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SKIPPED DIYNES—VI

TRIETHYNYLCARBINOLS, RELATED DIYNES AND ALLENE DIMERS[a]

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Abstract—The *tris*(t-butylethynyl)carbonium ion (δ_{CH_3} 1·86) has been prepared in chlorosulfonic acid from the corresponding carbinol. Apart from a few esters, triethynylmethyl derivatives appear to be unknown, contary to previous claims. *Tris*(t-butylethynyl) carbinol (**1a**) may, however, be converted into 1,1-di-t-butylethynyl-3-t-butylallenes, e.g., chloride, bromide, and carboxylic acid. These haloallenes dimerize (~25°) to give one of the fourteen possible structures, the unsymmetrical 1,2-dimethylenecyclobutane (*Z*-I). *Tris*(1-propynyl) carbinol is generally similar to **1a**, although its chloroallene leads directly to two dimers (Eq 4). Upon heating (~100°) dimer *Z*-I (Cl) is quantitatively isomerized to the *trans*-II (Cl) dimer. Thus far, the known chemistry of I and II is largely associated with replacement of the halogen by acetate, alkoxide and hydroxide.

This is one of a series of papers on the chemistry of skipped diynes.[1,2] Our interest in triethynylcarbinols (1) was directed towards the preparation of new triethynyl compounds of the type $(RC{\equiv}C)_3CX$. In the course of this work, we discovered that one could not go very far in this area without encountering, first the isomeric allenes, $(RC{\equiv}C)_2C{=}C{=}CXR$, then their dimers.[2] An account of this progression and diversion from our original goals follows.

Triethynylcarbinol chemistry. A survey of most of the reported work on triethynylcarbinols has been given,[3] but the chief contributions of interest here were made in the period 1925–1937 by Marvel, *et al.* We have repeated some of the synthetic work: understandably, some of Marvel's structural assignments have to be revised.

Among the triethynylcarbinol compounds that we sought were the halides, the Grignard reagent, and the hydrocarbon. From our chart of the reactions (Fig 1) it is apparent that this search was unsuccessful, notwithstanding some of Marvel's early claims. Our work began with *tris*(phenylethynyl) methanol (**1c**), but we were unable to convert the hydroxyl function to the halide or tosylate. Because there were reports on their chemistry and because they contained a convenient handle for PMR identification, much of our work then focused on the *tris*(t-butylethynyl)methyl (**1a**) and *tris*(1-propynyl)methyl (**1b**) systems.

At room temperature, **1a** reacted vigorously with strong acids, but a stable solution of the carbonium ion (**2a**) could be obtained at temperatures below 3° in chlorosulfonic acid. The PMR spectrum in this acid showed a single methyl proton resonance which we ascribe to the *tris*(t-butylethynyl) methyl carbonium ion (**2a**).

Stable solutions of the *tris*(1-propynyl)methyl cation (**2b**) has previously been prepared by the addition of fluorosulfonic acid to solutions of **1b** in liquid SO_2 at −78°.[4] A comparison of the PMR shifts of the carbinols and carbonium ions follows:

$(Me_3CC{\equiv}C)_3COH$ (**1a**), δ_{CH_3} 1·70
$(MeC{\equiv}C)_3COH$ (**1b**), δ_{CH_3} 1·87

$(Me_3CC{\equiv}C)_3C^+$ (**2a**), δ_{CH_3} 1·86
$(MeC{\equiv}C)_3C^+$ (**2b**), δ_{CH_3} 2·76

In the case of **1b** and **2b**, there is a downfield shift of 0·89 ppm for the carbonium ion relative to the carbinol which has been attributed to charge delocalization[4] at the site of the attached methyl group. The much smaller shift of 0·16 ppm in **2a** relative to **1a** is difficult to appreciate in isolation. For comparison, the pair di-t-butylcyclopropenone (δ 1·34)-tri-t-butylcyclopropenium ion (δ 1·58),[5a] shows an increment of 0·24. Clearly, the well known insensitivity of t-butyl PMR shifts relative to methyl shifts is not appreciably changed in the carbocations.[5b]

In strong acids, **1** give intriguing colour reactions.[3,6–9] The course of these reactions seems to be complex, but in a few cases, the carbinol can be recovered by dilution of the acidic solution with water, or other products can be isolated. Following Salzberg and Marvel,[9] we treated **1a** in glacial acetic

