45 ± 5°. After standing for 15 minutes the mixture was poured onto 50 cc. of ice-water. The acid was neutralized by adding 12 g. of KOH, then $NaHCO_3$ and the product was extracted with ether. The crude ketone weighed 208.1 mg. A chromatographic procedure on alumina in pentane gave 187.2 mg. (89%) of 10-methyl-2-decalone which could not be crystallized.

The 2,4-dinitrophenylhydrazone was prepared from 163.0 mg. of ketone and 220 mg. of 2,4-dinitrophenylhydrazine in 25 cc. of ethanol with 1 cc. of H_2SO_4; yield 320 mg. (94%), m.p. 130–147°. When recrystallized from ethanol or ethanol–pyridine, a crystalline form melting at 125–128° mixed with higher melting material (148–154°) was observed. Several crystallizations from ethanol and from ether raised the m.p. to 174–176°; yield 220 mg. (64%). When this sample was mixed with an authentic sample of the 2,4-dinitrophenylhydrazone of *trans*-10-methyl-2-decalone, m.p. 173–175°,[9] it melted at 172–175°. Admixture of the present sample with the 2,4-dinitrophenylhydrazone of *cis*-10-methyl-2-decalone, m.p. 175–177°,[8,9] produced a m.p. of 150–158°.

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Tetrakis-(trimethylsiloxy)-titane[1]

BY W. D. ENGLISH AND L. H. SOMMER

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In the work published by various authors[2] about trimethylsilanol, the only esters of this compound with inorganic acids reported were the phosphate,[2a] the sulfate,[2b,c,3] the silicate[2d,4] and the borate.[5] Perhaps the lead derivative,[2b] $(Me_3SiO)_2Pb$ should also be mentioned. Because of reports that titanium alkoxides form heat-resistant materials[6] and because of the well-known thermal stability of organosiloxanes, we became interested in a molecule which combined both structures.

We have synthesized trimethylsilyl titanate (or *tetrakis*-(trimethylsiloxy)-titane) from trimethylsilanol and titanium tetrachloride in the presence of ammonia.[7] This siloxy titane is a water-white, mobile liquid which boils at 106° at 7 mm., almost the same boiling point as *t*-butoxy titanate, 108° at 10 mm.[8] In this connection it is interesting to note that hexamethyldisiloxane boils at 100°[9] and di-*t*-butyl ether boils at 101°,[10] both at atmospheric pressure.

Trimethylsilyl titanate resembles the alkyl titanates but does not hydrolyze as vigorously. A film formed by baking trimethylsilyl titanate on steel appeared to have interesting properties.

Experimental

Synthesis of Trimethylsilyl Titanate.—Gaseous NH_3 was bubbled through a solution of 80 g. (0.89 mole) of trimethylsilanol[11] in 50 ml. of dry benzene in a 3-liter flask fitted with a reflux condenser. From a dropping funnel was slowly added 24 g. (0.125 mole) of $TiCl_4$ in 50 ml. of benzene.[12]

$$\mathrm{-TiCl + HOSi- \longrightarrow -Ti{-}O{-}Si- + HCl}$$

$$\mathrm{TiCl_4 + HCl \longrightarrow TiCl_5^- + H^+}$$

$$\mathrm{2Me_3SiOH \xrightarrow{H^+} (Me_3Si)_2O + H_2O}$$

The reaction was vigorous. It evolved white fumes and a white precipitate formed. When the reaction mixture became too thick, 100 ml. more of benzene was added. Toward the end of the addition of $TiCl_4$, the white precipitate turned yellow. After addition was complete, the reaction mixture was heated at reflux for one hour, maintaining the flow of NH_3. The mixture was then cooled, the gas stream turned off, and the precipitate filtered out, rinsed with benzene and the benzene solutions combined.

Benzene and unreacted trimethylsilanol were fractionated from the mixture at atmospheric pressure, then the residual liquid was fractionated at reduced pressure. The yield was 9.2 g. (18% based on Ti) of a pale yellow-green liquid boiling at 106° at 7 mm. On standing for a short time the liquid became colorless; properties: n^{20}_{D} 1.4278, d^{20} 0.9078, MR_{D} 114.6.

