The Preparation and Reaction of *tert*-Butyl Trimethylsilyl Carbonate and Related Compounds[1]

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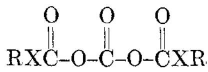
tert-Butyl trimethylsilyl carbonate (**4a**) and the thiol analog **3** have been prepared from the corresponding *tert*-butyl carbonate salts and chlorotrimethylsilane. Similar compounds were prepared with primary and secondary alkyl groups; the *n*-butyl compound proved to be too unstable to isolate, but the ethyl analog was obtained pure. The compounds **3** and **4** react with a variety of secondary and primary amines to form the silylcarbamates **5**. Action of butyl trimethylsilylcarbonate (**4a**) and acetyl chloride gives the *tert*-butyl acetic anhydride **7**, which was also prepared by the standard procedure. *tert*-Butyl ethyl dicarbonate was obtained by the action of ethyl chlorocarbonate on *tert*-butyl trimethylsilyl carbonate.

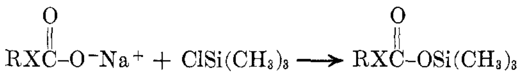
Recent work has shown that di-*tert*-butyl tricarbonates **1** and **2** can be readily prepared as crystalline compounds,[2-4] the kinetics and mechanisms of decomposition of these compounds have been examined,[4] and reactions of some nucleophiles with these tricarbonates have been studied.[5]



$$\mathrm{RX}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{-O-}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{-O-}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{XR}$$

1, X = O; R = *tert*-Bu
2, X = S; R = *tert*-Bu

In connection with further syntheses and studies in this general field, we have prepared the *tert*-butyl trimethylsilyl carbonates **3** and **4a** and some related compounds, and have studied their behavior.[6]



$$\mathrm{RX}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{-O^-Na^+} + \mathrm{ClSi(CH_3)_3} \longrightarrow \mathrm{RX}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{-OSi(CH_3)_3}$$

3, R = *tert*-Bu; X = S
4a, X = 0; R = *tert*-Bu
4b, X = 0; R = *i*-Pr
4c, X = 0; R = 2,4-dimethyl-3-pentyl
4d, X = 0; R = *n*-Bu (unstable)
4e, X = 0; R = Et

The thiol compound **3** and the oxygen analogs **4a**–**4e** were obtained as stable liquids with the exception of **4d**, with the physical properties shown in Table I.[7] Attempts to prepare the *n*-butyl analog led to CO_2 evolution below room temperature, and distillation yielded $n\text{-}C_4H_9OSi(CH_3)_3$, which was identical with a sample prepared from sodium *n*-butoxide and chlorotrimethylsilane. The formation and existence of the *n*-butyl analog at low temperatures is supported by two strong bands at 1760 and 1725 $\mathrm{cm^{-1}}$, similar to those of the other compounds in Table I; these bands gradually disappeared at room temperature, and also when distillation was attempted at room temperature.

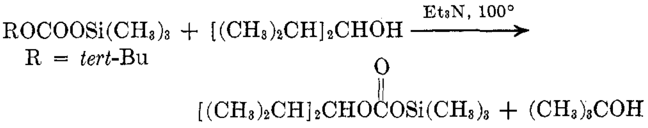
The *tert*-butyl compound **4a** reacted with a variety of secondary amines to form the silylcarbamates[8] indicated in Table II, and a similar reaction was given by the thiol compound **3**. The *i*-Pr compound **4b** and the *tert*-Bu compound **4a** yielded **5e** with aniline, and the same compound was prepared from the thiol compound **3** (mixture melting point) The physical properties of the silylcarbamates are given in Table II.

$$\mathrm{ROCOOSi(CH_3)_3} + \mathrm{R'_2NH} \longrightarrow \mathrm{R'_2NCOOSi(CH_3)_3}$$

R = *tert*-Bu

5a, $R'_2 = (CH_2)_4$
b, $R'_2 = (CH_2)_5$
c, $R'_2 = (CH_2)_2O(CH_2)_2$
d, $R'_2 = C_6H_5, CH_3$
e, $R'_2 = C_6H_5$, H

An ester interchange took place as follows.

