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SILYLATION AS A PROTECTIVE METHOD IN ACETYLENE CHEMISTRY

POLYYNE CHAIN EXTENSIONS USING THE REAGENTS, $Et_3Si(C{\equiv}C)_mH$ ($m = 1,2,4$) IN MIXED OXIDATIVE COUPLINGS

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Abstract. The reagents, $Et_3Si(C{\equiv}C)_mH$ ($m = 1,2,4$), employed as one component in mixed oxidative couplings (Hay technique), allow extension of terminal polyyne chains by up to four yne-units in a single step, thereby providing competitive and moderately efficient alternatives to older polyacetylene syntheses founded upon elimination processes. The following examples illustrate the method: (R = Mesityl) $R(C{\equiv}C)_2H$ (IV) + $Et_3SiC{\equiv}CH$ (excess) $\rightarrow$ $R(C{\equiv}C)_3SiEt_3$ (VI); IV + $Et_3Si(C{\equiv}C)_2H \rightarrow R(C{\equiv}C)_4SiEt_3$ (IX); $Et_3SiC{\equiv}CH + R(C{\equiv}C)_4H$ [X, prepared by base-catalysed cleavage (desilylation) of IX] $\rightarrow$ $R(C{\equiv}C)_5SiEt_3$ (XII). Likewise, $PhC{\equiv}CH + Et_3Si(C{\equiv}C)_4H \rightarrow Ph(C{\equiv}C)_5SiEt_3$ (XV); t-$BuC{\equiv}CH$ (XVIII) + $Et_3Si(C{\equiv}C)_4H \rightarrow$ t-$Bu(C{\equiv}C)_5SiEt_3$ (XX) and t-$Bu(C{\equiv}C)_2H$ (XIX) + $Et_3Si(C{\equiv}C)_4H \rightarrow$ t-$Bu(C{\equiv}C)_6SiEt_3$ (XXIII). Quantitative desilylation of VI, XV, XX and XXIII yield $R(C{\equiv}C)_3H$ (VII), $Ph(C{\equiv}C)_5H$ (XVI), t-$Bu(C{\equiv}C)_5H$ (XXI) and t-$Bu(C{\equiv}C)_6H$ (XXIV) which, in addition to X, may be separately coupled by the Hay or Eglington-Galbraith procedures to give $R(C{\equiv}C)_6R$ (VIII), $Ph(C{\equiv}C)_{10}Ph$ (XVII), t-$Bu(C{\equiv}C)_{10}Bu$-t (XXII), t-$Bu(C{\equiv}C)_{12}Bu$-t (XXV) and $R(C{\equiv}C)_8R$ (XI) respectively. $R(C{\equiv}C)_5H$ (XIII) prepared by desilylation of XII, cannot be oxidatively coupled by these techniques. Provided excess of silyl reagent is used, the method compares favourably with Cadiot-Chodkiewicz syntheses for lower polyynes (e.g. IV + $BrC{\equiv}CSiEt_3 \rightarrow$ VI) and is superior when longer polyyne chains are desired. The UV spectra of the products are correlated by means of relationships, λ^2 or $\Delta\lambda$ vs n (number of conjugated polyyne units) previously established for polyacetylenes.

INTRODUCTION

THE rapid progress in naturally-occurring polyacetylene chemistry over the past decade was preceded by a period of intense synthetic activity during the course of which three fully conjugated systems were prepared:

$Me(C{\equiv}C)_nMe$	$n = 2 - 6$	(ref 1)
$Ph(C{\equiv}C)_nPh$	$n = 2 - 6, 8$	(refs 2, 3)
t-$Bu(C{\equiv}C)_nBu$-t	$n = 2 - 8, 10$	(refs 4, 5)

Modes of synthesis for the higher members of each series, subsequently employed for other bisarylpolyynes,[6] consisted for the most part of couplings between an aldehyde and an acetylene Grignard reagent, conversion of the resulting glycol to its chloride followed by dehydrohalogenation to give either an internal or terminal polyyne, the latter being oxidatively coupled to yield a higher internal polyyne.

The advent of a variety of protective groups for terminal alkynes[7] provide for an alternative approach based upon well-established oxidative coupling methods[8] in

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which acetylene chains may be built up in stepwise fashion, the often troublesome dehydrohalogenation stage being thus avoided. We have found trialkylsilyl groups to be of particular value in this context allowing construction, for example, of the parent polyynes, $H(C{\equiv}C)_nH$, in solution, containing up to twelve conjugated triple bonds,[9] via symmetrical or mixed Glaser couplings (Hay modification: e.g. eqn. 1) and also of aryl-butadiynes and -hexatriynes[10] by a two-step procedure based upon the Cadiot–Chodkiewicz reaction (eqn. 2)

$$Et_3Si(C{\equiv}C)_xH + H(C{\equiv}C)_ySiEt_3 \rightarrow Et_3Si(C{\equiv}C)_{x+y}SiEt_3 \rightarrow H(C{\equiv}C)_{x+y}H \quad (1)$$

$$Ar(C{\equiv}C)_xH + BrC{\equiv}CSiEt_3 \rightarrow Ar(C{\equiv}C)_{x+1}SiEt_3 \rightarrow Ar(C{\equiv}C)_{x+1}H \quad (2)$$

In this paper, we assess the relative merits of these two coupling methods as a means of extending longer polyyne chains.

RESULTS AND DISCUSSION

Choice of end groups, R, *in* $R(C{\equiv}C)_nR$ ($n \geqslant 8$)

As discovered by previous workers,[1–5] the stability of long-chain polyynes is profoundly influenced by the nature of the end groups, R. For practical purposes the limit in the methyl series (R = Me) is reached when n = 6, whereas the phenyl (R = Ph) and t-butyl (R = t-Bu) analogues possess greater stability. We have sought therefore to extend the last two series and, with a combination of stabilization factors in mind, to synthesize a range of bismesitylpolyynes, $Mes(C{\equiv}C)_nMes$.*

Synthesis of the mesityl series (n = 2, 4, 6, 8)

1,4-*Bismesitylbutadiyne* (II). In order to prepare the first member of the series (n = 2), ethynylmesitylene (I), synthesized according to the literature instructions[11] and purified via its silver derivative,[12] was oxidatively coupled using the Hay procedure[13] which requires passage of air through an acetone solution of I in the presence of a CuCl:TMEDA complex. The yield (42%) of II was lower than is normally the case for such couplings and may arise from insolubility of the organocopper intermediate or from difficulty encountered with its formation (the two flanking *ortho*-Me groups may well hinder π-complexation with copper: *vide infra*).

1,8-*Bismesityloctatetrayne* (V). When the Cadiot–Chodkiewicz procedure, used to couple a range of arylactylenes with the reagent, $BrC{\equiv}CSiEt_3$,[10] (eqn. 2) was applied to coupling of I, the yield (14%) of desired product, $Mes(C{\equiv}C)_2SiEt_3$ (III), was disappointingly low. Modifications to the reaction conditions, e.g. use of anhydrous deoxygenated reactants and solvents, increase in Cu(I) content and a longer reaction time, merely resulted in a diminished yield of III. These facts also partly argue for difficulty in copper complex formation. Batches of III which were obtained in this way, upon treatment with aqueous methanolic alkali[10, 14] gave a quantitative yield of mesityldiacetylene (IV) (estimated by UV spectroscopy[10]). Further batches of IV, required for extension of the mesityl series, were prepared from acetoacetylmesitylene via chlorination (PCl_5) followed by dehydrohalogenation with sodamide,[15] the overall yield (45%) of IV (obtained as white needles which darkened rapidly at room temp.) clearly making this route the method of choice. Oxidative coupling of IV by the Hay procedure gave V as yellow crystals, m.p. 230–231°.

