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METHYLSILICON ESTERS. ESTERS IN AN ORGANOSILICON "CONVERSION SERIES"

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In a recent "conversion series" for organosilicon halides, halogenoids, oxides, and sulfides Eaborn (1) included cyanide, isocyanate, isothiocyanate, and hydride; he omitted the generic ester group, such as acetate or propionate.

Our present report places the ester group in reactions involving silver salts. Using silver salts the "conversion series" is $Me_3SiI \rightarrow (Me_3Si)_2S \rightarrow Me_3SiBr \rightarrow Me_3Si(CN)$ and $Me_3SiCl \rightarrow Me_3SiNCS \rightarrow Me_3SiNCO \rightarrow (Me_3Si)_2O$ and $Me_3SiOCOCH_3 \rightarrow Me_3SiF$, in which the appropriate silver salt converts an organosilicon compound into any organosilicon compound to the right of it in the series. Reactions do not proceed to the left. Our "conversion series" differs from the previous (1) chiefly through inclusion of the ester group and also through placement of fluoride at the right of oxide, with omission of the difficultly-placed hydride. Oxide and acetate are left paired since silver oxide took approximately 80% of the trifluoroacetate from $Me_2Si(OCOCF_3)_2$, but gave a complex mixture with the more-easily oxidized $Me_2Si(OCOC_2H_5)_2$.

A study of the forward and reverse reactions in the system $2\ AgOCOCF_3 + Me_2Si(OCOC_2H_5)_2 \rightleftarrows 2\ AgOCOC_2H_5 + Me_2Si(OCOCF_3)_2$ showed that equilibrium required 40 mol-% $Me_2Si(OCOCF_3)_2$ and 60 mol-% $Me_2Si(OCOC_2H_5)_2$.

Table I lists the properties of eleven new methylsilicon esters, some made by transesterifications (2).

EXPERIMENTAL

I. REACTIONS FOR "CONVERSION SERIES"

Equipment used. Throughout this paper every reaction employed borosilicate glass equipment with 10/30 standard taper ground joints, accepting a thermometer, assorted receivers, and a drying tube filled with fresh anhydrous $CaCl_2$—except for the cyanide runs, which required P_4O_{10}.

Iodide and chloride to acetate. Twenty-minutes reflux under 100 mm. pressure of exactly 2 g. of Et_2SiClI (3) and 4 g. of silver acetate furnished 1.2 g. of $Et_2Si(OCOCH_3)_2$ free of chloride or iodide, boiling at 192° under 760 mm.; n^{25} 1.417.

Sulfide to acetate. Reaction of Et_3SiI and Ag_2S furnished $(Et_3Si)_2S$ (1). Exactly 1 g. of $(Et_3Si)_2S$ and 2 g. of silver acetate upon five minutes reflux under atmospheric pressure yielded 0.8 g. of $Et_3SiOCOCH_3$, boiling at 170°, free of sulfide.

Bromide to acetate. Preparation of Me_3SiBr involved reaction of PBr_3 and $Me_3Si(HNC_6H_5)$ (4). A 15-minute reflux of exactly 1 g. of Me_3SiBr and 1.70 g. of $AgOCOCH_3$ yielded bromide-free $Me_3SiOCOCH_3$ boiling at 102° [Lit. b.p. of 103.5° (5)].

Cyanide to trifluoroacetate. Reaction of Et_3SiI and AgCN furnished $Et_3Si(CN)$ (1). Exactly 0.5 g. of $Et_3Si(CN)$ and 1 g. of $AgOCOCF_3$ after three minutes of reflux under 760 mm. yielded 0.4 g. of cyanide-free $Et_3SiOCOCF_3$, b.p. 153° (2).

Isothiocyanate to acetate or trifluoroacetate. Fifteen-minutes reflux under 760 mm. pressure

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of 1.6 g. of $Et_2Si(NCS)_2$ (6) and 3 g. of $AgOCOCH_3$ yielded 1.1 g. of $Et_2Si(OCOCH_3)_2$, b.p. 193°, n^{20} 1.423, d_4^{20} 1.013, bearing only a trace of thiocyanate. Reflux of 8 g. of $Me_3Si(NCS)$ (7) and 16 g. of $AgOCOCF_3$ for an hour in 40 ml. of isopropylbenzene ultimately furnished thiocyanate-free $Me_3SiOCOCF_3$, b.p. 90.3°, n^{20} 1.334, d_4^{20} 1.100, neutralization equivalent 179—a little less pure than material made from Me_3SiCl.

