EXPERIMENTAL[4]

Tetrahydro-3,3,5,5-tetrakis(hydroxymethyl)pyran (Id). To 236 g. (3.30 moles) of 42% aqueous formaldehyde solution adjusted to *p*H 11.0 by addition of 50% sodium hydroxide solution was added 200 g. (0.50 mole) of 25% aqueous glutaraldehyde (Union Carbide Chemicals Co.) at 40–45° over a 1-hr. period. Thereafter, the temperature of the mixture was held at 50, 60, and 70° for 4, 3, and 2 hr., respectively. A *p*H of 11.0 was maintained throughout by intermittent addition of base. Theoretical base consumption was observed following the complete heating period. Deionization of the total crude reaction solution by passage through columns of Dowex 50 and Dowex 1 exchange resin, in that order, gave 60.6 g. of crystalline to semicrystalline product in the initial portions of effluent. Further rinsing gave an additional 10.3 g. of oily by-product considered to represent lower condensation products. The major portion of the latter material was absorbed by the exchange resin and not recovered. The main product contained 55.5% Id (32.6% yield) as determined by quantitative isolation of its dibenzylidene derivative. Preparation of an analytical sample of Id by water recrystallization gave a white crystalline solid; m.p. 176.5°.

Anal. Calcd. for $C_9H_{18}O_5$: C, 52.41; H, 8.80; OH, 32.99; mol. wt., 206.23. Found: C, 52.64, 52.51; H, 8.80, 8.96; OH (acetylation), 32.3, 31.9; mol. wt. (cryoscopic in ethanol), 206, 206.

Derivatives of tetrahydro-3,3,5,5-tetrakis(hydroxymethyl)-pyran (Id). (1) *Tetraacetate.* A mixture of 10 g. (0.049 mole) of Id, 40 g. (0.39 mole) of acetic anhydride, and 4 ml. of glacial acetic acid was heated under reflux for 1 hr., allowed to stand overnight, and then poured into 100 ml. of water. The crystalline, white solid which separated amounted to 7.8 g. (43% yield), m.p. 91–95°, recrystallized from *n*-hexane, 94°.

Anal. Calcd. for $C_{17}H_{26}O_9$: C, 54.54; H, 7.00; mol. wt., 374.38; Sapon. No., 599.48. Found: C, 54.81, 55.00; H, 7.09, 7.17; mol. wt. (Rast), 386, 381; Sapon. No., 604.

(2) *Dibenzylidene acetal.* A mixture of 5.0 g. (0.024 mole) of impure Id, 25 ml. of water, 25 ml. of methanol, and 5 ml. of concd. hydrochloric acid was reacted with 10 ml. of benzaldehyde for 45 min. at steam bath temperature. There was obtained 8.14 g. (89% yield) of crude, white solid which upon recrystallization from butyl acetate melted at 232–234°.

Anal. Calcd. for $C_{23}H_{26}O_5$: C, 72.22; H, 6.85; mol. wt., 382.43. Found: C, 72.37, 72.47; H, 7.01, 7.02; mol. wt. (Rast), 388, 403.

Tests with pure Id showed the dibenzylidene reaction to be quantitative and applicable to the determination of Id in mixtures, or compounds hydrolyzed under the reaction conditions.

(3) *Diisopropylidene ketal.* A mixture of 10 g. (0.048 mole) of Id, 150 ml. of acetone, 5 drops of concd. sulfuric acid, and 15 g. of 2,2-dimethoxypropane (Dow Chemical Co.) was heated under reflux overnight. Concentration of the reaction mixture gave 11.6 g. (91.4% yield) of white crystals. Recrystallization from acetone gave a melting point of 201–205°.

Anal. Calcd. for $C_{15}H_{26}O_5$: C, 62.91; H, 9.15. Found: C, 63.27, 63.25; H, 9.39, 9.29.

The Id content of the recrystallized product was determined by conversion to its dibenzylidene derivative: calcd., 72.02; found, 71.2. Various samples of Id diisopropylidene ketal melted over a range of 153–206°, suggesting the presence of allotropic crystalline forms.

