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SILYLATION AS A PROTECTIVE METHOD FOR TERMINAL ALKYNES IN OXIDATIVE COUPLINGS

A GENERAL SYNTHESIS OF THE PARENT POLYYNES[1] $H(C{\equiv}C)_nH$ (n = 4–10, 12)

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Abstract—Individual polyynes in the series $H(C{\equiv}C)_nH$ (n = 4–10, 12) have been prepared in solution by sequences involving Cu-catalysed oxidative couplings (Hay technique) of silyl-protected terminal alkynes, partial cleavage (desilylation) of the products by alkali, recoupling and complete desilylation. Thus using the conditions established in a model coupling, $Et_3SiC{\equiv}CH$(I) → $Et_3Si(C{\equiv}C)_2SiEt_3$(II), coupling of the silyldiyne $Et_3Si(C{\equiv}C)_2H$(III) gives $Et_3Si(C{\equiv}C)_4SiEt_3$(IV) which upon controlled cleavage yields a chromatographically separable mixture of IV, $Et_3Si(C{\equiv}C)_4H$ (V) and $H(C{\equiv}C)_4H$ (VI). Coupling of V in turn gives $Et_3Si(C{\equiv}C)_8SiEt_3$ (VII) which upon cleavage yields $Et_3Si(C{\equiv}C)_8H$ (VIII) and $H(C{\equiv}C)_8H$ (IX), and coupling of VIII gives the bissilylhexadecaacetylene $Et_3Si(C{\equiv}C)_{16}SiEt_3$ (X). Hexa- and dodeca-acetylene may be synthesized analogously: $Et_3Si(C{\equiv}C)_3SiEt_3$ (XII) → $Et_3Si(C{\equiv}C)_3H$ (XI) → $Et_3Si(C{\equiv}C)_6SiEt_3$ (XIII) → $Et_3Si(C{\equiv}C)_6H$ (XIV) → $H(C{\equiv}C)_6H$ (XV): XIV → $Et_3Si(C{\equiv}C)_{12}SiEt_3$ (XVI) → $H(C{\equiv}C)_{12}H$ (XVII). Other members of the series are prepared via mixed couplings: I + V → $Et_3Si(C{\equiv}C)_5SiEt_3$ (XVIII) → $H(C{\equiv}C)_5H$ (XIX): I + XIV → $Et_3Si(C{\equiv}C)_7SiEt_3$ (XX) → $H(C{\equiv}C)_7H$ (XXI): I + VIII → $Et_3Si(C{\equiv}C)_9SiEt_3$ (XXII) → $H(C{\equiv}C)_9H$ (XXIII): III + VIII → $Et_3Si(C{\equiv}C)_{10}SiEt_3$ (XXIV) → $H(C{\equiv}C)_{10}H$ (XXV). The principal UV light absorption maxima of compounds IV → XXV within each of the series $Et_3Si(C{\equiv}C)_nSiEt_3$, $Et_3Si(C{\equiv}C)_nH$ and $H(C{\equiv}C)_nH$ correlate excellently with relationships previously established for polyyne spectra: $\lambda^2 = kn$ (λ = longest wavelength high intensity band) and $\Delta\lambda = k'n$ ($\Delta\lambda$ = average vibrational spacing of the intense bands).

INTRODUCTION

ADVANCES in preparative acetylene chemistry during the early 1950's resulted in viable laboratory syntheses of the lower members of the polyyne series, $H(C{\equiv}C)_nH$ (n = 2–5). The most successful approach to these highly unstable compounds was based upon low-temperature sodamide dehydrohalogenation of α, ω-bis(chloromethyl)alkynes, $ClCH_2(C{\equiv}C)_{n-1}CH_2Cl$ in liquid ammonia, a technique which provided a convenient route to diacetylene[2] but which proved increasingly troublesome for tri-[3] and for tetra-acetylene.[4] Pentaacetylene,[4] the highest member of the series to be described,† was obtained in *ca* 1% yield from the difficultly accessible precursor, $ClCH_2(C{\equiv}C)_4CH_2Cl$, and the authors concluded at the time[4] that "the general method could not usefully be extended further without modification in the reaction conditions." Other reports, notably of triacetylene, have appeared at intervals‡ but it is doubtful whether any of the preparative methods could be adapted for higher polyyne synthesis.

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† Octaacetylene is reported to result from treatment of diacetylene with $O(^3P)$ atoms in a flow discharge system as revealed by mass spectroscopy.[5]

‡ Triacetylene is formed as a by-product of the arc process for acetylene manufacture,[6] and can be generated in the laboratory by treating either octachlorohexa-1,3,5-triene with Zn dust in boiling EtOH[7] or $ClCH_2(C{\equiv}C)_2CH_2Cl$ with $NaOH/Et_2O$.[3a, 8] It is also found in nature as a fungal metabolite.[9]

Copper-catalysed oxidative coupling procedures are employed extensively in the preparation of internal polyacetylenes and provide an alternative approach to the problem.[10, 11] Coupling of acetylene itself however, with one exception,[12] leads to polymeric species as a result of uncontrolled chain growth[13] and discrete oligomers have yet to be isolated from such reactions. Clearly, if the method is to be adapted for parent polyyne synthesis, protective groups are needed which will survive the coupling step but which can easily be removed under mild and strictly controlled conditions, *preferably in dilute solution*, in view of the extreme sensitivity of the products. The carboxyl group has been employed in this capacity in the synthesis of terminal polyacetylenes, $R(C{\equiv}C)_mH$ ($m = 2, 3$) by the Cadiot–Chodkiewicz method and may be removed, for example, by treatment with copper powder in refluxing dioxan.[14] However, as v. Baeyer noted many years ago,[15] the tetraacetylenedicarboxylic acid, $HO_2C(C{\equiv}C)_4CO_2H$, is quite unstable so that it is doubtful whether decarboxylation even of this acid, let alone higher polyacetylenedicarboxylic acids (if indeed such compounds could be prepared) could be achieved with the desired degree of control. Other allied protective groups, e.g. COOEt,[16] CH_2OH,[11] CMe_2OH[11, 17] require comparatively vigorous conditions for removal.

Some years ago, a kinetic study of the base-catalysed cleavage of the ethynyl–silicon bond in arylethynyl(trimethyl)silanes[18] and of ethynyl–hydrogen exchange in ethynylbenzenes[19] revealed that the cleavage proceeded *ca* 10^3–10^4 times slower than the exchange under comparable conditions: both processes are inhibited at pHs < 7. Since terminal alkynes can be oxidatively coupled over a pH range within which the ethynyl–silicon bond is relatively stable, it seemed likely in principle that silylacetylenes, $R_3Si(C{\equiv}C)_nH$ could be coupled to give bissilylpolyynes, $R_3Si(C{\equiv}C)_{2n}SiR_3$ from which the parent polyacetylenes, $H(C{\equiv}C)_{2n}H$, could be liberated in solution merely by raising the pH. Other criteria made this approach to the problem attractive at the outset. Firstly, the UV absorption bands characteristic of acetylenes (and of polyacetylenes in particular) are displaced to longer wavelengths when the alkyne moiety is attached directly to silicon.[20] Secondly the base-catalysed cleavage is a quantitative bimolecular process (kinetically first order with respect to base),[18] so that progress of the cleavage (pseudo first-order under the chosen conditions) can, therefore, be monitored accurately in dilute solution by UV spectroscopy. Finally, the profile geometry of the trialkylsilyl and t-butyl groups are similar. It is generally held[21] that the thermal and/or photochemical stability of $t\text{-}Bu(C{\equiv}C)_nBu\text{-}t$ compounds is associated with a spatial effect whereby polyyne chains are held apart and are thus prevented from approaching one another to the optimum distance for electrocyclic cross-linking. A comparable effect is therefore to be anticipated for the silyl analogues.

