# Chemistry of Electron-rich Conjugated Polyenes. Part 4.[1] A Simple and General Synthesis of 1-Alkoxy-3-trimethylsilyloxybuta-1,3-dienes

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Acid-catalysed addition of ketens to 1-alkoxyalkenes yields alkoxycyclobutanones, which on trimethylsilylation under basic conditions give *trans*-3-alkoxy-1-trimethylsilyloxycyclobutenes. These derivatives undergo electrocyclic ring opening below 100 °C to give the title compounds in which the 1-alkoxy-group and the 4-substituent are *trans*. Some reactions to illustrate the synthetic application of these highly functionalized electron-rich butadienes are given.

ALKOXYBUTADIENES (1) with a 3-trimethylsilyloxy-group are attractive reagents for cycloadditions. They can be used for the preparation of six-membered ring compounds containing a ketone or enone function (Scheme 1). The reaction has been demonstrated for
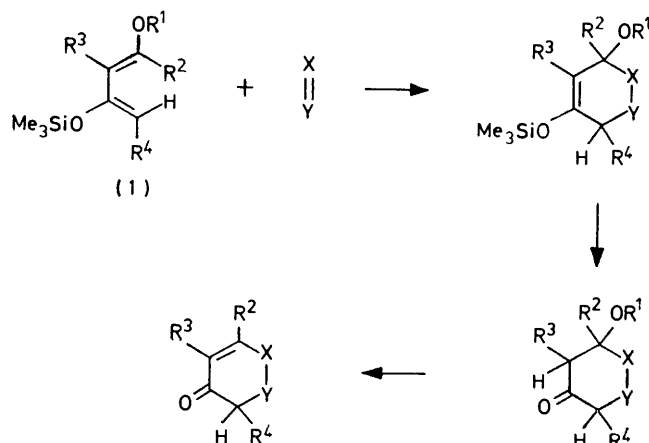
SCHEME 1

compounds (1), having $R^1 = Me$, $R^2 = R^3 = R^4 = H$; $R^1 = Me$, $R^2 = OMe$, $R^3 = R^4 = H$; and $R^1 = Me$, $R^2 = R^3 = H$, $R^4 = SePh$, in reactions with various olefinic derivatives.[2-4]

The trimethylsilyloxy-derivatives (1) are good alternatives for the less readily available 3-alkoxy-derivatives in these reactions.[2,5] They are electron-rich butadienes with a preferred *cisoid* conformation, and react smoothly even with weakly electrophilic double-bond systems.[3-5]

RESULTS AND DISCUSSION

Initial studies have shown that the compounds (1) react also with carbonyl compounds. With ZnCl₂ as catalyst they react with a variety of aldehydes at room temperature to yield γ-dihydropyrones [6] (Scheme 1: X = O, Y = CHR). Under the same conditions the more electron-rich 1,1-dimethoxybutadienes yield polymeric products or complex reaction mixtures.[1] Our preliminary results and those from other studies [4,6-8] indicate that even highly functionalized compounds (1) are useful reagents in Diels–Alder reactions, and thus valuable starting compounds in the synthesis of extensively substituted six-membered ring compounds.
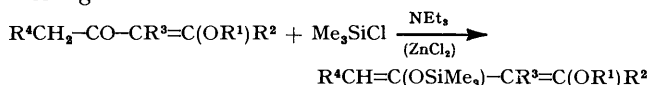
Relatively few 1-alkoxy-3-trimethylsilyloxybutadienes have been prepared. The methods used depend on the availability of the appropriate α,β-unsaturated carbonyl compound, which is silylated according to Scheme 2.

A more general procedure is now described in which 3-alkoxycyclobutanones (2) are treated with trimethylsilyl chloride in the presence of a base (Scheme 3) to yield buta-1,3-dienes (1).
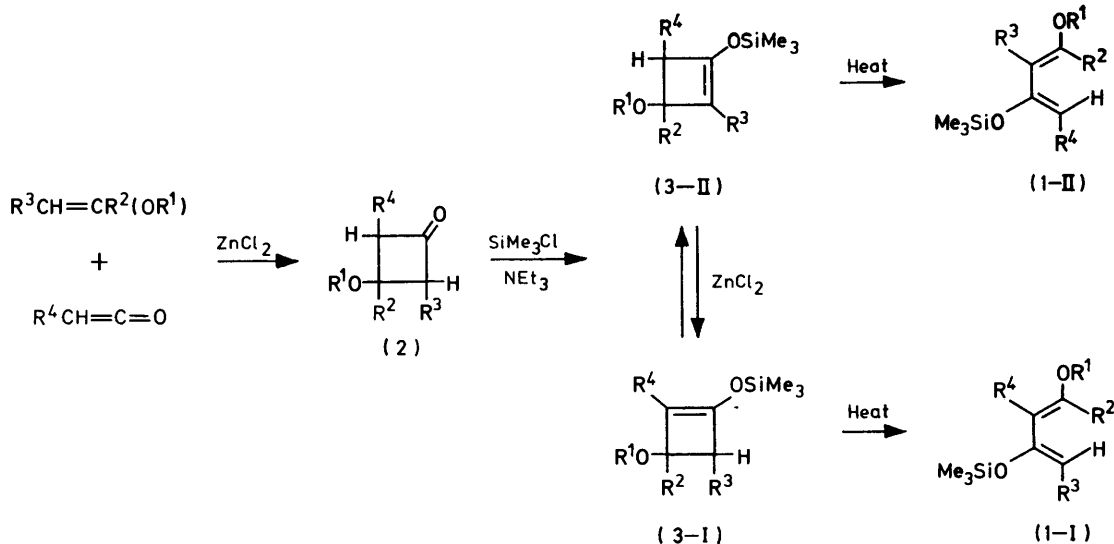
A useful aspect of the procedure is that it yields products in which the alkoxy-group at C-1 and the substituent at C-4 are *trans* to each other, thus avoiding tedious isomer separation. It further implies that the intermediates (3) must also be *trans*-isomers, since the thermal ring-opening in the final step is a concerted and conrotatory process. The exclusive formation of *trans*-isomers in the second step is guaranteed by the basic conditions used in the silylation reaction. *cis,trans*-Isomers, mixtures of 3-alkoxycyclobutanones (2), are almost completely transformed into the *trans*-isomers (*trans,trans*-isomers when $R^3,R^4 = H$) when treated with a base, *e.g.* NEt₃. The regioselectivity of the ring opening (3)→(1) from (3-I) or (3-II) is discussed below.

