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1, 5-BIS(TRIMETHYLSILOXY)-1, 5-DIMETHOXY-1, 4-PENTADIENES

PRECURSORS FOR THE SYNTHESIS OF CYCLOPROPANES AND CYCLOBUTANES

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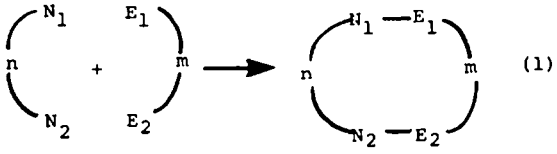
Abstract—1, 5-Bis(trimethylsiloxy)-1, 5-dimethoxy-1, 4-pentadienes (**7**) can be prepared in good yield by silylation of the dianions of dimethyl glutarates (**8**). On treatment with titanium tetrachloride, **7** cyclise stereoselectively to dimethyl *trans*-cyclopropane-1, 2-dicarboxylates **10**. Reaction of **7** with acetic anhydrode and titanium tetrachloride gives substituted cyclobutanes **22b–d**.

Recently[1] we proposed a general approach (eqn 1) to the construction of carbocyclic compounds involving the condensation of two fragments—one fragment (**1**) containing two nucleophilic sites in the form of enol silyl ehters (represented in **1** as N), and the other fragment (**2**) containing two electrophilic sites in the form of CO groups or their equivalents (represented in **2**, as E). Such a strategy has been applied to the synthesis of 6, 7- and 8-numbered carbocycles.[2,3] It is especially useful for the

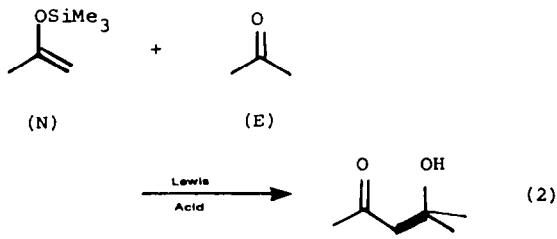


(1)

1 **2** **3**

regio-controlled synthesis of phenolic compounds [1,2] including two natural products, sclerin[4] and Δ^1-tetrahydrocannabinol.[5]

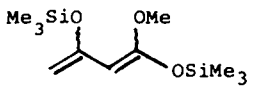
The chemistry utilised in this method of carbocyclic synthesis is the condensation of enol silyl ethers with CO compounds, often with Lewis acid as catalyst (eqn 6).[6] There are certain advantages in using enol silyl ethers instead of the more classical enolate anions as the nucleophilic components in eqn (1). It is now possible to prepare, purify and characterise bis-enol silyl ethers (**1**)[7,8] whereas in enolate anion chemistry, the anions



(2)

would have to be generated and used *in situ*. For compounds where the two enol silyl ethers are not of identical structure, (represented in **1** as N_1 and N_2), their reactivities may be sufficiently different so that a reactivity order can be assigned (say, N_1 more reactive than N_2 in **1**). Finally, because the reaction is carried out under acid-catalysed conditions, a number of CO equivalents in the form of ortho-esters, acetals, and the conjugated position of β-oxy-α, β-unsaturated CO compounds can be used as the electrophilic sites as well. This allows for greater flexibility in designing the structure of **2** where E_1 and E_2 will also have reactivity difference (say, E_1 more reactive than E_2 in **2**). The regiochemistry of the cyclisation reaction can then be controlled by the differential reactivities of these sites as in eqn (1).

We have explored several types of bis-enol silyl ethers as the nucleophilic component. 1, 3-Bis(trimethylsiloxy)-1-methoxy-1,3-butadiene (**4**, dianion equivalent of methyl acetoacetate)[1,3], 2,4-bis(trimethylsiloxy)-1, 3-pentadiene (**5**, dianon equivalent of acetylacetone)[2] and 2, 5-bis(trimethylsiloxy) furan (**6**, dianion equivalent of succinic anhydride)[9] have thus far been used in the condensation reaction. In this paper, we wish to examine the chemistry of 1,5-bis(trimethylsiloxy)-1,5-dimethoxy-1, 4-pentadienes (**7**),[10] the dianion equivalents of dimethyl glutarates, and their use in the synthesis of 3- and 4-membered rings.



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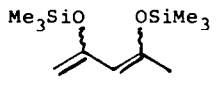

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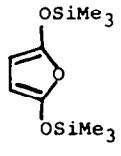

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Preparation of 1, 5-*bis*(*trimethylsiloxy*)-1, 5-*dimethoxy*-1,4-*pentadienes*(**7**)

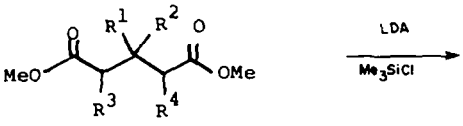
The parent compound, 1, 5-bis(trimethylsiloxy)-1, 5-dimethoxy-1, 4-pentadiene (**7a**), has previously been

