The Synthesis and Pyrolytic Rearrangement of Phthalate Esters of Some Tertiary Silanols. An Attempt to Prepare a Silicon Carbon Double Bond Species

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The synthesis and pyrolysis of the methyl phthalate esters of diphenylmethylsilyl, *t*-butylsilyl, benzyldiphenylsilyl, and optically active 2-octanol yielded corresponding silyl ethers and phthalic anhydride. In the case of the latter compound, almost complete retention of configuration was observed about the asymmetric carbon atom. A mechanism is proposed for this rearrangement.

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La synthèse et la pyrolyse des phtalates de méthyle et de diphénylméthylsilyle, de *t*-butylsilyle, de benzyldiphénylsilyle et de l'octyl-2 optiquement actif conduit aux éthers silylés et à l'anhydridre phtalique. Dans le cas du dernier ester, on a observé une rétention pratiquement complète de la figuration autour du carbone asymétrique. On propose un mécanisme pour ce réarrangement. [Traduit par le journal]

Introduction

Over the past several years, our laboratory has been engaged in an exhaustive study on the pyrolysis of tertiary hydrogen phthalate esters which at abnormally low temperatures (below 150°) decompose to afford near quantitative yields of olefins and phthalic acid (1). Mechanistic studies have shown that the decomposition of such esters occurs through a reversibly formed ion pair with *ortho*-carboxylate hydrogen participation, followed by a kinetically controlled elimination of phthalic acid and olefin (2, 3). A natural extrapolation would be to study the pyrolysis of tertiary silyl hydrogen phthalates which presumably might lead to a stable Si=C system especially if these derivatives decomposed at low temperatures and contained within the compounds resonance and/or steric stabilization.

There is a scarcity of such derivatives in the literature. Gilman and co-workers (4) recorded an unsuccessful attempt at the preparation of a silyl hydrogen phthalate upon reacting triphenylsilanol with phthalic anhydride. A patent reference (5) reports the chloroplatinic acid catalyzed preparation of silyl derivatives of dicarboxylic acids, including phthalic acid, although the report indicates that a mixture of silyl hydrogen phthalate and disilyl ester was produced. We were not successful in obtaining pure monosilyl derivatives from the reaction of potassium phthalate with several tertiary silyl chlorides. The disilyl esters were the predominating products. It is interesting to report that an attempt to prepare the monosilver hydrogen phthalate salt using an obvious exchange reaction of the corresponding monopotassium salt and silver nitrate gave only the disilver salt in quantitative yield. Although silver salts of acids are generally water insoluble, it appears that this salt has sufficient solubility to allow further selective reaction with silver nitrate under more homogeneous conditions. In any event, a preparation of silver hydrogen phthalate does not appear in the literature.

The reaction of phthalic acid with tertiary silyl chlorides (pyridine catalysis) under homogeneous conditions, again lead to mixtures. The procedure of Sommer and co-workers (ref. 6 and references cited therein) which involves the treatment of an organosilicon hydride with an organic acid in the presence of 10% palladium on carbon to yield esters did not prove fruitful with phthalic acid and diphenylmethylsilane. Here again, mixtures were obtained.

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It was decided to prepare *t*-silyl methyl phthalate esters for pyrolytic studies to circumvent the problems previously encountered with the preparation of the monosilyl derivatives. Thus methyldiphenylsilyl, trimethylsilyl, and benzyldiphenylsilyl methyl phthalates (**1**, **2**, and **4**) were prepared in excellent yields from anhydrous potassium methyl phthalate with the appropriate silyl chloride (Scheme 1).

Thermal decomposition of **1** was effected only very slowly at 250° to give phthalic anhydride (**5**) and diphenylmethylmethoxysilane (**6**) as the major products. A more rapid decomposition was realized at 400°. The silyl ester (**2**) decomposed in a similar manner over the temperature range 400–470° to give **5** and methoxytrimethylsilane (**7**). Decomposition of **4** at 400° yielded **5** and benzyldiphenylmethoxysilane (**8**). No silicoolefin nor products which could be construed as arising from such an intermediate were observed.