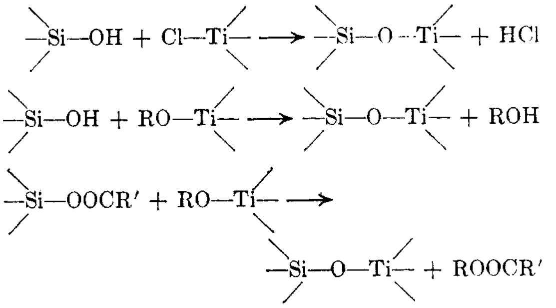
RESEARCH CENTER
HERCULES POWDER CO.
WILMINGTON, DEL.

Reaction of Trimethylacetoxysilane with Tetraisopropoxytitanium[1]

J. B. RUST, H. H. TAKIMOTO, AND G. C. DENAULT[2]

Received April 25, 1960

The preparations of organotitanium derivatives containing the silicon-oxygen-titanium linkage have been reported by several investigators.[3–9] These compounds have been prepared by any one of the following methods:



(1)

(2)

(3)

Although these three methods have been utilized in the synthesis of the tetrasubstituted triorganosiloxy titanium derivatives, only Danforth[8] has reported the preparation of monomeric, partially substituted trimethylsiloxy titanium esters. He studied the reaction of trimethylsilanol with tetraisopropoxytitanium. The reaction was reported to proceed as follows:

$$n(CH_3)_3SiOH + Ti(OC_3H_7)_4 \longrightarrow [(CH_3)_3SiO]_nTi(OC_3H_7)_{4-n} + nC_3H_7OH \quad (4)$$

where *n* is 1, 2, or 4. The extent of the substitution may be controlled by the stoichiometry of the reactants used.

The condensation reaction of trimethylacetoxysilane with tetrabutoxytitanium as reported by Andrianov and Ganina[10] results not in the desired tetrakis(trimethylsiloxy)titanium but rather in

---

(4) All melting points are uncorrected.

(1) This work was supported in part by the Office of Naval Research under Contract No. Nonr 2540(00).

(2) Hughes Research Laboratories, A Division of Hughes Aircraft Company, Malibu, Calif.

(3) W. D. English and L. H. Sommer, *J. Am. Chem. Soc.*, **77**, 170 (1955).

(4) V. A. Zeitler and C. A. Brown, *J. Am. Chem. Soc.*, **79**, 4616 (1957).

(5) D. N. Dolgov and N. F. Orlov, *Izvest. Akad. Nauk. S.S.S.R., Otdel. Khim Nauk*, 1395 (1957). *Doklady Akad. Nauk S.S.S.R.*, **117**, 617 (1957).

(6) K. A. Andrianov, A. A. Zhdanov, N. A. Kurasheva, and V. G. Dulova, *Doklady Akad. Nauk. S.S.S.R.*, **112**, 1050 (1957).

(7) D. C. Bradley and I. M. Thomas, *Chem. and Ind.*, **17** (1958).

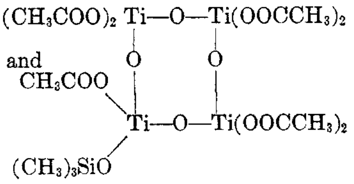
(8) J. D. Danforth, *J. Am. Chem. Soc.*, **80**, 2585 (1958).

(9) H. H. Takimoto and G. C. Denault, *Reactions of Acetoxysilanes with Tetraisopropyl Titanate*, Pacific Southwest Regional Meeting of the American Chemical Society, Redlands, Calif., October 1958.

(10) K. A. Andrianov and T. N. Ganina, *Z. Obschei Khimii S.S.S.R.*, **29**, 605 (1959).

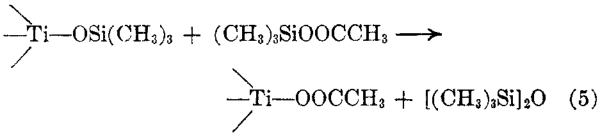
solid infusible substances. Among the products characterized and reported were

$[TiO(OOCCH_3)_2]_4$ and



These authors concluded that the basic reaction between trimethylacetoxysilane and tetrabutoxytitanium resulted in the substitution of the butoxy group by acetoxy groups with the formation of cyclic structures.

