Cassida, Ed. Academic Press, New York, 1973, p 68, and references cited therein.
(5) For other examples of malonate condensations with epoxides see: (a) E. E. van Tamelen and S. R. Bach, *Chem. Ind., (London)*, 1308 (1956); (b) L. Maat, A. Sinnema, and H. C. Beyerman, *Recl. Trav. Chim. Pays-Bas*, **86**, 97 (1967); (c) T. Wieland and V. Georgi, *Justus Liebigs Ann. Chem.*, **700**, 133 (1966); (d) L. H. Dreger and W. N. Hubbard, *J. Am. Chem. Soc.*, **83**, 606 (1961).
(7) (a) A. P. Krapcho and A. J. Lovey, *Tetrahedron Lett.*, 957 (1973); (b) A. P. Krapcho, E. G. E. Jahngen, Jr., and A. J. Lovey, *ibid.*, 1091 (1974).

(8) (a) M. Julia, S. Julia, and M. Langlois, *Bull. Soc. Chim. Fr.*, 1014 (1965); (b) M. Julia, S. Julia, C. Jeanmart, and M. Langlois, *ibid.*, 2243 (1962); (c) M. Julia, S. Julia, and C. Jeanmart, *C. R. Hebd. Seances Acad. Sci.*, **251**, 249 (1960); (d) M. Matsui and M. Uchiyama, *Agric. Biol. Chem.*, **26**, 532 (1962).
(9) A. Takeda, T. Sakai, S. Shinohara, and S. Tsuboi, *Bull. Chem. Soc. Jpn.*, **50**, 1133 (1977).
(10) One of these was identified as the acetylenic ester **19**: NMR (CDCl$_3$) δ 1.22 (3 H, t, J = 7 Hz), 1.78 (3 H, s), 1.98 (3 H, s), 3.14 (2 H, s), 4.14 (2 H, q, J = 7 Hz); IR (neat) 2200, 1735, 1442 cm^{-1}.

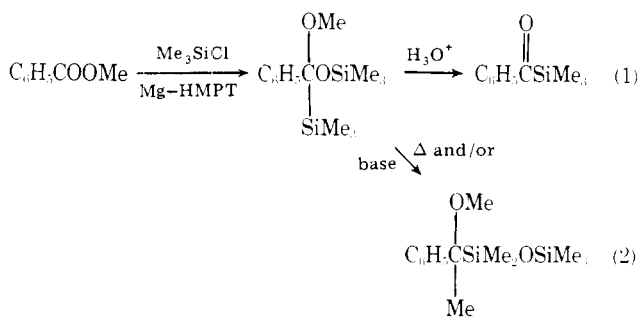# Reductive Silylation of Benzoates: Convenient Synthesis of Aroylsilanes[1]

Jean-Paul Picard,* Raymond Calas, Jacques Dunoguès, Norbert Duffaut, Jacqueline Gerval, and Paulette Lapouyade

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Reductive silylation of benzoates Σ-C$_6$H$_4$COOR (1) by means of trimethylchlorosilane/magnesium/hexamethylphosphorictriamide affords a very convenient synthesis of a wide variety of aroyltrimethylsilanes Σ-C$_6$H$_4$C(O)-SiMe$_3$ (3), through the formation of the corresponding ketals 2 which can be isolated. Scope and limitations of this new synthesis have been studied. The intermediate ketals undergo an unusual quantitative isomerization in the presence of base and/or heat, yielding substituted disiloxanes 8.

We have reported the use of the reagent trimethylchlorosilane/magnesium/hexamethylphosphorictriamide (Me$_3$-SiCl/Mg/HMPT) to reductively silylate two benzoates.[2] With methyl benzoate we showed that reaction 1 led to benzoyltrimethylsilane upon hydrolysis of the intermediate ketal and at the same time that this intermediate ketal underwent the unusual isomerization into the substituted disiloxane under the influence of heat and/or base (reaction 2).

$$C_6H_5COOMe \xrightarrow[\text{Mg-HMPT}]{Me_3SiCl} \underset{\substack{|\\ SiMe_3}}{C_6H_5\overset{OMe}{\underset{|}{C}}OSiMe_3} \xrightarrow{H_3O^+} C_6H_5\overset{O}{\overset{\|}{C}}SiMe_3 \quad (1)$$

$$\text{base} \searrow \Delta \text{ and/or}$$

$$C_6H_5\overset{OMe}{\underset{\underset{Me}{|}}{\underset{|}{C}}}SiMe_2OSiMe_3 \quad (2)$$

With trimethylsilyl benzoate we showed that the reductive silylation leads directly to a trisilylated compound and postulated the possible intermediacy of a ketal.
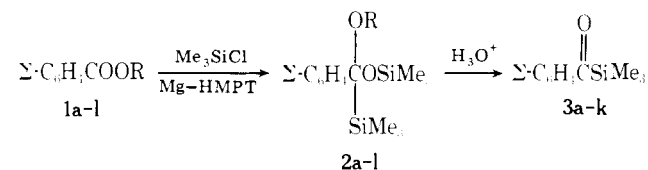
In order to learn the scope and limitations of reaction 1 as a very useful synthetic route to aroyltrimethylsilanes and to learn more about the factors governing the formation and the stability of the intermediate ketal, and its isomerization, we studied the behavior of a wide variety of substituted benzoates 1 (Table I) in the presence of Me$_3$SiCl/Mg/HMPT.