RESULTS AND DISCUSSION

Preparation of $H(C{\equiv}C)_nH$ *compounds* ($n = 4, 8$)

Ethynyl(triethyl)silane (I) selected for study,* was prepared without difficulty from Et_3SiBr and $HC{\equiv}CMgBr$ in THF.[23, 24] For oxidative coupling of I, the Hay

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* The Et_3Si- is cleaved less readily than the Me_3Si-group from acetylene (viz. $PhC{\equiv}CSiMe_3/PhC{\equiv}CSiEt_3 = 277$ in aqueous methanolic alkali[18]) so the former was chosen as the protective group in order both to reduce the likelihood of cleavage during oxidative coupling and to gain working margin for control of the subsequent desired cleavage. It should be noted however that the compounds $Me_3SiC{\equiv}CH$ and $Me_3Si(C{\equiv}C)_2H$ can be separately coupled without difficulty to give $Me_3Si(C{\equiv}C)_2SiMe_3$ and $Me_3Si(C{\equiv}C)_4SiMe_3$ respectively in good yield,[22] although the bissilyltetrayne is cleaved rapidly in 'neutral' methanol.[27]

technique[25] using the CuCl:TMEDA complex proved most effective, the advantage of this method being that the reaction can be speedily carried out with aerial oxidation in acetone solution. Only a minute quantity of catalyst is required, a vital factor since at higher concentrations of copper salt or of base the alkynyl-Si bond may be cleaved. 1,4-Bistriethylsilylbutadiyne (II) was isolated in excellent yield, however since the cleavage of II is a somewhat trivial exercise for preparative purposes, attention was focused on the next member of the series, butadiynyl(triethyl)silane (III). Synthesis of III was accomplished in moderate yield from $H(C{\equiv}C)_2MgBr$ and Et_3SiBr. Although the Grignard procedure necessitated isolation of C_4H_2 followed by metallation with EtMgBr in THF,[23] exploratory studies revealed this route to be superior to the more direct method, i.e. coupling involving $Na(C{\equiv}C)_2H$ in liquid NH_3, since the solvent reacts rapidly with Et_3SiBr to give silylamines thus resulting in a minute yield of III. [The yield is not improved if NH_3 is replaced by a high-boiling inert solvent.] Compound III, which can be stored for several days at −20° without significant decomposition was oxidatively coupled by the Hay method to give 1,8-bistriethylsilyloctatetrayne (IV) in 80% yield, as a stable crystalline solid which could, if necessary, be distilled without decomposition *in vacuo*.

Examination of the UV spectrum of IV in hexane solution revealed a characteristic visible shift (*ca* 30 nm) coupled with a 10% increase in extinction coefficient of the highest intensity band compared to octatetrayne (VI) [λ_{max} 227 nm, ε 280,000 (pentane solution)].[4] This pattern was reflected in the other band maxima (*cf* Fig. 3) and is considered in detail below. When a MeOH solution of IV was treated with dilute aqueous NaOH, the principle max (256·0 nm in the mixed solvent) gradually disappeared and was replaced by a new max (241·0 nm) attributed to triethylsilyloctatetrayne (V). This max. in turn decreased in intensity and was replaced by a band for VI, (225·5 nm). Eventually only VI remained.* Neutralisation and extraction into petroleum followed by chromatography on alumina (to remove silanol and siloxane) gave a solution of VI whose UV spectrum was identical to that previously reported.[4] The whole procedure was repeated on a larger scale and the cleavage was quenched by neutralization with dilute acid at the precise moment when the peak due to V was maximal. Chromatography of a petrol concentrate (*cf* Exptl) resulted in a clean separation with elution of residual IV followed by V and finally by VI. Closer examination of methanol solutions of IV and of pure V under identical conditions of temperature and added base revealed that the rate of desilylation of IV was approximately twice that of V.† This result is to be expected since IV contains essentially two sites for attack and also because the Et_3Si-group exerts a substituent effect which is little different from that of hydrogen, any inductive electron release by Et_3Si being counteracted by p_π–d_π bonding between the polyyne group and silicon.[28] These observations highlight a most useful inbuilt advantage as regards the synthesis of V from IV based upon careful kinetic control and the conversion serves as a model for other transformations (*vide infra*). Compound V like VI[4] proved to be too unstable to isolate however dilution of a petrol solution of V with acetone followed by oxidative coupling by the established procedure gave a product whose UV spectrum, after

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* The alkaline conditions were too dilute to catalyse addition of water or of methanol to the product.[26]

† A detailed kinetic account of this process and of the cleavages of other silylpolyynes described here will be discussed in a forthcoming publication.[27]

chromatographic purification of a petrol concentrate, showed an ultra high intensity band at 336 nm attributable to 1,16-bistriethylsilylhexadecaoctayne (VII). Attempts to isolate VII were unsuccessful, the white crystals obtained by removal of solvent *in vacuo* at −30° decomposing rapidly above −20°, so that the geometric similarity between the R_3Si- and t-Bu-groups cited above does not confer the same degree of stability upon the analogous compounds (viz. t-Bu$(C{\equiv}C)_8$Bu-t m.p. 130° dec).[29]

Treatment of a MeOH solution of VII with dilute alkali resulted in successive disappearance of the 336 nm max, growth of a new band at 324·5 nm (triethylsilylhexadecaoctayne, VIII) disappearance of this band and emergence of a new max. at 315·0 nm (hexadecaoctayne, IX). Petrol solutions of VIII or IX were obtained by the techniques adopted for preparing solutions of V or VI, namely, a large scale cleavage was allowed to proceed to completion whereupon a petrol concentrate was chromatographed to remove silanol leaving a pure solution of IX, or alternatively the reaction was quenched with acid when the intensity of the 324·5 nm band for VIII was maximal,* and a petrol concentrate containing VII, VIII, and IX was cleanly separated on alumina. Prolonged oxygenation of an acetone–petrol solution of VIII in the presence of Hay catalyst lead to development of a new principal max at 426·0 nm attributed to the hexadecaacetylene, $Et_3Si(C{\equiv}C)_{16}SiEt_3$ (X) on the basis of spectral correlations (*vide infra*). The percentage conversion remained small however and repeated chromatography failed to free X entirely from unreacted VIII. Similar difficulties, encountered previously in attempted oxidative coupling of longer terminal polyynes, were overcome using the Eglinton–Galbraith technique,[29] however it is doubtful whether the Si—C≡C bonds would stand up to the high concentrations of cupric ion and pyridine required for this alternative procedure.[10] Efforts to transfer X from acetone–petrol to MeOH were also unsuccessful owing to the not-unexpected extreme insolubility of X in the more polar solvent. The alkali cleavage of X could not therefore be studied. The preparative sequence leading to compounds IV → X is summarised in Chart 1 and spectral data are recorded in Table 2.

Preparation of $H(C{\equiv}C)_nH$ *compounds* ($n = 6, 12$)

In view of the anticipated instability of $Et_3Si(C{\equiv}C)_3H$ (XI) and difficulties encountered in preparing this compound directly from either $H(C{\equiv}C)_3Na$ or $H(C{\equiv}C)_3MgBr$† and Et_3SiBr, the bissilylhexatriyne, $Et_3Si(C{\equiv}C)_3SiEt_3$ (XII), was selected as the starting point for the cleavage—coupling sequence. The methyl analogue, $Me_3Si(C{\equiv}C)_3SiMe_3$, has been synthesized directly, albeit in low yield (5%) from $Na(C{\equiv}C)_3Na$ and excess of Me_3SiCl in liq. NH_3[20] however our efforts to prepare XII analogously were unsuccessful. A mixed Hay coupling was therefore conducted between I and III and the three resulting products, II, IV and XII were

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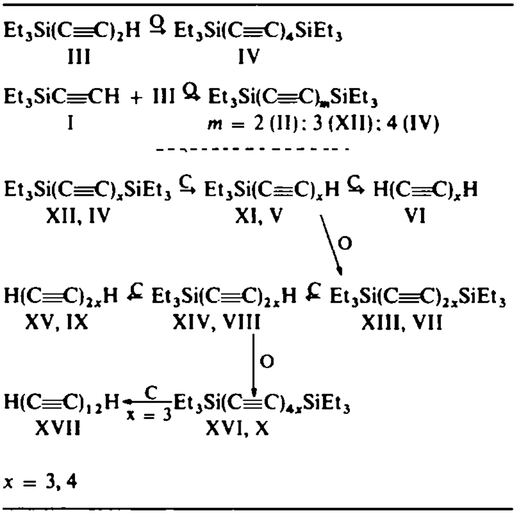
* Knowledge of the rate for conversion of VII to VIII which is exactly twice the rate for conversion of VIII to IX[27] allows this reaction time to be calculated exactly from series first-order rate equations.[30] After one half life (VII → VIII), the mixture contains unreacted VII (25%) together with VIII (50%) and IX (25%).

