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SILYLATION AS A PROTECTIVE METHOD IN CADIOT–CHODKIEWICZ COUPLINGS

SYNTHESIS OF ARYL-BUTADIYNES AND -HEXATRIYNES

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Abstract—Cadiot-Chodkiewicz couplings of arylacetylenes (I), $XC_6H_4C{\equiv}CH$ (X = H; *m*-Br, —Me; *p*-F, —NO_2, —OMe) with bromoethynyl(triethyl)silane(II), $BrC{\equiv}CSiEt_3$, yield the silylated diynes, $XC_6H_4(C{\equiv}C)_2SiEt_3$ from which the terminal diynes(III), $XC_6H_4(C{\equiv}C)_2H$, are quantitatively liberated by treatment with aqueous methanolic alkali. Reactions of II with III in turn yield the silylated triynes, $XC_6H_4(C{\equiv}C)_3SiEt_3$, which, with alkali, give the free arylhexatriynes, $XC_6H_4(C{\equiv}C)_3H$(IV). The germanium analogue of II, $BrC{\equiv}CGeEt_3$, likewise couples with I (X = H, *p*-NO_2) to give $XC_6H_4(C{\equiv}C)_2GeEt_3$ or with III to give $XC_6H_4(C{\equiv}C)_3GeEt_3$. The products (X = H) are identical with those obtained from the Grignard reagents, $C_6H_5(C{\equiv}C)_nMgBr$ (n = 2, 3), and bromotriethylgermane. Other $XC_6H_4(C{\equiv}C)_nGeEt_3$ compounds (n = 2, 3; excluding X = NO_2) were also prepared by the Grignard method. Couplings between phenylacetylene and the reagents, $BrC{\equiv}CSiMe_3$(V), and $IC{\equiv}CSiR_3$ (R = Me, Et) give the appropriate silylated phenylbutadiynes in poor yield because of symmetrical oxidative coupling (iodo compounds) or of base-sensitivity of the trimethylsilyl-acetylene bonds.

INTRODUCTION

THE coupling of a terminal alkyne with a bromoacetylene in the presence of cuprous ions and a simple amine, as formulated by Cadiot and Chodkiewicz, constitutes the best method yet devised for preparing unsymmetrical polyacetylenes containing an even or odd number of triple bonds, Eq. (1).[1–3]

$$R(C{\equiv}C)_nH + Br(C{\equiv}C)_mR' \longrightarrow R(C{\equiv}C)_{n+m}R' \qquad (1)$$

With few exceptions,[4] the reaction cannot easily be employed to prepare terminal polyacetylenes directly with any degree of efficiency, because such syntheses would require either a parent acetylene, $H(C{\equiv}C)_nH$ or bromoacetylene $H(C{\equiv}C)_mBr$. Since the reaction is conducted at a pH > 7 and since the acidity of ethynyl-hydrogen in terminal polyacetylenes increases with increasing chain length,[5] any initial coupling product would be more reactive than the starting materials with the result that uncontrolled chain growth, or even chain stopping by symmetrical coupling as noted by Bohlmann,[4] is likely to ensue.

In consequence, a number of protecting groups have been devised† the most successful of which incorporate the carboxylate[7] and primary[8] or tertiary[9] alcohol functions. For the most part these are used to protect the bromo-component and, with the exception of the carboxylate group[7] require one or more steps for removal.

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[†] For a detailed account *cf* Ref 6.

Our interest in this area originated in a study of the rates of base-catalysed ethynyl-hydrogen exchange in arylacetylenes[10] and base-catalysed cleavage of ethynyl-silicon bonds in arylethynyl(trialkyl)silanes[11] which revealed that, under comparable conditions, the $ArC{\equiv}C{-}SiMe_3$ bond was broken in aqueous methanol at a $pH > 7$ *ca* $10^3 \sim 10^4$ times more readily than an ethynyl-hydrogen underwent exchange, and that both processes could be halted by acidification. These simple facts coupled with our need of silyl- and germyl-substituted polyacetylenes for kinetic studies,[12] prompted an investigation into the feasibility of using silicon as a basis for protecting terminal acetylenes in organometallic syntheses. The results of this work in relation to the Cadiot–Chodkiewicz reaction are presented here and an account of applications in other copper-catalysed oxidative couplings is described in the accompanying paper.[13]*