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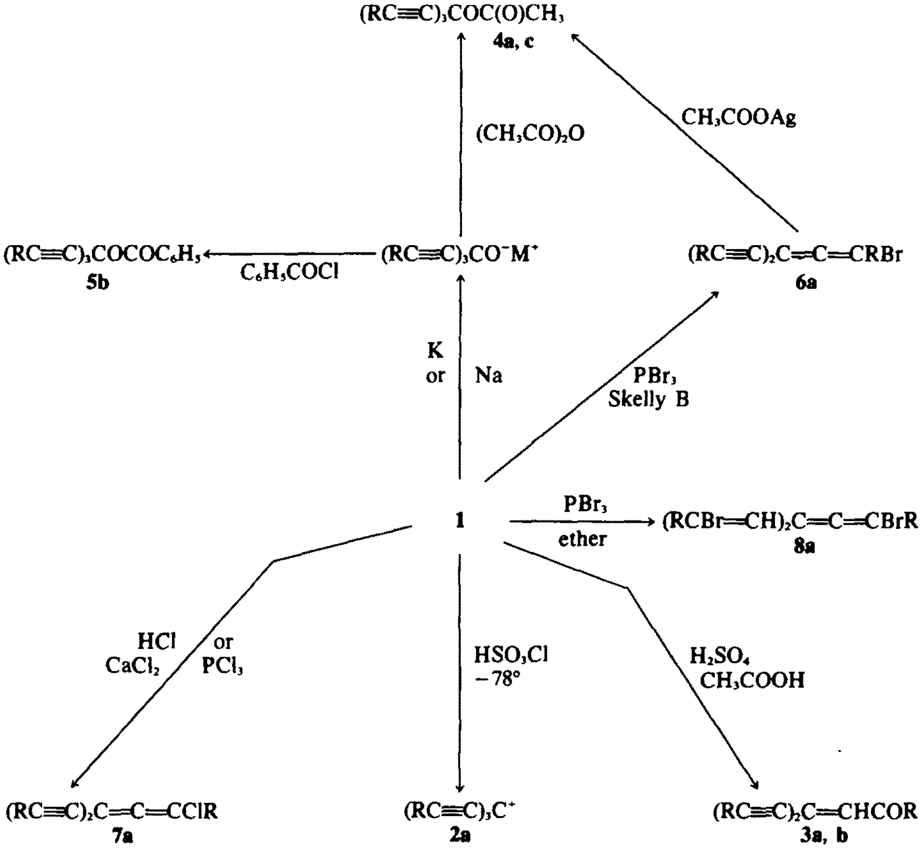


Fig 1. Reactions of $(RC\equiv C)_3COH$ **1** (**1a** R=Me$_3$C; **1b** R=Me; **1c** R=Ph)

acid with sulfuric acid and obtained the ketone **3a** (Fig 1). Evidently this is a typical Meyer–Schuster rearrangement, which probably goes through **2a**. In like manner, an attempted reaction of **1b** with wet phosphorus trichloride led to **3b**. As for **1c**, we confirmed its halochromy in strong acid,[3,6,7] but isolated no new products.

Apart from **1**, the only triethynylcarbinyl compounds we could prepare were the esters. The procedure indicated in Fig 1 for forming the acetate **4a** from the potassium salt of **1a** is that of Marvel and Salzberg.[9] Using the analogous salts of **1b** and **1c** with acetic anhydride or benzoyl chloride, we also prepared three additional esters.

1,1-*Diethynylallene chemistry*. Marvel *et al.*, claimed that **1** led to triethynylhalomethanes when treated with phosphorus trihalides (or acyl halides).[9-11] Here, we found that **1a**, at least, gave haloallenes **6a** and **7a** as products. The bromoallene (**6a**) could be converted to the triethynylcarbinyl acetate (**4a**) with silver acetate,[9] and to 2,2-di-t-butylethynyl-1-t-butylallene carboxylic acid (**9a**) by the path:

$$\mathbf{6a}\xrightarrow{Mg}\xrightarrow{CO_2}\underset{\mathbf{9a}}{(Me_3CC\equiv C)_2C{=}C{=}C(CMe_3)COOH} \qquad (1)$$

Without our spectral data on compounds **4a**, **6a**, **7a**, and **9a**, it would be plausible, of course, to suppose that **1a**→**6a**→**4a** (Fig 1) and only triethynyl compounds were involved.[9]

When **1a** was treated with phosphorus tribromide in the solvent ether, instead of petroleum ether as above, a tribromide (**8a**) was obtained. If, as we suspect, the phosphorus tribromide was slightly "wet", the hydrogen bromide effects the conversion **6a**→**8a**. Elemental analysis and spectral data are consistent with structure **8a**; we further suppose that the hydrogen bromide additions to the triple bond were in the *anti* sense and that the isomeric structure, with the bromine and hydrogen atoms interchanged, is improbable. Treatment of **8a** with sodium methoxide appears to involve an overall S_N2' process, in which the allenic system disappears. IR evidence ($\nu_{C\equiv C}$ 2240 cm^{-1}) supports

$$\mathbf{8a}\xrightarrow[CH_3OH]{CH_3O^-}\underset{\mathbf{10}}{(Me_3CCBr{=}CH)_2C(OCH_3)C\equiv CCMe_3} \qquad (2)$$

our structural assignment of **10**. The fact that allenic carbon to oxygen bonds form less readily or are less favored than standard carbon to oxygen bonds seems to have some precedent and may be a general phenomenon.[12]

A comment on Salzberg and Marvel's self-coupling of **6a** is in order here. Following these workers, we treated **6a** with silver and probably obtained the same product as theirs (Experimental).[9,13] The three possible coupling products would be:

$$[(Me_3CC{\equiv}C)_3C]_2$$

11

$$[Me_3CC{\equiv}C)_2C{=}C{=}CCMe_3]_2$$

12

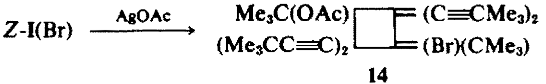
$$(Me_3CC{\equiv}C)_3C{-}C(Me_3C){=}C{=}C(C{\equiv}CCMe_3)_2$$

13

Our spectral evidence is not conclusive, but it would seem that the product is **13**, rather than **11** as was claimed.[9] Thermal rearrangement of the first product presumably led to one of the other dimers.[13]

Allene dimers. Marvel *et al.*, had shown that the compounds they thought to be *tris*(t-butylethynyl)methyl bromide or chloride dimerized fairly readily on heating.[9,10] Sparks and Marvel explained this result by postulating a facile rearrangement to **6a** or **7a** followed by dimerization of these allenes.[14] We confirmed the formation of these dimers, which in fact are often found exclusively, or along with monomer in preparations of the monomer. Since their number has been underestimated[3,14] and we shall have to refer to them later, we set down in Fig 2 the possible structures of the allenic dimers, exclusive of optical isomers. (Note that **I–VI** derive from **6a** and **7a** and **Ib–VIb** derive from **6b** and **7b**.)

