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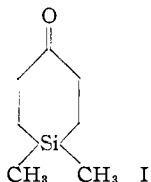
## A Silicon Analog of Cyclohexanone. The Preparation and Reactivity of 4,4-Dimethyl-4-silacyclohexanone

BY ROBERT A. BENKESER AND EVERETT W. BENNETT

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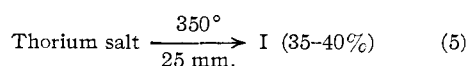
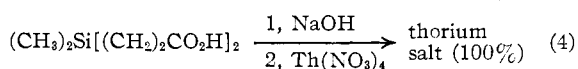
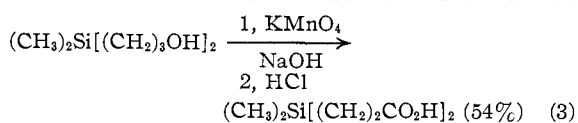
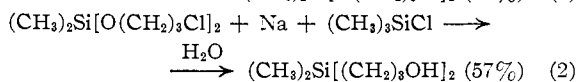
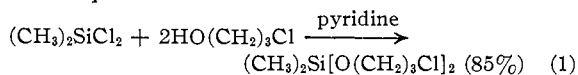
A silicon analog of cyclohexanone, 4,4-dimethyl-4-silacyclohexanone, has been prepared in a four-step synthesis and its reactivity compared with its carbon analog, 4,4-dimethylcyclohexanone. The dissociation constants of the cyanohydrins of these two ketones have been determined, and the results interpreted in terms of the I-strain theory. Spectral evidence is presented which would indicate that the ring size of the silicon ketone is somewhat larger than that of its carbon analog.

The literature contains a rather considerable number of examples of cyclic organosilanes.<sup>1</sup> However, probably as a result of the synthetic difficulties involved, there has been only one example of a cyclic silane reported which contains a functional group in the ring itself.<sup>2</sup> It seemed particularly desirable to investigate the chemistry of such compounds to ascertain whether the presence of the bulky silicon atom would in any manner alter the reactivity of the functional group. Toward this end we are hereby reporting the successful preparation of 4,4-dimethyl-4-silacyclohexanone (I). The dissociation of the cyanohydrin



of this compound has been measured as well as that of its carbon analog, 4,4-dimethylcyclohexanone.

**Syntheses.**—The synthesis of 4,4-dimethyl-4-silacyclohexanone was accomplished by the reaction sequence



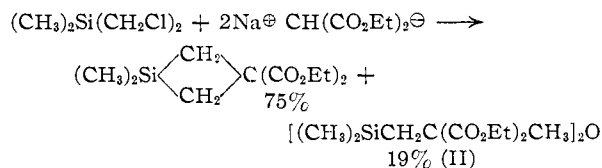
The thorium salt was used for the final ring closure (step 5) in view of the study by Ruzicka, *et al.*,<sup>3</sup> on the pyrolytic closure of various sized rings by the use of heavy metal salts.

(1) (a) A. Bygden, *Ber.*, **48**, 1236 (1915); (b) R. H. Krieble and C. A. Burkhard, *This Journal*, **69**, 2689 (1947); (c) R. West, *ibid.*, **76**, 6012 (1954); (d) **77**, 2339 (1955); (e) L. H. Sommer and co-workers, *ibid.*, **79**, 1008, 3295 (1957).

(2) A silacyclopentene has been reported; see A. D. Petrov and co-workers, *Bull. Acad. Sci. U.S.S.R., Div. Chem. Sci.*, **5**, 861 (1955). Unfortunately we have not yet been successful in duplicating the results of these workers.

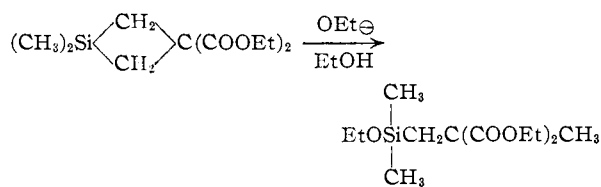
(3) L. Ruzicka, W. Brugger, M. Pfeiffer, H. Schinz and M. Stoll, *Helv. Chim. Acta*, **9**, 330, 499 (1926).

