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STUDIES IN SILICO-ORGANIC COMPOUNDS: XVI. REACTIONS OF ALKYL THIOETHERS OF SILICON WITH ACETIC ANHYDRIDE AND WITH BENZOYL CHLORIDE

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INTRODUCTION

In a previous paper (1) data were presented covering the preparation of compounds of the type $HSi(SR)_3$ in which R was methyl, ethyl, *n*-propyl, isopropyl, *n*-butyl, isobutyl, and *tert*-butyl. The work herein reported was a continuation of the problem and covered the interaction of most of these mercaptosilanes with acetic anhydride. A limited series of reactions with benzoyl chloride was carried out for comparison.

REACTIONS WITH ACETIC ANHYDRIDE

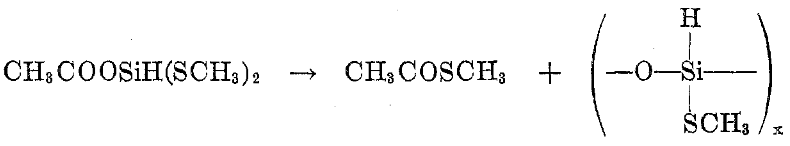
Reilly and Post (3) have shown that acetic anhydride reacts with triethoxysilane and with tri-*n*-propoxysilane with interchange of alkoxyl for acetate. The action of acetic anhydride on the corresponding sulfur compounds is analogous.

It is believed that the initial reaction between a trialkylmercaptosilane and acetic anhydride takes the following course:

$$\text{I.}\quad HSi(SCH_3)_3 + (CH_3CO)_2O \rightarrow CH_3COSCH_3 + CH_3COOSiH(SCH_3)_2$$

Alkyl thiolacetates were always isolated in much more than 100% yields, on the basis of Equation I. It was therefore concluded that the other product, dimethylmercaptosilicyl acetate broke down before reaching its boiling point:

II.



$$CH_3COOSiH(SCH_3)_2 \rightarrow CH_3COSCH_3 + \left(-O-\overset{\displaystyle H}{\underset{\displaystyle SCH_3}{Si}}- \right)_x$$

No evidence could be obtained however for the existence of the second product of Equation II, since analyses of the non-separable residue after distillation of isolable products did not correspond to any favorable atomic ratio. A similar reaction was noted when acetic anhydride was allowed to react with triethyl-, tri-*n*-propyl-, triisopropyl-, and triisobutyl-mercaptosilane.

The polymerized product from tri-*n*-propylmercaptosilane, however, seemed to be more stable than any of the others having a composition approximating that of the proposed analysis. Data covering these reactions will be found in Table I.

[1] A portion of the thesis presented by the first author in partial fulfillment of the requirements for the degree of Doctor of Philosophy at the University of Buffalo.

REACTIONS WITH BENZOYL CHLORIDE

Jenkins and Post (2) have shown that benzoyl chloride and various substituted benzoyl chlorides react with tribenzylsilane and triethylsilane. Reilly and Post (3) later showed that benzoyl chloride reacts with triethoxysilane and with tri-*n*-propoxysilane at high temperatures with interchange of chlorine for alkoxyl. It should be pointed out that the reactions with benzoyl chloride reported here all took place at low temperatures. The first reaction between triethylmercaptosilane and benzoyl chloride is:

TABLE I

THE ACTION OF ACETIC ANHYDRIDE

REACTANT	PRODUCT	B.P., °C.	MM.	n^{25}_{D}	d^{25}_{25}	YIELD, %
$HSi(SCH_3)_3$	CH_3COSCH_3	95–96	752	1.4622		149
$HSi(SC_2H_5)_3$	$CH_3COSC_2H_5$	115–116	744	1.4553	0.9740	122
$HSi(SC_3H_7\text{-}n)_3$	$CH_3COSC_3H_7\text{-}n$	135	750	1.4540	.9688	152
$HSi(SC_3H_7\text{-}i)_3$	$CH_3COSC_3H_7\text{-}i$	26	4	1.4498		148
		124–126	750			
$HSi(SC_4H_9\text{-}i)_3$	$CH_3COSC_4H_9\text{-}i$	55	20			134
		148	760			

TABLE II

THE ACTION OF BENZOYL CHLORIDE ON TRIETHYLMERCAPTOSILANE

YIELDS, %		SOLVENT	TEMP., °C.	TIME, HOURS
$(C_2H_5S)_2SiHCl$	$C_6H_5COSC_2H_5$			
12	78	Pet. ether	35	12
14	58	Pet. ether	0	12
?	64	Toluene	111	18
?	47.5	Toluene	111	8
?	6.5	None	boiling	12

$$\text{III.}\quad HSi(SC_2H_5)_3 + C_6H_5COCl \rightarrow (C_2H_5S)_2SiHCl + C_6H_5COSC_2H_5$$

Further studies have indicated that triethylmercaptochlorosilane decomposes at distillation temperatures. A summary of yields appears in Table II.

EXPERIMENTAL

All materials used were of satisfactory quality and showed acceptable physical properties: ethyl mercaptan, b.p. 34.5–35.5°; *n*-propyl mercaptan, b.p. 67–68°, isopropyl mercaptan, b.p. 50.0–52.5°; isobutyl mercaptan, b.p. 87–89°; acetic anhydride, b.p. 138–139° and benzoyl chloride, b.p. 194–196°.

Silane hydrogen was determined by the action of caustic alkali.

Silicon was determined gravimetrically (7).

Halogens were determined volumetrically following hydrolysis to halide ion (8).

Sulfur was determined gravimetrically (9, 10).