Results and Discussion

Ketals 2: Their Formation, Stability, and Hydrolysis to Acylsilanes 3.
Under well-defined experimental conditions (i.e., excess of trimethylchlorosilane relative to HMPT, reaction and workup temperatures lower than 50–60 °C, and contact between basic reagent and ketal avoided), alkyl benzoates 1a–l lead to the stable and isolable ketals 2 (Table II).[3] All these O-alkyl O-silyl mixed ketals of acylsilanes belong to a new class of compounds; symmetric ketals only have been

reported to date.[4] A mechanism accounting for this silylation reaction has been previously proposed by us.[2]
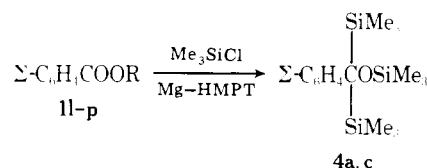
Acidic hydrolysis of these ketals 2a–l leads to the corresponding acylsilanes 3a–k.

$$\Sigma\text{-}C_6H_4COOR \xrightarrow[\text{Mg-HMPT}]{Me_3SiCl} \underset{\substack{|\\ SiMe_3}}{\Sigma\text{-}C_6H_4\overset{OR}{\underset{|}{C}}OSiMe_3} \xrightarrow{H_3O^+} \Sigma\text{-}C_6H_4\overset{O}{\overset{\|}{C}}SiMe_3$$

$$\text{1a-l} \qquad\qquad\qquad \text{2a-l} \qquad\qquad\qquad \text{3a-k}$$

This pathway is very convenient for the synthesis of substituted aroyltrimethylsilanes[5] and presents the advantage, in comparison with the two most usual methods,[6] of using directly commercially available starting compounds, of having a very easy and rapid workup, and of giving good yields (Table II).

The yields of ketals and acylsilanes seem to be not greatly affected by the nature and the position of the Σ group in 1. In contrast, the nature of the R group seems to be more important as illustrated by *tert*-butyl *p*-methylbenzoate 1l, which gives a poor yield of the corresponding acylsilane 3c; also trimethylsilyl benzoate 1m does not afford any acylsilane.[2]

As 1m, compounds 1l–q[7] undergo reductive silylation of the

$$\Sigma\text{-}C_6H_4COOR \xrightarrow[\text{Mg-HMPT}]{Me_3SiCl} \underset{\substack{|\\ SiMe_3}}{\Sigma\text{-}C_6H_4\overset{SiMe_3}{\underset{|}{C}}OSiMe_3}$$

$$\text{1l-p} \qquad\qquad\qquad \text{4a, c}$$

ester function leading to the trisilylated derivatives 4 in good yields[8] (Table III), regardless of whether there is an excess of HMPT or not.

In order to explain the reductive silylation of such esters, we postulated the formation of an unstable ketal;[2] the acylsilane resulting from its decomposition would then be silylated, giving 4.

Further evidence for this pathway is found in the behavior

Table I. Benzoates 1 Submitted to Reductive Silylation (Σ-C$_6$H$_4$COOR)

	registry no.	Σ	R		registry no.	Σ	R
1a	93-58-3	H	Me	**1j**	610-96-8	o-Cl	Me
b	93-89-0	H	Et	**k**	118-61-6	o-OH	Et
c	99-75-2	p-Me	Me	**l**	13756-42-8	p-Me	Me$_3$C
d	99-36-5	m-Me	Me	**m**	2078-12-8	H	Me$_3$Si
e	89-71-4	o-Me	Me	**n**	65-85-0	H	H
f	26537-19-9	p-Me$_3$C	Me	**o**	93-97-0	H	C$_6$H$_5$C(O)
g	22515-30-6	p-Me$_3$Si	Me	**p**	120-51-4	H	C$_6$H$_5$CH$_2$
h	1126-46-1	p-Cl	Me	**q**	1018-20-8	H	Et$_3$Si
i	2905-65-9	m-Cl	Me	**r**	774-65-2	H	Me$_3$C