† Preparation of $H(C{\equiv}C)_3MgBr$ from EtMgBr and triacetylene, and its coupling with transition metal halides has been reported recently.[8] We thank Professor Hagihara for generously providing us with full experimental details in advance of publication. Our attempts to couple $H(C{\equiv}C)_3MgBr$ with Et_3SiBr have so far been unsuccessful (experiments by M. Ford).

separated by preparative GLPC without undue difficulty yielding pure III as a stable, low melting solid. This operation is obviously unattractive for large scale operations but appears to be the only available option at present.

CHART 1. PREPARATIVE SEQUENCES FOR $H(C\equiv C)_nH$ COMPOUNDS ($n = 4, 6, 8, 12$)



$Et_3Si(C\equiv C)_2H \xrightarrow{O} Et_3Si(C\equiv C)_4SiEt_3$
III IV

$Et_3SiC\equiv CH + III \xrightarrow{O} Et_3Si(C\equiv C)_mSiEt_3$
I $m = 2$ (II): 3 (XII): 4 (IV)

$Et_3Si(C\equiv C)_xSiEt_3 \xrightarrow{C} Et_3Si(C\equiv C)_xH \xrightarrow{C} H(C\equiv C)_xH$
XII, IV XI, V VI

$\xrightarrow{O}$

$H(C\equiv C)_{2x}H \xleftarrow{C} Et_3Si(C\equiv C)_{2x}H \xleftarrow{C} Et_3Si(C\equiv C)_{2x}SiEt_3$
XV, IX XIV, VIII XIII, VII

$\xrightarrow{O}$

$H(C\equiv C)_{12}H \xleftarrow[x=3]{C} Et_3Si(C\equiv C)_{4x}SiEt_3$
XVII XVI, X

$x = 3, 4$

O denotes oxidative coupling (Hay technique)
C denotes cleavage with aqueous methanolic alkali

Treatment of a MeOH solution of XII with aqueous alkali lead to disappearance of its max (230 nm in the mixed solvent), development of a new max at 216 nm ascribed to XI, then disappearance of this max. and appearance of a max for triacetylene at 281·0 nm. Repetition of the cleavage with acid quenching after the appropriate interval resulted in a solution containing XII together with XI and triacetylene. A petroleum extract of this mixture was chromatographically separated to give a pure solution of XI. Isolation of XI was not attempted: the solution was

TABLE 1. CONVERSION OF $Et_3Si(C\equiv C)_nSiEt_3$ COMPOUNDS TO THE PARENT POLYYNES $H(C\equiv C)_nH$ IN AQUEOUS MeOH AT 20°

n	[NaOH][a] M	λ[b] nm $Et_3Si(C\equiv C)_nSiEt_3$	$H(C\equiv C)_nH$	Reaction time (min)
4	3	256	225·5	30
5	3	278	250·5	30
6	1	298·5	273·5	63
7	1	317·5	295	63
9	1	349	331·5	44
10	1	365	348	44
12	1	388	375	44

[a] Strength of aqueous NaOH one drop of which was added to a MeOH solution (100 ml) of bissilylpolyyne.

[b] Principle absorption maxima of the bissilylpolyyne and parent polyyne in methanol solution.

diluted with acetone and oxidatively coupled to give bistriethylsilyldodecahexayne [XIII: λ_{max} 299·5 (hexane)]. In turn, a purified solution of XIII (not isolated) was completely cleaved according to the conditions stated in Table 1 to give dodecahexayne $H(C{\equiv}C)_6H$ [XV, λ_{max} 273·5 (MeOH)]. A controlled cleavage of XIII quenched by acidification resulted in a mixture of XIII, XIV and triethylsilyldodecahexayne $Et_3Si(C{\equiv}C)_6H$ [XIV; λ_{max} 287·0 (MeOH)] from which a pure petrol solution of XIV was obtained by extraction followed by chromatography. An acetone–petrol solution of XIV was then oxidatively coupled without difficulty to give bistriethylsilyltetracosadodecayne $Et_3Si(C{\equiv}C)_{12}SiEt_3$ [XVI: λ_{max} 390·0 (hexane)] and extraction of XVI into MeOH followed by alkali cleavage yielded dodecaacetylene $H(C{\equiv}C)_{12}H$ [XVII: λ_{max} 375·0 (MeOH)].

CHART 2. MIXED HAY OXIDATIVE COUPLINGS LEADING TO $H(C{\equiv}C)_nH$ COMPOUNDS (n = 5, 7, 9, 10)

$$\text{V} + \text{I (excess)} \xrightarrow{O} \text{II} + \text{VII} + \underset{\text{XVIII}}{Et_3Si(C{\equiv}C)_5SiEt_3} \xrightarrow{C} \underset{\text{XIX}}{H(C{\equiv}C)_5H}$$

$$\text{XIV} + \text{I (excess)} \xrightarrow{O} \text{II} + \text{XVI} + \underset{\text{XX}}{Et_3Si(C{\equiv}C)_7SiEt_3} \xrightarrow{C} \underset{\text{XXI}}{H(C{\equiv}C)_7H}$$

$$\text{VIII} + \text{I (excess)} \xrightarrow{O} \text{II} + \underset{\text{XXII}}{Et_3Si(C{\equiv}C)_9SiEt_3} \xrightarrow{C} \underset{\text{XXIII}}{H(C{\equiv}C)_9H}$$

$$\text{IX} + \text{III (excess)} \xrightarrow{O} \text{IV} + \underset{\text{XXIV}}{Et_3Si(C{\equiv}C)_{10}SiEt_3} \xrightarrow{C} \underset{\text{XXV}}{H(C{\equiv}C)_{10}H}$$

O denotes oxidative coupling
C denotes cleavage by aqueous methanolic alkali

Preparation of $H(C{\equiv}C)_nH$ *compounds* (n = 5, 7, 9, 10)

Access to the odd members of the series, n = 5, 7, 9 necessitated mixed Hay couplings which potentially suffer from the disadvantage that in each case three possible products may result. For the lowest member, n = 5, the combination V + I (excess) was selected for two reasons. Firstly, excess of the *less* reactive (least acidic component) minimises the chance of symmetrical coupling, V → VII, thus reducing the number of major products to two [II + required bistriethylsilyldecapentayne (XVIII)] and secondly, the products II, VII, and XVIII, differing from each other by three (or six) yne-units offers a better chance for clean chromatographic separation during the work-up than does the alternative combination: III + XI → IV + XVIII + XIII, which differ by two (or four) yne-units. In practice, V was coupled with a twelve-fold excess of I and upon chromatography, II eluted rapidly followed by XVIII [(λ_{max} 279 (hexane)] containing a trace (<5%) of VII. Treatment of a MeOH solution of XVIII with aqueous alkali (Table 1) resulted in a solution of $H(C{\equiv}C)_5H$ XIX [λ_{max} 250·5 (MeOH)] which could be entirely freed from IX (resulting from desilylation of VII) by chromatography.

Comparable criteria governed the combination choice, XIV + I (excess) for the preparation of the bissilyltetradecaheptayne (XX) [λ_{max} 319·0 (hexane)] which was obtained in intermediate chromatography fractions free from II and XVI (trace).

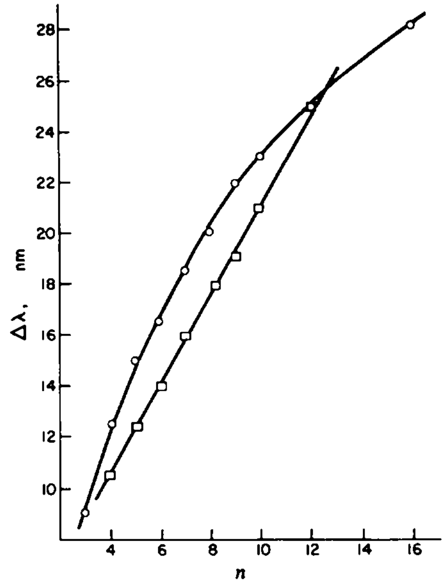


Fig 1. Plot of *n* vs Δλ (wavelength difference between the two highest (adjacent) intensity bands for $\mathrm{Et_3Si(C{\equiv}C)_nSiEt_3}$ (circles) or $\mathrm{H(C{\equiv}C)_nH}$ (squares) compounds.

