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SILYLATION AS A PROTECTIVE METHOD IN ACETYLENE CHEMISTRY. SYNTHESES IN THE POLYENEYNE SERIES, $R_3Si(C{\equiv}C)_n(CH{=}CH)_4(C{\equiv}C)_nSiR_3$ AND $H(C{\equiv}C)_n(CH{=}CH)_4(C{\equiv}C)_nH$ (n = 1, 2)

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Abstract—The Grignard reagents $R_3Si(C{\equiv}C)_nMgBr$ (R = Me, n = 1; R = Et, n = 1, 2) couple with cyclooctatetraene dibromide **1** in THF to give, as major products, the silyl-stabilised E, Z, Z, E-polyeneynes, $Me_3SiC{\equiv}C(CH{=}CH)_4C{\equiv}CSiMe_3$ **3a**, $Et_3SiC{\equiv}C(CH{=}CH)_4C{\equiv}CSiEt_3$ **4a** and $Et_3Si(C{\equiv}C)_2(CH{=}CH)_4(C{\equiv}C)_2SiEt_3$ **6a** together with minor proportions of configurational isomers Z, E, Z, Z **3c**, all -E **3b**, **4b**, **6b** and compounds in which a bicyclo-octadiene structure **2**, **5** and **7** is retained. Irradiation converts the *cis*(Z)-rich isomers e.g. **3c** into the all-*trans*(E) products. Treatment of the bissilyl compounds **3**, **4** and **6** with aqueous base liberates the respective parent polyeneynes, $H(C{\equiv}C)_n(CH{=}CH)_4(C{\equiv}C)_nH$, in each case.

Synthesis within the polyeneyne series, $R'(C{\equiv}C)_n(CH{=}CH)_m(C{\equiv}C)_nR'$‡, was advanced usefully by Müller and his associates[3] who reported that cyclo-octatetraene dibromide **1** coupled with alkynyl Grignard reagents, $R'C{\equiv}CMgBr$, to yield diynetetraenes, $R'C{\equiv}C(CH{=}CH)_4C{\equiv}CR'$. The authors confined their account to products containing non-labile R' groups (e.g. alkyl or aryl) with one exception namely the unstable 3,5,7,9 - dodecatetraene - 1,11 - diyne, $HC{\equiv}C(CH{=}CH)_4C{\equiv}CH$, of unspecified configuration which was obtained in unstated yield by reaction of **1** with $HC{\equiv}CMgBr$.[3]

Silylation is a versatile preparative procedure in terminal acetylene chemistry,[4] conferring thermal stability upon polyynes[5] whilst providing both controlled protection under basic[6,7] conditions yet excellent leaving groups for electrophilic displacement.[8,9] We have examined the behaviour of the Grignard reagents $R_3Si(C{\equiv}C)_nMgBr$ (R = Me, n = 1; R = Et, n = 1, 2) towards **1** with a view to preparing silyl-ended tetraenepolyynes, $R_3Si(C{\equiv}C)_n(CH{=}CH)_4(C{\equiv}C)_nSiR_3$, potentially useful starting materials for acetylene functionalisation in the eneyne series, and as efficient sources for the parent compounds, $H(C{\equiv}C)_n(CH{=}CH)_4(C{\equiv}C)_nH$.

RESULTS AND DISCUSSION

Coupling of $Me_3SiC{\equiv}CMgBr$ *with* **1**. The Grignard reagent, $Me_3SiC{\equiv}CMgBr$ reacted readily with **1** in THF during 3 hr at the reflux temperature and the organic concentrate, obtained after an aqueous work up of the mixture, was chromatographed on neutral alumina carefully shielded from light. Upon elution with petroleum ether, foreruns containing $Me_3Si(C{\equiv}C)_2SiMe_3$ and $Me_3SiC{\equiv}CH$ were obtained, followed by fractions which, upon concentration, gave a pale-yellow oil (27%). The ^1H NMR spectrum in CCl_4 of this oil (Table 1) was consistent with a *bicyclic* structure **2** as evidenced by: (i) distinctive singlet resonances at 9.74 τ (9H) and 9.84 τ (9H) commensurate with *endo* (X) and *exo* (Y) -cyclic trimethylsilylethynyl substituents on the 4-membered ring, (ii) modified proton triplets (2H), Hd and Hd', centred at *ca.* 8.28 and 8.01 τ on the same ring (iii) allylic multiplets (2H), Hc and Hc' centred at 7.65 and 7.27 τ and (iv) vinyl multiplets (4H), Ha, Ha', Hb and Hb' centred at 3.96 and 4.18 τ.

Additional confirmation of structure **2** was provided by the position of its principal UV minimum at 262 nm and maximum at 295.5 nm (MeOH) and the characteristic blue shifts (*ca.* 10 nm) of these bands when the trimethylsilyl groups were removed from their terminal alkyne sites by treatment of a MeOH solution of **2** with aqueous alkali (Table 2).