Bradley and Thomas,[11] on the other hand, obtained a 95% yield of the tetrakis(trimethylsiloxy)titanium by the reaction of trimethylacetoxysilane with tetraisopropoxytitanium; furthermore, they also found that the treatment of tetrakis(trimethylsiloxy)titanium with trimethylacetoxy silane resulted in a solid product containing acetoxy groups. Thus, the following reaction appears to take place readily:



$$\rangle Ti{-}OSi(CH_3)_3 + (CH_3)_3SiOOCCH_3 \longrightarrow \rangle Ti{-}OOCCH_3 + [(CH_3)_3Si]_2O \quad (5)$$

It is apparent from this work that the use of an excess of the acetoxysilane would result in the destruction of the trimethylsiloxy titanium derivative formed initially in the condensation reaction.

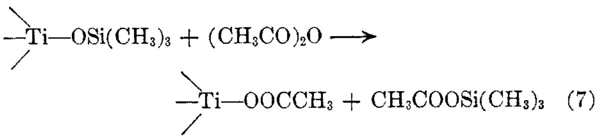
The apparent anomaly of the ester-interchange reaction reported by Andrianov and Ganina becomes clear upon the re-examination of their experimental procedures. These workers used a six to one molar ratio of trimethylacetoxysilane to tetrabutoxytitanium, whereas stoichiometry would require a ratio of four to one. In addition, the titanium orthoester was added to the acyloxysilane, and consequently the latter compound was in considerable excess at all times. Under these reaction conditions, then, it is expected that the formation of $Ti{-}OOCCH_3$ compounds would be favored to the point of exclusion of tetrakis(trimethylsiloxy)titanium.

In the present study the findings of Bradley and Thomas have been confirmed. Under proper reaction conditions, the condensation of trimethylacetoxysilane with tetraisopropoxytitanium proceeds smoothly to yield trimethylsiloxy titanium derivatives. By the control of the stoichiometry of the reaction as well as of the order of addition, the mono-, di-, tri-, and tetrasubstituted trimethylsiloxy titanium esters have been produced in good yields.

$$n(CH_3)_3SiOOCCH_3 + Ti(OC_3H_7)_4 \longrightarrow [(CH_3)_3SiO]_nTi(OC_3H_7)_{4-n} + nC_3H_7OOCCH_3 \quad (6)$$

To obtain a high yield of the desired product, the purity of the starting materials is very important. Strict care must be taken to exclude moisture from the reaction mixture, as both the acyloxysilane and the titanium esters are readily hydrolyzed. In our later work on the synthesis of tetrakis(trimethylsiloxy)titanium, we found that cooling of the reaction mixture during the slow addition of the trimethylacetoxysilane and minimizing the subsequent period of heating resulted in an improved yield. The use of this modified procedure would probably give higher yields of the partially substituted trimethylsiloxy titanium esters than that reported here.

In analogy to the reaction of tetrakis(trimethylsiloxy)titanium with trimethylacetoxy silane as reported by Bradley and Thomas, the treatment of the former compound with acetic anhydride was investigated. The use of acetic anhydride was of interest in our work on metalloxane polymers. Trimethylacetoxysilane was liberated with the formation of a white, solid product containing acetoxy groups. The reaction may be written as



$$\rangle Ti{-}OSi(CH_3)_3 + (CH_3CO)_2O \longrightarrow \rangle Ti{-}OOCCH_3 + CH_3COOSi(CH_3)_3 \quad (7)$$

and is analogous to the acetylation of $(CH_3)_3SiO{-}Ti$ with trimethylacetoxysilane.

EXPERIMENTAL

Materials. Trimethylacetoxysilane was prepared by the method of Schuyten[12] using freshly distilled trimethylchlorosilane. A commercially available tetraisopropoxytitanium was distilled and the product, boiling at 89–91°/3–4 mm., n_D^{25} 1.4608, was used.

Trimethylsiloxytriisopropoxytitanium. Trimethylacetoxysilane (13.2 g., 0.10 mole) was slowly added to 28.4 g. (0.10 mole) of tetraisopropoxytitanium (n_D^{25} 1.4630) in a flask equipped with a stirrer and an addition funnel. Drying tubes were used to protect the mixture from moisture. The addition of acetoxysilane caused the temperature of the mixture to rise. The contents of the flask were stirred for 1.5 hr. and the condensation by-product, isopropyl acetate, was then removed.