Table II. Syntheses of Ketals 2 and Aroylsilanes 3

	Σ-C$_6$H$_4$COOR Σ		registry no.	Σ-C$_6$H$_4$C(SiMe$_3$)(OSiMe$_3$)OR		% yield[b]		registry no.	Σ-C$_6$H$_4$CO—SiMe$_3$	% yield[b]
				Σ	R				Σ	
1a	C$_6$H$_5$COOMe	**2a**	23998-91-6	H	Me	90	**3a**	5908-41-8	H	75
b	C$_6$H$_5$COOEt	**b**	68185-87-5	H	Et	80	**a**		H	66
c	p-Me-C$_6$H$_4$COOMe	**c**	68185-88-6	p-Me	Me	70	**c**	68185-94-4	p-Me	54
d	m-Me-C$_6$H$_4$COOMe	**d**	68185-89-7	m-Me	Me	85	**d**	68185-95-5	m-Me	62
e	o-Me-C$_6$H$_4$COOMe					c	**e**	65284-33-5	o-Me	59
f	p-Me$_3$C-C$_6$H$_4$COOMe	**f**	68185-90-0	p-Me$_3$C	Me	60	**f**	68185-96-6	p-Me$_3$C	48
g	p-Me$_3$Si-C$_6$H$_4$COOMe	**g**	68185-91-1	p-Me$_3$Si	Me	65	**g**	22364-51-8	p-Me$_3$Si	55
h	p-Cl-C$_6$H$_4$COOMe[a]	**g**			p-Me$_3$Si	Me	89	**g**		p-Me$_3$Si	75
i	m-Cl-C$_6$H$_4$COOMe[a]	**i**	68185-92-2	m-Cl	Me	75	**i**	68185-97-7	m-Cl	71
j	o-Cl-C$_6$H$_4$COOMe[a]	**j**	68185-93-3	o-Cl	Me	94	**j**	68185-98-8	o-Cl	65
k	o-HO-C$_6$H$_4$COOEt					c	**k**	68185-99-9	o-HO	54
l	p-Me-C$_6$H$_4$COOCMe$_3$					c	**c**		p-Me	5

[a] In the course of the silylation, the chlorine atom in the para position is entirely substituted by a trimethylsilyl group contrarywise to the meta and ortho isomers. [b] Calculated on ester engaged. [c] Reference 3.

Table III. Synthesis of Alkoxysilanes 4 (Σ-C$_6$H$_4$C(SiMe$_3$)$_2$OSiMe$_3$) from Various Benzoates

starting ester 1	4	registry no.	Σ	yield, %
l	c	68186-00-5	p-Me	40
m	a	23998-93-8	H	69
n	a		H	65
o	a		H	70
p	a		H	80
q	a		H	51
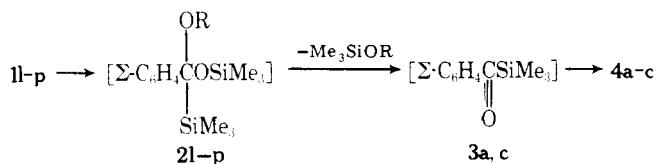
of **1l**, which affords a partially stable ketal **2l**, since the corresponding acylsilane **3c** is isolated in poor yield after hydrolysis of the reaction mixture.

Ketal **2** appears as the key compound in the reductive silylation of benzoates, and its stability seems to be related to the nature of the R group and its inductive effect: the greater the inductive effect, the more unstable the ketal is ($^+I_{Me,Et}$ < $^+I_{CMe_3}$ < $^+I_{SiMe_3}$).[9] Its decomposition can be interpreted as follows.
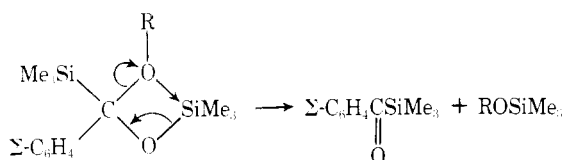
The oxygen of C–OR could form a dative bond with the silicon of C–OSi, the strength of which increases with the inductive

effect of R. This can afford cleavage via a four-center concerted transfer which leads to the acylsilane and the alkoxysilane (when R = CMe$_3$) or the siloxane (when R = SiMe$_3$). When R = Me or Et, the dative bond apparently is not strong enough to initiate the cleavage.

The role of the steric hindrance of R is also important. With bulky groups such as *tert*-butyl and triethylsilyl (and only when Σ = H), the silylation of the corresponding benzoates, **1q,r**, occurs preferentially at the para position of the phenyl ring, leading to a semiquinonoid compound **5**, isomeric from

C$_6$H$_5$COOR
1q, R = SiEt$_3$
   r, R = CMe$_3$
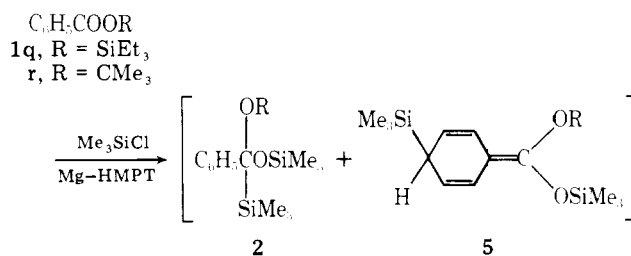
2. Finally, p-silylated derivatives are obtained from these benzoates: **6** from **1q** (beside **4a**), p-trimethylsilylbenzoic acid, **4g** or **7** (depending upon the ratio ester/reagent)[10] from **1r**. In support of the importance of the steric hindrance in the formation of **2** is the observation that the use of tetramethylurea (TMU) instead of HMPT increases the yield of **6** from
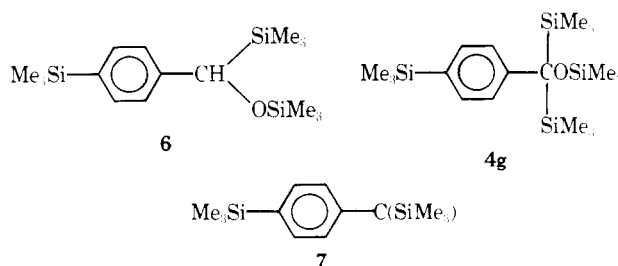
Table IV. Syntheses of Siloxane 8