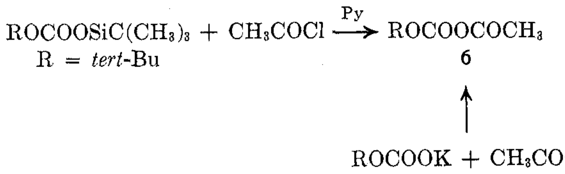


$$\mathrm{ROCOOSi(CH_3)_3} + \mathrm{[(CH_3)_2CH]_2CHOH} \xrightarrow{\mathrm{Et_3N,\ 100°}} \mathrm{[(CH_3)_2CH]_2CHO}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{OSi(CH_3)_3} + \mathrm{(CH_3)_3COH}$$

R = *tert*-Bu

4c

Of interest to us were reports that trimethylsilyl derivatives reacted with acyl halides.[9] We have prepared the mixed carboxylic carbonic anhydride **6** as below; the product was identical with that prepared by the usual method.



$$\mathrm{ROCOOSiC(CH_3)_3} + \mathrm{CH_3COCl} \xrightarrow{\mathrm{Py}} \mathrm{ROCOOCOCH_3} \quad (\mathbf{6}) \longleftarrow \mathrm{ROCOOK} + \mathrm{CH_3COCl}$$

R = *tert*-Bu

Treatment of *tert*-butyl trimethylsilyl carbonate with ethyl chlorocarbonate in the presence of a trace of pyridine yielded *tert*-butyl ethyl dicarbonate **7**, previously

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[2] A. W. Friederang and D. S. Tarbell, *Tetrahedron Lett.*, 5535 (1968).

[3] C. S. Dean and D. S. Tarbell, *Chem. Commun.*, 728 (1969).

[4] C. S. Dean, D. S. Tarbell, and A. W. Friederang, *J. Org. Chem.*, **35**, 3393 (1970).

[5] C. S. Dean and D. S. Tarbell, *J. Org. Chem.*, **36**, 1180 (1971).

[6] For reviews of the use of silyl compounds as synthetic reagents, see among others (a) L. Birkofer and A. Ritter, *Angew. Chem.*, **77**, 414 (1965); (b) "Organosilicon Chemistry," IUPAC Symposium, Prague, 1965, particularly paper by R. C. Mehrotra, p 111 ff; (c) V. Bayant, V. Chvalvosky, and J. Rathovsky, "Organosilicon Compounds," Academic Press, New York, N. Y., 1965; (d) R. J. H. Voorhoeve, "Organohalosilanes; Precursors to Silicones," Elsevier, Amsterdam 1967; (e) L. F. Fieser and M. Fieser, "Reagents for Organic Syntheses," Vol. 2, Wiley, New York, N. Y., 1969, p 435 ff; (f) J. F. Klebe, H. Finkbeiner, and D. M. White, *J. Amer. Chem. Soc.*, **88**, 3390 (1966), and accompanying papers; (g) C. A. Buehler and D. E. Pearson, "Survey of Organic Syntheses," Wiley, New York, N. Y., passim; (h) Y. K. Yur'ev and Z. V. Belyakova, *Russ. Chem. Rev.*, 383 (1960); (i) J. F. Klebe, *Accounts Chem. Res.*, **3**, 299 (1970); G. Urry, *ibid.*, **3**, 306 (1970).

[7] Compounds of type $R_3MSCOOEt$, where M = Si, Ge, Sn, Pb, have been made from KSCOOEt + R_3MX by M. Schmidt, *et al.*, *J. Organometal. Chem.*, **17**, 277 (1969). The Si compound is very unstable.

[8] Several groups have prepared silylcarbamates by action of CO_2 or CS_2 as follows: $R_2NSi(CH_3)_3 + CO_2 \rightarrow R_2NCOOSi(CH_3)_3$ [G. Oertel, H. Malz, and H. Holtschmidt, *Chem. Ber.*, **97**, 891 (1964); R. H. Cragg and M. F. Lappert, *J. Chem. Soc., A*, 82 (1966); J. F. Klebe, J. B. Bush, Jr., and J. E. Lyons, *J. Amer. Chem. Soc.*, **86**, 4400 (1964), using phenyl isocyanate; S. S. Washburn and W. R. Peterson, Jr., *J. Organometal. Chem.*, **21**, 59 (1970)]; E. A. V. Ebsworth, *et al.*, *J. Chem. Soc. A*, 362 (1967); H. Breederveld, *Recl. Trav. Chim. Pays-Bas*, **81**, 276 (1962).