Similarly, oxidative coupling of a mixture containing VIII and I (20—fold excess) gave, upon chromatography, II followed by the desired bissilyloctadecanonayne (XXII) [λ_{max} 350·5 (hexane)] essentially free of X which is not surprising in view of the extremely slow rate of symmetrical coupling: VIII → X. Alkali cleavage (*cf* Table 1) of XX and XXII then gave $\mathrm{H(C{\equiv}C)_7H}$(XXI) [$\lambda_{max}$ 295·0 (MeOH) and $\mathrm{H(C{\equiv}C)_9H}$ (XXIII) [λ_{max} 331·5 (MeOH)] respectively.

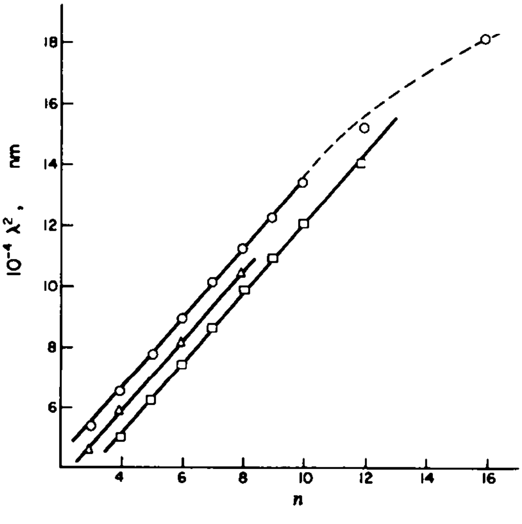


Fig 2. Plot of *n* vs λ^2 (highest intensity band) for $\mathrm{Et_3Si(C{\equiv}C)_nSiEt_3}$ (circles), $\mathrm{Et_3Si(C{\equiv}C)_nH}$ (triangles) or $\mathrm{H(C{\equiv}C)_nH}$ (squares) compounds.

Since insufficient XVIII was available to allow partial cleavage, separation of $Et_3Si(C{\equiv}C)_5H$ and oxidative coupling, the bissilyleicosadecayne $Et_3Si(C{\equiv}C)_{10}SiEt_3$ (XXIV) was prepared by a mixed coupling between VIII and III (30-fold excess), the product XXIV [λ_{max} 367·0 (hexane)] being easily separable from the detected by-product, IV, of symmetrical coupling, III → IV. Desilylation of XXIV (Table 1) gave the decaacetylene $H(C{\equiv}C)_{10}H$ [λ_{max} 348·0 (MeOH)].

UV absorption spectra. Polyacetylenes display a series of distinctive fine-structured electronic absorption bands the vibrational analysis of which is both challenging to the spectroscopist and diagnostically useful to the experimental chemist. Each set of the well established series, $Me(C{\equiv}C)_xMe$, t-$Bu(C{\equiv}C)_xBu$-t, $Ph(C{\equiv}C)_xPh$ and $Aryl(C{\equiv}C)_xAryl$* may be correlated by means of the Lewis–Calvin equation[31] (originally formulated and applied to polyenes) commonly written $\lambda^2 = kn$ (λ = wavelength of corresponding bands for polyynes containing n conjugated triple bonds) and by the empirical relationship $\Delta\lambda = k'n$ ($\Delta\lambda$ = average vibrational spacing of corresponding adjacent bands in each polyyne). (For a summary of previous work *cf* Ref 32).

A detailed knowledge of oscillator strengths is necessary for meaningful theoretical treatment and since our absorption intensity data for both silylated and higher parent polyynes is incomplete at this time, we confine our comments here to a brief consideration of wavelengths at which maxima occur and wavelength spacing correlations with emphasis on the characteristic high or ultra-high intensity bands detailed in Table 2. A selection of these spectra is depicted in Fig 3.

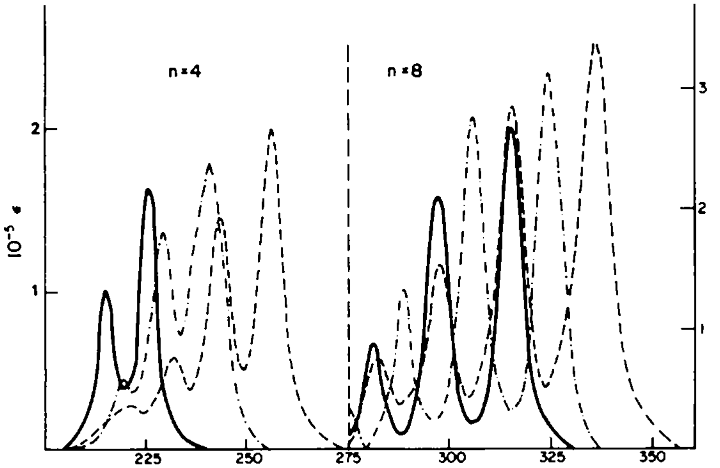


Fig 3. UV spectra (MeOH solution) of highest intensity bands for $Et_3Si(C{\equiv}C)_nSiEt_3$ (- - - - -), $Et_3Si(C{\equiv}C)_nH$ (-·-·-·-) and $H(C{\equiv}C)_nH$ (———) Compounds.

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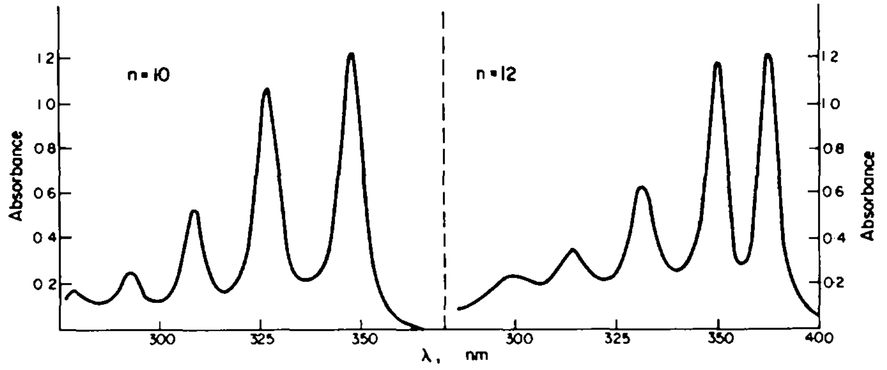
* The empirical correlation, $\lambda = An^* + B$ is preferred for certain polynuclear-substituted polyynes.[33]



$Et_3Si(C{\equiv}C)_nSiEt_3$ *compounds.* All spectra exhibit distinct solvent dependence with a small shift (1–2 nm) to longer wavelengths for all maxima in hexane as compared to MeOH. Bands are generally broader in the protic solvent and extinction coefficients are considerably greater in hexane [IV: λ_{max}, ε: 256 nm, 195000 (MeOH): 256·5 nm, 271000 (hexane)]. For the high intensity bands, the *average* vibrational spacing in either solvent, initially 2000 ± 90 cm^{-1} ($n = 4$–6), decreases with increase in chain length [1800 ± 100 cm^{-1} ($n = 10$)] and then to 1650 ± 40 cm^{-1} ($n = 16$). A comparable decrease is observed in the di-t-butylpolyyne series.[29] A regular indication of this trend is shown in a plot (Fig 1) of n versus the solvent-independent wavelength difference ($\Delta\lambda$) between the two most intense (adjacent) bands. Lewis–Calvin plots of λ^2 for corresponding maxima (MeOH or hexane) versus n are linear for $3 \leqslant n \leqslant 8$ but a regular deviation from each line is apparent for $n > 8$ as illustreated in Fig 2 for the most intense band. A similar deviation was observed previously for the α,ω-diphenylpolyynes.[34] The slope of the linear portion is 11·9 10^3 $(nm)^2$ per triple bond for the bissilylpolyynes which is close the value (11·7 10^3 $(nm)^2$/triple bond) observed for the bis-t-butylpolyynes.[3]

Some of the medium-to-low intensity bands at longer wavelengths were also recorded ($n = 2, 3, 4, 6$) and a Lewis–Calvin plot (not shown) of n versus the highest observed wavelength (λ^2) for these bands is also a good straight line with slope 28 10^3 $(nm)^2$/triple bond. The slope of the equivalent plot for the $Me(C{\equiv}C)_nMe$ series is 30 10^3 $(nm)^2$/triple bond.[4] These bands decrease in intensity and the average vibrational spacing [*viz* 2150 cm^{-1} ($n = 3$), 2050 cm^{-1} ($n = 4$), 1950 cm^{-1} ($n = 6$)] decreases as n increases.

