

FRIEDEL-CRAFTS REACTIONS OF BIS(TRIMETHYLSILYL)POLYIYNES WITH ACYL CHLORIDES; A USEFUL ROUTE TO TERMINAL-ALKYNYL KETONES

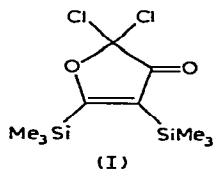
D. R. M. WALTON and F. WAUGH

School of Molecular Sciences, University of Sussex, Brighton BN1 9QJ, (Great Britain)

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SUMMARY

Bis(trimethylsilyl)acetylenes, $\text{Me}_3\text{Si}(\text{C}\equiv\text{C})_n\text{SiMe}_3$, react with acyl chloride-aluminium chloride complexes, $\text{XC}_6\text{H}_4\text{COCl}\cdot\text{AlCl}_3$ in methylene chloride at $0-20^\circ$ to form the corresponding ketones $\text{XC}_6\text{H}_4\text{CO}(\text{C}\equiv\text{C})_n\text{SiMe}_3$ in excellent ($n=1$) or moderate ($n=2, 4$) yield. Treatment of the products with aqueous methanolic borax results in virtually quantitative liberation of the terminal alkynyl ketones $\text{XC}_6\text{H}_4\text{CO}(\text{C}\equiv\text{C})_n\text{H}$. The method provides the first practical route to the ketotetraynes ($n=4$) and usefully supplements existing oxidative methods for keto-monoynes and -diynes synthesis. The oxalyl chloride-aluminium chloride complex reacts with $\text{Me}_3\text{SiC}\equiv\text{CSiMe}_3$ to give the novel silyl-substituted heterocycle (I):



INTRODUCTION

The lower reactivity of ethynyl Grignard and allied reagents as compared to their alkyl and aryl counterparts permits the former to be used in couplings leading directly to ethynyl ketones in certain circumstances¹. In recent years these reagents have been largely superseded by ethynyl derivatives of less electropositive metals such as cadmium², copper³, lead⁴, silver⁵, tin⁶ and zinc⁷ whereby side products arising from additions to the carbonyl group are avoided, however the latter cannot be used directly to synthesise terminal ethynyl ketones, $\text{RCOC}\equiv\text{CH}$, because of a pronounced tendency for certain $\text{MC}\equiv\text{CH}$ species to disproportionate to the acetylides, $\text{MC}\equiv\text{CM}$, which are either insoluble, unreactive polymers (*e.g.* $\text{M}=\text{Cu}, \text{Ag}$) or simply give non-terminal diketones. For these reasons coupled with problems of stability, they also cannot be used to prepare higher terminal-alkynyl ketones, $\text{RCO}(\text{C}\equiv\text{C})_n\text{H}$ ($n > 1$).

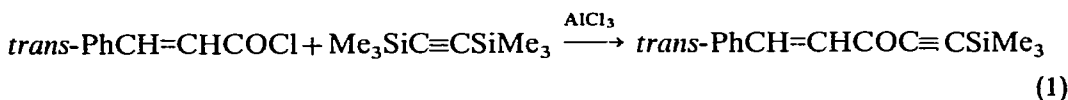
Some years ago, Birkofer, Ritter and Uhlenbrauk⁸ successfully reacted bis(trimethylsilyl)acetylene with acyl halides under Friedel-Crafts conditions and ob-

tained trimethylsilylethynyl ketones, $\text{RCOC}\equiv\text{CSiMe}_3$, in good yield. The reaction was conceived as an electrophilic displacement of one trimethylsilyl moiety by an acyl group which proceeded cleanly because the electron-withdrawing power of the acyl substituent deactivated the ethynyl-silicon bond of the product towards further attack.

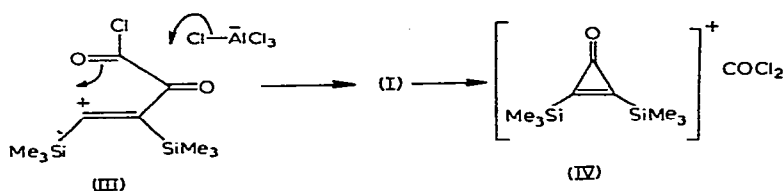
We considered further investigation of this reaction to be timely, firstly because advances in oxidative coupling techniques⁹ have made available a range of bisilyl polyacetylenes¹⁰ for exploitation in synthesis, and, secondly, because detailed knowledge derived from kinetic studies¹¹ permits the base-catalysed cleavage of ethynyl-silicon bonds to be carried out rapidly and quantitatively. These two factors serve as a basis for terminal-alkynyl ketone synthesis described in this paper.

RESULTS AND DISCUSSION

Birkofer and coworkers isolated the ketone, $p\text{-NO}_2\text{C}_6\text{H}_4\text{COC}\equiv\text{CSiMe}_3$ (II) in 43% yield by reacting bis(trimethylsilyl)acetylene with p -nitrobenzoyl chloride and aluminium chloride in carbon disulphide in the temperature range 2–8°. Higher yields were reported for reactions involving acetyl and propionyl chloride⁸. We obtained (II) in considerably improved yield (93%) using the preformed p -nitrobenzoyl chloride-aluminium chloride complex in methylene chloride solution, a technique employed by us in allied aryl ketone syntheses from reaction of such complexes with aryltrimethylsilanes¹². Comparable yields were obtained with other acyl halides, $\text{XC}_6\text{H}_4\text{COCl}$, as detailed in Table 1 whilst cinnamoyl and 2-furoyl chloride furnished β -styryl and 2-furoyl trimethylsilylethynyl ketones respectively in moderate yield [e.g. eqn. (1)].



