Rate increases in the latter instances were probably the result of appreciable increases in ionizing power of the solvent, to which the S_N1 reaction is very sensitive.

TABLE II

ARRHENIUS PARAMETERS AND DERIVED DATA

Compound	E_a kcal. mole^{-1} ($\pm$0.20)	$\log_{10} A$ ($\pm$0.1)	$\Delta\Delta H^+$ kcal. mole^{-1}	$T\Delta\Delta S^{\ddagger}_{25°}$ kcal. mole^{-1}
I	20.45	11.67	−1.01	0.30
II	21.04	12.01	−0.43	0.76
IV	21.47	11.45	(0.00)	(0.00)
V	23.38	11.24	1.91	−0.29
VI	23.32	11.17	1.85	−0.38
VII	23.20	10.00	1.73	−1.97

In calculating ρ for the reaction, only *meta* substituent data were used and the linear plot of $\log_{10} k_{25°}$ *versus* σ was fully satisfactory. Relevant information on the plot is given by the figures: $\rho = -4.030$; $r = 0.996$; $s = 0.14$; $n = 5$, where the symbols have their standard significance.[7]

Where comparison is possible, the rate constants of Hughes, Ingold, and Taher are consistently higher than those of Norris by a reasonably constant difference which has been commented upon by the first-named group. The value now reported for diphenylcarbinyl chloride agrees closely with that of Hughes *et al.* and a "correction" factor has been applied to the results of Norris to make them comparable with the data of Hughes and of the present work. Results then lead to the figures in Table III.

TABLE III

σ^+ PARAMETERS

Substituent	$k_{25°} \times 10^5$ (sec.$^{-1}$)	σ^+ (Present Work)	σ^+ (Okamoto & Brown)
m-NO_2	0.0103[a]		
m-Cl	0.124[a]		
m-Br	0.132[a]		
m-CH_3	13.7[a]		
H	5.41[a]		
3:4-C_6H_4	40.3[a]	−0.207	−0.132
p-CH_3	123.0[b]	−0.327	−0.306
p-C_2H_5	120.0[b]	−0.324	−0.291
p-*iso*-C_3H_7	106.0[b]	−0.311	−0.276
p-*tert*-C_4H_9	98.7[b]	−0.303	−0.250
p-Cl	1.48[c]	−0.158	−0.112
p-Br	1.23[c]	−0.179	−0.148
p-OC_6H_5	1170.0[c]	−0.555	−0.63[d]
p-C_6H_5	50.2[c]	−0.218	−0.12[d]

[a] Present work. [b] Ref. 4. [c] Refs. 5 and 6. [d] See ref. 3.

Agreement between the last two columns is seen to be good. The effect of the 3:4 C_6H_5 substituent in a number of reactions is currently being reviewed by us and comment on this substituent is at present withheld.

Acknowledgment. The authors are grateful to the Research Committee of the University of New Zealand for financial assistance and to Dr. A. D. Campbell for the microanalyses.

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF CANTERBURY
CHRISTCHURCH, NEW ZEALAND

Reactions of Some Organochlorosilanes in Acetone

TOSHIO TAKIGUCHI

Received February 4, 1958

The author wishes to report on the conversion of some organochlorosilanes to siloxanes in acetone. When solutions of organochlorosilanes in acetone are allowed to stand at room temperature for extended periods, conversion to organopolysiloxanes occurs, all of the silicon-chlorine bonds being replaced by silicon-oxygen bonds.

EXPERIMENTAL

Reagents and general procedure. Silicon tetrachloride (hereafter called STC), methyltrichlorosilane (MTS), dimethyldichlorosilane (DDS), diphenyldichlorosilane (DPDS) provided in purified grades by the Shin-etsu Chemical Industrial Company were used. Acetone was purified according to the ordinary method; titration with Karl Fischer reagent showed 0.2% (mean) water content. Each solution of the chlorosilane in acetone was enclosed in a Pyrex glass tube of 2 cm. in diameter and 15 cm. in length and allowed to stand at room temperature. After several days, the solution developed a yellowish color which became dark gradually. Ultimately it turned dark red, nearly black, and at the same time the corresponding polysiloxane was formed. The time required for these changes, and the character of polysiloxane finally formed, varied with the concentration and with the chemical identity of the chlorosilane used, but much more with the water content of acetone used. For example, the addition of a small amount of water (or methanol) to the initial mixture promoted the coloration and the formation of polysiloxanes remarkably.