Subsequent chromatographic fractions, upon concentration, yielded two minor products **3c** (5%) and **3b** (5%) separated by a major component, **3a** (25%). The ^1H NMR

Table 1. ^1H NMR spectra of E-7,8-bis(trialkylsilylalkynyl)-bicyclo[4,2,0]octa-2,4-dienes

COMPOUND	R_3Si (exo)	R_3Si (endo)	Hd	Hd'	Hc	Hc'	Hb Hb'	Ha Ha'
	[18 or 30 H]		[2H]		[2H]		[4H]	
2[a)]	9.84s	9.74s	8.28t[c)]	8.01m	7.65m	7.27m	4.18m	3.96m
5[b)]	9.00q	8.40t	8.30t[c)]	8.13m	7.78m	7.32m	4.23m	3.98m
7[a)]	9.00q	8.40t	8.13t[c)]	8.06m	7.71m	7.28m	4.16m	3.79m

a) In CCl_4 b) In $CDCl_3$ c) . J = ca. 6Hz

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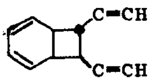
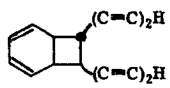
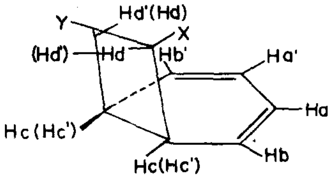
† Address enquiries to this author.

‡ For synthesis of lower members of the series (R' = H, n = 1) see Refs. 1 (m = 1) and 2 (m = 2).

Table 2. UV spectra of E-7,8-bis(trialkylsilylalkynyl)-bicyclo[4,2,0]octa-2,4-dienes and E-7,8-bis(alkynyl)-bicyclo[4,2,0]octa-2,4-dienes

COMPOUND	λ_{max} nm (log ε)	Solvent
2	296(4.11)	Hexane
	295.5	MeOH
	285	MeOH[a)]
5	296(4.10)	Hexane
	296	MeOH
7	317	Hexane
	318	MeOH
	308	MeOH[a)]

a) MeOH (30 vol) containing aqueous NaOH (1 vol).



X,Y = 2 $Me_3SiC{\equiv}C$
5 $Et_3SiC{\equiv}C$
7 $Et_3Si(C{\equiv}C)_2$

spectra of each of the three compounds (Table 3) exhibited one singlet resonance (18 H) in the 9.77–9.80 τ (Me_3Si) region and a doublet (2H) centred at 4.40–4.52 τ compatible with vinylic protons α to a triple bond.[3] The crucial distinguishing feature as regards the latter resonances is the coupling constant, J : 15.5 Hz for **3a** and **3b** assignable to *trans*-ene units, and 10.0 Hz for **3c** assignable to *cis*-ene units. Compound **3c** additionally exhibited multiplets (totalling 6 H) in the range 3.05–3.60 τ, whilst the comparable resonances for **3a**, included a doublet of doublets at 2.95 τ incorporating J = 15.5 and 12.0 Hz, a multiplet at 3.88 τ (including J = 12.0 Hz) and a doublet at 3.50 τ (J = 9.5 Hz). Compound **3b** exhibited a multiplet centred at 3.42 τ incorporating J = 15.5 Hz.

All three products had sharp m.p's, the highest corresponded to the compound of longest chromatographic retention time.

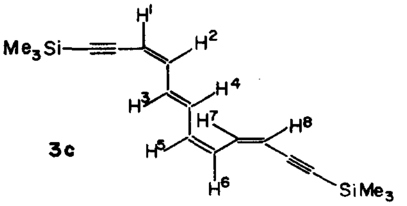
The following structures are compatible with the NMR spectral data considered in conjunction with these physical properties. Compound **3c** possessing the greatest number of *cis*-ene units has the lowest m.p. (76°) and, being the thermodynamically least stable of the three, is the isomer most prone to configurational change (*vide infra*).

The essential tetraenediyne element in compounds **3a**–**c** is corroborated by the positions of the longest wavelength high intensity UV bands in the 365–373.5 nm range (Table 4), however the fact that substitution of each *cis*-ene for a *trans*-ene unit brings about a blue shift of *ca* 3 nm is unusual and is considered in greater detail later.