The reaction between oxalyl chloride and bis(trimethylsilyl)acetylene took an interesting course in that instead of the anticipated α,β -diketone, the dihydrofuranone (I) was obtained, presumably via intramolecular cyclisation of intermediate (III) without loss of the trimethylsilyl group, e.g.:



The mass spectral cracking pattern of (I) is interesting in that in addition to the parent ion, pronounced lines were present corresponding to loss of phosgene ($m/e=99$) and appearance of the bis(trimethylsilyl)cyclopropenone (IV) ($m/e=200$).

1,4-Bis(trimethylsilyl)butadiyne reacted similarly with a range of acyl chloride-aluminium chloride complexes to give the stable aryl trimethylsilylbutadiynyl

TABLE I

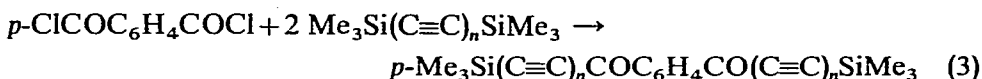
ARYL TRIMETHYLSILYLALKYNYL KETONES $\text{XC}_6\text{H}_4\text{CO}(\text{C}\equiv\text{C})_n\text{SiMe}_3$ PREPARED FROM $\text{XC}_6\text{H}_4\text{COCl}\cdot\text{AlCl}_3$ COMPLEXES AND $\text{Me}_3\text{Si}(\text{C}\equiv\text{C})_n\text{SiMe}_3$ COMPOUNDS IN METHYLENE CHLORIDE BY METHODS A OR B

X	n	Yield (%)	M.p. ($^{\circ}\text{C}$) or b.p. ($^{\circ}\text{C}/\text{mm}$)	Found (%)		Calcd. (%)	
				C	H	C	H
<i>p</i> -Me ^a	1	94 ^g	74–78/10 ⁻³	72.2	7.5	72.2	7.45
<i>p</i> -Cl ^b	1	85 ^g	80–84/10 ⁻³	60.9	5.6	60.9	5.5
<i>p</i> -NO ₂	1	93	109 ^c				
H	2	48	13–15 ^d	74.6	6.7	74.3	6.2
<i>p</i> -Me	2	49	33–34	75.0	6.9	74.95	6.7
<i>p</i> -NO ₂	2	74	128–129	62.2	5.0	61.95	4.8
<i>p</i> -OMe	2	76	104–105	70.4	6.5	70.3	6.3
<i>p</i> -Cl	4	49	100 dec ^e	69.8	4.6	70.0	4.2
<i>p</i> -OMe	4	64	102 dec ^e	75.0	5.1	75.0	5.3
<i>p</i> -NO ₂	4	40	105 dec ^{e,f}	65.9	4.2	67.7	4.1

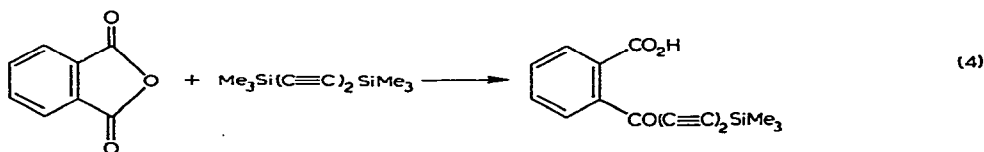
^a n_D^{20} 1.5321. ^b n_D^{20} 1.5446. ^c Lit.⁸ m.p. 107 $^{\circ}$. ^d B.p. 90–94 $^{\circ}$ /10⁻³ mm. ^e The product was recrystallized from ether/petrol at –15 $^{\circ}$ and darkened rapidly at room temperature. ^f Despite repeated recrystallization to constant m.p., the carbon elemental analysis was in error by ca. 3%. ^g Method A.

ketones (*cf.* Table 1) although the yields (50–75%) were somewhat lower than those obtained with bis(trimethylsilyl)acetylene. Use of up to two equivalents of acyl chloride did not lead to displacement of the second trimethylsilyl group thus demonstrating that the electron withdrawing effect of the acyl group is still operative in the product despite the increase in acetylene chain length. This result is compatible with the rates of acid-catalysed cleavage of ethynyl–germanium bonds in $\text{YC}_6\text{H}_4\text{-(C}\equiv\text{C)}_n\text{GeEt}_3$ compounds which show that substituents, Y, continue to influence the rate when $n=2$ (*viz.* $\rho = -1.4$) despite their distance from the site of reaction¹³.

Additional syntheses of interest in the mono- and di-acetylene series are exemplified by eqns. (2)–(4):



$n=1, 2$



The instability of terminal tetraynes $\text{R}(\text{C}\equiv\text{C})_4\text{H}$ and particularly of octatetrayne itself has hitherto considerably restricted the use of these polyacetylenes in

TABLE 2

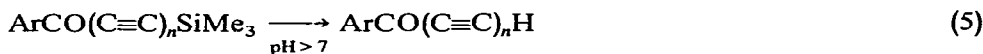
SPECTRAL DATA FOR $\text{XC}_6\text{H}_4\text{CO}(\text{C}\equiv\text{C})_n\text{SiMe}_3$ COMPOUNDS^a