Corresponding long wavelength bands for bissilylpolyynes ($n > 6$) were not recorded as the compounds proved to be difficult to handle at concentrations required to detect the bands and measure their extinction coefficients with any degree of reliability.

$H(C{\equiv}C)_nH$ *compounds.* The ultra-high intensity bands show a solvent dependence similar to that of their silylated precursors and, for those compounds whose extinction coefficients could be measured, a comparable intensity increase in going from MeOH to hexane.

The magnitude of the visible shift (MeOH or hexane) incurred by the presence of the two triethylsilyl groups steadily decreases as n increases: e.g. for the highest intensity band $\Delta\lambda$ = 30·5 nm ($n = 4$) and 13·0 nm ($n = 12$). This effect contrasts with

TABLE 2. UV SPECTRAL DATA FOR $Et_3Si(C{\equiv}C)_nSiEt_3$, $Et_3Si(C{\equiv}C)_nH$ AND $H(C{\equiv}C)_nH$ COMPOUNDS

Compound	Solvent[a]	λ_{max} (nm), log ε or relative intensity†
$Et_3Si(C{\equiv}C)_2SiEt_3$	m	279·5 (2·51), 271* (1·85), 263·5 (2·66), 249·5 (2·57), 236 (2·36)
II	h	280 (2·49), 271·5* (1·78), 264 (2·64), 250 (2·54), 237 (2·28)
$Et_3Si(C{\equiv}C)_3SiEt_3$ XII	m	332 (2·32), 329* (1·95), 320 (1·60), 310·5 (2·52), 307·5* (2·28), 300* (1·95), 291 (2·48), 288·5* (1·90), 282·5* (2·00), 274 (2·30), 270 (2·08), 230 (5·04), 221 (4·95), 211 (4·65)
	h	332 (2·26), 329* (1·95), 321* (1·60), 311 (2·49), 308* (2·23), 300* (1·95), 291·5 (2·42), 289* (2·23), 283* (2·00), 274·5 (2·20), 270 (2·08), 231·5 (5·11), 211 (4·99), 211·5 (4·64)
$Et_3Si(C{\equiv}C)_3H$	m	215
XI	h	216
$Et_3Si(C{\equiv}C)_4SiEt_3$ IV	m	375 (2·04), 369 (1·95), 361* (1·48), 348·5 (2·28), 344 (2·18), 336* (1·70), 325 (2·20), 321 (2·15), 314* (1·78), 256 (5·29), 243·5 (5·14), 232 (4·80), 221 (4·54)
	h	376 (2·04), 370 (1·95), 361* (1·30), 348·5 (2·26), 344·5 (2·18), 336* (1·60), 326 (2·18), 321·5 (2·15), 314* (1·60), 256·5 (5·43), 244 (5·27), 232 (4·82), 221·5 (4·32)
$Et_3Si(C{\equiv}C)_4H$	m	241 (5·27), 229·5 (5·18), 219·5 (4·79)
V	h	242·5, 230·5, 220·5
$H(C{\equiv}C)_4H$[b]	m	337·5, 316, 297·5, 281·5, 263,* 225·5 (5·25), 215 (5·06)
VI	h	226 (5·28), 215·5 (5·12)
$Et_3Si(C{\equiv}C)_5SiEt_3$	m	278, 263, 250·5, 238·5
XVIII	h	279, 263·5, 250·5, 238·5
$H(C{\equiv}C)_5H$[c]	m†	250·5 (1·0), 238 (0·7), 226 (0·33)
XIX	h	251·5, 239, 227·5
$Et_3Si(C{\equiv}C)_6SiEt_3$	m	298·5 (5·50), 282 (5·40), 267 (5·01), 253 (4·61), 240·5 (4·32)
XIII	h	299·5 (5·61), 282·5 (5·51), 267·5 (5·11), 254 (4·63), 242 (4·62)
$Et_3Si(C{\equiv}C)_6H$	m	287 (5·49), 270·5 (5·38), 256·5 (5·01), 244 (4·64), 233·5 (4·36)
XIV	h	288·5, 272·5, 257·5, 245, 234
$H(C{\equiv}C)_6H$	m	273·5 (5·47), 259·5 (5·38), 246·5 (4·49), 235 (4·69), 225 (4·51)
XV	h	275 (5·51), 260·5 (5·41), 247·5 (5·02), 236 (4·74), 225·5 (4·59)
$Et_3Si(C{\equiv}C)_7SiEt_3$	m	317·5 (1·00), 299 (0·85), 282 (0·47), 268 (0·17), 255 (0·10)
XX	h	319, 300, 283·5, 269, 256
$H(C{\equiv}C)_7H$	m†	295 (1·0), 279 (0·85), 264 (0·48), 252 (0·17), 236·5 (0·12)
XXI	h	297, 281, 266, 253, 237
$Et_3Si(C{\equiv}C)_8SiEt_3$	m	335 (5·52), 315 (5·47), 297·5 (5·18), 282 (4·75), 268·5 (4·32)
VII	h	336 (5·65), 316 (5·60), 298·5 (5·26), 283 (4·84), 269·5 (4·30)
$Et_3Si(C{\equiv}C)_8H$	m	324·5 (5·50), 306 (5·44), 289 (5·14), 274·5 (4·74), 261·5 (4·48)
VIII	h	327·5, 307·5, 290, 275·5, 262·5
$H(C{\equiv}C)_8H$	m	315 (5·48), 297 (5·36), 281 (5·01), 267 (4·60), 255 (4·30)
IX	h	316 (5·54), 298 (5·44), 281·5 (5·19), 268 (4·72), 255·5 (4·51)
$Et_3Si(C{\equiv}C)_9SiEt_3$	m	349, 328, 309·5, 294, 279
XXII	h	350·5, 330, 311·5, 295·5, 280
$H(C{\equiv}C)_9H$	m†	331·5 (1·0), 312·5 (0·88), 295 (0·44), 280 (0·21), 266·5 (0·11)
XXIII	h	331·5, 312·5, 296·5, 287·5, 267
$Et_3Si(C{\equiv}C)_{10}SiEt_3$	m†	365 (1·0), 341 (0·86), 321 (0·43), 304·5 (0·20), 289 (0·14)
XXIV	h	367, 343, 323, 306·5, 291·5
$H(C{\equiv}C)_{10}H$	m†	348 (1·0), 327 (0·86), 308·5 (0·43), 292·5 (0·20), 278 (0·14)
XXV	h	349, 328, 310, 294, 279·5
$Et_3Si(C{\equiv}C)_{12}SiEt_3$	m	388, 363, 342·5, 323, 307·5
XVI	h	390, 365, 343, 325, 309

TABLE 2—*continued*

Compound	Solvent[a]	λ_{max} (nm), log ε or relative intensity†
$H(C{\equiv}C)_{12}H$ XVII	m†	375 (1·0), 350 (0·95), 331 (0·49), 314 (0·24), 300 (0·16)
$Et_3Si(C{\equiv}C)_{16}SiEt_3$	p	426, 398, 374, 352

[a] MeOH (m): hexane (h): petrol (p)

[b] Lit[4] [λ_{max} (nm), log ε (pentane)]: 227 (5·45), 217, 207

[c] Lit[4] [λ_{max} (nm), pentane]†: 254 (1·83), 240 (1·65), 229 (1·0)

* Inflexion

† Relative Intensity (arbitrary scale)

the difference between the $H(C{\equiv}C)_nH$ and t-$Bu(C{\equiv}C)_nBu$-t series which remains fairly constant (14·7 ± 0·7 nm) for $4 \leqslant n \leqslant 10$.

For the intense bands again the average vibrational spacing for $H(C{\equiv}C)_nH$ compounds decreases as n increases; $\Delta v = 2170\ \text{cm}^{-1}$ $(n = 4) \rightarrow 1730 \pm 100\ \text{cm}^{-1}$ $(n = 12)$ and the Lewis–Calvin plot of n *vs* λ^2 for the band of highest intensity is an excellent straight line (Fig 2) whose slope (12·2 10^3 nm^2/triple bond in MeOH) is slightly greater than the slope for the $Et_3Si(C{\equiv}C)_nSiEt_3$ series.

Again, considerations of stability prevented accurate intensity assessments of the long wavelength bands for values of $n > 4$.

