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

RECEIVED JULY 23, 1954

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]

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

$$TiCl_4 + HCl \longrightarrow TiCl_5^- + H^+$$

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

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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acid upon treatment with hydrogen chloride yields *n*-butanesulfonyl chloride.[2] An attempt to extend this reaction, however, to the preparation of benzenesulfonyl bromide by reaction of benzenesulfonic anhydride and anhydrous hydrogen bromide resulted instead in bis-(*p*-bromophenyl) disulfide as the principal product.[3]

Owing to this divergence of results, both a confirmation of the Proell procedure and a determination of the effect of hydrogen bromide upon an alkanesulfonic anhydride became of interest.

Although more vigorous conditions than those of Proell were found to be desirable with pure methanesulfonic anhydride, nevertheless methanesulfonyl chloride was obtained in 59% yield.

More vigorous conditions were necessary in the reaction of methanesulfonic anhydride with hydrogen bromide than had been used in the reaction of benzenesulfonic anhydride,[3] in order to effect completeness of reaction. Methanesulfonyl bromide was obtained in 44% yield. No dimethyl disulfide could be isolated; conceivably, sulfenyl halides could have been formed and overlooked in the isolation procedure, although a disulfide and not a sulfenyl halide is the principal product with benzenesulfonic anhydride.[3] Nevertheless, bromine vapors were evident during the reaction, and titration of the residue for methanesulfonic acid after distillation of the sulfonyl bromide showed an excess over that anticipated from equation 1, which represents simple cleavage.

$$(CH_3SO_2)_2O + HBr \longrightarrow CH_3SO_2Br + CH_3SO_3H \quad (1)$$

Both of these results, as well as the relatively lower yield in comparison to the chloride, point to the probability of a certain amount of reduction, as formulated for example in equation 2 (in which equation 1 probably figures as an intermediate step).

$$6(CH_3SO_2)_2O + 10\ HBr \longrightarrow (CH_3S)_2 + 5\ Br_2 + 10\ CH_3SO_3H \quad (2)$$

None the less, the principal reaction product is evidently the sulfonyl halide rather than the disulfide.

Klamann and Hofbauer[4] found that *p*-toluenesulfonyl chloride was reduced to di-*p*-tolyl disulfide by hydrogen bromide, but only in the presence of substances such as N-ethylaniline, phenol, and sodium sulfite which were deemed to accept bromine, formed as an oxidation product, and thereby to prevent its reoxidation of the disulfide. If this view is correct, the formation of the sulfonyl bromide rather than the disulfide may result from the inability of dimethyl disulfide to consume bromine by substitution in the manner of diphenyl disulfide. On the other hand, possibly the presumed acceptors of Klamann and Hofbauer function in a manner actually unrelated to the present question, for example by conversion of the sulfonyl chloride to an intermediate form which is more readily reducible to the disulfide. In this event, an alternative explanation for the reduction of benzenesulfonic anhydride in contrast to the seemingly simple cleavage of methanesulfonic anhydride becomes more appealing, namely, that the aromatic anhydride is reduced more easily because of an electronic interaction between the ring and the sulfonyl group which is impossible in the aliphatic anhydride; Truce and Vriesen have ascribed the stability of the ion $C_6H_5SO_2^+$ to an electronic interaction which is absent in the less stable $CH_3SO_2^+$ ion.[5]

Experimental[6]

Reaction of Methanesulfonic Anhydride with Hydrogen Chloride.—Passage of anhydrous hydrogen chloride through stirred molten methanesulfonic anhydride[7] for periods of about 2 hours first at 55–65° and then at 75–80° did not effect complete reaction, and a recrystallized sample of the solid which formed on cooling had m.p. 63–65.5°, undepressed by the original anhydride. After continued passage for 3.5 hours at 105°, solidification no longer occurred on cooling, but distillation yielded anhydride (16% recovery) as well as methanesulfonyl chloride (36%, $n^{25}\mathrm{D}$ 1.4496. *Anal.* Calcd. for CH_3ClO_2S: C, 10.49; H, 2.64. Found: C, 10.84; H, 2.90).

A better result was obtained by passage of hydrogen chloride during 3 hours into 17.4 g. of molten anhydride with stirring at 105°; the mixture was then allowed to stand overnight, after which the process was repeated. Combined benzene extracts of the dark oily product were then distilled through an 8-cm. Vigreux column, and yielded 6.80 g. (59%) of colorless lachrymatory methanesulfonyl chloride, b.p. 54–56° (13 mm.), $n^{25}\mathrm{D}$ 1.4497; reported b.p.[8] 55° (11 mm.), $n^{25}\mathrm{D}$ 1.4490.[9]

Reaction of Methanesulfonic Anhydride with Hydrogen Bromide.—Anhydrous hydrogen bromide was passed during 6 hours into 24.6 g. (0.141 mole) of molten methanesulfonic anhydride[7] (m.p. 68–69.5°) while it was stirred and heated at 95°. The reaction mixture solidified on standing overnight, and a recrystallized portion had m.p. 59.5–63°, undepressed by the original anhydride. Passage of the gas was accordingly continued for 6 hours at 105°; rather dense red fumes, presumably of bromine, were then observed after two hours. The mixture was allowed to stand at 30° for 40 hours after completion of the gas passage. Exit gases were collected in a trap immersed in Dry Ice. When the reaction was concluded, the trap contents were warmed slowly to 25° (dimethyl disulfide has b.p. 109.5° (774 mm.)),[10] and bromine present was reduced with sulfurous acid; there remained only a trace of water-insoluble residue.

Distillation of the reaction mixture yielded 7.4 g. (33%) of pale yellow lachrymatory liquid, b.p. 57–58° (12 mm.), $n^{25}\mathrm{D}$ 1.5120; reported[9] for methanesulfonyl bromide, b.p. 80–80.5° (22 mm.), $n^{25}\mathrm{D}$ 1.5080; a forerun boiling mainly at 55–57° (12 mm.) amounted to an additional 2.5 g. (11%) of methanesulfonyl bromide, but was red and apparently contaminated with bromine. No significant amount of material distilled before the sulfonyl bromide. Titration of the distillation residue (17.5 g.) showed the neut. equiv. to be 99 (calcd. for methanesulfonic acid, 96); it therefore consisted of the equivalent of 0.18 mole of methanesulfonic acid.

Redistillation of the crude bromide gave material of b.p. 64–66.5° (13 mm.) and $n^{25}\mathrm{D}$ 1.5079; it contained halogen, and 165.9 mg. gave 42.3 mg. of methanesulfonamide (43%) after recrystallization, m.p. and mixture m.p. 89–91°.[11] *Anal.* Calcd. for CH_3BrO_2S: S, 20.16. Found: S, 20.09.

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(11) Derivatization by John R. Holsten.