The above stereochemical aspects further imply that the order of the silylation and thermal ring-opening cannot successfully be reversed. The heating of (2) in the presence of acids could provide a route to α,β-unsaturated carbonyl compounds (see Scheme 2) through a Grob-type fragmentation.[9] Initial experiments showed, however, that such a fragmentation, needing elevated temperatures (80 °C) and acid catalysis, is usually accompanied by side reactions resulting in poor yields.

The cyclobutanones (2) (Table 1) were prepared by heating a solution of a vinyl ether in acetonitrile containing ZnCl₂ as a catalyst with a keten. The yields of the cycloadditions were dependent on the vinyl ether used. Less electron-rich (*e.g.* $H_2C=CHOCH_2CH_2Cl$, *ca.* 20%) gave much lower yields than olefins having a higher electron density (*e.g.* EtOH=CHOEt, 60%). The presence of two β-substituents as in $Me_2C=CHOEt$ (yield *ca.* 5%) prevented cyclobutanone formation on steric grounds.

$$R^4CH_2-CO-CR^3=C(OR^1)R^2 + Me_3SiCl \xrightarrow[\text{(ZnCl}_2)]{\text{NEt}_3}$$

$$R^4CH=C(OSiMe_3)-CR^3=C(OR^1)R^2$$

SCHEME 2

Scheme 3

Generally, the use of a catalyst at low reaction temperatures was preferred to heating in an autoclave at higher temperatures. It is an easier method and leads to better yields than those previously obtained, *cf.* ethoxyethylene (30—40%) and dihydropyran (40—50%) (lit. yields 25 and 12%, respectively [10,11]).

The more reactive keten acetals can be used in place of vinyl ethers. Although the use of the catalyst is unnecessary for a sufficiently high reaction rate at low temperature, it can assist in forming the desired product. Tetramethoxyethene adds to keten in the presence of $ZnCl_2$ to give the thermodynamically more stable cyclobutanone [(2g) see Table 1] in 80% yield. In the absence of a catalyst the oxetan (4) is a significant side-product [9,12] (Scheme 4).

N.m.r. spectra of the reaction products from the cycloadditions showed that in some cases ring-opened products $[R^4CH_2-CO-CR^3=C(OR^1)R^2]$ were also present, especially when higher reaction temperatures were used (Scheme 5). These could be eliminated by careful fractional distillation of the cyclobutanones using a spinning-band column.

It was stated earlier than it is not necessary to use the pure *cis* or *trans* form of the vinyl ethers. The cycloadditions lead to *cis–trans* mixtures of (2), which are converted into the racemic *trans*-3-alkoxycyclobutanone, under the influence of triethylamine used in the subsequent step. The *cis* and *trans* isomers of (2) can be separated for identification purposed by careful fractional distillation. The *cis* isomer of 2,3-diethoxycyclobutanone (2h) has a larger coupling constant [13] (J_{AB} 6.5 Hz) and a larger shift difference between H_C and H_D than the *trans*-isomer (2i) (see Table 1) (J_{AB} 5 Hz).
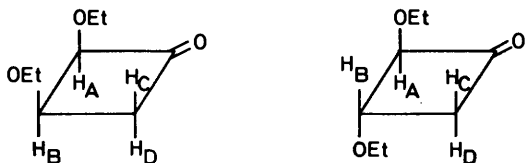
The dialkoxycyclobutanones (2h—j) were obtained from ethoxyketen, prepared *in situ*, and vinyl ether or *cis,trans*-1-ethoxybut-1-ene. Minh and Strausz [13] obtained only the *cis*-2,3-diethoxycyclobutanone on heating ethyl vinyl ether, ethoxyacetyl chloride, and triethylamine in an autoclave at 100 °C. In the present study a
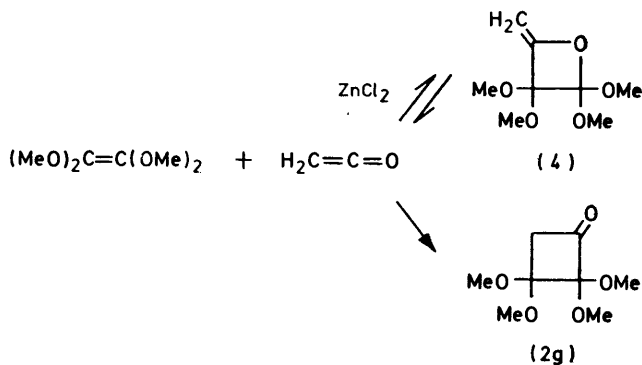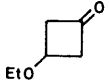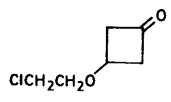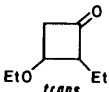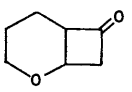

