

Synthesis of Esters from Silyl Ethers and Acyl Chlorides: Catalysis by Quaternary Ammonium Chlorides

Svante Brandänge,* Hans Leijonmarck and Teclay Minassie

Department of Organic Chemistry, Arrhenius Laboratory, Stockholm University, S-106 91 Stockholm, Sweden

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The formation of esters from silyl ethers and acyl chlorides is catalysed by quaternary ammonium chlorides, the other halide ions being less efficient. Evidence for the intermediacy of the alcohol formed by protodesilylation of the silyl ether is presented. Excellent regioselectivities (>99%) were obtained in the monoacylations of the bis-silyl ether **3** made from 1-*O*-benzylglycerol.

Cleavage of the Si–OR bond by acyl chlorides to form a chlorosilane plus a carboxylic ester is a reaction that has been known since the nineteenth century (Scheme 1).¹ Later it was found that Lewis acids catalyse the reaction. Zinc chloride² and tin(II) chloride or bromide³ have been used successfully. Alternatively, acetic anhydride can be used as acylating agent in combination with either a Lewis acid (FeCl₃, BF₃ or TiCl₄–AgClO₄)^{4–6} or a Brønsted acid (acetic acid–pyridine).⁷ Triflic and trifluoroacetic anhydride⁸ and sulfinyl chlorides⁹ have been used without catalyst to convert trimethylsilyl (TMS) ethers into esters.

We here report that quaternary ammonium chlorides, too, are efficient catalysts for the formation of esters from silyl ethers and acyl chlorides (Table 1). It should be noted that dilute solutions were used in the reactions of Tables 1 and 2 in order to demonstrate the catalytic



Scheme 1.

Table 1. Effect of added tetraethylammonium chloride on the yield of octyl benzoate obtained from benzoyl chloride and *n*-C₈H₁₇OSiMe₃.^a

Et ₄ N ⁺ Cl ⁻ (mmol)	Yield of octyl benzoate (%) ^b
0	0.1
0.5	13
1.0	31
2.0	61

^aThe reactions between *n*-C₈H₁₇OSiMe₃ (1.00 mmol) and BzCl (1.10 mmol) were run in refluxing, alcohol-free CHCl₃ (5.0 ml) for 90 min. ^bGLC yields.

*To whom correspondence should be addressed.

Table 2. Effect of added tetraalkylammonium halides on the yield of octyl benzoate obtained from benzoyl chloride and *n*-C₈H₁₇OSiMe₃.^a

Quaternary salt (1.0 mmol)	Yield of octyl benzoate (%) ^b
Bu ₄ N ⁺ F ⁻ , 3 H ₂ O	17
Bu ₄ N ⁺ F ⁻ , <3 H ₂ O	10
Et ₄ N ⁺ Cl ⁻	31
Bu ₄ N ⁺ Cl ⁻	40
Bu ₄ N ⁺ Br ⁻	24
Bu ₄ N ⁺ I ⁻	3

^aThe reactions between *n*-C₈H₁₇OSiMe₃ (1.00 mmol) and BzCl (1.10 mmol) were run in refluxing, alcohol-free CHCl₃ (5.0 ml) for 90 min. ^bGLC yields.

effect. Reactions in more concentrated solution gave higher yields. Thus the yield in the third reaction of Table 1 was 95% (GLC) when 1.0 ml of chloroform was used instead of 5.0 ml. Triethylamine hydrochloride proved less active than the quaternary chlorides; use of 0.5 or 2.0 equiv. of this salt under the standard conditions (Table 1) led to octyl benzoate in 0.4 and 3.0% yield, respectively. Acylation of a TMS ether was slower than that of the corresponding alcohol as shown by two benzoylations performed under identical conditions; the third reaction of Table 1 led to a yield of 66% when 1-octanol served as starting material (31% with the TMS ether). As expected, acetyl chloride reacts faster than benzoyl chloride and trimethylsilyl ethers react faster than *tert*-butyldimethylsilyl or *tert*-hexyldimethylsilyl ethers (cf. Refs. 2 and 3). In an acylation similar to the third reaction of Table 1, a 53% yield of octyl acetate was formed after only 10 min at 22 °C using 1.5 mmol of acetyl chloride.