Fractionation of the residual material was carried out at reduced pressure to give 26.10 g. (93.1% yield) of product boiling at 91°/5 mm., n_D^{25} 1.4509.

Anal. Calcd. for $C_{12}H_{30}O_4SiTi$: C, 45.85; H, 9.62. Found: C, 45.80, H, 9.56.

Bis(trimethylsiloxy)diisopropoxytitanium. Trimethylacetoxysilane (132.0 g., 1.00 mole) was slowly added to 142.0 g. (0.50 mole) of tetraisopropoxytitanium. A considerable amount of heat was evolved upon addition of the acetoxysilane. The reaction mixture was stirred for 2 hr. and the isopropyl acetate was removed. The product (131.6 g., 76% yield) distilling at 103°/9 mm., n_D^{25} 1.4378 was collected.

Anal. Calcd. for $C_{12}H_{32}O_4Si_2Ti$: C, 41.85; H, 9.37. Found: C, 41.66; H, 9.22.

---

(11) D. C. Bradley and I. M. Thomas, *J. Chem. Soc.*, 3404 (1959).

(12) H. A. Schuyten, J. W. Weaver, and J. D. Reid, *J. Chem. Soc.*, **69**, 2110 (1947).

Tris(trimethylsiloxy)isopropoxytitanium. Trimethylacetoxysilane (26.4 g., 0.20 mole) was treated with 19.0 g. (0.067 mole) of tetraisopropoxytitanium as described previously. Isopropyl acetate was removed. Fractionation of the residual material yielded 16.3 g. (65.3% yield) of product boiling at 107°/8 mm., $n_{\rm D}^{25}$ 1.4321.

Anal. Calcd. for $C_{12}H_{34}O_4Si_3Ti$: C, 38.49; H, 9.15. Found: C, 38.48; H, 9.08.

Tetrakis(trimethylsiloxy)titanium. This compound was prepared by the addition of 26.4 g. (0.20 mole) of trimethylacetoxysilane to 14.3 g. (0.05 mole) of tetraisopropoxytitanium. After isopropyl acetate was removed, fractionation of the reaction mixture gave 16.6 g. 82.5% yield of product distilling at 125°/8 mm., $n_{\rm D}^{25}$ 1.4283.

Anal. Calcd. for $C_{12}H_{36}O_4Si_4Ti$: C, 35.62; H, 8.98. Found: C, 35.42, H, 8.73.

Reaction of tetrakis(trimethylsiloxy)titanium with acetic anhydride. Acetic anhydride (5.1 g., 0.05 mole) was added over a period of 10 min. to 10.1 g., (0.025 mole) of tetrakis(trimethylsiloxy)titanium. The temperature of the reaction mixture rose from 28° to 51° during the addition, and a low boiling material was observed refluxing on the wall of the flask. The contents of the flask became increasingly cloudy and a viscous, opaque gel appeared after 15 min. After 30 min. the gel turned into a white solid. The reaction mixture was heated for 30 min. At this time the mixture consisted of two phases, a clear fluid and a white solid. Distillation of the volatile material yielded 9.4 g. of the product boiling at 102°, $n_{\rm D}^{25}$ 1.3810. The infrared spectrum taken on the volatile product was similar to that of trimethylacetoxysilane. The white solid pot residue weighed 4.5 g. (Si, 10.7%; Ti, 13.8%).

HUGHES RESEARCH LABORATORIES
HUGHES AIRCRAFT CO.
CULVER CITY, CALIF.