Scheme 4
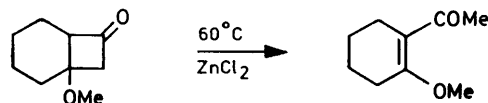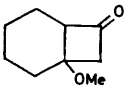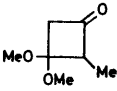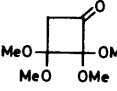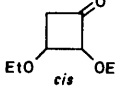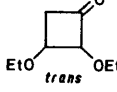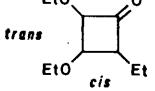
Scheme 5

cis–trans mixture was obtained when an excess of the acid chloride was used for the generation of the keten (acetonitrile, 80 °C); *trans*-2,3-diethoxycyclobutanone was the only product when excess of triethylamine was present. Pure *cis*-, pure *trans*-, or *cis,trans*-1-ethoxybut-1-ene all yielded the same compound (2j) by this reaction. Decoupling experiments showed J_{AB} 5 Hz and J_{AC} 4 Hz, in agreement with the proposed structure.

The cyclobutanones were best silylated with trimethylsilyl chloride–triethylamine. Of the solvents tried (diethyl ether, tetrahydrofuran, benzene, and acetonitrile) acetonitrile gave the highest conversion rate. The re-

Table 1

3-Alkoxycyclobutanones (2a—j)

| Compound	Reaction temp. (°C)	Yield (%)	B.p. (°C/mmHg)	¹H N.m.r. (δ) (CCl₄)	Analysis Found (Calc.) (%)
(2a)	40	ca. 30	55/12 [a]	4.33—4.00 (m, 1 H); 3.43 (q, J 7 Hz, 2 H); 2.97 (br s, 2 H); 3.07 (br s, 2 H); 1.20 (t, J 7 Hz, 3 H)	
(2b)	50	20	62/0.2	4.50—4.10 (m, 1 H); 3.97 (narrow m, 4 H); 3.12 (br s, 2 H); 3.03 (br s, 2 H)	C, 48.2 (48.48); H, 5.9 (6.06)
(2c)	35	55	70—73/15	4.00—3.63 (m, 1 H); 3.43 (q, J 7 Hz, 2 H); 2.17—2.80 (m, 1 H); 2.97 (s, 1 H); 2.87 (s, 1 H); 1.80—0.80 (m, 8 H)	C, 67.75 (67.71); H, 10.15 (9.86)
(2d)	45	45	60/0.5 [b]	4.30 (dd, J 5.0 and 5 Hz); 3.90—3.50 (m, 1 H); 3.40—2.90 (m, 3 H); 2.55 (AB, J_{AB} 17 Hz, 1 H); 2.33—1.27 (m, 4 H)	
(2e)	60	60	59/0.7 [c]	3.22 (s, 3 H); 3.27—2.83 (m, 2 H); 2.62 (d, J ca. 1 Hz) and 2.37 (d, J ca. 1 Hz, AB, J_{AB} 14 Hz); 1.80—1.10 (m, 8 H)	C, 70.5 (60.13); H, 9.2 (9.09)
(2f)	25	35	74/15	3.08 (s, 3 H); 3.05 (s, 3 H); 2.97 (d, J 1 Hz, 2 H); 1.10 (d, J 7 Hz, 2 H)	C, 58.05 (58.33); H, 8.42 (8.33)
(2g)	25	~40	44/0.2	3.33 (s, 6 H); 3.25 (s, 6 H); 2.82 (s, 2 H) [d]	
(2h)	80	85	56/0.4	4.57—4.10 (m, 2 H); 3.97—3.33 (m, 4 H); 3.27—2.20 (m, 2 H); 1.20 (t, J 7 Hz, 3 H)	
(2i)	80	85	43/0.4	4.40 (dd, J 5.3 and 1 Hz, 1 H); 3.35—4.17 (m, 5 H); 2.60—2.50 (m, 2 H); 1.20 (t, J 7 Hz, 3 H); 1.17 (t, J 7 Hz, 3 H)	C, 60.75 (60.76); H, 9.1 (8.86)
(2j)	60	45	54/0.3	4.27 (dd, J 5 and 4 Hz, 1 H); 4.00—3.30 (m, 5 H); 2.90—2.47 (m, 1 H); 1.60—0.80 (m, 11 H)	C, 64.05 (64.52); H, 9.81 (9.68)

[a] Lit. b.p.[10] 65° C at 20 mmHg. [b] Lit. b.p.[11] 50—55 °C at 0.5 mmHg. [c] Distilled with a Teflon spinning-band (25 plates). [d] Cf. ref. 12.

action could be accelerated using ZnCl₂ * as a catalyst. As indicated in Scheme 3 two isomeric products can arise, which are dependent upon the solvent used, the presence of the catalyst, and the reaction temperature.

