[Contribution from the Chemistry Department, Drexel Institute of Technology]

ETHYLSILICON ESTERS AND TRANSESTERIFICATIONS

HERBERT H. ANDERSON[1] AND GEORGE M. STANISLOW

Received June 24, 1953

Previous publications on organosilicon esters have concentrated primarily on acetates (1) or on trimethylsilicon esters (2, 3). Some transesterifications of alkoxysilanes are known (4–6). Decomposition often limited studies made, and sometimes boiling points under 760 mm. were not listed.

Recent studies of tri-*n*-propylgermanium esters (7) showed that the equilibrium $R_3GeOCOR' + HOCOR'' \rightleftarrows R_3GeOCOR'' + HOCOR'$ shifted to the right quantitatively when HOCOR′ could be removed easily from the mixture by fractional distillation. The individual reader may call this reaction a transesterification, a displacement, or an ester exchange.

Trimethylsilicon esters (2, 3) and the corresponding organic acids boil too close together to permit decisive study of trimethylsilicon transesterifications. Therefore the present publication emphasizes triethylsilicon esters, which are separable by distillation from the organic acids, and which are thermally relatively stable.

In the present paper there are fourteen new ethylsilicon esters, nine containing halogens; bromoesters or iodoesters could not be prepared from silver salts. Pure triethyltrichloroacetoxysilane and diethylbis- (trichloroacetoxy) silane, isolated herein, are much more stable than tri-*n*-propylgermanium trichloroacetate, which quickly (7) yielded decomposition products containing hydrolyzable chlorine. The present paper includes ten successful organosilicon transesterifications, four transesterifications which took place at least partially, and the two transesterifications shown not to occur at all. These six combinations show an unexpected limitation to the transesterification process; together with difficulties in preparing organosilicon formates, this justifies the observation that *acetates* offer the best compounds for transesterification. A boiling point of 118° for acetic acid is also a vital factor in reaching this conclusion.

Triethyl-α-chloropropionoxysilane did not react at all with either 100% sulfuric acid or benzoic acid; neither combination yielded free α-chloropropionic acid, while unreacted benzoic acid was present in essentially the original amount. The chloropropionate (5 g.) and a slightly-less-than-equivalent quantity of either free acid may not have reacted because of steric factors.

Either incomplete reaction or decomposition blocked four other transesterifications involving halogenoacids; these experiments are described in the experimental section.

Trifluoroacetoxysilanes are surprisingly volatile; diethylbis-(trifluoroacetoxy)-silane (2), triethyltrifluoroacetoxysilane, and ethyltris-(trifluoroacetoxy)silane

---

[1] Kindly address communications to this author. Experiments performed by both authors.

all boil between 148° and 155°. The triester is quite easily hydrolyzed, but may be distilled at atmospheric pressure.

On comparing the stability of organosilicon esters and organogermanium esters, one finds that organogermanium esters containing no halogen are more stable both to heat and to water; organogermanium esters containing organic halogen are more stable to water, but usually less stable to heat.

Malatesta (5, 6), in closely related work, has shown that silicon disulfide reacts with organic acids to give hydrogen sulfide and tetraesters such as $Si(ClCH_2COO)_4$, melting at 154° with decomposition; he slowly distilled a mixture of $(C_2H_5O)_4Si$ and phenol to get $(C_6H_5O)_4Si$.

Peppard, Brown, and Johnson studied reactions of alkoxysilanes (4), perhaps typical of which was the reaction $(C_2H_5O)_3SiF + 3\ n\text{-}C_4H_9OH \rightarrow (n\text{-}C_4H_9O)_3SiF + 3\ C_2H_5OH$.

EXPERIMENTAL

This article includes the preparation of fourteen new esters, ten successful transesterifications, and six other reactions either only partially successful or not taking place. We are giving reasonably complete information in some typical instances, and are giving only starting quantities in other cases.

Starting materials consisted of ethyltrichlorosilane and diethyldichlorosilane, from Dow Corning Corp., Midland, Mich.; triethyliodosilane, prepared from tetraethylsilane (8); commercial silver acetate; carefully prepared silver trifluoroacetate, silver propionate, and silver *n*-butyrate; and Eastman Kodak halogenoacids, several of which needed further purification to remove water absorbed from the air.

Borosilicate glass equipment, with standard taper ground joints, was used for all of the reactions and purifications. Micropipets and self-adjusting (in the final stage) micropycnometers were used in analytical work, which featured analysis by measuring liquids in self-filling micropipets and later titrating the acidity (9) using sodium hydroxide dissolved in 95% ethanol.