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* Mes = $1,3,5\text{-}Me_3C_6H_2$

1,12-*Bismesityldodecahexayne* (VIII). In spite of the difficulties encountered in coupling $BrC{\equiv}CSiEt_3$ with I, a Cadiot–Chodkiewicz reaction between IV and $BrC{\equiv}CSiEt_3$ was comparatively successful and gave 1-mesityl-6-triethylsilylhexatriyne (VI) in 36% yield. As an alternative route to VI, a mixed Hay coupling was conducted between IV and the readily available silane, $Et_3SiC{\equiv}CH$.[9] Normally such couplings are regarded as inefficient since, in principle, three products may ensue as a result of competing symmetrical couplings: in this case giving rise to I and the bissilylbutadiyne, $Et_3Si(C{\equiv}C)_2SiEt_3$. Production of one component, V, was minimised by using excess of (expendable) $Et_3SiC{\equiv}CH$ (a device used previously by us for preparing bissilylpolyynes containing an odd number of triple bonds[9]) and any V formed, which is relatively insoluble, was removed entirely from the crude products of reaction simply by filtration. The desired product, VI, and unwanted $Et_3Si(C{\equiv}C)_2SiEt_3$, were easily separated by column chromatography, the overall yield (30%) of VI comparing favourably with that obtained by the Cadiot–Chodkiewicz procedure. Desilylation of VI and oxidative coupling of the resulting terminal triyne (VII) (not isolated), afforded VIII as yellow needles (dec. > 170°).

1,16-*Bismesitylhexadecaoctayne* (XI). Several attempts were made to couple VII with $BrC{\equiv}CSiEt_3$. All were unsuccessful despite operation within or above the minimum temperature range, 30–40°, recommended for triyne couplings in the Cadiot–Chodkiewicz reaction,[8] furthermore UV spectral monitoring of the reaction mixture at intervals revealed a steady decline in absorptions due to VII. Presumably thermal decomposition of unprotected VII took place at the reaction temperature which may account for the substantial quantity of red tar eluted during the chromatographic work up procedure (*cf* Exptl. section).

A mixed Hay coupling between IV and excess of the silylbutadiyne, $Et_3Si(C{\equiv}C)_2H$,[9] gave more satisfactory results. Traces of relatively insoluble V were easily removed by filtration from the oily product mixture and the required component, 1-mesityl-8-triethylsilyloctatetrayne (IX), was obtained as a stable crystalline solid in 30% yield after chromatographic separation from the unwanted by-product, $Et_3Si(C{\equiv}C)_4SiEt_3$,[9] formed by self-coupling of $Et_3Si(C{\equiv}C)_2H$. The free mesityloctatetrayne (X), liberated by treatment of IX with aqueous methanolic alkali, was not isolated but was oxidatively coupled directly to give XI (25% yield), obtained as dark red needles (dec. >150°).

Attempted synthesis of 1,20-*bismesityleicosadecayne* (XIV)

Since it seemed unlikely that a Cadiot–Chodkiewicz coupling would lead to $Mesityl(C{\equiv}C)_5SiEt_3$ (XII), the essential precursor for XIV, a mixed Hay coupling was conducted between X and excess of $Et_3SiC{\equiv}CH$. Traces of insoluble XI were filtered from the oily product concentrates and the filtrate, containing XII together with $Et_3Si(C{\equiv}C)_2SiEt_3$, was separated by column chromatography. The silylated mesitylpentaacetylene (XII) was found to be surprisingly unstable and underwent rapid decomposition upon attempted isolation at room temperature. Solutions of XII were sufficiently stable however and, upon treatment with base according to the procedure established for the lower members of the series, gave mesityldecapentayne (XIII). Attempts to couple XIII by the Hay technique were uniformly unsuccessful even upon prolonged oxygenation. In every case a thick precipitate, presumably the cuprous derivative of XIII, formed so that the homogeneous conditions, characteristic of the Hay method, were not attained. Similar behaviour has been observed previously for other long chain terminal polyynes in Glaser type couplings[5] and the problem overcome employing the Eglinton–Galbraith method, i.e. coupling in pyridine solution in the presence of cupric acetate. Use of this technique for XIII did not yield better results however, and attempts to prepare XIV were therefore abandoned.

General and spectral properties of the mesitylpolyynes

Of the precursor series, the terminal mesitylpolyynes (IV, VII, X) proved to be thermally less stable than their silyl derivatives (III, VI, IX) for like values of n, an order of stability usually found for terminal as compared to internal polyacetylenes. The bismesitylpolyynes (II, V, VIII and XI), whose stabilities were clearly greater than those of their bisphenyl analogues (*cf* Table 1), were obtained as highly crystalline substances whose insolubility in common organic solvents increased with increasing chain length. Elemental analyses for the higher members of the series were unsatisfactory, the carbon percentages always being lower than required. Since a linear modification of carbon is known to be thermally stable to 2300° before conversion to graphite[16] this analytical result is perhaps not surprising. Quantitative semimicro scale catalytic hydrogenations of the polyyne units gave good results however and the αω-bismesitylalkanes so prepared analysed correctly for both carbon and hydrogen.

The UV spectra of the four silylated mesitylpolyynes (MeOH solution) exhibit a series of definitive bands at long wavelength accompanied by more intense absorptions at shorter wavelength somewhat lacking in vibrational fine structure. The intensities at longer wavelength increase as n increases whilst the reverse is true for the shorter wavelength bands. Comparison with the spectrum reported for the compound $Ph(C{\equiv}C)_3SiEt_3$[10] reveals little difference in the bands at longer wavelength save that the maximum tends to be broader, whereas the bands at shorter wavelengths are relatively less intense and broader in the mesityl analogue (VI). The Et_3Si-groups cause a visible shift with accompanying intensity increase in all bands relative to the terminal mesitylpolyynes, $Mes(C{\equiv}C)_nH$, as illustrated for compounds IX and X in Fig 1. The magnitude of this shift decreases as n increases as exemplified by the band at longest wavelength: viz. $n = 2$, $\Delta\lambda = 14$ nm; $n = 5$, $\Delta\lambda = 8$ nm. A Lewis–Calvin plot[17] of the square of the longest wavelength absorption versus n

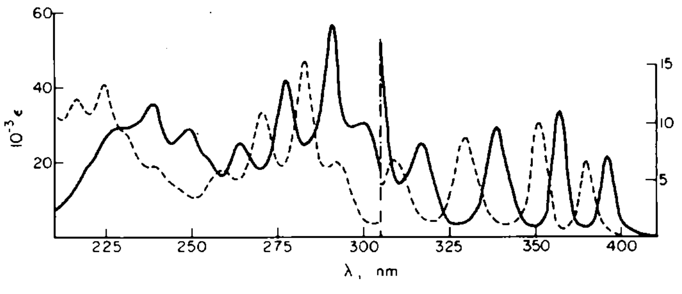

FIG 1. UV spectrum (MeOH solutions) of $Mes(C{\equiv}C)_4SiEt_3$(———) and $Mes(C{\equiv}C)_4H$ (- - - -)

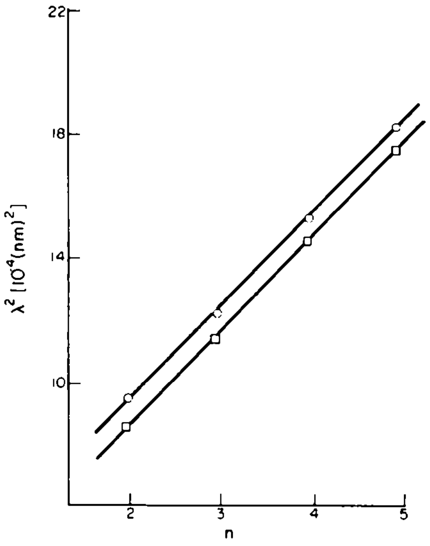

FIG 2. Lewis Calvin plot of λ^2 *vs* n for the longest wavelength band in Mes$(C{\equiv}C)_nSiEt_3$ (circles) and Mes$(C{\equiv}C)_nH$ (squares) (MeOH solution)

within each series is a straight line (Fig 2) with slope 29 × 10^3 and 30 × 10^3 (nm)^2/triple bond for the silylated and terminal mesitylpolyynes respectively. These values compare favourably with those observed in similar λ^2 vs. n plots for the equivalent low intensity bands in the bissilylpolyynes (28 × 10^3 (nm)^2/triple bond)[9] and in the Me$(C{\equiv}C)_n$Me series (30 × 10^3 (nm)^2/triple bond).[1]

The UV spectra of the bismesitylpolyynes similarly exhibit two regions of absorption (e.g. Fig 3) as do the bisphenylpolyynes,[3] the bands at longer wavelength possessing a more regular fine structure and declining in intensity as n increases. The higher intensity bands at lower wavelengths are somewhat more intense than the corresponding bands for the bisphenyl series but the fine structure is not as regular as is observed in both the aliphatic[1,4,5] and silylated[9] polyynes. A Lewis–Calvin plot λ^2 vs. n (Fig. 4) for the longest wavelength observed band is a good straight line