(2j)
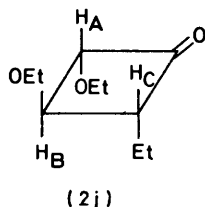
It is known [14] that silylation of the kinetically controlled enolate intermediate yields the silylenol ether with the least alkylated double bond. This product yields the thermodynamically more stable isomer on treatment with an acid catalyst, especially at higher temperatures. It is apparent that kinetic control in the deprotonation step is realised in silylations at room temperature in acetonitrile, since (2c) provides the less-substituted cyclobutene (3c-II) as the main product under these conditions. When ZnCl₂ is present (in acetonitrile or benzene as the solvent) the other isomer (3c-I) is the main product (Scheme 6).

Since the Lewis-acid-catalysed isomerization of (3c-II)→(3c-I), at room temperature, will be slow, the thermodynamically more stable (3c-I) may also be formed via silylation of the more stable enol derivative of (2c).

* Benzene is preferred as the solvent for ZnCl₂-catalysed reactions since the end-product (1) is more stable in this solvent in the presence of a Lewis acid.
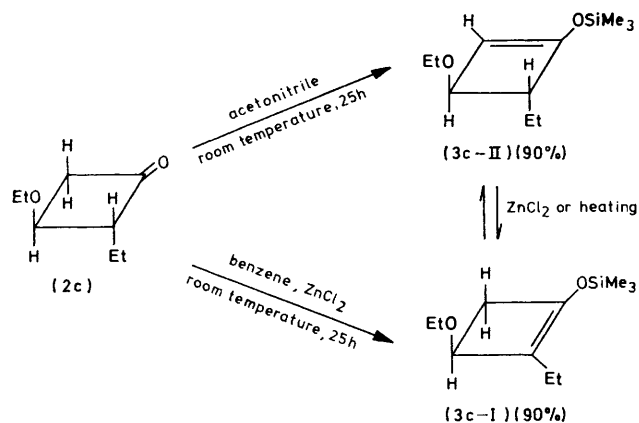
SCHEME 6

In the final thermal ring-opening reaction it is necessary to heat (3c-II) to a temperature above 50 °C. This unfortunately also causes partial conversion to (3c-I), and *trans→cis* isomerization to *cis*-(3c-II). Thus the end product from (3c-II) is a mixture of Z,E and E,E isomers of (1c-II) ($R^1 = R^4 = Et$; $R^2 = R^3 = H$).

In other examples (3i: $R^1 = Et$, $R^2 = R^3 = H$, $R^4 = OEt$) the thermal ring openings of the I,II-isomers of (3) proceed at sufficiently different rates to yield only one end-product (1) in high yield, *i.e.* that, which arises from the most labile intermediate (3). This could best be achieved by keeping the reaction mixture for 25 h at 55 °C. Silylation of (2i) and subsequent ring opening at room temperature (8 h) in acetonitrile gave 60% of the end-product (1i-II), formed from (3i-II) and 40% of (3i-I) (see Scheme 7).

The same reaction sequence, but carried out in benzene and in the presence of $ZnCl_2$, yielded the same products but in a reversed ratio (40 and 60%, respectively). It is probable that the ring-opening of (3i-I) occurs only above

80 °C, apparent from the experiment with the pure isomer, and that the isomerization (3i-I) ⇌ (3i-II) is slow at room temperature.

Silylation of (2j) in acetonitrile or in benzene containing $ZnCl_2$, at 55 °C, yielded a mixture of (1j-I) and (1j-II) (see Scheme 8) with (1j-I) as the main product (75% in acetonitrile and 86% in benzene–$ZnCl_2$). At room temperature (1j-II) and (3j-I) were the only products. Isomerization of (3j-I) to (3j-II) appeared to be very slow at 30 °C, taking 8 d to yield 50% of (1j-II). The low temperature that was necessary to prevent ring-opening of (3j-I), together with the slight variation in boiling points between (1j-I) and (1j-II) probably accounts for (1j-I) being the only pure product obtained. It is not quite clear whether in benzene–$ZnCl_2$ (1j-II) is formed in such a low amount.

The thermal, conrotatory ring-opening of the silyloxy-derivatives (3) can be accomplished below 100 °C, but only when vicinal hydrogen atoms at C-3 and C-4 are present. Double substitution at one of these positions [*e.g.* (3e), (3f), and (3g)] necessitates higher temperatures, causing unwanted side-reactions [9,15] (see Scheme 9). The temperatures required for the thermal ring-opening are lower for compounds with electron-donating substituents on C-3 and C-4, whereas similar substituents on the C-1 and C-2 olefinic carbons have the opposite effect. A temperature of 180 °C was required for the successful opening of 1,2-bis(trimethylsilyloxy)cyclobutene.[8] These electronic effects can be accounted for by Frontier Orbital theory.[16]