$Et_3Si(C{\equiv}C)_nH$ *compounds.* Because of isolation difficulties and quantities of bissilylpolyynes available, only those monosilylpolyynes $Et_3Si(C{\equiv}C)_nH$ (n = 2, 3, 4, 6, 8) were characterised which were needed for the synthesis of the higher polyynes. The visible shift and intensity increases arising from the presence of the single Et_3Si-group in these compounds is approximately half of the shift and intensity incremental difference between the parent and the bissilylpolyynes and a Lewis–Calvin plot for the first intensity band (MeOH) versus n was likewise linear with slope 11·8 10^3 (nm)^2 (Fig. 2).

This brief summary reflects the range and scope of correlations existing between the three series $Et_3Si(C{\equiv}C)_nSiEt_3$, $Et_3Si(C{\equiv}C_nH$ and $H(C{\equiv}C)_nH$ and allows band assignments for each compound to be made with confidence. A detailed spectral analysis will be published later.

EXPERIMENTAL

General precautions and procedures recommended by other workers for handling sensitive polyacetylenes were adopted.

AnalaR grade acetone, MeOH and CCl_4 were used and other solvents [EtOH and petrol (light petroleum, b.p. 40–60°)] were carefully scanned for interfering absorptions (e.g. CO) where appropriate

Proton NMR spectra were recorded on a Varian A60 instrument using 10% solutions in CCl_4 with TMS as internal standard. IR spectra were recorded on a Perkin-Elmer 257 instrument.

UV spectra which played a critical role in product characterization were scanned rapidly on a Unicam SP 800 spectrophotometer whereas maxima and extinction coefficients (*vide infra*) were measured accurately using matched 10 mm quartz cells in conjunction with a manually operated SP500 instrument. Full spectral details are given in Table 2 but wavelengths for diagnostic high or ultra-high intensity bands [hexane solution (BDH spectroscopic grade)] are also quoted for clarity and convenience in the discussion and in the experimental sections below.

Estimation of UV extinction coefficients (The following techniques were used)

(a) *Weighed residue method.* A freshly eluted petrol solution containing (*ca* 2·2 mg) of polyyne was concentrated under reduced pressure and a 5 ml aliquot was diluted (*ca* × 400) with hexane for UV measurements. Three further 5 ml aliquots were pipetted into clean dry tared flasks, solvent was removed by rotary evaporation and the flasks plus residues were dried to constant weight *in vacuo*. Average values for extinction coefficients were then calculated from the weights of residue.

(b) *Direct or correlated reading methods.* For stable compounds, $Et_3Si(C\equiv C)_{3,4}SiEt_3$, standard solutions were prepared and evaluated in the usual way. Extinction coefficients for the parent polyynes $H(C\equiv C)_nH$ (n = 3, 4, 6, 8) in MeOH were determined by treating solutions of the appropriate bissilyl precursor, $Et_3Si(C\equiv C)_nSiEt_3$, of known strength with aqueous NaOH (Table 1) and assuming cleavage to be quantitative. MeOH solutions of unstable $Et_3Si(C\equiv C)_nH$ (n = 4, 6, 8) compounds were likewise treated with alkali and coefficients were evaluated from known coefficients for $H(C\equiv C)_nH$ compounds. In order to obtain coefficients for the latter in hexane solution, identical aliquots of MeOH concentrates were diluted at least 100-fold with equal volumes of MeOH or hexane. Optical densities of both solutions were then compared and values of the coefficients in hexane calculated from the coefficients in MeOH previously determined.

Ethynyl(triethyl)silane $Et_3SiC\equiv CH$ (I). Et_3SiBr (175 g, 0·9 mole) was added during 15 min to a soln of $HC\equiv CMgBr$[23] (1·1 mole) in THF (500 ml) maintained at 0°. The reaction mixture was subsequently set aside at 20° for 12 hr, then poured onto aqueous 2N H_2SO_4. The H_2O layer was extracted with petrol (3 × 200 ml) and the combined organic phases were dried (Na_2SO_4) and distilled to give I (94 g, 75%) b.p. 53–55°/31 mm, n_D^{20} 1·4310 (lit.[35] b.p. 138°, n_D^{20} 1·4302). IR spectrum (film); $\nu_{C\equiv C-H}$ 3290 cm^{-1}; $\nu_{C\equiv C}$ 2030 cm^{-1}.

Butadiynyl(triethyl)silane $Et_3Si(C\equiv C)_2H$ (III). To $H(C\equiv C)_2MgBr$[23] prepared from EtMgBr (0·25 mole) and $H(C\equiv C)_2H$ (10 g, 0·2 mole) in THF (250 ml) was added Et_3SiBr (19·5 g, 0·1 mole). The mixture was set aside at 20° for 12 hr, then poured onto a slurry of ice and 2N H_2SO_4 and worked up as described for I to give III (10·2 g, 62% based upon Et_3SiBr used) b.p. 35–37°/0·4 mm, n_D^{20} 1·4790. (Found: C, 72·9; H, 10·0. $C_{10}H_{16}Si$ requires: C, 73·2; H, 9·8%). An ^1H NMR spectrum had the correct integration and showed resonances as follows: (τ =) $C\equiv C-H$ 8·00 (s) and $(C_2H_5)_3Si$ multiplet centred at 9·30. IR spectrum (film): $\nu_{C\equiv C-H}$ 3310 cm^{-1}; $\nu_{(C\equiv C)_2}$ 2190, 2140 cm^{-1}.

Preparation of Hay catalyst[25] *for oxidative couplings*

Freshly pptd. CuCl (*ca* 1·0 g) was added to a stirred mixture of TMEDA (0·5 ml) in acetone (20 ml). The resulting blue green suspension of CuCl:TMEDA complex in acetone was decanted from excess of CuCl, stored under N_2, and aliquots, referred to as Hay catalyst below, were used as required.

Synthesis of α-ω-bistriethylsilylpolyynes $Et_3Si(C\equiv C)_nSiEt_3$

1,4-Bistriethylsilylbutadiyne $Et_3Si(C\equiv C)_2SiEt_3$ (II). Hay catalyst (5 ml) was added to a stirred soln of I (14·0 g, 0·1 mole) in acetone (50 ml) and air was bubbled through the mixture for 6 hr. Aqueous 2N H_2SO_4 (150 ml) was then added and organic products were extracted with petrol (3 × 50 ml). The petrol extracts were dried and distilled to give II (12·0 g, 86%) b.p. 139–140°/0·4 mm, n_D^{20} 1·5040 (lit.[36] b.p. 136°/0·2 mm, n_D^{18} 1·5035). IR (film): $\nu_{(C\equiv C)_2}$ 2070 cm^{-1}.

1,6-Bistriethylsilylhexatriyne $Et_3Si(C\equiv C)_3SiEt_3$ (XII). Air was passed for 2 hr through a stirred mixture of Hay catalyst (5 ml), III (10·0 g, 0·06 mole) and I (8·4 g, 0·06 mole) in acetone (100 ml). The mixture was then poured onto an ice-2N H_2SO_4 slurry and organic products were extracted with petrol (3 × 100 ml). The petrol extracts were dried and concentrated by rotary evaporation and the residual pale brown oil (25 ml) was chromatographed on an activated alumina (DuPont: Grade H; column dimensions 150 × 50 mm) using petrol as eluent. Successive fractions (25 ml) which showed little or no absorption due to terminal $C\equiv C-H$ in the IR region (3300 cm^{-1}) were concentrated and submitted to preparative scale GLPC on a 7′ 20% SE 30 column at 250° (sample size, 100 μl; N_2 flow, 150 ml min^{-1}). Hexaethyldisiloxane eluted first (identified by R_T comparison with an authentic sample) followed successively by II and XII (205 mg) which crystallized as a white solid, m.p. 16·5–17·5°, in the receiver. (Found: C, 70·8; H, 10·2. $C_{18}H_{30}Si_2$ requires: C, 71·4; H, 10·0%). The identity of XII was confirmed by its principle UV absorption [216 nm (hexane)] and mass spectrum [m/e = 302. MW (calc) = 302]. IR (CCl_4): $\nu_{(C\equiv C)_3}$ 2160, 2170 cm^{-1}. The product discoloured upon prolonged storage in the dark at 0° but impurities could not be detected in such samples.