An attempt to prepare the dibasic acid (equation 3) *via* the sodium salt of malonic ester failed because of a surprisingly facile cyclization which occurred resulting in the formation of a silacyclobutane. Despite the presence of a 200% excess



of diethyl malonate, a 75% yield of 1,1-dimethyl-3,3-dicarbethoxysilacyclobutane was obtained. Previously<sup>4,5</sup> these conditions had been employed successfully to avoid cyclizations in similar reactions.

The physical properties of the silacyclobutane agreed well with those previously reported for this compound by West.<sup>6</sup> The disiloxane structure (compound II above) was not rigorously established. An elemental analysis agreed well for the compound shown and an infrared spectrum showed the presence of a siloxane linkage. The formation of such a material could be rationalized easily in terms of a base-catalyzed ring opening of 1,1-dimethyl-3,3-dicarbethoxysilacyclobutane. The eth-



oxysilane thus produced would quite likely condense to the disiloxane during the process of isolation. Saponification of compound II produced a tetrabasic acid which could be decarboxylated to a product which analyzed reasonably well for some type of cyclic anhydride. Since these reactions were not directly connected with the main phase of the project they were not investigated further. Consequently it must be emphasized that structure II must be considered as only tentative.

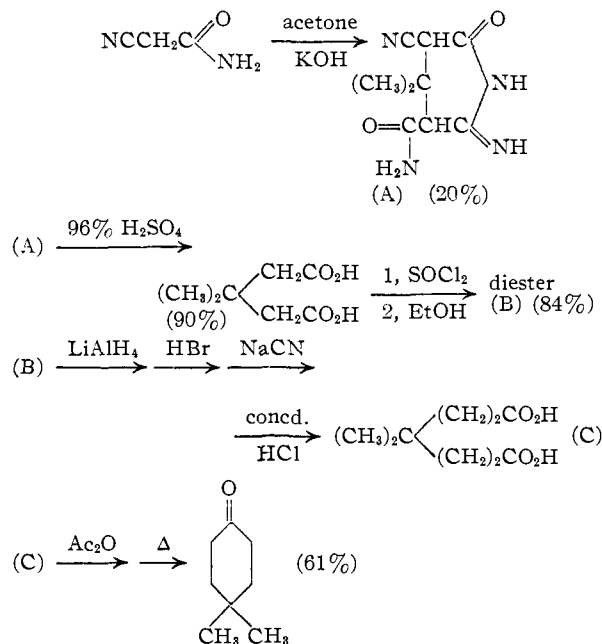
Compound I was reduced successfully with lithium aluminum hydride in 66% yield to 4,4-dimethyl-4-silacyclohexanol.

The synthesis of 4,4-dimethylcyclohexanone was accomplished by the sequence

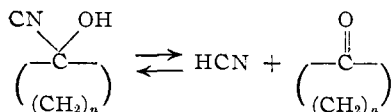
(4) J. Cason and C. F. Allen, *J. Org. Chem.*, **14**, 1063 (1949).

(5) A. T. Blomquist and J. Wolinsky, *ibid.*, **21**, 1371 (1956).

(6) R. West, *This Journal*, **77**, 2339 (1955).



It is of interest that the final ring closure in this sequence was accomplished by Blanc's pyrolysis method in approximately a 61% yield. This same procedure, when applied to the closure of the silicon ring, afforded only a 6% yield of ketone.



**Cyanohydrin Dissociation Constants.**—Equilibrium constants for the cyanohydrin dissociation were determined for cyclohexanone, 4-methylcyclohexanone, 4,4-dimethylcyclohexanone and 4,4-dimethyl-4-silacyclohexanone. The results are given in Table I.