An interesting application of these highly reactive butadienes, in addition to those mentioned above,[6] is in the Diels–Alder reaction with quinones. The adduct between 1-ethoxy-3-trimethylsilyloxybuta-1,3-diene and naphthaquinone (5) undergoes mild (acidic) hydrolysis to yield (6), which is quite stable and can be crystallized from ethanol (Scheme 10).
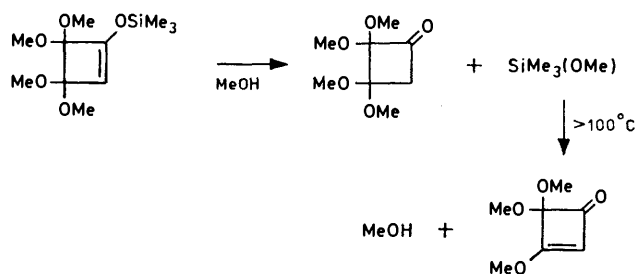
The reaction of quinones with the other butadienes (1)
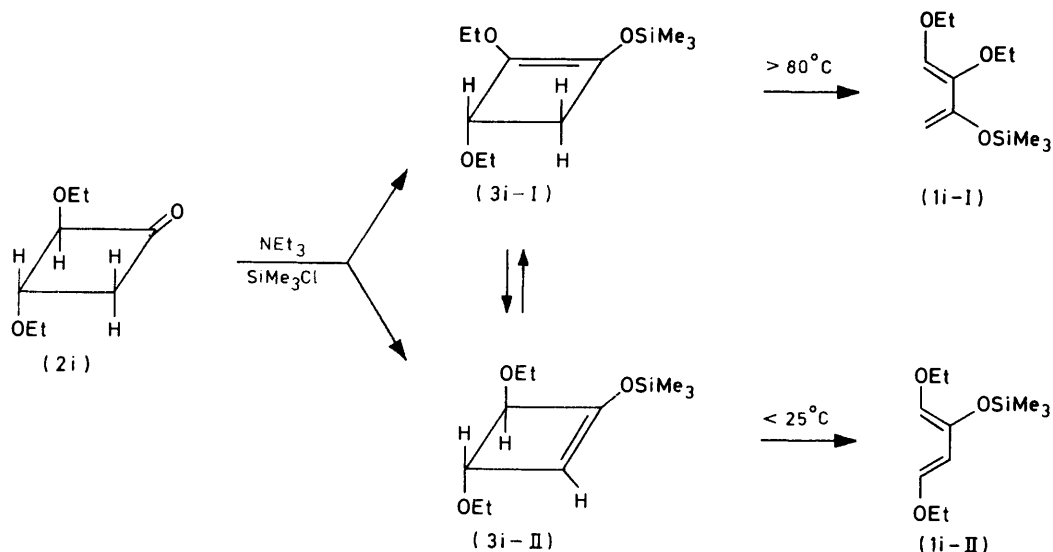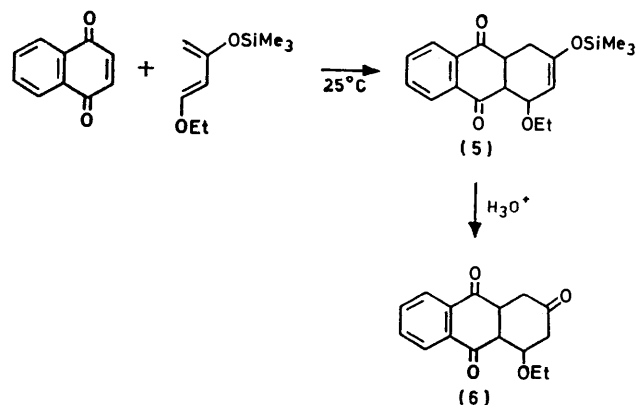

SCHEME 7
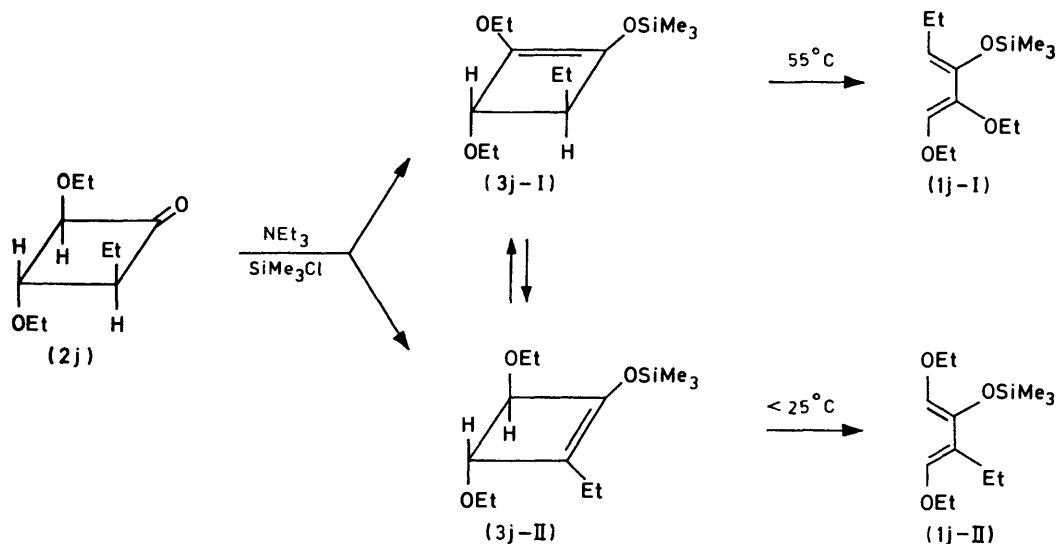
SCHEME 8

is currently under investigation as a possible route to adriamycin analogues.[17]

SCHEME 9

SCHEME 10

EXPERIMENTAL

I.r. spectra were determined on a Perkin-Elmer spectrophotometer, model 257. Hydrogen-1 n.m.r. spectra were measured on Varian T-60 or a Brucker WH-90 spectrometers (for decoupling experiments) in carbon tetrachloride solutions. Chemical shifts (δ) are relative to tetramethylsilane as internal standard. Mass spectra were obtained with a double focusing Varian Associates SM1-B mass spectrometer.