Table 1. Preparation of bis-ketene silyl acetals from glutarate esters

Structure	Bpt (°C/mmHg)	Yield (%) (dist)	Isomer Distribution[a] EE	EZ	ZZ%
7a	72–76(0.06)	52 (54)	38 (62)	47 (31)	15 (7)
7b	91–96(0.5)	– (68)	41 (53)	46 (42)	13 (5)
7c	78–79(0.9)	– (64)	100 (100)	0 (0)	0 (0)
7d	78–83(0.3)	73	not determined[b]		
7e	72–76(0.07)	(56)	(84)	(15)	(0[c])

[a]Calculated from nmr integration, figures in parenthesis are ratios obtained when TMEDA (2.5 mol equiv) is used in conjunction with LDA as base. [b]Although peaks due to isomers are observed in the nmr (in C_6D_6) they cannot be assigned with confidence. [c]From GC integration, supported by gcms and nmr.

prepared by the reductive silylation of 1, 2-dicarbomethoxycyclopropane.[11] A more convenient approach would be to trap the dianion of dimethyl glutarate with trimethylchlorosilane. Indeed, when a solution of dimethyl glutarate (**8a–e**) in dry THF was added to a solution of lithium di-isopropylamide (LDA) at −78°, and the mixture was treated with trimethylchlorosilane, the expected bis-ketene acetals **7a–e** could be obtained in reasonable yields (Table 1).



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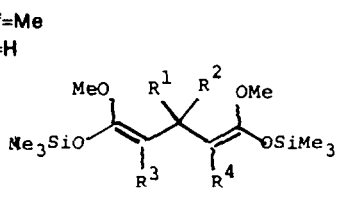
(a) $R^1=R^2=R^3=R^2=H$
(b) $R^1=R^3=R^4=H$, $R^2=Me$
(c) $R^1=R^2=Me$, $R^3=R^4=H$



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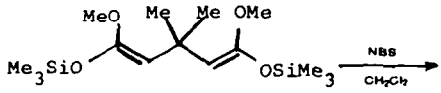
(d) $R^1=R^2=R^4=H$, $R^3=Me$
(e) $R^1=R^2=H$, $R^3=R^4=Me$

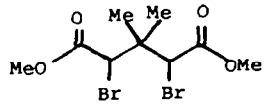
Three different geometrical isomers, *EE*, *EZ* and *ZZ* are possible for the bis-ketene silyl acetals, and for **7a** and **b** all three are observed (Table 1). The assignment of stereochemistry is based on the chemical shifts of the vinyl protons using Ireland's value for *E* and *Z* monoketene acetals.[12] The relative ratio of isomers were determined by integrating the OMe peaks in the 200 MHz NMR in deuterobenzene. It can be seen for Table 1 that **2c** exists exclusively as the *EE* isomer, perhaps because of the steric repulsion expected in the *Z*-geometry. Another observation is that if the reaction is carried out using a TMEDA–LDA complex as the base, the proportion of *EE* isomer in the case of **7a** and **b** increases somewhat. This is opposite to the effect observed for monoesters[12] which is the subject of some discussion.[13,14]

The bisketene silyl acetals 7 are reasonably stable and may be stored at toom temperature in well sealed containers for an extended period. When exposed to the air, they are converted back to the dimethyl esters **8**. The hydrolysis of **7** to **8** is accelerated by a few drops of 0.1 M HCl.

The bisketene silyl acetals (*e.g.* **7c**) react with 2 equivalent of bromine or N-bromosuccinimide (NBS) to give α, α'-dibromoesters (**9c**) as a 1 : 1 dl and meso mixture in good yield. NBS is the reagent of choice, since trace amount of HBr in the bromine convert the substrate to the ester **8**. When one equivalent of NBS was used in the bromination, little monobromide was formed and the major products were the dibromide and diester, after an aqueous work-up. This suggests that the rate of bromination of the bromo-monoketene silyl acetal intermediate is significantly faster than the bisketene silyl acetal.



7c

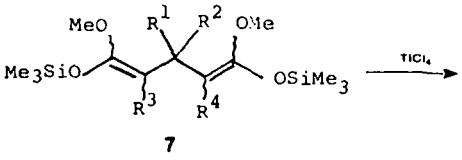


9c

Cyclopropane synthesis via oxidative intramolecular coupling of 7 with titanium tetrachloride

Since $TiCl_4$ is often the Lewis acid of choice to catalyse the reaction outlined in eqn (2), and it is also known that ketene silyl acetals undergo an oxidative coupling reaction with $TeCl_4$ to give 1, 4-diesters,[15,16] it became of interest to us to investigate the intramolecular coupling of **7** as a way to synthesize cyclopropane-1, 2-dicarbpxylate esters. Indeed, when **7a** was allowed to react with $TiCl_4$ in a fairly dilute CH_2Cl_2 solution (20 mM) at 20° for 1 hr, dimethyl *trans*-cyclopropane-1, 2-dicarboxylate (**10a**) can be obtained.