The experimental procedure employed in these determinations involved treating a known weight of the ketone with a definite volume of a standard solution of hydrogen cyanide in ethanol. After the solution was permitted to equilibrate for approximately a day, an excess of standard silver nitrate was added. The excess silver nitrate was then back-titrated with potassium thiocyanate in a typical Volhard procedure. The values obtained by this method were checked by a direct titration of the cyanide with mercuric nitrate, utilizing diphenylthiocarbazonate as the indicator.

TABLE I  
CYANOHYDRIN DISSOCIATION CONSTANTS

	$K^*_{\text{D}} \times 10^4$ , mole/l.
Cyclohexanone	8.26 (5.91) <sup>a</sup>
4-Methylcyclohexanone	4.92 (3.15) <sup>a</sup>
4,4-Dimethylcyclohexanone	20.8
4,4-Dimethyl-4-silacyclohexanone	94.7

<sup>a</sup> The values in parentheses are those of O. H. Wheeler and J. Z. Zabicky, *Chemistry & Industry*, 1388 (1956).

**Results and Discussion.**—It will be noted from Table I that the dissociation constant of 4,4-dimethyl-4-silacyclohexanone is approximately five times larger than that of its carbon analog 4,4-

dimethylcyclohexanone. This behavior is perhaps best explained in terms of the I-strain theory.<sup>7</sup> Enlargement of a 6-membered ring by the substitution of a silicon atom for a carbon will decrease the symmetry of the ring and hence increase the hydrogen-hydrogen repulsions to some extent. A change in coordination number from four to three (which occurs in cyanohydrin dissociation) will be favored in such a compound since the introduction of an atom with a preferred angle of 120° (C=O) results in a decrease in internal strain. Stated in another way, the reactivity of the six-membered silicon ring approaches (albeit in a small way) the reactivity of the corresponding seven-membered carbon ring. The failure of the Blanc pyrolysis method to effect ring closure in the case of the silicon ketone can also be taken as evidence for its increased ring size. It is to be noted that cycloheptanone is formed in only low yields by this method.

Additional evidence for the increased ring size of the silicon ketone was obtained from infrared spectra (see Experimental). The frequency of the carbonyl band of 4,4-dimethyl-4-silacyclohexanone was found to be 1702 cm.<sup>-1</sup> while that of its carbon analog was 1709 cm.<sup>-1</sup> (Scott and Tarbell<sup>8</sup> have reported a value of 1699 cm.<sup>-1</sup> for cycloheptanone). Several workers<sup>9</sup> have observed the decrease in carbonyl frequencies of alicyclic ketones as the ring size increases from C<sub>5</sub> to C<sub>7</sub>.

### Experimental

**Dimethyldi-(3-chloropropoxy)-silane** was prepared in 85% yield essentially as described by Speier<sup>10</sup> from 258.2 g. (2.0 moles) of dimethyldichlorosilane, 378.2 g. (4.0 moles) of 3-chloro-1-propanol and 632.8 g. (8.0 moles) of pyridine. The product boiled at 95–100° (3 mm.),  $n_{\text{D}}^{20}$  1.4436 (reported<sup>10</sup>  $n_{\text{D}}^{25}$  1.4413).

**Dimethyldi-(3-hydroxypropyl)-silane** was synthesized in 57% yield from dimethyldi-(3-chloropropoxy)-silane by the method outlined by Speier.<sup>10</sup> A typical run utilized 81.4 g. (3.54 g. atoms) of sodium, 400 ml. of toluene, 195.6 g. (1.8 moles) of trimethylchlorosilane and 199.7 g. (0.814 mole) of the diester. The product boiled at 177° (24 mm.),  $n_{\text{D}}^{22}$  1.4667 (reported<sup>10</sup> b.p. 176° (24 mm.),  $n_{\text{D}}^{25}$  1.4649).