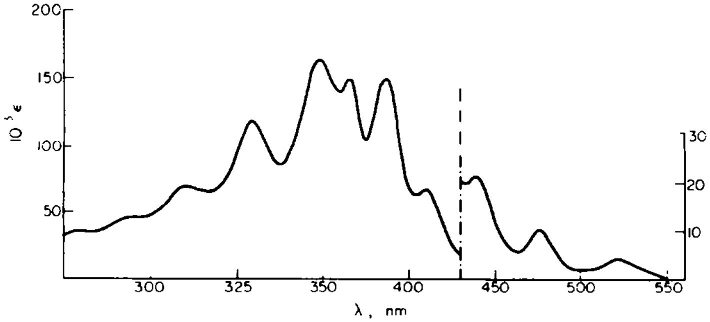

FIG 3. UV spectrum of Mes$(C{\equiv}C)_8$Mes ($CHCl_3$ solution)

of slope 26·5 × 10^3 $(nm)^2$/triple bond [compare 28 × 10^3 $(nm)^2$/triple bond for the $Ph(C{\equiv}C)_nPh$ series]. The first band of the high intensity region is often difficult to locate in the bisarylpolyynes,[3] however a similar plot for this band (Fig 4) has a slope ca. 16 × 10^3 $(nm)^2$/triple bond (compare 15 × 10^3 $(nm)^2$/triple bond for the $Ph(C{\equiv}C)_nPh$ series).

Full details of absolute or relative absorption intensities (where measured) are given in Table 2 for compounds II → XIII.

Synthesis and properties of 1,20-*bisphenyleicosadecayne* (XVII)

The model syntheses for extending longer polyyne chains in the mesityl series establish the superiority of the mixed Hay method which possesses the added advantage, as demonstrated by the preparation of IX, that more than one triple bond may be added to a polyyne chain in a single step.*

In order to develop this approach and, at the same time, to extend the range of known bisphenylpolyynes, a mixed coupling was conducted between phenylacetylene and excess of the silyltetrayne, $Et_3Si(C{\equiv}C)_4H$, solutions of which are readily prepared by controlled cleavage of $Et_3Si(C{\equiv}C)_4SiEt_3$.[9] Under the standard Hay conditions for coupling, the reaction mixture in this case became turbid. Precipitated material was removed by filtration and extracted with MeOH and UV examination of the extracts

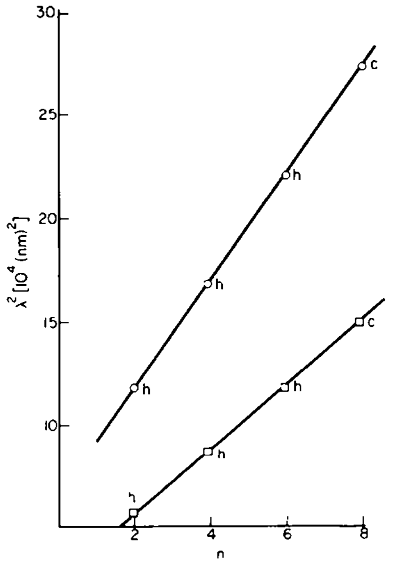

FIG 4. Lewis–Calvin plot of λ^2 *vs* n for the longest wavelength absorption (circles) and for the first band in the high intensity region (squares) for $Mes(C{\equiv}C)_nMes$ compounds in hexane (h) or $CHCl_3$ (c) solution

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* Arylacetylenes may be extended by two yne-units at a time using the reagent, $Br(C{\equiv}C)_2SiEt_3$ in conjunction with the Cadiot-Chodkiewicz procedure[18] however we have encountered considerable difficulties in devising an economic and convenient synthesis for the silylated bromobutadiyne.[19]

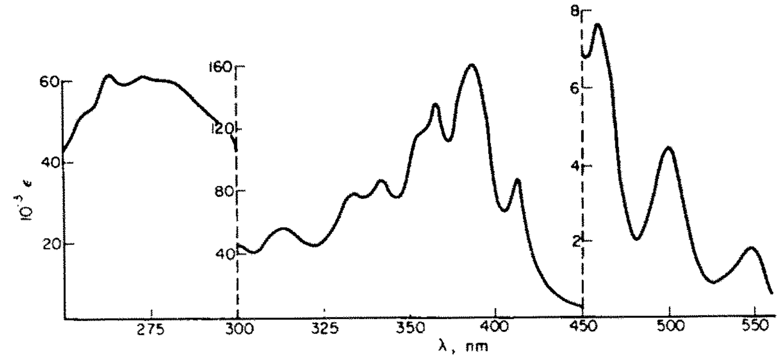


FIG 5. UV spectrum of $Ph(C{\equiv}C)_{10}Ph$ ($CHCl_3$ solution)

showed only the presence of bands due to 1,4-bisphenylbutadiyne and no absorptions attributable to higher polyynes. In view of the insolubility encountered within the mesityl series, the solids were extracted with $CHCl_3$ and spectral examination of these extracts revealed, surprisingly, the presence of the bisphenyldecaacetylene (XVII). It is assumed that the Cu(I) and/or base concentration of the reaction mixture was sufficient to cleave both initially formed 1-phenyl-10-triethylsilyldecapentayne (XV) and symmetrically coupled product, $Et_3Si(C{\equiv}C)_8SiEt_3$, [to give $H(C{\equiv}C)_8H$ which would doubtless polymerise by further oxidative coupling][9] followed by *in*

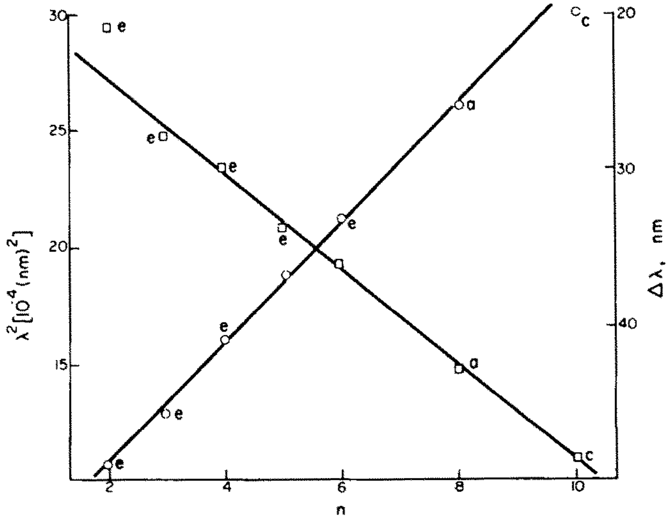


FIG 6. Lewis-Calvin plot (λ^2 *vs* n) for the longest wavelength absorption (circles) and a plot of $\Delta\lambda$ *vs* n (squares), where $\Delta\lambda$ = wavelength separation between the two longest wavelength absorptions, for $Ph(C{\equiv}C)_nPh$ compounds in EtOH (e), MeCOOEt (a) or $CHCl_3$ (c) solution. (Data from this work and from refs. 2, 3)

situ coupling of liberated phenyldecapentayne (XVI) to yield XVII. Such a course of reaction is likely in view of the considerable sensitivity of silyl-polyyne bonds towards base[20]. Concentration of the $CHCl_3$ extracts resulted in dark red needles of XVII which decomposed exothermically upon attempted isolation at room temperature so that the practical limit in stability of the series has clearly been attained at $n = 8$ (Table 1). Extinction coefficients of XVII were estimated by the residual weighing technique[9] and its identity was confirmed by qualitative hydrogenation of the decayne unit (in solution) to give 1,20-bisphenyleicosane.