The reaction appears to be general and has been applied to the other substituted bis-ketene silyl acetals (**7b–e**) (Table 2). The reaction gave similar results (e.g. **7b**) when run in hexane at the same dilution. The use of MeCN, THF or DMSO gave no reaction and only diester **8** was obtained after aqueous work-up. When one equivalent of $TiCl_4$ was used, no cyclopropane compound was observed in the crude mixture according to NMR. The reaction is accompanied by the formation of polymeric material. However at higher dilution, the reaction gave diminished yields of **10**, even though great pains were taken to dry the solvent to avoid hydrolysis of the bis-ketene silyl acetals.



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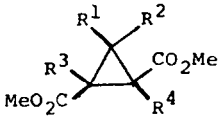

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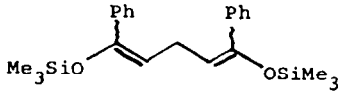
An interesting feature of this reaction is that the cyclopropane **10** is formed stereoselectively. In the case of **10a, c, d** and **e**, the stereochemistry is exclusively *trans* as determined by NMR and GC. With **10b**, two isomers; 1r-2t-3t and 1r-2c-3t are formed in a 1 : 1 ratio. The other possible isomers, 1r-2c-3c and 1r-2t-3c were not detected. It appears that the stereochemical course of the reaction is controlled by the thermodynamical stability of the products. The geometrical isomer distribution in the starting bis-ketene silyl acetals **7** does not influence the stereochemical outcome of the products. Thus, results were identical when **7a**, prepared from either LDA or TMEDA-LDA, was cyclised.

The mechanism for this cyclisation is not presently known for certain but is expected to be similar to that postulated by Ojima[15] for the oxidative dimerisation of monoketene silyl acetals. The bisketene silyl acetal **7** is first converted to an enoxy radical **11a** via the titanium enolate **11b**; intermolecular coupling of the diradical **11a** then give the product **10** (Scheme 1).

In essence, the reaction is similar to the $Cu(OTf)_2$ induced cyclisation of dienolates reported recently by Kobayashi[17] or the coupling of enol silyl ethers by metal salts.[18,19] In the Ti(IV) induced formation of cyclopropanes, however, the reaction is more stereoselective. Furthermore, it seems that titanium tetrachloride causes coupling only of ketene silyl acetals and not of enol silyl ethers derived from ketones. Thus, when the bis-enol silyl ether **12** was treated with $TiCl_4$ under identical conditions, *no* cyclopropane product **13** was observed.[19]



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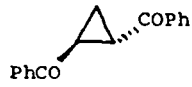

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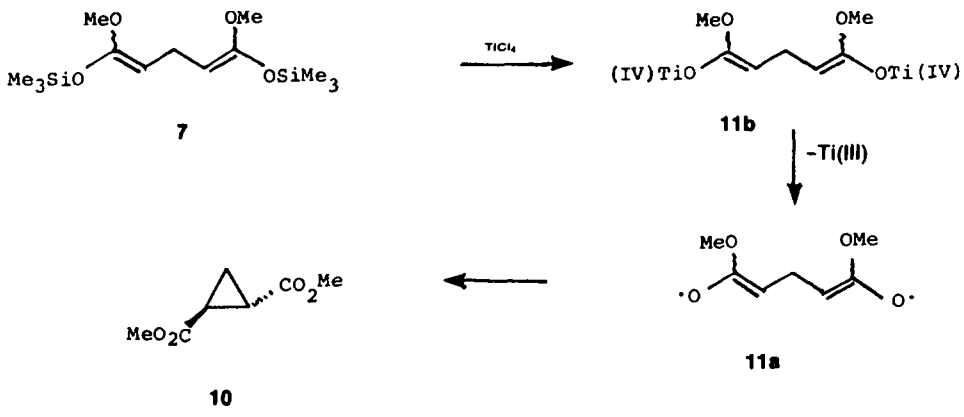
Table 2. Oxidative cyclisation of the bisketene acetals (7) with titanium tetrachloride

Substrate	Product	Stereochemistry[ab]	distilled yield %[c] (bpt °C/mmHg)	literature Reference
7a	10a	> 95% trans	20% (70-75/0.3)	25
7b	10b	50% 1r-2t-3t 50% 1r-2c-3t	41% (104-108/14)	26
7c	10c	> 99% trans	69% (48-49/10.05)	24
7d	10d	> 98% trans	59% (65-69/0.2)	27
7e	10e	> 95% trans	not determined	28

a. Structure assigned by comparison of nmr with reported data.

b. Isomer ratios determined by GLC (Hewlett-Packard 5570 gas chromatograph using a 10' x 0.25" 5% GEXP 1150 on chromosorb W column[29]).

c. Other product is polymer.



Scheme 1.