I. REACTIONS USING SILVER SALTS

Triethyltrifluoroacetoxysilane. In the absence of a solvent, 9.95 g. of pure triethyliodosilane and 11.92 g. of dry silver trifluoroacetate were refluxed 30 minutes while protected from the air by a calcium chloride tube. Then total distillation under 100 mm. pressure yielded 8.80 g. of crude triethyltrifluoroacetoxysilane, which later was redistilled with collection of an iodine-free center fraction. This was an apparently quantitative reaction, followed by a nearly complete recovery of the product—with an over-all yield of 93%. Table I lists the properties of a center fraction collected at 153.0–153.5°.

Triethylpropionoxysilane and triethylbutyroxysilane. In a process similar to that employed with triethyltrifluoroacetoxysilane above, exactly 9 g. of triethyliodosilane and 8.34 g. (a 30% excess) of silver propionate furnished 6.1 g. of triethylpropionoxysilane, a yield of 86%. Similarly, 5.34 g. of triethyliodosilane and 7.28 g. of silver *n*-butryate yielded fairly pure triethyl-*n*-butyroxysilane, which seemed to be a little less pure than other preparations. Perhaps the use of a solvent would have been more appropriate for the butyrate. Table I lists the properties of center fractions of these two esters.

Ethyltris-(trifluoracetoxy)silane. Exactly 5 g. of ethyltrichlorosilane and 26 g. of dry silver trifluoroacetate reacted in the absence of a solvent with considerable warming. After 30 minutes of reflux, distillation of the product furnished 12.0 g. of ethyltris-(trifluoroacetoxy)silane, an essentially quantitative yield. Table I lists the properties of the chlorine-free center fraction, which fumed in moist air.

TABLE I
PROPERTIES OF ETHYLSILICON ESTERS

COMPOUND	B.P.,[a] °C.	MM.	d_4^{20}	n_D^{20}	R	MOL. WT.		NEUT. EQUIV.	
						Calc'd	Found	Calc'd	Found
$Et_3SiOCOC_2H_5$	188 124–126	760 100	0.892	1.424_2	53.89	188.3	192	188.3	191, 191.5
Et_3SiOCO-*n*-C_3H_7	195.5 68–70	760 4	0.888	1.422	57.9	202.3	212	202.3	206
$Et_3SiOCOCF_3$	153.0	760	1.050	1.372_0	49.38	228.3	244	228.3	227, 228.5
$Et_3SiOCOCCl_3$	234 67–69	760 1	1.167	1.451_2	64.06	277.6	290	277.6	279.5, 280.5
$Et_3SiOCOCH_2Cl$	215 137–140	760 75	1.025	1.444_9	54.18	208.7	—	208.7	213, 212
$Et_3SiOCOCHClCH_3$	216 54–55	760 1	0.998	1.439_9	58.77	222.7	227	222.7	224, 225
$Et_3SiOCOCH_2CH_2I$	232 83–84	760 1	1.345	1.485_9	67.06	314.2	302	314.2	315.5, 315.0
$Et_2Si(OCOC_2H_5)_2$	220.5 59–60	760 1	0.997	1.417_0	60.00	232.3	233	116.2	117.5, 118.0
$Et_2Si(OCO$-*n*-$C_3H_7)_2$	248 80–81	760 1	0.972	1.428_2	69.23	260.4	—	130.2	132.5, 133
$Et_2Si(OCOCH_2Cl)_2$	257 100–101	760 2	1.215	1.453_4	60.82	273.2	—	136.6	135.8, 136.2

$Et_2Si(OCOCCl_3)_2$	273 123–125	760 1	1.416	1.473_8	81.52	411.0	—	205.5	211, 210
$Et_2Si(OCOCHBrCH_3)_2$	278 105–106	760 1	1.444	1.474_5	75.98	390.1	—	195.1	193.5, 196
$Et_2Si(OCOC_6H_5)_2$	344 170–172	760 1	1.105	1.519_2	90.20	328.4	—	164.2	165.8, 166.3
$EtSi(OCOCF_3)_3$	148.5 90–91	760 90	1.483	1.322_5	53.37	396.2	421	132.1	133, 133.5

[a] All compounds were distilled at the lowest pressure listed.