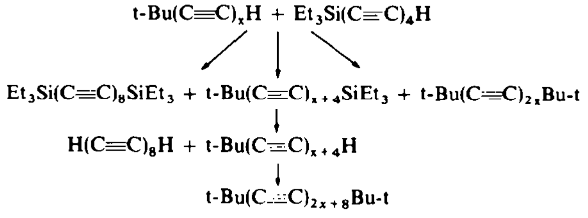
The UV spectrum of XVII (Fig 5; Table 2) exhibits the two anticipated regions of absorption together with an additional area of high intensity at lower wavelengths presumably corresponding to the bands observed in this region for di-t-butyldeca-acetylene.[5] The long wavelength medium intensity bands possess the more distinctive fine structure and the longest wavelength absorption (549 nm) accords with the slight curvature of the published[3] Lewis–Calvin plot (Fig 6) for the $Ph(C{\equiv}C)_nPh$ series, notwithstanding the variation in solvent. The average vibrational spacing ($\Delta\lambda$) for the two bands observed at highest wavelength increases uniformly as n increases (Fig 6).

An alternative synthesis of $t\text{-}Bu(C{\equiv}C)_{10}Bu\text{-}t$ (XXII) *and extension of the polyyne series to* $t\text{-}Bu(C{\equiv}C)_{12}Bu\text{-}t$ (XXV)

In 1960, Jones *et al.*[5] formulated elegant syntheses of bis-t-butyl-hexadecaoctayne and -eicosadecayne (XXII). Preparation of the decayne, starting from the diynal, $t\text{-}Bu(C{\equiv}C)_2CHO$, involved several problems of purification, nevertheless the synthesis was carried through to a satisfactory conclusion in which the characteristic ultra-high intensity UV absorption bands in the region 280–365 nm (hexane solution) of XXII, the longest fully conjugated polyyne then known, played a crucial diagnostic role.

The mixed Hay coupling, employing $Et_3Si(C{\equiv}C)_4H$ to extend the polyyne chain by four triple bonds in one step, now provides for a conceptually simple route to XXII and to higher members of the series, e.g. $t\text{-}Bu(C{\equiv}C)_{12}Bu\text{-}t$, as summarised in Scheme 1.

Scheme 1



$t\text{-}Bu(C{\equiv}C)_xH + Et_3Si(C{\equiv}C)_4H$

$Et_3Si(C{\equiv}C)_8SiEt_3 + t\text{-}Bu(C{\equiv}C)_{x+4}SiEt_3 + t\text{-}Bu(C{\equiv}C)_{2x}Bu\text{-}t$

$H(C{\equiv}C)_8H + t\text{-}Bu(C{\equiv}C)_{x+4}H$

$t\text{-}Bu(C{\equiv}C)_{2x+8}Bu\text{-}t$

$x = 1$ (XXII), 2 (XXV)

Thus a coupling between excess of (expendable) t-butylacetylene (XVIII) and $Et_3Si(C{\equiv}C)_4H$ afforded a mixture of $Et_3Si(C{\equiv}C)_8SiEt_3$,[9] $t\text{-}Bu(C{\equiv}C)_2Bu\text{-}t$ and the required 1-t-butyl-10-triethylsilyldecapentayne (XX). Chromatography on alumina at this stage did not lead to separation of products, however treatment with base gave a cleanly separable mixture of t-butyldecapentayne (XXI), $H(C{\equiv}C)_8H$[9] and unchanged $t\text{-}Bu(C{\equiv}C)_2Bu\text{-}t$. Without isolation, XXI was oxidatively coupled (Hay method) to give XXII in good yield. The spectral properties of both XXI and XXII were in good agreement with data recorded previously.[5]

For the dodecayne (XXV), t-butyldiacetylene (XIX) was required. The reported routes to this compound are based upon pivalaldehyde (t-BuCHO) which is difficult to synthesise in quantity and after some experimentation a method of preparation (analogous to that used for mesityldiacetylene) starting from pivaloylacetone was employed.* Coupling of $Et_3Si(C{\equiv}C)_4H$ with excess of XIX gave a mixture of $Et_3Si(C{\equiv}C)_8SiEt_3$, $t\text{-}Bu(C{\equiv}C)_4Bu\text{-}t$[4] and the silylated t-butylhexaacetylene, $t\text{-}Bu(C{\equiv}C)_6SiEt_3$ (XXIII), which, without characterisation, was treated with base to yield a chromatographically separable mixture of $H(C{\equiv}C)_8H$, $t\text{-}Bu(C{\equiv}C)_4Bu\text{-}t$ and $t\text{-}Bu(C{\equiv}C)_6H$ (XXIV). Solubility problems were encountered with the Cu(I) derivative of XXIV and in an attempted Hay coupling only trace quantities of the desired dodecaacetylene (XXV) were obtained. The Eglinton–Galbraith method gave marginally better results however and hexane solutions of XXV, upon concentration, precipitated red-brown needles which when heated, immediately following isolation, decomposed ~50°. The product also gradually decomposed to an insoluble black mass during 8 min at 20°.

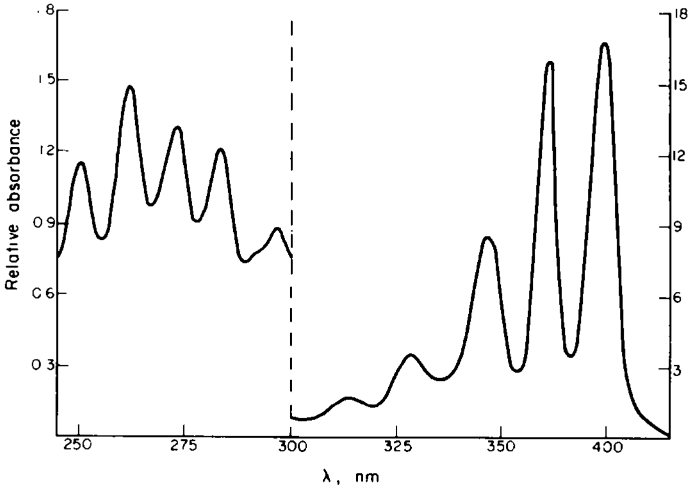


Fig 7. UV spectrum of $t\text{-}Bu(C{\equiv}C)_{12}Bu\text{-}t$ ($CHCl_3$ solution)

The UV spectrum of XXV ($CHCl_3$ solution, Fig 7) reveals the features similar to those of the decayne (XXII), namely a series of well-defined high intensity bands, attaining a maximum at 396·5 nm, together with a series of medium intensity bands at lower wavelengths (250–300 nm). The long wavelength set of low intensity bands (not shown) is ill-defined and two shoulders only could be detected (compare the spectrum of XXII[5]). The Lewis–Calvin plot for the highest intensity bands of the

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* This method also yields XIX free from enyne.[5]

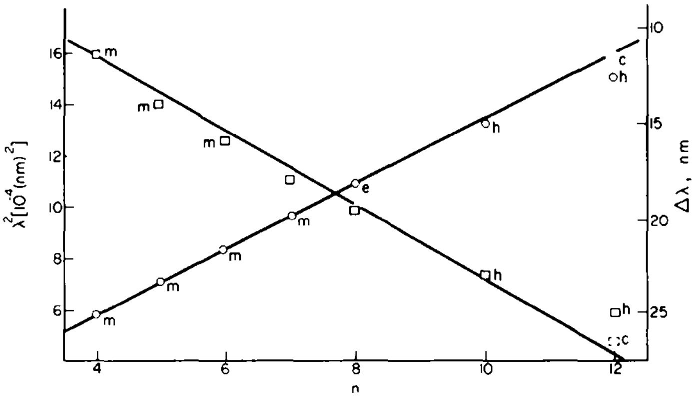

FIG 8. Lewis–Calvin plot (λ^2 *vs* n) for the highest intensity band (circles) and a plot of Δλ *vs* n (squares), where Δλ = wavelength separation of the two bands of highest intensity, for t-Bu(C≡C)$_n$Bu-t compounds in $CHCl_3$ (c), ether (e), hexane (h) or MeOH (m) solution. (Data from this work and from refs. 4, 5)

t-butyl series [slope *ca* 12 × 10^3 $(nm)^2$/triple bond] may now be extended to include the dodecayne (Fig 8), however it should be noted that the position of the maxima in XXV exhibit considerable solvent dependance [e.g. λ_{max} = 387 nm (hexane), 396·5 nm ($CHCl_3$)] so that interpretation of curvature (Fig 8) should be attempted with caution.

The difference in wavelength between the two adjacent bands of highest intensity increases uniformly as n increases (Fig 8. For a similar plot based upon the *average* vibrational spacing in the high intensity band series *cf* ref 5) for 4 ≤ n ≤ 10. Solubility difficulties in methanol prevent direct incorporation of XXV in the plot, furthermore, since the spacing is also solvent-dependent (Table 2) the exact significance of the point for the dodecayne is subject to reservation.