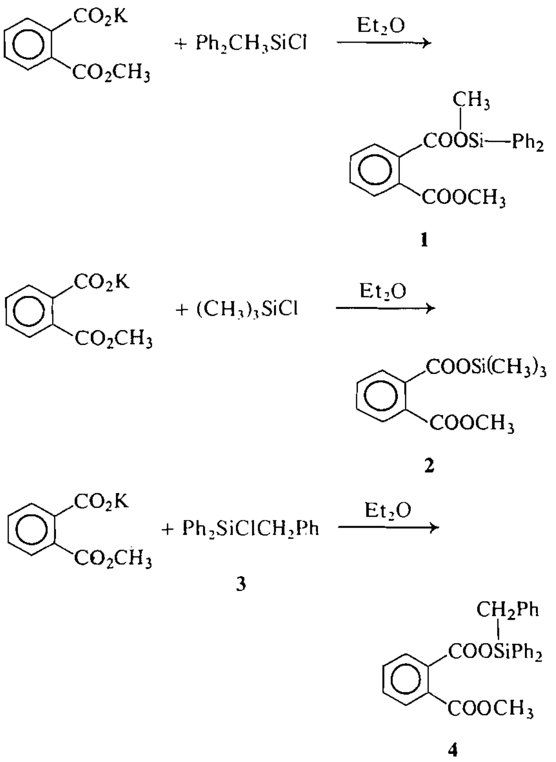
Isolation of silyl ethers (**6**, **7**, and **8**) from the pyrolysis of **1**, **2**, and **4** contrasts with the pyrolysis of methyl alkyl phthalates which give the appropriate alkene, methanol, and **5** (7). The reaction is postulated to initially involve the formation of alkenes and methyl hydrogen phthalate, followed by decomposition of this acid ester to methanol and **5** (8).

In order to provide some idea of the stereochemical aspects of our results, optically active trimethylsilyl-2-octyl phthalate (**10**) was prepared and subjected to pyrolysis. The synthesis of **10**, the pyrolysis, and proof of retention of configuration about the asymmetric carbon atom is shown in Scheme 2.

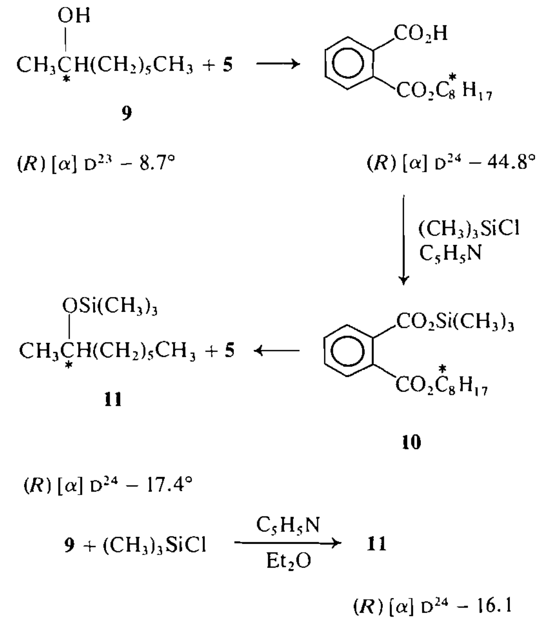
It is proposed then that the reaction proceeds in a concerted manner as indicated in Scheme 3 with essentially complete retention of configuration about the asymmetric carbon atom.