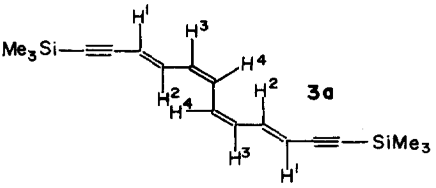
Table 3. ^1H NMR spectra of $R_3Si(C{\equiv}C)_n(CH{=}CH)_4(C{\equiv}C)_nSiR_3$ compounds in CCl_4

COMPOUND	R	H^1(d) (2H)	H^2 (2H)	H^3 (2H)	H^4 (2H)
3a	9.77[a]	4.42[b]	2.95dd[be]	3.88m[e]	3.50d[f]
4a	8.95[c]	4.38[b]	2.95dd[be]	3.89m[e]	3.49d[f]
6a	8.94[c]	4.33[b]	2.80dd[be]	3.83m[e]	3.49d[f]
3b	9.77[a]	4.40[b]	3.42m[d]	3.73m	
4b	8.95[c]	4.42[b]	3.42m[d]	3.73m	
6b	8.95[c]	4.41[b]	3.23m[d]	3.70m	
3c	9.80[a]	4.52[g]	3.60 - 3.05 m[h]		

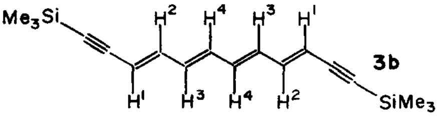
[a] CH_3s (18H); [b] $J_{12} = J_{21} = 15.5$ Hz; [c] C_2H_5 8.40 t + 9.00 q (30H);
[d] Incl. $J_{21} = 15.5$ Hz; [e] Incl. $J_{23} = J_{32} = 12.0$ Hz; [f] Incl. $J_{43} = 9.5$ Hz;
[g] H^1, H^8; $J_{12} = J_{87} = 10.0$ Hz; [h] H^2–H^7.



3c



3a



3b

Table 4. UV spectra of $R_3Si(C\equiv C)_n(CH{=}CH)_4(C\equiv C)_nSiR_3$ and $H(C\equiv C)_n(CH{=}CH)_4(C\equiv C)_nH$ compounds

COMPOUND	λ_{max} nm (log ε)				Solvent
3a	316.5(4.48)	332(4.78)	348(4.96)	368(4.87)	hexane
	316	332	348	368	MeOH
$HC\equiv CCH\overset{t}{=}CH(CH\overset{c}{=}CH)_2CH\overset{t}{=}CHC\equiv CH$	302.5(4.46)	317.5(4.72)	333.5(4.88)	350(4.82)	MeOH[a)]
$HC\equiv C(CH{=}CH)_4C\equiv CH$	-	318	334	353	hexane[b)]
3b	320(4.47)	336(4.78)	352(5.01)	373.5(5.05)	hexane
	319	336	352	373	MeOH
$HC\equiv C(CH\overset{t}{=}CH)_4C\equiv CH$	305(4.46)	320.5(4.73)	337.5(4.93)	355(4.97)	MeOH[acd)]
	305	320	336	354	hexane
3c	315(4.47)	330(4.76)	346(4.94)	365(4.86)	hexane
4a	317(4.49)	333(4.77)	349(4.95)	369(4.89)	hexane
	317	332	349	368.5	MeOH
4b	321.5(4.46)	337.5(4.78)	355(5.01)	375(5.05)	hexane
	321	337	354.5	374.5	MeOH
6a	342(4.47)	358(4.79)	378(5.00)	401.5(4.97)	hexane
	342	358	378	401	MeOH
$H(C\equiv C)_2CH\overset{t}{=}CH(CH\overset{c}{=}CH)_2CH\overset{t}{=}CH(C\equiv C)_2H$	-	347.5(4.76)	366(4.94)	387(4.90)	MeOH[a)]
6b	349.5(4.51)	365(4.82)	385(5.05)	409(5.09)	hexane
		365	385	408	MeOH
$H(C\equiv C)_2(CH\overset{t}{=}CH)_4(C\equiv C)_2H$	-	352.5	372	392.5	MeOH[ad)]

a) MeOH (30 vol) containing aqueous NaOH (1 vol)

b) Unspecified configuration (ref. 3)

c) Produced by exposure of $HC\equiv CCH\overset{t}{=}CH(CH\overset{c}{=}CH)_2CH\overset{t}{=}CHC\equiv CH$ solutions to light or by desilylation of 3b

d) *Absorption maxima of the all-trans isomers are sharper than those of the isomers containing cis-ene units.*

The results can best be accounted for in terms of Müller's proposals.[3] In such a scheme, **1**, reacting via its valence-isomer **1b**, couples with $Me_3SiC\equiv CMgBr$ to give the *trans* - 7,8 - bisalkynycycloocta - 1,3,5 - triene (A) (not isolated) which undergoes either thermally allowed conrotatory ring-opening to give **3** or disrotatory ring closure to give **2**. [Direct conversion of the predominant valence isomer, **1a**, is ruled out because of the anticipated low reactivity of the non-allylic bromine atoms towards displacement in Grignard-type couplings.[3]] Intermediate A can ring-open by conrotation in two ways; mode (i) (*exo*) which would yield directly the (predominant)*trans*, *cis*, *cis*, *trans* isomer, **3a**, and mode (ii) (*endo*) which would give the all-*cis*-isomer.