A convenient technique for some preparative acylations involves the use of cetylpyridinium chloride monohydrate (Rpy⁺Cl⁻) without solvent. Heating a mixture

of $n\text{-C}_8\text{H}_{17}\text{OSiMe}_3$ (2.00 mmol), BzCl (2.00 mmol) and Rpy^+Cl^- (1.0 mmol) formed a melt which produced octyl benzoate in a 96% yield (90 °C, 40 min). A 100% yield was obtained (GLC) when Rpy^+Cl^- in the reaction flask was treated with chlorotrimethylsilane (1 ml) at reflux for 10 min, and volatile compounds then evaporated off under reduced pressure before running the reaction.

This investigation was initiated assuming that the pentavalent silicon compound which could be formed from the silyl ether and halide ion would display enhanced nucleophilicity on oxygen which would lead to faster ester formation. Although fluoride has proved to be the most efficient halide ion in the activation or cleavage of Si–O or Sn–O bonds,^{10–13} the results in Table 2 show that chloride ion is superior in the present reaction type. The lower efficiency of fluoride is probably largely due to rapid and extensive formation of benzoyl fluoride, which presumably here, too, is a less reactive acylating agent^{14,15} than the corresponding chloride. After aqueous work-up of the second reaction of Table 2, GLC indicated a ca. 80% yield of benzoyl fluoride.

Mechanistic considerations. To elucidate the reaction mechanism we performed acylation experiments in which *N*-ethyl-diisopropylamine was used as an additive. This amine is sterically hindered and therefore a poor nucleophile. Any effect from it should most likely be due mainly to its basic character. The yield in the fourth reaction of Table 1 dropped from 61 to 5% when 0.20 mmol of the amine was included (2.0 mmol of BzCl) and to less than 1% when 0.50 mmol was used (1.5 mmol of BzCl). These results indicate a catalytic role of hydrogen chloride, presumably formed from the acyl chloride and traces of water. A pathway to the ester which accounts for this finding is proposed in Scheme 2. The above-outlined acylation of a pentavalent silicon compound intermediate seems less likely but cannot be ruled out since a second mechanistic role of hydrogen chloride is also conceivable, namely activation of the acyl chloride by hydrogen bonding to it during its reaction with the pentavalent silicon compound intermediate. The first half of the Scheme 2 pathway is well known in the reverse direction but not in the forward direction. However, the reaction forming a separate layer of chlorotriethylsilane from triethylsilanol plus conc. hydrochloric acid¹⁶ is analogous to the forward reaction. It may be expected that added chloride ions (from the quaternary ammonium chloride) would catalyse the formation of the intermediate alcohol irrespective whether the silyl ether reacts first with hydro-

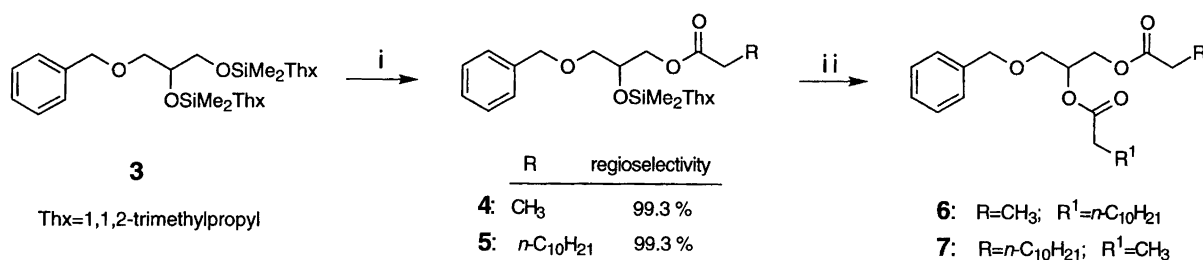


Scheme 2. Proposed main pathway for the formation of esters from silyl ethers and acyl chlorides under the given reaction conditions.

gen chloride and then with chloride ion or in the opposite order.

