**1-Chloro-1,5-hexadiene** was prepared from allylmagnesium bromide and 1,3-dichloropropane. The distilled product was treated with potassium hydroxide in ethanol for one hour to remove 3% 1,3-dichloropropylene. The redistilled product boiled at 82° at 200 mm. and had a refractive index of $n^{20}_{D}$ 1.4503. Infrared spectra showed all chlorine atoms to be of the type $—C{=}CHCl$.

*Anal.* Calcd. for $C_6H_9Cl$: Cl, 30.4. Found: Cl, 30.9.

**4-Phenylbutene-1** was prepared from benzylmagnesium chloride and allyl bromide; b.p. 107° at 78 mm., $n^{20}_{D}$ 1.5079 (lit.[5] b.p. 175–178°, $n^{20}_{D}$ 1.5090).

**Biallyl** was purchased from the Farchan Laboratories and had a boiling point of 59.2° and refractive index $n^{20}_{D}$ 1.4034 (lit.[6] b.p. 59.4°, $n^{20}_{D}$ 1.4040).

**Procedure and Analyses.**—Reactants were passed from calibrated flowmeters through 6 mm. Pyrex preheaters into a 700 ml. Pyrex tube of 40 mm. internal diameter. The temperatures at four evenly spaced thermocouples in a central well were held constant by automatically controlled furnace sections. The effluent was passed through a water-cooled condenser, a water scrubber to remove hydrogen chloride, and was condensed in a Dry Ice trap. Propylene and other gases were then topped through a short Vigreux column. The residue was washed, dried with calcium chloride and fractionated in a vacuum jacketed column packed with glass helices. Liquid products were usually determined by infrared analyses and gases by mass spectrometry. The identity of significant compounds was confirmed by the following derivatives or constants and in each case was supported by elemental analyses: cyclohexadiene–maleic anhydride adduct, m.p. 147° (lit.[7] 147°); biallyl, b.p. 60°[2]; $n^{20}_{D}$ 1.4041 (lit.[8] 59.6°, 1.4040)[7]; naphthalene, m.p. 79.7 (lit.[9] 80.2°); 4-phenylbutene-1, ultraviolet spectrum, bromine no. calcd. 121, found, 117; bibenzyl, m.p. 53.8° (lit.[10] 52.5°); stilbene, m.p. 123° (lit.[11] 124°).

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[6] A. L. Henne, H. Chanan and A. Turk, THIS JOURNAL, **63**, 3474 (1941).

[7] "Organic Reagents for Organic Analysis," Chemical Publishing Company, New York, N. Y., 1950.

[8] A. Turk and H. Chanan, *Org. Syntheses*, **27**, 7 (1947).

[9] A. Jaquerod and E. Wassmer, *Ber.*, **37**, 2531 (1904).

[10] E. C. Kleiderer and E. C. Kornfeld, *J. Org. Chem.*, **13**, 455 (1948).

[11] E. Buchta and W. Kallert, *Ann.*, **573**, 220 (1951).

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[CONTRIBUTION FROM THE RESEARCH LABORATORY OF J. T. BAKER CHEMICAL CO.]

# Preparation of Esters from the Reaction of Alkyl Orthosilicates with Organic Acids

BY GENE SUMRELL AND GEORGE E. HAM

RECEIVED MARCH 15, 1956

A convenient new preparative method for aliphatic esters is described, involving the reaction of alkyl orthosilicates with aliphatic acids. Results with certain other acids are also discussed. Improved procedures for preparing methyl and isopropyl orthosilicate are given, and the method extended to the preparation of *t*-butoxytrichlorosilane and di-*t*-butoxydichlorosilane.

It has been noted in the literature[1,2] that ethyl orthosilicate reacts sluggishly with benzoic acid to give ethyl benzoate, and "ethylates" acetic acid, implying the formation of ethyl acetate. However, no data are given and the reaction of alkyl orthosilicates with organic acids as a preparative method for esters does not seem to have been investigated.[3]

During an investigation of the properties of various silicon-containing compounds, it was discovered that methyl orthosilicate reacts readily with several aliphatic acids producing methyl esters in high yield. Since the method seemed to be a convenient means of preparing esters where the desired alkyl orthosilicate is available, the scope of the reaction has been further investigated and the results are reported here.

