The α-Alk-1-ynylation of β-Dicarbonyl Compounds and Nitronate Salts by Alk-1-ynyl-lead Triacetates

Mark G. Moloney, John T. Pinhey,* and Eric G. Roche
Department of Organic Chemistry, University of Sydney, Sydney 2006, Australia

Di(alk-1-ynyl)mercury compounds and alk-1-ynyltrimethylstannanes have been shown to react with lead tetra-acetate to give alk-1-ynyl-lead triacetates, unstable intermediates which may be used for the *C*-alkynylation of β-dicarbonyl compounds and the salts of nitroalkanes. A comparative study of the two methods has shown that the tin–lead exchange route to the alkynyl-lead intermediate results in better yields, and in an examination of the scope of this alkynylation procedure the acetylene derivatives (**5**), (**9**)—(**14**), (**27**)—(**30**), (**32**), (**34**), (**36**)—(**41**), (**43**), (**45**), (**47**)—(**49**), and (**51**)—(**56**) have been produced in moderate to good yields.

We have recently shown that aryl-lead triacetates[1] and vinyl-lead triacetates[2] are useful reagents for the arylation and vinylation respectively of soft carbon nucleophiles such as the enolates of β-dicarbonyl compounds and nitronate salts. In this paper we report the extension of this work to the formation of alk-1-ynyl-lead triacetates, which, although unstable, can be employed *in situ* for the alkynylation of the same carbon nucleophiles.[3]

Recent work on the generation of alkynyl cations[4,5] would suggest that the dissociative production of such species is unlikely to be synthetically useful. Thus, nucleophilic substitution at acetylenic carbon is achieved by the use of alkynyl cation equivalents, and there has been considerable interest in this area of synthesis.[6,7] The most commonly used compounds of this type have been halogenoacetylenes, which will react with vinylic and acetylenic cuprates to give enynes[8] and diynes[9] respectively. Also, it has been known for some time that the sodium salt of diethyl ethylmalonate can be converted into the α-chloroacetylene derivative by reaction with dichloroacetylene,[10] and this reaction has recently been extended by Kende,[11] who has shown that a variety of enolates can be made to react with a limited range of halogenoacetylenes. The reaction is thought to proceed by nucleophilic addition–elimination, since only acetylenes in which the intermediate anion would be stabilised give significant yields of the α-alkynyl derivative. No reaction occurred with 1-chlorohex-1-yne.

The only previous report of an alk-1-ynyl-lead triacetate was that of Moon and Campbell,[12] who proposed phenylethynyl-lead triacetate as an intermediate in a reaction of phenylacetylene and lead tetra-acetate in acetic acid; however, there was no direct evidence for its existence. Our initial approach to the synthesis of these compounds involved mercury–lead exchange which we had successfully employed for the generation of vinyl-lead triacetates.[2] Bis(phenylethynyl)mercury (**1**) was found to react rapidly with lead tetra-acetate in a mixture of chloroform and pyridine, and addition of ethyl 2-oxocyclopentanecarboxylate (**4**) to the solution after 10 min resulted in formation of the α-alkynylated β-keto ester (**5**) in 25% yield (entry 1, Table 1). In analogy with the chemistry of diarylmercury[13] and divinylmercury[2] compounds, the proposed route to compound (**5**) is that outlined in Scheme 1. No direct evidence was obtained for the formation of phenylethynyl-lead triacetate (**2**) or the corresponding mercury compound (**3**); however, we believe that the lead compound (**2**) is the species responsible for the alkynylation. The time allowed for the mercury–lead exchange, and to a lesser extent the solvent, were found to affect the success of the alkynylation reaction (see Table 1). When the exchange time was decreased to 0.5 min the yield of product (**5**) was increased to 53% (entry 2, Table 1), while a reaction performed in dimethyl sulphoxide (DMSO)–pyridine with a 5 min exchange time afforded compound (**5**) in 60% yield (entry 3, Table 1).

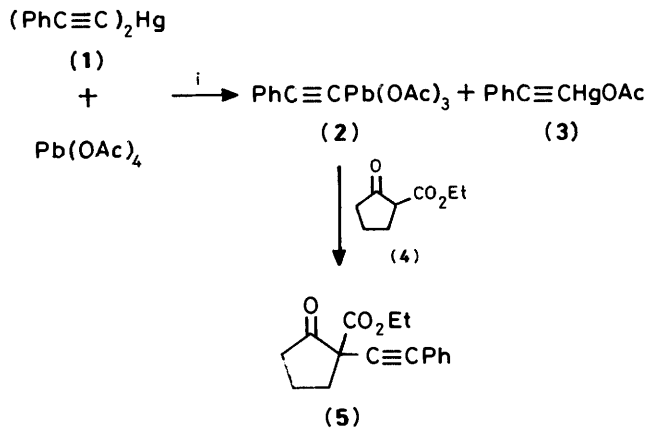
Bis-(*p*-methoxyphenylethynyl)mercury (**6**) behaved similarly in the sequence outlined in Scheme 1, giving moderate yields of the α-alkynyl β-keto ester (**9**) by use of mercury–lead exchange times of 0.5 to 2.5 min (entries 4, 5, and 6, Table 1). When di(oct-1-ynyl)mercury (**7**) was subjected to the same reaction sequence the analogous β-keto ester (**10**) was obtained, albeit in somewhat lower yield (entries 7 and 8, Table 1). This was possibly due to the low solubility of the mercury compound (**7**) and to a slower mercury–lead exchange.

In an attempt to improve the above alkynylation reaction,

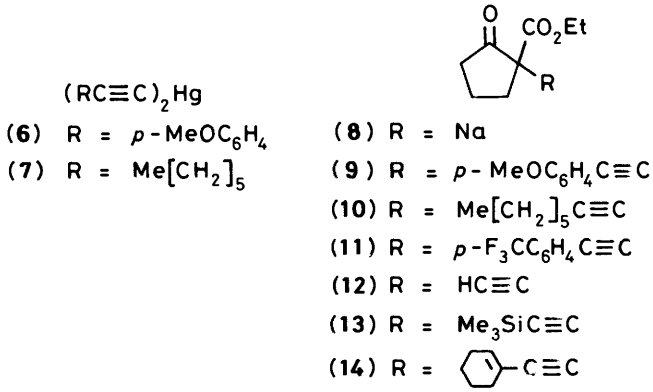
Table 1. Reactions of β-keto ester (4) with alk-1-ynyl-lead triacetates produced *in situ* by reaction of bis(alk-1-ynyl)mercury compounds with lead tetra-acetate (LTA)

Entry	$(RC{\equiv}C)_2Hg$	Mol equiv.[a] $R^1{}_2Hg$	Mol equiv.[a] LTA	Time (min)[b]	Solvent	Product	Isolated yield (%)
1	(**1**)	1.0	1.0	10	$CHCl_3$–py	(**5**)	25
2	(**1**)	0.95	1.0	0.5	$CHCl_3$–py	(**5**)	53
3	(**1**)	0.8	0.9	5	DMSO–py	(**5**)	60
4	(**6**)	0.8	0.8	0.5	$CHCl_3$–py	(**9**)	46
5	(**6**)	0.9	1.0	0.5	DMSO–py	(**9**)	51
6	(**6**)	0.95	1.0	2.5	$CHCl_3$–py	(**9**)	50
7	(**7**)	0.7	0.7	5	$CHCl_3$–MeCN	(**10**)	11
8	(**7**)	0.6	0.6	2	$CHCl_3$–MeCN	(**10**)	18

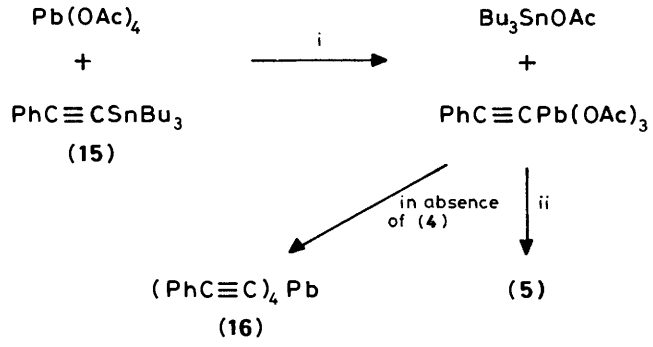
[a] Relative to (**4**). [b] Time allowed for mercury–lead exchange before addition of (**4**).



Scheme 1. *Reaction conditions:* i, $CHCl_3$–py, room temp. 10 min



and to gain evidence for the intermediacy of alk-1-ynyl-lead triacetates, we turned to tin–lead exchange, a method which we had found to be particularly useful for the synthesis of aryl-lead triacetates[14] and vinyl-lead triacetates.[2] When tributyl(phenylethynyl)stannane (**15**) was stirred with lead tetra-acetate in chloroform at room temperature, a rapid reaction occurred, as shown by the formation of tributyltin acetate in high yield. If after 2 min a dry 1:1 ether–light petroleum mixture was added, a yellow precipitate was obtained. We believe that this unstable material, which was free of stannanes (n.m.r. spectroscopy), contained the lead compound (**2**) since, when mixed with the β-keto ester (**4**), the acetylene derivative (**5**) was produced in 19% yield (see Scheme 2). Evidence for the fate of the lead compound



Scheme 2. *Solvent or reagent:* i, $CHCl_3$; ii, (**4**)

(**2**), in the absence of a nucleophile, came from the isolation of tetrakis(phenylethynyl)lead (**16**) in 46% yield from a chloroform solution of compound (**15**) and lead tetra-acetate which was kept at room temperature for 3 h. Compound (**16**), which is inert to the keto ester (**4**), presumably arises as indicated in Scheme 3. The absence of lead tetra-acetate from the reaction mixture after 3 h is thought to be due to its oxidation of the phenylethynyl group, and this would account for the low yield of compound (**16**).