Regioselectivity aspects. Highly regioselective transformation of primary TMS ethers into acetate esters in the presence of secondary TMS ether groups in the carbohydrate/mannitol series has been accomplished by using an acetic acid–acetic anhydride–pyridine reagent system.⁷ Acetic anhydride was used in large excess; no other esters have been synthesized using this method. Because of the biological importance of various derivatives of glycerol, we chose 1-*O*-benzylglycerol (**1**) as starting diol. This compound, as well as the corresponding *p*-methoxybenzyl ether, is available in either *R* or *S* form and these have been widely used for the synthesis of enantiomerically pure glycerol derivatives.^{17,18} We converted racemic **1** into the bis-TMS ether **2** and the bis(dimethylhexylsilyl) ether **3**. Reaction between **2**, hexanoyl chloride (0.82 or 1.50 equiv.) and Bu_4NCl (0.35 equiv., CHCl_3 , 22 °C) led mainly to the primary monohexanoate (partially desilylated) with regioselectivities in the 75–90% range. In contrast, acylations of the less reactive silyl ether **3** to the monoesters **4** or **5** occurred with excellent regioselectivities (Scheme 3). These two reactions were followed by GLC and showed a similar change in isomer ratio with time. After 1 h (22 °C) the conversion into **4** was ca. 30% and the regioselectivity 96.6%. The latter increased with time and reached a value of 99.3% after 7 h. A similar effect was observed in the synthesis of **5**. This should be due to a rate difference between the conversions of the two isomeric monoesters to diester. The minor monoester contains a primary silyl ether unit and should thus undergo a further acylation faster than the major isomer (**4** or **5**) which contains a secondary silyl ether unit. We stopped the reactions at the 99.3% level in order to keep the amount of diester below 15%. Unlike the monoesters of 1-*O*-benzylglycerol, the silylated analogues **4** and **5** could be purified by chromatography on silica gel with no isomerization problems¹⁹ at all. In fact there was actually some isomer enrichment of **5** from 99.3 to 99.8%. The remaining secondary silyl ether group in **4** or **5** could also be transformed into an ester group albeit more reluctantly (105 °C, 3 h) than the primary silyl ether in **3**. Reaction between **4** and dodecanoyl chloride led to a mixed diester (**6**) of 1-*O*-benzylglycerol. Similar acylation of **5** with propionyl chloride gave the isomeric diester **7**. The preferred catalyst was Bu_4NCl since it gave less emulsion during work-up. Unfortunately, during these second acylations there was some decrease in isomeric purity: from 99.3 to 98.2% in the reaction with **4** and from 99.8 to 98.0% in the reaction with **5**. The proposed mechanism (Scheme 2) is compatible with a decrease in isomeric purity since the protodesilylation gives the primary monoester of **1** as a reaction intermediate and a small part of this could well undergo isomerisation by acyl migration before being converted into diester.

A single attempt to convert **4** into **6** with tin(IV)



Scheme 3. Technique for a highly regioselective preparation of esters in the glycerol series. Reagents: (i) RCH₂COCl, Bu₄NCl, 22 °C, (ii) R¹CH₂COCl, Bu₄NCl, 105 °C. In step (ii) the regioisomeric purities decreased to 98.2% (**6**) and 98.0% (**7**).

chloride as catalyst (0.05 equiv.) instead of the quaternary chloride was made. Despite the use of a smaller amount of acyl chloride, the isomeric purity of **6** was 98.9% which indicates that this method of conversion is more efficient than the acylation catalysed by Bu₄NCl.

Regioselective derivatisation of the primary hydroxy group in **1** has previously been achieved, e.g., by direct esterification,¹⁸ silylation^{20,21} or (*p*-methoxy)tritylation.^{22,23} In the strategy described here **1** is instead disilylated prior to a regioselective acylation step. The isomeric purities of **6** and **7** seem to be similar to the highest found (estimated¹⁸ as ≥98%) for diesters of **1** in other studies. Potential advantages of the present technique are the possibility of isolating the product obtained after the first acylation step without loss in regioisomeric purity, and also regioselectively derivatising **3** with a group even more prone to migrate than a fatty acid acyl group, e.g., a phosphoryl group.