A plausible explanation of the observed result is that the all-*cis* compound may be indeed formed, but that being the thermodynamically least stable isomer it transforms rapidly by geometric isomerisation of one double bond to the *cis*, *trans*. *cis*, *cis*. product **3c**. In support of this hypothesis, the second minor component all-*trans* **3b**, is formed presumably by partial isomerisation of **3a**, a process which can be demonstrably accelerated by exposing hexane solutions of **3a** to sunlight (**3b** is obtained in high yield). Since **3c** is a minor product†, it seems likely that **3a** is formed in preference to the all-*cis* isomer in competing conrotational ring-opening proces-

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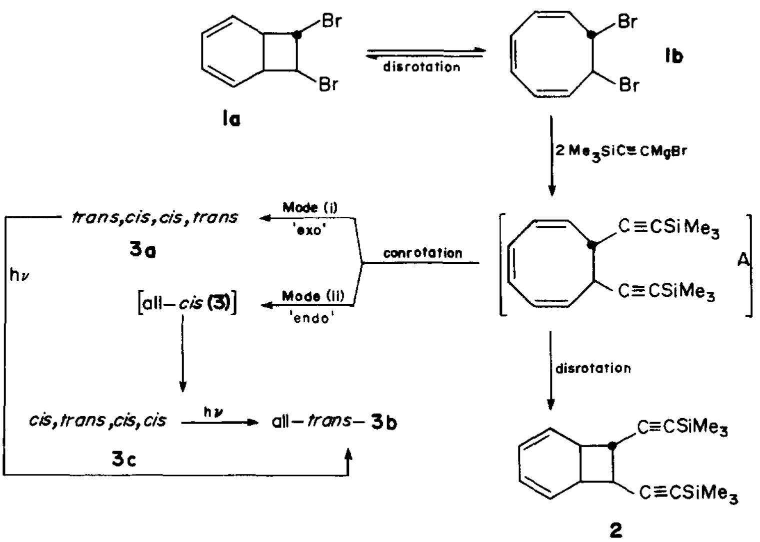
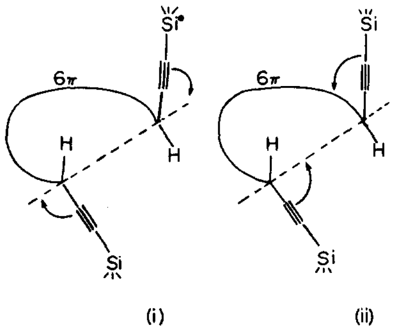
†It should be borne in mind that the total yield of all products is 60–65%.



Scheme I.

ses. (This fact may be understood in terms of steric interactions inherent in the transition state of the "*endo*" mode (ii) which requires the two trimethylsilylethynyl groups to approach one another thus raising the activation energy of this particular ring opening; crowding would be much less in the *exo* mode (i) as illustrated below.)



The main difference between these results and those reported elsewhere[3] lies in the isolation of the bicyclic compound, **2**, equal in molar quantity to **3a**. Unlike other systems which exhibit temperature variable equilibria between valence isomers, **2** showed no tendency to convert into detectable amounts of the mono-cyclic isomer (A) at low temperatures. It is doubtful whether the mild π-delocalising effect of the silyl groups would really exert such a profound influence on the equilibrium position.

Coupling of $Et_3SiC{\equiv}CMgBr$ *with* **1**. In view of the possibility that the modest yields of **2** and **3** arise from inadvertent cleavage of trimethylsilyl groups in the products during chromatographic work up of the reaction mixtures†, an analogous coupling was carried out between **1** and triethylsilylethynylmagnesium bromide, since the triethylsilyl group is known to be less susceptible to attack by base and therefore to provide a greater degree of protection both during the Grignard coupling and initial work up. In practice, use of this Grignard reagent did not lead to overall improved product yields: *ca* equimolar amounts of the corresponding bicyclic compound, **5**, (25%) and *trans*, *cis*, *cis*, *trans* product, **4a**, (30%) were obtained together with a small quantity (8%) of the all-*trans* isomer **4b**. The NMR and UV data for all three products were compatible with simple replacement of triethyl- for trimethyl-silyl groups, (Tables 1–4), whilst **4a** is isomerised readily to **4b** in hexane solution by the action of light. Careful chromatography did not reveal the presence of any *cis*, *trans*, *cis*, *cis* isomer **3c**.