Experimental

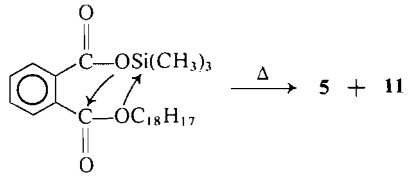
Melting points were determined on a Fisher–Johns apparatus and are uncorrected. Infrared spectra were recorded on Beckman IR-10 and IR-12 spectrometers in chloroform or deuterochloroform solutions unless otherwise noted. Nuclear magnetic resonance spectra were obtained with a Jeolco C-60 HL spectrometer in deuterochloroform with methylene chloride as an internal standard (τ 4.70) unless otherwise specified. Optical rotation measurements were determined with a Rudolph Model 80 polarimeter equipped with a sodium lamp (λ 589 nm) using 2 dm polarimeter tubes. Gas chromatography (g.c.) was performed on Hewlett Packard 720 and 5750 instruments. Columns utilized were as follows: 6 ft × 1/4 in. 10% SE 30 on 60–80 Chromosorb W, 8 ft × 1/4 in. 20% SE 30 on 60–80 Chromosorb W, 8 ft × 3/8 in.



SCHEME 1. Synthesis of diphenylmethylsilyl, trimethylsilyl, and diphenylbenzylsilyl methyl phthalates (**1**, **2**, and **4**).



SCHEME 2. Synthesis and pyrolysis of optically active trimethylsilyl-2-octyl phthalate (**10**) and synthesis of optically active trimethylsilyl-2-octanol (**11**)



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SCHEME 3. Postulated thermal decomposition pathway for *t*-silyl alkyl phthalates.

10% SE 30 on 60–80 Chromosorb W, and 6 ft × 1/4 in. 10% Dexsil 300 on 60–80 Chromosorb W. All nonaqueous reactions were run in dried apparatus under an atmosphere of nitrogen and the silyl chlorides utilized were distilled prior to use. All ethereal solvents were purified by distillation from lithium aluminum hydride and pyridine was distilled from calcium hydride. Anhydrous sodium sulfate was used for all drying operations unless otherwise noted. Microanalyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, N.Y. and A. B. Gygli Microanalyses Laboratory, Toronto, Ontario.

Methyldiphenylsilyl Methyl Phthalate (1)

To 1.09 g (5 mmol) of potassium methyl phthalate in 50 ml of ether was added 0.83 g (4 mmol) of diphenylmethylsilyl chloride. The resultant heterogeneous mixture was vigorously stirred for 4 h at room temperature and then allowed to stand for an additional 4 h. The mixture was filtered through Super Cel under an atmosphere of nitrogen and concentrated overnight at 35° (1 mm) to give 1.2 g (82%) of **1** as a pale yellow viscous liquid: i.r. 5.78, 5.85, and 8.93 μ (PhSi); n.m.r. 2.4 (m, 14), 6.34 (s, 3, OCH_3), and 8.98 (s, 3, CH_3Si).

Anal. Calcd. for $C_{22}H_{20}O_4Si$: C, 70.18; H, 5.35; Si, 7.46. Found: C, 70.13; H, 5.41; Si, 7.45.

Trimethylsilyl Methyl Phthalate (2)

To 3.27 g (15 mmol) of potassium methyl phthalate in 80 ml of ether was added 1.53 g (12 mmol) of chlorotrimethylsilane and the mixture was vigorously stirred for 4 h. The mixture was filtered through Super Cel under an atmosphere of nitrogen and concentrated overnight at 40° (0.5 mm) to give 2.4 g (80%) of **2** as a yellow liquid: i.r. 5.78, 5.85, and 11.7 μ (CH_3Si); n.m.r. 2.4 (m, 4), 6.1 (s, 3, OCH_3), and 9.61 (s, 9, CH_3Si).

Anal. Calcd. for $C_{12}H_{16}O_4Si$: C, 57.11; H, 6.39; Si, 11.13. Found: C, 57.48; H, 6.55, Si, 11.21.