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TABLE I

PHYSICAL PROPERTIES OF $RXOCOOSi(CH_3)_2$

$RXC(=O)OSi(CH_3)_3$					
R	X	Bp, °C (mm)	Yield, %	Ir,[a] ν (C=O)	Nmr[b,c]
tert-Bu	O	71–72 (22)	60	1755, 1720	0.30 (9 H, s) 1.48 (9 H, s)
i-Pr	O	66–67 (28)	53	1760, 1720	0.31 (9 H, s) 1.08 (6 H, d, J = 6.5 Hz) 4.85 (1 H, quintet, J = 6.5 Hz)
2,4-Dimethyl-3-pentyl	O	59 (2)	39	1755, 1720	0.33 (9 H, s) 0.91 (12 H, d, J = 6.5 Hz) 1.6–2.2 (2 H, m) 4.36 (1 H, t, J = 6.5 Hz)
Et	O	42–43 (11)	62	1760, 1725	0.30 (9 H, s) 1.31 (3 H, t, J = 7 Hz) 4.16 (2 H, q, J = 7 Hz)
tert-Bu	S	47–49 (3.5)	47	1690	0.31 (9 H, s) 1.45 (9 H, s)

[a] In cm^{-1} in liquid film. [b] In parts per million from $(CH_3)_4Si$ in $CDCl_3$: s = singlet, d = doublet, t = triplet, q = quartet. [c] All compounds gave C and H analyses within 0.4% of the calculated values. The data were made available to the editors.

TABLE II

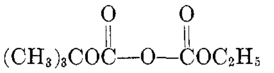
PHYSICAL PROPERTIES OF SILYLCARBAMATES[a]

R_2NCOOR' [$R' = Si(CH_3)_3$]

Compd[a]	Bp, °C (mm)	Yield, %	Ir, ν (C=O), in CCl_4
$R_2 = (CH_2)_4$	79–80 (6)	55	1680 (liquid film) 1680
$R_2 = (CH_2)_5$	64–65 (2)	70	1675 (liquid film)
$R_2 = (CH_2)_2O(CH_2)_2$	Mp 44–46	57	1670 (in $CHCl_3$)
$R_2 = CH_3$ and C_6H_5	70.5–72 (1)	77	1682
R_2 = H and C_6H_5	Mp 134–136	64	1720

[a] All compounds gave C and H analyses within 0.4% of the calculated values. The analytical data were made available to the editors.

obtained by action of ethanol on di-*tert*-butyl tricarbonate.[5]



$$(CH_3)_3CO\overset{O}{\overset{\|}{C}}{-}O{-}\overset{O}{\overset{\|}{C}}OC_2H_5$$

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Further investigations of carbonate syntheses *via* silicon-containing intermediates are under way.

Experimental Section[10]

***tert*-Butyl Trimethylsilylcarbonate (4a).**—Dry carbon dioxide was passed into a solution of 20 g of potassium *tert*-butoxide to 250 ml of THF at −10–0° over a period of 30 min with stirring, and 50 ml of THF was added to dilute the thick gel. To the mixture was added 20 g of chlorotrimethylsilane in 50 ml of THF over a period of 30 min. The thick gel changed to a white slurry. The mixture was stirred and chilled with ice-salt bath for an additional hour. The mixture was centrifuged to separate it into an organic layer and a semisolid material. The semisolid was washed with 100 ml of THF and centrifuged, and the organic layer was combined with the washing. Solvent was removed at ambient temperature under reduced pressure by an aspirator, and the residue was distilled and had the recorded boiling point (Table I).

Anal. Calcd for $C_8H_{18}O_3Si$: C, 50.49; H, 9.58; Si, 14.76. Found: C, 50.44; H, 9.37; Si, 14.57.

***tert*-Butylthiol trimethylsilylcarbonate (3)** was prepared by carbonation of sodium *tert*-butyl mercaptide[4] followed by treatment with chlorotrimethylsilane as described above.

Anal. Calcd for $C_8H_{18}O_2SSi$: C, 46.60; H, 8.73. Found: C, 46.82; H, 8.42.

The other compounds in Table I were made by similar procedures and had similarly acceptable carbon and hydrogen analyses.