Because of difficulty experienced with the removal of tributyltin acetate from the product (**5**), when the lead compound (**2**) was generated *in situ* from tributyl(phenylethynyl)stannane (**15**), we turned to the use of alkynyltrimethylstannanes. These compounds had the additional advantage of undergoing faster tin–lead exchange with lead tetra-acetate. In the case of trimethyl(phenylethynyl)stannane (**17**), reaction with lead tetra-acetate in chloroform produced trimethyltin acetate in almost quantitative yield (n.m.r. spectroscopy) after 0.5—1 min. When the β-keto ester (**4**) was added 0.5 min after mixing of compound (**17**) and lead tetra-acetate, the α-alkynyl derivative (**5**) was produced rapidly and in good yield (Scheme 4; entry 1, Table 2).

$$PhC{\equiv}CSnMe_3 \xrightarrow{i,ii} (5) + Me_3SnOAc + Pb(OAc)_2 + HOAc$$
(**17**)

Scheme 4. *Reagents and conditions:* i, LTA, $CHCl_3$, 0.5 min; ii, (**4**)

The reaction was rather insensitive to the solvent, with best results being obtained in chloroform, and unlike analogous arylation reactions of aryl-lead triacetates,[15] pyridine had no effect on the yield of compound (**5**). The procedure outlined in Scheme 4 was applied to trimethyl(oct-1-ynyl)stannane (**18**), to yield the α-octynyl β-keto ester (**10**) in 54% yield (entry 2, Table 2), a marked improvement on the result obtained with the corresponding mercury compound (**7**). The instability of the intermediate oct-1-ynyl-lead triacetate is reflected in the considerably higher yield of compound (**10**) which was achieved by use of 2.0 mol equiv. of the lead reagent (entry 3, Table 2).

The scope of the alkynylation reaction outlined in Scheme 4 was examined for the alkynyltrimethylstannanes (**17**)—(**25**), the β-dicarbonyl compounds (**4**), (**26**), (**31**), (**33a**), (**35a**), (**42**), and (**44a**), and the nitro compounds (**46a**) and (**50a**), and the results are recorded in Table 2. In most cases the conditions used were those indicated in Scheme 4, and as can be seen in Table 2 the yields were generally moderate to good, indicating that the method should be widely applicable. In the majority of cases the rate of tin–lead exchange was similar to that of tin compound (**17**) and the alkynyl-lead intermediates showed similar instability to that of (**2**), thus yields may be increased by the use of excess of reagent.

In the alkynylation of the β-keto lactone (**26**) (entries 4 and 5, Table 2) care was required in the work-up, since hydrolytic cleavage of the acetyl group of the products (**27**) and (**28**) occurred very readily. Thus, if the chloroform was evaporated off at the completion of the alkynylation and the residue refluxed in aqueous acetone for 10 min, synthetically useful yields of the α-alkynyl γ-lactones (**29**) and (**30**) were obtained.

Of particular interest was the reaction of the androstan-3β-ol keto ester (**31**) (entry 6, Table 2), which proceeded in high yield to give the two possible products (**32a**) and (**32b**), with a ratio of 16α-epimer:16β-epimer of 4:1. It would therefore appear that protection of the hydroxy functionality, a group which may be

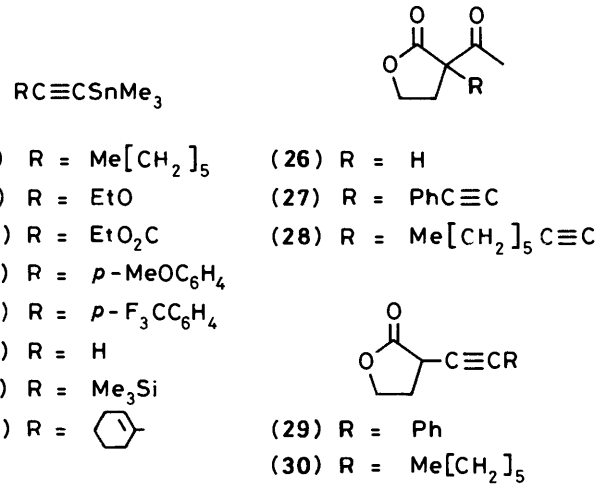
$$2PhC{\equiv}CPb(OAc)_3 \rightleftharpoons (PhC{\equiv}C)_2Pb(OAc)_2 + Pb(OAc)_4$$
$$PhC{\equiv}CPb(OAc)_3 + (PhC{\equiv}C)_2Pb(OAc)_2 \rightleftharpoons (PhC{\equiv}C)_3PbOAc + Pb(OAc)_4$$
$$PhC{\equiv}CPb(OAc)_3 + (PhC{\equiv}C)_3PbOAc \rightleftharpoons (PhC{\equiv}C)_4Pb + Pb(OAc)_4$$

Scheme 3.

Table 2. Reaction of β-dicarbonyls, and their enolate salts, and nitronate salts with alk-1-ynyl-lead triacetates produced *in situ* by reaction of alk-1-ynyltrimethylstannanes with lead tetra-acetate

Entry	Substrate	$RC{\equiv}CSnMe_3$	Reactant proportions	Solvent	Product	Isolated Yield (%)
1	(4)	(17)	*a*	$CHCl_3$	(5)	73
2	(4)	(18)	*a*	$CHCl_3$	(10)	54
3	(4)	(18)	*b*	$CHCl_3$	(10)	77
4	(26)	(17)	*a*	$CHCl_3$	(27)	60
5	(26)	(18)	*a*	$CHCl_3$	(28)	57
6	(31)	(17)	*c*	$CHCl_3$	(32)	82[e]
7	(33a)	(17)	*a*	$CHCl_3$	(34)	14
8	(33b)	(17)	*a*	DMSO	(34)	58
9	(35a)	(17)	*a*	$CHCl_3$	(36)	87
10	(35a)	(18)	*a*	$CHCl_3$	(37)	75
11	(42)	(17)	*a*	$CHCl_3$	(43)	47
12	(44a)	(17)	*a*	$CHCl_3$	(45)	17
13	(44b)	(17)	*a*	DMSO	(45)	25
14	(8)	(21)	*d*	DMSO	(9)	75
15	(35b)	(21)	*d*	DMSO	(38)	76
16	(4)	(22)	*a*	$CHCl_3$	(11)	75
17	(35a)	(22)	*a*	$CHCl_3$	(39)	77
18	(4)	(23)	*a*	$CHCl_3$	(12)	57
19	(35a)	(23)	*a*	$CHCl_3$	(40)	69
20	(4)	(24)	*a*	$CHCl_3$	(13)	78
21	(35a)	(24)	*a*	$CHCl_3$	(41)	77
22	(4)	(25)	*a*	$CHCl_3$	(14)	59
23	(46b)	(17)	*a*	DMSO	(47)	72
24	(46b)	(18)	*a*	DMSO	(48)	47
25	(46b)	(21)	*d*	DMSO	(49)	59
26	(50b)	(17)	*a*	DMSO	(51)	62
27	(50b)	(18)	*a*	DMSO	(52)	53
28	(50b)	(21)	*d*	DMSO	(53)	59
29	(50b)	(22)	*a*	DMSO	(54)	50
30	(50b)	(23)	*a*	DMSO	(55)	48
31	(50b)	(24)	*a*	$CHCl_3$	(56)	60

[a] Proportions of substrate:stannane:LTA 1.0:1.2:1.1. [b] Proportions of substrate:stannane:LTA 1.0:2.0:2.0. [c] Proportions of substrate:stannane:LTA 1.0:1.4:1.3. [d] Proportions of substrate:stannane:LTA 1.0:1.65:1.5. [e] A mixture of diastereoisomers, ratio of (32a):(32b) was 4:1.

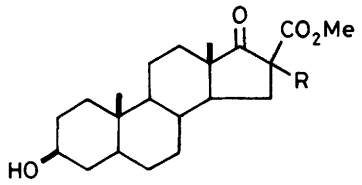


oxidised by lead tetra-acetate, will not be necessary. Less success was experienced with alkynylation of the acyclic β-keto ester (**33a**) (entry 7, Table 2), which gave only 14% of the phenylethynyl derivative (**34**). The yield of compound (**34**) can, however, be improved considerably by use of the sodium salt of the keto ester (**33b**) (entry 8, Table 2); here the tin–lead exchange was successfully achieved in DMSO and the sodium salt was added after a 0.5 min exchange time.

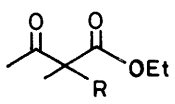
Two β-diketones, (**35a**) and (**42**), and the Meldrum's acid derivative (**44a**), were included in the study. Compound (**35a**) gave the α-phenylethynyl and α-octynyl derivatives, (**36**) and (**37**) respectively, in high yields under the standard conditions (entries 9 and 10, Table 2); however, diketones (**42**) and (**44a**), which undergo high yielding arylations with aryl-lead triacetates,[16,17] were somewhat less reactive (entries 11 and 12 respectively, Table 2), resulting in formation of significant amounts of tetrakis(phenylethynyl)lead (**16**). Unlike the β-keto ester (**33a**), use of the lithium salt (**44b**) did not result in much improvement in the yield of the Meldrum's acid derivative (**45**) (entry 13, Table 2).

The scope of the procedure with respect to the alkynylstannane was examined with the keto ester (**4**) and the diketone (**35a**), and only in the case of (ethoxyethynyl)trimethylstannane (**19**) and the ethoxycarbonyl-substituted compound (**20**) did the reaction fail. The reaction of stannane (**19**) and lead tetra-acetate was highly exothermic, and even at low temperature only a trace of the expected alkynylated product was observed with diketone (**35a**), presumably due to thermal decomposition of the lead intermediate. On the other hand, the stannane (**20**), bearing a strongly electron-withdrawing group, failed to undergo the metal–metal exchange with lead tetra-acetate even with catalysis by mercury(II) trifluoroacetate.