Anal. Calcd. for $C_{12}Si_4TiH_{36}O_4$: Si, 27.8; Ti, 11.8. Found: Si, 28.1, 28.0; Ti, 11.6, 11.9.

There are no bond refractions for Ti–O in the literature, so calculation of the molecular refraction was impossible. Instead, the bond refraction was calculated from the observed molecular refraction; bond ref. Ti–O, 4.02.

Reactions and Properties of Trimethylsilyl Titanate.—This compound is soluble in ether, acetone and benzene. It is insoluble in water. Samples of trimethylsilyl titanate were dropped onto water, 0.1 *N* NaOH and dilute HCl. The liquids lay quietly with no signs of reaction even at the interfaces. Mixing the liquids by shaking produced immediate reaction in each case, but the reaction was mild with no noticeable heat effect or gas evolution. In water and base a curdy, white precipitate formed. In acid a layer of oil formed on the surface, smaller in volume than the layer of titanate had been. No odor of silanol was noticeable from any of the three.

The steel blade of a spatula was carefully cleaned with steel wool and a few drops of trimethylsilyl titanate placed on it. The blade was held high over the flame of a Meker burner and then slowly brought closer to the flame in order to bake the titanate onto the blade without igniting it. A colorless, smooth and apparently continuous film was produced. When the spataula blade and film were subsequently heated to bright red heat several times at the maximum temperature of the burner there was no apparent change in the film.

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[1] Paper 45 in a series on organosilicon chemistry. For paper 44 see THIS JOURNAL, **76**, 5002 (1954).

[2] (a) R. O. Sauer, *ibid.*, **66**, 1707 (1944); (b) W. J. Patnode and F. C. Schmidt, *ibid.*, **67**, 2272 (1945); (c) L. H. Sommer, E. W. Pietrusza and F. C. Whitmore, *ibid.*, **68**, 2282 (1946); (d) L. H. Sommer, L. Q. Green and F. C. Whitmore, *ibid.*, **71**, 3253 (1949).

[3] L. H. Sommer, E. W. Pietrusza, G. T. Kerr and F. C. Whitmore, *ibid.*, **68**, 156 (1946); L. H. Sommer, G. T. Kerr and F. C. Whitmore, *ibid.*, **70**, 445 (1948); L. H. Sommer, L. J. Tyler and F. C. Whitmore, *ibid.*, **70**, 2872 (1948).

[4] N. Wright and M. J. Hunter, *ibid.*, **69**, 803 (1947).

[5] R. H. Krieble, U. S. Patent 2,440,101 (Apr. 20, 1948) (*C. A.*, **42**, 6376 (1948)).

[6] For a review of the work on preparing and formulating titanium alkoxides, see M. Kronstein, *Paint and Varnish Production*, **30**, [No. 8] 10, 20 (1950).

[7] J. Nelles, U. S. Patent 2,187,821 (Jan. 23, 1940) (from *C. A.*, **34**, 3764 (1940)); D. C. Bradley and W. Wardlaw, *J. Chem. Soc.*, 280 (1951).

[8] R. J. Speer, *J. Org. Chem.*, **14**, 655 (1949).

[9] E. G. Rochow, "An Introduction to the Chemistry of the Silicones," 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., p. 184.

[10] Boiling point given as 214°F., H. E. Alquist and L. K. Tower, *Natl. Adv. Comm. Aeronaut.*, Wartime Report M. R. No. E5A04 (from *C. A.*, **42**, 4736 (1948)).

[11] Prepared from trimethylfluorosilane in 94% yield by the method of L. H. Sommer, E. W. Pietrusza and F. C. Whitmore, reference 2c.

[12] The $TiCl_4$ and silanol cannot be mixed and then the NH_3 bubbled through because acid released would cause the condensation of the silanol to hexamethyldisiloxane.

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Reaction of Methanesulfonic Anhydride with Hydrogen Halides[1]

BY LAMAR FIELD AND PAUL H. SETTLAGE

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Proell recently disclosed that a mixture of *n*-butanesulfonic anhydride and *n*-butanesulfonic

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