X	n	NMR [τ (ppm)]		UV
		$(\text{CH}_3)_3\text{Si}^b$	C_6H_4	λ_{max} (nm) ($10^{-4} \epsilon$)
<i>p</i> -Me ^c	1	9.69	2.40(q)	279(1.49)
<i>p</i> -Cl	1	9.70	2.27(q)	275(1.67)
<i>p</i> -NO ₂	1	9.64	1.68(s)	271(1.96)
H	2	9.74	2.18(m) ^g	264(1.18), 272(1.54), 285(1.79), 303(1.35)
<i>p</i> -Me ^d	2	9.74	2.40(q)	289(1.83), 306(1.79)
<i>p</i> -NO ₂	2	9.71	1.67(s)	275(2.12), 290(1.93), 307(1.45)
<i>p</i> -OMe ^e	2	9.75	2.55(q)	322(1.99)
<i>p</i> -Cl	4	9.75	2.26(q)	218(4.66), 227(7.09), 236(7.77), 245(sh)(5.14), 263(4.08), 277(4.66), 299(4.10), 316(1.71), 338(0.89), 362(0.89), 391(0.56)
<i>p</i> -OMe ^f	4	9.76	2.55(q)	217(4.65), 226(7.00), 236(8.66), 245(sh)(5.86), 262.5(4.93), 274(5.08), 323(1.77), 340(2.03), 362(1.64), 390(0.77)
<i>p</i> -NO ₂	4	9.75	1.67(s)	230, 236, 273(sh), 283, 290, 317(sh), 340, 365, 393

^a All IR spectra showed bands in the range 1630–1665 s (C=O), and bands for $(\text{C}\equiv\text{C})_n$ as follows: $n=1$, 2150–2160 m; $n=2$, 2205–2212 m and 2100–2110 s; $n=4$, 2194 s, 2148 m, 2130 s and 2060 s. ^b Singlet. ^c 7.63(s) CH₃. ^d 7.60(s) CH₃. ^e 6.13(s) CH₃O. ^f 6.12(s) CH₃O. ^g C₆H₅.

synthesis, for example the sole recorded substitution [apart from oxidative couplings of $\text{R}(\text{C}\equiv\text{C})_4\text{H}$]^{14,15} is the reaction of the disodio derivative, $\text{Na}(\text{C}\equiv\text{C})_4\text{Na}$ ¹⁶, generated *in situ*, with acetone in liquid ammonia to give the diol, $\text{Me}_2\text{C}(\text{OH})(\text{C}\equiv\text{C})_4\text{C}(\text{OH})\text{Me}_2$. Bis(trimethylsilyl)octatetrayne on the other hand, a stable substance readily prepared by oxidative coupling of butadiynyl(trimethyl)silane, reacted with $\text{XC}_6\text{H}_4\text{COCl}\cdot\text{AlCl}_3$ complexes in methylene chloride at ambient temperatures to give aryl trimethylsilyloctatetraynyl ketones, $\text{XC}_6\text{H}_4\text{CO}(\text{C}\equiv\text{C})_4\text{SiMe}_3$, in moderate to good yield (*cf.* Table 1).

Liberation of terminal-alkynyl ketones from their silyl precursors [eqn. (5)]



Ethynyl–silicon bonds are readily broken by aqueous methanolic alkali¹¹, the reactions following well established substituent effect rules for nucleophilic substitution: *i.e.* electron-supplying groups attached to silicon or to the ethynyl group retard, whereas electron-withdrawing groups enhance the rate of cleavage. Thus the acyl groups which inhibit breaking of the alkynyl–silicon bonds in the ketone products of the Friedel–Crafts reactions enhance the reactivity of these bonds towards base with the result that the aryl trimethylsilylalkynyl ketones are cleaved by extremely weak bases such as dilute borax. Furthermore the substituent effect is augmented by cumulative electron-withdrawal of additional acetylene units in the chain. For terminal ketone synthesis care needs to be exercised since the cleavage products are susceptible to base-catalysed Michael type additions to the triple bond¹¹. Fortunately the rate of cleavage is faster than the rate of addition and the transformation can

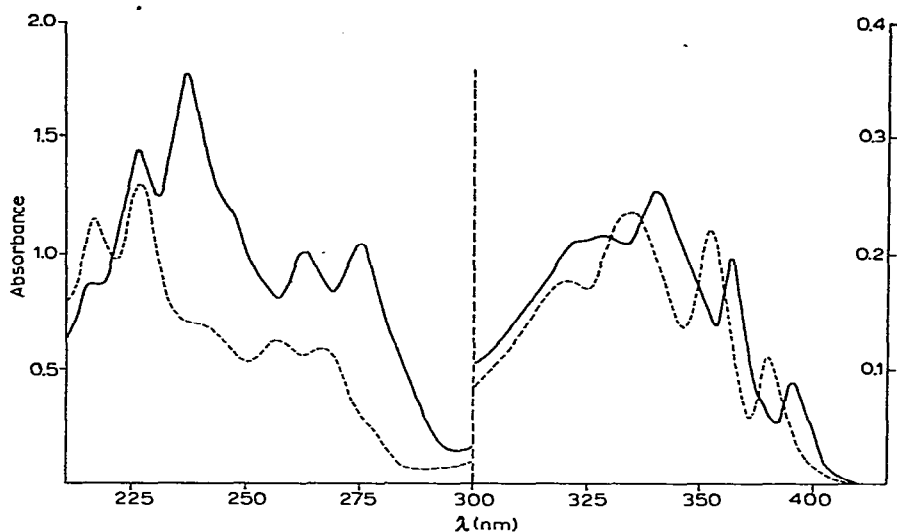
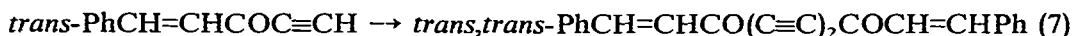