**Dimethyldi-(2-carboxyethyl)-silane.**—The oxidation procedure employed was patterned after that of Fournier.<sup>11</sup> A solution of 11.67 g. (0.291 mole) of sodium hydroxide in 200 ml. of water was mixed with 51.9 g. (0.294 mole) of dimethyldi-(3-hydroxypropyl)-silane and chilled to 0°. A solution of 124.1 g. (0.786 mole) of potassium permanganate in 2357 ml. of water was chilled to 10° and added to the vigorously stirred diol over a 10-minute period. The mixture was stirred for 6 hours at ice-bath temperature and for 16 additional hours while it was permitted to warm to room temperature. Excess permanganate was destroyed with sodium sulfite; the precipitate filtered off, and the water removed at aspirator vacuum on a steam-cone. The residue was acidified with hydrochloric acid and ether extracted. The ether was replaced by benzene, traces of water azeotroped out, and the benzene solution concentrated. Chilling yielded 32.6 g. (54.4%) of the dibasic acid melting at 96–98°. Recrystallization raised the melting point to 97–98°.

*Anal.* Calcd. for C<sub>8</sub>H<sub>16</sub>O<sub>4</sub>Si: C, 47.03; H, 7.89. Found: C, 46.94; H, 7.64.

(7) H. C. Brown and M. Gerstein, *THIS JOURNAL*, **72**, 2926 (1950); H. C. Brown, R. S. Fletcher and R. B. Johannesen, *ibid.*, **73**, 212 (1951).

(8) G. P. Scott and D. S. Tarbell, *ibid.*, **72**, 240 (1950).

(9) (a) A. J. Birch, *Ann. Reports*, 194 (1951); (b) E. J. Corey, *THIS JOURNAL*, **75**, 2301 (1953); (c) W. M. Schubert and W. A. Sweeney, *ibid.*, **77**, 4172 (1955).

(10) J. L. Speier, *ibid.*, **74**, 1003 (1952).

(11) M. H. Fournier, *Bull. soc. chim. France*, **5**, 920 (1909).

**Preparation of 4,4-Dimethyl-4-silacyclohexanone by Blanc's Anhydride Pyrolysis.**<sup>12</sup>—A solution of 20.0 g. (0.097 mole) of dimethyldi-(2-carboxyethyl)-silane in 54.7 g. (0.535 mole) of freshly distilled acetic anhydride was heated on a spiral Todd column, 11 ml. (98.2%) of acetic acid ( $n_D^{20}$  1.3725) was collected using a 50:1 reflux ratio. Excess acetic anhydride was removed at 54–55° (30 mm.) and the residual liquid placed in a 50-ml. flask equipped with a simple still-head. A Wood's metal-bath was used to heat the material slowly to 310°. The distillate was redistilled yielding 0.8 g. (5.8%) of material boiling in the proper range, 75–78° (10 mm.),  $n_D^{20}$  1.4551. That this material contained the ketone was shown by the formation of the semicarbazone, m.p. 191–192° dec.

**Thorium Salt of Dimethyldi-(2-carboxyethyl)-silane.**—A procedure described by Ruzicka and co-workers<sup>13</sup> was used. Three drops of phenolphthalein indicator were added to a solution of 31.7 g. (0.155 mole) of dimethyldi-(2-carboxyethyl)-silane in 50 ml. of hot 95% ethanol. The acid was neutralized with 20% sodium hydroxide. A solution of 60 g. (0.108 mole) of thorium nitrate tetrahydrate<sup>14</sup> in 100 ml. of warm water was added rapidly with stirring. When the gelatinous precipitate had given way to a powdery suspension the salt was filtered off and washed with 200 ml. of water. After drying over phosphorus pentoxide at 20 mm. for 24 hours the salt weighed 51.1 g. (103%).