Our spectral analysis of the chloro and bromo dimers eliminates four of the six gross structures given in Chart 2. The PMR spectrum is partly diagnostic: six different resonances of equal intensity suggest that forms with equivalent t-Bu groups, i.e. **II**, **III**, **IV**, **V**, must be ruled out. In addition to elemental analyses and molecular weight determinations, Marvel *et al.*, found that in **I**(Br) (from **6a**), one of the Br atoms was reactive and one was relatively inert to hydrolysis with alcohols, esterification with silver acetate, and coupling with silver.[9,10,14] Both **I** and **VI** should have one halogen that is more reactive with such reagents:



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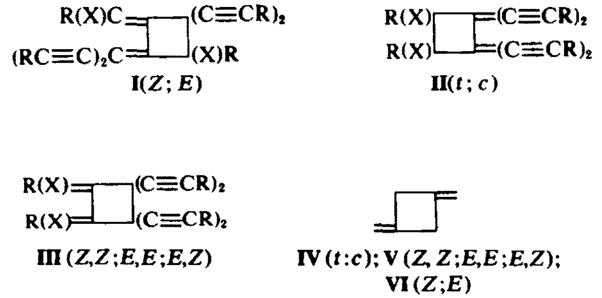
(3)

Other chemical observations, e.g., on oxidation or thermal rearrangement carried out by us or by Marvel *et al.*, would not allow one to assign the dimeric structure.[14] Our attempts to effect Diels–Alder reactions with maleic anhydride or tetracyanoethylene were inconclusive, either because no addition occurred or no adduct was isolated. Since similar 1,2-dimethylenecyclobutanes either do not react, or react very slowly, with dienophiles,[15,16] we cannot reject structure **I** on this basis. As between structures **I** and **VI** we must favor **I**, since 1,3-dimethylenecyclobutanes have never been observed as products of the dimerization of substituted allenes; allene itself dimerizes to give a mixture of 1,2- and 1,3-dimethylenecyclobutanes, the 1,3-isomer being a minor product (< 15%).[15] It is interesting that Sparks and Marvel also favored structure **I**.[14]

The UV spectrum of the dimer from **6a** does, however, appear to be more appropriate to **I** rather than **VI**. The example of 1-bromo-3-methyl-1,2-butadiene and its dimer is apropos.[16] The enhanced absorption and lower energy bands in the diene can presumably be associated with the 1,3-diene moiety. Our dimer formed from **6a** shows similar behavior. This appears to be a larger effect than one can ascribe to the cross-conjugated enediyne moiety, for which 3-methylene-1,4-diyne is the model compound.[17] In structure **VI**, there is no additional conjugation over the monomeric form, except perhaps for the methylene interactions diagonally across the cyclobutane ring; in structure **I** (Br) there would be 1,3-diene conjugation in the adjacent methylene groups. The details of our UV comparison, which follows, clarify our preference for **I**.



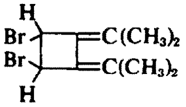
I(*Z*; *E*)

II(*t*; *c*)

III (*Z,Z*;*E,E*;*E,Z*)

IV (*t*:*c*); **V** (*Z, Z*;*E,E*;*E,Z*); **VI** (*Z*;*E*)

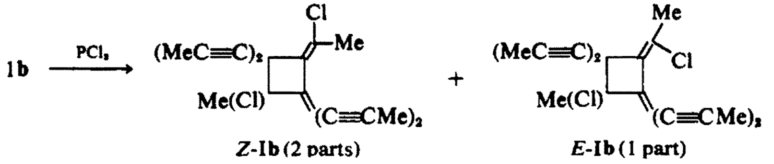
Fig 2. Fourteen possible dimers of **6** or **7** (R = CMe$_3$ or Me; X = Br or Cl; *t* = *trans*, *c* = *cis*, *E* = *seqtrans*, *Z* = *seqcis*); the substituents in the 1,3-dimethylene forms, **IV–VI**, are the same as those in **I–III**.

		λ, nm (ε)
$(CH_3)_2C=C=CHBr$[16]	95% C_2H_5OH	221 (7000)
	95% C_2H_5OH	285 (8300), 221 (13400)
$(HC\equiv C)_2C=CH_2$[17]	isooctane	233
$(Me_3CC\equiv C)_2C=C=CBrCMe_3$	CH_3OH	276 (15000), 238 (7600)
Dimer I (Br)	C_2H_5OH	350 (21000), 342 (20000), 267 (13000)