3-Alkoxycyclobutanones (2a—g) *by the Reaction of Vinyl Ethers or Keten Acetals and Keten.*—Keten (3 equiv.), generated from acetone with a keten lamp (*ca.* 0.5 mol h^{-1}) was passed into a solution of a vinyl ether (1 mol) or keten acetal (0.2 mol) in acetonitrile (50 ml), containing zinc chloride (0.5 g) where necessary, at the reaction temperature given in Table 1. The reaction mixture was then concentrated *in vacuo* (20 mmHg) and the residue treated with pentane–diethyl ether (1 : 1). The mixture was filtered, the filtrate was evaporated *in vacuo*, and the residual oil was distilled through a Vigreux column (50 × 1.2 cm) under reduced pressure. It was necessary to use a Teflon spinning band for the distillation of 1-methoxybicyclo[4.2.0]octan-7-one (2e) in order to obtain material free from ring-opened by-products. 2-Ethyl-3-ethoxycyclobutanone (2c) was obtained as a *cis–trans* mixture. Heating the mixture for 8 h at 50 °C in the presence of 10 mol % triethylamine yielded a product containing >90% of the *trans*-isomer. I.r. spectra of all products showed $\nu_{C=O}$ between 1 775 and 1 795 cm^{-1}, in agreement with the cyclobutanone structures. All mass spectra showed M^+ and ($M^+ - C_2H_4O$) peaks.[9,18] Molecular weights of the new cyclobutanones, determined from their mass spectra, agreed with the calculated values within 0.003 mass units. The microanalysis data of these compounds agreed with the calculated values within 0.5%. Further physical data are given in Table 1.

2,3-Diethoxycyclobutanones (2h—j) *from Vinyl Ethers, Ethoxyacetyl Chloride, and Triethylamine.*—Monoethoxyacetyl chloride (0.4 mol, 49.4 g) was added dropwise over 20 min to a well stirred solution of ethoxyethylene or 1-ethoxybut-1-ene (*cis* + *trans*) (0.5 mol) and triethylamine (0.45 mol, 45.5 g) in acetonitrile (150 ml). The temperature was allowed to rise to *ca.* 50 °C during the addition. The mixture was heated at 80 °C (60 °C for the reaction with 1-ethoxybut-1-ene) for 12 h, the solvent was then evaporated off *in vacuo*, and diethyl ether was added to the residue. The precipitated triethylamine hydrochloride was removed by filtration and washed with ether, and the combined filtrate and washings were evaporated to give an oil which was distilled through a Vigreux column (40 × 1.2 cm) to give the pure product, 2,3-diethoxycyclobutanone, mainly as the *trans*-isomer (2i). When less triethylamine (0.38 mol)

was used a *cis–trans* mixture [(2h) + (2i)] was obtained containing 20—60% (2h). It could be separated by distillation through a Vigreux column (100 × 1.2 cm). Pure *cis*- or pure *trans*-1-ethoxybut-1-ene yielded the same cyclobutanone (2j). With *cis*-1-ethoxybut-1-ene a mixture of cyclobutanones was isolated which on treatment with an additional 10 mol % of triethylamine for 3 h gave (2j). Physical constants of the products are given in Table 1.
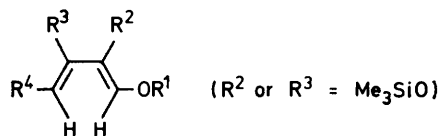
1-Alkoxy-3-(or 2)trimethylsilyloxybuta-1,3-dienes [(1a—c, i, j); (*Table* 2)].—Trimethylsilyl chloride (1.4 equiv.) was added dropwise to a solution of an alkoxycyclobutanone (2) (see Table 1) and triethylamine (3 equiv.) in acetonitrile, or benzene containing 1 mol % zinc chloride. The solutions contained *ca.* 3 mol of the cyclobutanone per litre of

3-Alkoxy-1-trimethylsilyloxycyclobutenes (3).—A number of 3-alkoxy-1-trimethylsilyloxycyclobutenes were obtained by carrying out the preceding experiments at lower temperatures. The products obtained after removal of precipitated triethylamine hydrochloride by filtration, and evaporation of the solvent *in vacuo*, could not be distilled because of ring-opening decomposition at elevated temperatures. The products, identified by their ¹H n.m.r. spectra (CCl₄) were considered to be at least 90% pure.

3-Ethoxy-1-trimethylsilyloxycyclobutene (3a). This was prepared by silylation of (2a) for 8 h in acetonitrile below 15 °C; δ 4.60 (s, 1 H, HC=), 4.03 (dd, 1 H, *H*COEt, $J < 1$ and 3 Hz), 3.33 (q, 2 H, CH_2O, J 7 Hz), 2.80 and 2.60 (d,