TABLE 1. MELTING OR DECOMPOSITION POINTS OF POLYACETYLENES PROTECTED BY ALKYL OR ARYL END-GROUPS

n	Me(C≡C)$_n$Me[a]	Ph(C≡C)$_n$Ph[b]	t-Bu(C≡C)$_n$Bu-t[c]	Mes(C≡C)$_n$Mes[d]
2	65	88	132	179·5–180
3	128	96	70	—
4	dec 80	144	100	230–231
5	—	dec 160	130	—
6	dec 5	dec 100	140	dec > 170
8	—	dec 20	dec 130	dec > 150
10	—	dec <20	dec ~ 100	—
12	—	—	dec ~ 50[d,e]	—

[a] Ref. 1; [b] Refs. 2, 3; [c] Refs. 4, 5; [d] This work (Mes = mesityl). [e] Spontaneously decomposes after *ca* 8 min at room temp.

TABLE 2. UV SPECTRAL DATA FOR NEW POLYYNES: $R(C{\equiv}C)_nR$, $R(C{\equiv}C)_nSiEt_3$ AND $R(C{\equiv}C)_nH$ WHERE R = Mes, Ph AND t-Bu.

Compound	Solvent[a]	λ_{max}(nm), log ε or rel. intensity*
$Mes(C{\equiv}C)_2Mes$ II	h	341·5 (4·56), 319·5 (4·64), 300 (4·55), 270† (4·60), 264 (4·61), 239† (4·56), 228 (4·68).
$Mes(C{\equiv}C)_2SiEt_3$ III	m	306·5 (4·43), 288·5 (4·51), 272·5 (4·30), 259 (3·95), 237 (4·76).
$Mes(C{\equiv}C)_3SiEt_3$ VI	m	349 (4·18), 326 (4·32), 306·5 (4·20), 288 (4·11), 269·5 (4·61), 264·5 (4·58), 257·5 (4·36), 251 (4·36), 236 (3·78).
$Mes(C{\equiv}C)_3H$ VII	m	336·5 (4·08), 315 (4·21), 296 (4·09), 279·5 (3·86), 256·5 (4·58), 244·5 (4·35), 233 (4·25).
$Mes(C{\equiv}C)_6Mes$ VIII	m	469 (4·02), 430 (4·18), 398 (4·49), 365·5 (5·06), 341 (5·24), 323 (5·07), 318·5 (5·09), 301 (5·05), 287·5 (4·85), 274 (4·66).
$Mes(C{\equiv}C)_4SiEt_3$ IX	m	390 (3·90), 363 (4·09), 338·5 (4·03), 316·5 (3·96), 296 (4·49), 290·5 (4·76), 277·5 (4·61), 264 (4·40), 249 (4·37), 239 (4·26), 228·5 (4·46).
$Mes(C{\equiv}C)_4H$ X	m	380 (3·87), 352 (4·05), 329·5 (3·99), 309 (3·89), 292·5 (4·30), 283 (4·68), 271 (4·52), 259 (4·24), 239 (4·27), 288·5† (4·45).
$Mes(C{\equiv}C)_8Mes$ XI	c	522 (3·67), 476 (4·09), 439 (4·34), 410 (4·84), 387 (5·18), 365 (5·18), 349 (5·19), 330 (5·07), 311 (4·84), 295·5 (4·66), 281·5 (4·52), 268 (4·45).
$Mes(C{\equiv}C)_5SiEt_3$ XII	m	426 (3·70), 394 (4·04), 367·5 (4·00), 344 (3·90), 329 (4·48), 318 (4·88), 307 (4·78), 304† (4·76), 291 (4·74), 276 (4·88), 264 (4·79), 255 (4·66), 245·5 (4·60).
$Mes(C{\equiv}C)_5H$ XIII	m	418 (3·68), 386 (3·88), 359 (3·84), 337 (3·61), 322·5 (3·10), 312 (4·61), 301 (4·45), 296 (4·45), 285·5 (4·41), 269 (4·45), 260·5 (4·44), 249 (4·37), 239 (4·36), 231 (4·41).
$Ph(C{\equiv}C)_{10}Ph$ XVII	c	549 (3·23), 500 (3·58), 460 (3·89), 414 (4·89), 386 (5·20), 365 (5·13), 356 (5·09), 342·5 (4·94), 333 (4·91), 313·5 (4·76), 273·5 (4·78), 263 (4·79), 255 (4·72).
$t\text{-}Bu(C{\equiv}C)_6H$ XXIV	m*	282 (1·00), 266 (0·82), 252 (0·44), 240 (0·25), 230† (0·26).
$t\text{-}Bu(C{\equiv}C)_{12}Bu\text{-}t$ XXV	c*	540,† 494,† 396·5 (1·00), 370 (0·95), 346·5 (0·51), 328 (0·20), 313·5 (0·095), 297 (0·053), 283 (0·071), 272·5 (0·077), 261 (0·087), 249·5 (0·069).
	h	387, 362, 339·5, 323, 307, 291·5, 278·5, 269, 257·5, 246, 236·5.

[a] $CHCl_3$ (c); hexane (h); MeOH (m)

* Relative Intensity (arbitrary scale)

† Inflexion

EXPERIMENTAL

The general procedures associated with handling sensitive polyacetylenes[1-5,9] were adopted. M.p's and b.p's are uncorrected. UV spectral profiles were recorded on a Unicam SP800 instrument and absorption maxima and extinction coefficients were checked manually on a SP500 spectrophotometer. Spectra of new polyacetylenes are collated in Table 2.

Petrol refers to reagent grade petroleum ether (40–60° fraction). Alumina (Du Pont, grade H) was used for column chromatography.

1. *Syntheses in the Bismesitylpolyyne Series*

1,4-Bismesitylbutadiyne (II). α-Chloro-2,4,6-trimethylstyrene, obtained from acetylmesitylene by treatment with PCl_5, was dehydrohalogenated by heating with $NaNH_2$ in mineral oil.[11] The resulting crude ethynylmesitylene (I) after purification via its silver salt,[12] had the following physical constants: b.p.

87·5°/11 mm, n_D^{25} 1·5443 (lit.[11] b.p. 103–107°/23 mm, NMR (10% CCl_4) τ: 6·72s (C≡C—H). Hay catalyst (10 ml), prepared from excess of CuCl and TMEDA in acetone,[9] was added to a solution of I (3·66 g) in acetone (75 ml), and air was bubbled through the mixture for 2 hr. Following treatment with 2N HCl (50 ml), precipitated solid was removed by filtration and recrystallized from acetone to give II (42%) as white needles m.p. 179·5–180° (Found: C, 92·1; H, 8·0. $C_{22}H_{22}$ requires: C, 92·3; H, 7·7%).

1,8-*Bismesityloctatetrayne* (V)

Preparation of mesityldiacetylene (IV): (i) *from acetoacetylmesitylene*[15]. Acetoacetylmesitylene (20·4 g, 0·1 mole) was added to a suspension of PCl_5 (45·9 g, 0·22 mole) in ice-cold C_6H_6 (200 ml). The mixture was heated on an oil bath at 50–60° for 14 hr, then poured onto ice (300 g) and organic products were extracted with petrol (3 × 200 ml). The petrol extracts were combined, washed with satd aq $NaHCO_3$ and dried (Na_2SO_4). Solvent was removed by rotary evaporation and the residual brown oil was added during 20 min to $NaNH_2$ (1·3 mole) in liquid NH_3 (250 ml). This mixture was stirred for 1 hr, then NH_4Cl (70 g) was added followed by ether (150 ml). After addition of 2N HCl, the ether layer was separated and dried and evaporation of the solvent left a viscous residue which was absorbed onto alumina (150 g). Elution with petrol gave fractions rich in IV which upon concentration yielded pure IV as white needles (45%) m.p. 42–44° (lit.[15] m.p. 42–44°); UV (MeOH) λ_{max} nm (log ε): 292·5 (4·29), 276·5 (4·39), 262 (4·16), 226·5 (4·51): NMR (CCl_4) τ: 7·97s (C≡C—H), 7·77s (p-CH_3), 7·62s (o-CH_3), 3·22s (m-C_6H_2): IR (CCl_4) ν(cm^{-1}): 3315s (C≡C—H), 2215m, 2190w, 2070w [$(C\equiv C)_2$]. The product darkened rapidly upon storage at room temperature.