**Pyrolysis of Thorium Salt.**—The general method outlined by Ruzicka and co-workers<sup>13</sup> was followed. The apparatus consisted of a 300-ml. round-bottom flask connected by 20-mm. tubing to a series of two ice-cooled Dewar traps and one Dry Ice-trichloroethylene Dewar trap that were in turn connected to a vacuum pump. The finely powdered thorium salt (51.1 g., 0.108 mole) was placed in the flask, the pressure reduced to 25 mm., and a Wood's metal-bath used to effect the pyrolysis. Decomposition commenced between 280 and 315° and was satisfactorily rapid at 320°. The temperature finally was raised to 460° to complete the pyrolysis. Fractionation of the distillate yielded 7.8 g. (35%) of the ketone boiling at 73–74° (11 mm.),  $n_D^{20}$  1.4635,  $d_4^{20}$  0.9285 g./ml.

*Anal.* Calcd. for  $C_7H_{14}OSi$ : C, 59.09; H, 9.91; *MR*, 42.04. Found: C, 59.04; H, 9.84; *MR*, 42.23.

The semicarbazone melted at 191–192° dec.

*Anal.* Calcd. for  $C_8H_{17}ON_3Si$ : C, 48.23; H, 8.59; N, 21.08. Found: C, 48.39; H, 8.39; N, 21.39.

The infrared spectrum of the ketone contained a C-H stretch band at 3.48  $\mu$ , a carbonyl band at 5.87  $\mu$ , and the characteristic  $CH_3-Si$  bands at 8.0 and 12.8  $\mu$ .

**4,4-Dimethyl-4-silacyclohexanol.**—A procedure outlined by Noyce and Denney<sup>15</sup> was used. A solution of 4.28 g. (0.030 mole) of the silacyclonone in 30 ml. of dry ether was added slowly to a suspension of 1.14 g. (0.030 mole) of lithium aluminum hydride powder in 50 ml. of ether. After 5 hours refluxing, 30 ml. of 20% by volume ethyl acetate in ether was added slowly, followed by 100 ml. of water and sufficient hydrochloric acid to acidify the material. Ether extraction, a 5% sodium carbonate wash, drying over calcium sulfate, and distillation yielded 2.85 g. (66%) of the alcohol as a rather viscous clear colorless liquid of pleasant odor boiling at 70–71° (5 mm.),  $n_D^{20}$  1.4648,  $d_4^{20}$  0.9225 g./ml. The infrared spectrum contained a C-H band at 3.51  $\mu$ , a hydroxyl band at 3.05  $\mu$ , and the  $CH_3-Si$  band at 8.02  $\mu$ .

*Anal.* Calcd. for  $C_7H_{16}OSi$ : C, 58.26; H, 11.17; *MR*, 43.59. Found: C, 58.03; H, 11.40; *MR*, 43.17.

The  $\alpha$ -naphthylurethan of the alcohol melted at 100–101°.

*Anal.* Calcd. for  $C_{15}H_{23}O_2NSi$ : C, 68.96; H, 7.39; N, 4.46. Found: C, 69.08; H, 7.63; N, 4.66.

**Reaction of Diethyl Sodiomaltonate with Dimethyldi-(chloromethyl)-silane.**—Sodium (14.6 g., 0.636 g. atom) was treated with 180 ml. of absolute ethanol, and 305.9 g.

(1.908 moles) of diethyl malonate (200% excess)<sup>4,5</sup> was added to the ethoxide solution. The mixture was stirred for 30 minutes while it was cooled to room temperature and then 50.0 g. (0.318 mole) of dimethyldi-(chloromethyl)-silane was added slowly. It was then refluxed for 24 hours. Next 154 ml. of ethanol was distilled out and replaced with 400 ml. of water. The mixture was extracted with 1500 ml. of ether in portions, and the ethereal solution dried over calcium sulfate. Distillation yielded 58.9 g. (74.6%) of 1,1-dimethyl-3,3-dicarboxy-1-silacyclobutane<sup>6</sup> boiling at 141–143° (15 mm.),  $n_D^{20}$  1.4321 (reported<sup>6</sup> b.p. 141–143° (15 mm.),  $n_D^{20}$  1.4318) and 15.7 g. of a material believed to be *sym*-tetramethyldi-(2,2-dicarboxy)-propyldisiloxane boiling at 150–160° (0.08 mm.),  $n_D^{20}$  1.4461. A similar run also yielded this material boiling at 155–161° (0.05 mm.),  $n_D^{20}$  1.4468. The infrared spectrum of the high boiling fraction contained a band at 9.5  $\mu$  indicating a Si-O bond.