The detailed structure of *E*-**I** and *Z*-**I** may now be specified. In *E*-**I**, the vinylic chlorine is directed in toward the double bond; in *Z*-**I** the vinylic *t*-butyl group is directed inward. **I**(Cl) (from **7a**) has a PMR spectrum consisting of six lines at $\delta = 1{\cdot}18$, 1·21, 1·24, 1·25, 1·32, and 1·43. **I**(Br) (from **6a**), has a very similar set of PMR lines, $\delta = 1{\cdot}18$, 1·21, 1·26, 1·27, 1·37 and 1·46. Since the t-Bu protons resonate at $\delta \sim 1{\cdot}23$ in t-butylethynyl, at $\delta \sim 1{\cdot}43$ in t-butylchlorocyclobutyl (see Dimer **II** (Cl)), and $\delta = 1{\cdot}17$ in 1-t-butyl-1-chloroethene, all of the resonances but one, δ 1·32, are accounted for. If this is assigned to the vinylic t-Bu group and this is pointed outward, δ should be ~1·17. If however, the t-Bu group were directed inward, its protons "should be deshielded both by "bumping" and the diamagnetic anisotropy of the opposing double bond."[18] Incidentally, the chemical shift of this t-Bu group, and it alone, shows a significant substituent effect as between the bromo (δ 1·37) and chloro (δ 1·32) dimers **I**. These observations are again consistent with the *Z*-**I** structure and in agreement with the curious preference of large groups (e.g., phenyl, mesityl) to occupy inward-facing methylene positions in allene dimers.[18]

In one of our attempts to make a triethynylmethyl derivative, we treated **1b** with phosphorus trichloride. In this case a 2/1 mixture of dimers was obtained.[11a] This structural assignment was made on the basis of the fact that in the NMR spectrum, inward-facing methylene substituents are deshielded relative to outward-facing methylene substituents.[18]

Our further findings on dimer chemistry essentially extend or correct the pioneering work of Marvel and Sparks.[14] On heating, *Z*-**I** (Cl) is quantitatively transformed into a second product which turns out to be *trans*-**II** (Cl)(Eq 5).[2] The lability of both halogen atoms, which we describe presently (Eq 5), is in accord with structure **II** but not **I** or **III**. The PMR spectrum of this compound showed two sets of two lines in the ratio 2:1, indicating that a symmetric structure was required; the presence of characteristic t-butylhalocyclobutyl (δ 1·42) and the absence of t-butylvinyl (δ ~ 1·18 or 1·32) chemical shifts supports structure **II** and rules out **III**.



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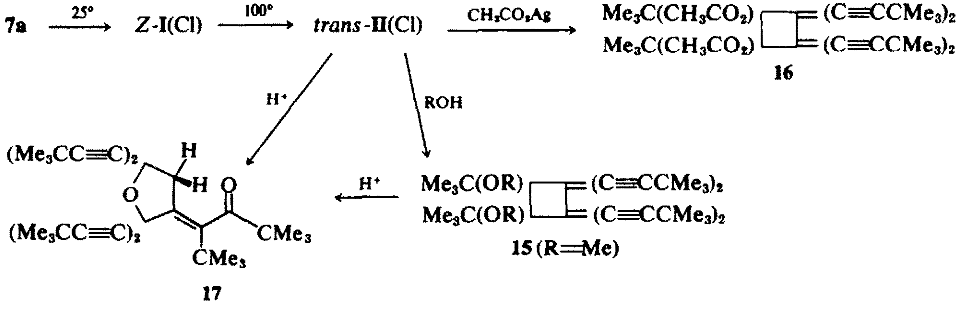


(5)

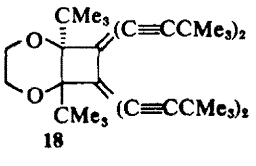
The UV spectrum of **II** (Cl) (λ_{max} 360 nm, ϵ 19000) showed a bathochromic shift relative to **I** (Cl), (λ_{max} 340 nm, ϵ 21000) also consistent with more extensive enyne conjugation in **II**(Cl). A related observation is the fact that **II** appears to be the most stable dimer–it is the end product of relatively long periods (3 days) of heating at 100°, conditions which appear to be conducive to possible isomerization.[2]

Among the other structural probes we have considered, e.g., X-ray, dipole moment, we were able to obtain chlorine nuclear quadrupole resonance (NQR) data for **I** (Cl) and **II**(Cl). Specifically we expected and found two lines of equal strength for **I** at 34·64 (Cl, ring) and 35·24 (Cl, vinyl) MHz; we expected and found one line for **II** at 33·93 MHz (Cl, ring). For comparison, some typical chlorine NQR resonances (in MHz) are: $(CH_3)_3CCl$, 31·065; $H_2C{=}CHCl$, 36·0; c-C_3H_5Cl, 34·063.[19,20] Lacking data on model compounds and allowing for some problems in interpreting data taken on solids,[20] we believe that the NQR results are nevertheless consistent with our structural assignments, although the choice of **II** over **III** could not be based on them.

As yet we have no evidence by which we could label **II** (Cl) as *trans* or *cis*. Although we calculate a difference of ~1·0 Debye unit in *cis* and *trans*-**II** (Cl), we were unable to measure the dipole moment by the usual methods due to the insolubility of **II** (Cl) in nonpolar solvents. However, judging by the relative instability of *t*-Bu groups in *cis*-1,2- as compared with *trans*-1,2-configurations,[21] e.g. di-t-butylethylene, we regard *cis*-**II** (Cl) as highly improbable and favor the *trans*-**II** (Cl) structure.

As was the case with *Z*-**I** (Cl), no Diels–Alder adduct could be obtained with **II**-Cl: here we used dimethyl acetylenedicarboxylate or 4-phenyl-1, 2, 4-triazoline-3,5-dione as the dienophiles. When *trans*-**II** (Cl) was heated in refluxing alcohols, both halogens were replaced by alkoxide to give ethers, e.g. **15** (Eq 5).[14] Such displacements from cyclobutyl halides under neutral or basic conditions are known.[22] All spectral data were consistent with this structure; in particular, the UV spectrum was identical with that of **II** (Cl). With ethylene glycol and **II** (Cl), the major product appears to be the cyclic diether **18**. Dimer **II** (Cl) was also found to react with silver acetate in acetic acid to give diacetate (**16**) analogous to **15** (Eq 5).