	registry no.	Σ-C₆H₄C(Me)(OR)SiMe₂OSiMe₃ Σ	R	% yield with procedure[a] A	B[b]	C
8a	31129-61-0	H	Me	2a,78		1a,71
b	68186-01-6	H	Et	2b,73		1b,75
c	68186-02-7	*p*-Me	Me		2c,65	
d	68186-03-8	*m*-Me	Me	2d, 80		
e	68186-04-9	*o*-Me	Me			1e,71
f	68186-05-0	*p*-Me₃C	Me		2f, 45	
g	68186-06-1	*p*-Me₃Si	Me		2g,40	1h, 65
i	68186-07-2	*m*-Cl	Me	2i, 80		
j	68186-08-3	*o*-Cl	Me	2j, 70		
k	68186-09-4	*o*-HO	Et			1k,62
l	68186-10-7	*p*-Me	CMe₃			1l, 40

[a] See text. [b] Yields are calculated on the basis of the ester involved to prepare 2.

25 to 60%. The lower dielectric constant of TMU[11] favors the formation of bulkier ion pairs, in contrast to HMPT[12] in which ions would be separated; it would be easier for the bulkier ion pairs to attack at the para position of the phenyl ring than at the benzylic carbon atom.

Ketals 2: Their Isomerization into Siloxanes 8. Ketals 2a–l isomerize very easily into disiloxanes 8a–l and this unusual rearrangement is induced by heat and/or by the presence of basic reagents. Siloxanes 8 are formed under three different circumstances (A, B, C in Table IV): (A) in 70–80% yield when ketals 2 are treated with base (HMPT or pyridine at 60 °C); (B) in 40–65% yield when ketals 2 are thermolyzed (attempted slow distillation under vacuum); and (C) in 65–75% yield directly from esters when HMPT is used in excess relative to Me₃SiCl.

On the basis of the thermal properties of symmetrical ketals of acylsilanes,[4] we earlier proposed a mechanism involving an intermediate alkoxycarbene in order to explain the transformation of 2a into 8a.[2] It now seems to us that this general
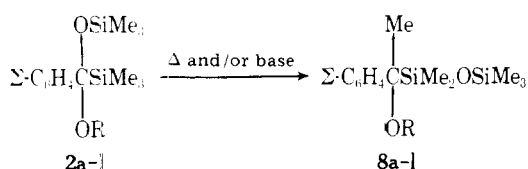
isomerization can be viewed as a new kind of sigmatropic rearrangement[13,14] induced by base and/or heat. The attack of the base B at Si$_\beta$ would make more basic the adjacent oxygen which would attack the Si$_\alpha$ inducing the cleavage of the C–O bond and the migration of the methyl group as depicted in the following scheme:
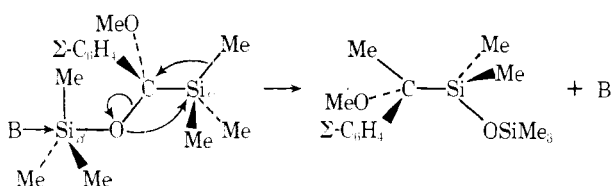
In the absence of base, the methoxy group could act as B and facilitate the thermal ionization.

Experimental Section

Infrared spectra were measured with a Perkin-Elmer 457 on neat compounds. The ¹H-NMR spectra were determined with either a Perkin-Elmer R-12 or a Varian A60 spectrometer using tetramethylsilane as an internal standard. All GLC analyses were performed on a FM 810 or 7570 apparatus with columns packed with 10% silicon SE 30 on Chromosorb P. Mass spectral data were obtained on a AEI-MS12 mass spectrometer. Elemental analyses were performed at the Centre de Microanalyse du CNRS; they were submitted for review and were in good agreement with the proposed structures.

Trimethylchlorosilane and HMPT were used after distillation.