Benzyldiphenylchlorosilane (3)

Benzylmagnesium chloride (200 mmol) in 150 ml of ether and chlorodiphenylsilane (53.2 g, 210 mmol) in 125 ml of ether were stirred for 15 min at 0° and then refluxed for 2 h. Upon cooling, the solution was filtered through Super Cel under a nitrogen atmosphere with the aid of another 150 ml of ether and the filtrate was concentrated *in vacuo*. Methylene chloride (50 ml) was added and the solution was refiltered and concentrated to a pale yellow liquid. Short-path distillation gave 40.9 g (66%) of the chlorosilane: b.p. 147–150° (0.003 mm); m.p. 52–57°; n_D^{25} 1.6085; i.r. 7.0, 8.97, and 19.0 μ (SiCl); n.m.r. 2.7 (m, 15) and 7.2 (s, 2).

Anal. Calcd. for $C_{19}H_{17}SiCl$: C, 73.87; H, 5.54; Cl, 11.47. Found: C, 73.76; H, 5.58; Cl, 11.38.

Benzyldiphenylsilyl Methyl Phthalate (4)

To 1.09 g (5 mmol) of potassium methyl phthalate in 50 ml of ether was added 1.23 g (4 mmol) of **3** in 1 ml of ether and the mixture was stirred for 4 h and then allowed to stand without stirring for 4 h. The mixture was filtered through Super Cel under an atmosphere of nitrogen and concentrated overnight at 45° (0.3 mm) to give 1.4 g (78%) of **4** as a pale yellow viscous liquid: i.r. 5.78, 5.84, and 8.90 μ (PhSi); n.m.r. 2.6 (m, 19), 6.38 (s, 3, OCH_3), and 6.85 (s, 2, CH_2Ph).

Anal. Calcd. for $C_{28}H_{24}O_4Si$: C, 74.30; H, 5.34; Si, 6.20. Found: C, 74.48; H, 5.45; Si, 5.90.

(R)-(−)-Trimethylsilyl-2-octyl Phthalate (10)

(*R*)-(−)-2-octanol (**9**), $[\alpha]_D^{23}$ − 8.7° was reacted with **5** according to the procedure of Kenyon (9) to give 26 g (74%) of (*R*)-(−)-2-octyl hydrogen phthalate; m.p. 69–70°; $[\alpha]_D^{24}$ − 44.8° (C 3.4, abs. ethanol) [lit. (7) m.p. 75°; $[\alpha]_D^{24}$ − 48.4°]. The trimethylsilyl derivative **10** was prepared from the potassium salt according to the procedure described for **1** to obtain **10** (72%) as a colorless liquid, i.r. 5.83 and 11.7 μ; n.m.r. ($CDCl_3$-*p*-dioxane), 8.7 (m, 16), and 9.6 (m, 9, CH_3Si).

Anal. Calcd. for $C_{19}H_{30}O_4Si$: C, 65.10; H, 8.62. Found: C, 65.24; H, 8.50.

(R)-(−)-2-Octyltrimethylsiloxane (11)

This was prepared in 64% yield by the method of Fertig *et al.* (10) using ether as a solvent: b.p. 99.0–99.5° (30 mm); n_D^{20} 1.4124; $[\alpha]_D^{24}$ − 16.1°.

Diphenylmethylmethoxysilane (6)

Diphenylmethylchlorosilane (**3**) was converted by the procedure of Sommer *et al.* (11) into **6** (53%): b.p. 87–90° (0.075 mm); n_D^{25} 1.5531 [lit. (11) n_D^{25} 1.5510].

Trimethylmethoxysilane (7)

Chlorotrimethylsilane was converted by the method of Sauer (12) into 7 (18%): b.p. 57.5°; n_D^{20} 1.3675 (lit. (12) b.p. 57°, n_D^{20} 1.3678).

