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Alcoholysis Reactions of Alkyl Silicates

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With ethyl orthosilicate available commercially as a starting material, the preparation of higher esters through alcoholysis reactions offers practical advantages as compared with methods starting from silicon tetrachloride. In the few cases reported, the alkoxy group interchange has been carried out under quite drastic conditions with the formation of mixtures of esters with presumably all possible combinations of alkoxy groups. It would be surprising, in view of the high level of reactivity of alkyl silicates in hydrolysis reactions, if the alcoholysis could not be made to proceed under relatively mild conditions which would permit removal of the ethanol as formed and hence the complete displacement of ethoxy groups.

Friedel and Crafts[2] prepared a mixed[3] ester, dimethyl diethyl silicate, by heating ethyl orthosilicate with an excess of methanol in a sealed tube at 210° for twenty hours. Some further examples of the preparation of mixed esters by alcoholysis are reported in the patent literature[4] and by Klein and Nienburg.[5] An example of the preparation of a homogeneous[3] ester by alcoholysis has been claimed in a patent,[6] namely, the formation of $Si(OCH_2CH_2NH_2)_4$ from ethyl orthosilicate and aminoethanol in aqueous solution.[7]

In our experience with mixtures of ethyl orthosilicate and higher alcohols, heated under reflux at atmospheric pressure, the alcoholysis reaction proved to be capricious. For example, mixtures of ethyl orthosilicate and allyl alcohol when heated under reflux for prolonged periods showed no evidence of reaction except on one occasion, when for no apparent reason the reaction proceeded smoothly. On this occasion the ethanol formed in the reaction was stripped off at hourly intervals and the conversion was complete after twenty hours. At about the same time a similar experiment with methallyl alcohol and ethyl orthosilicate resulted in a quantitative yield of methallyl orthosilicate. Since these results could not be duplicated in numerous attempts, it was evident that either the apparatus or the materials had been contaminated by some catalytic agent.

No difficulty was experienced in effecting alkoxy group interchange with cyclohexanol, *s*-butanol, crotyl alcohol, and ethylene glycol, but in view of the above findings some doubt must exist as to whether these reactions may have been due to spurious catalysis.

Catalytic effects in the alcoholysis reactions have not been reported, but considering the analogy with the hydrolysis reactions of alkyl silicates, which are sensitive to acid catalysis, such effects are to be expected. The effect of added acid was first investigated using aqueous hydrochloric acid, but as this resulted in the formation of polysilicate esters, the later experiments were carried out either by passing dry hydrogen chloride into the refluxing mixture, or by adding small portions of silicon tetrachloride at frequent intervals. The latter procedure was preferred.

In the presence of added acid, alcoholysis reaction involving allyl and methallyl alcohols could be carried out at will, and in other cases the alcoholysis could be accelerated. The procedure is believed to be generally applicable in the preparation of silicate esters (including di- and polysilicates) of primary and secondary alcohols. It is not uniformly successful with tertiary alcohols. Ethyl orthosilicate and *t*-butyl alcohol could not be made to react in the presence of silicon tetrachloride, but a mixture of *t*-amyl alcohol and ethyl orthosilicate yielded nearly the theoretical quantity of ethanol, although *t*-amyl orthosilicate was not isolated.

If the device of stripping off the ethanol is not made use of to drive the reaction to completion, mixtures containing the various possible mixed esters in very nearly statistical proportions should be obtained. This is illustrated in the preparation of the series of allyl-ethyl orthosilicates, and again in the series of methallyl-ethyl orthosilicates. However, in the allyl-methyl series, and also in the methallyl-methyl series, some discrepancy in yields was encountered.

Alcoholysis reactions involving di- and trialkoxysilanes have been found likewise to be greatly accelerated by the addition of silicon tetrachloride in catalytic amounts. Post and Hofrichter[8] found that while ethyltriethoxysilane exchanged alkoxy groups with higher alcohols, only slight exchange occurred when the alkyl group on silicon was larger than ethyl. Our procedure has given satisfactory results for both amyl- and allylsilane derivatives.

Experimental

Ethyl Orthosilicate and Cyclohexanol: (A) In the Absence of Acid.—A mixture of 40 g. of ethyl orthosilicate

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[2] Friedel and Crafts, *Ann. chim. phys.*, [4] **9**, 5 (1866).

[3] The term, mixed, is used to designate esters containing unlike alkyl groups, as opposed to those containing all like groups which are designated homogeneous.

[4] German Patent 662,732 (July 30, 1938).

[5] Klein and Nienburg, *Ber.*, **69B**, 2066 (1936).

[6] German Patent 637,532 (Oct. 30, 1936).