*Anal.* Calcd. for  $C_{22}H_{42}O_9Si_2$ : C, 53.44; H, 7.97. Found: C, 53.63; H, 8.27.

**Hydrolysis of  $C_{22}H_{42}O_9Si_2$  Compound.**—A solution of 11.8 g. (0.023 mole) of the ester and 12.0 g. (0.213 mole) of potassium hydroxide in 60 ml. of 50% aqueous ethanol was refluxed for 6 hours and then worked up in a standard manner. There was isolated 5.89 g. (64.1%) of solid acid melting at 131–133° dec.<sup>6</sup> (mixed m.p. with an authentic sample was undepressed). In addition there was obtained 2.16 g. of yellow gum containing crystals that could not be freed of the liquid. The liquid may have resulted from partial decarboxylation.

*Anal.* Calcd. for  $C_{14}H_{26}O_9Si_2$ : C, 42.61; H, 6.64. Found: C, 42.69; H, 6.60.

**Decarboxylation of Tetrabasic Acid  $C_{14}H_{26}O_9Si_2$ .**—A 30.0-g. (0.076 mole) sample of the acid was heated for 7 hours at 170°, at which time the weight loss was 6.6 g. (calculated 6.7 g.). The product was a liquid that could not be induced to crystallize.<sup>6</sup> This material was distilled at 90–92° (0.15 mm.),  $n_D^{20}$  1.4574. The distillate nearly completely crystallized on standing and when recrystallized from petroleum ether (60–70°) the solid melted at 110.5–111.5°. It was apparently quite hygroscopic as exposure to air caused it to liquefy and attempts at recrystallization were unsuccessful. This same solid was also obtained in a similar manner from the acid hydrolysis of 1,1-dimethyl-3,3-dicarboxy-1-silacyclobutane and analyzed approximately for the cyclic anhydride of the expected dibasic acid.

*Anal.* Calcd. for  $C_{12}H_{24}O_4Si_2$ : C, 49.95; H, 8.38. Found: C, 50.31; H, 8.05.

**$\beta,\beta$ -Dimethylglutaric Acid.**—The procedure was that of Thole and Thorpe.<sup>16</sup> A solution of 200 g. (2.38 moles) of cyanoacetamide, 90 g. (1.55 moles) of acetone and 2 ml. of 30% potassium hydroxide in 600 ml. of water was allowed to react for two days at room temperature. The yield of crude iminopiperidone in several such runs was always around 20%. The yields quoted in the reference could not be duplicated. The iminopiperidone was converted in 90% yield to the dibasic acid, melting point 101–102°, using 96% sulfuric acid.

**Diethyl  $\beta,\beta$ -Dimethylglutarate.**—The method of Reid and Gompf<sup>17</sup> was used to prepare the ester in 84% yield. The ester boiled at 91–93 (3 mm.),  $n_D^{20}$  1.4270,  $d_4^{20}$  0.9923 g./ml. (reported b.p. 90–91° (3 mm.),<sup>17</sup>  $d_4^{20}$  0.9929 g./ml.<sup>18</sup>).

**3,3-Dimethyl-1,5-pentandiol and 3,3-Dimethyl-1,5-dibromopentane.**—The method was that as outlined by Reid and Gompf<sup>17</sup> except that the 8-day ether extraction of the diol was avoided by using ethyl acetate to extract the lithium aluminum hydride reduction mixture. The crude diol was converted to the dibromide by the method of Kamm and Marvel.<sup>19</sup> The physical constants of the dibromide were redetermined insofar as those in the reference could not be duplicated. The dibromide boiled at 98° (3 mm.),  $n_D^{20}$  1.5088,  $d_4^{20}$  1.5435 g./ml. (reported<sup>17</sup> b.p. 98–105° (5 mm.)  $n_D^{20}$  1.4537).