Isocyanate to trifluoroacetate. Without a solvent, a two-hour reflux of exactly 1 g. of $Me_2Si(NCO)_2$ (8) and 4 g. of $AgOCOCF_3$ yielded 2.00 g. of $Me_2Si(OCOCF_3)_2$, n^{20} 1.3332, d_4^{20} 1.345, free of isocyanate according to a Nessler test.

Acetate to fluoride. Without a solvent, reflux for a half-hour of exactly 2 g. of $Et_3SiOCOCH_3$ and 5 g. of AgF at 760 mm. gave an essentially quantitative yield of Et_3SiF, b.p. 108.5°, n^{20} 1.388, d_4^{20} 0.846.

Reactions which did not occur. Reflux of 1 g. of $Me_3SiOCOCH_3$ and 1 g. of each silver salt for one hour without a solvent failed to produce any reaction with silver iodide, sulfide, bromide, or chloride, and very little reaction with silver cyanide. Fifty-minutes reflux of 5 g. of $Me_3SiOCOCF_3$ and 10 g. of AgNCS gave unaltered $Me_3SiOCOCF_3$, free of thiocyanate content in a test with $AgNO_3$. A one-hour reflux of exactly 2 g. each of $Me_2Si(OCOCF_3)_2$ and AgNCO yielded unchanged $Me_2Si(OCOCF_3)_2$, d_4^{20} 1.354, n^{20} 1.331. Without a solvent, a 90-minute reflux of 3 g. of Et_3SiF and 5 g. of silver acetate yielded 2.4 g. of unchanged Et_3SiF, b.p. 108, n^{20} 1.387. Similarly Et_3SiF and $AgOCOCF_3$ did not react. However, a 3-hour reflux of 3 g. of $Et_3SiOCOCF_3$ and 10 g. of AgF furnished a product with only 30% of the silicon as Et_3SiF; we are not including this partial reaction in view of decisive results with fluoride and acetate.

Partial reactions. Two hours reflux of exactly 2 g. of $Me_2Si(OCOC_2H_5)_2$ and 2.27 g. of Ag_2O furnished a cloudy liquid at first, probably containing a little water; the final product boiled at 110–130° under 70 mm. pressure. With n^{20} 1.400 and neutralization equivalent 93, this was probably mainly $Me_2Si(OCOC_2H_5)_2$ with polymers of (Me_2SiO), and either propionic acid or propionic anhydride. Forty-minutes free reflux of exactly 2 g. of $Me_2Si(OCOCF_3)_2$ and 1.66 g. of silver oxide furnished a white silver solid, chiefly $AgOCOCF_3$, and only 0.33 g. of crude $Me_2Si(OCOCF_3)_2$ with neut. equivalent 170, due to presence of some $(Me_2SiO)_n$. After the first vigorous evolution of hydrogen, exactly 1 g. of diphenylsilane and 2.60 g. of silver acetate were subjected to an hour of reflux under one mm. pressure, and later distilled chiefly at 156–158° under 1 mm. A neutralization equivalent of 190 indicated a mixture of $(C_6H_5)_2Si(OCOCH_3)_2$ and polymers of $(C_6H_5)_2SiO$; the method demonstrates replacement of hydride hydrogen by ester, although too vigorous for preparative value.

System $2\ AgOCOCF_3 + Me_2Si(OCOC_2H_5)_2 \rightleftarrows 2\ AgOCOC_2H_5 + Me_2Si(OCOCF_3)_2$. Two-hours reflux of exactly 2 g. of $Me_2Si(OCOC_2H_5)_2$ and 4.33 g. of $AgOCOCF_3$ yielded a liquid organosilicon product of d_4^{20} 1.114, n^{20} 1.379 and neut. equivalent 120. Fractional microdistillation substantiated the composition 40 mol-% $Me_2Si(OCOCF_3)_2$ and 60 mol-% $Me_2Si(OCOC_2H_5)_2$. Warming a mixture of exactly 2 g. of $Me_2Si(OCOCF_3)_2$ and 2.55 g. of $AgOCOC_2H_5$ gave a single liquid phase only; after 17-minutes free reflux the organosilicon product was distilled at 80–150° under 70 mm. pressure. Bearing d_4^{20} 1.138, n^{20} 1.379 and neut. equivalent 120, the product was very nearly 40 mol-% $Me_2Si(OCOCF_3)_2$ and 60 mol-% $Me_2Si(OCOC_2H_5)_2$.

II. PREPARATION OF NEW ESTERS. SEE TABLE I

$Me_3SiOCOCF_3$. Fifteen-minutes reflux of 5.4 g. of Me_3SiCl and 14.5 g. of $AgOCOCF_3$, without a solvent, furnished 7 g. of chloride-free $Me_3SiOCOCF_3$. Upon redistillation the lowest-boiling 50% was rejected, and the next 35% was collected at 89.5–89.8° under 750 mm. pressure.

