 42.9, 43.0.

n-Octyltrichlorosilane from silicon tetrachloride and *n*-octylmagnesium bromide boils 233° at 731 mm.; 119° at 28 mm.[9]

Treatment of a portion of the product with ethanolic potassium hydroxide gave no hydrogen, indicating the absence of Si-H bonds.[10]

Reaction of the product, 24.8 g., 0.1 mole, with 0.35 mole of methylmagnesium bromide (using a procedure known to form the tetraalkylsilane from *n*-octyltrichlorosilane)[9] gave 13.0 g. of *n*-octyltrimethylsilane, b. p. 201.5° at 733 mm., $n^{20}D$ 1.4242, 74% yield. Constants for this compound[9] are: b. p. 202° at 760 mm., $n^{20}D$ 1.4242. All the data thus conclusively confirm equation (1).

Olefin, Trichlorosilane, and Ultraviolet Light.—1-Octene, 22.4 g., 0.2 mole, and trichlorosilane, 81.3 g., 0.6 mole, were placed in a 500 cc. quartz flask with thermometer and a reflux condenser connected through a trap cooled in Dry Ice–acetone to a mercury seal of 20 cm. height. The system was swept with nitrogen for a half hour, and the reaction mixture was heated to 46° under the slight extra pressure of the mercury. Ultraviolet light was applied from an external source and the solution was heated for twenty-four hours at a temperature range of 46–52°.

After removal of excess trichlorosilane, the residue was distilled at reduced pressure and then redistilled at atmospheric pressure, giving 15.3 g. of clear, colorless liquid, b. p. 231–232° at 728 mm., $n^{20}D$ 1.4481, 31% yield.

Anal. Calcd. for $C_8H_{17}SiCl_3$: Cl, 43.0. Found: Cl, 42.8, 42.9.

Treatment of a portion of the product with ethanolic potassium hydroxide gave no hydrogen, indicating the absence of Si-H bonds.[10]

The above product corresponds completely to the product of the peroxide catalyzed reaction. When ultraviolet light is applied for longer periods of time, better yields of the octyltrichlorosilane are obtained.

Reactions of 1-Octene with Other Silicon Hydrides.—These were carried out under essentially the same conditions as those described above.

Summary

1. A new synthesis of organosilicon compounds is described which involves the addition of trichlorosilane to olefins differing widely in structural type. These reactions are catalyzed by small amounts of diacetyl peroxide or ultraviolet light.

2. New alkyltrichlorosilanes of varying complexity were prepared by this method in good yield.

STATE COLLEGE, PA. RECEIVED MAY 28, 1947

---

[7] (a) Gambarjan, *Ber.*, **42**, 4010 (1909); (b) Kharasch, *J. Org. Chem.*, **10**, 393 (1945).

[8] Kokatnur and Jelling, THIS JOURNAL, **63**, 1432 (1941).

[9] Whitmore, Sommer, DiGiorgio, Strong, Van Strien, Bailey, Hall, Pietrusza and Kerr, THIS JOURNAL, **68**, 475 (1946).

[10] *Cf.* Sauer, Scheiber and Brewer, *ibid.*, **68**, 962 (1946).

[CONTRIBUTION FROM THE NAVAL RESEARCH LABORATORY, WASHINGTON, D. C.]

Reaction of Lithium Aluminum Hydride with Compounds Containing Active Hydrogen

BY J. A. KRYNITSKY, J. E. JOHNSON AND H. W. CARHART

The new compound, lithium aluminum hydride, discovered by Finholt, Schlesinger, *et al.*,[1,2] has been shown to be a vigorous agent for the reduction of various types of organic compounds.[3] In addition, many compounds containing active hydrogen decompose the reagent to liberate hydrogen. The purpose of this investigation was to study the latter type of reaction and to explore the possibility of using lithium aluminum hydride as a reagent for the determination of active hydrogen.

In a previous study, it was found that ether solutions of lithium aluminum hydride could be analyzed quantitatively by decomposing with excess water at 0° and measuring the evolved hydrogen by changes in pressure.[4] In the present work, an apparatus was devised so that a known amount of material could be added to an excess of lithium aluminum hydride–ether solution at 0° and the liberated gas measured by changes in pressure. By this method, the apparent active hydrogen content of a number of organic compounds was determined.

Experimental

Apparatus.—A diagram of the apparatus used is shown in Fig. 1. The reaction flask consisted of a 500-ml. round-bottom flask bearing a 35/20 spherical socket joint. A take-off arm was attached to the neck and connected to a manometer by small bore tubing through a T-tube. The T-tube was joined to a drying tube with rubber tubing which could be closed by a pinch clamp. The reaction flask was closed by a spherical ball joint carrying a 12 × 130 mm. guide tube. A clamp with an efficient locking

---

[1] Finholt, Schlesinger and Wilzbach, Division of Physical and Inorganic Chemistry, A. C. S., Chicago Meeting, September, 1946.

[2] Finholt, Bond and Schlesinger, THIS JOURNAL, **69**, 1199 (1947).

[3] Nystrom and Brown, *ibid.*, **69**, 1197 (1947).

[4] Krynitsky, Johnson and Carhart, *Anal. Chem.*, in press.