[7] In the absence of experimental evidence, the structure indicated for this product may be questioned. The conditions for its formation suggest that it may be an aminolysis product.

[8] Post and Hofrichter, *J. Org. Chem.*, **5**, 572 (1940).

and 100 g. of cyclohexanol (30% excess over 4 moles) after refluxing for three hours was subjected to distillation first at atmospheric pressure, yielding 3 g. of distillate below 130°, and then at 22 mm. pressure, yielding a fraction at 68–73° of 97 g. (unchanged ethyl orthosilicate and cyclohexanol) and a fraction up to 130° of 23 g. which presumably consisted chiefly of triethyl cyclohexyl orthosilicate. In a second experiment the reaction mixture was heated in a flask fitted with a Vigreux column with a view toward removing ethanol preferentially from the mixture, but the formation of ethanol occurred so slowly that this was not practical.

(B) **In the Presence of Concentrated Hydrochloric Acid.**—A mixture of 52 g. of ethyl orthosilicate, 50 g. of cyclohexanol, and 8 ml. of concentrated hydrochloric acid was heated under reflux for six hours. After removal of volatile products by distillation there remained 31 g. of a viscous liquid which set to a glassy solid on cooling. This solid was easily soluble in organic solvents from which it deposited transparent films. The volatile products included, in addition to ethanol and unchanged starting materials, a 23-g. fraction boiling at 73–82° at 13 mm.

(C) **In the Presence of Silicon Tetrachloride.**—A mixture of 94.0 g. of ethyl orthosilicate, 146.0 g. of cyclohexanol (3.2 moles), and 1 ml. of silicon tetrachloride, the latter added in portions of 0.05 ml. at hourly intervals, was heated for twenty-five hours. Fractionation yielded 38 g ethanol, unchanged starting materials, a 14-g. fraction at 124.0–124.2° (22 mm.), and fractions from 218 to 257° at 3 mm. which solidified immediately. The 124.0–124.2° fraction was shown by analysis to be triethyl cyclohexyl orthosilicate. *Anal.* Calcd. for $Si(OC_2H_5)_3(OC_6H_{11})$: Si, 10.69; mol. wt., 262.4. Found: Si, 10.44, 10.53, mol. wt. (cryoscopic in benzene), 268.0, 273.4. Recrystallization of the solid fractions and residue from acetone yielded 61 g. pure cyclohexyl orthosilicate (39% yield).

Cyclohexyl Orthosilicate and Ethanol.—Cyclohexyl orthosilicate was recovered quantitatively after heating for three hours with a large excess of ethanol (5 g. ester, 50 g. ethanol). In a similar experiment in which 10 drops of silicon tetrachloride were added, the residue after removing distillate up to 180° at 14 mm. amounted to approximately 1 g. and the residue, moreover, could not be made to solidify, thus indicating extensive conversion of the starting ester. In the presence of concentrated hydrochloric acid, a mixture of cyclohexyl orthosilicate and ethanol yielded a thermoplastic polysilicate similar to that described under B above.

Ethyl Orthosilicate and Allyl Alcohol.—A mixture of 208 g. of ethyl orthosilicate and 255 g. (4.4 moles) of allyl alcohol was heated under total reflux in the stillpot of a 26-inch glass helices-packed column. At one-hour intervals the ethanol present in the mixture was removed by operating the column at a 5:1 reflux ratio. After twenty hours, 183 g. of ethanol (theoretical, 184.3) had been removed. Fractionation of the product yielded 234 g. of pure allyl orthosilicate (91% yield).

Earlier attempts to effect this reaction had failed completely. At a later date the following experiment, showing clearly the catalytic effect of silicon tetrachloride, was carried out.

Ethyl orthosilicate, 312 g., and allyl alcohol, 418 g. (7.2 moles), were heated as above, but after three hours no ethanol had been formed. One ml. of silicon tetrachloride was then added and, after one and one-half hours, 66 g. of ethanol was removed. Stripping was continued hourly and after six hours a further portion of 0.2 ml. silicon tetrachloride was added. Nearly the theoretical yield of ethanol was removed over a total period of twenty-one hours. The yield of redistilled allyl orthosilicate was 86%.

Preparation of Mixed Allyl-ethyl Esters.—Ethyl orthosilicate, 417 g. (2 moles), and allyl alcohol, 232 g. (4 moles), were heated as in the above experiment, 2 drops of silicon tetrachloride being added initially and at the end of every hour. The ethanol was removed as formed and the theoretical quantity was obtained after eight and one-half hours. Fractional distillation of the residue at 34 mm. pressure yielded the products shown in Table I.