HMPT should be handled with great care since it has recently been found to cause cancer in laboratory animals.[15] Magnesium powder and most of the products used were commercially available, except some esters which were prepared by conventional or reported methods: 1g,[16] 1l,[17] 1m,[18,19] 1q,[20,21] 1r.[19]

Silylation Reactions: General Procedure. HMPT, powdered magnesium, and chlorosilane were introduced into a four-necked round-bottomed flask equipped with a mechanical stirrer, a thermometer, a dropping funnel, and a reflux condenser protected by a calcium chloride tube. After stirring 0.5 h, the product to be silylated was added dropwise, maintaining a temperature between 40 and 50 °C. During the course of the reactions, MgCl₂·(HMPT)₂ crystals[22] appeared in the cold part of the vessel. After the addition, the reaction mixture was left overnight at 40–50 °C using an oil bath. MgCl₂·(HMPT)₂ precipitated out during the cooling. Next the mixture was poured onto crushed ice (eventually acidified by HCl when the Me₃SiCl/HMPT molar ratio was lower than unity after reaction). The pH of the aqueous layer was kept between 4 and 6. The organic layer was extracted with ether, washed several times with water, and dried over sodium sulfate. Ether and volatile products (essentially Me₆Si₂O resulting from the hydrolysis of the excess Me₃SiCl) were removed at 40 °C under reduced pressure (25 torr).

Silylation of Benzoates Yielding Ketals (2a–k). Benzoates 1a–g,i,j. Ester (0.2 mol), 7.2 g of magnesium (0.3 g-atom), 87 g of Me₃SiCl (0.8 mol), and 108 g of HMPT (0.6 mol) were reacted following the general procedure which gave ketal the purity of which was about 90%; it was not distilled because of its thermal instability. Ketal 2e was never obtained because of its high sensitivity to hydrolysis, and the corresponding acylsilane 3e was obtained directly.

Benzoates 1h,k. Because of the presence of another reactive function in the molecule, the amounts of reagents were modified as follows for 0.2 mol of ester: magnesium, 11 g (0.45 g-atom); Me₃SiCl, 110 g (1 mol); and HMPT, 135 g (0.75 mol). The same procedure was used. Benzoate 1h gave the same ketal 2g as benzoate 1g. Acylsilane 3k was obtained directly instead of the expected ketal 2k.

Benzoate 1l. A sample of 19.2 g (0.1 mol) of this ester was silylated according to the general procedure using 7.5 g of magnesium, 85 g of Me₃SiCl, and 105 g of HMPT. GLC analysis gave the composition of the resulting crude mixture obtained after workup (38 g): acylsilane 3c (5% yield), siloxane 8l (40% yield), and trisilylated derivative 4c (40% yield). When the reaction was carried out with the same relative amounts of reagents as above in the case of the silylation of the benzoates 1a–g, the same products were obtained in about the same relative yields and 20% of the starting ester was recovered. Compounds 4c and 8l were separated by column chromatography (1 m × 2 cm, silica gel): 4c was eluted first (pentane) and then 8l (pentane/benzene, 2:1). Compound 8l was identified by ¹H and ¹³C NMR spectroscopy. ¹H: −0.05 (s, 9 H) 0.11 (s, 9 H) 2.18 (s, 3 H), and 5.96 (s, 4 H). The ¹³C spectrum was recorded on a spectrospin Brucker apparatus and calibrated on the center of the signal given by the deuteriochloroform used as solvent (δ 76.9/Me₄Si). The data were: 0.82 (q, CSiCH₃) 4.63 (q, OSiCH₃), 21.27 (q, C₆H₄CH₃), 79.88 (s, benzylic C), 124.43 and 128.88 (d, aromatic CH), 133.62 and 144.03 (s, aromatic C).

Table V gives the NMR data for ketals 2.

Hydrolysis of Ketals Yielding Aroylsilanes (3a–k). The crude ketals 2 obtained from 0.2 mol of ester were dissolved in a mixture of 100 mL of acetone, 20 mL of water, and 10 drops of concentrated hydrochloric acid, and the solution was refluxed for 3 h. Acetone was removed under reduced pressure and the residue was dissolved in 100 mL of ether. After washing twice with a 5% sodium bicarbonate so-

Table V. NMR Data for Ketals 2[a]

	SiMe$_3$	R of O–R	phenyl
2a	−0.02 (s) and +0.16 (s)	Me 3.25 (s)	7.24 (m)
b	0.0 (s) and 0.1 (s)	CH$_3$ 1.15 (t, J = 6 Hz) CH$_2$ 3.30 (q, J = 6 Hz)	7.30 (m)
c	0.02 (s) and 0.24 (s)	Me 3.30 (s)	7.15 m) p-Me 2.35 (s)
d	−0.08 (s) and +0.13 (s)	Me 3.22 (s)	7.05 (m) m-Me 2.33 (s)
f	−0.05 (s) and +0.18 (s)	Me 3.24 (s)	7.33 (m) p-CMe$_3$ 1.32 (s)
g	0.05 (s) and 0.25 (s)	Me 3.32 (s)	7.38 (m) p-SiMe$_3$ 0.25 (s)
i	−0.04 (s) and +0.17 (s)	Me 3.25 (s)	7.20 (m)
j	0.0 (s) and 0.18 (s)	Me 3.24 (s)	7.18 (m)

[a] s, singlet; t, triplet; q, quartet; m, multiplet.