Trimethylsilyl 1-Pyrrolidinocarbamate (5a).—A solution of 3 g of *tert*-butyl trimethylsilyl carbonate (4a) and 1.1 g of pyrrolidine was refluxed in 15 ml of dry ether for 1 hr, the solvent was removed, and the product obtained by distillation had the properties given in Table II.

Anal. Calcd for $C_8H_{17}NO_2Si$: C, 51.83; H, 9.15. Found: C, 51.65; H, 9.19.

The other compounds in Table II were prepared similarly except that the solids were purified by crystallization.

The aniline derivative **5e** was prepared from both the *tert*-butyl and isopropyl compounds **4a** and **4b**.

***tert*-Butylcarbonic Acetic Anhydride (6).** **A.**—To a solution of 2.5 g of *tert*-butyl trimethylsilylcarbonate and 1.25 g of pyridine in 5 ml of THF was added dropwise 1.25 g of acetyl chloride in 45 ml of THF at room temperature with stirring over a period of 3.5 hr. The reaction mixture was evaporated under reduced pressure, pentane was added, the suspension was filtered, and the filtrate was evaporated under reduced pressure. Distillation of the residual liquid gave two fractions: (1) a mixture of *tert*-butyl trimethylsilyl carbonate and *tert*-butylcarbonic acetic anhydride (in an approximate ratio of 2:1), 0.3 g, bp 57–58° (9 mm); (2) *tert*-butylcarbonic acetic anhydride, **6**, 0.5 g (24%), bp 60–62° (9 mm).

Anal. Calcd for $C_7H_{12}O_4$: C, 52.50; H, 7.50. Found: C, 52.55; H, 7.58.

The ir spectra in both liquid film and CCl_4 solution showed a broad carbonyl band at 1760–1830 cm^{-1} and the nmr ($CDCl_3$) showed two singlets at 1.55 (9 H) and 2.18 (3 H). These ir and nmr spectra were identical in all respects with those of an authentic sample, prepared as below.

B.—Potassium *tert*-butoxide (5.6 g) was carbonated in 100 ml of THF in an ice-salt bath in the usual way,[4] and 3.9 g of acetyl chloride in 10 ml of THF was added dropwise. The mixture yielded, after usual work-up, two centrifugations, and washings, 3.3 g (41%) of *tert*-butylcarbonic acetic anhydride (**6**), bp 63–64° (10 mm).

***tert*-Butyl Ethyl Dicarbonate (7).**—A mixture of 2.85 g of *tert*-butyl trimethylsilyl carbonate, 1.78 g of ethyl chlorocarbonate, and about 0.05 g of pyridine in 10 ml of $CHCl_3$ (alcohol free) was stirred for 30 min at room temperature. An additional 0.95 g of *tert*-butyl trimethylsilyl carbonate in 5 ml of $CHCl_3$ was added. Stirring was continued for 15 min. The reaction mixture was evaporated under aspirator pressure. The residue was washed with dry ether and the solid was filtered off. The ether layer was evaporated and the residue gave after distillation 0.65 g of *tert*-butyl ethyl dicarbonate, bp 38° (0.2 mm). The ir spectrum (liquid film) was identical in all respects with that of the authentic sample.[5]

***n*-Butyl trimethylsilylcarbonate** was found to liberate CO_2 even below room temperature, and was found in two runs to be much less stable than the corresponding ethyl compound **4e**. Distillation of the supposed *n*-butyl compound gave complete loss of

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[10] Analyses and instrumentation were as previously described.[4] Glass apparatus was dried under a nitrogen stream with a heating mantle, and THF was distilled from $LiAlH_4$ directly before use.

CO_2, forming the known *n*-butoxytrimethylsilane, whose boiling point and ir and nmr properties agreed completely with those of an authentic sample.[11]

Registry No.—**3**, 30882-86-1; **4a**, 30882-87-2; **4b**, 30882-88-3; **4c**, 30882-89-4; **4e**, 30882-90-7; **5a**, 30882-91-8; **5b**, 30882-92-9; **5c**, 30882-93-0; **5d**, 30882-94-1; **5e**, 30882-95-2; **6**, 30882-96-3.