TABLE I

MIXED ALLYL-ETHYL ESTERS FROM ETHYL ORTHOSILICATE BY ALCOHOLYSIS

Cpd.	B. p., °C. (34 mm.)	$n^{20}D$	Yield, g.	Yield, mole
$Si(OC_2H_5)_4$	78.5– 81.0	1.3835	24.2	0.117
$Si(OC_2H_5)_3(OC_3H_7)$	93.5– 94.0	1.3973	95.6	.434
$Si(OC_2H_5)_2(OC_3H_7)_2$	107.5–108.0	1.4098	124.8	.537
$Si(OC_2H_5)(OC_3H_7)_3$	121.0–121.5	1.4230	63.2	.259
$Si(OC_3H_7)_4$	134.0–134.5	1.4329	23.5	.092

Ethyl Orthosilicate and Methallyl Alcohol—Preparation of Mixed Esters.—The preparation of the series of mixed ethyl-methallyl esters was carried out in a similar way except that a diluent, dioxane, was used. The value of this modification is doubtful. Ethyl orthosilicate, 208 g. (1 mole), methallyl alcohol, 144 g. (2 moles), and 200 g. of dioxane were heated with the occasional addition of a drop of silicon tetrachloride. After five hours the theoretical amount of ethanol had been removed. The products shown in Table II were separated by fractional distillation at 18 mm. pressure.

TABLE II

MIXED ETHYL-METHALLYL ESTERS FROM ETHYL ORTHOSILICATE BY ALCOHOLYSIS

Cpd.	B. p., °C. (18 mm.)	$n^{20}D$	Yield, g.	Yield, moles
$Si(OC_2H_5)_4$	67.5– 68.0	1.3840	19.0	0.091
$Si(OC_2H_5)_3(OC_4H_7)$	92.5– 93.0	1.4051	76.2	.325
$Si(OC_2H_5)_2(OC_4H_7)_2$	115.5–116.0	1.4200	57.8	.222
$Si(OC_2H_5)(OC_4H_7)_3$	133.0–133.5	1.4320	14.8	.052

Ethyl Orthosilicate and Crotyl Alcohol.—Crotyl alcohol was prepared by the aluminum isopropoxide reduction of crotonaldehyde following the procedure of Young, Hartung and Crossley.[9] Ethyl orthosilicate, 41.6 g. (0.2 mole), and crotyl alcohol, 72 g. (1 mole), heated under reflux with periodic stripping yielded the theoretical quantity of ethanol in five and one-half hours. No catalyst was added. Crotyl orthosilicate, b. p. 126–128° at 4 mm., $n^{20}D$ 1.4430, was obtained in 75% yield. *Anal.* Calcd. for $Si(OC_4H_7)_4$: Si, 8.98. Found: Si, 9.05, 9.08.

Ethyl Orthosilicate and Ethylene Glycol.—Ethylene glycol was refluxed with a 30% excess over 1 mole of ethyl orthosilicate for six hours. Volatile products, consisting chiefly of ethanol and ethyl orthosilicate, were removed by distillation and there remained a white solid, insoluble in ether, benzene and cold alcohol, but soluble in boiling alcohol. The solubility of the polymeric glycol silicate in hot alcohol is possibly due to reversal of the alcoholysis reaction.

Preparation of Methyl Orthosilicate.—In the preparation of methyl orthosilicate by the addition of an excess of methanol to silicon tetrachloride, or by the addition of silicon tetrachloride to a large excess of methanol, the yields varied from 40 to 60%. The formation of polysilicate esters in considerable amounts indicated that water, formed by the interaction of methanol and hydrogen chloride, was reacting with the orthosilicate to form polymeric esters. The low yield was also due in part to the use of too large an excess of methanol which with methyl orthosilicate and hydrogen chloride forms a ternary mixture boiling at 69°.

These losses are minimized, and yields up to 80% are obtained, by adding the silicon tetrachloride as rapidly as possible to the methanol (ice–salt-bath), with the latter in slight excess only, and fractionally distilling the mixture immediately thereafter. Because of the solubility of hydrogen chloride in the mixture the evolution of hydrogen chloride is scarcely noticeable throughout the first two thirds of the addition.

Methyl Orthosilicate and Allyl Alcohol—Formation of Mixed Esters.—A mixture of 152 g. (1 mole) of methyl orthosilicate and 116 g. (2 moles) of allyl alcohol was

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[9] Young, Hartung and Crossley, THIS JOURNAL, **58**, 100 (1936).