Table VI. Data for Acylsilanes 3

	$\nu_{C=O}$, cm^{-1} (film)	NMR (δ)	bp, °C/torr
3a	1618[a]	(SiMe$_3$) 0.37 (s), (Ph) 7–8 (m)[a]	84/2[a]
c	1620	(SiMe$_3$) 0.33 (s), (Ph) 7.1–7.7 (m), (p-Me) 2.33 (s)	85/1
d	1612	(SiMe$_3$) 0.33 (s), (Ph) 7.1–7.6 (m), (m-Me) 2.38 (s)	83–86/1
e	1608	(SiMe$_3$) 0.28 (s), (Ph) 6.9–7.5 (m), (o-Me) 2.36 (s)	85–88/0.5
f	1605	(SiMe$_3$) 0.34 (s), (Ph) 7.1–7.8 (m), (p-CMe$_3$) 1.30 (s)	104–105/0.5
g	1616[b]	(SiMe$_3$) 0.35 (s), (Ph) 7.56 (m),[b] (p-SiMe$_3$) 0.27 (s)	95–96/1[b]
i	1621	(SiMe$_3$) 0.36 (s), (Ph) 7.3–7.8 (m)	97–98/1
j	1620	(SiMe$_3$) 0.25 (s), (Ph) 7.2 (m)	90–92/1
k	1620	(SiMe$_3$) 0.37 (s), (Ph) 6.7–7.2 (m), (OH) 12.1 (s)	79/0.6

[a] In agreement with ref 6. [b] In agreement with ref 9.

Table VII. Data for Siloxane 8

	bp, °C/torr	NMR, δ
8a	93–94/2	(SiMe$_2$) −0.07 and +0.08 (s), (SiMe$_3$) 0 (s), (CMe) 1.55 (s), (OMe) 3.18 (s), (Ph) 7.16 (m)
b	92–95/1	(SiMe$_2$OSiMe$_3$) 0 (m), (CMe) 1.55 (s), (OEt) 1.10 and 3.25 (t + q, J = 7 Hz), (Ph) 7.10 (m)
c	90–91/1	(SiMeOSiMe$_3$) 0–0.4 (m), (CMe) 1.62 (s), (MePh) 2.35 (s), (MeO) 3.12 (s), (Ph) 7.1–7.2 (m)
d	91–94/1	(SiMe$_2$) −0.1 and +0.03 (s), (SiMe$_3$) −0.03 (s), (CMe) 1.53 (s), (MePh) 2.32 (s), (MeO) 3.05 (s), (Ph) 6.85–7.15 (m)
e	90–92/1	(SiMe$_2$OSiMe$_3$) 0 (m), (CMe) 1.67 (s), (MePh) 2.44 (s), (OMe) 3.0 (s), (Ph) 6.8–7.2 (m)
f	110–115/1	(SiMe$_2$) 0.04 (s), (SiMe$_3$) −0.07 (s), (CMe$_3$) 1.33 (s), (CMe) 1.58 (s), (OMe) 3.11 (s), (Ph) 7.3 (m)
g	107–112/0.5	(SiMe$_2$) 0.02 (s), (SiMe$_3$) −0.05 (s), (PhSiMe$_3$) 0.32 (s), (CMe) 1.57 (s), (OMe) 3.07 (s), (Ph) 7.25 (m)
i	100–105/1	(SiMe$_2$) 0.03 (s), (SiMe$_3$) −0.03 (s), (CMe) 1.55 (s), (OMe) 3.07 (s), (Ph) 7–7.4 (m)
j	110–112/0.5	(SiMe$_2$OSiMe$_3$) 0 (m), (CMe) 1.83 (s), (OMe) 3.12 (s), (Ph) 7–7.4 (m)
k	112–113/1	(SiMe$_2$OSiMe$_3$) 0.03 (m), (CMe) 1.75 (s), (OEt) 1.2 and 3.35 (t + q, J = 7 Hz), (Ph) 6.7–7 (m), (OH) 12.4 (s)
l	108–110/0.5	(SiMe$_2$) −0.1 and +0.03 (s), (SiMe$_3$) −0.03 (s), (OCMe$_3$) (CMe) 1.7 (s), (MePh) 2.26 (s), (Ph) 7.0 (m)

spectroscopy on a sample of the reaction mixture: ethylenic protons appeared in the 5–6.2-ppm range. When the silylation was carried out in tetramethylurea (TMU) solvent instead of HMPT, the procedure was the same; the semiquinonoid intermediate was shown by NMR and 19.5 g (60% yield) of **6** was obtained after distillation. Compound **6** oxidized rapidly in air and gave p-trimethylsilylbenzoic acid.[24]