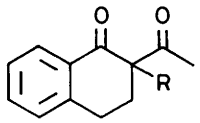
(4-Methoxyphenylethynyl)trimethylstannane (**21**) was very moisture sensitive and underwent a rapid exchange with lead tetra-acetate. With the β-keto ester (**4**) under the conditions of Scheme 4, the expected product (**9**) was obtained in only 23% yield, and it was accompanied by *p*-methoxyphenylacetylene (34%). Thus, it appeared that the acetic acid produced in the alkynylation reaction resulted in protodemetallation of the



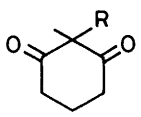
(31) R = H
(32a) R = α-PhC≡C
(32b) R = β-PhC≡C



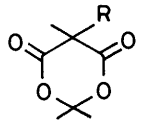
(33a) R = H
(33b) R = Na
(34) R = PhC≡C



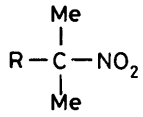
(35a) R = H
(35b) R = Na
(36) R = PhC≡C
(37) R = $Me[CH_2]_5C\equiv C$
(38) R = p-$MeOC_6H_4C\equiv C$
(39) R = p-$F_3CC_6H_4C\equiv C$
(40) R = HC≡C
(41) R = $Me_3SiC\equiv C$



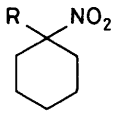
(42) R = H
(43) R = PhC≡C



(44a) R = H
(44b) R = Li
(45) R = PhC≡C



(46a) R = H
(46b) R = Na
(47) R = PhC≡C
(48) R = $Me[CH_2]_5C\equiv C$
(49) R = p-$MeOC_6H_4C\equiv C$



(50a) R = H
(50b) R = Na
(51) R = PhC≡C
(52) R = $Me[CH_2]_5C\equiv C$
(53) R = p-$MeOC_6H_4C\equiv C$
(54) R = p-$F_3CC_6H_4C\equiv C$
(55) R = HC≡C
(56) R = $Me_3SiC\equiv C$

alkynyl-lead intermediate. These problems were overcome by employing a metal–metal exchange time of 15 s and by using the sodium salts of the dicarbonyl compounds, (**8**) and (**35b**). Under these conditions good yields of the α-alkynyl derivatives (**9**) and (**38**) were produced (entries 14 and 15, Table 2). In contrast to the *p*-methoxy derivative (**21**), trimethyl(*p*-trifluoromethylphenylethynyl)stannane (**22**) was less susceptible to protodemetallation, and the tin–lead exchange reaction required 2 min for completion, which is in keeping with an electrophilic addition–elimination mechanism for the metal substitution. Good yields of the α-(*p*-trifluoromethylphenylethynyl) derivatives (**11**) and (**39**) were obtained by use of the standard conditions with a considerably longer time for the tin–lead exchange (entries 16 and 17, Table 2).

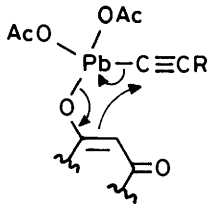
Of particular interest was the application of the alkynylation reaction to ethynyltrimethylstannane (**23**) and the trimethylsilyl-protected compound (**24**). Although very sensitive to moisture, the stannane (**23**) reacted in the usual way to give the α-ethynyl derivatives (**12**) and (**40**) in moderate yields (entries 18 and 19, Table 2). The trimethylsilyl derivative (**24**) was much less sensitive to moisture and reacted quite slowly with lead tetra-acetate; nevertheless, with an exchange time of 20 min good yields of the α-trimethylsilylethynyl derivatives (**13**) and (**41**) were obtained (entries 20 and 21, Table 2).

The final stannane to be examined was the readily available enyne (**25**). Its reaction with lead tetra-acetate was very rapid, giving rise to an extremely unstable alkynyl-lead intermediate. With the usual 0.5 min exchange time, reaction with the β-keto ester (**4**) produced only 18% of the expected alkynylated product (**14**) with 72% recovery of (**4**); however, by reducing the exchange time to 5 s the yield of product (**14**) could be increased to 59% (entry 22, Table 2).

The *C*-arylation of nitro compounds and nitronate salts by aryl-lead triacetates[18] prompted an investigation of these substrates in place of dicarbonyls in the procedure outlined in Scheme 4. Not unexpectedly, owing to their low kinetic acidity and the low stability of the alkynyl-lead compounds no alkynylation of the nitro compounds (**46a**) and (**50a**) was observed. On the other hand, their sodium salts, (**46b**) and (**50b**), underwent rapid alkynylation, and the α-alkynyl nitro compounds (**47**)—(**49**) and (**51**)—(**56**) were produced in synthetically useful yields by use of the procedures indicated above for generating the alkynyl-lead intermediates (entries 23—31, Table 2).

In the above reactions the alk-1-ynyl-lead triacetates are behaving as alk-1-ynyl cation equivalents, which is analogous to the reactivity shown by aryl-lead triacetates[1] and alk-1-enyl-lead triacetates.[2] The mechanism of the reaction remains obscure, but we believe that a nucleophilic addition to the triple bond followed by elimination can be excluded because of the similar reactivities of a wide range of alkynyl-lead intermediates, which may bear either an electron-withdrawing group or electron-releasing group on the β-carbon. Strong support for this conclusion is to be found in the work of Kende[11] referred to above. In an important recent paper by Barton[19] on the arylation of CH-acids by aryl-lead and arylbismuth compounds, radical pathways have been excluded, and a mechanism involving ligand exchange followed by a collapse of the intermediate has been suggested. In terms of such a mechanism, the reactions reported in this work may be represented as

proceeding as shown for a β-dicarbonyl compound in structure (**57**).



(**57**)

Synthesis of Alk-1-ynyltrimethylstannanes.—The previously unreported stannanes (**18**), (**21**), and (**22**) were prepared from the corresponding alkyne by a standard procedure. The alkynyl-lithium reagent was generated by treatment with butyl-lithium and this was treated with chlorotrimethylstannane at −30 to −70 °C. All were readily hydrolysed by moisture, especially (ethoxyethynyl)trimethylstannane (**19**), which could not be completely characterised.

Assignment of Structures to the Androstane Derivatives (**32a**) *and* (**32b**).—The assignment of configuration at C-16 in the diastereoisomers (**32a**) and (**32b**) was achieved by n.m.r. spectroscopy in conjunction with shift reagents. The greatest differences between the spectra of the two compounds were in the chemical shifts of the C-15 and C-18 protons, and also in the ^{13}C n.m.r. spectra, but these were insufficient for assignment of stereochemistry. An attempt to assign the C-15 protons by observation of an n.O.e. between the C-18 protons and 15-H_β in the major isomer was unsuccessful due to the similar chemical shifts of the two protons; however, in the minor isomer (**32b**), the C-15 protons had quite different chemical shifts and their couplings to 14-H (13.7 and 6.0 Hz) allowed assignment of the more upfield signal to 15-H_β ($J_{14,15}$ 13.7 Hz, J_{gem} 13.7 Hz).

Although addition of the shift reagent Eu(fod)$_3$* gave rise to downfield movements of similar magnitude for both C-15 protons of (**32b**), the use of a mixture of Eu(fod)$_3$ and Ag(fod)$_3$, which has been employed for assignment of stereochemistry in olefins,[20] proved successful. The 15β-proton suffered a significantly greater downfield shift, indicating that the acetylene group, to which silver would co-ordinate, was also on the β-face of the molecule.

Experimental

For general experimental procedures see our earlier paper.[21] Previously reported methods were used to prepare bis(phenylethynyl)mercury,[22] bis-(*p*-methoxyphenylethynyl)mercury,[23] di(oct-1-ynyl)mercury,[22] and (ethynyl)trimethylstannane.[24] light petroleum refers to the fraction boiling in the range 60—80 °C.

Synthesis of Alk-1-ynylstannanes.—Butyl-lithium in hexane (1.5M; 20 ml, 30 mmol) was added to a solution of the alkyne (30 mmol) in anhydrous ether (50 ml) at −30 °C, and the mixture was stirred at this temperature for 15 min under dry nitrogen. A solution of the trialkylchlorostannane (30 mmol) in ether (10 ml) was added, and the mixture was stirred for 30 min under the same conditions. The temperature was allowed to rise to room temperature during 1 h, and dry light petroleum (100 ml) was added. The mixture was filtered under a stream of dry nitrogen, and the solvent was evaporated off. The crude product was then purified by distillation at reduced pressure.

* Eu (fod)$_3$ = tris-(6,6,7,7,8,8,8-heptafluoro-2,2-dimethyloctane-3,5-dionato)europium.

The following compounds were prepared according to the above general method.

(a) Tributyl(phenylethynyl)stannane (**15**) (90%), b.p. 190 °C at 1 mmHg (lit.,[25] 184 °C at 1—2 mmHg).

(b) Trimethyl(phenylethynyl)stannane (**17**) (94%), b.p. 101—103 °C at 2.5 mmHg, m.p. 61—63 °C (lit.,[26] b.p. 60 °C at 0.2 mmHg; m.p. 67 °C).

(c) *Trimethyl(oct-1-ynyl)stannane* (**18**) (81%) was obtained as a very moisture-sensitive oil, b.p. 86—87 °C at 3.0 mmHg (Found: C, 49.5; H, 8.1. $C_{11}H_{22}Sn$ requires C, 48.4; H, 8.1%); $\nu_{max.}$(film) 2 150 cm^{-1}; δ_H($CDCl_3$) 2.20 (2 H, t, *J* 6.9 Hz), 1.58—1.46 (2 H, m), 1.40—1.22 (6 H, m), 0.88 (3 H, t, *J* 6.9 Hz), and 0.25 (9 H, s, $^{117Sn}J$ 57, $^{119Sn}J$ 60 Hz); δ_C($CDCl_3$) 111.1 (C-1), 81.8 (C-2), 31.3 (C-6), 29.0 (C-4 or -5), 28.5 (C-5 or -4), 22.5 (C-7), 20.1 (C-3), 14.0 (C-8), and −7.8 ($^{117Sn}J$ 25.8, $^{119Sn}J$ 27.3 Hz, $SnMe_3$).