The reaction seems to be general, and is represented by the equation

$$2RCO_2H + (R'O)_4Si \longrightarrow 2RCO_2R' + 2R'OH + SiO_2 \quad (1)$$

However, it probably is not as simple as indicated by this equation since distillation of the reaction mixture leaves behind a dry, friable silicious residue which always amounts to more than the theoretical value for silica and evidently still has bound alkoxy groups and probably acyloxy groups (see reference 3). However, in most cases the ester and alcohol are obtained in 85–90% yields as indicated by equation 1 if two moles of acid are used per mole of alkyl orthosilicate. The esters so produced are easily purified by fractional distillation if their boiling points are sufficiently different from that of the alcohol which is formed simultaneously. If the ester is not appreciably soluble in water and the alcohol contains three carbons or less, it is possible to remove the latter by washing with water, as illustrated by the separation of allyl alcohol and allyl acetate in the Experimental Part.

Methyl, ethyl, isopropyl and allyl orthosilicate were allowed to react with various acids. The course of the reaction was easily followed by observing the temperature of the reaction mixture under reflux. As the reaction progressed the temperature of the boiling reaction mixture dropped and finally became constant. The time for complete reaction varied with the alkyl group in the orthosilicate, as well as with the organic acid. For example, methyl orthosilicate (b.p. 121°) and acetic acid (b.p. 118°) react so readily that appreciable reaction evidently occurred during the initial heating period and the mixture initially boiled at about 100°, dropping rapidly to a constant value of about 55° within an

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[1] A. W. Dearing and E. E. Reid, THIS JOURNAL, **50**, 3058 (1928).

[2] H. W. Post, "The Chemistry of the Aliphatic Orthoesters," Reinhold Publishing Corp., New York, N. Y., 1943, pp. 120–151.

[3] The authors are indebted to the referee for calling to their attention the disclosure by Langkammer, U. S. Patent 2,490,691 (1949, to du Pont), in which aliphatic acids were heated with various alkyl orthosilicates, yielding a distillate of the appropriate alcohol and ester. The reaction was not taken to completion, however, and the desired product was the residue which is a liquid high molecular weight alkyl polysilicate. The referee also points out that this reaction is used in the formation of silicone-alkyd resins. For a discussion of similar exchange reactions involving alkyl orthosilicates and other alkoxysilanes with carboxylic anhydrides, esters, aldehydes, ketones and alcohols see reference 2 and the references cited therein.

hour. With butyric or caprylic acid about two hours were required for the temperature to drop to a constant value. Ethyl orthosilicate reacted somewhat more slowly than did the methyl orthoester, and isopropyl orthosilicate reacted even slower, the latter compound requiring about five hours for complete reaction with butyric acid.

Like the reaction of benzoic acid and ethyl orthosilicate,[1] the reaction of this acid and methyl orthosilicate was extremely slow, not being complete in 43 hours of refluxing. The yield of methyl benzoate at this time was 79%. Similar results were obtained from the reaction of methyl orthosilicate and crotonic acid.

When methyl orthosilicate and nicotinic acid were heated together no reaction was observed, possibly owing to the insolubility of this acid in the orthosilicate at its boiling point.

In the case of methyl orthosilicate and butyric acid, the ratio of acid to orthosilicate was increased above 2 to 1 on several runs to see whether or not the presence of excess acid would cause the reaction to take the course

$$4RCO_2H + (CH_3O)_4Si \longrightarrow 4RCO_2CH_3 + SiO_2 + 2H_2O \quad (2)$$

Some success was achieved, but even with four moles of acid per mole of methyl orthosilicate the yield of methyl butyrate was only 65% based on equation 2 (130% based on equation 1). From this run one-fourth of the acid was recovered and the fractionation was complicated by the slow distillation of water during the entire fractionation. The yield of methanol from this run was about 35% of the theory based on equation 1.

Variations of this method in which the alkyl orthosilicate is not isolated are described in the Experimental Part. For example, 0.5 mole of silicon tetrachloride was added dropwise to a mixture of one mole of butyric acid and two moles of methanol, followed by a reflux period. The yield of methyl butyrate was 81%. In another run, two moles of ethanol was added to a cooled, stirred mixture of one-half mole of silicon tetrachloride and two moles of butyric acid, followed by refluxing. The yield of ethyl butyrate was 90%. In another example, allyl alcohol was added to a mixture of acetic acid and silicon tetrachloride, yielding 78% of allyl acetate. In these runs there appeared to be little reaction between the acids and silicon tetrachloride during the short time before addition of the alcohol.