Coupling of $Et_3Si(C{\equiv}C)_2MgBr$ *with* **1**. Despite the lack of success over improving yields in the tetraenediyne series, the relative stability of the silylated products together with their ease of separation by column chromatography was considered sufficiently encouraging to warrant attempted extension of the unsaturation by introducing terminal butadiyne units. To achieve this, butadiynyltriethylsilane was metallated with EtMgBr and the resulting Grignard reagent, $Et_3Si(C{\equiv}C)_2MgBr$, was coupled with **1**. Work up according to the established procedure gave *ca* 4% yield of the anticipated bicyclic compound, **7**, whose NMR spectrum (Table 1) correlated closely with **2** and **5** as regards common structural features. The UV spectrum of **7** (Table 2) revealed a *ca.* 20 nm red shift of the absorption maximum compared with **2** and **5**, commensurate with the presence of additional ethynyl groups. Continuation of the chromatography gave, in order of elution, the *trans*, *cis*, *cis*, *trans*-bis(triethylsilyl)tetraenetetrayne **6a** (33%), followed by the all-*trans* isomer **6b** (5%); the NMR spectral features correlate with those of **4a** and **4b** respectively (Table 3). The UV spectra of **6a** and **6b** (Table 4) likewise showed *ca.* 30 nm red shifts of all band maxima compared to **4a** and **4b** as expected for extension of the conjugated system at each end by single *yne* units. Exposure of hexane solutions to daylight in the laboratory resulted in rapid conversion of **6a** to **6b**. No isomer corresponding to *cis*, *trans*, *cis*, *cis*- **3c** could be detected during chromatography.

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†The trimethylsilylpolyynepolyene bonds are likely to be sensitive to the mild conditions by analogy with the results for the silylpolyynes. For example, methanol alone cleaves bistrimethylsilyloctatetrayne slowly at room temperature.[8]

Liberation of the parent polyeneynes. Alkynyl-silicon bonds are broken in homogeneous H_2O:MeOH solution under the catalytic influence of added alkali. The process which has been studied kinetically by UV spectroscopy[10] is quantitative and, commensurate with rate determining nucleophilic attack at silicon, electron-withdrawing groups (steric factors being equal) attached either to silicon or to the alkyne moiety enhance the rate of cleavage. Thus in view of the electronegativity of both sp (alkyne) and sp^2 (alkene) units, the polyeneynes would be expected to cleave under relatively mild conditions. This proved to be the case, for example, treatment of a dilute (*ca.* 10^{-5} M) MeOH (20 vol) solution of compound **3a** with 0.02 M aqueous NaOH (1 vol) at 30° resulted in complete desilylation and liberation of the parent polyeneyne, $\mathrm{HC{\equiv}CCH\overset{t}{=}CH(CH\overset{c}{=}CH)_2CH\overset{t}{=}CHC{\equiv}CH}$, within 5 h†. The characteristic spectral blue shifts (*ca.* 18 nm for each band) associated with the removal of both terminal silyl groups are shown in the Figure.

Treatment of **3b**, **6a**, **6b**, **2** and **7** with aqueous methanolic alkali in an analogous fashion yielded the corresponding polyeneynes: $\mathrm{HC{\equiv}C(CH\overset{t}{=}CH)_4C{\equiv}CH}$, $\mathrm{H(C{\equiv}C)_2CH\overset{t}{=}CH(CH\overset{c}{=}CH)_2CH\overset{t}{=}CH(C{\equiv}C)_2H}$, $\mathrm{H(C{\equiv}C)_2(CH\overset{t}{=}CH)_4(CH{\equiv}C)_2H}$, E - 7,8 - bis(ethynyl)bicyclo[4,2,0]octa - 2,4 - diene and E - 7,8 - bis(butadiynyl)bicyclo[4,2,0]octo - 2,4 - diene respectively.

UV spectra. The UV spectra of the parent polyeneynes and their bissilyl derivatives (Table 4) exhibit high intensity ($\log \epsilon > 4.0$) absorptions in the 300–400 nm region with characteristic regular band spacing of *ca.* 18 ± 3 nm for the tetraenediynes and *ca.* 20 ± 4 nm for the tetraenetetraynes respectively. Plots (not shown) of λ^2_{max} (longest wavelength band) vs n for corresponding bands in each of the $\mathrm{Me_3SiC{\equiv}C(CH\overset{t}{=}CH)_nC{\equiv}CSiMe_3}$ and $\mathrm{HC{\equiv}C(CH\overset{t}{=}CH)_nC{\equiv}CH}$ series are linear as observed previously for polyyne and analogous spectra (see Ref. 5 for leading references). The presence of two silyl end-groups causes a red shift of 18–19 nm compared to the parent tetraenediyne and 14–15 nm compared to the parent tetraenetetrayne for each absorption maximum.

An interesting feature within both series is that replacement of a *cis*-ene by a *trans*-ene moiety results in absorption at *longer* wavelengths for all bands. Similar behaviour is apparent in the n = 1 series[1] whereas for n = 2^2, introduction of *cis*-ene in place of *trans*-ene units leads to longer wavelength absorptions. In each situation, the absorption bands of the *trans*-compounds are of higher intensity. The wavelength changes involved are in all cases small (1–3 nm), nevertheless they are quite distinct. The *cis* > *trans* wavelength phenomenon is reported to be general for dienes and for simple unbranched polyenes;[12] our results show that such systems may be easily perturbed however.