$Me_3SiOCOC_2H_5$. Forty-minutes reflux of 23 g. of $AgOCOC_2H_5$ and 30 g. of Me_3SiCl, without a solvent, was followed by careful filtration. After distilling the excess Me_3SiCl, the $Me_3SiOCOC_2H_5$ weighed 12 g., a 65% yield. Center-fraction $Me_3SiOCOC_2H_5$, collected at 124.5–125.0°, was chloride-free, colorless, mobile, and with a weak odor of free acid.

$Me_2Si(OCOCF_3)_2$. One-hour reflux of exactly 8 g. of Me_2SiCl_2 and 30 g. of $AgOCOCF_3$,

TABLE I

PROPERTIES OF NEW COMPOUNDS

COMPOUND	B.P.,[a] °C.	MM.	d_4^{20}	n^{20}	R	ANALYSES			
						Mol. Wt.		Neut. Equiv.	
						Calc'd	Found	Calc'd	Found
$Me_3SiOCOCF_3$	90.2	760	1.077	1.338	36.0	186.1	199	186.1	182, 182.5
$Me_3SiOCOC_2H_5$	124.8	760	0.877	1.396_5	40.1	146.2	143	146.2	144.6, 144.4
$Me_2Si(OCOCF_3)_2$	128.2	760	1.361	1.331	42.7	284.2	295	142.1	142.0, 142.6
$Me_2Si(OCOCH_2Cl)_2$	245	760	1.305	1.453_5	50.8	245.1	261	122.6	122.1, 123.1
	98–99	3							
$Me_2Si(OCOCHCl_2)_2$	248	760	1.376	1.460_6	62.6	314.0	330	157.0	154.0, 154.3
	94–96	1							
$Me_2Si(OCOCCl_3)_2$	257	760	1.495	1.472_0	71.7	382.9	364	191.5	192.8, 193.0
	102–104	1							
$Me_2Si(OCOC_2H_5)_2$	191.4	760	1.011	1.415_6	50.7	204.3	210	102.1	103.8, 103.9
	80–82	9							
$Me_2Si(OCO_n\text{-}C_4H_9)_2$	233	760	0.952	1.415	68.5	260.4	290	130.2	131.7, 132.1
	80–82	1							
$Me_2Si(OCOC_6H_5)_2$	343	760	1.148	1.539_0	81.9	300.3	—	150.1	151.0, 151.8
	150–152	1							
$MeSi(OCOCF_3)_3$	140.0	760	1.540	1.319	49.1	382.2	—	127.4	127.2, 127.8
$MeSi(OCOC_2H_5)_3$	239.5	760	1.094	1.421_0	60.8	262.3	280	87.4	87.7, 87.3
	90–92	1							

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

without a solvent, furnished chloride-free $Me_2Si(OCOCF_3)_2$ almost quantitatively. Upon redistillation the lowest-boiling 40% was set aside and the next 50% collected at 128.0–128.5° for study.

$MeSi(OCOCF_3)_3$. Two-hours reflux of exactly 3.4 g. of $MeSiCl_3$ and 21 g. of $AgOCOCF_3$ yielded 9 g. of $MeSi(OCOCF_3)_3$ upon distillation from the silver salt—a nearly quantitative yield. Redistillation furnished center-fraction triester at 139.3–140.3° under 750 mm.

$Me_2Si(OCOCH_2Cl)_2$. Two hours of reflux produced no reaction between Me_2SiCl_2 and $AgOCOCH_2Cl$. A 20-minute transesterification (2) of exactly 5.7 g. of $Me_2Si(OCOCF_3)_2$ with 3 g. of vacuum-refluxed $CH_2ClCOOH$ yielded CF_3COOH easily, distilled first under atmospheric pressure and finally under 70 mm. Disregarding the small amount lost in completing the removal of CF_3COOH, a yield of 3.49 g. of $Me_2Si(OCOCH_2Cl)_2$ was 90%. Distilling under 3 mm. pressure, the first 1.3 g. were rejected and a center fraction (free of hydrolyzable chlorine) of 1.8 g. was collected at 98–99°, leaving behind 0.3 g. of ester.

$Me_2Si(OCOCCl_3)_2$. Transesterification of 3.30 g. of $Me_2Si(OCOCF_3)_2$ with 3.50 g. of dry CCl_3COOH produced the expected amount of CF_3COOH over a 75-minute period, also 3.85 g. of $Me_2Si(OCOCCl_3)_2$ or a yield of 94% based upon original CCl_3COOH. Upon distillation under one mm. pressure, the first 40% was set aside and the next 55%, collected at 102–104°, was taken for study. The moderately viscous compound hydrolyzed easily in air to give solid CCl_3COOH.