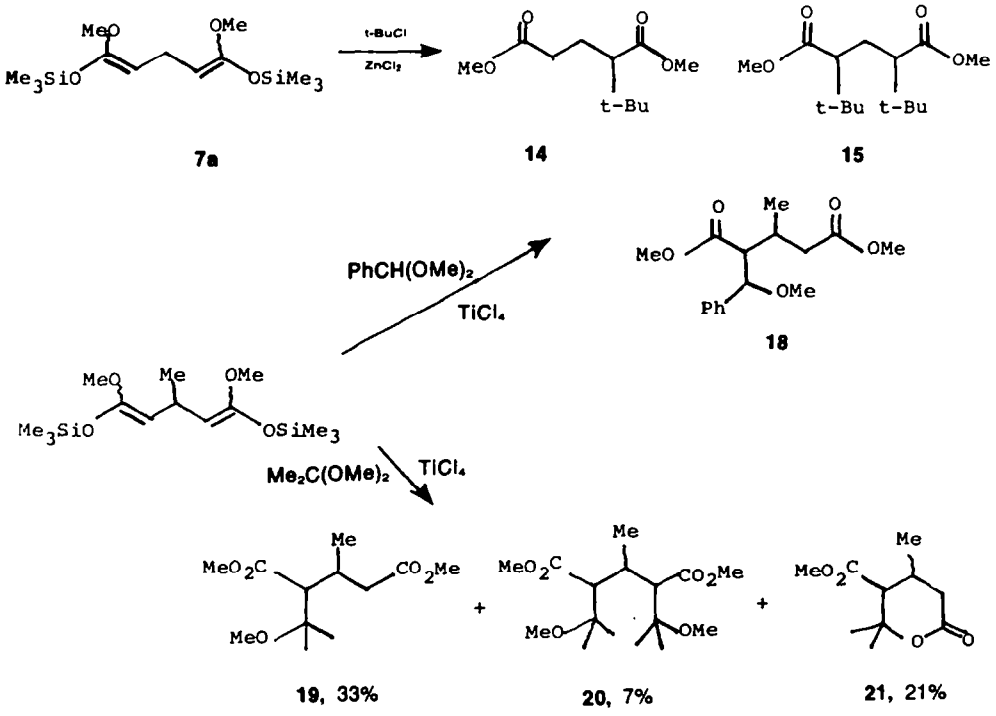
Reaction of 7 with carbon electrophiles and synthesis of cyclobutyl compounds

We have examined the condensation of **7** with a number of carbon electrophiles. When t-butyl chloride in the presence of a catalytic amount of $ZnCl_2$ is used as the electrophilic reagent, α-butylation product was obtained.[20,21] When 1 equivalent of t-butyl chloride was used in the reaction with **7a**, only dimethyl 2-t-butylglutarate (**14**) was obtained with no di-alkylation product **15**. Dimethyl glutarate was also formed, presumably due to the hydrolysis of **7a** either during or after the reaction. The use of excess of t-butyl chloride led to only a small yield to **15** with **14** still as the major component (ratio 14 : 15 ≅ 6 : 1). This result is to be contrasted with the bromination reaction mentioned previously where the dibromo compound **9c** is the major product.

The preference for reaction with only one site persists when benzaldehyde dimethyl acetal (**16**) or 2, 2-dimethoxypropane (**17**) was used as the carbon electrophile. Compound **7b**, on reaction with **16**-$TiCl_4$ (1 : 2, −78°) gave the methoxy-diester **18** as the only product in the form of a mixture of diastereoisomers in 69% yield. Similarly, reaction with 2, 2-dimethoxypropane gave a mixture of compounds **19**, **20** and **21** again with reaction at one site predominating.

When the more reactive carbon electrophile, acetic anhydride, is used in conjunction with $TiCl_4$, reaction with the substituted bis-ketene silyl acetals **7b–d** gave substituted 2, 4-dicarbomethoxycyclobutanols (**22b–d**) in moderate yields. Cyclobutane compound **23** was also obtained on the reaction of **7c** with benzoic anhydride–$TiCl_4$.

The four cyclobutyl compounds (**22b–d**, **23**) are apparently formed with high stereoselectivity. In each case,



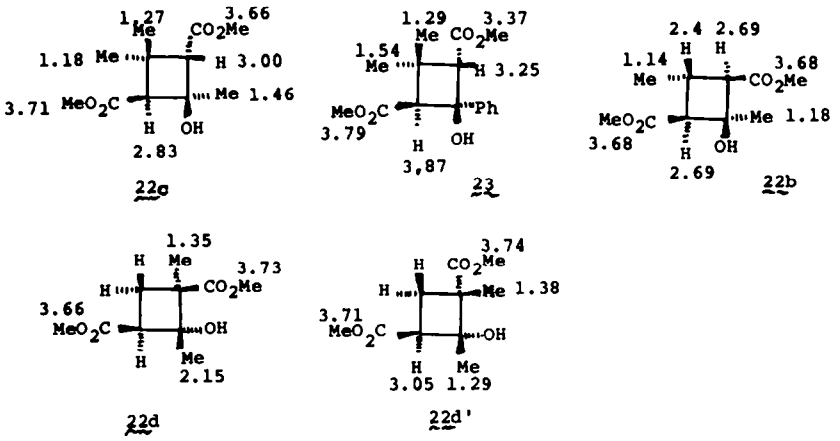


Fig. 1. ^{1}H NMR spectea of cyclobutyl compounds **22b–d** and **23**.

only one stereoisomer was detected and isolated. The assignment of stereochemistry of these high substituted cyclobutanol was not an easy task, but, by comparison of the ^{1}H NMR chemical shifts, a reasonable argument for the structures postulated could be made. Firstly, cyclobutanols **22c** and **23** show two signals for their ester Me protons, implying a *trans*-arrangement. Comparison of the other signals in the ^{1}H NMR spectrum of **22c** with those from **23** enable the assignment to be made with some confidence as in Fig. 1.