Marvel reported that both **II** (Cl) and its dimethoxy derivative (**15**) were hydrolyzed in acid solution to give "the expected diketone",[14] presumably $(RCOC{=}C(C{\equiv}CR)_2)_2$. We have repeated this work many times but have not been able to obtain a pure product. Our material, assigned as **17** (Eq 5), melts over a 5° range and this is ~10° higher than that previously reported.[14] In its IR spectrum there are possible carbonyl and ether bands (1695, 1060, 1000 cm^{-1}). Its NMR spectrum has six distinct t-Bu resonances as well as a multiplet (δ ~ 1·7), presumably indicative of a completely unsymmetric structure. From its UV spectrum (λ_{max} = 294 nm, ϵ 25000), it is evident that the 1,2-diene character of **II** has vanished. In its mass spectrum, the "parent" peak at *m/e* 544 coincides with a molecular weight that would be obtained by replacing both Cl in **II** with OH; this is also consistent with its reported elemental analysis.[14] Of the many structures considered by us (K.G.M. Ph.D. thesis), **17** appears to best fit the observations at this time.



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EXPERIMENTAL

M.ps were determined on a Mel-Temp apparatus and are uncorrected. PMR spectra are given with respect to TMS as an internal standard. IR spectra of solids were taken in KBr pellets or as dilute solns in CCl_4 or $CHCl_3$, IR spectra of liquids were taken as films. NQR spectra obtained on a Wilks NQR-1 Spectrometer at 77°K, are probably accurate to ±0·05 MHz.

Tris(t-butylethynyl)carbinol (**1a**) was prepared by a standard method.[8,10] 2,2-Dichloro-3, 3-dimethylbutane, NMR (neat) δ 1·23 (9H), 2·17 (3H), and 2-chloro-3, 3-dimethyl-1-butene, NMR (neat) δ 1·17 (s, 9H), 5·09 (q, 2H, J = 1·5 Hz) were prepared from pinacolone,[23] and dehydrochlorinated with KOH in a stainless steel reactor to give t-butylacetylene, NMR (neat) δ 1·2 (s, 9H), 1·92 (s, 1H). This was converted to an ethynyl Grignard reagent, which on treatment with diethyl carbonate, gave **1a**, m.p. 102–103° (lit.[14] m.p. 100–102·2°) from n-hexane: IR (CCl_4) 3540 (OH), 2240 ($C{\equiv}C$) cm^{-1}; NMR (CCl_4) δ 1·25 (s, 27H) and 2·09 (s, 1H).

In preparing **4a**, we followed both routes (Fig 1).[9] The acetate had: m.p. 143–144° (lit.[9] m.p. 143·5–144·5°); IR 2220 ($C{\equiv}C$) 1750 (CO) cm^{-1}; NMR ($CDCl_3$) δ 1·21 (s, 27H), 2·07 (s, 3H).

Tris(t-butylethynyl)carbonium ion (**2a**). Compound **1** reacted vigorously with chlorosulfonic or sulfuric acids. In the range −70° to 3°, a stable soln can be obtained in chlorosulfonic acid; δ_{CH_3} 1·86 and δ_{H^+} 11·47. The PMR spectrum is the same at 3° and −20°. In trifluoroacetic acid (90%)-sulfuric acid (10%), the PMR spectrum had δ 1·53 and 1·43, with areas in the ratio 2:1; in trifluoroacetic acid (50%)—sulfuric acid (50%) the resonances were δ 1·70 and 1·62, again with areas in the ratio 2:1; in sulfuric acid only one broad peak was observed. Trifluoroacetic acid is apparently not strong enough an acid to generate the carbonium ion; it is possible that an allenic trifluoroacetate analogous to **6** and **7** does form, however.

Tris(1-propynyl)carbinol (**1b**). An ethereal soln of propynylmagnesium bromide (1 mole; prepared from EtMgBr and propyne) was added slowly with stirring to an ice-cooled ethereal soln of diethyl carbonate (39·3 g, 0·33 moles). When the addition was completed (~2 h), the mixture was stirred at 0° for 1 h and at ~25° for ~12 h. The mixture was refluxed for 1 h and then poured slowly into cold sat aq NH_4Cl. Workup yielded a brown oil which crystallized to a brown solid upon treatment with ligroin.

This solid, sublimed at 120° (1 mm), was recrystallized from dichloromethane-ligroin to give white crystals in 30% yield: m.p. 138–139° (lit.[11a] 134–135°); IR ($CHCl_3$) 3540, 3300, 2280, 2240 cm^{-1}; NMR δ ($CDCl_3$) 1·92 (s, 9H), 2·99 (s, 1H).

Tripropynylmethyl benzoate (**5b**). A soln of **1b** (0·5 g) in dry THF was stirred with an excess of freshly-cut Na metal until all gas evolution ceased (*ca* 2 h). This soln was then decanted from the unreacted Na metal and treated with benzoyl chloride (0·5 g) at 25° for 12 h. Workup yielded a white solid, m.p. 111–113° (dec), from ligroin-benzene: IR (CCl_4) 2260 (C≡C), 1740 (C≡O), 1280, 1090 (C—O) cm^{-1}; NMR ($CDCl_3$) δ 1·98 (s, 9H), 7·7 (m, 3H), 8·4 (m, 2H). (Found: C, 81·93 H, 5·31. Calc for $C_{17}H_{14}O_2$: C, 81·58: H, 5·61%).