Silylation of *tert*-Butyl Benzoate (1r). A 17.8-g (0.1 mol) sample of this ester was reacted with 7.5 g of magnesium and 85 g of Me$_3$SiCl in 105 g of HMPT. Isobutene and hydrogen evolved and 24 g of the p-trimethylsilyl alkoxide **4g** (60% yield) was obtained by distillation: bp 107 °C/0.7 torr; NMR 0.10 (s, 18 H), 0.28 (s, 9 H), 0.30 (s, 9 H), 7.15–7.45 (AA'XX' spectrum, J = 8 Hz, 4 H). When a deficiency of reagent (2.5 g of magnesium, 45 g of Me$_3$SiCl, and 60 g of HMPT for 0.1 mol of the ester) is used, 5 g of p-trimethylsilybenzoic acid was obtained and 9.5 g of the ester recovered. With an excess of reagent (12 g of magnesium, 110 g of Me$_3$SiCl, and 145 g of HMPT for 0.1 mol of the ester) and at 70–80 °C, 21 g of the tetrasilylated hydrocarbon **7** (55% yield) was distillated: bp 120 °C/1 torr; NMR 0.18 (s, 36 H), 7.15 (s, 4 H).

Synthesis of Siloxanes 8a–l. Procedure A. The isomerization of ketals **2** in HMPT or pyridine at 60 °C was conducted as described previously[2] with **2a. Procedure B.** A sample of the ketal (10 g) was heated for 2 h with an oil bath at 150 °C and then the siloxane was distilled. A liquid nitrogen trap contained a small amount of hexamethyldisiloxane and methoxy- (or ethoxy) silane. **Procedure C.** Silylation of benzoates in the presence of an excess of HMPT was done following the general silylation procedure and for 0.1 mol of ester, 2.5 g of magnesium, 25 g of Me$_3$SiCl, and 50 g of HMPT (respectively 5 g, 40 g, and 75 g in the case of benzoates **1h** and **1k**) were used. Siloxane **8** was separated by distillation. Yields are listed in Table IV and physicochemical data in Table VII.

lution, then with water, drying over anhydrous sodium sulfate, and concentrating, the acylsilane was separated by distillation. Physicochemical data are reported in Table VI.

Silylation of Benzoates Yielding the Alkoxysilane 4a. The alkoxysilane **4a** has been previously obtained from trimethylsilyl benzoate **1m** and benzoyltrimethylsilane **3a** and described.[2] It was prepared by reductive silylation of benzoates **1m–p** following the general procedure and the amounts of reagents used depend upon the starting ester. When 12.2 g (0.1 mol) of benzoic acid **1n** was dissolved in 100 g hot HMPT and reacted with 6.5 g of magnesium and 100 g of Me$_3$SiCl in 200 g of HMPT, 21 g of the alkoxysilane **4a** (65% yield) was obtained. During the reaction, hydrogen was evolved, but the collected amount (1.12 L, 0.05 mol) was lower than theoretically expected, as previously observed and reported.[23] The silylation of 22.6 g (0.1 mol) of benzoic anhydride, **1o**, dissolved in 100 g of HMPT, by 10 g of magnesium and 100 g of Me$_3$SiCl in an additional 100 g of HMPT gave 45.5 g of **4a** (70% yield) and 2.5 g of benzoic acid. During the reaction each drop of anhydride solution led to the appearance of a yellow color in the reaction mixture. A 21.2 g (0.1 mol) sample of benzyl benzoate **1p** was reacted with 7.5 g of magnesium and 75 g of Me$_3$SiCl in 150 g of HMPT. Distillation gave 13 g of benzyltrimethylsilane (80% yield) identified by comparison with an authentic sample and 26 g of **4a** (80% yield).

Silylation of Triethylsilyl Benzoate (1q). A 23.6-g (0.1 mol) sample of triethylsilyl benzoate was silylated using 4.8 g of magnesium, 65 g of Me$_3$SiCl, and 110 g of HMPT, giving 24.6 g of a mixture (bp 85–90 °C/0.5 torr) of the isomeric trisilylated derivatives **4a** and **6** (2/1 by GLC). The physicochemical data of **6** were: bp 85–87 °C/0.05 torr; NMR 0.0 (s, 18 H), 0.16 (s, 9 H), 1.65 (s, 1 H), 7.10 (m, 4 H). The semiquinonoid intermediate structure **5** was established by NMR

References and Notes

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Reactions of Lithio Derivatives of Carboxylic Acids. 2. Alkylations and Cyclizations of Substituted Acrylic Acids