Fig. 1. UV spectra (petrol solution); —, $p\text{-MeOC}_6\text{H}_4\text{CO}(\text{C}\equiv\text{C})_4\text{SiMe}_3$; ----, $p\text{-MeOC}_6\text{H}_4\text{CO}(\text{C}\equiv\text{C})_4\text{H}$.

conveniently be followed spectrophotometrically in the UV region by observing associated optical density changes. (cf. Fig. 1). This difference is not always clear cut, particularly for aryl butadiynyl and ethynyl ketones. However, the spectrum of the base-catalyzed addition product differs considerably from that of the terminal-

its spectrophotometric solution was described in our recent synthesis of aryl ethynyl sulphones from bis(trimethylsilyl)acetylene¹⁸. As anticipated, the stability of the terminal-alkynyl ketones $\text{RCO}(\text{C}\equiv\text{C})_n\text{H}$ decreased rapidly as n increased and it proved impossible to isolate the ketotetraynes ($n=4$). Fortunately the cleavage is quantitative and the by-products, trimethylsilanol or hexamethyldisiloxane, are easily removed by column chromatography to leave pure solutions of the ketotetrayne.

Selected butadiynyl and ethynyl ketones were further characterized by oxidative coupling as exemplified in eqns. (6) and (7).



Attempts to oxidatively couple the ketotetrayne $\text{PhCO}(\text{C}\equiv\text{C})_4\text{H}$ were unsuccessful, doubtless because of the insolubility of its cuprous derivative.

EXPERIMENTAL

Petrol refers to light petroleum b.p. $< 40^\circ$. Chromatography was performed on silica gel columns using chloroform/petrol or ether/petrol mixtures in varying proportions as eluent. IR spectra were recorded on a Perkin-Elmer 257 instrument. Proton NMR spectra had the correct integration and chemical shifts (τ) were measured on a Varian A60 instrument using 5% solutions in CCl_4 or CDCl_3 with TMS as

internal standard. UV spectra were recorded on a Unicam SP800 instrument using slightly acidified methanol solutions, unless stated otherwise.

Bis(trimethylsilyl)acetylene

Tetrahydrofuran (250 ml) was added to butyllithium (2.0 moles) in ether (1250 ml) maintained at -20° by external cooling and dry acetylene gas was bubbled through the solution for 2–3 h producing a copious white precipitate. The mixture was subsequently boiled under reflux for 12 h (to ensure disproportionation of any ethynyllithium) then cooled in ice and chlorotrimethylsilane (217 g, 2.0 moles) in THF (120 ml) was added. Following a further 8 h of reflux the reaction mixture was treated with ice-cold dilute hydrochloric acid, the aqueous layer was separated and extracted with petrol and the combined petrol and ether layers were dried (MgSO_4) and fractionated to give bis(trimethylsilyl)acetylene (86%) b.p. $134\text{--}136^{\circ}$ which solidified in the receiver (lit.¹⁹ b.p. $134\text{--}136^{\circ}$; m.p. 26°). NMR: τ 9.79 (s) [$(\text{CH}_3)_3\text{Si}$] ppm.

1,4-Bis(trimethylsilyl)butadiyne

Cuprous chloride (20 g) was added to a stirred solution of tetramethylethylene diamine (10 ml) in acetone (250 ml). The resulting blue-green suspension of $\text{CuCl}\cdot\text{TMEDA}$ complex⁹ was decanted from excess of CuCl , then diluted with more acetone (100 ml) and ethynyl(trimethyl)silane²⁰ (25 g, 0.255 mole) in acetone (100 ml) was added with stirring during 30 min whilst oxygen was bubbled through the mixture. Passage of oxygen was continued for a further 2 h, then the reaction mixture was poured into ice-cold dilute HCl and extracted with petrol. The petrol layer was dried and solvent was removed under reduced pressure to leave a pale yellow solid which was recrystallized from aqueous methanol (slightly acidified) to give 1,4-bis(trimethylsilyl)butadiyne (93%) m.p. 107° (lit.²¹ m.p. $107\text{--}108^{\circ}$). IR (CCl_4): 2070 vs, 2046 w [$(\text{C}\equiv\text{C})_2$] cm^{-1} . UV (λ_{max}): 226, 237, 249, 261.8, 277.5 nm. NMR: τ 9.85 (s) [$(\text{CH}_3)_3\text{Si}$] ppm.

Butadiynyl(trimethyl)silane

Chlorotrimethylsilane (108.5 g, 1.0 mole) diluted with THF (50 ml) was added during 1 h to a solution of butadiynylmagnesium bromide prepared from diacetylene (55 g, 1.1 mole) and ethylmagnesium bromide (1.0 mole) in THF (550 ml)²². The mixture was initially stirred at 20° for 2 h, then boiled under reflux for 30 min and finally set aside at room temperature for 12 h. Dilute HCl was then added slowly and organic products were extracted with petrol. The petrol extracts were dried and distilled to give butadiynyl(trimethyl)silane (29%) b.p. $35\text{--}37^{\circ}/27$ mm, n_{D}^{20} 1.4665 (lit.²³ b.p. $40^{\circ}/30$ mm, n_{D}^{20} 1.4666), as a colourless liquid which rapidly turned red at room temperature. IR (film): 3300 vs ($\text{C}\equiv\text{C}\text{--H}$); 2190 s, 2035 vs [$(\text{C}\equiv\text{C})_2$] cm^{-1} . UV (λ_{max}): 225, 236, 248.4, 262.5 nm. The pale brown residue, following removal of butadiynyl(trimethyl)silane, was recrystallised from acidified methanol to give 1,4-bis(trimethylsilyl)butadiyne (24 g) m.p. 107° .