Experimental

Chloroform was passed through a column of basic alumina to remove the stabilizing alcohol. The reactions in Tables 1 and 2 were run using flame-dried glassware and a blue silica gel drying tube but without a protective atmosphere. In the work-up most of the solvent was evaporated off and the residue was partitioned between water and Et₂O. The solvent (Et₂O) was evaporated off, CH₂Cl₂ was added and the solution was dried (Na₂SO₄). The yields of octyl benzoate were determined by GLC with triphenylmethane as an internal standard. These and other GLC analyses were performed using fused silica SPB-5 (column A) and DB-225 (column B) capillary columns (30 m) mounted in a Hewlett-Packard 5830 A gas chromatograph linked to a 18850 A GC terminal (electronic integrator); H₂ was the carrier gas. The retention times of the minor isomers formed in the acylations of the silyl ethers **2** and **3** were found by using GLC reference mixtures prepared by acylation of **1** with acyl chloride–pyridine–CH₂Cl₂, followed by silylation. The isomer ratios in these mixtures were roughly 7:1. Reference samples of **6** and **7** were prepared in a similar way.

(*R,S*)-3-(Phenylmethoxy)-1,2-propanediol (**1**) was prepared by a modified lit.²⁴ procedure; *O*-benzylation of

2,2-dimethyl-1,3-dioxolan-4-ylmethanol was performed by cautiously adding BnCl (1 equiv.) to the mixture formed from the dioxolanylmethanol and KOBu^t (1 equiv.) in HOBu^t (3.2 equiv.) at 110 °C. After 1 h at this temperature the mixture was cooled and partitioned between Et₂O and 0.5 M aq. NaOH; the benzylation product was distilled, the acetal was hydrolysed and **1** was distilled. The two best (of three) fractions showed GLC purities of 99.2 and 98.7%. Compound **1** (≥97%) is commercially available.

2,3,3,4,4,9,9,10,10,11-Decamethyl-6-[(phenylmethoxy)methyl]-5,8-dioxa-4,9-disiladodecane (**3**) was prepared in a stoppered flame-dried flask from **1** (1.90 g, 98.7% purity, 10.3 mmol), chlorodimethylthexylsilane (Fluka, 4.86 g, 27.2 mmol) (thexyl=1,1,2-trimethylpropyl) and imidazole (4.94 g, 72.6 mmol) in distilled *N,N*-dimethylformamide (10 ml). After being stirred for 19 h (22 °C) the reaction mixture was partitioned between water (10 ml) and *n*-hexane (30 ml). The hexane layer was washed with water (2 × 30 ml), dried (Na₂SO₄) and then concentrated. Purification on a silica gel column (5 × 28 cm) using 2,2,4-trimethylpentane–toluene (2:1) as the eluant gave **3** in a purity (GLC) of 99.9% (81% yield). ¹H NMR: δ 7.1–7.4 (m, 5 H), 4.52 (s, 2 H), 3.82 (quintet, 1 H), 3.6–3.3 (m, 4 H), 2.75 (m, 2 H), 0.88, 0.88, 0.86, 0.85, 0.83 (in all 24 H), 0.10 (s, 6 H), 0.07 (s, 6 H). ¹³C NMR: δ 138.7, 128.2, 127.5, 127.4, 73.3, 72.5, 72.3, 64.6, 34.1, 25.2, 24.9, 20.4, 20.3, 18.6, 18.5, –2.6, –3.5.

2-[Dimethyl-1,1,2-(trimethylpropyl)silyloxy]-3-(phenylmethoxy)propyl propanoate (**4**). A mixture of **3** (2.507 g, 5.37 mmol), propanoyl chloride (0.994 g, 10.7 mmol), Bu₄NCl (0.448 g, 1.61 mmol) and CHCl₃ (1 ml) in a stoppered flame-dried flask was stirred at 22 °C. Samples were withdrawn at 1 h intervals and analysed by GLC. The regioisomeric purity of **4** increased continuously from 96.6% (1 h) to 99.3% (7 h). The reaction was stopped after 7 h. Partition between Et₂O and aqueous NaHCO₃ and purification on a column of silica gel (4 × 35 cm) using 2,2,4-trimethylpentane–ethyl acetate (9:1) gave a 72% yield of **4**, regioisomeric purity, 99.2%. ¹H NMR: δ 7.35–7.25 (m, 5 H), 4.53 (s, 2 H), 4.20 (m, 1 H), 4.03 (m, 2 H), 3.45 (d, 2 H, *J* 5.5 Hz), 2.32 (q, 2 H, *J* 7.5 Hz), 1.61 (m, 1 H), 1.13 (t, 3 H, *J* 7.5 Hz),

0.86 (d, 6 H, J 6.6 Hz), 0.82 (s, 6 H), 0.11 (s, 3 H) and 0.10 (s, 3 H). ^{13}C NMR: δ 174.3, 138.1, 128.3, 127.6, 73.4, 71.8, 69.5, 66.2, 34.1, 27.5, 24.9, 20.2, 18.5, 9.1, -2.7, -2.9.

