Anal. Calcd. for $C_{12}H_{20}ClNO$: Cl, 15.43. Found: Cl, 15.50.

Davies, Haworth, Jones and Lamberton[11] have reported melting points for this phenolic amine and its hydrochloride in each case about nine degrees lower than our values.

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t-Alkyl-*n*-alkyl Orthosilicates

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Mixed alkyl orthosilicates are produced by the interaction of ethyl orthosilicate and an alcohol in the presence of a basic catalyst, provided that the ethanol formed is continuously removed.

$$(EtO)_4Si + x\,ROH \xrightarrow{NaOR} (RO)_xSi(OEt)_{4-x} + x\,EtOH$$

Furthermore, this reaction is applicable to the synthesis of mixed alkyl orthosilicates containing tertiary alkoxy groups.[1,2] We have applied this method of synthesis to the preparation of six mixed alkyl orthosilicates. The pertinent data on synthesis and properties are summarized in Table I.

Experimental

Intermediates.—The ethyl orthosilicate was purchased from Carbide and Carbon Chemicals Company and used as received. Distillation of other samples had indicated that this material is of high quality. The *n*-butyl alcohol, *t*-butyl alcohol and *t*-amyl alcohol were the ordinary materials of commerce used without further purification.

Synthesis of *t*-Alkyl-*n*-alkyl Orthosilicates.—All six compounds were prepared in essentially the same manner. The following detailed description of the synthesis of *t*-amyltriethyl silicate (V) and di-*t*-amyldiethyl silicate (VI) is illustrative of the method used. Yields, properties and analyses of the six compounds prepared may be found in Table I.

In a round-bottom flask was placed 1040 g., 5.0 moles, of ethyl orthosilicate and 440 g., 5.0 moles, of *t*-amyl alcohol. Several pea-sized chunks of sodium were added and the reaction flask was attached to a glass helix-packed rectification column having an estimated efficiency of twenty theoretical plates. As heat was applied to the reaction vessel, the sodium went into solution and reflux appeared at the head of the column. The reaction was stopped after 233 g. of distillate had been taken off at 78° over a period of six hours; the theoretical yield of ethanol was 230 g.

TABLE I

		Unreacted $(EtO)_4Si$, %	Yield,[a] %	B.p., uncorr.[b] °C.	Mm.	$n^{25}D$[b]	d^{25}[b]	R_D[c] Calcd.	Obsd.	Analyses, % Carbon Calcd.	Obsd.	Hydrogen Calcd.	Obsd.	Mol. wt.[d] Calcd.	Obsd.
I	*n*-$BuOSi(OEt)_3$[e]		49	128	77	1.3939	0.919	0.2585	0.2602	50.8	50.7	10.2	11.1	...	...
II	$(n\text{-}BuO)_2Si(OEt)_2$[e]	27	24	155	78	1.4019	.912	.2661	.2669	54.5	54.4	10.7	10.9	...	...
III	*t*-$BuOSi(OEt)_3$		54	95	40	1.3872	.905	.2585	.2602	50.8	51.3	10.2	10.4	236	231
IV	$(t\text{-}BuO)_2Si(OEt)_2$	32	11	101	34	1.3899	.887	.2661	.2675	54.5	55.7	10.7	11.1	264	266
V	*t*-$AmOSi(OEt)_3$[f]		53	116	55	1.3859	.910	.2625	.2640	52.8	53.3	10.5	10.8	250	242
VI	$(t\text{-}AmO)_2Si(OEt)_2$	24	19	141	59	1.4052	.900	.2722	.2724	57.5	57.7	11.0	11.1	278	290

[a] Based on unrecovered ethyl orthosilicate and calculated from distillation curves. [b] These physical properties are those of a center fraction of the particular distillation flat. [c] The calculated values were obtained by use of bond refractions given by K. G. Denbigh, *Trans. Faraday Soc.*, **36**, 936 (1940), and by E. L. Warrick, THIS JOURNAL, **68**, 2455 (1946). Similar results may be obtained by use of the method of R. O. Sauer, *ibid.*, **68**, 954 (1946). [d] Determined cryoscopically in cyclohexane. [e] H. W. Post and C. H. Hofrichter, *J. Org. Chem.*, **5**, 576 (1940), reported the synthesis of these two compounds in 22 and 30% yields, respectively, by prolonged heating of ethyl orthosilicate with *n*-butyl orthosilicate. These workers found that the *n*-butylethyl orthosilicates disproportionate on heating at their atmospheric boiling points. [f] G. W. Pedlow and C. S. Miner, Jr., U. S. Patent 2,566,365 (September 4, 1951), reported the synthesis of this compound by the reaction of *t*-amoxytrichlorosilane with ethanol in the presence of pyridine.