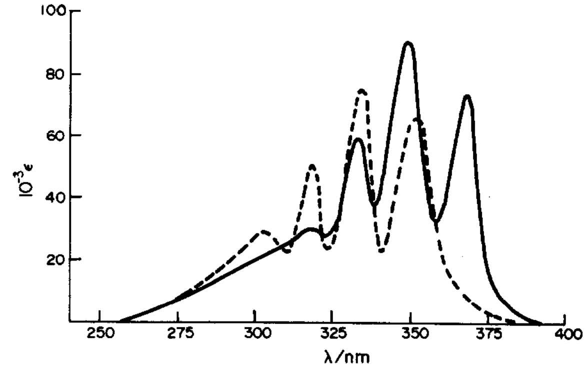

Fig. 1. UV spectra (MeOH solution) of $\mathrm{Me_3SiC{\equiv}CCH\overset{c}{=}CH(CH\overset{t}{=}CH)_2CH\overset{c}{=}CHC{\equiv}CSiMe_3}$ and $\mathrm{HC{\equiv}CCH\overset{c}{=}CH(CH\overset{t}{=}CH)_2CH\overset{c}{=}CHC{\equiv}CH}$.

EXPERIMENTAL

The general techniques employed previously for handling polyynes were adopted.[5] In view of the anticipated photosensitivity of the products, reaction vessels, chromatography columns and all solutions were carefully shielded from light with metal foil unless stated otherwise.

Petrol refers to Analar grade slightly acidified petroleum ether (40–60° fraction). Alumina (La Porte, grade H) was used for column chromatography. U.v. spectral profiles were recorded on a Unicam SP800 instrument whereas absorption maxima and extinction coefficients were measured on a SP1700 spectrophotometer.

Coupling of Grignard reagents $\mathrm{R_3Si(C{\equiv}C)_nMgBr}$ *with cyclooctatetraene dibromide* **1** 1,12 - *Bis(trimethylsilyl)dodeca* - 3,5,7,9 - *tetraene* - 1,11 - *diyne* **3** $\mathrm{Me_3SiC{\equiv}C(CH{=}CH)_4C{\equiv}CSiMe_3}$

A soln of **1** (3.96 g, 15 mmole) in THF (15 ml) was added at 0° to $\mathrm{Me_3SiC{\equiv}CMgBr}$ (40 mmole) prepared from $\mathrm{Me_3SiC{\equiv}CH}$[11] and EtMgBr in THF (30 ml). The mixture was stirred and boiled under reflux for 3 hr to give an orange-red soln which was poured onto ice and NH_4Cl and extracted with Et_2O. The organic phase was dried (Na_2SO_4) and the solvent was removed under reduced pressure to leave a red oil which was chromatographed using petrol as eluent to give successively traces of $\mathrm{Me_3Si(C{\equiv}C)_2SiMe_3}$, [8]$\mathrm{Me_3SiC{\equiv}CH}$ and the following products in order of elution:

(a) E - 7,8 - *Bis(trimethylsilylethynyl)bicyclo*[4,2,0]*octa* - 2,4 - *diene* **2** as a pale-yellow oil (27%) n_D^{25} 1.5341 (Found: C, 72.1; H, 8.8. $C_{18}H_{26}Si_2$ requires: C, 72.4; H, 8.8%); IR (film) ν (cm^{-1}): 3020w (C=C–H), 2955s (CH_3), 2150s, 2135s (C≡C), 1575w (C=C), 1250s, 845s, 755s (CH_3Si); MS: P (298), P–Me (283), P–Me–2H (281), Me_3Si (73).

(b) Z,E,Z,Z - 1,12 - *Bis(trimethylsilyl)dodeca* - 3,5,7,9 - *tetraene* - 1, 11 - *diyne* **3c** as a lemon powder (5%) m.p. 76° (isomerisation); IR ν (cm^{-1})‡: 3020w (C=C–H), 2955s (CH_3), 2150sh, 2135s, 2115m (C≡C), 1595w (C=C), 1250s (CH_3Si), 1086s, 975s, 940vw ($\mathrm{CH\overset{t}{=}CH}$). (The $\mathrm{CH\overset{c}{=}CH}$ band is obscured by Me_3Si bands at 850 and 750 cm^{-1}); MS: P (298), P–2H (296), P–Me–H (281), Me_3Si (73).