Trimethylmercaptosilane and acetic anhydride. Trimethylmercaptosilane, (17 g., 0.1 mole) was reacted with 9.5 cc. (0.1 mole) of acetic anhydride at a temperature slightly above the boiling point of the major product to be expected, methyl thiolacetate. The flask was attached to an efficient fractionating column to provide for the distillation of methyl thiolacetate as formed. During later fractionation, a Dry Ice-acetone trap was placed in series with the distillation system to catch by-products. Nothing was isolated, however, beyond unidentifiable material. *Methyl thiolacetate,* b.p. found and literature (4), 95–96° (752 mm.), n_D^{25} 1.4620, 13.4 g., 149% yield (based on Equation I.)

Anal. Calc'd for C_3H_6OS: S, 35.56. Found: S, 35.21.

There was a strong tendency toward the formation of polymerized material in all of these experiments. These unidentifiable products accounted for nearly all of the material not otherwise identified.

Triethylmercaptosilane and acetic anhydride. In a similar manner, 0.142 mole of triethylmercaptosilane (28.6 cc.) and 0.142 mole of acetic anhydride (13.4 cc.) were refluxed for 20 hours with isolation, on fractionation, of *ethyl thiolacetate,* b.p. found and literature (5) 115–116° (744 mm.); d_4^{25}, found 0.9740, literature (5) 0.9739; 18.4 g., 122% (based on Equation I).

Anal. Calc'd: S, 30.77. Found: S, 30.98.

Analysis of the residue did not produce evidence for the existence of any compounds therein.

Tri-n-propylmercaptosilane and acetic anhydride. Tri-*n*-propylmercaptosilane (0.1 mole, 25.48 cc.) and 0.1 mole of acetic anhydride (9.5 cc.) were refluxed for two hours and then slowly distilled at 135°. There was formed *n-propyl thiolacetate,* b.p. (750 mm.) found 135°, literature (5) 135–137°, n_D^{25} 1.4540, d_{25}^{25} 0.9688; 15.8 g., 152% yield (based on Equation I). Here as before, analysis of the residue showed values approximating the expected polymer but not sufficiently close to the calculated to serve as evidence.

Triisopropylmercaptosilane and acetic anhydride. Triisopropylmercaptosilane and acetic anhydride, 0.1 mole each, were slowly distilled with the fractionating column at 120°, forming *isopropyl thiolacetate,* b.p. (750 mm.) found 124–126°, literature (5) 124–127°; found b.p. (4 mm.) 26°; 11.3 g., 148% yield (based on Equation I).

Anal. Calc'd: S, 27.12. Found: S, 27.18.

The residue could not be identified.

Triisobutylmercaptosilane and acetic anhydride. Triisobutylmercaptosilane and acetic anhydride, 0.1 mole each, were refluxed for 4 hours, then fractionated, yielding *isobutyl thiolacetate,* b.p. found 148°, literature (5) 148–150°; found b.p. (20 mm.) 55°; 17.7 g., yield 134% (based on Equation I).

Anal. Calc'd for $C_6H_{12}OS$: S, 24.35. Found: S, 24.48.

Analysis of the residue produced no dependable results.

Triethylmercaptosilane and benzoyl chloride. Triethylmercaptosilane (20.2 cc., 0.1 mole) and benzoyl chloride (11.6 cc., 0.1 mole) were refluxed in 100 cc. of dry petroleum ether at 35° for 12 hours. The deep red solution was fractionated yielding products in accordance with Equation III. *Diethylmercaptochlorosilane,* b.p. 63–64° (2.5 mm.), n_D^{25} 1.5160, d_{25}^{25} 1.1250; 2.3 g., yield 12%.

Anal. Cal'd for $C_4H_{11}ClS_2Si$: Si, 15.02; S, 34.33; Cl, 18.98; Silane H, 0.535; M.R., 51.40.
Found: Si, 14.45; S, 33.50; Cl, 18.73; Silane H, 0.532; M.R., 50.11.

Ethyl thiolbenzoate, b.p. found 251°, literature (6) 252–253°; found b.p. 83–84° (2.5 mm.), n_D^{25} 1.5678, d_{25}^{25} 1.1010; 12.0 g., yield 78%.

Anal. Calc'd for $C_9H_{10}OS$: S, 20.79. Found: S, 21.08.

Ethyl thiolbenzoate prepared by the interaction of ethyl mercaptan, benzoyl chloride, and pyridine had b.p. 84° (2.5 mm.), n_D^{25} 1.5678, d_{25}^{25} 1.0998.

The experiment was repeated at 0° in petroleum ether giving a 14% yield of diethylmercaptochlorosilane and 58% of ethyl thiolbenzoate.

When the synthesis was repeated in dry toluene, refluxing at 111° for 18 hours, a 64% yield of ethyl thiolbenzoate was obtained but nothing else was isolated. Refluxing the original mixture in toluene for 8 hours gave only ethyl thiolbenzoate, yield 47.5%.

A 12-hour reflux of 0.1 mole each of triethylmercaptosilane and benzoyl chloride, with no solvent, gave a 26.5% yield of ethyl thiolbenzoate. Nothing else was isolable although quantities of residue were obtained.

SUMMARY

1. The action of acetic anhydride on five trialkylmercaptosilanes—methyl, ethyl, *n*-propyl, isopropyl, and isobutyl—is reported. In each case the alkyl thiolacetate was formed. It is assumed that dialkylmercaptosilicyl acetates were also formed, decomposing to give alkyl thiolacetate and polymerized material.

2. Benzoyl chloride reacts with triethylmercaptosilane to form diethylmercaptochlorosilane and ethyl thiolbenzoate.

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