The ^{1}H NMR spectrum of **22b** has only one CO_2Me signal (Me and C=O of the two esters both also resonate as single peaks in the ^{13}C NMR spectrum of **22b**) and is therefore *cis* at these centres. The two C–Me groups of **22b** have similar chemical shifts and resonate at higher field then those in **22c**, indicating that the C–Me in **22b** are *cis* to each other but *trans*- to the ester group.

Finally, the assignment for **22d** is more tentative. The particularly low field Me_3 (2.15 ppm) signal suggests that this Me group is *cis*- to both ester groups. Furthermore, when **22d** is passed through a column of silica gel in chromatographic purification, a mixture of two diastereomers is obtained. The new isomer **22d'** is assigned the structure indicated on the basis of the chemical shifts of the two ring Me groups, and the ester α-proton.

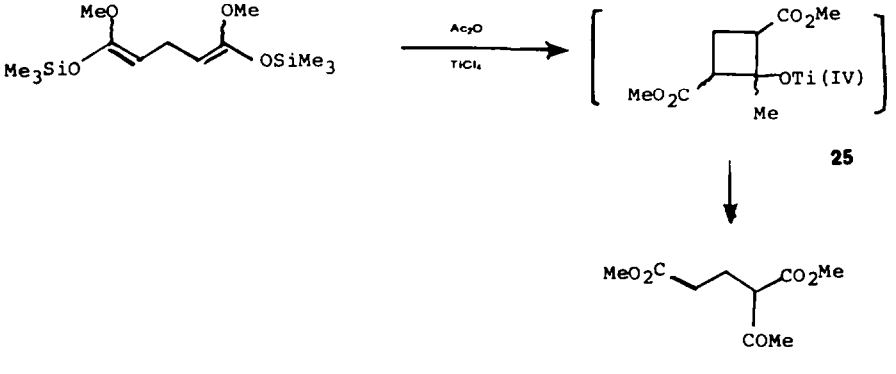
When the parent compound **7a** was treated even with an excess of acetic anhydride-$TiCl_4$, the only product isolated was dimethyl 2-acetylglutarate (**24**) apart from dimethyl glutarate. The formation of **24** and the absence of diacylation product is indicative that cyclobutyl compound **25** may well be the product in the reaction which however on hydrolytic work-up ring opens to give **24**. Such ring opening and reclosure accounts also for the isomerisation of **22d** and **22d'**.

There are only a limited number of non-photochemical routes to cyclobutanes.[22,23] The present methodology, involving as it does, a 3C + 1C cyclisation under acidic conditions, may offer a viable alternative route.

EXPERIMENTAL

General. M and b ps are uncorrected. IR spectra were obtained from films on NaCl plates for liquids and from solns in 0.1 mm NaCl cells for solids, using a Perkin–Elmer 297 spectrophotometer. ^{1}H NMR spectra were recorded on Varian T-60A and XL-200 instruments, with Me_4Si as internal standard. Mass spectra were obtained on a Hewlett–Packard 5984A or an LKB 9000 machine operating at 70 eV. Column chromatography was performed on silica gel 60 (Merck). Et_3N, i-Pr_2NH, and TMEDA were dried by distillation from CaH_2; hexane, CCl_4 and benzene from P_2O_5; CH_2Cl_2 from P_2O_5 and then from CaH_2. THF was distilled under N_2 from sodium–benzophenone directly into the reaction vessel. Microanalyses were preformed by Guelph Chemical Laboratories Ltd.

General procedure for the preparation of 1, 5-*bis*(*trimethylsiloxy*)-1, 5-*dimethoxy*-1, 4-*pentadienes* **7a–e**. A soln of dimethyl 3, 3-dimethylglutarate (4.26 g, 0.03 mol) in dry THF (50 ml) was added to a stirred soln of lithium di-isopropylamide (0.075 mol) in THF (25 ml) under N_2 at −78°. After 20 min, trimethylchlorosilane (9.7 ml, 0.075 mol) was added and the mixture was allowed to warm and stand at room temp for 2 hr. The solvent was removed *in vacuo* and hexane was added to the residue. The soln was filtered and evaporated, then distilled to give **7c**, (6.42 g, 64%) as a colorless oil, b.p. 78–79% 0.9 mm. It showed: IR (neat),



1670, 1255 and 843 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.91 (s, 2H), 3.48 (s, 6H), 1.18 (s, 6H), 0.21 (s, 18H); MS, *m/z* 332 (M^+, 10%), 317 (50%), 213 (80%), 119 (100%), 73 (80%).