*Anal.* Calcd. for  $C_7H_{14}Br_2$ : C, 32.58; H, 5.46; Br, 61.94; *MR*, 49.90. Found: C, 32.88; H, 5.63; Br, 61.98; *MR*, 49.89.

(16) F. B. Thole and J. F. Thorpe, *J. Chem. Soc.*, **99**, 422 (1911).

(17) E. B. Reid and T. E. Gompf, *J. Org. Chem.*, **18**, 661 (1953).

(18) G. Komppa, *Ber.*, **32**, 1421 (1899).

(19) O. Kamm and C. S. Marvel, "Organic Syntheses," Coll. Vol. I, 2nd ed., John Wiley and Sons, Inc., New York, N. Y., 1956, p. 30.

(12) H. G. Blanc, *Compt. rend.*, **144**, 1356 (1907).

(13) L. Ruzicka, M. Stoll and H. Schinz, *Helv. Chim. Acta*, **9**, 249 (1926).

(14) Thorium chloride is preferable. When the nitrate is used the resulting thorium salt must be very carefully freed of excess nitrate to avoid explosions during the pyrolysis. The sensitive diphenylamine-sulfuric acid test is a useful check on the purity of the salt.

(15) D. S. Noyce and D. B. Denney, *THIS JOURNAL*, **72**, 5743 (1950).

**3,3-Dimethyl-1,5-dicyanopentane and 4,4-Dimethylheptane-dioic Acid.**—A solution of 87.4 g. (0.338 mole) of 3,3-dimethyl-1,5-dibromopentane in 137 ml. of 95% ethanol was added over 45 minutes to a solution of 40.34 g. (0.823 mole) of sodium cyanide in 45 ml. of water.<sup>20</sup> After refluxing for 36 hours the solvent was removed at aspirator vacuum and the residue extracted five times with 100-ml. portions of ethyl acetate. The solvent was distilled off and the crude nitrile hydrolyzed by refluxing for five hours with 148 ml. of concentrated hydrochloric acid.<sup>21</sup> When worked up in the standard manner and crystallized from 1:1 ether-petroleum ether (60–70°) there was obtained 56.2 g. (88%) of acid melting at 96.5–97.5° (reported<sup>17</sup> m.p. 95–96°).

**4,4-Dimethylcyclohexanone.**—Blanc's anhydride pyrolysis method was used.<sup>12</sup> A solution of 25.0 g. (0.133 mole) of 4,4-dimethylheptanedioic acid in 64.9 g. (0.636 mole) of acetic anhydride was heated on a Vigreux Todd column and 15.6 ml. of acetic acid removed. Excess acetic anhydride was removed at 52–54° (28 mm.) and the residue pyrolyzed in a 100-ml. flask with a small still-head attached directly to it. Gas evolution started at 230° and as the pot temperature was raised slowly to 300° 10.3 g. (61%) of material boiling at 173–176° which crystallized in the receiver was collected. Recrystallization from low boiling petroleum ether entailed high loss of material. After three crystallizations the ketone melted at 43–44.5° (reported<sup>17,22</sup> 38–40°, 38–41°). The semicarbazone melted at 200–201° dec., but, as indicated,<sup>22</sup> the melting point varied with the rate of heating.

**Purification of Model Ketones.**—Commercial cyclohexanone was dried over Drierite for 24 hours and then distilled through a 60 cm. X 20 mm. helices packed column. The middle cuts ( $n_D^{20}$  1.4483,  $n_D^{20}$  1.4405) were redistilled through a spiral Todd column at a 25:1 reflux ratio to obtain material boiling at 151.5° (742 mm.),  $n_D^{20}$  1.4505 (reported<sup>23</sup> 155.7° C (760 mm.),  $n_D^{19}$  1.4506).