1,8-Bis(trimethylsilyl)octatetrayne

Butadiynyl(trimethyl)silane (14.2 g, 0.12 mole) was oxidatively coupled in acetone (250 ml) during 2 h in the presence of $\text{CuCl}\cdot\text{TMEDA}$ complex (0.1 mole) and oxygen as described above. Removal of solvent under reduced pressure from the

worked up petrol extracts afforded a yellow solid which was recrystallised from acidified aqueous methanol to give 1,8-bis(trimethylsilyl)octatetrayne (nc) (82%) m.p. 94–95°. (Found: C, 69.5; H, 7.6. $C_{14}H_{18}Si_2$ calcd.: C, 69.3; H, 7.5%) IR (CCl_4): 2179 w, 2046 vs $[(C\equiv C)_4]$ cm^{-1} . UV $[\lambda_{max}(\epsilon)]$: 221(20000), 227(50000), 238(170000), 250.5(260000) nm.

Preparation of aryl trimethylsilylalkynyl ketones

Phenyl trimethylsilylethynyl ketone (Method A). A solution of benzoyl chloride (14 g, 0.1 mole) in anhydrous methylene chloride (50 ml) was added during 30 min to a suspension of finely powdered aluminium chloride (20 g, 0.15 mole) in ice-cold methylene chloride (100 ml). The mixture was subsequently stirred at 0° for 30 min, the dark brown solution was decanted from excess of aluminium chloride, filtered quickly through glass wool under nitrogen, and added during 1 h to bis(trimethylsilyl)acetylene (17 g, 0.1 mole) in methylene chloride (100 ml) at 0°. After stirring for 3 h the resulting black mixture was shaken vigorously with sufficient ice-cold dilute hydrochloric acid to dissolve the aluminium salts. The organic layer was separated and the aqueous layer was extracted with ether. The combined organic phases were dried and the solvent was removed under reduced pressure, leaving a dark brown oil which was chromatographed. Elution with 1/2 chloroform/petrol afforded a yellow liquid which was concentrated and distilled to give phenyl trimethylsilylethynyl ketone (89%) b.p. 60–63°/0.001 mm, n_D^{20} 1.5295 (lit.²⁴ b.p. 103–104°/2.5 mm, n_D^{20} 1.5311). UV $[\lambda_{max}(\epsilon)]$: 267(14900) nm. NMR: τ 9.70 (s) $[(CH_3)_3Si]$, 2.19 (m) (C_6H_5) ppm.

trans- β -Styryl trimethylsilylethynyl ketone (Method B). Powdered aluminium chloride (14.7 g, 0.11 mole) was added in portions during 30 min to an ice-cold solution of cinnamoyl chloride (16.7 g, 0.1 mole) and bis(trimethylsilyl)acetylene (17 g, 0.1 mole) in methylene chloride (300 ml). The mixture was stirred at 20° for 3 h then added to dilute hydrochloric acid and worked up as described in method A. The resulting brown oil was chromatographed and the eluted fractions were concentrated and distilled to give *trans- β -styryl trimethylsilylethynyl ketone* (nc) (71%) b.p. 110–112°/0.01 mm, n_D^{20} 1.5735. (Found: C, 73.6; H, 7.1. $C_{14}H_{16}OSi$ calcd.: C, 73.6; H, 7.1%) UV $[\lambda_{max}(\epsilon)]$: 312(24800) nm. NMR: τ 9.70 (s) $[(CH_3)_3Si]$, 2.79 (q) (*trans*-C₆H=CH), 2.58 (m) (C_6H_5) ppm.

2-Furyl trimethylsilylethynyl ketone. A similar reaction between 2-furoyl chloride (13.1 g, 0.1 mole), bis(trimethylsilyl)acetylene (17 g, 0.1 mole) and aluminium chloride (14.7 g, 0.11 mole) in methylene chloride (300 ml) during 1.5 h at 20° gave 2-furyl trimethylsilylethynyl ketone (nc) (51%) b.p. 72–74°/0.03 mm, n_D^{20} 1.5208. (Found: C, 62.2; H, 6.3. $C_{10}H_{12}O_2Si$ calcd.: C, 62.5; H, 6.3%) UV $[\lambda_{max}(\epsilon)]$; 298-(16800) nm. NMR: τ 9.75 (s) $[(CH_3)_3Si]$ ppm.

Reaction between oxalyl chloride and bis(trimethylsilyl)acetylene. A solution of bis(trimethylsilyl)acetylene (25.5 g, 0.15 mole) and oxalyl chloride (7.4 g, 0.058 mole) in methylene chloride (250 ml) was cooled to –78° and powdered aluminium chloride (16.7 g, 0.125 mole) was added. No visible change resulted at this temperature, however on warming to –30°, the mixture turned brown and eventually black at 0°. It was set aside at 0° for 1 h, then poured into dilute hydrochloric acid and worked up in the usual way to give, after chromatography (elution with 1/10 ether/petrol) a dark brown liquid which solidified upon cooling. Repeated recrystallisation of this

solid from acidified methanol followed by sublimation at reduced pressure (10^{-4} mm) gave white crystalline 2,2-dichloro-2,3-dihydro-4,5-bis(trimethylsilyl)-3-furanone (nc) (27%) m.p. 55–56°. (Found: C, 40.7; H, 6.4; Cl, 24.2. $C_{10}H_{18}Cl_2O_2Si_2$ calcd.: C, 40.4; H, 6.1; Cl, 23.9%.) IR (nujol): 1740 s (C=O), 1260 s, 1245 m ($SiMe_3$) cm^{-1} . NMR: τ 9.69 (s) and 9.59 (s) [$(CH_3)_3Si$] ppm.