TABLE 2

1-Alkoxy-3(or 2)-trimethylsilyloxybutadienes,

$(R^2$ or $R^3 = Me_3SiO)$

Compd.	R²	R³	R₄	R¹	Solvent, reaction temp. (°C)	Yield (%)	B.p. (°C/mmHg)	¹H N.m.r. δ (CDCl₃)
(1a)	H	Me₃SiO	H	Et	CH₃CN 50	85	79/15	6.70 and 6.50 (AB, J_{AB} 12 Hz, 1 H); 5.30 and 5.10 (AB, J_{AB} 12 Hz, 1 H); 3.93 (br s, 2 H); 3.41 (q, J 7 Hz, 2 H); 1.30 (t, J 7 Hz, 3 H); 0.23 (s, 9 H)
(1b)	H	Me₃SiO	H	Cl[CH₂]₂	CH₃CN 50	73	64/0.3	6.73 and 6.53 (AB, J_{AB} 12 Hz, 1 H); 5.38 and 5.18 (AB, J_{AB} 12 Hz, 1 H); 3.97 (⁻, 2 H); 4.07—3.47 (m, 4 H); 0.20 (s, 9 H)
(1c–I)	Et	Me₃SiO	H	Et	C₆H₆ ᵃ 70	67 ᵇ	34/0.1	6.30 (s, 1 H); 4.10 (br s, 1 H); 3.97 (br s, 1 H); 3.78 (q, J 7 Hz, 2 H); 2.11 (q, J 7 Hz, 2 H); 1.25 (t, J 7 Hz, 3 H); 0.96 (t, J 7 Hz, 3 H); 0.20 (s, 9 H)
(1c–II) (E,E + E,Z-mixture)	H	Me₃SiO	Et	Et	CH₃CN 50	*ca.* 45 ᶜ (E,Z/E,E = 2.75)	52—54/0.2	6.60 and 6.40 (AB, J_{AB} 12 Hz, =CHOEt *E,E* isomer); 6.47 and 6.27 (AB, J_{AB} 12 Hz, =CHOEt, *Z,E* isomer); 5.47 and 5.27 (AB, J_{AB} 12 Hz, H–C=, *E,E* isomer); 5.23 and 5.03 (AB, J_{AB} 12 Hz, H–C=, *Z,E* isomer); 4.37 (t, J 7 Hz, =C*H*Et, *E,E* isomer); 4.33 (t, J 7 Hz, =C*H*Et, *Z,E* isomer)
(1i–I)	OEt	Me₃SiO	H	Et	C₆H₆ ᵃ 70	40 ᵈ	60/0.2	6.00 (s, 1 H); 4.47 (s, 1 H); 3.93 (s, 1 H); 4.00—3.53, (2 × q, 4 H); 1.40—1.07 (2 × t, 6 H); 0.18 (s, 9 H)
(1i–II)	H	Me₃SiO	OEt	Et	CH₃CN 50	70	74/0.4	6.43 and 6.23 (AB, J_{AB} 12 Hz, 1 H); 5.30 (s, 1 H); 5.10 and 4.90 (AB, J_{AB} 12 Hz, 1 H); 3.63 (q, J 7 Hz, 4 H); 1.23 (t, J 7 Hz, 6 H); 0.17 (s, 9 H)
(1j–I)	Me₃SiO	OEt	Et	Et	C₆H₆ ᵃ 70	55	70/0.2 ᵉ	5.80 (s, 1 H); 4.83 (t, 1 H); 3.97—3.53 (2 × q, 4 H); 2.33—1.73 (m, 2 H)

ᵃ 1 mol % ZnCl₂ was added. ᵇ A higher-boiling fraction gave 8% (1cI-I). ᶜ A lower-boiling fraction gave *ca.* 25% (1c-I). ᵈ A higher-boiling fraction gave 30% (1i-II). ᵉ Distilled with a Teflon spinning-band column (25 plates).

the solvent. The reaction mixture was kept for 25 h at the reaction temperatures given in Table 1. The solvent was then evaporated off *in vacuo*, diethyl ether–pentane (1 : 1, 400 ml mol⁻¹ of the cyclobutanone) added, and the precipitated triethylamine hydrochloride was removed by filtration and washed several times with pentane. The combined filtrate and washings were concentrated *in vacuo* and distilled through a Vigreux column (100 × 1.2 cm) or, where necessary, a Teflon spinning-band column (25 plates). Yields and physical constants are given in Table 2.

The molecular weights of all products, determined from their mass spectra, agreed with the calculated values within 0.003 mass units. The compounds decomposed on contact with atmospheric moisture, and it was therefore not possible to obtain reproducible microanalysis data. The compounds were considered to be at least 95% pure as shown by their ¹H n.m.r. spectra.

part of AB quartet, 1 H in CH₂, J 3 and J_{AB} 12 Hz), 2.70 and 2.17 (br s, part of AB quartet, 1 H in CH₂, J_{AB} 12 Hz), 1.13 (t, 3 H, J 7 Hz), and 0.23 (s, 9 H). The product was converted rapidly into (1a) at 50 °C.

3-Ethoxy-4-ethyl-1-trimethylsilyloxycyclobutene (3c-II). This was prepared by silylation of (2c) in acetonitrile below 20 °C, and contained *ca.* 10% of the isomeric 3-ethoxy-2-ethyl-1-trimethylsilyloxycyclobutene (3c-I), apparent from the integration of the signals for the *H*C= and *H*COEt protons. Furthermore, (3c-II) existed as a *cis–trans* mixture (1 : 5) as shown by the occurrence of two singlets at δ 4.67 and 4.64 for the HC= proton.

3-Ethoxy-2-ethyl-1-trimethylsilyloxycyclobutene (3c-I). This was obtained as the main product by silylation of (2c) below 20 °C in benzene containing ZnCl₂; δ 4.60 (d, 1 H, *H*COEt, J 3 Hz) and 2.80—1.77 (m, 2 H, CH₂). The product was contaminated with a small amount of the

isomer (3c-II) (*ca.* 10% by ¹H n.m.r.). Heating (3c-I) at 40 °C yielded the butadiene (1c-I) (see Table 2).