RESULTS AND DISCUSSION

Synthesis of arylbutadiynes (III) *from arylacetylenes* (I)

Our initial approach as regards reactants and conditions for the Cadiot–Chodkiewicz coupling was influenced by Krüerke's report[15] of a successful coupling between phenylacetylene and bromoethynyl(trimethyl)silane (V) and also by the commercial availability of chlorotrimethylsilane from which V is easily prepared in two steps. Using the standard procedure[15] with anhydrous $EtNH_2$ as base, DMF as co-solvent, CuCl as catalyst and added NH_2OH,HCl to reduce unwanted cupric ion, at most 5% of $Ph(C{\equiv}C)_2SiMe_3$ was isolated together with much unreacted $PhC{\equiv}CH$. Reduction of the ethylamine content had little effect upon the yield initially, but a point was eventually reached where *both* $PhC{\equiv}CH$ and V were recovered which suggests that V was being attacked by base with or without participation by copper ion (vide infra). Attempts to improve the yield by substituting the more reactive substrate, $IC{\equiv}CSiMe_3$, whilst reducing the concentration of both $EtNH_2$ and cuprous ion were likewise unsuccessful. Phenylacetylene was again recovered together with a small quantity of bis(trimethylsilyl)diacetylene, $Me_3Si(C{\equiv}C)_2SiMe_3$, presumably a result of symmetrical coupling, known to occur readily with iodoalkynes.[2] Use of the triethylsilyl analogue, $BrC{\equiv}CSiEt_3$ (II), prepared from bromotriethylsilane (*cf* Exptl.) gave more promising results and under the established conditions with $PhC{\equiv}CH$, the desired product $Ph(C{\equiv}C)_2SiEt_3$, was obtained pure as a stable liquid in 50% yield, free from symmetrically coupled material. This result supports the contention that failure of the initial experiments lay in the enhanced base sensitivity of the ${\equiv}Si{-}C{\equiv}C{-}$ bonds in $XC{\equiv}CSiMe_3$ ($X = Br, I$) as a result of electron-withdrawal by halogen, X, so that bromoacetylene is presumably liberated and rapidly polymerised for reasons outlined in the introductory section. This explanation is preferred to a sequence in which the desired coupling occurs followed by cleavage of the highly base-sensitive $Me_3Si{-}(C{\equiv}C)_2{-}$ bonds in the product, since no trace of $Ph(C{\equiv}C)_2H$ was found, furthermore, $PhC{\equiv}CH$ was recovered in quantity. Direct participation by cuprous ion can be discounted by reference to aryl-trimethyl- and aryl-triethyl-silanes which display little difference in reactivity towards electrophiles (e.g. acids).[16] Indirect assistance, for example π-complexing between copper and the $-C{\equiv}C-$ bond in $XC{\equiv}CSiMe_3$ (which would assist nucleophilic attack at silicon), cannot be ruled out

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* For a preliminary account, *cf* Ref 14.

however, and the success of the experiment with II is ascribed to the comparative resistance of the $Et_3Si—C{\equiv}C—$ bond to attack by base.*

Attempts to couple $PhC{\equiv}CH$ with $IC{\equiv}CSiEt_3$ were also unsuccessful and $PhC{\equiv}CH$ was recovered together with traces of bis(triethylsilyl)butadiyne $Et_3Si(C{\equiv}C)_2SiEt_3$, the product of symmetrical coupling.

Clearly, modifications to the reaction enabling Me_3Si derivatives, particularly $Me_3SiC{\equiv}CI$ for which a convenient synthesis is now available,[17] to be used would be desirable, but we have not sought out such conditions at this time.