Triphenylethynylmethyl acetate (**4c**). Triphenylethynylcarbinol (**1c**) was prepared as described,[6,7] m.p. 131·5–132·5° (lit.[7] m.p. 131°). To **1c** (1·7 g) in ether was added potassium. After 0·5 h, the supernatant liquid was decanted and treated with Ac_2O (1 g). Workup of the mixture gave a product (1·5 g) which had: m.p. 90–91°, from ether-Skelly B: IR (KBr) 2225 (C≡C), 1725 (C=O) cm^{-1}; NMR ($CDCl_3$) δ 2·18 (s, 3H), *ca* 7·4 (m, 15H). (Found: C, 86·21; H, 5·16, Calc for $C_{27}H_{18}O_2$: C, 86·63; H, 4·82%).

Triphenylethynylmethyl benzoate (**5c**). The K- salt of **1a**, formed as above for **4a**, was treated with benzoyl chloride (1 g). The product (0·5 g) had: m.p. 134° dec, from Skelly B; IR (KBr) 2220 (C≡C), 1730 (C=O) cm^{-1}; NMR ($CDCl_3$) δ *ca* 7·4 (m, 18H), *ca* 8·2 (m, 2H). (Found: C, 88·44; H, 4·68, Calc for $C_{32}H_{20}O_2$: C, 88·05; H, 4·62%).

2,2,8,8-*Tetramethyl-5-t-butylethynylnon-4-en-6-yn-3-one* (**3a**). This yellow ketone was prepared from **1a** as described.[9] It had: m.p. 108–109·5 (lit.[9] m.p. 109·5–110·5°): IR (KBr) 2200 (C≡C), 1670 (C=O), 1540 (C=C) cm^{-1}; NMR ($CDCl_3$) δ 1·13 (s, 9H), 1·27 (s, 9H), 1·30 (s, 9H), 6·77 (s, 1H).

4-Propynylhept-3-en-5-yn-2-one (**3b**) *and its 2,4 DNP*. A soln of **1b** (0·5 g) in ether was treated with an excess of freshly-distilled PCl_3 at 25° for 30 min. Workup yielded a yellow-green solid from ligroin. Attempts to purify this solid only resulted in further darkening and tar formation. NMR and IR analysis of this oily solid showed that it was **3b**: IR (CCl_4)2250, 2270 (C≡C), 1665 (C=O), 1560 (C=C) cm^{-1}; NMR ($CDCl_3$) δ 2·0 (s, 3H), 2·08 (s, 3H), 2·38 (s, 3H), 6·4 (s, 1H). This material was dissolved in EtOH and treated with 2,4-dinitrophenylhydrazine in ethanolic phosphoric acid. The resulting red solid was filtered off and recrystallized twice from EtOAc to give dark red plates, m.p. 202–204° (dec): IR ($CHCl_3$) 3280 (NH), 2250 (C≡C), 1620 (C=N), 1540 (C=C), 1530 (NO_2) cm^{-1}; NMR ($CDCl_3$) δ 2·03 (s, 3H), 2·1 (s, 3H), 2·43 (s, 3H), 6·66 (s, 1H), 8·3 (m, 3H), 11·1 (broad, 1H). (Found: C, 58·88; H, 4·29. Calc for $C_{16}H_{14}N_4O_4$: C, 58·89; H, 4·33%).

1,1-*Di-t-butylethynyl-3-t-butyl-3-bromoallene* (**6a**). This allene, previously considered to be tri-t-butylethynylbromomethane, was prepared as described.[9] It had: m.p. 70–71° (lit.[9] m.p. 69–70°); IR (KBr) 2200 (C≡C), 1940 (C=C=C), 650 (C—Br) cm^{-1}; NMR ($CDCl_3$) δ 1·2 (s, 9H), 1·23 (s, 18H); UV (methanol) λ_{max} (ε) 276 (15000), 238 (7600) nm.

Following Salzberg and Marvel, we coupled **6** with molecular silver.[9] The white product had: m.p. 126–127° (lit.[9] m.p. 130–131°); IR (KBr) 2260, 2220 (C≡C) cm^{-1}; NMR (C_6H_6) δ 1·15, 1·20 and 1·65 with peak areas in the ratio 2:3:1. This was not **11**, as had been claimed.[9] Although we perfer structure **13**, the absence of an allenic IR band (*ca* 1950 cm^{-1}) remains unexplained.

4,4-*Di-t-butylethynyl-2-t-butylbutadienoic acid* (**9**). This acid, previously considered to be tri-t-butylethynylacetic acid, was prepared as described.[9] It had: m.p. 204–205° (lit.[9] m.p. 202–205°); IR (KBr)3040 (OH), 2205 (C≡C), 1915 (C=C=C), 1685 (C=O) cm^{-1}; NMR (C_6H_6) δ 1·27 (s, 18H), 1·43 (s, 9H).

3,7-*Dibromo-2,2,8,8-tetramethyl-5-(3,3-dimethyl-2-bromo-1-butenyl)-3,4,6-nonatriene* (**8a**). Compound **1a** (4g) was treated with an old, possibly wet sample of PBr_3 (1 g) in toluene (30 ml) at 0° for 1·5 h. The product was worked up and vacuum distilled (125 Torr, pot temp 100°). The residue was recrystallized from acetone to give a solid, m.p. 84–85° (4·3 g). This had: IR (KBr) 1930 (C=C=C), 1610 (C=C) cm^{-1}; NMR ($CDCl_3$) δ 1·18 (s, 9H), 1·23 (s, 18H), 6·23 (s, 2H). (Found: C, 45·73: H, 5·79. Calc for $C_{19}H_{29}Br_3$: C, 45·89; H, 5·89%).