TABLE III

METHYL-ALLYL ORTHOSILICATES

Cpd.	B. p., °C. (34 mm.)	n^{20}_D	Yield, moles	Anal., % Si Calcd.	Anal., % Si Found
$Si(OCH_3)_4$	42.5- 43.0	....	0.083	...	....
$Si(OCH_3)_3(OC_3H_5)$	70.5- 70.8	1.3919	.242	15.75	15.89 15.89
$Si(OCH_3)_2(OC_3H_5)_2$	94.7- 95.0	1.4110	.145	13.73	13.82 13.85
$Si(OCH_3)(OC_3H_5)_3$	116.0-116.3	1.4252	.047	12.18	12.21 12.20
$Si(OC_3H_5)_4$	134.5-135.0	....	.170	...	....

TABLE IV

METHYL-METHALLYL ORTHOSILICATES

Cpd.	B. p., °C.	Mm.	n^{20}_D	Yield, mole	Anal. Si, % Calcd.	Anal. Si, % Found
$Si(OCH_3)_4$	43.0- 43.2	34	....	0.039	...	... ...
$Si(OCH_3)_3(OC_4H_7)$	83.0- 83.5	34	1.4003	.196	14.60	14.68 14.63
$Si(OCH_3)_2(OC_4H_7)_2$	114.5-115.0 103.0-103.5	34 18	1.4156	.231	12.08	12.16 12.12
$Si(OCH_3)(OC_4H_7)_3$	128.0-128.5	18	1.4320	.080	10.30	10.48 10.51
$Si(OC_4H_7)_4$	148.0-148.5	18	....	.127	...	... ...

heated with periodic stripping of the methanol formed for three hours without added catalyst. Fractional distillation of the residue at 34 mm. yielded the products shown in Table III.

Methyl Orthosilicate and Methallyl Alcohol—Formation of Mixed Esters.—An experiment similar to the preceding, with a mixture of 137 g. (0.9 mole) of methyl orthosilicate and 130 g. (1.8 moles) of methallyl alcohol, again with no added catalyst, resulted in the products shown in Table IV.

Hexamethallyl Disilicate.—A mixture of 34.2 g. (0.1 mole) of hexaethyl disilicate (prepared by the controlled, partial hydrolysis of ethylorthosilicate) and 86.6 g. (1.2 mole) of methallyl alcohol was refluxed for three hours. Throughout this interval the temperature at the still head remained at 100-101°, indicating that no ethyl alcohol had been formed. The mixture was then cooled and a 0.2-ml. portion of silicon tetrachloride was added. After standing for a time, an ethanol fraction amounting to 16.5 g. was removed by distillation. The repetition of this procedure, until a total of 0.6 g. of silicon tetrachloride had been added, yielded 27.4 g. of ethanol (theoretical, 27.6 g.). The residue, after removal of excess methallyl alcohol, was thrice fractionated at 4 mm. pressure (no column) yielding 25.0 g. (50%) of hexamethallyl disilicate, b. p. 175.0-178.0° (4 mm.), n^{20}_D 1.4414. *Anal.* Calcd. for $Si_2O(OC_4H_7)_6$: Si, 11.25. Found: Si, 11.16, 11.16.

***n*-Amyltriallyloxysilane.**—From a mixture containing 46.9 g. (0.2 mole) of *n*-amyltriethoxysilane, 69.7 g. (1.2 mole) of allyl alcohol, and 3 drops of silicon tetrachloride, ethanol was distilled slowly and continuously until a total of 26.9 g. had been collected (four hours). Fractionation of the residue yielded 46.9 g. (84%) of *n*-amyltriallyloxysilane, b. p. 153.5° (32 mm.), n^{20}_D 1.4383. *Anal.* Calcd. for $C_5H_{11}Si(OC_3H_5)_3$: Si, 10.38. Found: Si, 10.49, 10.45.

Allyltri-*n*-amyloxysilane.—This compound was obtained similarly, in 61% yield, from allyltriethoxysilane and *n*-amyl alcohol; b. p. 180.5-181.0° (23 mm.), n^{20}_D 1.4421.

Anal. Calcd. for $C_3H_5Si(OC_5H_{11})_3$: Si, 8.49. Found: Si, 8.44, 8.46.

Di-*n*-amyldiallyloxysilane.—This compound was prepared in 81% yield from di-*n*-amyldiethoxysilane and allyl alcohol by a similar procedure; b. p. 163.0-163.5° (23 mm.), n^{20}_D 1.4415. *Anal.* Calcd. for $(C_5H_{11})_2Si(OC_3H_5)_2$: Si, 9.86. Found: Si, 9.82, 9.82.

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Summary

It is shown that many alkyl silicates can be prepared advantageously by means of alcoholysis reactions. In several instances in which the reaction failed to proceed spontaneously, it could be promoted by the addition of hydrogen chloride or silicon tetrachloride. Examples are given of the preparation of homogeneous (all like alkyl groups) and of mixed (unlike alkyl groups) orthosilicates, disilicates, di- and trialkoxysilanes.

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