(ii) *Cadiot-Chodkiewicz coupling of* I *with* BrC≡$CSiEt_3$ → Mes$(C\equiv C)_2SiEt_3$ (III) *followed by alkali cleavage to give* IV. I (14·5 g, 0·1 mole) was added to a soln of $EtNH_2$ (7·5 g), CuCl (0·2 g) and $NH_2OH \cdot HCl$ (1·0 g) in DMF (120 ml). Bromoethynyl(triethyl)silane[10] (22 g, 0·1 mole) in DMF (25 ml) was added dropwise during 15 min, then the mixture was maintained at 20° for 1 hr, subsequently acidified, and extracted with petrol (3 × 100 ml). The petrol extracts were dried, solvent was removed under reduced pressure and the residue was distilled to give III (14%) b.p. 138–140°/0·1 mm, n_D^{25} 1·5754, which solidified in the receiver to give material, m.p. 36–38° (Found: C, 80·7; H, 9·4. $C_{19}H_{26}Si$ requires: C, 80·9; H, 9·2%). When freshly distilled DMF (from P_2O_5 and n-Bu_3N (in place of $EtNH_2$) were used the yield of III fell to 2%, and when double the quantity of CuCl was employed or when the reaction time was increased to 3 hr the yield was marginally reduced (12%). 25 nl of a solution of KOH (3 g) in 10% aqueous MeOH (100 ml) were then added to III (1·23 g) in MeOH (50 ml) followed by hexane (1 ml) to facilitate soln. The mixture was maintained at 20° for 25 min, then treated with ice (100 g) and 2N HCl (50 ml). Extraction of organic products into petrol followed by the established working up procedure gave IV in 95% yield.

Hay coupling of IV → V

A soln of IV (5 mmole) in acetone (50 ml) was treated with Hay catalyst (5 ml) followed by passage of air for 1 hr. After acidification, the resulting yellow solid was recrystallized from petrol: $CHCl_3$ (1:1) to give V (80%) m.p. 230–231° (lit.[15] m.p. 227–228°); UV (hexane) [λ_{max} nm (log ε)]: 407 (4·34), 376 (4·57), 349 (4·53), 322·5 (4·87), 306·5 (4·82), 293·5 (4·99), 276·5 (4·70), 267 (4·48), 254 (4·41), 246 (4·57), 236 (4·58), 220 (4·69): NMR (CCl_4) τ: 7·72s (p-CH_3), 7·60s (o-CH_3), 3·12s (m-C_6H_2); IR(CCl_4) ν(cm^{-1}): 2190s, 2193w, 2075w [$(C\equiv C)_4$].

1,12-*Bismesityldodecahexayne* (VIII)

Preparation of 1-*mesityl*-6-*triethylsilylhexatriyne* (VI): (i) *Cadiot-Chodkiewicz coupling of* IV with BrC≡$CSiEt_3$ → VI. The petrol extracts from a coupling between IV (0·065 mole) and BrC≡$CSiEt_3$ (0·07 mole) in DMF (120 ml) and $EtNH_2$ (7·6 g) in the presence of CuCl (0·2 g) and $NH_2OH \cdot HCl$ (1 g) at 40° for 25 min were concentrated and chromatographed. Elution with petrol gave successive fractions containing DMF (trace), unreacted BrC≡$CSiEt_3$ and VI followed by traces of mesitylhexatriyne (VII) (*vide infra*) and IV. Subsequent elution with 1:10 $CHCl_3$: petrol gave V (identified by its UV spectrum and mixed m.p. with an authentic sample). Concentration of petrol fractions rich in VI left a yellow oil (n_D^{21} 1·5400) which was dissolved in EtOH (50 ml). Dropwise addition of 2N HCl afforded a cloudy solution which, at − 20°, deposited white crystals of VI (36%) m.p. 27–27·5° (Found: C, 82·2; H, 8·6. $C_{21}H_{26}Si$ requires: C, 82·5; H, 8·5%); NMR (CCl_4) τ: 8·70–9·60m [$(C_2H_5)_3Si$], 7·72s(p-CH_3), 7·60s(o-CH_3), 3·29s(m-C_6H_2): IR (CCl_4) ν(cm^{-1}): 2170m, 2125s, 2075m [$(C\equiv C)_3$].

(ii) *Mixed Hay coupling*: IV + HC≡$CSiEt_3$ → VI. Hay catalyst (20 ml) was added to a mixture of IV (12 g, 0·076 mole) and HC≡$CSiEt_3$ (20 g, 0·144 mole) dissolved in acetone (100 ml) and air was bubbled through the homogeneous solution for 20 min. Addition of ether and acidification resulted in a precipitate which was removed by filtration and identified as V. The filtrate was extracted with petrol (2 × 100 ml), the extracts were dried and concentrated and the residue absorbed onto alumina (50 g). Elution with petrol gave initial fractions containing predominantly $Et_3Si(C\equiv C)_2SiEt_3$, identified by its UV spectrum (λ_{max} 264 nm, hexane).[9] Removal of solvent from subsequent fractions gave 7·5 g of pale yellow oil (n_D^{20} 1·5380) which when treated as under (i) above, deposited crystals of VI (30%).

Alkali cleavage of VI → VII *and oxidative coupling* → VIII

To a solution of VI (2·0 g) in MeOH (200 ml) was added 1 ml of a solution of NaOH (20 g) in H_2O (30 ml) and after 6 min at 18° the mixture was poured onto a slurry of ice (100 g), 2N HCl (100 ml). The aqueous layer was separated and extracted with petrol (2 × 100 ml) and the combined petrol extracts were dried, then cooled to − 10° and concentrated by evaporation under reduced pressure. UV spectral examination of 0·1 ml of concentrate dissolved in excess of MeOH revealed the presence of VII (λ_{max} 244·5 nm). The main bulk of the concentrate was dissolved in acetone (100 ml), Hay catalyst (10 ml) was added, and oxygen was passed through the mixture for 2 hr. Solid material which separated upon subsequent acidification was recrystallized from $CHCl_3$:petrol to give yellow needles of VIII (22%) dec > 170° (Found: C 90·7; H, 5·6. $C_{30}H_{22}$ requires: C, 94·2; H, 5·8%); NMR ($CDCl_3$) τ: 7·66s (p-CH_3), 7·52s(o-CH_3), 3·13s(m-C_6H_2); IR (CCl_4) ν(cm^{-1}): 2175m, 2100m, 2065w [$(C\equiv C)_6$]. Extraction of the aqueous acetone filtrate with petrol afforded a further 11% of VIII.

1,16-*Bismesitylhexadecaoctayne* (XI)

Preparation of 1-*mesityl*-8-*triethylsilyloctatetrayne* (IX): (i) *attempted Cadiot–Chodkiewicz coupling of* VII *with* $BrC\equiv CSiEt_3$. DMF (50 ml) was added to a petrol concentrate (100 ml) of VII (0·02 mole) and the solution was concentrated under reduced pressure to *ca* 50 ml. CuCl (0·1 g), $EtNH_2$ (3·75 g) and $NH_2OH{\cdot}HCl$ (0·5 g) were then added followed by a solution of $BrC\equiv CSiEt_3$ (5·5 g, 0·025 mole) in DMF (10 ml) during 10 min. The mixture was maintained at 40° for 1 hr, then acidified and extracted with petrol. Chromatography of the dried concentrated extract using petrol as eluent gave fractions rich in $BrC\equiv CSiEt_3$ and further elution with $CHCl_3$:petrol gave a quantity of red tar which could not be identified.