Diethyldi-n-butyroxysilane and diethyldipropionoxysilane. Exactly 9 g. of diethyldichlorosilane and 26 g. of silver butyrate suspended in 100 ml. of benzene were allowed 30 minutes of reflux. After filtration of silver salts, with washing, the solvent was distilled, at first under atmospheric pressure, but finally at 70 mm. The dibutyrate was distilled at 1 mm. to avoid decomposition. Table I lists the physical properties of the dibutyrate, a compound with very little odor. When 15 g. of diethyldichlorosilane and 30.5 g. of silver propionate reacted in the absence of a solvent, a nearly-pure center fraction with the properties listed in Table I was obtained; solvent benzene would have been preferable in this case.

II. PREPARATION OF NEW COMPOUNDS BY TRANSESTERIFICATION

Triethyltrichloroacetoxysilane. Exactly 3.5 g. of purified trichloroacetic acid and 4.02 g. of triethylacetoxysilane, after a 30-minute period of distillation of acetic acid as it was being formed, yielded 1.65 g. of acetic acid and 5.87 g. of triethyltrichloroacetoxysilane. This figure for acetic acid includes a little unchanged triethylacetoxysilane; the lowest apparent boiling point was 123°. During such a process the lowest-boiling component often gives too high a thermometer reading; the true boiling point is obtained by remeasurement later in a separate container.

This represents an essentially quantitative reaction. It is advisable to use a quantity of the less volatile acid 10% less than the original number of moles of the more volatile ester.

Table I lists the properties of center-fraction trichloroacetate distilled at 1 mm., with rejection of the first third and last tenth. There was no hydrolyzable chlorine present.

Triethyl(monochloroacetoxy)silane. Exactly 4.5 g. of triethylacetoxysilane and 2.08 g. of monochloroacetic acid in a 30-minute period of controlled distillation yielded 1.34 g. of crude acetic acid. After rejection of a low fraction, a center fraction of the properties listed in Table I contained no hydrolyzable chlorine. Even after measurement of the boiling point under 760 mm. pressure the sample contained no hydrolyzable chlorine. This is unlike the behavior of germanium (7).

Triethyl-α-chloropropionoxysilane. A somewhat slower reaction of 4.85 g. of triethylacetoxysilane and 2.87 g. of α-chloropropionic acid over a period of 60 minutes reflux at 760 mm. yielded 5.8 g. of crude α-chloropropionate, also 1.9 g. of crude acetic acid which carried some acetate with it. No hydrolyzable chlorine was present in the center fraction, which had a partly camphoraceous odor.

Triethyl β-iodopropionoxysilane. Distillation at 75 mm. pressure with 3.73 g. of triethylacetoxysilane and 3.57 g. of β-iodopropionic acid yielded 5.75 g. of the β-iodopropionate and 1.45 g. of crude acetic acid (at approximately 75°) carrying a little excess acetate. As distilled the center fraction of the β-iodopropionate was essentially colorless, although it soon became a light yellow.

Diethylbis-(monochloroacetoxy)silane and acetic acid resulted when exactly 5 g. of diethyldiacetoxysilane and 3.1 g. of monochloroacetic acid reacted under reflux at atmospheric pressure. There was slight decomposition of the sample during measurement of the boiling point.

Diethylbis-(α-bromopropionoxy)silane and acetic acid resulted from the reaction of exactly 4 g. of diethyldiacetoxysilane and 5.45 g. of α-bromopropionic acid during reflux under 70 mm. pressure, with distillation of acetic acid at approximately 80°.

Diethylbis-(trichloroacetoxy)silane. Exactly 5 g. of purified trichloroacetic acid and 3.83 g. of diethyldiacetoxysilane were refluxed with distillation of acetic acid, first at 760 mm. and later at 70 mm. After distillation of the excess acetate the trichloroacetate was distilled at 1 mm., with some formation of a light brown color in the last (undistilled) fraction. Even the center fraction probably contained some decomposition products, although in small amounts. Table I lists the properties.

Diethyldibenzoxysilane. A combination of 6.17 g. of diethyldi-*n*-butyroxysilane and 4.25 g. of benzoic acid upon distillation at 63 mm. yielded approximately 3 g. of butyric acid at 120°. After distilling excess dibutyrate, the dibenzoate was distilled at 170–172° under 1 mm. and the *last* fraction (last third) was collected for study. It was a clear, colorless liquid of fairly high viscosity.

III. TRANSESTERIFICATIONS NOT YIELDING NEW COMPOUNDS

Formation of bis-(triethylsilicon)sulfate. Distillation at atmospheric pressure of 1.34 g. of acetic acid from an original mixture of 3.75 g. of triethylacetoxysilane and 0.94 g. of 100% sulfuric acid left a residue containing a small amount of excess acetate. Nearly 3.05 g. of bis-(triethylsilicon) sulfate resulted, the main portion of which had the normal boiling point of 278° and a refractive index of 1.4440 at 20°. This appears to be an excellent method of preparation (10).