The diacylation product 3-(phenylmethoxy)-2-(propanoyloxy)propyl propanoate (11% yield) was eluted later: ^1H NMR: δ 7.40–7.25 (m, 5 H), 5.24 (m, 1 H), 4.54 (AB, 2 H, J 12.2 Hz), 4.36 (dd, 1 H, J 11.9 and 3.9 Hz), 4.20 (dd, 1 H, J 11.9 and 6.4 Hz), 3.60 (d, 2 H, J 5.1 Hz), 2.35 (q, 2 H, J 7.6 Hz), 2.31 (q, 2 H, J 7.6 Hz), 1.14 (t, 3 H, J 7.7 Hz), 1.12 (t, 3 H, J 7.7 Hz).

2-[Dimethyl-1,1,2-(trimethylpropyl)silyloxy]-3-(phenylmethoxy)propyl dodecanoate (**5**). The reaction between **3** (1.614 g, 3.46 mmol), dodecanoyl chloride (2.00 g, 9.14 mmol) and Bu_4NCl (0.316 g, 1.14 mmol) in chloroform (1 ml) was run and followed similarly. After 5 h the regioisomeric purity had increased to 99.3% and the reaction was then worked up as for **4** to give a crude product which was purified on silica gel with toluene as the eluant. Elution order: **3** (1.4%), then **5** (69%; isomeric purity, 99.8%), and finally the diester (ca. 12%). ^1H NMR of **5**: δ 7.2–7.4 (almost s, 5 H), 4.52 (s, 2 H), 4.20 (m, 1 H), 4.02 (m, 2 H), 3.45 (d, 2 H, J 5.1 Hz), 2.28 (t, 2 H), 1.61 (m, 3 H), 1.26 (s, 16 H), 0.95–0.80 (15 H), 0.11 (s, 3 H) and 0.10 (s, 3 H). ^{13}C NMR: δ 173.7, 138.2, 128.4, 127.6, 73.4, 71.9, 69.5, 66.1, 34.3, 34.1, 31.9, 29.6, 29.5, 29.3, 29.3, 29.2, 24.9, 22.7, 20.2, 18.6, 14.1, -2.7, -2.8. Column A gave baseline separation of **5** and its regioisomer; retention times, 25.46 and 24.28 min, respectively ($150^\circ\text{C}/10^\circ\text{C min}^{-1}/300^\circ\text{C}$).

2-(Dodecanoyloxy)-3-(phenylmethoxy)propyl propanoate (**6**). A mixture of **4** (0.576 g, 1.51 mmol), dodecanoyl chloride (1.66 g, 7.58 mmol, 5.0 equiv.), and Bu_4NCl (0.328 g, 1.18 mmol) was heated in a stoppered flask (105°C) for 3 h. After cooling, the product was worked up by being partitioned between diethyl ether and half-satd. aq. NaHCO_3 . Compound **6** showed a regioisomeric purity of 98.2% (GLC). Purification (twice) on silica gel columns eluting, in the first run with toluene and in the second with toluene–ethyl acetate (3:1) gave **6** (92%). ^1H NMR: δ 7.40–7.25 (m, 5 H), 5.25 (m, 1 H), 4.54 (AB, 2 H, J 12.1 Hz), 4.35 (dd, 1 H, J 11.9 and 3.9 Hz), 4.19 (dd, 1 H, J 11.9 and 6.4 Hz), 3.59 (d, 2 H, J 5.1 Hz), 2.32 (t, 2 H, J 7.5 Hz), 2.31 (q, 2 H, J 7.6 Hz), 1.59 (m, 2 H), 1.25 (br s, 16 H), 1.12 (t, 3 H, J 7.5 Hz), 0.88 (t-like, 3 H, J 6.6 Hz). ^{13}C NMR: δ 174.0, 173.1, 137.7, 128.4, 127.8, 127.6, 73.3, 70.0, 68.3, 62.8, 34.3, 31.9, 29.6, 29.5, 29.3, 29.3, 29.1, 27.4, 25.0, 22.7, 14.1, 9.0. Apart from the trivial differences due to having dodecanoyl instead of hexadecanoyl, the ^1H and ^{13}C NMR spectra of **6** were indistinguishable from those of compound **9a** in Ref. 18. The GLC retention time of contaminant **7** was indistinguishable from that of **7** prepared as described below. For the GLC separation of **6** and **7**, see below. An experiment with 2.0 instead of 5.0 equiv. of