(d) (Ethoxyethynyl)trimethylstannane (**19**) was obtained in 87% yield, b.p. 60—62 °C at 7.0 mmHg, as an oil which was too moisture sensitive to obtain an elemental analysis; δ_C ($CDCl_3$) 112.3 (O*C*≡C), 92.7 (OC≡*C*), 74.6 (OCH_2), 14.3 (Me), and −7.5 ($^{119Sn}J$ 408.0 Hz, $SnMe_3$) (lit.,[27] δ_C 112.1, 93.3, 74.2, 14.2, −7.8, $^{119Sn}J_{Sn,Me}$ 406.6 Hz).

(e) (Ethoxycarbonylethynyl)trimethylstannane (**20**) (67%), b.p. 62—70 °C at 0.2 mmHg (lit.,[28] 100 °C at 0.01 mmHg).

(f) (p-*Methoxyphenylethynyl)trimethylstannane* (**21**) was obtained as a moisture-sensitive oil (85%), b.p. 107—108 °C at 0.6 mmHg (Found: C, 48.6; H, 5.4. $C_{12}H_{16}OSn$ requires C, 48.9; H, 5.5%); $\lambda_{max.}$(cyclohexane) 260, 269sh, 286sh, and 298 nm (ε 26 900, 22 100, 3 000, and 1 400); $\nu_{max.}$(film) 2 140 cm^{-1}; δ_H($CDCl_3$) 7.42 and 6.82 (4 H, AA′BB′, 2-, 6-H and 3-,5-H respectively), 3.77 (3 H, s, OMe), and 0.32 (9 H, s, $^{117Sn}J$ 58, $^{119Sn}J$ 61 Hz, $SnMe_3$); δ_C($CDCl_3$) 159.3 (C-4), 133.3 (C-2 and C-6), 115.8 (C-3 and C-5), 109.0 (C≡), 91.3 (C≡), 55.1 (OMe), and 7.7 ($^{117Sn}J$ 388, $^{119Sn}J$ 407 Hz, $SnMe_3$).

(g) *Trimethyl*(p-*trifluoromethylphenylethynyl)stannane* (**22**) (82%) was obtained as a moisture-sensitive oil which solidified on keeping, b.p. 142—144 °C at 35 mmHg; m.p. 27—30 °C (Found: C, 42.5; H, 4.3. $C_{12}H_{13}F_3Sn$ requires C, 43.3; H, 3.9%); $\lambda_{max.}$(cyclohexane) 254 and 266 nm (ε 22 300 and 2 060); $\nu_{max.}$(film) 2 135 cm^{-1}; δ_H($CDCl_3$) 7.53 (4 H, br s) and 0.37 (9 H, s, $^{117Sn}J$ 58.3, $^{119Sn}J$ 60.9 Hz, $SnMe_3$); δ_C($CDCl_3$) 132.9 (q, $J_{C,F}$ 3.0 Hz, C-2 and C-6), 130.4 (q, $J_{C,F}$ 32 Hz, CF_3), 128.2 (q, $J_{C,F}$ 1.5 Hz, C-4), 126.0 (C-1), 125.8 (q, $J_{C,F}$ 3.9 Hz, C-3 and C-5), 107.9 ($^{117Sn}J$ 78, $^{119Sn}J$ 82 Hz, Ar*C*≡), 97.5 ($^{117Sn}J$ 378, $^{119Sn}J$ 396 Hz, SnC≡), and −9.75 ($^{117Sn}J$ 378, $^{119Sn}J$ 396 Hz, $SnMe_3$).

(h) Trimethyl(trimethylsilylethynyl)stannane (**24**) (92%), b.p. 73—74 °C at 39 mmHg (lit.,[29] 25 °C at 1 mmHg).

(i) (Cyclohex-1-enylethynyl)trimethylstannane (**25**) (87%), b.p. 107—108 °C at 4 mmHg (lit.,[30] 68—70 °C at 3 mmHg).

Tetrakis(phenylethynyl)plumbane (**16**).—A solution of trimethyl(phenylethynyl)stannane (0.32 g, 1.2 mmol) in dry chloroform (1.5 ml) was added rapidly to a solution of lead tetra-acetate (0.48 g, 1.1 mmol) in dry chloroform (2.5 ml) and the mixture was stirred at room temperature for 3 h. Ether (10 ml) was added, the mixture was filtered, and the crude product was fractionated by radial chromotography (Chromatotron) with light petroleum–ether (4:1). Tetrakis(phenylethynyl)plumbane (84 mg, 49%) was obtained as pale yellow needles, m.p. 130—135 °C (decomp.) [lit.,[31] 135 °C (decomp.)], identical (i.r. and n.m.r. spectra) with an authentic sample.

Preparation of the α-Alkynyl β-Keto Esters Reported in Table 1.—Dry lead tetra-acetate (0.6—1.0 mol equiv.) was added to a solution of the mercury compound (0.6—1.0 mol equiv.) in chloroform or DMSO (1.0 ml) containing pyridine (0.2 ml) or acetonitrile (0.5 ml), and the mixture was stirred at room temperature for the time indicated. A solution of the keto ester (**4**) (0.25 mmol) in chloroform or DMSO (0.5 ml) was added,

and the mixture was stirred overnight at room temperature. The mixture was diluted with chloroform, washed successively with hydrochloric acid (3M) and water, dried (Na_2SO_4), and the solvent was evaporated off. The residue was dissolved in ether, washed successively with aq. sodium hydroxide (3M) and water, and the solvent was evaporated off. The product was purified for analysis by chromatography followed by h.p.l.c. (Water Associates μ-Porasil column).

The following compounds were prepared according to the above general method.

(a) *Ethyl 2-oxo-1-(phenylethynyl)cyclopentanecarboxylate* (**5**) (60%) was obtained as an oil after preparative t.l.c. (p.l.c.) (chloroform) and h.p.l.c. in light petroleum–ethyl acetate (47:3) (Found: C, 75.0; H, 6.1. $C_{16}H_{16}O_3$ requires C, 75.0; H, 6.3%); $\lambda_{max.}$ (MeOH) 243 and 253 nm (ε 17 900 and 18 600); $\nu_{max.}$(film) 1 760, 1 720, and 1 600 cm^{-1}; $\delta_H(CDCl_3)$ 7.58—7.21 (5 H, m, Ph), 4.27 (2 H, q), 2.90—1.94 (6 H, m, 3 × CH_2), and 1.32 (3 H, t).

(b) *Ethyl 1-(p-methoxyphenylethynyl)-2-oxocyclopentanecarboxylate* (**9**) was obtained as an oil (51%) after p.l.c. (dichloromethane) and h.p.l.c. in light petroleum–ethyl acetate (22:3) (Found: C, 71.1; H, 6.4; M^+, 286.1202. $C_{17}H_{18}O_4$ requires C, 71.3; H, 6.3%; M^+, 286.1205); $\lambda_{max.}$(cyclohexane) 256 and 262 nm (ε 28 900 and 29 800); $\nu_{max.}$(film) 2 230, 1 760, 1 720, and 1 600 cm^{-1}; $\delta_H(CDCl_3)$ 7.37 and 6.80 (4 H, AA′BB′, 2-, 6-H and 3-, 5-H respectively), 4.25 (2 H, q), 3.78 (3 H, s, OMe), 2.85—1.90 (6 H, m, 3 × CH_2), and 1.30 (3 H, t).

(c) *Ethyl 1-(oct-1-ynyl)-2-oxocyclopentanecarboxylate* (**10**) was obtained as an oil (19%) after column chromatography [light petroleum–ethyl acetate (19:1)] and h.p.l.c. [light petroleum–ethyl acetate (19:1)] (Found: C, 72.8; H, 9.4; M^+, 264.1725. $C_{16}H_{24}O_3$ requires C, 72.7; H, 9.2%; *M*, 264.1716); $\delta_H(CDCl_3)$ 4.22 (2 H, q), 2.63—2.25 (4 H, m, 2 × CH_2), 2.22 (2 H, t), 2.13—2.05 (2 H, m), 1.55—1.20 (11 H, m), and 0.89 (3 H, t); $\delta_C(C_6D_6)$ 207.1 (C-2), 169.1 (*C*O_2Et), 86.4 and 76.4 (C≡C), 62.0 (OCH_2), 56.6 (C-1), 37.3, 36.5, 31.7, 29.0, 28.8, 22.9, 20.1 (7 × CH_2), 19.2 (≡C*C*H_2), and 14.3, 14.2 (2 × Me).

Preparation of α-Alkynyl β-Dicarbonyls and α-Alkynyl Nitroalkanes Reported in Table 2.—Method A. A solution of the alkynyltrimethylstannane (1.2 mmol) in dry chloroform (1 ml) was added rapidly to a solution of dry lead tetra-acetate (1.1 mmol) in dry chloroform (2 ml), and the mixture was stirred at room temperature for 0.5 min. A solution of the substrate (1.0 mmol) in dry chloroform (1 ml) was added rapidly, and the mixture was stirred at room temperature for 1 h in a stoppered flask. Ether (10 ml) was added and the mixture was filtered. The residue was washed with ether (2 × 5 ml), and the combined ether filtrates were washed successively with water (2 × 10 ml) and brine (10 ml), dried ($MgSO_4$), and the solvent was evaporated off. The crude product was purified by radial chromatography (Chromatotron).

Method B. As for method A except that the stannane (0.7 mmol) in dry chloroform (0.5 ml) was added to lead tetra-acetate (0.65 mmol) in dry chloroform (1 ml), and after 0.5 min the dicarbonyl compound (0.5 mmol) was added.

