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1,5-BIS(TRIMETHYLSILOXY)-1,5-DIMETHOXY-1,4-PENTADIENES. CYCLOPROPANE SYNTHESIS VIA INTRAMOLECULAR COUPLING.

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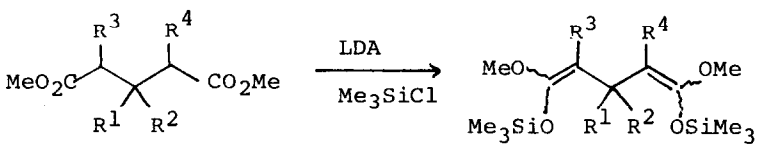
Summary: *The title compounds (1a-e) can be prepared in good yield by silylation of the dianions of dimethyl glutarates (2a-e). On treatment with titanium tetrachloride, they cyclise stereoselectively to dimethyl trans-cyclopropane-1,2-dicarboxylates.*

Recently we have been examining the chemistry and synthetic potential of the silyl ethers of a number of enolate dianions. The rationale is that while the dianions are strongly basic and very reactive, their silyl ethers remain neutral and have more easily controllable reactivity. Enol silyl ethers such as 1,3-bis(trimethylsiloxy)-1-methoxy-1,3-butadiene (dianion equivalent of methyl acetoacetate)[1] and 1,5-bis(trimethylsiloxy)furan (dianion equivalent of succinic anhydride)[2] have proved useful intermediates in organic synthesis. The chemistry of 1,5-bis(trimethylsilyl)-1,5-dimethoxypenta-1,4-diene (1a), the dianion equivalent of dimethyl glutarate (2) has not been explored[3]. In this communication we wish to report on a simple preparation of 1a and the alkyl derivatives (1b-e), and on their cyclisation to give cyclopropane derivatives.



2 1

(a) R_1=H R_2 = H R_3 = H R_4 = H; (b) R_1 = H R_2 = Me R_3 = H R_4 = H; (c) R_1 = Me R_2 = Me R_3 = H R_4 = H; (d) R_1 = H R_2 = H R_3 = Me R_4 = H; (e) R_1 = H R_2 = H R_3 = Me R_4 = Me

Preparation. A solution of the dimethyl glutarate (2a-e) (0.05 mol) in dry THF (50 ml) was added to a THF solution of LDA (0.125 mol) under argon at -78°C. After 10 minutes, trimethylchlorosilane (0.125 mol) was added and the mixture was allowed to warm to room temperature. The solvent was removed in vacuo and dry hexane was added to the residue. The precipitated

Table 1. Preparation of the bioketene silyl acetals 1

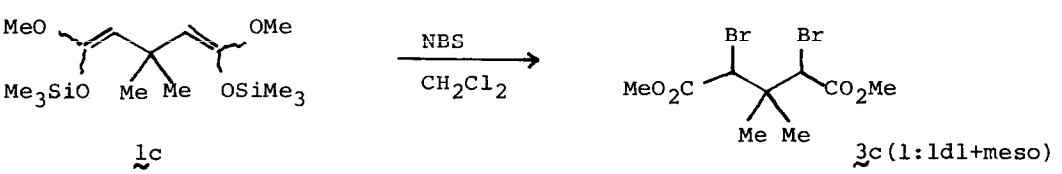
Substrate	Product	Conditions	isomer ratio[a] %EE	%EZ	%ZZ	distilled yield %	bpt °C/mmHg
2a	1a	LDA	38	47	15	52	
		LDA-TMEDA	62	31	7	54	72-76/0.025 lit.[3] 98-104/0.65
2b	1b	LDA	41	46	13	-	
		LDA-TMEDA	53	42	5	68	66-7/0.06
2c	1c	LDA	100	0	0	-	
		LDA-TMEDA	100	0	0	64	78-79/0.9
2d	1d	LDA	not determined			73	78-82/0.3
2e	1e	LDA-TMEDA	86	15	0	56	72-76/0.07

a. assigned by chemical shift correlation with data reported for monoketen acetals: R.E. Ireland, R.H. Mueller and A.K. Willard, J. Am. Chem. Soc., 98, 2868 (1976).

lithium salts were filtered off, and the solution was evaporated to dryness, eventually under high vacuum, to give the crude 1, usually in quantitative yield (Table 1). These bisketen acetals could be distilled in vacuo, although some decomposition occurred on heating. Generally the crude product was pure enough to be used in subsequent reactions.