3,3-Dimethoxy-4-methyl-1-trimethylsilyloxycyclobutene (3f-I). This was obtained by silylation of (2f) in acetonitrile at 25 °C; δ 4.67 (s, 1 H, HC=), 3.20 (s, 6 H, OMe), 2.60 (q, 1 H, *H*-CMe, *J* 7 Hz), and 1.03 (d, 3 H, MeC, *J* 7 Hz). Distillation of the crude reaction product (Kugelrohr, 100 °C, 15 mmHg) yielded a mixture containing (3f-I) and (3f-II) (2-methyl isomer) in 50% yield, but with no ring-opening. Heating the product above 100 °C led to elimination of the trimethylsilyloxy-group. According to the ¹H n.m.r. spectra the complex reaction mixture contained no butadienes.

3,3,4,4-Tetramethoxy-1-trimethylsilyloxycyclobutene (3g). This was prepared by silylation of (2g) in acetonitrile, and could be purified by distillation (Kugelrohr, 100—110 °C 0.5 mmHg), yield 60%; δ 5.07 (s, 1 H, HC=), 3.33 (s, 6 H, OMe), 3.20 (s, 6 H, OMe), and 0.27 (s, 9 H, Me₃Si). Prolonged heating above 100 °C led to a mixture from which 1,4,4-trimethoxycyclobuten-3-one could be isolated by distillation, b.p. 90 °C at 0.5 mmHg (Kugelrohr); δ 5.47 (s, 1 H, HC=), 4.03 (s, 3 H, OMe), and 3.43 (s, 6 H, OMe) (*cf.* ref. 9).

Reaction of (1a) *with Naphthoquinone.*—A solution of (1a) (5.3 g, 0.03 mol) in acetonitrile (20 ml) was treated with naphthoquinone (3.2 g, 0.02 mol) and set aside for 16 h at room temperature. The reaction mixture was concentrated *in vacuo* (100 °C at 0.5 mmHg) to yield an oil, which was further purified by column chromatography on silica gel, with toluene–chloroform (3 : 1) as eluant, to yield (5); δ (CDCl₃) 8.07—7.37 (m, 4 H), 5.10 (br d, *J* 6 Hz, HC=), 4.30—4.10 (m, *H*COEt), 3.93—2.80 (m, 6 H), 0.53 (t, *J* 7 Hz, 3 H), and 0.30 (s, 9 H).

Treatment of the oil with 0.1M aqueous hydrochloric acid (10 ml) for 1 h at room temperature, followed by concentration *in vacuo* (40 °C, 15 mmHg) yielded a crystalline product, which was washed with ether and recrystallized from ethanol to yield compound (6) (80%) (Found: C,

70.45; H, 5.93. C₁₆H₁₁O₄ requires C, 70.58; H, 5.92%); δ (CDCl₃) 8.17—7.57 (m, 4 H), 4.40—4.17 (m, *H*COEt), 3.83—2.30 (m, 8 H), and 0.53 (t, *J* 7 Hz, 3 H); ν_{C=O} 1 685 and 1 727s; ν_{C=C} 1 595s cm⁻¹ (no LH absorptions).

REFERENCES

¹ Part 3, H. C. J. G. van Balen, A. A. Broekhuis, J. W. Scheeren, and R. J. F. Nivard, *Rec. Trav. chim.*, 1979, **98**, 36.
² S. Danishefsky and T. Kitahara, *J. Amer. Chem. Soc.*, 1974, **96**, 7807.
³ (*a*) J. Banville and P. Brassard, *J.C.S. Perkin I*, 1976, 1852; (*b*) S. Danishefsky, R. K. Singk, and R. B. Gammill, *J. Org. Chem.*, 1978, **43**, 379.
⁴ S. Danishefsky, C. F. Yan, and P. M. McCurry, *J. Org. Chem.*, 1977, **42**, 1819.
⁵ M. E. Jung and C. A. McCombs, *Tetrahedron Letters*, 1976, 2935.
⁶ R. W. Aben, A. A. Broekhuis, and H. W. Scheeren, unpulished results.
⁷ K. Yanamato, S. Suzuki, and J. Tsugi, *Chem. Letters*, 1978, 649 and refs. cited therein.
⁸ D. Anderson and T. H. Koch, *J. Org. Chem.*, 1978, **43**, 2726.
⁹ O. Bellus, H. Fischer, H. Greuter, and P. Martin, *Helv. Chim. Acta*, 1978, **61**, 1784.
¹⁰ J. B. Sieja, *J. Amer. Chem. Soc.*, 1971, **93**, 130.
¹¹ C. D. Hurd and R. D. Kimbrough, *J. Amer. Chem. Soc.*, 1960, **82**, 1373.
¹² R. W. Hoffmann, U. Bressel, J. Gehlhaus, and H. Haüser, *Chem. Ber.*, 1971, **104**, 873.
¹³ T. D. Minh and O. P. Strausz, *J. Amer. Chem. Soc.*, 1970, **92**, 1766.
¹⁴ H. O. House, L. J. Czuba, M. Gall, and H. D. Olmstead, *J. Org. Chem.*, 1969, **34**, 2324.
¹⁵ H. Mayr and R. Huisgen, *Angew. Chem.*, 1975, **87**, 491.
¹⁶ I. Fleming, 'Frontier Orbitals and Organic Chemical Reactions,' John Wiley, Chichester, New York, Brisbane, Toronto, 1978.
¹⁷ F. Farina and P. Prados, *Tetrahedron Letters*, 1979, 477.
¹⁸ B. M. Trost and M. J. Bogdanowicz, *J. Amer. Chem. Soc.*, 1973, **95**, 5321.