In general, the experimental procedure was as follows. The reaction mixture, consisting of several small pieces of sodium and equimolar amounts of ethyl orthosilicate and the appropriate alcohol, was heated, and the resulting reflux was rectified through an efficient column. Distillate was removed slowly at the boiling point of ethyl alcohol until the refluxing slowed and the weight of distillate approximately equalled the theoretical amount of ethyl alcohol. The reaction mixture was allowed to cool, washed thoroughly with water, dried and fractionally distilled. The mixed-alkyl silicates thus obtained were water-white mobile liquids having an odor similar to the alcohol from which they were prepared. Yields ranged from 10% to 50%. Table I summarizes physical properties and analyses.

The crude reaction product was washed thoroughly with four 300-ml. portions of distilled water and dried for several days over Drierite. Fractional distillation was carried out at reduced pressure in a glass helix-packed column having an estimated efficiency of thirty theoretical plates. Graphical analysis of the distillation data revealed three plateaus identified as ethyl orthosilicate (physical properties and molecular weight), *t*-amyltriethyl silicate (V) and di-*t*-amyldiethyl silicate (VI).

Other compounds prepared by this method were: *n*-butyltriethyl silicate (I), di-*n*-butyldiethyl silicate (II), *t*-butyltriethyl silicate (III) and di-*t*-butyldiethyl silicate (IV).

In the case of the *t*-butyl compounds the proximity of the boiling points of ethanol and *t*-butyl alcohol necessitated a slightly modified procedure. The distillate consisted of a mixture of the two alcohols whose composition was determined by refractive index. More *t*-butyl alcohol was added to the reaction mixture and distillation was continued until one mole of ethanol had been removed for each mole of ethyl orthosilicate used.

(1) We learned of this reaction through a private communication from Dr. C. S. Miner, Jr., and co-workers of the Miner Laboratories of Chicago, Illinois.

(2) (a) D. F. Peppard, W. G. Brown and W. C. Johnson, THIS JOURNAL, **68**, 73 (1946), reported that acid-catalyzed alcoholysis of ethyl orthosilicate did not occur with *t*-butyl alcohol; while *t*-amyl alcohol did react to give ethyl alcohol, these workers did not report any *t* amyl silicate. (b) D. Ridge and M. Todd, *J. Chem. Soc.*, 2637 (1949), reported that uncatalyzed alcoholysis of ethyl orthosilicate occurred to a slight extent with *n*-butyl alcohol but not at all with *t*-butyl alcohol or with *t*-amyl alcohol.

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Dimethylvinylethoxysilane and Methylvinyldiethoxysilane

BY M. COHEN AND J. R. LADD

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A mixture of magnesium (2.63 moles) and absolute ether (800 ml.) was placed in a two-liter, three-necked, round-bottom flask equipped with a mercury-sealed stirrer, Dry Ice condenser and a gas inlet tube. A stopcock had been previously sealed to the bottom of the reaction flask. Methyl bromide was bubbled into the stirred mixture until all the magnesium had dissolved.

After excess methyl bromide had been allowed to evaporate from the solution, the methylmagnesium bromide solution was added to a stirred solution of 500 g. (2.63 moles) of vinyltriethoxysilane[1] and 960 ml. of ether in a three-liter, three-necked, round-bottom flask equipped with a mercury-sealed stirrer and a water condenser. All outlets were protected with calcium chloride tubes. The rate of addition was such that the ether refluxed gently.

The mixture was stirred under reflux one hour, and the ether distilled off. The distillation was continued at atmospheric pressure until the temperature of the distillate reached 100°. The remainder of the silanes was separated from the residue of magnesium salts at reduced pressure (40 mm.). On fractionation of the combined silanes there was obtained 19 g. (5.6% yield) of vinyldimethylethoxysilane, b.p. 99°, $n^{20}D$ 1.3983, d^{20}_4 0.790; *MR* calcd.[2] 39.8, obsd. 39.8; and 241 g. (57.4% yield) of vinylmethyldiethoxysilane, b.p. 133 to 134°, $n^{20}D$ 1.4000, d^{20}_4 0.858; *MR* calcd.[2] 45.2, obsd. 45.3.

Anal. Calcd. for $C_6H_{14}OSi$: C, 55.3; H, 10.8; Si, 21.5. Found: C, 55.4; H, 11.1; Si, 21.0. Calcd. for $C_7H_{16}O_2Si$: C, 52.5; H, 10.1; Si, 17.5. Found: C, 52.5; H, 10.2; Si, 17.2.

(1) Linde Air Products, New York, N. Y.

(2) E. L. Warrick, THIS JOURNAL, **68**, 2455 (1946).

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Thiosemicarbazones of Thiophene Derivatives[1]

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Due to the effectiveness of *p*-acetaminobenzaldehyde thiosemicarbazone (Tibione)[2] as an antituberculous agent, a number of thiosemicarbazones have been prepared for biological testing. Among these have been a number of heterocyclic derivatives, including several of the thiophene series. 2-Thenaldehyde thiosemicarbazone has been reported to have a relatively high order of activity against the tubercle bacillus *in vitro*.[3,4] In addition, Anderson, *et al.*,[4] reported *in vitro* tests on the thiosemicarbazones of 2-acetothienone, 2-propiothienone, 2-butyrothienone and 2,5-dimethyl-3-acetothienone. Of these, 2-propiothienone thiosemicarbazone afforded the best protection. A later report[5] indicated that 2-thenaldehyde thiosemicarbazone gave weak protection to mice infected with tuberculosis.