3,7-*Dibromo-2,2,8,8-tetramethyl-5-(3,3-dimethyl-2-methoxy-1-butenyl)-3,4,6-nonatriene* (**10**). The tribromide **8a** (1 g) was treated with NaOMe (2·5 g) in MeOH (30 ml) for 24 h. After work-up and recrystallization from EtOH, the product had: m.p.: 54–55°; IR (KBr) 2240 (C≡C), 1630, 1615 (C=C), 1080 (C—O) cm^{-1}; NMR ($CDCl_3$) δ 1·2 (s, 18 H), 1·25 (s, 9H), 3·29 (s, 3H), 6·28 (s, 2H). (Found: C, 53·56; H, 7·41. Calc for $C_{20}H_{32}Br_2O$: C, 53·57: H, 7·21%).

trans-**II** (Br). As indicated by Marvel in the preparation of **6a**,[14] the first crops of crystals from EtOH may contain the dimer. This had m.p. 177–178° (lit.[14] m.p. 177–178°, from acetone; IR (KBr) 2210 (C≡C) cm^{-1}; NMR ($CDCl_3$) δ 1·46 (s, 9H), 1·18 (s, 9H), 1·37 (s, 9H), 1·27(s, 9H), 1·26 (s, 9H), 1·21 (s, 9H); UV (EtOH) λ_{max} (ε) 350 (21000), 342 (20000), 267 (13000) nm. The monoacetate (**14**) formed from **II** (Br) and silver acetate[14] had: m.p. 114–115° (lit.[14] m.p. 108–110·): IR (KBr) 2210 (C≡C), 1760 (C=O) cm^{-1}; NMR ($CDCl_3$) δ 1·14 (s, 9H), 1·21 (s, 18H), 1·26 (s, 9H), 1·32 (s, 9H), 1·45 (s, 9H), 2·17 (s, 3H). Attempts to prepare Diels–Alder adducts from **II** (Br) and maleic anhydride or tetracyanoethylene were unsuccessful.

Dimers Z-**1b** (*Eq 5*). Carbinol **1b** (0·5 g) in dry benzene was stirred with an excess of PCl_3 at 25° for 5 min. The dark red mixture was then quenched with sat $NaHCO_3$aq and extracted with ether. Removal of the ether gave a red oil which crystallized upon the addition of abs EtOH. Recrystallization from EtOH gave a yellow solid, m.p. 150–152° (lit,[11a] 153–154°): IR 2250 (C≡C), 1630 (C=C) cm^{-1}; NMR ($CDCl_3$) δ 1·9–2·08 (m, 15H), 2·41 s, 2·59 s (total 3H); UV (EtOH) λ_{max} (ε) 342 (17900), 328 (19000), 250 (500) nm; mass spectrum *m*/*e* (rel abundance) 329 (P^+, 7), 294 (100), 279 (21), 259 (50). TLC (silica, C_6H_6) showed one major and one minor component. Integration of the NMR spectrum gave a relative ratio of *Z*-**Ib**/*E*-**Ib** of 2/1 based on the following tentative spectral assignments: *Z*-**Ib**; δ 2·59, 2·08, 2·00, 1·99, 1·93, 1·90; *E*-**Ib** δ 2·41, 2·03, 1·98, 1·94, 1·93, 1·91.

1,1-*Di-t-butylethynyl-3-t-butyl-3-chloroallene* (**7a**) *and dimer Z*-**I** (Cl). The monomer (**7a**), previously considered to be tri-t-butylethynylchloromethane, was prepared essentially as described.[14] The crude product had: m.p. 66–69° (lit.[14] 73–74°); IR (KBr) 2210 (C≡C), 1935 (C=C=C) cm^{-1}; NMR ($CDCl_3$) δ 1·22 (s, 18H), 1·18 (s, 9H).

Four recrystallizations from ether-EtOH, gave a white solid, m.p. 173°, (lit.[14] m.p. 177–178°) (this is not a true m.p., but rather the temp range within which the dimeric chloride (white solid) changes to a yellow crystalline compound): IR (CCl_4) 2240 (C≡C), 1595 (C=C), 1395, 1365 (t-Bu) cm^{-1}; NMR ($CDCl_3$ 1·18 (s, 9H), 1·21 (s, 9H), 1·24 (s, 9H), 1·25 (s, 9H), 1·32 (s, 9H) 1·43 (s, 9H);

UV (EtOH)λ_{max} (ϵ) 340 (21000), 326 (20000), 265 (6000), 242 (7000) nm; mass spectrum *m/e* (rel abundance) 582 (15), 580 (P$^+$, 20), 547 (15), 545 (20), 525 (70), 523 (75), 510 (25), 467 (95), 431 (100).

trans-**II** (Cl). *Z*-**I** (Cl) was heated to 180° under N_2 for 90 min. After cooling, the dark red mass was pulverized in a mortar and recrystallized from benzene. This produced light yellow crystals, m.p. 253–257° (dec) lit.[14] 257°): IR (CCl_4) 2260 ($C{\equiv}C$), 1605 ($C{=}C$), 1395, 1370 (t-Bu) cm^{-1}; NMR ($CDCl_3$) δ 1·23 (s, 18H), 1·42 (s, 9H), 1·43 (s, 9H); UV (EtOH) λ_{max} (ϵ) 360 (19000), 345 (17000), 256 (19000), 248 (21500) nm; mass spectrum *m/e* (rel abundance) 582 (80), 580 (P$^+$, 100), 545 (20), 547 (15), 525 (30), 523 (25), 467 (80), 431 (90).