$Me_2Si(OCOC_2H_5)_2$. A 90-minute reflux of 14 g. of Me_2SiCl_2 and 41 g. of $AgOCOC_2H_5$ gave 18 g. of $Me_2Si(OCOC_2H_5)_2$ upon distillation under 17 mm. pressure—an 80% yield. Upon redistillation under 9 mm. the lowest-boiling 7 g. was set aside and then a chloride-free center fraction taken at 80–82°.

$Me_2Si(OCOCHCl_2)_2$. In a 40-minute reflux under 70 mm. pressure 6.65 g. of

$Me_2Si(OCOC_2H_5)_2$ and 6.50 g. of $CHCl_2COOH$ (76% of the equivalent amount) yielded 3.7 g. of propionic acid. Further distillation furnished 1.9 g. of crude excess dipropionate boiling as high as 145° under 70 mm.; 7.55 g. of $Me_2Si(OCOCHCl_2)_2$ remained in the distilling unit. More distillation furnished a 1.9 g. low fraction, a 4.3-g. center fraction at 94–96°, and a 1.4-g. residue left in the distilling unit. The center fraction was odorless and fairly viscous.

$Me_2Si(OCOC_6H_5)_2$. An hour of reflux under 70 mm. pressure using 4.45 g. of $Me_2Si(OCOC_2H_5)_2$ and 4.15 g. of benzoic acid yielded 2.5 g. of propionic acid at 92°; distillation under 9 mm. furnished 0.8 g. of excess $Me_2Si(OCOC_2H_5)_2$ at 80–90°. Next, distillation under 1 mm. yielded 0.6 g. as low fraction, then 3.0 g. of highly-viscous center fraction dibenzoate boiling at 150–152°.

$Me_2Si(OCO_n\text{-}C_4H_9)_2$. Very gentle heating of 12 g. of silver valerate and 3.1 g. of Me_2SiCl_2 for an hour was followed by distillation of the divalerate under 1 mm. pressure into a second distilling unit. Six g. of chlorine-free product furnished a low and then a center fraction, the latter boiling at 80–82°/1 mm.

$MeSi(OCOC_2H_5)_3$. Using 18 ml. of CCl_4 as solvent, a 30-minute reflux of exactly 3 g. of $MeSiCl_3$ and 12.3 g. of $AgOCOC_2H_5$ yielded 4.3 g. of $MeSi(OCOC_2H_5)_3$—after filtering, washing the silver salts, and then carefully distilling CCl_4 under 85 mm. pressure. Distillation of the triester under 1 mm. pressure furnished an 0.8-g. low fraction, a 2.7-g. center fraction at 90–92°, and also an 0.8-g. residue. This mobile liquid contained no chlorine.

Analysis consisted of finding molecular weights by gas densities at rather high temperatures, also of using self-filling micropipets and 0.0304 *M* ethanolic NaOH (9) in titrations.

SUMMARY

1. Now including the ester group, the "conversion series" for organosilicon compounds (using silver salts) becomes $Me_3SiI \rightarrow (Me_3Si)_2S \rightarrow Me_3SiBr \rightarrow Me_3Si(CN)$ and $Me_3SiCl \rightarrow Me_3SiNCS \rightarrow Me_3SiNCO \rightarrow (Me_3Si)_2O$ and $Me_3SiOCOCH_3 \rightarrow Me_3SiF$. In this series an organosilicon ester forms not at all from Me_3SiF, forms partially from the organosilicon oxide, and forms completely from all the other compounds.

Equilibrium in the system $2\ AgOCOCF_3 + Me_2Si(OCOC_2H_5)_2 \rightleftarrows 2\ AgOCOC_2H_5 + Me_2Si(OCOCF_3)_2$ required 60 mol-% $Me_2Si(OCOC_2H_5)_2$ and 40 mol-% $Me_2Si(OCOCF_3)_2$.

2. Table I lists the properties of eleven new esters: $Me_3SiOCOCF_3$, $Me_3SiOCOC_2H_5$, $Me_2Si(OCOCF_3)_2$, $Me_2Si(OCOCH_2Cl)_2$, $Me_2Si(OCOCHCl_2)_2$ $Me_2Si(OCOCCl_3)_2$, $Me_2Si(OCOC_2H_5)_2$, $Me_2Si(OCO_n\text{-}C_4H_9)_2$, $Me_2Si(OCOC_6H_5)_2$, $MeSi(OCOCF_3)_3$, and $MeSi(OCOC_2H_5)_3$.

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