In the course of this investigation improved procedures were developed for the preparation of methyl and isopropyl orthosilicates. This involved the addition of the alcohol slowly to a cold, stirred solution of silicon tetrachloride in ether, followed by refluxing and fractionation. This method gave a 93% yield of methyl orthosilicate, and an 80% yield of isopropyl orthosilicate. Attempts to extend this procedure to the reaction of *t*-butyl alcohol with silicon tetrachloride met with only limited success, due to the slowness of the reaction and the ease with which this alcohol reacts with hydrogen chloride.[4] No reaction was noted at 0°. A moderately rapid dropwise addition of -butyl alcohol to an ether or benzene solution of silicon tetrachloride, maintained at reflux, gave a vigorous reaction and a deposit of silica gel which quickly stopped the stirrer, thus bearing out the work of previous investigators[4b, 4c] on the course of this reaction. However, the very slow addition of one mole of *t*-butyl alcohol to one mole of silicon tetrachloride in ether gave a 60% yield of *t*-butoxytrichlorosilane, which was converted to di-*t*-butoxydichlorosilane in 35% yield by a similar procedure.

In these reactions it seems likely that the ether functions mainly to coördinate with most of the hydrogen chloride and then to carry it out upon distillation at a moderate temperature, hence minimizing alkyl chloride formation and attendant hydrolysis.

## Experimental Part

Unless otherwise indicated, distillations were carried out using an 80-cm. Podbielniak type column with heated jacket and partial take-off head similar to that described by Cason and Rapoport.[5] Boiling points are uncorrected.

**The Alkyl Orthosilicates.**[6]—Methyl orthosilicate was prepared by adding 2 moles of methanol dropwise to 0.5 mole of silicon tetrachloride in 200 ml. of diethyl ether with stirring and cooling in ice, followed by a 2-hour reflux period and fractionation. The ether proved to be surprisingly easy to remove without sweeping over appreciable quantities of the moderately volatile product. After removal of the ether (containing much hydrogen chloride), there was obtained 73.6 g. (93%) of methyl orthosilicate of b.p. 118–121°, $n^{25}D$ 1.3700 (lit.[4e] b.p. 121°).

A similar procedure for isopropyl orthosilicate, except for an overnight reflux period, gave a yield of 80% of product of b.p. 183–185°, $n^{25}D$ 1.3853 (lit.[4a] b.p. 185°).

Ethyl orthosilicate was prepared in the usual manner[7] from ethanol and silicon tetrachloride. The product (85% yield) had b.p. 165-166°, $n^{25}D$ 1.3818 (lit.[4e] b.p. 165.3°, $n^{20}D$ 1.3831).

**Methyl Esters.**—A mixture of 15.2 g. (0.1 mole) of methyl orthosilicate and 28.8 g. (0.2 mole) of caprylic acid was heated under reflux for 4 hours. The temperature of the boiling mixture gradually dropping from 130 to 73° during the first 2 hours and remained unchanged thereafter. Fractionation yielded 5.4 g. (85%) of methanol at 65°, 1.5 g. of intermediate fraction at 65–190°, $n^{25}D$ 1.3990, and 28.6 g. (90%) of methyl caprylate at 190–192°, $n^{25}D$ 1.4135 (lit.[8] b.p. 193–194°), leaving 9 g. of white, powdery residue (theory for silica, 6 g.).

A similar procedure employing methyl orthosilicate and butyric acid, except that the reflux period was shortened to 2 hours, gave a forerun of 7.3 g. consisting mainly of methanol, followed by 18.3 g. (90%) of methyl butyrate distilling at 99–102°, $n^{25}D$ 1.3847 (lit.[9] b.p. 102.3°, $n^{20}D$ 1.3879). The

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[4] For discussions of the difficulties experienced by others in the reaction of methanol and secondary and tertiary alcohols with silicon tetrachloride see reference 1 and also: (a) D. C. Bradley, R. C. Mehrotra and W. Wardlaw, *J. Chem. Soc.*, 5020 (1952); (b) W. Gerrard and A. H. Woodhead, *ibid.*, 519 (1951); (c) D. Ridge and M. Todd, *ibid.*, 2637 (1949); (d) A. P. Kreshkov and G. D. Nessonova, *Zhur. Obshchei Khim.*, **19**, 660 (1949); (e) M. G. Voronkov and B. N. Dolgov, *Zhur. Priklad. Khim.*, **24**, 93 (1951); and (f) D. F. Peppard, M. C. Brown and W. C. Johnson, THIS JOURNAL, **68**, 73 (1946).

(5) J. Cason and H. Rapoport, "Laboratory Text in Organic Chemistry," Prentice-Hall, Inc., New York, N. Y., 1950, p. 237.

(6) Since fractionation alone was relied upon to purify the orthosilicates and no check was made to be sure that they were free of chlorides, the question has been raised by the referee as to whether the reactions with acids were catalyzed by traces of acidic chlorides, and whether "neutral" alkyl orthosilicates would react similarly. This matter has not been investigated by the authors.