Addition of aqueous alkali to a methanol solution of $Ph(C{\equiv}C)_2SiEt_3$ resulted in cleavage of the $Si—C{\equiv}C$ bond and liberation of the diyne, $Ph(C{\equiv}C)_2H$. This process is quantitative[12] and can be accurately monitored because of characteristic shifts and intensity changes of the vibrational fine structure bands in the UV associated with removal of the trialkylsilyl group from the polyyne (*cf* Tables 2 and 3). This method is attractive, firstly because the reaction conditions can be accurately controlled and are relatively mild and, secondly because after neutralisation, solvent extraction and chromatography to remove silanol, pure solutions of the unstable diyne are obtained in accurately known concentration. The technique therefore, compares very favourably with existing protective procedures for terminal akynes in Cadiot–Chodkiewicz couplings.[6]

Couplings of I with II were used to synthesize a range of silylated diynes, $XC_6H_4(C{\equiv}C)_2SiEt_3$, (X = *m*-Br, —Me; *p*-F, $—NO_2$ and —OMe) the physical properties of which are given in Table 1. The products were mostly high boiling oils which in general survived distillation but which could be also efficiently purified by column chromatography. Treatment of the protected diynes with aqueous methanolic alkali afforded the parent arylbutadiynes (III) in quantitative yield. Examination of the spectral data in Tables 2 and 3 reveals a fairly constant shift ($\Delta\lambda = 14{\cdot}8 \pm 0{\cdot}5$ nm) in the longest wavelength high intensity band accompanying desilylation for the compounds (X = *m*-Br, —Me; *p*-F) and slightly smaller shifts in this band for other X-compounds (*p*-OMe, $\Delta\ \lambda = 12{\cdot}5$ nm; *p*-NO_2, $\Delta\ \lambda = 10{\cdot}0$ nm). Progressively smaller shifts *viz* $\Delta\ \lambda = 12{\cdot}2 \pm 0{\cdot}2$ nm, $10{\cdot}9 \pm 0{\cdot}2$ nm, $9{\cdot}4 \pm 0{\cdot}4$ nm, are associated with successive high intensity bands moving to shorter wavelengths. Correspondingly smaller shifts occur for the *p*-methoxy compound. (Diffuse fine structure does not permit comparable correlations to be drawn for the *p*-nitro compounds).

The germanium analogue of II, $BrC{\equiv}CGeEt_3$, was also coupled with $PhC{\equiv}CH$ and with $p\text{-}NO_2C_6H_4C{\equiv}CH$ to give the corresponding germyl-substituted arylbutadiynes which upon treatment with aqueous methanolic alkali gave the appropriate arylbutadiynes (III; X = H, *p*-NO_2). Since germanium-acetylene bonds may also be broken with acids[12a, 18] without hydration of the triple bond occurring (unlike their silicon counterparts) these cleavages serve as useful prototypes for the synthesis of alkali-sensitive polyynes.†

Synthesis of arylhexatriynes (IV) *from arylbutadiynes* (III)

Solutions of III in DMF, prepared as described in the Experimental, coupled cleanly with II under identical conditions to those used for couplings between I and II.

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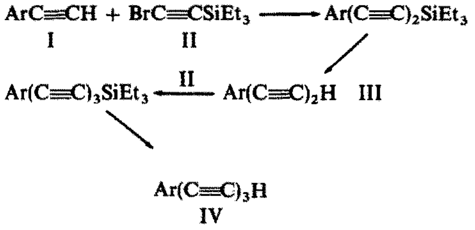
[*] In aqueous methanolic alkali at 29·4°, the relative rate of cleavage: $(PhC{\equiv}CSiEt_3/PhC{\equiv}CSiMe_3) = 277$.[11]

[†] The silicon-acetylene bond is however cleanly broken with $AgNO_3$.[19]

The liquid products could not be distilled without extensive decomposition, however, a single chromatographic purification step yielded uncontaminated $XC_6H_4(C{\equiv}C)_3SiEt_3$ compounds as stable oils which were characterized by their UV spectra (Table 2). Identical couplings between III($X = H$, p-NO_2) and $Et_3GeC{\equiv}CBr$ gave the germyl-substituted analogues, $XC_6H_4(C{\equiv}C)_3GeEt_3$. Treatment of the silyl- or germyl-triynes with aqueous methanolic alkali afforded the parent triynes (IV) in qualitative yield. As with the diynes (III), regular UV spectral shifts were associated with the cleavages as exemplified in Fig. 1. No attempt was made to isolate the products (IV) in view of the reported instability of the parent, $Ph(C{\equiv}C)_3H$.[7]

In conclusion scheme 1 summarises the essential details whereby ethynyl units may be successively added to a terminal arylacetylene in a simple two-step sequence.