"*Dimethoxydimer*" (**15**). Dimer **II** (Cl) was suspended in MeOH and refluxed until the yellow color was no longer visible (*ca* 30 min/ 0·5 g). The resulting white solid was filtered off and used directly. It had m.p. 259–260° (sublimes; sealed tube) (lit.[14] m.p. 250°): IR (CCl_4) 2820 (OMe), 2260 ($C{\equiv}C$), 1605 ($C{=}C$), 1395, 1365 (t-Bu); 1110, 1090, 1080 (C—O—C) cm^{-1}; NMR ($CDCl_3$) δ 1·12 (s, 18H), 1·23 (s, 18H), 1·35 (s, 18H), 3·25 (s, 6H); UV (EtOH) λ_{max} (ϵ) 360 (19000), 345 (17000), 256 (18500), 247 (20500) nm; mass spectrum *m/e* (rel abundance) 572 (P$^+$, 70), 515 (100), 458 (20).

trans **18**. A soln of dimer **II** (Cl) in dioxane was treated with ethylene glycol at 100° for 30 min. Upon cooling, a white solid formed. Chromatography of this solid on alumina with benzene eluant gave a small amount of white solid in the first fractions. This material exhibited a broad, m.p. range. It had: IR (KBr) 2960–2820 (C—H), 2220 ($C{\equiv}C$), 1695w ($C{=}O$?), 1605 ($C{=}C$), 1100, 1115 (C—O) cm^{-1}; NMR ($CDCl_3$) δ 1·18 (s, 18H), 1·24 (s, 18H), 1·35 (s, 18H), 3·23 (m, 4H); UV (EtOH) λ_{max} (ϵ) 360 (2000), 349 (18000), 298 sh (7500), 288 sh (6250), 256 (21500), 248 (24200) nm; mass spectrum *m/e* (rel abundance) 572 (P$^+$, 50), 515 (100), 459 (60). The presence of the weak 1605 cm^{-1} band in the IR spectrum indicated the presence of an impurity similar to the hydrolysis product **17**. We were unable to purify **18** further.

"*Dimer diacetate*" (**16**). To a solution of **II** (Cl) (0·5 g) in glacial AcOH (50 ml) at 110° was added a slurry of AcOAg (0·5g) in glacial AcOH (20 ml) at 110°. This soln was stirred in the dark for 24 h, after which the solid ppt was filtered off and the filtrate was poured onto crushed ice. Workup yielded a white solid, m.p. 262–264°, (dec) from ether–ligroin: IR (CCl_4) 2220 ($C{\equiv}C$), 1750 ($C{=}O$), 1610 ($C{=}C$), 1395, 1365 (t-Bu), 1250 (C—O)cm^{-1}; NMR ($CDCl_3$) δ 1·15 (s, 18H), 1·22 (s, 18H), 1·26 (s, 18H), 2·02 (s, 6H); UV (EtOH) λ_{max} (ϵ) 360 (18500), 345 (17000), 256 (18800), 246 (21900) nm; mass spectrum *m/e* (rel abundance) 630 (50), 629 (P$^+$, 100), 529 (80). (Found: C, 79·86; H, 9·83. Calc for $C_{42}H_{60}O_4$: C, 79·95; H, 9·9%).

Hydrolysis of **II** (Cl) *and the product* (**17**). Following the standard procedure,[14] **II**(Cl) (0·2 g) was refluxed in 50% H_2SO_4 (25 ml) for 2 h. The resulting soln was poured onto crushed ice and extracted with ether. The combined extracts were washed with aq$NaHCO_3$ and sat aqNaCl. Removal of the ether and recrystallization of the residue from MeOH gave a white solid, m.p. 177–181° (lit.[14] m.p. 169–170°). TLC with CCl_4 on silica gel showed a major and minor component; there was evidence of decomposition of the material on the plate. Further recrystallizations or sublimations proved to be ineffective in improving purity. Spectral data were as follows: IR (CCl_4) 2960, 2840 (CH), 2250 ($C{\equiv}C$), 1700 ($C{=}O$?), 1395, 1370 (t-Bu), 1100 (C—O—C?) cm^{-1}; NMR ($CDCl_3$) δ 0·93 (s, 9H), 1·18, 1·21, 1·22, 1·23 (m, 36H), 1·3 (s, 9H), 1·7 (m, 4H); UV (EtOH) λ_{max} (ϵ) 294 (25000), 284 (25500), 228 (22200) nm; mass spectrum *m/e* (rel abundance) 545 (10), 544 (P$^+$, 30), 529 (5), 488 (55), 487 (100), 436·5 (1, m*), 431 (20), 432 (10), 382 (1, m*). Found: C, 83·60; H, 10·75. Calc for $C_{38}H_{56}O_2$: C, 83·77; H, 10·36%).

The following test reagents gave negative or inconclusive tests with **17**: bromine in carbon tetrachloride; 2,4-dinitrophenylhydrazine; hydroxylamine hydrochloride; ceric nitrate; periodic acid; chromium trioxide.

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