The reactions of individual silanes in acetone thus observed are described below.

STC, MTS. Each of them shows an entirely similar reaction in acetone; solutions in acetone finally form dark red gels. Especially when the solution consists of 1 mole of silane and 3–5 moles of acetone, the whole mixture solidifies, transforming into a dark red, brittle gel. The reaction takes a period of 3 or 4 weeks. In a previous publication,[1] this red gel was described as an addition compound of STC and acetone, but no information about its structure or composition was given.

The author now concludes that these red gels are polysiloxane $(SiO_2)_n$ and methylpolysiloxane $(CH_3SiO_{1.5})_n$, respectively. For evidence, the gel was decolorized gradually on being extracted with fresh acetone, ultimately turned to white and translucent, while acetone acquired a deep red color and emitted a characteristic terpene-like odor. The X-ray powder pattern for white gels showed broad halos

---

[7] H. H. Jaffé, *Chem. Revs.*, **53**, 191 (1953).

[1] W. R. Trost, *Nature*, **169**, 289 (1952).

at 3.90 Å (for gel from STC), at 4.09 Å (for gel from MTS) respectively, in good agreement with those of two polysiloxanes prepared by direct hydrolysis of STC and of MTS.

Anal. For STC gel (Calcd. for $n\text{SiO}_2$: Si, 46.75; Found: Si, 46.54), for MTS gel (Calcd. for $n\text{CH}_3\text{SiO}_{1.5}$: Si, 41.85; Found: Si, 41.57). No chlorine was detected by an argentometric titration carried out after ignition with sodium peroxide.

On shaking the red acetone with 5% sodium hydroxide solution, a deep red oily layer was separated at the top, from which mesityl oxide (b.p. 131°/760 mm., d_D^{25} 0.8535) was isolated; the distillation residue was a tarlike, black material from which no pure substances were isolated hitherto. It is considered to be a high order condensation product of acetone.

DDS. From DDS solution in acetone, when it contained not less than 5 moles of acetone per 1 mole of DDS, a colorless transparent oily layer separated at the bottom after standing for about 2 weeks. Fractional distillation under atmospheric pressure showed that it consisted of hexamethylcyclotrisiloxane (b.p. 134°/760 mm.), octamethylcyclotetrasiloxane (b.p. 175°/760 mm., n_D^{25} 1.3966) as the main products, and of higher polymers of dimethylsiloxane. The polymer fraction was very difficult to purify, because it gave no distillate below 200° under 2 mm. and its molecular weight changed (measured cryoscopically in benzene) on heating.

DPDS. From DPDS solution in acetone, hexaphenylcyclotrisiloxane (hereafter called trimer) crystallized upon standing. From a solution of suitable composition (*e.g.* DPDS, 8 g.; acetone, 25 g.; chloroform, 5 g.), trimer was obtained as large hexagonal plates of 5–10 mm. in width. Thorough investigations[2] on the relation between mixing ratio and yield of trimer, have been made recently in this laboratory. Properties of trimer produced here are as follows: m.p. 189°, d_4^{25} 1.23, mol. wt. 579–609 (in benzene).

Anal. Calcd. for $C_{36}H_{30}Si_3O_3$: Si, 14.16; C, 72.68; H, 5.09. Found: Si, 14.06; C, 72.77; H, 4.83.

The X-ray powder pattern data are in complete agreement with those given by Hyde[3] as type I_3 (trimer in orthorhombic system).