In recent papers[6,7] Hamre, *et al.*, reported that *p*-aminobenzaldehyde thiosemicarbazone caused a significant delay in death of chick embryos and mice infected with vaccinia virus. This observation was confirmed by Thompson, Price and Minton[8] who reported that benzaldehyde thiosemicarbazone prevents multiplication of vaccinia virus in check embryonic tissue, but that substitution in the *p*-position of the benzene nucleus reduced virostatic activity.

In pursuing a program of virus chemotherapy, we have synthesized a number of heterocyclic thiosemicarbazones, and report here a group of thiophene derivatives. All of the carbonyl compounds used in preparing the thiosemicarbazones have been reported previously, either from these laboratories, or from other sources. The compounds prepared, their melting points and analyses are presented in the table. The biological testing data have been reported elsewhere by Dr. R. L. Thompson.[9]

TABLE I

THIOSEMICARBAZONES OF THIOPHENE DERIVATIVES

Cmpd. No.		M.p., °C.[a]	Formula	Nitrogen, % Calcd.	Found
	3-Thenaldehydes				
1	Unsubstituted	151–152	$C_6H_7N_3S_2$	22.78	22.70
2	2-Chloro-	196–198 dec.	$C_6H_6N_3S_2Cl$	19.15	19.06
3	2-Bromo-	192–194 dec.	$C_6H_6N_3S_2Br$	15.91	15.64
4	2,5-Dichloro-	232–233 dec.	$C_6H_5N_3S_2Cl_2$	...[b]	...[b]
	2-Thenaldehydes				
5	5-Chloro-	164–165	$C_6H_6N_3S_2Cl$[c]	19.15	19.27
6	5-Bromo-	182–184	$C_6H_6N_3S_2Br$	15.91	15.97
7	5-Nitro-	252–255 dec.	$C_6H_6N_4O_2S_2$	24.36	24.05[d]
8	5-Acetamido-	231–233	$C_8H_{10}N_4OS_2$	23.15	23.05[d]
9	5-Methyl-	160–161	$C_7H_9N_3S_2$	21.08	21.02[d]
10	3-Methyl-	185–187	$C_7H_9N_3S_2$	21.08	21.40[d]
11	5-*t*-Butyl-	182–183	$C_{10}H_{15}N_3S_2$	17.42	17.40
	2-Acetothienones				
12	Unsubstituted[e]	147–148	$C_7H_9N_3S_2$	21.08	21.12[d]
13	5-Bromo-	200–201	$C_7H_8N_3S_2Br$	15.11	14.99[d]
14	5-Methyl-	161–163	$C_8H_{11}N_3S_2$	19.73	19.72[d]
15	4-Nitro-5-methyl-	232–235 dec.	$C_8H_{10}N_4O_2S_2$	21.72	21.48[d]

[a] All melting points uncorrected. [b] Calcd.: S, 25.2; Cl, 28.0. Found: S, 25.2; Cl, 27.9. [c] Calcd.: S, 29.16. Found: 29.06. [d] Analyses by H. L. Clark, Urbana, Ill. [e] Previously reported by F. E. Anderson, C. J. Duca and J. V. Scudi, THIS JOURNAL, **73**, 4967 (1951), m.p. 148–149° uncor.

(1) Contribution No. 571 from the Chemistry Laboratory of Indiana University. This work was supported by a contract between the Office of Naval Research, Department of the Navy, and Indiana University.

(2) R. Behnisch, F. Mietzsch and H. Schmidt, *Am. Rev. Tuberc.*, **61**, 1 (1950).

(3) R. Donovick, F. Pansy, G. Stryker and J. Bernstein, *J. Bact.*, **59**, 667 (1950).

(4) F. E. Anderson, C. J. Duca and J. V. Scudi, THIS JOURNAL, **73**, 4967 (1951).

(5) C. J. Duca, M. V. Rothlauf and J. V. Scudi, *Antibiotics and Chemo.*, **2**, 16 (1952).

(6) D. Hamre, J. Bernstein and R. Donovick, *Proc. Soc. Exp. Biol. Med.*, **73**, 275 (1950).

(7) K. A. Brownlee and D. Hamre, *J. Bact.*, **61**, 127 (1951).

(8) R. L. Thompson, M. L. Price and S. A. Minton, Jr., *Proc. Soc. Exp. Biol. Med.*, **78**, 11 (1951).

(9) R. L. Thompson, S. A. Minton, Jr., and J. E. Officer, *J. Immunology*, in press.