dodecanoyl chloride gave a somewhat lower regioisomeric purity (97.5%).

2-(Propanoyloxy)-3-(phenylmethoxy)propyl dodecanoate (**7**). A mixture of **5** (0.603 g, 1.19 mmol), propanoyl chloride (0.220 g, 2.38 mmol), and Bu_4NCl (0.105 g, 0.38 mmol) was heated in a stoppered flask (105°C) for 3 h. After cooling, the product mixture was shaken for 3 min with diethyl ether (40 ml) and half-satd. aq. NaHCO_3 (30 ml). The organic phase was separated, washed again with aq. NaHCO_3 (1/5-satd.) and finally dried (Na_2SO_4). GLC retention times of **6** and **7**: 25.62 and 25.79 min, respectively; column A; resolution $R_s \approx 1.5$; $R_s = (t_2 - t_1)/0.5(W_1 + W_2)$, where W_1 and W_2 are the base widths (in time units) of the triangulated peaks; $150^\circ\text{C}/5^\circ\text{C min}^{-1}/300^\circ\text{C}$; regioisomeric purity 98.0%. The GLC retention time of contaminant **6** was indistinguishable from that of **6** prepared as described above. Purification on a silica gel column (4×33 cm) eluting first with toluene–ethyl acetate (50:1) and finally with ethyl acetate gave **7** in a 93% yield. ^1H NMR: δ 7.40–7.25 (m, 5 H), 5.24 (m, 1 H), 4.54 (AB, 2 H, J 12.1 Hz), 4.35 (dd, 1 H, J 11.8 and 3.8 Hz), 4.19 (dd, 1 H, J 11.8 and 6.2 Hz), 3.59 (d, 2 H, J 5.1 Hz), 2.35 (q, 2 H, J 7.6 Hz), 2.28 (t, 2 H, J 7.7 Hz), 1.59 (m, 2 H), 1.26 (br s, 16 H), 1.14 (t, 3 H, J 7.6 Hz), 0.88 (t-like, 3 H, J 6.6 Hz). ^{13}C NMR: δ 173.7, 173.4, 137.7, 128.4, 127.8, 127.6, 73.3, 70.1, 68.2, 62.6, 34.1, 31.9, 29.6, 29.5, 29.3, 29.3, 29.1, 27.6, 24.9, 22.7, 14.1, 9.1. Apart from the trivial differences due to having dodecanoyl instead of hexadecanoyl, the ^1H and ^{13}C NMR spectra of **7** were indistinguishable from those of compound **9b** in Ref. 18.

Tin(IV) chloride-catalysed synthesis of **6**. A mixture of **4** (0.391 g, 1.03 mmol), dodecanoyl chloride (0.229 g, 1.05 mmol) and SnCl_4 (0.013 g, 0.05 mmol) in CH_2Cl_2 (7.3 ml) in a stoppered flask was stirred for 21 h (22°C). Pyridine (26 mg) was added. A light ppt. was filtered off and the solution was washed with half-satd. aq. NaHCO_3 (5 ml). After being washed with water the organic phase was dried (Na_2SO_4) and concentrated. The crude product was passed through a silica gel column (0.6×6 mm, toluene–EtOAc, 10:1) with the sole purpose of removing small amounts of dodecanoic acid; care was taken not to separate **6** and **7**. GLC analysis, performed as above, of the product mixture (0.510 g) showed the isomeric purity of **6** to be 98.9%, the amount of **4** was 1.2%.

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