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Preparation, Characterization, and Photofragmentation of the Isomeric 1,4-Bis(2,3-diphenyloxiranyl)benzenes

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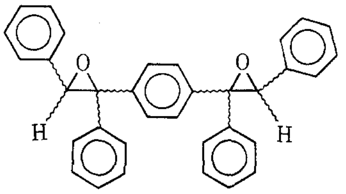
The preparation and separation of the three isomeric 1,4-bis(1,2-diphenylvinyl)benzenes and their epoxidation to give the six diastereoisomeric 1,4-bis(2,3-diphenyloxiranyl)benzenes are described. One of the dialkenes and the two bisoxiranes derived from it are unambiguously assigned cis–trans geometry on the basis of pmr data. Tentative structural assignments for the remaining cis–cis and trans–trans isomers in the alkene and oxirane series are made on the basis of the ultraviolet spectra of the respective dialkenes. The photofragmentation of the bisoxiranes in solution has been studied and the primary mode of cleavage determined.

Previous studies have demonstrated that aryl-substituted oxiranes fragment photochemically yielding aryl carbenes and carbonyl compounds.[2–6] Esr and optical spectral investigations have provided direct evidence for the formation of diphenylmethylene upon photofragmentation of tri- and tetraphenyloxirane.[7] More recently optical spectroscopic evidence for the formation of phenylmethylene upon photolysis of the isomeric 2,3-diphenyloxiranes also has been obtained.[6] In independent studies Trozzolo and coworkers have observed the esr spectra of two dicarbenes, namely *m*- and *p*-phenylenebis(phenylmethylene), upon irradiation of 1,3- and 1,4-bis(α-diazobenzyl)benzene, respectively, in rigid matrices.[8,9] The esr spectra of quintet *m*-phenylenebis(phenylmethylene) was independently reported by Itoh[10] who oriented the diazo precursor in a single crystal of benzophenone.

The observation that the unsymmetrical oxirane, triphenyloxirane, fragments preferentially (85%) to give diphenylmethylene and benzaldehyde[6] suggested that the isomeric 1,4-bis(2,3-diphenyloxiranyl)benzenes (**1**) would fragment in a similar manner and perhaps provide additional precursors for *p*-phenylenebis(phenylmethylene) (**2**), a transient of considerable theoretical as well as potential practical interest as a cross-linking agent for a broad variety of polymers having functionality known to react with carbenes. Observation of the dicarbene *per se* will undoubtedly require low temperature rigid matrices, a stepwise fragmentation of the bisoxiranes in solution being likely.



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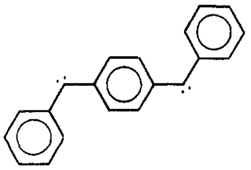

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The bisoxiranes **1** in principle may exist in six diastereoisomeric forms and we were also interested in the possibility that the mode of fragmentation might vary as a function of the stereochemistry of the precursor. Therefore we have prepared, separated, and characterized the three isomeric 1,4-bis(1,2-diphenylvinyl)benzenes and the six diastereoisomeric 1,4-bis(2,3-diphenyloxiranyl)benzenes derived from them by peracid oxidation and studied the fragmentation pattern of the latter in methanol.

Results and Discussion

1,4-Bis(1,2-diphenylvinyl)benzenes.—A mixture of the three isomeric alkenes was prepared from *p*-dibenzoylbenzene *via* a Grignard addition–dehydration sequence previously described by Buu-Hoi and coworkers.[11] These authors report the preparation of "α"-distilbenzylbenzene, mp 74°, a substance characterized only by elemental analyses. No structural assignment or mention of the other potential isomers was made. Microscopic examination revealed that amorphous materials were obtained in our attempts to repeat the earlier work and to crystallize the product from ethanol as described. Neither heating under reflux in ethanol containing a trace of iodine nor in toluene containing *p*-toluenesulfonic acid converted the mixture to a single, stable isomer. One of the isomers, mp 172–174°, eventually crystallized from *n*-heptane

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[1] (a) Taken from the dissertation submitted by N. R. B. in partial fulfillment of the Ph.D. requirements, Louisiana State University in New Orleans, New Orleans, La. (b) Author to whom inquiries regarding this communication should be directed, Louisiana State University in New Orleans. (c) One of the laboratories of the Southern Marketing and Nutrition Research Division, Agricultural Research Service, U. S. Department of Agriculture.

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