(7) H. D. Cogan and C. A. Setterstrom, *Ind. Eng. Chem.*, **39**, 1364 (1947).

(8) I. M. Heilbron, "Dictionary of Organic Compounds," revised ed., Oxford University Press, New York, N. Y., 1953.

(9) "Handbook of Chemistry and Physics," 36th ed., Chemical Rubber Publishing Co., Cleveland, Ohio, 1954, p. 822

dry, nearly colorless residue amounted to 8.5 g. Since rather vigorous heating is necessary to distil the products from the silica gel, poor fractionation occurred on some runs and a refractionation was necessary to achieve separation.

When methyl orthosilicate and benzoic acid were heated together in a similar manner, the reaction evidently proceeded very slowly. The mixture initially boiled at 137°. The temperature of the boiling mixture had dropped to 133° after 4 hours, to 115° after 15 hours, and to 108° after 43 hours. At this point the mixture was distilled yielding a mixture of methanol and methyl benzoate which could not be separated completely since the reaction producing ester and methanol continued during the distillation. A residue of 11.8 g. of brown residue remained. The distillate was fractionated yielding a forerun of 6.8 g., followed by 21.6 g. (79.5%) of methyl benzoate at 198–200°, $n^{25}\text{D}$ 1.5150 (lit.[8] b.p. 199.6°, $n^{15}\text{D}$ 1.5205).

Crotonic acid reacted with methyl orthosilicate in a similar sluggish manner to that described above for benzoic acid. When 0.2 mole of the acid and 0.1 mole of the orthosilicate were heated together the temperature of the boiling mixture slowly dropped from 128 to 109° in the first 24 hours, and to 104° during the next 15 hours. At this point the mixture was distilled, leaving a viscous liquid residue of 14.8 g. of material. The distillate was fractionated, yielding a 5.7-g. forerun, followed by 12.9 g. (64%) of methyl crotonate at 118–121°, $n^{25}\text{D}$ 1.4215 (lit.[8] b.p. 121°).

An alternate procedure for methyl butyrate is the following: To a mixture of one mole of butyric acid and 2 moles of methanol, with stirring and cooling in ice, was added dropwise 0.5 mole of silicon tetrachloride. The mixture was refluxed for 2 hours and distilled to dryness giving 34 g. of a white residue (theory for silica, 30 g.). The distillate was washed twice with half-saturated sodium chloride solution, dried over sodium sulfate and fractionated, yielding 82.9 g. (81%) of methyl butyrate, b.p. 101–102°, $n^{25}\text{D}$ 1.3867.

**Ethyl Butyrate.**—A mixture of 20.8 g. (0.1 mole) of ethyl orthosilicate and 17.6 g. (0.2 mole) of butyric acid was refluxed (temperature dropping from 135 to 93°) for 3 hours and fractionated. There was obtained a forerun of 8.3 g. consisting mainly of ethanol, followed by 21 g. (90%) of ethyl butyrate at 118–120°, $n^{25}\text{D}$ 1.3900 (lit.[8] b.p. 120°, $n^{18}\text{D}$ 1.3930), leaving 9 g. of residue.

An alternate procedure involved the addition of 2 moles of absolute ethanol to a stirred, ice-cooled mixture of one mole of butyric acid and 0.5 mole of silicon tetrachloride, followed by overnight refluxing and fractionation. After a forerun of 47.4 g., there was obtained 104.2 g. (90%) of ethyl butyrate at 118–120°. The dry, brownish residue amounted to 44 g. (theory for silica, 30 g.).

**Isopropyl Butyrate.**—A mixture of 52.8 g. (0.2 mole) of isopropyl orthosilicate and 35.2 g. (0.4 mole) of butyric acid was heated under reflux overnight. The boiling temperature dropped from 137 to 97° in five hours and no further change occurred. Fractionation gave 22.2 g. of forerun and 46.5 g. (89%) of isopropyl butyrate at 131–132°, $n^{25}\text{D}$ 1.3922 (lit.[8,10] b.p. 134–135°, b.p. 128°), leaving 13.5 g. of dry residue (theory 12.0 g.).

**Allyl Acetate.**—Three moles of allyl alcohol was added dropwise to a stirred, cooled mixture of 1.5 moles of acetic acid and 0.75 mole of silicon tetrachloride. The mixture was then heated under reflux for 2 hours and distilled. A total of 225 g. of distillate was taken at 79–92°, leaving 50 g. of dry powdery residue. The distillate was washed several times with water to remove the allyl alcohol, then dried over sodium sulfate and fractionated. After a small forerun, there was obtained 117 g. (78%) of allyl acetate at 101–103°, $n^{35}\text{D}$ 1.3970 (lit.[8] b.p. 103–104°, $n^{20}\text{D}$ 1.4049).