Benzyldiphenylmethoxysilane (8)

Benzyldiphenylchlorosilane (**3**) (5.17 g) was converted by the method of Sauer (12) into **8** (3.9 g, 76%): b.p. 142–144° (0.005 mm); n_D^{25} 1.5923; i.r. 3.52, 7.0, 8.93, and 9.17 μ; n.m.r. 2.7 (m, 15), 6.42 (s, 3), and 7.24 (s, 2).

Anal. Calcd. for $C_{20}H_{20}OSi$: C, 78.89; H, 6.62, Si, 9.22. Found: C, 78.55; H, 6.78; Si, 8.90.

General Pyrolysis Procedure

The thermal rearrangements were effected by a calibrated variac controlled heating mantle or by the use of a bunsen flame (the results were not altered by this method). The sample was placed in a dried single-necked flask which was attached to a cooled flask for trapping of volatile products. All pyrolyses were conducted under an atmosphere of nitrogen. After the pyrolysis assembly cooled, pentane was added and the insoluble phthalic anhydride was filtered, washed with pentane, dried, and identified by comparison of its infrared spectrum and its melting point with authentic material. The combined pentane fractions were concentrated to yield oils. The components which constituted the oils were identified by i.r., n.m.r., and g.c. (retention time) comparison with authentic material and the relative amounts were calculated by n.m.r. integration.

*Pyrolysis of Diphenylmethylsilyl Methyl Phthalate (**1**)*

Pyrolysis of 1.1 g of **1** with a bunsen flame for 15 min and then for 3 min (0.5 mm) to remove volatile material from the reaction flask gave **5** (0.4 g, 88%) and a yellow oil (0.64 g) which contained four components as indicated by i.r. and n.m.r. inspection. The components were identified as diphenylmethylmethoxysilane (**6**, 85%), sym-tetraphenyldimethyldisiloxane (7%), m.p. 45–46° (lit. (13), m.p. 50°), methyl hydrogen phthalate, and undecomposed **1** (6%). Pyrolysis of **1** at 250° indicated *ca.* 90% decomposition at the end of 6 h.

*Pyrolysis of Trimethylsilyl Methyl Phthalate (**2**)*

Pyrolysis of 2.3 g of **2** at 400° and then at 470° (0.5 h) gave **5** (0.75 g, 48%) and methoxytrimethylsilane (**7**) (0.37 g, 38%). The remaining material (0.87 g) from concentration of the pentane layer, was shown by i.r. and n.m.r. inspection to consist of methyl hydrogen phthalate along with small amounts of trimethylsilanol, hexamethyldisiloxane, undecomposed **2** as well as **5**.

*Pyrolysis of Benzyldiphenylsilyl Methyl Phthalate (**4**)*

Pyrolysis of 0.96 g of **4** at 400° (1 h) and then with a Bunsen flame for 3 min (0.5 mm) gave **5** (0.28 g, 90%) and a yellow oil (0.24 g) which was identified as **8** along with trace amounts of starting material.

*Pyrolysis of (R)-(−)-Trimethylsilyl-2-Octyl Phthalate (**10**)*

Pyrolysis of 5.5 g of **10** at 400° (1.5 h) and then at 470° (0.5 h) gave **5** (2.2 g, 93%) and a colorless volatile liquid (2.6 g) which contained five components by g.c. analysis. The products were separated by preparative g.c. and were identified by spectral comparison and retention time with authentic samples. The first two components were identified as trimethylsilanol (1%) and hexamethyldisiloxane (2%). The third peak (4%) consisted of at least three components tentatively identified as a mixture of octenes by g.c. and spectral comparison with an authentic sample of 1-octene. The fourth component (10%) was identified as 2-octanol (**9**): $[\alpha]_{\mathrm{D}}^{24}$ − 8.8° (C, 1.7, abs. ethanol). The last component (83%) was identified as the (*R*)-(−)-2-octyltrimethylsilyl ether **11**: $[\alpha]_{\mathrm{D}}^{24}$ − 17.4° (C, 3.4, isooctane).

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