Reaction of bis(trimethylsilyl)-acetylene and -butadiyne with terephthaloyl chloride. A mixture of bis(trimethylsilyl)acetylene (17.8 g, 0.105 mole), terephthaloyl chloride (10.1 g, 0.05 mole) and aluminium chloride (16.1 g, 0.12 mole) in methylene chloride (200 ml) was maintained at 20° for 3 h. Following the established working up procedure, evaporation of solvent from chromatographed extracts left a solid which was recrystallised from petrol to give the diketone *p*- $Me_3SiC\equiv CCOC_6H_4CO-C\equiv CSiMe_3$ (nc) (80%) m.p. 145–146°. (Found: C, 66.4, H, 6.9. $C_{18}H_{22}O_2Si_2$ calcd.: C, 66.2; H, 6.8%.) UV [$\lambda_{max}(e)$]: 281 (28500) nm. NMR: 9.65 (s) [$(CH_3)_3Si$], 1.80 (s) (*p*- C_6H_4) ppm. A similar reaction between terephthaloyl chloride (9.85 g, 0.049 mole), 1,4-bis(trimethylsilyl)butadiyne (18.9 g, 0.097 mole) and aluminium chloride (13.4 g, 0.1 mole) in methylene chloride (200 ml) gave the diketone *p*- $Me_3Si(C\equiv C)_2COC_6H_4CO(C\equiv C)_2SiMe_3$ (nc) (50%) m.p. 133–134° (from petrol). (Found: C, 70.4; H, 6.1. $C_{22}H_{22}O_2Si_2$ calcd.: C, 70.5; H, 5.9%.) UV [$\lambda_{max}(e)$]: 282 (27000), 294 (32300), 311 (30500) nm. NMR: τ 9.72 (s) [$(CH_3)_3Si$] ppm.

Reaction between 1,4-bis(trimethylsilyl)butadiyne and phthalic anhydride. Phthalic anhydride (7.4 g, 0.05 mole), 1,4-bis(trimethylsilyl)butadiyne (12.7 g, 0.065 mole) and aluminium chloride (13.4 g, 0.1 mole) were reacted together in methylene chloride (300 ml) at 0–20° during 3 h, and the mixture was worked up by the established method to give the keto acid *o*- $Me_3Si(C\equiv C)_2COC_6H_4CO_2H$ (nc) (60%) m.p. 123–124° (from ether/petrol). (Found: C, 66.9; H, 5.4. $C_{15}H_{14}O_3Si$ calcd.: C, 66.65; H, 5.2%.) IR (CCl_4): 2200 m, 2102 s [$(C\equiv C)_2$], 1650 s (C=O), 1700 s (CO_2H) cm^{-1} . NMR: τ 9.73 (s) [$(CH_3)_3Si$], 2.21 (m) (*o*- C_6H_4) ppm.

Reaction between 1,4-bis(trimethylsilyl)butadiyne and acetyl chloride. A filtered solution of complex prepared from acetyl chloride (4.07 g, 0.052 mole), aluminium chloride (8.7 g, 0.065 mole) in methylene chloride (70 ml) was added to an ice-cold solution of 1,4-bis(trimethylsilyl)butadiyne (9.7 g, 0.05 mole) in methylene chloride (75 ml). The mixture was set aside at 0° for 2 h then worked up in the usual way to give, after chromatography, a red-brown liquid. Distillation of this liquid at reduced pressure (10^{-4} mm) in conjunction with a cold finger probe (-78°) resulted in a pale yellow solid (47%) which was recrystallised from petrol at -78° but which melted at room temperature to give a red oil. IR (film): 2212 m, 2102 s [$(C\equiv C)_2$], 1680 s (C=O) cm^{-1} . UV (λ_{max}): 234, 246, 259, 273.5, 289.5 nm, characteristic for methyl trimethylsilylbutadiynyl ketone (nc). The (2,4-dinitrophenyl)hydrazone derivative, prepared in acid solution in the usual way was a stable yellow solid m.p. 210–212° (from methanol). (Found: C, 52.1; H, 4.9; N, 16.0. $C_{15}H_{16}N_4O_4Si$ calcd.: C, 52.3; H, 4.7; N, 16.3%.)

Analytical and spectral data for other aryl trimethylsilylalkynyl ketones, $XC_6H_4CO(C\equiv C)_nSiMe_3$ prepared by methods A and B are given in Tables 1 and 2 respectively.

Preparation of alkynyl aryl ketones

Ethynyl phenyl ketone. Aqueous 0.01 M borax (25 ml) was added to a methanol

solution (200 ml) of phenyl trimethylsilylethynyl ketone (3.25 g, 0.016 mole). The mixture was set aside at 20° for 5 min then added to cold dilute hydrochloric acid and organic products were extracted with petrol. The petrol layer was dried and concentrated at reduced pressure to leave crude material, which was chromatographed, using 1/4 ether/petrol as eluent, to give ethynyl phenyl ketone (89%) m.p. 51° (from methanol) (lit.²⁵ m.p. 50–51°). NMR: τ 6.68 (s) (C \equiv C–H), 2.25 (m) (C₆H₅) ppm.