Method C. A solution of the stannane (1.2 mmol) in dry DMSO (1 ml) was added to a solution of lead tetra-acetate (1.1 mmol) in dry DMSO (3 ml), and the mixture was stirred at room temperature for 0.5 min. The enolate or nitronate salt (1.0 mmol) was added, and the mixture was stirred at room temperature for 1 h. Water (50 ml) was added and the mixture was extracted with ether (3 × 40 ml). The ether extract was worked up as in method A.

Method D. A solution of the stannane (1.65 mmol) in dry DMSO (1 ml) was added to a solution of lead tetra-acetate (1.5 mmol) in dry DMSO (2 ml) and the reaction mixture was stirred at room temperature for 15 s. The sodium salt (1.0 mmol) was added, the mixture was stirred at room temperature for 1 h, and the reaction mixture was worked up as in method C.

Method E. As for method A except that the tin–lead exchange reaction was allowed to proceed for 2 min before addition of the substrate.

Method F. As for method A except that the tin–lead exchange reaction was allowed to proceed for 20 min before addition of the substrate.

Method G. As for method C except that the lead tetra-acetate was dissolved in DMSO (2 ml), and the tin–lead exchange reaction was allowed to proceed for 2 min before addition of the substrate.

The following compounds were synthesised by the above methods.

(i) Ethyl 2-oxo-1-(phenylethynyl)cyclopentanecarboxylate (**5**), prepared by method A, was obtained as an oil (73%) after chromatography [light petroleum–ether (4:1)]. It was identical (i.r. and n.m.r. spectra) with the material above.

(ii) Ethyl 1-(*p*-methoxyphenylethynyl)-2-oxocyclopentanecarboxylate (**9**), prepared by method D, was obtained as an oil (75%) after chromatography [light petroleum–ether (4:1)]. It was identical (i.r. and n.m.r. spectra) with the material above.

(iii) Ethyl 1-(oct-1-ynyl)-2-oxocyclopentanecarboxylate (**10**), prepared by method A, was obtained after chromatography [light petroleum–ether (4:1)] as an oil (54%). It was identical (i.r. and n.m.r. spectra) with the material above.

(iv) *Ethyl 2-oxo-1-(p-trifluoromethylphenylethynyl)cyclopentanecarboxylate* (**11**) was obtained [method E and chromatography in light petroleum–ether (9:1)] as an oil (75%) (Found: C, 62.9; H, 4.8. $C_{17}H_{15}F_3O_3$ requires C, 63.0; H, 4.7%); $\lambda_{max.}$(EtOH) 248 and 256 nm (ε 18 500 and 20 300); $\nu_{max.}$(film 2 225, 1 755, 1 725, and 1 605 cm^{-1}; $\delta_H(CDCl_3)$ 7.57 (4 H, br s, ArH), 4.30 (2 H, q), 2.90—2.04 (6 H, m, 3 × CH_2), and 1.32 (3 H, t); $\delta_C(CDCl_3)$ 207.6 (C-2), 168.1 (*C*O_2Et), 132.2 (C-2′ and -6′), 130.2 (q, $J_{C,F}$ 32.5 Hz, CF_3), 126.3 (C-4′), 125.2 (C-1′), 125.1 (q, $J_{C,F}$ 4.1 Hz, C-3′ and -5′), 86.8 (C≡C), 84.0 (C≡C), 62.6 (OCH_2), 56.6 (C-1), 36.8 (C-3 and -5), 20.0 (C-4), and 14.0 (Me).

(v) *Ethyl 1-ethynyl-2-oxocyclopentanecarboxylate* (**12**) was obtained [method A and chromatography in light petroleum–ether (4:1)] as an oil (57%) (Found: C, 66.5; H, 6.9. $C_{10}H_{12}O_3$ requires C, 66.7; H, 6.7%); $\nu_{max.}$(film) 2 115, 1 760, and 1 730 cm^{-1}; $\delta_H(CDCl_3)$ 4.25 (2 H, q), 2.68—2.08 (6 H, m, 3 × CH_2), 2.44 (1 H, s, acetylenic H), and 1.31 (3 H, t); $\delta_C(CDCl_3)$ 207.4 (C-2), 167.8 (ester C=O), 116.7 (*C*≡CH), 73.6 (C≡CH), 62.4 (OCH_2), 55.7 (C-1), 36.5 (C-3 and -5), 19.7 (C-4), and 13.8 (Me).

(vi) *Ethyl 2-oxo-1-(trimethylsilylethynyl)cyclopentanecarboxylate* (**13**) was obtained [method F and chromatography in light petroleum–ether (4:1)] as an oil (78%) (Found: C, 61.9; H, 7.9. $C_{13}H_{20}O_3Si$ requires C, 61.9; H, 8.0%); $\lambda_{max.}$(EtOH) 298 nm (ε 200); $\nu_{max.}$(film) 2 180, 1 765, and 1 730 cm^{-1}; δ_H4.27 (2 H, q), 2.81—1.80 (6 H, m, 3 × CH_2), 1.31 (3 H, t), and 0.18 (9 H, s, $SiMe_3$); $\delta_C(CDCl_3)$ 207.4 (C-2), 168.0 (ester C=O), 99.9 (C≡*C*Si), 90.3 (*C*≡CSi), 62.2 (OCH_2), 58.9 (C-1), 36.8 (C-3 or -5), 36.5 (C-5 or -3), 19.6 (C-4), 13.8 (Me), and 0.4 ($SiMe_3$).

(vii) *Ethyl 1-(cyclohex-1-enylethynyl)-2-oxocyclopentanecarboxylate* (**14**) was prepared by method A (except that tin–lead exchange time was 5 s) followed by chromatography in light petroleum–ether (4:1). It was obtained as an oil (59%) (Found: C, 74.0; H, 8.0. $C_{16}H_{20}O_3$ requires C, 73.8, H, 7.7%); $\lambda_{max.}$(EtOH) 231 and 299 nm (ε 11 400 and 700); $\nu_{max.}$(film) 2 210, 1 760, and 1 720 cm^{-1}; δ_H 6.13 (1 H, m, vinyl H), 4.24 (2 H, q), 2.65—1.53 (14 H, m, 7 × CH_2), and 1.29 (3 H, t); δ_C ($CDCl_3$) 208.1 (C-2), 168.7 (ester C=O), 135.7 (C-2′), 120.0 (C-1′) 87.3 (*C*≡C), 81.2 (C≡*C*), 62.3 (OCH_2), 56.6 (C-1), 36.9 (C-3 and -5), 29.0 (C-3′), 25.6 (C-6′), 22.2 (C-4′), 21.4 (C-5′), 19.8 (C-4), and 14.0 (Me).

(viii) *3-Acetyl-3-(phenylethynyl)-4,5-dihydrofuran-2(3 H)-one*

(**27**) was obtained [method A and chromatography in light petroleum–ether (4:1)] as an oil (60%) (Found: C, 74.0; H, 5.2. $C_{14}H_{12}O_3$ requires C, 73.7; H, 5.3%); $\lambda_{max.}$(CH_3CN) 242 and 252 nm (ε 18 000 and 17 500); $\nu_{max.}$($CHCl_3$) 2 220, 1 775, and 1 720 cm^{-1}; δ_H($CDCl_3$) 7.48—7.45 (2 H, m, 2′- and 6′-H), 7.38—7.31 (3 H, m, 3′-, 4′-, and 5′-H), 4.46 (1 H, ddd, J_{gem} 8.9, $J_{5\alpha,4\alpha}$ 7.0, $J_{5\alpha,4\beta}$ 7.4 Hz, 5-H_α), 4.37 (1 H, ddd, J_{gem} 8.9, $J_{5\beta,4\alpha}$ 7.9, $J_{5\beta,4\beta}$ 5.7 Hz, 5-H_β), 3.11 (1 H, ddd, J_{gem} 13.0, $J_{4\beta,5\alpha}$ 7.4, $J_{4\beta,5\beta}$ 5.7 Hz, 4-H_β), 2.65 (3 H, s, Me), and 2.54 (1 H, ddd, J_{gem} 13.0, $J_{4\alpha,5\alpha}$ 7.0, $J_{4\alpha,5\beta}$ 7.9 Hz, 4-H_α); δ_C($CDCl_3$) 198.6 (*C*OMe), 170.6 (C-2), 131.7 (C-2′ and -6′), 129.0 (C-4′), 128.3 (C-3′ and -5′), 121.5 (C-1′), 86.4 (C≡C), 83.4 (C≡C), 66.6 (C-5), 56.0 (C-3), 33.1 (C-4), and 26.7 (Me).

(ix) 3-*Acetyl*-3-(*oct*-1-*ynyl*)-4,5-*dihydrofuran*-2(3 H)-*one* (**28**) was obtained [method A and chromatography in light petroleum–ether (4:1)] as an oil (57%) (Found: C, 71.3; H, 8.2. $C_{14}H_{20}O_3$ requires C, 71.2; H, 8.5%); $\nu_{max.}$(film) 2 240, 1 780, and 1 720 cm^{-1}; δ_H($CDCl_3$) 4.38 (1 H, ddd, $J_{5\alpha,4\alpha}$ 5.7, $J_{5\alpha,4\beta}$ 7.8, J_{gem} 8.9 Hz, 5-H_α), 4.30 (1 H, ddd, $J_{5\beta,4\alpha}$ 7.5, $J_{5\beta,4\beta}$ 6.9, J_{gem} 8.9 Hz, 5-H_β), 3.00 (1 H, ddd, J_{gem} 12.9, $J_{4\alpha,5\alpha}$ 5.7, $J_{4\alpha,5\beta}$ 7.5 Hz, 4-H_α), 2.56 (3 H, s, Me), 2.38 (1 H, ddd, J_{gem} 12.9, $J_{4\beta,5\beta}$ 6.9, $J_{4\beta,5\alpha}$ 7.8 Hz, 4-H_β), 2.25 (2 H, t, CH_2), 1.57—1.49 (2 H, m, CH_2), 1.42—1.25 (6 H, m, 3 × CH_2), and 0.89 (3 H, t, Me).