Three different geometrical isomers, EE, EZ and ZZ are possible for the bisketene silyl acetals, and for 1a and b all three are observed[4,5]. Prepared as above, the EZ and EE isomers are in roughly equal proportions with the ZZ isomer as a minor component (Table 1). However, if the reaction is repeated using a TMEDA-LDA[6] complex as the base the proportion of Z isomers in the mixture decreases significantly. This is opposite to the effect observed for monoesters, where the use of TMEDA increases the proportion of the Z isomer.

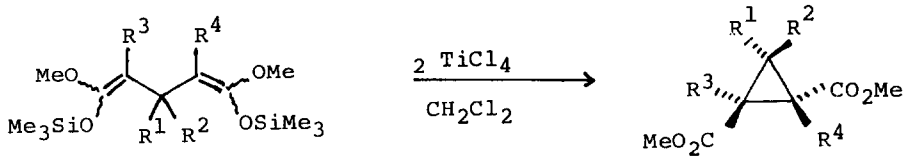
The bisketene silyl acetals (1) are reasonably stable and may be stored at room temperature in well sealed containers for an extended period. When exposed to the air, they are converted back to the dimethyl esters 2. The hydrolysis to 2 is accelerated by a few drops of 0.1M HCl. The bisketene silyl acetals (1c) react with 2 equivalents of bromine or N-bromosuccimide (NBS) to give α,α'-dibromoesters (3c) in good yield. NBS is the reagent of choice, since trace amount of HBr in the bromine convert the substrate to the ester 2.



1c 3c (1:1dl+meso)

An interesting observation is that these bisketene acetals can be oxidatively cyclised by titanium tetrachloride to give 1,2-cyclopropane-1,2-dicarboxylates. Thus, to a solution of 1a (3 mmol) in 150 ml dry dichloromethane at 0°C, was added titanium tetrachloride (6 mmol; 6 ml of a 1M solution in dichloromethane). The reaction was stirred at 20°C for 1 h, then quenched with saturated sodium bicarbonate. Evaporation of the organic layer and distillation gave dimethyl trans-cyclopropane-1,2-dicarboxylate (4a), identical in all respects with an

authentic sample prepared by the cyclopropanation of dimethyl fumarate[7].



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The reaction appears to be general and has been applied to the other substituted bisketene acetals (1b,c,d,e) (table 2). The stereochemistry suggests that the reaction is under thermodynamic control; the bisketene acetals symmetrically substituted at C3 gave cyclopropanes with exclusive trans stereochemistry, while 1b, unsymmetrically substituted, gave a mixture of two isomers, 1r-2t-3t and 1r-2c-3t (4b). The geometric isomer distribution in the starting bisketene silyl acetal has no influence in the stereochemical outcome of the final product 4. When 1a prepared by either LDA or LDA-TMEDA was cyclised, the same trans-4a was obtained.

Table 2. Oxidative cyclisation of the bisketene acetals (1) with titanium tetrachloride

Substrate	Product	Stereochemistry[ab]	distilled yield %[c] (bpt °C/mmHg)	Reference
1a	4a	> 95% trans	20% (70-75/0.3)	9
1b	4b	50% 1r-2t-3t 50% 1r-2c-3t	41% (104-108/14)	10
1c	4c	> 99% trans	69% (48-49/10.05)	11
1d	4d	> 98% trans	59% (65-69/0.2)	12
1e	4e	> 95% trans	not determined	13