Ethynyl trans- β -styryl ketone. *trans- β -Styryl trimethylsilylethynyl ketone* (8.78 g, 38.4 mmole) in methanol (250 ml) was similarly treated with 0.01 M borax (25 ml) at 20° for 5 min and the mixture was subsequently acidified and worked up as described above to give ethynyl *trans- β -styryl ketone* (nc) (91%) m.p. 64° (from ether/petrol). (Found: C, 84.3; H, 5.3. C₁₁H₁₈O calcd.: C, 84.6; H, 5.2%) NMR: τ 6.85 (s) (C \equiv C–H), 2.84 (q) (*trans*-CH=CH), 2.60 (m) (C₆H₅) ppm.

p-Chloro- and p-nitrophenyl ethynyl ketone. *p-Chloro- and p-nitrophenyl trimethylsilylethynyl ketones* were similarly treated with aqueous methanolic borax at 20° for 5 min to give *p-chlorophenyl ethynyl ketone* (90%) m.p. 106° (from ether/petrol) (lit.²⁶ m.p. 106–107°) [IR (CCl₄): 2100 s (C \equiv C), 3300 s (C \equiv C–H), 1660 s (C=O) cm⁻¹; NMR: τ 6.67 (s) (C \equiv C–H), 2.24 (q) (*p*-C₆H₄) ppm] and ethynyl *p-nitrophenyl ketone* (nc) (93%) m.p. 134–135° (from ether/petrol at –15°). (Found: C, 61.8; H, 3.1. C₉H₅NO₂ calcd.: C, 61.7; H, 2.9%) IR (CCl₄): 2100 s (C \equiv C), 3290 s (C \equiv C–H), 1664 s (C=O) cm⁻¹. NMR: τ 6.38 (s) (C \equiv C–H), 1.60 (s) (*p*-C₆H₄) ppm.

Butadiynyl phenyl ketone. A mixture of phenyl trimethylsilylbutadiynyl ketone (4.63 g, 0.02 mole), aqueous 0.01 M borax (25 ml) and methanol (250 ml) was set aside at 20° for 5 min, then treated with dilute hydrochloric acid and worked up in the usual way to give a concentrate which was absorbed directly onto silica gel (10 g). This material was transferred to a chromatography column and elution with 1/4 ether/petrol afforded a colourless solution. Upon concentration of the solution at reduced pressure a pink solid was deposited which was dissolved in a minimum quantity of ether/petrol. The solution was quickly filtered and cooled at –15° whereupon crystals of butadiynyl phenyl ketone (92%) m.p. 105° decompn. (lit.²⁷ m.p. 106°) reprecipitated. IR (CCl₄): 3305 s (C \equiv C–H), 2241 m, 2200 m, 2065 m [(C \equiv C)₂], 1650 s (C=O) cm⁻¹. UV [λ_{\max} (ϵ): 257 (sh)(9300), 266 (sh)(12700), 274(15100), 286(12300) nm. NMR: τ 7.26 (s) (C \equiv C–H), 2.14 (m) (C₆H₅) ppm. The product was stored unchanged at –15° for several hours, but rapidly turned deep blue upon warming to 20° even in the absence of light.

p-Anisyl butadiynyl ketone. Treatment of *p-anisyl trimethylsilylbutadiynyl ketone* (2.85 g, 0.01 mole) with 10% aqueous methanolic 0.01 M borax in the same way resulted in a blue solid which was partially ether-soluble. Recrystallization of this ether-soluble portion from ether/petrol at –15° gave blue needles, whereas recrystallization at –78° gave white crystals which rapidly darkened at room temperature. The crystalline *p-anisyl butadiynyl ketone* (nc) (94%) obtained at –78° had m.p. 78–79°. (Found: C, 78.4; H, 4.5. C₁₂H₈O₂ calcd.: C, 78.25; H, 4.4%) IR (CCl₄): 3315 s (C \equiv C–H), 2250 m, 2208 m, 2074 m [(C \equiv C)₂], 1652 s (C=O) cm⁻¹. NMR: τ 7.30 (s) (C \equiv C–H), 6.10 (s) (CH₃O), 2.44 (q) (*p*-C₆H₄) ppm. UV [λ_{\max} (ϵ): 319(17300) nm.

Butadiynyl p-tolyl ketone. *p-Tolyl trimethylsilylbutadiynyl ketone* was likewise treated with 0.01 M aqueous borax in methanol (13 mmole scale reaction) and after 5 min at 20° the mixture was worked up to give butadiynyl *p-tolyl ketone* (nc)

(91 %) m.p. 98–100° (from ether/petrol at -78°) as white needles which rapidly turned purple at 20°. (Found: C, 85.4; H, 4.9. $C_{12}H_8O$ calcd.: C, 85.7; H, 4.8%) IR (CCl_4): 3300 s ($C\equiv C-H$), 2248 m, 2207 m, 2072 m [$(C\equiv C)_2$], 1650 s ($C=O$) cm^{-1} . NMR: τ 7.57 (s) (CH_3), 7.40 (s) ($C\equiv C-H$), 2.41 (q) ($p-C_6H_4$) ppm.