When non-purified acetone was used, the trimer was obtained much sooner (2 or 3 days after mixing, with the yield of 80% max.). These results would suggest that this "acetone method" is a convenient method for preparation of the trimer which is usually synthesized after the method of Burkhard.[4]

Reaction of other ketones. The author confirmed the statement by Rochow and Gingold[5] that acetophenone did not react with any of the chlorosilanes. Methyl ethyl ketone was found to react with chlorosilanes used here in just the same manner of acetone, except that the siloxane formation was far slower and the color developed was a dark somewhat greenish red.

Acknowledgment. The helpful discussions with Dr. F. Hirata, in whose laboratory this work was carried out, and the generous supply of silanes by the Shin-etsu Chemical Industrial Company are greatly appreciated.

DEPARTMENT OF APPLIED CHEMISTRY
FACULTY OF TECHNOLOGY
GUMMA UNIVERSITY
KIRYU, JAPAN

---

(2) T. Takiguchi, *J. Chem. Soc. Japan (Ind. Chem. Sect.)*, **61**, 478 (1958).

(3) J. F. Hyde, L. K. Frevel, H. S. Nutting, P. S. Petrie, and M. A. Purcell, *J. Am. Chem. Soc.*, **69**, 488 (1947).

(4) C. A. Burkhard, *J. Am. Chem. Soc.*, **67**, 2173 (1945).

(5) E. G. Rochow, K. Gingold, *J. Am. Chem. Soc.*, **76**, 4852 (1954).

Dicyclopropylmercury and Divinylmercury

Received February 5, 1958

G. F. REYNOLDS,[1] RAYMOND E. DESSY, and H. H. JAFFÉ

In the course of an investigation of the electrophilic cleavage of dialkylmercury compounds, two new mercury compounds, dicyclopropyl- and divinyl-mercury, were prepared in good yield by the action of mercuric chloride on the corresponding Grignard reagent in tetrahydrofuran.

It might be expected that since dialkylmercury compounds in general, with the exception of dimethylmercury, decompose on standing to give hydrocarbons and metallic mercury,[2] these compounds would exhibit considerable instability. However, dicyclopropylmercury stood for several weeks at room temperature exposed to sunlight without giving noticeable evidence of decomposition, while during the same period of time di-*n*-propylmercury showed considerable decomposition. Divinylmercury can be stored in the cold for several weeks without apparent decomposition, although over the same period of time at room temperature some deposition of mercury is detectable. It should be noted that although no previous preparation of divinylmercury has been reported, a series of substituted vinylmercury compounds were prepared and studied by Nesmeyanov and co-workers,[3] and the vinylmercuric halides were recently prepared by reaction of tetravinyltin with the corresponding mercuric halides.[4]

The identities of the two compounds were established by their infrared spectra and carbon-hydrogen analysis. The spectrum of dicyclopropylmercury resembles that of cyclopropyl bromide[5] with strong absorptions at 809, 880, 1030, and 2990 cm.$^{-1}$. The spectrum of divinylmercury shows four strong absorptions at 938, 1010, 1250, and 2980 cm.$^{-1}$, and two medium adsorptions at 1400 and 3040 cm.$^{-1}$. The absorption peaks at 2980 and 3040 cm.$^{-1}$ are attributed to CH stretching vibrations, those at 938 and 1010 cm.$^{-1}$ to CH_2 and CH out-of-plane deformation vibrations, and that at 1400 cm.$^{-1}$ to a CH_2 in-plane deformation vibration. The medium absorption peak at 1250 cm.$^{-1}$ is unaccounted for and appears also in the spectrum of dicyclopropylmercury.

This method of preparing the dialkylmercuries involving the addition of a tetrahydrofuran solution of mercuric chloride to a tetrahydrofuran solu-

---

[1] Fulbright Fellow, University of Paris, France (1956–57).

(2) Rochow, Hurd, and Lewis, *The Chemistry of Organometallic Compounds*, John H. Wiley and Sons, Inc., New York, 1957, p. 117.

(3) A. N. Nesmeyanov and A. E. Borisov, *Tetrahedron*, **I**, 158 (1957).

(4) D. Seyferth, *J. Org. Chem.*, **22**, 478 (1957).

(5) J. D. Roberts and V. C. Chambers, *J. Am. Chem. Soc.*, **73**, 5030 (1951).