Eastman Kodak Co. 4-methylcyclohexanone was dried over Drierite and distilled through the 60-cm. helices packed column and then the Todd column to obtain material boiling at 165.5° (743 mm.),  $n_D^{20}$  1.4451 (reported<sup>24</sup>  $n_D^{20}$  1.44506). Since other values for the index of refraction may be found in the literature the purity of the compound was checked by passing it through a Perkin-Elmer 154C vapor refractometer using a type "A" packing, column pressure of 29.4 p.s.i.g., nitrogen flow rate of 30 cc./min., and a column temperature of 163°. Only one peak was obtained and authentic mixtures with 4-methylcyclohexanol showed two peaks.

The 4,4-dimethylcyclohexanone was a sample melting at 43–44.5° after three crystallizations.

The 4,4-dimethyl-4-silacyclohexanone was a freshly distilled sample whose physical constants agreed with those obtained for an analytical sample.

**Cyanohydrin Dissociation Constants.**—The method used was similar to that of Lapworth and Manske,<sup>25</sup> and Wheeler *et al.*,<sup>26,27</sup> except that instead of filtering off the silver cy-

nide in the Volhard titration as in Lapworth's procedure some nitrobenzene was added and the titration performed in the presence of the protected precipitate.<sup>28</sup> Samples ranging from 0.2500 to 0.3500 g. of the pure ketones were weighed into 50-ml. volumetric flasks, 45.00 ml. of 0.1005 *N* hydrogen cyanide in redistilled 95% ethanol,<sup>29</sup>  $n_D^{20}$  1.3636, was pipetted in, 1.00 ml. of catalyst solution composed of 2.00% by volume of triethylamine (b.p. 88° (745.0 mm.),  $n_D^{20}$  1.4010; reported<sup>30</sup> b.p. 89.4°,  $n_D^{20}$  1.40101) was added and the solutions brought to volume with 95% ethanol. After several hours in a 25.0 ± 0.1° constant temperature bath it was necessary to readjust the volumes due to a contraction. The solutions were allowed to equilibrate for 24–30 hours and then 10.00-ml. aliquots were quenched in 20.00 ml. of 0.1163 *N* silver nitrate (standardized against sodium chloride) containing 3.0 ml. of 6 *N* nitric acid and 3.0 ml. of purified nitrobenzene. The excess silver nitrate was back-titrated with 0.09377 *N* potassium thiocyanate using 21 drops of saturated ferric alum indicator. Duplicate runs and duplicate titrations were made.

The Volhard determinations were checked by Prelog's<sup>31</sup> direct mercurimetric titration procedure using diphenylthiocarbazono as the indicator. The same relative order of the  $K_D$  values was found.

**Hydrogen Cyanide Solution.**—A saturated aqueous solution of 11.96 g. of sodium cyanide was added slowly to 300 ml. of concentrated sulfuric acid. The gas was passed through a calcium sulfate drying tower and then bubbled into purified 95% ethanol. Unabsorbed gas was led through two concentrated sodium hydroxide scrubbing towers. The ethanolic solution was standardized by the same Volhard procedure used in the dissociation constant determinations.

**Infrared Spectra of Ketones.**—The infrared spectra of the ketones were obtained from dilute solutions of the compounds in purified carbon tetrachloride using a Perkin-Elmer model 21 recording spectrophotometer. A polystyrene calibration curve was run with the ketone spectra to allow correction of the observed carbonyl frequencies.

Compound	Carbonyl band, cm. <sup>-1</sup>
Cyclohexanone	1709 (lit. <sup>9</sup> 1710)
4-Methylcyclohexanone	1710
4,4-Dimethylcyclohexanone	1710
4,4-Dimethyl-4-silacyclohexanone	1702

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