(x) *Methyl* 3β-*hydroxy*-17-*oxo*-16α-(*phenylethynyl*)-5α-*androstane*-16β-*carboxylate* (**32a**) was obtained [method B and chromatography in light petroleum–ether (4:1) followed by light petroleum–ether (1:1)] as crystals (65%), m.p. 123—125 °C (from ether–light petroleum) (Found: C, 77.1; H, 8.5. $C_{29}H_{36}O_4$ requires C, 77.6; H, 8.1%); $\lambda_{max.}$ (EtOH) 244, 255, 280, and 302 nm (ε 16 900, 17 800, 500, and 350); $\nu_{max.}$(Nujol) 3 255, 2 140, 1 765, and 1 746 cm^{-1}; δ_H($CDCl_3$) 7.47—7.41 (2 H, m, 2 × *ortho* H), 7.32—7.27 (3 H, m, ArH), 3.82 (3 H, s, OMe), 3.75—3.56 (1 H, br m, 3-H), 2.43 (2 H, br d, 15-H_2), 1.98—0.74 (19 H, m), 1.03 (3 H, s, 13-Me), and 0.85 (3 H, s, 10-Me); in benzene solution, the doublet at δ 2.43 collapsed to an AB system, δ 2.42 and 2.39 (J_{AB} ~ 7 Hz), upon irradiation of 14-H at δ 1.72; δ_C($CDCl_3$) 209.0 (C-17), 169.2 (ester C=O), 131.9 (C-2′ and -6′), 128.4 (C-4′), 128.1 (C-3′ and -5′), 122.5 (C-1′), 85.6 (*C*≡CPh), 83.6 (C≡*C*Ph), 71.0 (C-3), 56.8 (C-16), 54.3 (C-9), 53.5 (OMe), 48.4 (C-13), 48.2 (C-14), 44.7 (C-5), 38.0 (C-4), 37.1 (C-15), 36.9 (C-1), 35.6 (C-10), 34.4 (C-8), 32.9 (C-12), 31.4 (C-7), 30.8 (C-2), 28.2 (C-6), 20.4 (C-11), 14.1 (C-18), and 12.2 (C-19).

(xi) *Methyl* 3β-*hydroxy*-17-*oxo*-16β-(*phenylethynyl*)-5α-*androstane*-16α-*carboxylate* (**32b**) was separated (17%) from the isomer (**32a**) as in (x) above. It was crystallised from aqueous ethanol, m.p. 145—147 °C (Found: C, 77.1; H, 8.4%); δ_H($CDCl_3$) 7.47—7.41 (2 H, m, 2 × *ortho* H), 7.32—7.27 (3 H, m, ArH), 3.81 (3 H, s, OMe), 3.76—3.56 (1 H, m, 3-H), 2.77 (1 H, dd which collapsed to a doublet on irradiation at δ 2.10, J_{gem} 13.7, $J_{15\alpha,14}$ 6.0 Hz, 15-H_α), 2.10 (1 H, dd, J_{gem} 13.7, $J_{15\beta,14}$ 13.7 Hz, 15-H_β), 1.96—0.74 (19 H, m), 1.16 (3 H, s, 13-Me), and 0.84 (3 H, s, 10-Me); δ_C($CDCl_3$) 209.6 (C-17), 169.3 (ester C=O), 131.7 (C-2′ and -6′), 128.3 (C-4′), 128.1 (C-3′ and -5′), 122.6 (C-1′), 86.9 (*C*≡CPh), 83.9 (C≡*C*Ph), 7.10 (C-3), 54.6 (C-16), 54.2 (C-9), 53.5 (OMe), 49.1 (C-13), 47.9 (C-14), 44.7 (C-5), 37.9 (C-15 and -4), 36.9 (C-1), 35.6 (C-10), 34.9 (C-8), 32.2 (C-12), 31.3 (C-7), 30.6 (C-2), 28.2 (C-6), 20.3 (C-11), 15.4 (C-18), and 12.2 (C-19).

(xii) *Ethyl* 2-*acetyl*-2-*methyl*-4-*phenylbut*-3-*ynoate* (**34**) was obtained [method C and chromatography in light petroleum–ether (19:1)] as an oil (58%) (Found: C, 73.9; H, 6.8. $C_{15}H_{16}O_3$ requires C, 73.8; H, 6.6%); $\lambda_{max.}$(EtOH) 242, 279, and 287 nm (ε 7 600, 500, and 400); $\nu_{max.}$(film) 1 748 and 1 726 cm^{-1}; δ_H($CDCl_3$) 7.54—7.25 (5 H, m, ArH), 4.28 (2 H, q), 2.46 (3 H, s, Ac), 1.68 (3 H, s, Me), and 1.30 (3 H, t); δ_C($CDCl_3$) 202.9 (*C*OMe), 168.9 (C-1), 131.6 (C-2′ and -6′), 128.5 (C-4′), 128.2 (C-3′ and -5′), 122.5 (C-1′), 86.4 and 85.9 (C≡C), 62.2 (OCH_2), 56.0 (C-2), 26.6 (CO*Me*), 21.8 (2-Me), and 13.8 (CH_2*Me*).

(xiii) 2-*Acetyl*-2-(*phenylethynyl*)-3,4-*dihydronaphthalen*-1-(2H)-*one* (**36**) was obtained [method A and chromatography in light petroleum–ether (4:1)] as an oil (87%) (Found: C, 83.3; H, 5.7. $C_{20}H_{16}O_2$ requires C, 83.3; H, 5.6%); $\lambda_{max.}$(EtOH) 243sh, 252, and 296sh nm (ε 23 000, 24 500, and 3 000); $\nu_{max.}$(film) 1 725, 1 685, and 1 600 cm^{-1}; δ_H($CDCl_3$) 8.04 (1 H, m, 8-H), 7.63—7.19 (8 H, m, ArH), 3.58—2.65 (2 H, m, CH_2), 2.63—2.15 (2 H, m, CH_2), and 2.64 (3 H, s, Me); δ_C($CDCl_3$) 203.8 (*C*OMe), 191.7 (C-1), 146.6 (C-4a), 134.1 (C-8), 131.9 (C-2′ and -6′), 128.8 (C-4′), 128.8 (C-5 or -6), 128.5 (C-6 or -5), 128.3 (C-3′ and -5′), 126.9 (C-7), 122.2 (C-1′), 74.8 and 59.9 (C≡C), 31.4 (C-4), 29.2 (Me), and 26.1 (C-3).

(xiv) 2-*Acetyl*-2-(*oct*-1-*ynyl*)-3,4-*dihydronaphthalen*-1(2H)-*one* (**37**) was obtained [method A and chromatography in light petroleum–ether (4:1)] as an oil (75%) (Found: C, 81.2; H, 8.2. $C_{20}H_{24}O_2$ requires C, 81.0; H, 8.2%); $\lambda_{max.}$(EtOH) 252 and 294 nm (ε 12 700 and 2 100); $\nu_{max.}$(film) 2 235, 1 725, 1 685, and 1 600 cm^{-1}; δ_H($CDCl_3$) 8.02 (1 H, m, 8-H), 7.62—7.14 (3 H, m, ArH), and 3.54—0.71 (20 H, m); δ_C ($CDCl_3$) 204.5 (*C*OMe), 192.2 (C-1), 143.6 (C-4a), 133.8 (C-8), 128.6 (C-5 or -6), 128.3 (C-6 or -5), 126.7 (C-7), 88.2 and 79.2 (C≡C), 59.2 (C-2), 31.4 (C-4), 31.1 (C-6′), 28.9 (CO*Me*), 28.3 (C-4′ and -5′), 25.9 (C-3), 22.4 (C-7′), 18.8 (C-3′), and 13.9 (C-8′).

(xv) 2-*Acetyl*-2-(p-*methoxyphenylethynyl*)-3,4-*dihydronaphthalen*-1(2H)-*one* (**38**) was obtained [method D and chromatography in light petroleum–ether (4:1)] as an oil (76%) (Found: C, 79.5; H, 6.1. $C_{21}H_{18}O_3$ requires C, 79.2; H, 5.7%); $\lambda_{max.}$(EtOH) 256 nm (ε 33 200); $\nu_{max.}$(film) 2 220, 1 725, 1 680, and 1 600 cm^{-1}; δ_H($CDCl_3$) 8.05 (1 H, dd, $J_{8,6}$ 1.4, $J_{8,7}$ 7.5 Hz, 8-H), 7.50 (1 H, dt, $J_{6,5}$ 7.5, $J_{6,7}$ 7.5, $J_{6,8}$ 1.4 Hz, 6-H), 7.33 and 6.79 (4 H, AA′BB′, 2′-, 6′- and 3′-, 5′-H respectively), 7.31—7.23 (2 H, m, 5- and 7-H), 3.78 (3 H, s, OMe), 3.37 (1 H, m), 3.02 (1 H, m), 2.73 (1 H, m), 2.63 (3 H, s, Ac), and 2.31 (1 H, m); δ_C($CDCl_3$) 204.0 (*C*OMe), 191.9 (C-1), 159.7 (C-4′), 143.5 (C-4a), 133.9 (C-8), 133.1 (C-2′ and -6′), 130.5 (C-8a), 128.6 (C-5 or -6), 128.3 (C-6 or -5), 126.7 (C-7), 114.1 (C-1′), 113.8 (C-3′ and -5′), 87.0 and 83.0 (C≡C), 59.9 (C-2), 55.2 (OMe), 31.4 (C-4), 29.1 (Me), and 26.0 (C-3).