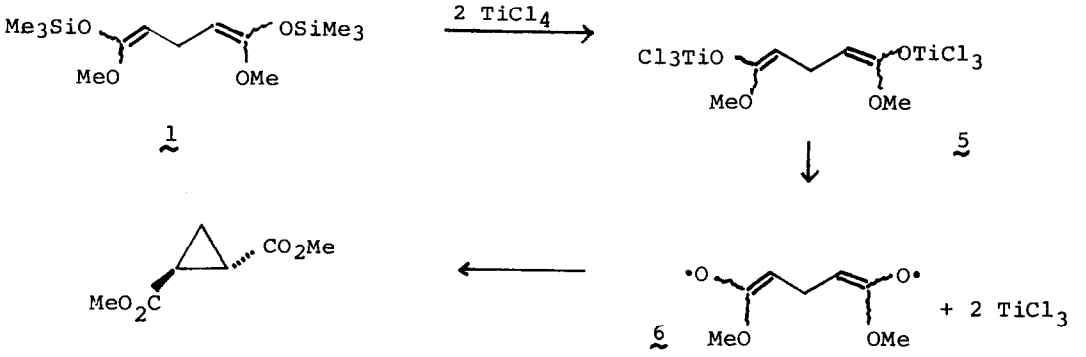
a. Structure assigned by comparison of nmr with reported data.

b. Isomer ratios determined by GLC (Hewlett-Packard 5570 gas chromatograph using a 10'x 0.25" 5% GEXF 1150 on Chromosorb w column[14]).

c. Other product is polymer.

The mechanism for this cyclisation is not presently known for certain but is expected to be similar to that postulated by Ojima for the oxidative dimerisation of monoketene silyl acetals[8]. The bisketene acetal (1) is first converted to an enoxy radical via the titanium enolate (5); intramolecular coupling of the diradical (6) then gives the product.

In view of the present interest in the chemistry of pyrethroids, the facile preparation of 4c in a stereoselective manner may be of potential interest. We are currently exploring the extension of this cyclisation to other ring systems and are looking at the reaction of the bisketene silyl acetals with electrophiles.



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References and Footnotes

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4. NMR data for the bisketene acetals (1): 1a, δ(C_6D_6) 4.09, (t, J=7.5 Hz, EZ Ha), 4.08 (t, J=7.5 Hz, EE Ha), 3.76 (t, J=7.5 Hz, ZZ Ha), 3.74 (t, J=7.5 Hz, EZ Ha), 3.54 (s, MeO EZ), 3.52 (s, MeO, EE), 3.31 (s, MeO, ZZ), 3.29 (s, MeO, EZ), 3.22 (t, J=7.5 Hz, Hb all isomers), 0.38 (s, Me_3Si ZZ), 0.36 (s, Me_3Si EZ), 0.29 (s, Me_3Si EZ), 0.28 (s, Me_3Si EE). 1b, δ(C_6D_6), 4.05 (d, J=10 Hz, Ha EZ), 4.03 (d, J=10 Hz, Ha EE); 4.00-3.85 (m, Hb), 3.68 (d, J=9 Hz, Ha ZZ), 3.66 (d, J=8 Hz, EZ Ha), 3.55 (s, MeO EZ), 3.53 (s, MeO EE), 3.31 (s, MeO ZZ), 3.28 (s, MeO ZE), 1.42 (d, J=4 Hz), EE Me), 1.40 (d, J=4 Hz, ZZ Me), 1.39 (d, J=4 Hz, EZ Me), 0.40 (s, Me_3Si ZZ), 0.38 (s, Me_3Si EZ), 0.30 (s, Me_3Si EZ), 0.29 (s, Me_3Si EE). 1c, δ($CDCl_3$), 3.91 (s, Ha), 3.48 (s, MeO), 1.18 (s, Me_2), 0.21 (s, Me_3Si). 1d, δ($CDCl_3$) 3.57 (d, J=8 Hz, Ha EZ), 3.55 (d, J=8 Hz, Ha EE), 3.50 (s, MeO), 3.48 (s, MeO), 2.58 (d, J=8 Hz, Hb), 1.51 (s, Me), 0.21 (s, Me_3Si), 0.19 (s, Me_3Si). 1e, δ($CDCl_3$) 3.51 s, MeO), 2.59 (s, Hb), 1.44 (s, Me_2), 0.20 (s, $SiMe_3$). All spectra were measured at 200 HMz using a Varian XL 200 nmr spectrometer. Chemical shifts in deuterobenzene referenced to δ(C_6H_6) = 7.30; chemical shifts in deuterochloroform referenced to δ($CHCl_3$) = 7.26.

5. 1c is formed at the EE isomer exclusively, no other isomers could be detected by ^1H or ^{13}CMR.

6. 2.5 equivalents of tetramethylethylenediamine (TMEDA) were added to the LDA prior to diester addition.

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