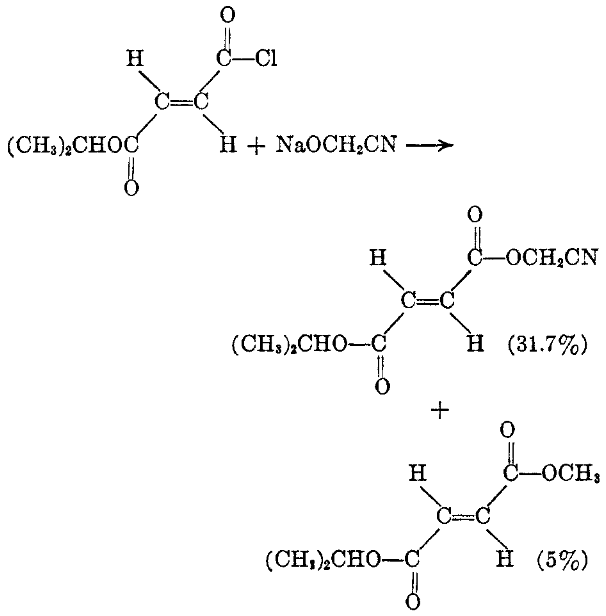
The Preparation of *i*-Propyl Cyanomethyl Fumarate

PAUL G. CAMPBELL AND CHARLES H. SCHRAMM

Received May 2, 1960

In the course of the preparation of new vinyl monomers, a convenient synthesis for alkyl fumaryl chlorides was developed. These acid chlorides served as intermediates for the preparation of various thiolfumarate esters and alkyl aryl fumarates *via* the Schotten-Baumann reaction.[1] As there are numerous examples of the synthesis and polymerization of cyanomethyl esters of α,β-unsaturated acids reported in the literature,[2] it was thought that alkyl cyanomethyl fumarates might also have useful properties.

Generally, the cyanomethyl esters of α,β-unsaturated acids have been prepared by alcoholysis of methyl or ethyl acrylates,[2d] the esterification reaction between an acyl halide and glycolonitrile,[2a,b,c,f] dehydrochlorination of the appropriate ester with quinoline,[2c] and the reaction of an acyl halide, formaldehyde, and an alkali metal cyanide.[2a,c] While Mowry was able to prepare a series of cyanomethyl esters by essentially a Schotten-Baumann reaction involving sodium cyanide and an appropriate acyl halide, these derivatives of dibasic acid halides, including fumaryl chloride, were formed in insignificant yield by this method. Instead biscyanomethyl fumarate was prepared from fumaryl chloride and glycolonitrile in the presence of a tertiary amine. However, as previously mentioned, the Schotten-Baumann reaction had been used successfully with various alkyl fumaryl chlorides, and the reaction between *i*-propyl fumaryl chloride, formaldehyde, and sodium cyanide was undertaken. The yield of *i*-propyl cyanomethyl fumarate obtained was 31.7%. However, material of the empirical formula $C_8H_{12}O_4$ was also formed. This was shown to be methyl *i*-propyl fumarate by comparison with an authentic sample prepared from *i*-propyl fumaryl chloride and methanol in the presence of pyridine. The probable explanation for the presence of this byproduct is the formation of methanol by the Cannizzaro reaction involving formaldehyde in the alkaline sodium cyanide solution. The methanol could then compete for the available acyl halide.



EXPERIMENTAL

Boiling points are uncorrected. Unless otherwise indicated, distillations were carried out through an 80-cm. Podbielniak-type column.

i-Propyl fumaryl chloride. A sample of crude *i*-propyl hydrogen maleate was prepared by warming a mixture of 0.5 mole each of maleic anhydride and *i*-propyl alcohol on the steam bath until a sirupy liquid resulted. To this

---

(1) P. G. Campbell, G. Sumrell, and C. H. Schramm, to be published.

(2a) D. T. Mowry, *J. Am. Chem. Soc.*, **66**, 371 (1944); (b) J. Harmon and C. J. Mighton, U. S. Patent **2,379,297** [*Chem. Abstr.*, **39**, 5128 (1945)]; (c) D. T. Mowry, U. S. Patents **2,380,061** and **2,380,062** [*Chem. Abstr.*, **40**, 91 (1946)]; (d) C. E. Rehberg, M. B. Dixon, and W. A. Faucette, *J. Am. Chem. Soc.*, **72**, 5199 (1950); (e) G. F. D'Alelio, U. S. Patent **2,583,062** [*Chem. Abstr.*, **48**, 11806 (1954)]; (f) C. S. Marvel, *et al.*, *Ind. Eng. Chem.*, **47**, 344 (1955).