1,8-Bistriethylsilyloctatetrayne $Et_3Si(C\equiv C)_4SiEt_3$ (IV). The mixture obtained following passage of air for 1·5 hr through a soln of III (5·0 g, 0·032 mole) and Hay catalyst (15 ml) in acetone (100 ml) was poured onto aqueous 2N HCl. Organic products were extracted with ether (3 × 100 ml) and the ether extracts were dried and concentrated to give an oily residue which was dissolved in a minimum quantity of slightly acidified EtOH. This soln was set aside at -20° whereupon creamy-white crystals slowly formed. These were removed by filtration and recrystallized from acidified EtOH to give pure IV (4·0 g, 80%) m.p. 39·5–40°. (Found: C, 73·5; H, 9·5. $C_{20}H_{30}Si_2$ requires: C, 73·6; H, 9·3%). Principle UV absorption [256·5 nm (hexane)]; mass spectrum [m/e = 328 MW (calc) = 328]. IR (CCl_4): $\nu_{(C\equiv C)_4}$ 2180, 2045 cm^{-1}. In some preparations the initially obtained oil was purified by distillation (b.p. 120°/0·55 mm) without decomposition. Crystals of IV, obtained in yields of 70% in this way were always coloured, however UV spectral examination showed all samples to be sufficiently pure for routine work.

Partial cleavage of IV, *isolation of* $Et_3Si(C\equiv C)_4H$ (V) *and oxidative coupling to give* $Et_3Si(C\equiv C)_8SiEt_3$ (VII)

Triethylsilyloctatetrayne $Et_3Si(C\equiv C)_4H$ (V). Aqueous N NaOH (1·0 ml) was added to a magnetically stirred soln of IV (2·47 g, 7·0 mmole) in MeOH (500 ml) and hexane (5 ml) thermostatted at 21°. After 80 sec, the reaction was quenched by pouring the mixture onto a slurry of ice (200 g) and 2N HCl (200 ml) and petrol (200 ml). The organic layer was separated and the aqueous layer was extracted with petrol (2 × 100 ml) and the combined organic phases were dried (Na_2SO_4) concentrated by rotary evaporation (to ca. 25 ml) and chromatographed on alumina (300 × 15 mm column) using petrol as eluent. IV (λ_{max} 256·5) eluted first followed successively by V (λ_{max} 241) and octatetrayne VI (λ_{max} 226). [*Caution*! Preferential evaporation of petrol from the tip of the column at this stage may lead to a build up of VI which ignites spontaneously. This hazard may be avoided by shielding the column from draughts]. Yields of V estimated (spectrophotometrically) at 40% based upon IV consumed and VI produced.

1,16-*Bistriethylsilylhexadecaoctayne* $Et_3Si(C\equiv C)_8SiEt_3$ (VII). A petrol soln (500 ml) of V (0·97 mmole, estimated by UV spectroscopy) was concentrated to ca. 100 ml and diluted with acetone (500 ml). Hay catalyst (20 ml) was added and air passed through the mixture for 2 hr. Subsequent treatment with acidified ice and working up by the established procedure gave a petrol concentrate which was chromatographed on alumina (120 × 10 cm column) shielded from daylight by aluminium foil. Elution with petrol gave VII (λ_{max} 336, estimated spectroscopically) followed by fractions containing traces of $Et_3Si(C\equiv C)_8H$ (VIII) (λ_{max} 327·5) *vide infra*, and V. Concentration of the petrol fractions rich in VII below -30° at reduced pressure gave pure white crystals which discoloured and charred rapidly above -20°.

Partial cleavage of VII, *isolation of* $Et_3Si(C\equiv C)_8H$ (VIII) *and oxidative coupling to give* $Et_3Si(C\equiv C)_{16}SiEt_3$ (X)

Triethylsilylhexadecaoctayne $Et_3Si(C\equiv C)_8H$ (VIII). The procedure used for controlled cleavage of IV was modified as follows. A petrol soln of VII (0·32 mmole) was concentrated (to ca. 20 ml), then diluted with MeOH (200 ml) and thermostatted at 17°. Aqueous 0·1N NaOH (1·5 ml) was added, the mixture was then stirred magnetically for 0·75 min then immediately poured onto a slurry of ice (100 g), N H_2SO_4 (100 ml) and petrol (100 ml). The petrol layer was separated, combined with petrol extracts (2 × 150 ml) of the aqueous layer, then dried and concentrated under reduced pressure to ca. 50 ml. At this point the mixture darkened so it was quickly cooled to -20° and aliquots were transferred to a foil-protected alumina column (100 × 10 mm). Elution with petrol gave recovered VII followed successively by fractions containing pure VIII (λ_{max} 327·5) and pure hexadecaoctayne. $H(C\equiv C)_8H$ IX (λ_{max} 316) (Estimated yield of VIII = 36%).

1,32-*Bistriethylsilyldotriacontahexadecayne* $Et_3Si(C\equiv C)_{16}SiEt_3$ (X). A freshly eluted petrol solution of VIII (ca. 1·0 mmole) was concentrated and diluted with acetone (100 ml). Hay catalyst (20 ml) was added and air was bubbled through the mixture for 30 min. Working up in the established manner culminating in chromatography of the concentrated extracts using petrol as eluent gave solns of $Et_3Si(C\equiv C)_{16}SiEt_3$ (λ_{max} 426) contaminated with VIII. Repeated chromatography both on alumina and silica gel did not improve the separation.

Attempts to render the coupling more efficient by passage of pure O_2 instead of air through the mixture for up to 24 hr with or without intermittant addition of further aliquots of Hay catalyst did not significantly improve the yield of X.

Partial cleavage of XII, *isolation of* $Et_3Si(C\equiv C)_3H$ (XI) *and oxidative coupling to give* $Et_3Si(C\equiv C)_6SiEt_3$ (XIII)

Triethylsilylhexatriyne $Et_3Si(C\equiv C)_3H$ (XI). Aqueous 0·01M NaOH (2·5 ml) was added to a soln of XII (0·1 g) in MeOH (25 ml) thermostatted at 20° and after 5 min the mixture was acidified and extracted with petrol (50 ml). The organic phase was combined with petrol extracts of the aqueous layer and the extracts were dried, reduced in volume by evaporation and the resulting concentrate was chromatographed on alumina (80 × 15 mm column) to give, upon elution with petrol, a forerun of XII followed successively by XI (λ_{max} 216) and triacetylene (λ_{max} 281).

1,12-*Bistriethylsilyldodecahexayne* $Et_3Si(C\equiv C)_6SiEt_3$ (XIII). A petrol soln (100 ml) containing XI (0·15 mmole) was reduced in volume (to ca. 20 ml) under reduced pressure. The concentrate was diluted with acetone (100 ml), Hay catalyst (10 ml) was added and air was bubbled through the mixture for 2 hr. The mixture was subsequently acidified, polyyne products were extracted into petrol and the petrol layer, after drying, was reconcentrated and chromatographed on a foil-protected column (100 × 15 mm) to give a pure petrol soln of XIII (λ_{max} 299·5). Upon concentration under reduced pressure the solution darkened. All the solvent was therefore removed by evaporation at −20° to leave a dark solid which rapidly blackened upon warming to 20°.

Partial cleavage of XIII, *isolation of* $Et_3Si(C\equiv C)_6H$ (XIV) *and oxidative coupling to give* $Et_3Si(C\equiv C)_{12}SiEt_3$ (XVI)

1,12-*Triethylsilyldodecahexayne*, $Et_3Si(C\equiv C)_6H$ (XIV). A 10 ml petrol concentrate of XIII (0·5 mmole) was dissolved in MeOH (500 ml). The solution was thermostatted at 19° and aqueous N NaOH (1 ml) was added with stirring. After 4 min the mixture was acidified and extracted with petrol (200 ml). The extracts were dried, then concentrated (to 25 ml) and the concentrate chromatographed (100 × 15 mm column). Elution with 10% ether–petrol gave unreacted XIII (λ_{max} 299·5) followed successively by XIV (λ_{max} 288·5) and by dodecahexayne $H(C\equiv C)_6H$ (λ_{max} 275) *vide infra*.

1,24-*Bistriethylsilyltetracosadodecayne* $Et_3Si(C\equiv C)_{12}SiEt_3$ (XVI). To a fresh eluted petrol solution containing XIV was added Hay catalyst and pure oxygen was bubbled through the solution for 5 hr. The mixture was then acidified and extracted with petrol and chromatography of the dried extracts (100 × 15 mm foil-protected column) gave initial fractions containing pure XVI (λ_{max} 390) followed by unreacted XIV.