(c) E, Z, Z, E - 1,12 - *Bis(trimethylsilyl)dodeca* - 3,5,7,9 - *tetraene* - 1,11 - *diyne* **3a** as lemon plates (25%) m.p. 88°; (Found: C, 72.1; H, 8.8. $C_{18}H_{26}Si_2$ requires: C, 72.4; H, 8.8%); I.R. ν (cm^{-1}): 3020w (C=C–H), 2955s (CH_3), 2166m, 2117s (C≡C), 1598w (C=C), 1250s (CH_3Si), 978m, 938vs (CH=CH), 846s, 756s (CH_3Si); MS: P (298), P–Me (283).

(d) all-E - 1,12 - *Bis(trimethylsilyl)dodeca* - 3,5,7,9 - *tetraene* - 1,11 - *diyne* **3b** as lemon needles (5%) m.p. 156–157°; (Found: C, 72.6; H, 8.9%) IR ν (cm^{-1}): 3020m (C=C–H), 2955s (CH_3), 2152m, 2109s (C≡C), 1605w (C=C), 1250s (CH_3Si), 996s, 965vw, 938w ($\mathrm{CH\overset{t}{=}CH}$), 846s, 756s, ($CH_3Si$); MS: P (298), P–Me (283).

1,12 - *Bis(triethylsilyl)dodeca* - 3,5,7,9 - *tetraene* - 1,11 - *diyne* **4** $\mathrm{Et_3SiC{\equiv}C(CH{=}CH)_4C{\equiv}CSiEt_3}$.

An identical procedure, using $\mathrm{Et_3SiC{\equiv}CMgBr}$ (prepared from $\mathrm{Et_3SiC{\equiv}CH}$[5] and EtMgBr) in place of $\mathrm{Me_3SiC{\equiv}CMgBr}$, gave traces of $\mathrm{Et_3SiC{\equiv}CH}$ and $\mathrm{Et_3Si(C{\equiv}C)_2SiEt_3}$[5] upon chromatography followed successively by:

E - 7,8 - *Bis(triethylsilylethynyl)bicyclo*[4,2,0]*octa* - 2,4 - *diene* **5** as a yellow oil (25%) n_D^{20} 1.5320; (Found: C, 74.8; H, 10.1. $C_{24}H_{38}Si_2$ requires: C, 75.3; H, 10.0%); IR ν (cm^{-1}): 3020w (C=C–H), 2947s, 2920sh, 2900m, 2867s (C_2H_5), 2153s, 2138s (C≡C), 1580w (C=C), 1455m, 1410m, 1375w, 1235m (C_2H_5Si); MS: P (382), P–Et + H (354), P–2Et + H (325), P–3Et + 2H (297).

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†The reaction can be accelerated by increasing the alkali concentration to which the rate of cleavage is proportional.

‡Powder obtained by evaporating a solution on the IR plate. Grinding the compound causes isomerisation.

(b) E,Z,Z,E - 1,12 - *Bis(triethylsilyl)dodeca* - 3,5,7,9 - *tetraene* - 1,11 - *diyne* **4a** as a yellow oil (30%) n_D^{22} 1.5885; (Found: C, 74.9; H, 10.0. $C_{24}H_{38}Si_2$ requires: C, 75.3; H, 10.0%); IR ν (cm^{-1}): 3020w (C=C–H), 2947s, 2920sh, 2900m, 2867s (C_2H_5), 2163m, 2140sh, 2118s (C≡C), 1596w (C=C), 1455m, 1410m, 1375w, 1235m (C_2H_5Si), 972m, 937s (CH=CH); MS: P (382).

(c) all - E - 1,12 - *Bis(triethylsilyl)dodeca* - 3,5,7,9 - *tetraene* - - 1,11 - *diyne* **4b** as a yellow oil (30%) n_D^{22} 1.5941; (Found: C, 75.0; H, 10.2%); IR ν (cm^{-1}): 3020w (C=C–H), 2947s, 2920sh, 2900m, 2867s (C_2H_5), 2154s, 2135sh, 2110m (C≡C), 1605w (C=C), 1455m, 1410m, 1375w, 1235m (C_2H_5Si), 995s (CH=CH); MS: P (382), P–Et + H (354), P–2Et + 2H (326), $Et_3SiC_6H_4$ (191), $Et_3SiC_4H_2$ (165), Et_3Si (115).