Other bis-ketene silyl acetals prepared by this method were:

1, 5-*Bis*(*trimethylsiloxy*)-1, 5-*dimethoxy*-1, 4-*pentadiene* (**7a**)

As an oil (52%) (b.p. 72–76°/0.06 mmHg). IR (neat): 673 cm^{-1}; ^1H NMR ($CDCl_3$): 3.64 (t, J = 7.5 Hz, *EZ* H), 3.62 (t, J = 7.5 Hz, *EE* H), 3.49 (s, MeO), 3.46 (s, MeO), 3.45 (s, MeO), 3.43 (t, J = 7.5 Hz, *ZZ* H), 2.60 (t, J = 7.5 Hz, E CH_2) 2.58 (t, J = 7.5 Hz, Z CH_2), 0.21 (s, Me_3Si *EZ*), 0.20 (s, Me_3Si *EE*), 0.18 (s, Me_3Si *ZZ*). This data is in agreement with the published spectra for this compound.[11]

3-*Methyl*-1, 5-*bis*(*trimethylsiloxy*)-1, 5-*dimethoxypenta*-1, 4-*diene* (**7b**)

As an oil (68%) (b.p. 91–96°/0.5 mmHg), IR (neat): 1 668 cm^{-1}; ^1H NMR, (C_6D_6): 3.65 (d, J = 10 Hz, *EZ* H), 3.63 (d, J = 10 Hz, *EE* H), 3.48 (d, J = 9 Hz, *ZZ* H), 3.2–3.4 (m, CHMe, all isomers), 3.51 (s, *EZ* MeO), 3.50 (s, *EE* MeO), 3.44 (s, *ZZ* MeO), 0.99 (d, J = 7 Hz, *EE* Me), 0.98 (d, J = 7 Hz, *ZZ* Me), 0.96 (d, J = 7 Hz, *EZ* Me), 0.21 (s, *ZZ* Me_3Si), 0.20 (s, *EZ* Me_3Si), 0.19 (s, *EE* MeSi).

2-*Methyl*-1, 5-*bis*(*trimethylsiloxy*)-1, 5-*dimethoxypenta*-1, 4-*diene* (**7d**)

As an oil (73%) (bp 78–83°/0.03 mmHG), IR (neat): 1 678 cm^{-1}; ^1H NMR, ($CDCl_3$): 3.57 (d, J = 8 Hz, *EZ* H), 3.55 (d, J = 8 Hz, *EE* H) 3.50 (s, MeO), 3.48 (s, MeO), 2.58 (d, J = 8 Hz, CH_2), 1.51 (s, Me) 0.21 (s, Me_3Si), 0.19 (s, Me_3Si).

2, 4-*Dimethyl*-1, 5-*bis*(*trimethylsiloxy*)-1, 5-*dimethoxypenta*-1, 4-*diene* (**7e**)

As an oil (56%) (bp 72–76°/0.07 mmHg), IR (neat): 1 691 cm^{-1}; ^1H NMR ($CDCl_3$): 3.51 (s, MeO), 2.59 (s, CH_2), 1.44 (s, Me_2), 0.20 (s, Me_3Si).

On GC (5% OV101 chrom. W, 100–200°, 8°C per min), **7a** decomposed while **7a–d** gave single peaks. Under the same conditions, **7e** gave two peaks, in 85 : 15 ratio, shown by MS to be isomeric bis-ketene silyl acetals.

If a TMEDA-LDA complex (2.5 TMEDA: 2.5 LDA: 1 diester) is used in the preparation, a different isomer ratio is observed, containing a greater proportion of E isomers. (Table 1).

Intramolecular coupling of 1, 5-*bis*(*trimethylsiloxy*)-1, 5-*dimethoxy*-1, 4-*pentadienes* (**7a–e**) *with titanium chloride*

The procedure used for the preparation of **10c** is illustrative.

A soln of $TiCl_4$ (60 mmol, 60 ml of a 1 M soln in CH_2Cl_2) was added to a stirred soln of **7c** (10 g, 30 mmol) in dry CH_2Cl_2 (300 ml) under N_2, at 5°. The mixture was stirred at room temp overnight then sat $KHCO_3$cl (5 ml) was added. The suspension was evaporated *in vacuo* and the residue was taken up in ether, dried ($MgSO_4$), filtered, evaporated and distilled to give **10c** (3.85 g, 69%) as an oil (b.p. 48.6° 0.05 mmHg).[24] It showed ^1H NMR and IR spectra in agreement with the lit data.[24]

Other dimethyl esters of cycloperopane-1, 2-dicarboxylic acids were prepared in a similar manner (Table 2). The geometric isomer distribution in **7** was not important; results were identical when **7a**, prepared from either TMEDA-LDA or LDA (Table 1) was cyclised.