Mixed couplings leading to $Et_3Si(C\equiv C)_nSiEt_3$ *compounds* (n = 5, 7, 9, 10)

1,10-*Bistriethylsilyldecapentayne* $Et_3Si(C\equiv C)_5SiEt_3$ (XVIII). A soln of V (0·025 mmole) in petrol (500 ml) was concentrated (to ca. 100 ml) and diluted with an equal vol of acetone, then I (0·30 mmole) and Hay catalyst (10 ml) were added successively. Following passage of air for 1 hr, the mixture was acidified, worked up and chromatographed (100 × 15 mm column) in the usual way. Elution with petrol gave II followed by XVIII (λ_{max} 279) contaminated with traces of VII followed by a main fraction of VII.

1,14-*Bistriethylsilyltetradecaheptayne*. $Et_3Si(C\equiv C)_7SiEt_3$ (XX). To a freshly chromatographed petrol soln of XIV (0·1 mmole) diluted with acetone was added I (2·0 mmole) followed by Hay catalyst (5 ml) and air was bubbled through the mixture for 1 hr. Acidification and working up with chromatography (100 × 15 cm column) and elution with petrol gave initial fractions containing II (trace) followed successively by XX (λ_{max} 319) and XVI also in trace amounts.

1,18-*Bistriethylsilyloctadecanonayne*. $Et_3Si(C\equiv C)_9SiEt_3$ (XXII). Air was bubbled for 1 hr through a mixture of VIII (0·05 mmole), I (1·1 mmole) and Hay catalyst (5 ml) in acetone (50 ml) and petrol (10 ml). Following the established working up procedure, chromatography (100 × 15 cm column) of concentrated petrol extract gave initial fractions containing II followed by XXII (λ_{max} 350·5).

1,20-*Bistriethylsilyleicosadecayne*. $Et_3Si(C\equiv C)_{10}SiEt_3$ (XXIV). A petrol concentrate (5 ml) of VIII (0·005 mmole) and III (1·6 mmole) was coupled in acetone soln (50 ml) in the presence of Hay catalyst (5 ml) with passage of air for 1 hr. Working up with petrol elution from a 100 × 15 mm column gave IV followed by XXIV (λ_{max} 367 nm).

Preparation of the parent polyynes $H(C\equiv C)_nH$

Hexadecaoctayne $H(C\equiv C)_8H$ (IX). A freshly eluted petrol soln of VII (*ca* 0·1 mmole) was concentrated (to *ca* 20 ml) and diluted with MeOH (100 ml). This soln was reconcentrated (to 50 ml), diluted with an equal vol of MeOH, then thermostatted at 20° and aqueous N NaOH (one drop) was added. Progress of the reaction was monitored by following the decrease in principal absorption band of VII (λ_{max} 335) and development of the max for IX at 315 nm. After 44 min when cleavage was judged to be complete, 2N HCl (one drop) was added followed by hexane (100 ml) and a further quantity (10 ml) of 2N acid and water (10 ml). Following vigorous shaking the hexane layer was separated and dried (Na_2SO_4) then concentrated (to 20 ml) and the concentrate chromatographed on alumina (100 × 15 cm column). Elution with hexane gave initial fractions containing Et_3SiOH and $(Et_3Si)_2O$ followed by pure IX. Details of other polyynes $H(C{\equiv}C)_nH$ prepared analogously are given in Table 1.

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REFERENCES

[1] Paper presented at the International Symposium on Acetylenes and Allenes, Nottingham, July 1971. For a preliminary account of part of this work cf. R. Eastmond and D. R. M. Walton, *Chem. Commun.* 204 (1968)

[2] J. B. Armitage, E. R. H. Jones and M. C. Whiting, *J. Chem. Soc.* 44 (1951)

[3] F. Bohlmann, *Chem. Ber.* **84**, 785 (1951): J. B. Armitage, C. L. Cook, E. R. H. Jones and M. C. Whiting, *J. Chem. Soc.* 2010 (1952)

[4] C. L. Cook, E. R. H. Jones and M. C. Whiting, *Ibid.* 2883 (1952)

[5] H. Niki and B. Weinstock, *J. Chem. Phys.* **45**, 3468 (1966)

[6] W. Hunsmann, *Chem. Ber.* **83**, 213 (1950)

[7] A. Roedig, G. Voss and E. Kuchinke, *Liebigs Ann.* **580**, 24 (1953)

[8] P. J. Kim, H. Masai, K. Sonogashira and N. Hagihara, *Inorg. Nucl. Chem. Lett.* **6**, 181 (1970)

[9] A. T. Glen, S. A. Hutchinson and N. J. McCorkindale, *Tetrahedron Letters* 4223 (1966)

[10] G. Eglinton and W. McCrae, *Adv. Org. Chem.* **4**, 225 (1963)

[11] P. Cadiot and W. Chodkiewicz in *Chemistry of Acetylenes* (Edited by H-G. Viehe) pp. 597–647: Marcel Dekker, New York (1969)

[12] F. Strauss, L. Kolleck and H. Hauptmann, *Chem. Ber.* **63**, 1886 (1930)

[13] V. V. Korshak, V. I. Kastochkin, A. M. Sladkov, Yu. P. Kudryartsov and K. Usenbaev, *Dokl. Akad. Nauk SSSR* **136**, 1342 (1961): V. I. Kastochkin, A. M. Sladkov, Yu. P. Kudryavtsev, N. M. Popov and V. V. Korshak, *Dokl. Akad. Nauk SSSR* **177**, 358 (1967)

[14] F. Bohlmann, W. Sucrow and I. Queck, *Chem. Ber.* **97**, 2586 (1964)

[15] A. v. Baeyer, *Ibid.* **18**, 674, 2269 (1885)

[16] H. E. Zimmerman and J. R. Dodd, *J. Am. Chem. Soc.* **92**, 6507 (1970)

[17] M. S. Shvartsberg, I. L. Kotlyarevsky, A. N. Kodzebnikova and V. N. Andrievsky, *Izv. Akad. Nauk SSSR, Ser. Khim.* 1144 (1970): L. Brandsma, *Preparative Acetylenic Chemistry* pp. 155–156: Elsevier, Amsterdam (1971)

[18] C. Eaborn and D. R. M. Walton, *J. Organometal. Chem.* **4**, 217 (1965)

[19] C. Eaborn, G. A. Skinner and D. R. M. Walton, *J. Chem. Soc.* (B), 922 (1966)

[20] For a summary cf. H. Bock and H. Seidl, *Ibid.* (B), 1158 (1968)

[21] F. Bohlmann, *Chem. Ber.* **86**, 657 (1953): *Angew. Chem.* **65**, 385 (1953)

[22] D. R. M. Walton and F. Waugh, *J. Organometal. Chem.* **37**, 45 (1972)

[23] E. R. H. Jones, L. Skattebol and M. C. Whiting, *J. Chem. Soc.* 4765 (1956)

[24] U. Krüerke, *J. Organometal. Chem.* **21**, 83 (1970)

[25] A. S. Hay, *J. Org. Chem.* **27**, 3320 (1962)

[26] F. Bohlmann, *Chem. Ber.* **88**, 1017 (1955)

[27] R. Eastmond, T. R. Johnson and D. R. M. Walton, *J. Organometal. Chem.* (1972) in press.

[28] C. Eaborn, G. A. Skinner and D. R. M. Walton, *Ibid.* **6**, 438 (1966)

[29] E. R. H. Jones, H. H. Lee and M. C. Whiting, *J. Chem. Soc.* 3483 (1960)

[30] A. A. Frost and R. G. Pearson, *Kinetics and Mechanism* (2nd Edn), pp. 166–169; Wiley, New York (1962)

[31] G. N. Lewis and M. Calvin, *Chem. Revs.* **26**, 237 (1939)

[32] J. Dale in Ref. 11, Ch. 1

[33] S. Akiyama and M. Nakagawa, *Bull. Chem. Soc. Japan* **44**, 2237 (1971) and Refs cited

[34] J. B. Armitage, N. Entwhistle, E. R. H. Jones and M. C. Whiting, *Ibid.* 147 (1954)

[35] A. D. Petrov, L. L. Shchukovskaya and Yu. P. Egorov, *Dokl. Akad. Nauk SSSR* **93**, 293 (1953): *Chem. Abstr.* **48**, 13616 (1954)

[36] I. A. Shikhiev, M. F. Shostakovskii and L. A. Kayutenko, *Dokl. Akad. Nauk Azerb. SSR* **15**, 21 (1959); *Chem. Abstr.* **53**, 15957 (1959)