***t*-Butoxytrichlorosilane.**—One mole of silicon tetrachloride and 115 ml. of diethyl ether were placed in a 3-necked flask fitted with a mechanical stirrer, dropping funnel and reflux condenser (calcium chloride tube). The mixture was cooled with ice and one mole of *t*-butyl alcohol was added dropwise with stirring during 3 hours. The mixture was then heated under reflux for 3 hours more and fractionated. After removal of the ether there was obtained 125 g. (60%) of *t*-butoxytrichlorosilane at 132–133°, $d^{20}_4$ 1.176 (lit.[11] b.p. 30° (9 mm.), $d^{20}_4$ 1.176), leaving 48 g. of dry silicious residue in the flask.

**Di-*t*-butoxydichlorosilane.**—Attempts to substitute a second *t*-butoxy group for chlorine by procedures similar to that described above failed, with the reaction mixture gelling long before the addition of the second mole of *t*-butyl alcohol was completed. A successful run was carried out as follows: to 0.5 mole of *t*-butoxytrichlorosilane in an equal volume of ether there was added during 24 hours with stirring and heating under reflux 0.5 mole of *t*-butyl alcohol. The mixture was then fractionated yielding 43 g. (35%) of di-*t*-butoxydichlorosilane at 160–165°, $d^{20}_4$ 1.035 (lit.[11] b.p. 70° (15 mm.), $d^{20}_4$ 1.034), leaving 40 g. of dry powdery residue.

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(10) "Lange's Handbook of Chemistry," 8th ed., Handbook Publishers, Inc., Sandusky, Ohio, 1952, p. 646.

(11) C. S. Miner, Jr., L. A. Bryan, R. P. Holysz, Jr., and G. W. Pedlow, Jr., *Ind. Eng. Chem.*, **39**, 1368 (1947); also see Pedlow and Miner, U. S. Patents 2,566,956; 2,566,957; 2,566,363; 2,566,364; and 2,566,365; or *C. A.*, **46**, 3068 (1952). It should be noted that the preparative method described in these references using pyridine as a hydrogen chloride acceptor appears superior to that given here for replacing a second chlorine with a *t*-alkoxy group, and was also successful in yielding tri-*t*-alkoxychlorosilanes.

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[CONTRIBUTION FROM THE CONVERSE MEMORIAL LABORATORY OF HARVARD UNIVERSITY]

# The Dimerization of Acetyl Cyanide

BY BRYCE E. TATE AND PAUL D. BARTLETT

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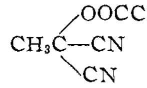
It is shown by a kinetic study that the conversion of acetyl cyanide (I) into α,α-dicyanoethyl acetate ("di-(acetyl cyanide)," DAC, II) proceeds according to sequences 2 and 3. The over-all dimerization is subject to basic catalysis because both cyanohydrin formation and acetylation are catalyzed by bases. Competing reactions are minimized by an excess of hydrogen cyanide which converts a maximum of the acetyl cyanide into the cyanohydrin. In acetonitrile solution in the presence of 0.5 *M* hydrogen cyanide and a pyridine–pyridinium chloride or perchlorate buffer, all three rate constants can be evaluated by following the initial fast and later slower stage of the reaction spectroscopically. There is a side reaction with chloride ion and a pronounced positive salt effect with tetraethylammonium perchlorate.

**Introduction.**—Acetyl cyanide (I) is readily converted in the presence of bases into a mixture of products including a dimer which has been shown to be α,α-dicyanoethyl acetate (II) ("di-(acetyl cyanide)," DAC)[1]

$CH_3COCN$
I



$CH_3C(OOCCH_3)(CN)CN$ II

This dimer is an intermediate in making the interesting monomer, vinylidene cyanide.[2] The related compound, benzoyl cyanide, forms an analogous dimer and possesses the ability to add to aldehydes in the presence of bases to yield cyanohydrin benzoates.[3] From what is known of the

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(1) K. Brunner, *Monatsh.*, **15**, 747 (1894).

(2) A. E. Ardis, S. J. Averill, H. Gilbert, F. F. Miller, R. F. Schmidt, F. D. Stewart and H. L. Trumbull, THIS JOURNAL, **72**, 1305 (1950).

(3) C. S. Marvel, N. O. Brace, F. A. Miller and A. R. Johnson, *ibid.*, **71**, 34 (1949).