(ii) *Mixed Hay coupling*: IV + $H(C\equiv C)_2SiEt_3$ → (IX). Air was passed through a mixture of IV (5·0 g, 0·042 mole), $H(C\equiv C)_2SiEt_3$[9] (8·0 g, 0·070 mole) and Hay catalyst (10 ml) in acetone (200 ml) for 2 hr. Dilute acid was then added and precipitated solid (1·6 g) was removed by filtration and identified as V by its m.p. (230–231°) and UV spectrum. The filtrate was extracted with petrol (3 × 150 ml), the petrol extracts were dried and concentrated and the residue was chromatographed using petrol as eluent. Removal of solvent from the initial fractions left an oil which was dissolved in a minimum of EtOH. Upon cooling to − 20°, creamy-white crystals of $Et_3Si(C\equiv C)_4SiEt_3$ (3·6 g) m.p. 38–39° (lit.[9] m.p. 39·5–40°) were obtained. Similar treatment of subsequent chromatography fractions gave IX as yellow plates (30%) m.p. 49·5–50·5° (Found: C, 83·4; H, 8·0. $C_{23}H_{26}Si$ requires: C, 83·6; H, 7·9%); NMR (CCl_4) τ: 8·70–9·60m [$(C_2H_5)_3Si$], 7·74s (*p*-CH_3), 7·58s(*o*-CH_3), 3·20s(*m*-C_6H_2); IR (CCl_4) ν (cm^{-1}): 2200m, 2135s, 2065 m [$(C\equiv C)_4$].

Alkali cleavage of IX → *mesityloctatetrayne* (X) *and oxidative coupling* → XI

Aqueous N NaOH (5 ml) was added to a soln of IX (3·1 g, 9 mmole) in MeOH (700 ml) previously thermostatted at 29°. After 2 min, the mixture was acidified and extracted with petrol and UV examination of the dried extract revealed the conversion, IX → X, to be complete. The extract was concentrated under reduced pressure, then diluted with acetone (100 ml). Hay catalyst (10 ml) was then added and air passed through the mixture for 24 hr. Upon acidification, a dark red solid precipitated which was filtered off and recrystallized from $CHCl_3$ to give XI (25%) dec > 150° (Found: C, 90·3; H, 4·9. $C_{34}H_{22}$ requires: C, 94·9; H, 5·1%); IR ($CHCl_3$) ν (cm^{-1}): 2180w, 2100m [$(C\equiv C)_8$].

Attempted preparation of 1,20-*bismesityleicosadecayne* (XIV)

Mixed Hay coupling: X + $HC\equiv CSiEt_3$ → 1-*mesityl*-10-*triethylsilyldecapentayne* (XII) *followed by cleavage* → *mesityldecapentayne* (XIII). A petrol concentrate (25 ml) containing X (2·4 g, 0·01 mole) was diluted with acetone (200 ml). $Et_3SiC\equiv CH$ (8·4 g, 0·06 mole) was added followed by Hay catalyst (10 ml) and air was bubbled through the mixture for 1 hr. Upon acidification, a dark red solid was obtained which, after washing with petrol, was identified as XI by its UV spectrum [λ_{max} 349 nm ($CHCl_3$)]. Petrol extracts of the filtrate were combined with these washings, then concentrated and absorbed onto alumina (50 g). Chromatography, using petrol as eluent, gave fractions which when concentrated left an oil (6·5 g) whose

UV spectrum showed it to consist mainly of $Et_3Si(C{\equiv}C)_2SiEt_3$. Further elution with ether:petrol (1:20) gave orange fractions which, upon concentration, left a dark red oil which was dissolved in a minimum quantity of EtOH. Upon cooling to − 20°, orange crystals of XII deposited during 12 hr which, upon filtration under N_2, conflagrated violently. In order to obtain spectra, the precipitated crystals were dissolved by addition of MeOH (UV details *cf* Table 2) or of CCl_4: IR ν (cm^{-1}): 2180w, 2095w, 2035m[$(C{\equiv}C)_5$]. A petrol soln (500 ml) containing XII (2·27 g, 5 mmole) estimated spectrophotometrically) was diluted with MeOH (500 ml), reconcentrated (to *ca* 35 ml) and then made up to 350 ml with MeOH. The solution was then thermostatted at 20° and N NaOH (1·5 ml) was added. After 16 min, when spectroscopic examination showed cleavage to be complete, the reaction mixture was acidified and extracted with petrol. The extracts containing XIII and triethylsilanol were used without further purification.

Attempted oxidative couplings of XIII → XIV

(i) *Hay method.* A petrol concentrate (50 ml) containing XIII (*ca* 0·5 mmole) was diluted with acetone (250 ml). Hay catalyst (20 ml) was added, the reaction vessel was shielded from daylight by a wrapping of aluminium foil, and air was bubbled through the mixture for 72 hr. Examination of petrol and $CHCl_3$ extracts following the established working-up procedure revealed only the presence of starting material. In a second reaction, the same quantity of XIII was used but the amount of catalyst was considerably increased [CuCl (0·1 mole) plus TMEDA (0·1 mole)] and oxygen was employed instead of air. Again, only starting material was recovered.

(ii) *Eglington–Galbraith method.* A MeOH soln (40 ml) of XIII (*ca* 0·5 mmole), prepared by diluting a petrol concentrate and removal of petrol by selective evaporation under reduced pressure, was shaken in the dark for 72 hr with $Cu(OAc)_2$ (15 g), pyridine (45 ml) and H_2O (40 ml). The mixture was diluted with an equal volume of water, then neutralized, and extracted with $CHCl_3$. UV spectral examination of the $CHCl_3$ extract showed only the presence of XIII.

2. *Synthesis of* 1,20-*bisphenyleicosadecayne* (XVII)

Mixed Hay coupling between $PhC{\equiv}CH$ *and* $H(C{\equiv}C)_4SiEt_3$ → 1-*Phenyl-5-triethylsilyldecapentayne* (XV) *followed by* in situ *cleavage and coupling of the liberated phenyldecapentayne* (XVI → XVII).

A petrol soln (250 ml) containing $Et_3Si(C{\equiv}C)_4H$[9] (4·4 mmole) was diluted with an equal volume of acetone then concentrated to *ca* 200 ml. Phenylacetylene (2·5 g, 24 mmole) and Hay catalyst (80 ml) were added and air was bubbled through the reaction for 3 hr, during which time the mixture turned black. After addition of ether (100 ml) and 2N H_2SO_4 (200 ml), solid products were removed by filtration and were digested with $CHCl_3$ (200 ml) during 24 hr. Following filtration, the $CHCl_3$ soln was concentrated and chromatographed and the eluent was concentrated by rotary evaporation until dark red needles appeared. When filtration was attempted under a stream of N_2, the crystals (subsequently identified as XVII) blackened and conflagrated violently. Spectral data were therefore recorded using the chromatographed $CHCl_3$ soln; UV (Table 2); IR ν (cm^{-1}): 2185w, 2070m, 2020w [$(C{\equiv}C)_{10}$].

Hydrogenation of the polyyne units in II, V, VIII, XI *and* XVII

In a typical preparative scale experiment, V (244 mg, 0·73 mmole) was dissolved in hexane (100 ml) and catalyst (*ca* 50 mg of 10% Pd on charcoal) was added. The mixture was shaken under a positive pressure of H_2 for 12 hr, whereupon the yellow colour of the soln gradually faded. The catalyst was removed by filtration and UV spectroscopic examination of the filtrate revealed that the tetrayne chromophore had entirely disappeared. Solvent was then removed by rotary evaporation to leave solid material which was recrystallized from acetone, and finally sublimed to give white needles of 1,8-bismesityloctane (75%) m.p. 80–80·5° (Found: C, 89·1; H, 10·7. $C_{26}H_{38}$ requires: C, 89·2; H, 10·8%); λ_{max} (hexane): 206, 218 nm; NMR (CCl_4) τ: 9·00–8·30 m [central − $(CH_2)_6$-], 7·80s(p-CH_3), 7·75s(o-CH_3), m centred at 7·50 (Mes-CH_2), 3·30s(m-C_6H_2). A semi-micro scale reaction using a Gallenkamp micro-hydrogenator and Pd/charcoal catalyst (*ca* 20 mg) gave 4·09 triple bonds per molecule of V (average of three runs). Analogous preparative and micro-scale reactions with the other polyynes gave the following results: II → $Mes(CH_2)_4Mes$ m.p. 122–123°. (Found: C, 89·7; H, 10·2. $C_{22}H_{30}$ requires: C, 89·8; H, 10·2%. 2·02 triple bonds per molecule); UV λ_{max} (hexane): 209, 219 nm. VIII → $Mes(CH_2)_{12}Mes$ m.p. 60·5–61·5° (Found: C, 88·8; H, 11·1. $C_{30}H_{46}$ requires: C, 88·7; H, 11·3%. 6·00 triple bonds per molecule: UV λ_{max}(hexane): 209, 219 nm. XI → $Mes(CH_2)_{16}Mes$ m.p. 19–20° (Found: C, 88·2; H, 11·4. $C_{34}H_{54}$ requires: C, 88·3; H, 11·7%. 8·01 triple bonds per molecule): UV λ_{max}(hexane): 214 nm. The NMR spectra of the products, $Mes(CH_2)_nMes$ (n = 4, 12, 16) showed resonances similar to those of $Mes(CH_2)_8Mes$.