Dimethyl 2-*t-butylglutarate* **14**. To a soln of **7a** (3.05 g, 0.01 mol) and t-BuCl (3.4 ml, 0.03 mol) in 50 ml CH_2Cl_2 anhyd $ZnCl_2$ (200 mg) was added. The mixture was stirred at room temp under argon for 36 hr. The mixture was washed with $NaHCO_3$aq, dried (Na_2SO_4) and evaporated to give 1.91 g colorless oil. GC analysis showed it to be a mixture of dimethyl glutarate (12%), dimethyl 2-t-butylglutarate (~50%) and other unidentified components. Dimethyl 2-t-butylglutarate was purified by preparative GC (S.E. 30 column, 6′ × ¼″ at 115°) or by preparative (Waters 500 A, Silica gel, hexane–ethyl acetate). It had ^1H NMR ($CDCl_3$): 3.67 (s, 3H), 3.66 (s, 3H), 2.34–2.07 (m, 3H), 1.98–1.82 (m, 2H), 0.96 (S, 9H). Found: C, 61.15, H 9.42. Calc: C 61.11, H 9.26%).

Treatment of bisketene Acetal **7b** *with dimethoxypropane-TiCl*$_4$. $TiCl_4$ (4.4 mmol, 4.4 ml of a 1M slon in CH_2Cl_2) was mixed with a soln of dimethoxypropane (0.229 g, 2.2 mmol), in Ch_2Cl_2 (10 ml) at −78°. After 5 min, this mixture was transferred (by syringe) to a soln of **7b** (0.638 g, 2 mmol) in CH_2Cl_2 (100 ml), at −78° giving a red colour that faded rapidly. After the colour had completely faded, the mixture was warmed and allowed to stand at room temp for 48 hr. The mixture was extracted with water (50 ml) and brine, then dried, evaporated and chromatographed (SiO_2, eluent: 20% EtOAc-hexane) to give the *methoxydiester* **19** (0.172 g, 35%) as an oil, R_f 0.36, IR (neat): 1 742 cm^{-1}, ^1H NMR ($CDCl_3$), 3.63 (s, CO_2Me). 3.15 (s, OMe (b) diastereomer), 3.12 (s, OMe (a) diastereomer), 2.87 (d, J = 5 Hz, CH (b) diastereomer), 2.79 (d, J = 4.5 Hz, CH (a) diastereomar) 2.68 − 2.00 (m, $CHCH_2$), 1.31 (s, MeO, diastereomer a), 1.29 (s, MeO diastereomer b), 1.18 (s, MeO diastereomer b), 1.14 (s, MeO diastereomer a), 1.04 (d, J = 7 Hz, Me diastereomer b), 0.90 (d, J = 6.4 Hz, Me diastereomer a), (a : b is 6 : 4 by integration), the dimethoxydiester **20** (0.045 g, 7%) as an oil, R_f 0.27, IR (neat); 1 740 cm^{-1}, ^1N NMR ($CDCl_3$) 3.66 and 3.65 (s, OMe's), 3.14 (s, CO_2Me), 2.82 (d, J = 10 Hz, CHE's), 2.64–2.30 (m, CHMe), 1.33, 1.25, 1.23, and 1.18 (s, Me_2C's) 1.12 (d, J = 7.0 Hz, MeCH), and the *lactone ester* **21** (0.083 *g*, 21%) as needles, m.p. 70–71° (hexane), R_f 0.17, IR (nujol): 1 750 sh (LACTONE), 1 733 cm^{-1} (ester), ^1H NMR ($CDCl_3$): (s, CO_2Me), 2.86 (d, J = 7 Hz CHE a), 2.77 (d, J = 6.5 Hz, CHE b) 2.60 − 2.40 (m, CH_2), 2.18 (d, J = 10 Hz, CHMe a), 2.09 (d, J = 10 Hz CHMe b) 1.44 and 1.43 (s, Me_2), 1.00 (d, J = 4.5 Hz, MeCH). Found: C 60.02, H 8.04. Calc: C 60.00, H 8.00%).

Dimethyl 1, 3-*Dimethylcyclobutan*-1-*ol*-2, 4-*dicarboxylate* (**22b**). $TiCl_4$ (6 mmol, 6 ml of a 1 M soln in $CHCl_2$) was added to a stirred soln of Ac_2O (0.612 g, 6 mmol) in dry CH_2Cl_2 (10 ml) under N_2 at −78°. After 5 min the mixture was added by syringe to a stirred soln of **7b** (0.954 g, 3 mmol) in CH_2Cl_2 (150 ml) at −78° under H_2, and the resulting mixture was stirred at low temp for 1 hr. The mixture was allowed to stand at room temp overnight then was extracted with sat $NaHCO_3$aq (2 × 30 ml) and brine (1 × 30 ml) then dried ($Mg SO_4$) and evaporated. Flash chromatography (SiO_2, eluent: 40% EtOAc–hexane) gave the *cyclobutanol* **22b** (0.339 g, 52%) as solid, m.p. 39–42°, R_f 0.26 (40% EtOAc), IR (neat): 1737 cm^{-1}, ^1H NMR ($CDCl_3$); 3.68 (s, 3H), 3.41 (br, 1H), 2.69 (d, J = 9 Hz, 2H), 2.56–2.32 (m, 1H), 1.18 (s, 3H), 1.14 (d, J = 7 Hz, 3H), ^{13}CMR ($CDCl_3$), 171.60 (ÇO), 74.45 (ÇOHMe), 56.16 (OMe), 51.57 (ÇHE), 26.49-MeÇH), 19.20 (MeCOH), 18.93 (MeÇH), MS: *m/z* Mo M, 185 (10%, M–MeO), 174 (18%, M–H_2CCO), 153 (13%, 185–MeOH), 142 (22%, 174–MeOH), 43 (100%, OCMe). (Found: C 55.56, H 7.47. Calcd: C 55.56, H 7.41%).