Preparation of aryl octatetraynyl ketones $p-XC_6H_4CO(C\equiv C)_4H$ ($X = Cl, NO_2, OMe$) in solution. In a typical experiment, *p*-chlorophenyl trimethylsilyloctatetraynyl ketone (0.54 g, 1.75 mmole) was dissolved in methanol (200 ml). The solution was thermostated at 20°, aqueous 0.01 M borax was added and after 5 min the mixture was poured into dilute hydrochloric acid. Organic material was quickly extracted with petrol and the petrol extract was dried and concentrated by rotary evaporation. Chromatography of the concentrate using 1/3 ether/petrol as eluent afforded yellow solutions of *p*-chlorophenyl octatetraynyl ketone, characterised by its UV spectrum [$\lambda_{max}(\epsilon)$]: 217(71200); 226(73000); 239(37200); 257(39100); 267(37900); 292(24800); 309(22500); 328(11400); 351(9100); 378(5800) nm. Isolation of the pure product was not attempted in view of its anticipated instability. An identical procedure was followed for preparing solution of other aryl octatetraynyl ketone; $X = NO_2$ (λ_{max}): 229, 266 (sh), 275, 285, 309 (sh), 331, 354, 380; $X = OMe$ (λ_{max}): 216, 226, 239, 256, 266, 320, 334, 354, 379.

Oxidative couplings of terminal-alkynyl ketones

1,6-Diphenylhexa-2,4-diyne-1,6-dione. Ethynyl phenyl ketone (2.57 g, 19.8 mmole) in acetone (100 ml) was added with stirring during 30 min to CuCl (2 g)/TMEDA (1 ml) in acetone (100 ml) whilst a stream of air was drawn through the mixture. The initial blue colour quickly discharged and the mixture gradually turned red. After 90 min, passage of air was discontinued and the mixture was acidified and extracted with ether. The dried ether extracts were concentrated under reduced pressure and the concentrate was chromatographed using 1/3 ether/petrol as eluent to give 1,6-diphenylhexa-2,4-diyne-1,6-dione (81 %) m.p. 136–138° (from ether/petrol) (lit.²⁸ m.p. 139–140°). IR (CCl_4): 2160 w, 2138 m [$(C\equiv C)_2$], 1660 vs ($C=O$) cm^{-1} . NMR: 2.13 (m) (C_6H_5) ppm. UV [$\lambda_{max}(\epsilon)$]: 278(18300), 290(18800), 309 (sh)(14200) nm.

trans,trans-1,10-Diphenyldeca-1,9-diene-4,6-diyne-3,8-dione. A similar oxidative coupling of ethynyl *trans*- β -styryl ketone (2.43 g, 0.016 mole) in acetone (160 ml) in the presence of CuCl (4 g)/TMEDA (2 ml) and passage of air for 2 h, gave upon working up by the established procedure, *trans,trans-1,10-diphenyldeca-1,9-diene-4,6-diyne-3,8-dione* (nc) (85 %) m.p. 140° decompn. (from ether/petrol). (Found: C, 84.9; H, 4.7. $C_{22}H_{24}O_2$ calcd.: C, 85.1; H, 4.55%) IR (CCl_4): 2140 m [$(C\equiv C)_2$], 1635 vs ($C=O$) cm^{-1} . NMR: τ 2.74 (q) (*trans*-CH=CH), 2.53 (m) (C_6H_5) ppm. UV [$\lambda_{max}(\epsilon)$]: 330(41700) nm.

1,10-Diphenyl- and 1,10-di-p-tolyldeca-2,4,6,8-tetrayne-1,10-dione. Butadiynyl phenyl ketone (2.12 g, 0.014 mole) was oxidatively coupled in acetone solution (250 ml) in the presence of CuCl (2 g)/TMEDA (1 ml) and air during 75 min. The reaction mixture was subsequently acidified and organic products were extracted with ether. The ether extracts were dried ($MgSO_4$) and concentrated by rotary evaporation and the residue was chromatographed using 1/3 ether/petrol as eluent. Product-rich fractions, as revealed by UV spectroscopy, were concentrated at reduced pressure and the solid thus obtained was recrystallized to constant m.p. from ether/petrol at

–15° to give yellow crystals of 1,10-diphenyldeca-2,4,6,8-tetrayne-1,10-dione (nc) (78%) m.p. 75° (decompn.). The product blackened rapidly at room temperature and characteristically gave poor elemental analysis figures. (Found: C, 84.4; H, 5.0. C₂₂H₁₀O₂ calcd.: C, 86.3; H, 3.3%) IR (CCl₄): 2198 s, 2075 m [(C≡C)₄], 1648 vs (C=O) cm⁻¹. UV [$\lambda_{\max}(\epsilon)$]: 230(37100), 251.5(43200), 265(53800), 299(40400), 338-(10500), 365(8800), 394(5600) nm.

In a similar way butadiynyl *p*-tolyl ketone was oxidatively coupled to give 1,10-di-*p*-tolyldeca-2,4,6,8-tetrayne-1,10-dione (nc) (60%) m.p. 90° (decompn.) (from ether/petrol at –78°) as an unstable solid which turned black rapidly at room temperature. (Found: C, 83.3; H, 5.1. C₂₄H₁₄O₂ calcd.: C, 86.2; H, 4.2%) IR (CCl₄): 2200 s, 2074 s [(C≡C)₄], 1648 vs (C=O) cm⁻¹. UV [$\lambda_{\max}(\epsilon)$]: 229(48300), 245(42200), 254(51400), 268(57700), 293(38100), 302(40200), 317(39900), 338(23600), 365(15100), 393(8400) nm.

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