3. *Syntheses of Bis-t-butylpolyynes*

t-Butylacetylene (XVIII)

t-Butyl methyl ketone was treated with PCl_5[21] and the resulting mixture of chlorohydrocarbons was dehydrohalogenated by heating with KOH pellets in refluxing EtOH to give XVIII (60%) b.p. 37–38° (lit.[21] b.p. 36·4–37·8°).

t-Butyldiacetylene (XIX)

Pivaloyl acetone (25 g, 0·17 mole) was added to a stirred soln of PCl_5 (73 g, 0·35 mole) in ice-cold C_6H_6 (400 ml). The mixture was initially maintained at 0° for 30 min, then heated to 50–60° on an oil bath for 14 hr, and finally poured onto ice. Organic products were extracted with petrol and the extracts were washed with satd aq $NaHCO_3$, then dried and solvent was removed under reduced pressure. The resulting oil was cautiously added to $NaNH_2$ (2 moles) in liquid NH_3 (300 ml) at $-$ 50° and the mixture was stirred at this temperature for 2 hr. NH_4Cl (150 g) was then added followed by anhydrous ether (500 ml) and the mixture was set aside for 12 hr. Following acidification with 2N H_2SO_4, the ether layer was separated, dried, and fractionated to give XIX (40%) b.p. 30–32°/25 mm, n_D^{25} 1·4562 (lit.[5] b.p. 34–35°/30 mm, n_D^{21} 1·4590–1·4600); UV (MeOH) λ_{max}: 251, 237·5, 225·5 nm (lit.[5] λ_{max}(ether): 250, 236·5, 225 nm); NMR (CCl_4) τ: 8·75s [$(CH_3)_3C$], 8·17s ($C{\equiv}C{-}H$); IR (film) ν (cm^{-1}): 3300s($C{\equiv}C{-}H$), 2320w, 2230m, 2060w [$(C{\equiv}C)_2$].

1,20-*Bis-t-butyleicosadecayne* (XXII)

Mixed Hay coupling: XVII + $H(C{\equiv}C)_4SiEt_3$ → *1-t-butyl-10-triethylsilyldecapentayne* (XX) *followed by cleavage* → *t-butyldecapentayne* (XXI) *and oxidative coupling* → XXII. Hay catalyst (20 ml) and XVIII (8·2 g, 0·1 mole) were added to an acetone soln (250 ml) of $Et_3Si(C{\equiv}C)_4H$ (5·1 mmole) and O_2 was passed through the stirred mixture for 90 min. Subsequent acidification, extraction with petrol (3 × 100 ml) and UV examination of the petrol extracts revealed the presence of t-Bu$(C{\equiv}C)_2$Bu-t, λ_{max}, 252·5, 239, 227·5, 217 nm [lit.[4] λ_{max}(MeOH): 252·5, 239, 227·5, 217 nm] and $Et_3Si(C{\equiv}C)_8SiEt_3$, λ_{max}(ultra high intensity bands), 326, 316, 298·5 nm [lit.[9] λ_{max}(hexane): 326, 316, 298·5 nm] together with the required product, t-Bu$(C{\equiv}C)_5SiEt_3$ (XX). Chromatography at this stage (elution with petrol) led to retention of $Et_3Si(C{\equiv}C)_8SiEt_3$ on the column, whereas t-Bu$(C{\equiv}C)_2$Bu-t and XX eluted together. Fractions rich in XX and t-Bu$(C{\equiv}C)_2$Bu-t were combined and concentrated (to *ca* 10 ml) then diluted with MeOH (250 ml). This solution was thermostatted at 22° and 0·1 N NaOH (1 ml) was added. After 7 min when UV spectral examination revealed no further changes, the mixture was acidified and extracted with petrol. The petrol extracts were dried and concentrated and chromatography (elution with petrol) gave t-Bu$(C{\equiv}C)_2$Bu-t followed by t-Bu$(C{\equiv}C)_5$H (XXI), λ_{max}(MeOH), 259, 245·5, 233, 222 nm [lit.[5] λ_{max}(ether), 259·5, 246·5, 234, 222 nm]. Petrol fractions containing XXI were concentrated, then diluted with acetone and subjected to Hay coupling in the presence of catalyst (100 ml) by passage of O_2 for 6 hr. The usual working-up procedure culminating in chromatography with $CHCl_3$:petrol (1:4) as eluent afforded fractions rich in t-Bu$(C{\equiv}C)_{10}$Bu-t (XXII). These fractions were reconcentrated then rechromatographed on an alumina column shielded from light. Elution with $CHCl_3$:petrol (1:20) gave orange-red fractions containing XXII identified by its UV spectrum: λ_{max}, 362·5, 339, 319·5, 302·5, 288, 275, 262, 255, 248 nm [lit.[5] λ_{max}(hexane), 362·5, 339·5, 320, 303, 288·5, 275, 263·5, 255·5, 247 nm]. Removal of solvent under reduced pressure left an orange-red solid, dec *ca* 90° (preheated block) (lit.[5] dec *ca* 100°).

1,24-*Bis-t-butyltetracosadodecayne* (XXV)

Mixed Hay coupling: XIX + $H(C{\equiv}C)_4SiEt_3$ → *1-t-butyl-10-triethylsilyldodecahexayne* (XXIII) *followed by cleavage* → *t-butyldodecahexayne* (XXIV) *and oxidative coupling* → XXV. The dried petrol extracts obtained from a coupling between XIX (0·02 mole) and $Et_3Si(C{\equiv}C)_4H$ (3·6 mmole) in acetone (200 ml) in the presence of Hay catalyst (20 ml) (passage of O_2 for 90 min) were concentrated and taken up in MeOH (500 ml). This solution was thermostatted at 20°, 0·1 N NaOH (5 ml) was added and after 2 min the mixture was acidified and extracted with petrol. Concentration of the petrol extracts and chromatography (elution with petrol) gave initial fractions rich in t-Bu$(C{\equiv}C)_4$Bu-t, λ_{max}(MeOH), 239·5, 228, 217 nm [lit.[4] λ_{max}(MeOH), 239·5, 228, 217·5 nm] followed by fractions containing t-Bu$(C{\equiv}C)_6$H (XXIV), λ_{max} values *cf* Table 2 and subsequently by fractions containing traces of $H(C{\equiv}C)_8H$,[9] λ_{max} (ultrahigh intensity bands), 316, 298, 281·5 nm. Fractions containing XXIV were diluted with acetone (200 ml) then reconcentrated (to *ca* 200 ml) and treated with Hay catalyst (20 ml) with passage of O_2 during 6 hr. The mixture was subsequently acidified and extracted with petrol. During this procedure, a black solid separated at the organic/aqueous layer interface. This solid was removed by filtration and digested with $CHCl_3$ (100 ml) during 24 hr. Examination of the petrol extract revealed the presence of starting material, XXIV, together with traces of t-Bu$(C{\equiv}C)_{12}$Bu-t (XXV); however neither extract contained sufficient product to permit further characterization. A MeOH solution (50 ml) containing XXIV (*ca* 5 mmole) was therefore submitted to Eglinton–Galbraith coupling during 72 hr as described for mesityldecapentayne (XIII) (*cf* ref 5 for coupling of XXI by this procedure). A black solid was likewise obtained upon dilution of the reaction mixture with water and was partially dissolved upon prolonged digestion with $CHCl_3$ (100 ml). The $CHCl_3$ soln, after filtration, was concentrated (to *ca* 10 ml) and chromatographed on a foil-protected column (elution with petrol). Solvent was removed under reduced pressure from the resulting fractions to leave reddish-brown needles of XXV (0·8 mg) which when heated, immediately following isolation, decomposed at *ca* 50° (preheated block). Upon standing at room temperature under N_2, the needles decomposed spontaneously during 8 min to give $CHCl_3$-insoluble black material.

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