(xvi) 2-*Acetyl*-2-(p-*trifluoromethylphenylethynyl*)-3,4-*dihydronaphthalen*-1(2H)-*one* (**39**) was obtained [method E and chromatography in light petroleum–ether (4:1)] as an oil (77%) (Found: C, 70.8; H, 4.3. $C_{21}H_{15}F_3O_2$ requires C, 70.8; H, 4.2%); $\lambda_{max.}$(EtOH) 251 sh and 257 nm (ε 26 500 and 28 300); $\nu_{max.}$(film) 2 235, 1 720, 1 680, and 1 600 cm^{-1}; δ_H($CDCl_3$) 8.06 (1 H, dd, $J_{8,6}$ 1.3, $J_{8,7}$ 7.6 Hz, 8-H), 7.54 and 7.50 (4 H, AA′BB′, 2′, 6′- and 3′-, 5′-H respectively), 7.52 (1 H, dt, $J_{6,5}$ 7.6, $J_{6,7}$ 7.6, $J_{6,8}$ 1.3 Hz, 6-H), 7.36—7.30 (2 H, m, 5- and 7-H), 3.34 (1 H, m), 3.06 (1 H, m), 3.00 (1 H, m), 2.62 (3 H, s, Me), and 2.36 (1 H, m); δ_C($CDCl_3$) 202.8 (*C*OMe), 191.3 (C-1), 143.5 (C-4a), 134.2 (C-8), 132.1 (C-2′ and -6′), 130.5 (C-8a), 130.3 (q, $J_{C,F}$ 32.7 Hz, CF_3), 128.8 (C-4′), 128.8 (C-5 or -6) 128.5 (C-6 or -5), 127.0 (C-7), 125.9 (C-1′), 125.2 (q, $J_{C,F}$ 4.2 Hz, C-3′ and -5′), 87.2 and 85.7 (C≡C), 60.0 (C-2), 31.3 (C-4), 28.9 (Me), 25.9 (C-3).

(xvii) 2-*Acetyl*-2-*ethynyl*-3,4-*dihydronaphthalen*-1(2H)-*one* (**40**) was obtained [method A and chromatography in light petroleum–ether (4:1)] as crystals (69%), m.p. 95—97 °C (Found: C, 79.4; H, 5.5. $C_{14}H_{12}O_2$ requires C, 79.2; H, 5.7%); $\lambda_{max.}$ (EtOH) 254 and 295 nm (ε 13 300 and 2 100); $\nu_{max.}$(Nujol) 1 720, 1 680, and 1 595 cm^{-1}; δ_H($CDCl_3$) 8.03 (1 H, m, 8-H), 7.54—7.22 (3 H, m, 5-, 6-, and 7-H), 3.28 (1 H, m), 3.02 (1 H, m), 2.70 (1 H, m), 2.56 (3 H, s, Me), 2.52 (1 H, s, C≡CH), and 2.26 (1 H, m); δ_C($CDCl_3$) 202.8 (*C*OMe), 191.4 (C-1), 143.4 (C-4a), 134.1 (C-8), 130.4 (C-8a), 128.7 (C-5 or -6), 128.5 (C-6 or -5), 126.8 (C-7), 79.4 (*C*≡CH), 75.5 (C≡*C*H), 59.2 (C-2), 31.2 (C-4), 28.6 (Me), and 25.7 (C-3).

(xviii) 2-*Acetyl*-2-(*trimethylsilylethynyl*)-3,4-*dihydronaphthalen*-1(2H)-*one* (**41**) was obtained [method F and chromatography in light petroleum–ether (4:1)] as crystals (77%), m.p. 72—73 °C (Found: C, 72.2; H, 7.4. $C_{17}H_{20}O_2Si$ requires C, 71.8;

H, 7.1%); $\lambda_{max.}$(EtOH) 254 and 295 nm (ε 13 700 and 2 100); $\nu_{max.}$(Nujol) 2 150, 1 720, 1 685, and 1 590 cm^{-1}; δ_H($CDCl_3$) 8.02 (1 H, m, 8-H), 7.53—7.23 (3 H, m, 5-, 6-, and 7-H), 3.31 (1 H, m), 2.98 (1 H, m), 2.66 (1 H, m), 2.60 (3 H, s, Me), 2.23 (1 H, m), and 0.12 (9 H, s, $SiMe_3$); δ_C($CDCl_3$) 203.8 (*C*OMe), 191.6 (C-1), 144.0 (C-4a), 133.9 (C-8), 130.5 (C-8a), 128.4 (C-5 and -6), 126.7 (C-7), 100.6 (C≡*C*Si), 92.6 (*C*≡CSi), 60.3 (C-2), 31.3 (C-4), 29.0 (Me), 25.8 (C-3), and 0.3 ($SiMe_3$).

(xix) 2-*Methyl*-2-(*phenylethynyl*)*cyclohexane*-1,3-*dione* (**43**) was obtained [method A and chromatography in light petroleum–ether (4:1)] as an oil (47%) (Found: C, 79.8; H, 6.1. $C_{15}H_{14}O_2$ requires C, 79.6; H, 6.2%); $\lambda_{max.}$(EtOH) 246sh and 253 nm (ε 14 900 and 16 900); $\nu_{max.}$(film) 1 745 and 1 715 cm^{-1}; δ_H($CDCl_3$) 7.32—7.10 (5 H, m, Ph), 3.47—1.58 (6 H, m, 3 × CH_2), and 1.47 (3 H, s, Me); δ_C($CDCl_3$) 201.7 (C-1 and -3), 131.4 (C-2′ and -6′), 128.7 (C-4′), 128.2 (C-3′ amd -5′), 121.8 (C-1′), 86.5 (*C*≡*C*), 62.2 (C-2), 37.1 (C-4 and -6), 17.9 (C-5), and 15.9 (Me).

(xx) 2,2,5-*Trimethyl*-5-(*phenylethynyl*)-1,3-*dioxane*-4,6-*dione* (**45**) was obtained [method C and chromatography in light petroleum–ether (4:1)] as an oil (25%) (Found: C, 69.6; H, 5.7. $C_{15}H_{14}O_4$ requires C, 69.8; H, 5.5%); $\lambda_{max.}$(EtOH) 242 and 253 nm (ε 17 200 and 16 400); $\nu_{max.}$(film) 2 240, 1 780, and 1 750 cm^{-1}; δ_H($CDCl_3$) 7.45—7.29 (5 H, m, Ph), 2.07 (3 H, s, 2-Me), 2.00 (3 H, s, 5-Me), and 1.80 (3 H, s, 2-Me); δ_C($CDCl_3$) 164.7 (C-4 and -6), 131.8 (C-2′ and -6′), 129.4 (C-4′), 128.8 (C-3′ and -5′), 106.1 (C-2), 83.4 (*C*≡*C*), 43.9 (C-5), 28.6 (Me), 27.7 (Me), and 24.5 (Me).

(xxi) 3-*Methyl*-3-*nitro*-1-*phenylbut*-1-*yne* (**47**) was obtained [method C and chromatography in light petroleum–ether (4:1)] as an oil (72%) (Found: C, 69.9; H, 5.8; N, 7.0. $C_{11}H_{11}NO_2$ requires C, 69.8; H, 5.9; N, 7.4%); $\lambda_{max.}$(EtOH) 240 nm (ε 17 300); $\nu_{max.}$(film) 2 240 and 1 555 cm^{-1}; δ_H($CDCl_3$) 7.53—7.24 (5 H, m, Ph and 1.94 (6 H, s, 2 × Me); δ_C($CDCl_3$) 131.7 (C-2′ and -6′), 129.0 (C-4′), 128.2 (C-3′ and -5′), 121.4 (C-1′), 87.0 and 86.0 (C≡C), 82.4 (C-3), and 28.6 (2 × Me).

(xxii) 2-Methyl-2-nitrodec-3-yne (**48**) was obtained (47%) as an oil by method C and chromatography in light petroleum–ether (97:3). It had spectroscopic data in agreement with previously prepared material.[32]

(xxiii) 1-(p-*Methoxyphenyl*)-3-*methyl*-3-*nitrobut*-1-*yne* (**49**) was obtained [method D and chromatography in light petroleum–ether (4:1)] as crystals, m.p. 43—44 °C (Found: C, 66.0; H, 5.8; N, 6.2. $C_{12}N_{13}NO_3$ requires C, 65.7; H, 6.0; N, 6.4%); $\lambda_{max.}$(EtOH) 256 nm (ε 21 900); $\nu_{max.}$(melt) 2 235, 1 600, and 1 545 cm^{-1}; δ_H($CDCl_3$) 7.41 and 6.85 (4 H, AA′BB′, 2′-, 6′- and 3′-, 5′-H respectively), 3.80 (3 H, s, OMe), and 1.93 (6 H, s, 2 × Me); δ_C($CDCl_3$) 160.4 (C-4′), 133.4 (C-2′ and -6′), 114.1 (C-3′ and -5′), 113.8 (C-1′), 87.5 and 85.2 (C≡C), 82.7 (C-3), 55.3 (OMe), and 28.8 (C-4 and 3-Me).

(xxiv) 1-*Nitro*-1-(*phenylethynyl*)*cyclohexane* (**51**) was obtained [method C and chromatography in light petroleum–ether (9:1)] as an oil (62%) (Found: C, 73.6; H, 6.3; N, 6.3. $C_{14}H_{15}NO_2$ requires C, 73.3; H, 6.6; N, 6.1%); $\lambda_{max.}$(EtOH) 240 nm (ε 17 600); $\nu_{max.}$(film) 2 240 and 1 545 cm^{-1}; δ_H($CDCl_3$) 7.56—7.24 (5 H, m, Ph) and 2.50—1.16 (10 H, m, 5 × CH_2); δ_C($CDCl_3$) 131.8 (C-2′ and -6′), 129.0 (C-4′), 128.2 (C-3′ and -5′), 121.6 (C-1′), 87.2 (*C*≡C and C-1), 84.8 (C≡*C*), 36.8 (C-2 and -6), 24.5 (C-4), and 23.1 (C-3 and -5).