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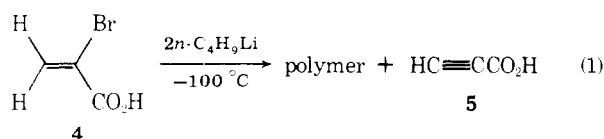
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2-Substituted 3-phenylcinnamic acids are obtained in good yields by effecting bromine–lithium exchange with 2-bromo-3-phenylcinnamic acid and 2 molar equiv of *n*-butyllithium at −100 °C and subsequent reaction with electrophiles (e.g., CH₃I, Ph₂CO, PhS₂Ph). Oxiranes afford γ-butyrolactones in modest yields. In contrast, 2-bromoacrylic acid polymerizes under such conditions and (*Z*)-2-bromocinnamic acid dehydrobrominates at −140 °C. Friedel–Crafts cyclization of 2-alkyl-3-phenylcinnamic acids affords 2-alkyl-3-phenylinden-1(1*H*)-ones in good yields.
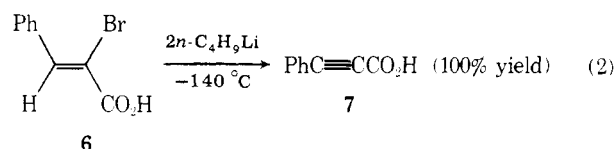
Bromine–lithium exchange at low temperature allows the preparation of organolithium compounds which contain electrophilic functionality or which are otherwise thermolabile.[2,3] For example, it was shown that techniques used for such exchange at −100 °C with bromoarylcarboxylic acids[2c] were applicable to an aliphatic bromo acid.[2b] The objectives of the present study were to establish more clearly the scope of this reaction in vinylic bromides[4] and to demonstrate its utility for introducing cyclic units.

2-Substituted 3-Phenylcinnamic Acids. Bromine–lithium exchange with 2-bromo-3-phenylcinnamic acid (1) and 2 molar equiv of *n*-butyllithium in THF at −100 °C was efficient, and good yields of 2-alkylated acids (3, Table I) were obtained with most electrophilic reagents tested. In contrast, attempts to condense the dilithio derivative of 1 (i.e., 2) with phenyl isothiocyanate or *tert*-butyl acrylate yielded polymeric material, and only 3a was obtained with allyl *p*-toluenesulfonate. Metalation of the 2 position of 3a was not effected by *n*-butyllithium in THF at −100 °C, even in the presence of Dabco (1,4-diazabicyclo[2.2.2]octane), although evidence for analogous metalation of the benzyl ester of 3a (by lithium 2,2,6,6-tetramethylpiperidide) has been described.[7]
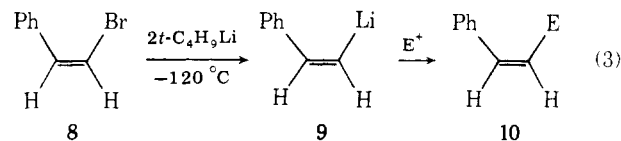
2-Bromo Acids with 3-Hydrogen. All attempts to effect bromine–lithium exchange with 2-bromoacrylic acid (4) were unsuccessful. Lithiation of 4 at −100 °C (eq 1) rapidly gave

$$
\underset{4}{\underset{\substack{H \diagup \diagdown Br \\ H \diagup \diagdown CO_2H}}{}} \xrightarrow[-100\ ^\circ C]{2n\text{-}C_4H_9Li} \text{polymer} + \underset{5}{HC\!\!\equiv\!\!CCO_2H} \quad (1)
$$

a polymeric mixture (whose NMR spectrum exhibited evidence for 5), and only phenylpropynoic acid (7) was obtained from the reaction of 6 with 2 molar equiv of *n*-butyllithium, even at −140 °C (eq 2) (Köbrich obtained similar results at

$$
\underset{6}{\underset{\substack{Ph \diagup \diagdown Br \\ H \diagup \diagdown CO_2H}}{}} \xrightarrow[-140\ ^\circ C]{2n\text{-}C_4H_9Li} \underset{7}{PhC\!\!\equiv\!\!CCO_2H} \ (100\% \text{ yield}) \quad (2)
$$

−115 °C[4c]). These results were not unexpected in view of the observation by Seebach that the vinyllithium compound 9, prepared as shown in eq 3, and others prepared analogously

$$
\underset{8}{\underset{\substack{Ph \diagup \diagdown Br \\ H \diagup \diagdown H}}{}} \xrightarrow[-120\ ^\circ C]{2t\text{-}C_4H_9Li} \underset{9}{\underset{\substack{Ph \diagup \diagdown Li \\ H \diagup \diagdown H}}{}} \xrightarrow{E^+} \underset{10}{\underset{\substack{Ph \diagup \diagdown E \\ H \diagup \diagdown H}}{}} \quad (3)
$$

were stable at −120 °C but at −110 °C dehydrobromination occurred rapidly.[3] In a related study, Köbrich found that bromine–lithium exchange could be effected with (*E*)-2-bromocinnamic acid (11) and *n*-butyllithium in a Trapp mixture at −115 °C, but protonation yielded a mixture of (*E*)- and (*Z*)-cinnamic acids.[4b,c]

It is improbable that the carboxylate anion renders the 3-proton of 6 more acidic, relative to the 3-proton of 8, by either inductive (weak for CO_2^-) or resonance (without invoking carbonium ion structures) effects. More attractive is the hypothesis that this difference in reactivity results from carboxylate-directed lithiation, through an arrangement such