Similarly, 3.25 g. of triethyltrichloroacetoxysilane and 1.01 g. of 100% sulfuric acid, upon distillation at 70 mm., also yielded bis-(triethylsilicon) sulfate, with approximately 0.5 g. of excess sulfuric acid. Although 1.70 g. of trichloroacetic acid resulted, this method is inferior to a reaction with an acetate, because of boiling points.

Triethyltrifluoroacetoxysilane and 100% sulfuric acid, upon similar treatment, reacted only partially.

Triethyltrifluoroacetoxysilane and β-chloropropionic acid also reacted only partially.

Triethylpropionoxysilane and β-chloropropionic acid yielded a moderate amount of propionic acid, but never gave a *pure* product.

Diethyldipropionoxysilane and β-iodopropionic acid reacted easily during reflux at 80 mm., but the product itself evidently partially lost hydrogen iodide gas, and was quite impure.

Ethyltris-(trifluoroacetoxy)silane and propionic acid reacted, but the tripropionate itelf decomposed too thoroughly to permit isolation. Even an effort to make the tripropionate from the silver salt failed.

IV. PHYSICAL PROPERTIES: SEE TABLE I

The physical properties of each compound were measured on the day of purification. Boiling points may be subject to some error because of decomposition, which also made it difficult to obtain molecular weights of some compounds.

SUMMARY

1. The fourteen new ethylsilicon esters, reported herein, consist of the following: $Et_3SiOCOC_2H_5$, $Et_3SiOCO\text{-}n\text{-}C_3H_7$, $Et_3SiOCOCF_3$, $Et_3SiOCOCCl_3$, $Et_3SiOCOCH_2Cl$, $Et_3SiOCOCHClCH_3$, $Et_3SiOCOCH_2CH_2I$, $Et_2Si(OCOC_2H_5)_2$, $Et_2Si(OCO\text{-}n\text{-}C_3H_7)_2$, $Et_2Si(OCOCH_2Cl)_2$, $Et_2Si(OCOCCl_3)_2$, $Et_2Si(OCOCHBrCH_3)_2$, $Et_2Si(OCOC_6H_5)_2$, and $EtSi(OCOCF_3)_3$.

2. Ten successful transesterifications — such as the reaction $Et_3SiOCOCH_3 + CH_2ClCOOH \rightarrow Et_3SiOCOCH_2Cl + CH_3COOH \uparrow$, carried out under gentle reflux with escape of acetic acid — demonstrate the general use of organosilicon transesterifications. Four transesterifications yielded impure products, while two reactions did not occur.

3. Organosilicon trifluoroacetates and trichloroacetates, the latter reported here for the first time, are surprisingly stable toward heat. Previous attempts to prepare the related tri-*n*-propylgermanium trichloroacetate always yielded decomposition products.

4. In organosilicon transesterifications involving two acids, the best method apparently consists of heating an acetate with a chosen less-volatile acid, followed by distillation of acetic acid.

PHILADELPHIA 4, PA.

REFERENCES

(1) Schuyten, Weaver, and Reid, *J. Am. Chem. Soc.*, **69,** 2110 (1947).
(2) Anderson, *J. Am. Chem. Soc.*, **74,** 2371 (1952).
(3) Étienne, *Compt. rend.*, **235,** 967 (1952).
(4) Peppard, Brown, and Johnson, *J. Am. Chem. Soc.*, **68,** 73, 76, 77 (1946).
(5) Malatesta, *Gazz. chim. ital.*, **78,** 747 (1948). See *Chem. Abstr.*, **43,** 5737^{i} (1949).
(6) Malatesta, *Gazz. chim. ital.*, **78,** 753 (1948). See *Chem. Abstr.*, **43,** 4630^{f} (1949).
(7) Anderson, *J. Am. Chem. Soc.*, **73,** 5798 (1951).
(8) Eaborn, *J. Chem. Soc.*, 2755 (1949).
(9) Anderson, *J. Am. Chem. Soc.*, **71,** 1801 (1949). Also *Anal. Chem.*, **24,** 579 (1952).
(10) Sommer, Kerr, and Whitmore, *J. Am. Chem. Soc.*, **70,** 445 (1948); The usual method of preparing bis-(triethylsilicon) sulfate, from oxide and sulfuric acid.