(xxv) 1-*Nitro*-1-(*oct*-1-*ynyl*)*cyclohexane* (**52**) was obtained [method C and chromatography in light petroleum–ether (49:1)] as an oil (53%) (Found: C, 71.2; H, 9.9; N, 6.2. $C_{14}H_{23}NO_2$ requires C, 70.9; H, 9.8; N, 5.9%); $\nu_{max.}$(film) 2 250 and 1 545 cm^{-1}; δ_H($CDCl_3$) 2.38 (2 H, t, *J* 7.0 Hz), 2.36—1.22 (18 H, m, 9 × CH_2), and 0.92 (3 H, t, *J* 7.0 Hz); δ_C($CDCl_3$) 90.5 and 87.0 (C≡C), 76.4 (C-1), 37.0 (C-2 and -6), 31.2 (C-6′), 28.5 (C-4′ or -5′), 28.3 (C-5′ or -4′), 24.6 (C-4), 23.1 (C-3 and -5), 22.5 (C-7′), 18.7 (C-3′), and 14.0 (Me).

(xxvi) 1-(p-*Methoxyphenylethynyl*)-1-*nitrocyclohexane* (**53**) was obtained [method D and chromatography in light petroleum–ether (4:1)] as crystals (59%), m.p. 40—42 °C (Found: C, 69.8; H, 6.8; N, 5.5. $C_{15}H_{17}NO_3$ requires C, 69.5; H, 6.6; N, 5.4%); $\lambda_{max.}$(EtOH) 256 nm (ε 21 400); $\nu_{max.}$(melt) 2 235, 1 600, and 1 545 cm^{-1}; δ_H ($CDCl_3$) 7.42 and 6.85 (4 H, AA′BB′, 2′- 6′- and 3′-, 5′-H respectively), 3.80 (3 H, s, OMe), 2.48—1.96 (4 H, m, 2 × CH_2), and 1.92—1.08 (6 H, m, 3 × CH_2); δ_C($CDCl_3$) 160.4 (C-4′), 133.4 (C-2′ and -6′), 114.8 (C-3′ and -5′), 113.8 (C-1′), 89.2 (*C*≡C), 87.3 (C-1), 83.9 (C≡*C*), 55.3 (OMe), 36.9 (C-2 and -6), 24.6 (C-4), and 23.2 (C-3 and -5).

(xxvii) 1-*Nitro*-1-(p-*trifluoromethylphenylethynyl*)*cyclohexane* (**54**) was obtained [method G and chromatography in light petroleum–ether (9:1)] as an oil (50%) (Found: C, 60.4; H, 4.6; N, 5.0. $C_{15}H_{14}F_3NO_2$ requires C, 60.6; H, 4.8; N, 4.7%); $\lambda_{max.}$ (EtOH) 245 and 252sh nm (ε 20 400 and 17 500), $\nu_{max.}$(film) 1 610 and 1 545 cm^{-1}; δ_H($CDCl_3$) 7.62 (4 H, m, ArH), 2.41—2.20 (4 H, m, 2 × CH_2), and 1.89—1.29 (6 H, m, 3 × CH_2) δ_C($CDCl_3$) 132.2 (C-2′ and -6′), 131.6 (q, $J_{C,F}$ 32.8 Hz, CF_3), 128.8 (C-4′), 125.3 (C-1′), 125.3 (q, $J_{C,F}$ 4.3 Hz, C-3′ and -5′), 87.8 (*C*≡C), 87.2 (C≡*C* or C-1), 87.1 (C-1 or C≡*C*), 36.7 (C-2 and -6), 24.5 (C-4), and 23.2 (C-3 and -5).

(xxviii) 1-*Ethynyl*-1-*nitrocyclohexane* (**55**) was prepared by method C except that the lead tetra-acetate was dissolved in DMSO (1.5 ml). Chromatography in light petroleum–ether (19:1) afforded the title compound as an oil (48%) (Found: C, 63.0; H, 6.9; N, 9.2. $C_8H_{11}NO_2$ requires C, 62.7; H, 7.2; N, 9.1%); $\nu_{max.}$(film) 2 105 and 1 540 cm^{-1}; δ_H($CDCl_3$) 2.81 (1 H, s, C≡CH) and 2.30—1.48 (10 H, m, 5 × CH_2); δ_C($CDCl_3$) 86.4 and 77.7 (C≡C), 36.5 (C-2 and -6), 30.8 (C-1), 24.3 (C-3 and -5), and 22.9 (C-4).

(xxix) 1-*Nitro*-1-(*trimethylsilylethynyl*)*cyclohexane* (**56**) was obtained [method F and chromatography in light petroleum–ether (19:1)] as an oil (60%) (Found: C, 58.6; H, 8.6; N, 5.9. $C_{11}H_{19}NO_2Si$ requires C, 58.6; H, 8.5; N, 6.2%); $\nu_{max.}$(film) 2 170 and 1 550 cm^{-1}; δ_H($CDCl_3$) 2.34—1.95 (4 H, m, 2 × CH_2), 1.92—1.53 (6 H, m, 3 × CH_2), and 0.22 (9 H, s, $SiMe_3$); δ_C($CDCl_3$) 100.5 (C≡*C*Si), 94.5 (*C*≡CSi), 86.6 (C-1), 36.7 (C-2 and -6), 24.5 (C-4), 23.0 (C-3 and -5), and 0.4 ($SiMe_3$).

3-(*Phenylethynyl*)-4,5-*dihydrofuran*-2(3H)-*one* (**29**).—The chloroform was evaporated from the crude reaction mixture obtained in the preparation of compound (**27**) above, and acetone (4 ml) and water (1 ml) were added. The mixture was heated at reflux for 10 min, then cooled, and work-up was effected as in method A (Table 2) above. Fractionation by radial chromatography [light petroleum–ether (1:1)] produced the *title compound* as an oil (63%) (Found: M^+, 186.0677. $C_{12}H_{10}O_2$ requires *M* 186.0681); $\lambda_{max.}$ (EtOH) 239 and 250 nm (ε 11 700 and 10 300); $\nu_{max.}$(film) 2 250 and 1 770 cm^{-1}, δ_H($CDCl_3$) 7.48—7.26 (5 H, m, Ph), 4.48 (1 H, ddd, $J_{5\alpha,4\alpha}$ 4.3, $J_{5\alpha,4\beta}$ 8.0, J_{gem} 9.2 Hz, 5-H_α), 4.31 (1 H, ddd, $J_{5\beta,4\alpha}$ 6.7, $J_{5\beta4\beta}$ 8.4, J_{gem} 9.2 Hz, 5-H_β), 3.71 (1 H, dd, $J_{3,4\alpha}$ 8.8, $J_{3,4\beta}$ 8.8 Hz, 3-H), 2.66 (1 H, dddd, $J_{4\alpha,3}$ 8.8, J_{gem} 12.8, $J_{4\alpha,5\alpha}$ 4.3, $J_{4\alpha,5\beta}$ 6.7 Hz, 4-H_α), and 2.48 (1 H, dddd, $J_{4\beta,3}$ 8.8, J_{gem} 12.8, $J_{4\beta,5\alpha}$ 8.0, $J_{4\beta,5\beta}$ 8.4 Hz, 4-H_β); δ_C($CDCl_3$) 173.6 (C-2), 131.7 (C-2′ and -6′), 128.5 (C-4′), 128.2 (C-3′ and -5′), 122.3 (C-1′), 83.8 and 83.1 (C≡C), 66.9 (C-5), 33.2 (C-3), and 30.7 (C-4).

3-(*Oct*-1-*ynyl*)-4,5-*dihydrofuran*-2(3H)-*one* (**30**) was synthesised by the procedure employed to obtained compound (**29**) above, and the same method of purification was used. *Compound* (**30**) was obtained as an oil (58%) (Found: M^+, 194.1304. $C_{12}H_{18}O_2$ requires *M*, 194.1307); $\nu_{max.}$(film) 2 250 and 1 780 cm^{-1}; δ_H($CDCl_3$) 4.42 (1 H, ddd, $J_{5\alpha,4\alpha}$ 4.3, $J_{5\alpha,4\beta}$ 7.8, J_{gem} 9.0 Hz, 5-H_α), 4.26 (1 H, ddd, $J_{5\beta,4\alpha}$ 6.8, $J_{5\beta,4\beta}$ 8.4, J_{gem} 9.0 Hz, 5-H_β), 3.45 (1 H, ddt, $J_{3,3'}$ 2.3, $J_{3,4\alpha}$ 9.0, $J_{3,4\beta}$ 9.0 Hz, 3-H), 2.56 (1 H, dddd, $J_{3,4\alpha}$ 9.0, J_{gem} 12.7, $J_{4\alpha,5\alpha}$ 4.3, $J_{4\alpha,5\beta}$ 6.8 Hz, 4-H_α), 2.33 (1 H, dddd, $J_{3,4\beta}$ 9.0, J_{gem} 12.7, $J_{4\beta,5\alpha}$ 7.8, $J_{4\beta,5\beta}$ 8.4

Hz, 4-H_β), 2.19 (2 H, dt, $J_{3,3'}$ 2.3 Hz, 3′-H_2), 1.51 (2 H, m, 4′-H_2), 1.41—1.22 (6 H, m, 3 × CH_2), and 0.89 (3 H, t, Me); δ_C ($CDCl_3$) 174.3 (C-2), 84.5 and 76.8 (C≡C), 66.7 (C-5), 32.6 (C-3), 31.2 (C-6′), 30.9 (C-4), 28.4 (C-4′ and -5′), 22.4 (C-7′), 18.6 (C-3′), and 13.9 (Me).

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