1,16 - *Bis(triethylsilyl)hexadeca* - 5,7,9,11 - *tetraene* - 1,3,13,15 - *tetrayne* **6** $Et_3Si(C{\equiv}C)_2(CH{=}CH)_4(C{\equiv}C)_2SiEt_3$

Solns of $Et_3Si(C{\equiv}C)_2MgBr$ [prepared from $Et_3Si(C{\equiv}C)_2H$[5] and EtMgBr] (40 mmole) and **1** (15 mmole) in THF were mixed and boiled under reflux for 4 hr, then treated with acidified ice water and extracted with Et_2O. The organic phase was dried (Na_2SO_4) and concentrated under reduced pressure to leave a dark-red oil which, when chromatographed on alumina, gave traces of $Et_3Si(C{\equiv}C)_4SiEt_3$[5] followed by E - 7,8 - *bis(triethylsilylbutadiynyl)bicyclo*[4,2,0]*octa* - 2,4 - *diene* **7** as a yellow oil (*ca.* 4%); IR ν (cm^{-1}): 3020w (C=C–H), 2947s, 2920sh, 2900m, 2867s (C_2H_5), 2215m, 2090m [$(C{\equiv}C)_2$], 1602vw, 1570vw (C=C), 1455m, 1410m, 1375w, 1235m (C_2H_5Si); MS: P (430), P–Et (401), P–2Et + H (373), P–3Et + 2H (345).

E,Z,Z,E - 1,16 - *Bis(triethylsilyl)hexadeca* - 5,7,9,11 - *tetraene* - 1,3,13,15 - *tetrayne* **6a** as yellow plates (33%) m.p. 71.5–73° (Found: C, 77.9; H, 8.8. $C_{28}H_{38}Si_2$ requires: C, 78.1; H, 8.9%); IR ν (cm^{-1}): 3020w (C=C–H), 2947s, 2920sh, 2900m, 2867s (C_2H_5), 2108s, 2090m [$(C{\equiv}C)_2$], 1587m (C=C), 1455m, 1410m, 1375w, 1235m (C_2H_5Si), 977m†, 932s (CH=CH); MS: P (430), P–Et (401), P–2Et + 2H (374), Et_3Si (115) and all - E - 1,16 - *Bis(triethylsilyl)hexadeca* - 5,7,9,11 - *tetraene* - 1,3,13,15 - *tetrayne* **6b** as bright orange microcrystals (5%) m.p. 147–149° (Found: C, 77.7; H, 9.0%); IR ν (cm^{-1}): 3020w (C=C–H), 2947s, 2920sh, 2900m, 2867s (C_2H_5), 2180s, 2090m [$(C{\equiv}C)_2$], 1597m (C=C), 1455m, 1410m, 1375w, 1235m (C_2H_5Si), 997s, 976m†, 932w (CH=CH); MS: P (430), P–Et (401).

Light-induced transformations (3a)→(3b)

A soln of **3a** (0.3 g, 1 mmole) in ice cold hexane [500 ml acidified with glacial AlOH (0.1 ml)] was exposed directly to bright sunlight for 4 hr. The colour of the soln (yellow) intensified during this period and regular monitoring of the UV spectrum revealed a progressive shift of the absorption maxima (316.5, 332, 348 and 368 nm) to longer wavelengths (320, 335, 351 and 373 nm), indicating near complete conversion of **3a** (E,Z,Z,E) into the all-E isomer, **3b**. Chromatography of the soln as described above gave a forerun of **3a** followed by material (70%), m.p. 154–156°, whose properties were identical with the compound (**3b**) isolated in minor quantity from the reaction of $Me_3SiC{\equiv}CMgBr$ with **1**.

In analogous experiments, acidified hexane solns (500 ml) containing *ca.* 1 mmole of **3c**, **4a** or **6a** were individually exposed to sunlight for periods of 1 to 4 hr. After isomerisation was judged to be complete, as evidenced by UV spectroscopic shifts viz. **3c** (315, 330, 346, 365 nm)→ **3b**, **4a** (317, 333, 349, 369 nm)→ **4b** (321.5, 336.5, 354.5, 374 nm) and **6a** (342, 358, 378, 401.5 nm)→ **6b** (349, 364.5, 384, 408.5 nm), the solns were chromatographed to give, in each case, foreruns of starting materials followed by the all-E isomers **3b**, **4b** and **6b** (each in *ca.* 70% yield) whose properties were identical with specimens isolated from the appropriate Grignard reagent couplings with **1**.

Desilylation procedure

In a typical experiment, a *ca.* 10^{-5} M soln of **3a** in MeOH (20 vol) was mixed with 0.02 M aqueous NaOH (1 vol) and the resulting soln was thermostatted at 30°. Progress of the desilylation was followed in the UV region by monitoring the disappearance of the 368 nm maximum and development of the corresponding band at 350 nm due to E,Z,Z,E - *dodeca* - 3,5,7,9 - *tetraene* - 1,11 - *diyne*. The half-life of this process was *ca.* 27 min and the reaction was considered complete after 2.25 hr (five half-lives).

Analogous treatment of **6a** using 0.1 M aqueous NaOH at 30° resulted in a soln of E,Z,Z,E - *hexadeca* - 5,7,9,11 - *tetraene* - 1,3,13,15 - *tetrayne*. The reaction was monitored at 402 nm and the half-life for complete desilylation was *ca.* 12 min.

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†The CH=CH bands at 977m and 976m cm^{-1} are partly obscured by Et_3Si.