Dimethyl 1, 3, 3-*trimethylcyclobutan*-1-*ol*-2, 4-*dicarboxylate* (**22c**) was prepared as above from **7c**. R_f 0.36 (20% EtOAc hexane), IR (neat): 3 490. 1 745 and 1 715 cm^{-1}, ^1H NMR ($CDCl_3$): 4.89 (s, 1H), 3.71 (s, 3H), 3.66 (s, 3H), 3.00 (s, 1H), 2.83 (s, 1H), 1.46 (s, 3H), 1.27 (s, 3H), 1.18 (s, 3H), ^{13}CMR ($CDCl_3$): 174.36 (Ç=O), 170.94 (Ç=O), 70.123 (MeHOÇ), 59.59 (MeO) 57.07 (MeO), 51.63 (ÇHE), 51.05 (ÇHE), 34.72 (MeCOH), 26.44 (Me), 25.54 (Me), MS: *m/z* No M, 115 (100%, $MeO_2CCH_2\overset{+}{C}Ce_2$) and 83 (97%, γ=C=CHCMe$_2$).

Dimethyl 1-*phenyl*-3, 3-*dimethylcyclobutan*-1-*ol*-2, 4-*dicarbaoxylate* (**23**) was prepared as above from benzoic anhydride and **7c**. As needles m.p. 92–93° (pet ether), R_f 0.15 (10%, EtOAc hexane), IR (nujol): 3500, 3460, 1735 cm^{-1}, ^1H NMR ($CDCl_3$): 7.28 (m, 5H), 4.76 (br, 1H), 3.87 (s, 1H), 3.79 (s, 3H), 3.37 (s, 3H), 3.25 (s, 1H), 1.54 (s, 3H), 1.29 (s, 3H). (Found:C 65.77, H 6.86. Calc: C.65.75, H 6.85%).

Dimethyl 2-*acetylglutarate* (**24**) was prepared from the reaction of **7a** with Ac_2O and $TiCl_4$ by using the same procedure described above for the preparation of **22b**. Instead of cyclobutanol compound, **24** was obtained as an oil which was purified by chromatography on silica (eluent: 20% EtOAc-hexane). Compound **24** (90% yield) had IR ($CDCl_3$): 1718 and 1737 cm^{-1}, ^1H NMR ($CDCl_3$): 3.74 (s, 3H), 3.68 (s, 3H), 3.58 (t, J = 7.0 Hz, 1H), 2.25 (s, 3H), 2.10–2.40 (m, 4H).[30]

Dimethyl 1, 2-*dimethylcyclobutan* -1-*ol*-2, 4-*dicarboxylate* (**22d**) was prepared from **7d**. When isolated by preparative GC, 29.6 min (10% SE30-1/4 in × 6 ft, 155°), it had IR (neat): 3.430 1740 and 1715 cm^{-1}, ^1H NMR ($CDCl_3$): 3.73 (s, 3H), 3.66 (s, 3H),

2.33–2.06 (m, 3H), 2.15 (s, 3H), 1.62 (br, 1H), 1.35 (s, 3H), MS: *m/z* No M, 185 (17%, M–OMe), 153 (51%, 185–MeOH), 125 (16%, 153–CO), 174 (49%, M–$OCCH_2$), 142 (45%, 174–MeOH), 114 (92%, $C_6H_{10}\overset{+}{O})_2$, 88 (100%, $MeCH_2CO_2\overset{+}{M}$). (Found: C 55.56, H 7.40. Calc: C 55.56, H 7.41%). When isolated on silica (40% EtOAc hexane) **22d** was obtained as a mixture of the above isomer (36%) and another (61%). The new isomer **22d'** had ^{1}H NMR ($CDCl_3$): 3.70 (s, 3H), 3.67 (s, 3H), 3.05 (dd, J = 6.0 and 10.5 Hz, 1H), 2.64 (dd, J = 10.5 and 12.4 Hz, 1H), 1.85 (dd, J = 6.0 and 12.4 Hz, 1H), 1.38 (s, 3H), 1.29 (s, 3H), MS: *m/z* No M, 185 (15%), 174 (25), 142 (53), 114 (100), 99 (47).

CONCLUSION

The chemistry of 1, 5-bis(trimethylsiloxy)-1, 5-dimethoxy-1, 4-pentadienes studied so far suggests that they may be useful precursors for the stereoselective synthesis of multifunctional cyclopropane and cyclobutane compounds. Reactions with other bifunctional electrophilic reagents to form cyclic compounds remain to be explored. Extension of bis-ketene silyl acetals chemistry to the higher homologs, e.g. the adipates and the pimilates, can be anticipated.

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