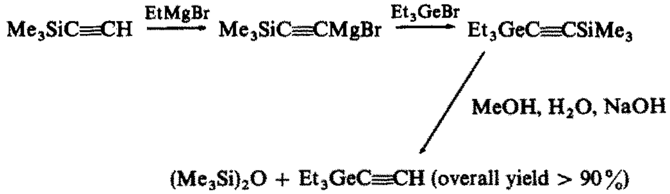


Scheme 1

Preparation of germyl-substituted aryl-butadiynes and -hexatriynes by a Grignard procedure.

In order to further characterise the free diynes and triynes, petrol solutions containing III or IV ($X = H$, m-Br, —Me; p-OMe) were treated withEtMgBr in ether and the resulting Grignard reagents, $XC_6H_4(C{\equiv}C)_nMgBr$ ($n = 2, 3$) were coupled with Et_3GeBr. The products, $XC_6H_4(C{\equiv}C)_nGeEt_3$, were not distilled but were purified by column chromatography in the manner of their silyl analogues.

A note on the preparation of $Et_3GeC{\equiv}CH$. The compound, $Et_3GeC{\equiv}CH$, has been prepared hitherto in 70% yield from a coupling between $HC{\equiv}CMgBr$ and Et_3GeBr in THF, a method which is somewhat wasteful in view of the high cost of germanium.



Scheme 2

We have adopted a procedure, using a trimethylsilyl group protectively, as outlined in scheme 2. Since the triethylgermyl group is removed from acetylene less readily than a triethylsilyl group[11] which, as already noted, is cleaved much less readily than a trimethylsilyl group, the silyl-acetylene bond in $Et_3GeC{\equiv}CSiMe_3$ can be selectively cleaved by aqueous methanolic alkali to give $Et_3GeC{\equiv}CH$ in virtually quantitative yield.

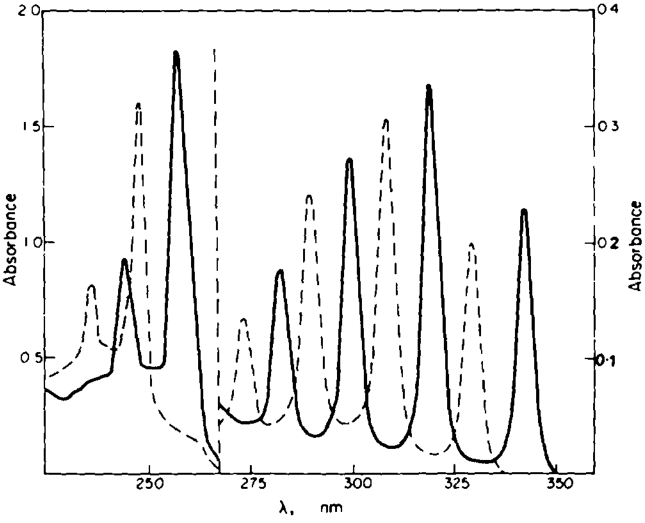


FIG 1. UV spectra of $Ph(C{\equiv}C)_3SiEt_3$(——), and $Ph(C{\equiv}C)_3H$(- - -) in MeOH solution.

TABLE 1. $XC_6H_4(C{\equiv}C)_2MR_3$ COMPOUNDS PREPARED BY CADIOT–CHODKIEWICZ COUPLINGS OF $XC_6H_4C{\equiv}CH$ WITH $YC{\equiv}CMR_3$

X	Y	MR_3	B.p.°/mm or M.p.°	n_D^{25}	Yield %	Found		Required	
						C	H	C	H
m-Br	Br	$SiEt_3$	185/0·8	1·5955	30	60·2	6·0	60·2	6·0
m-Me	Br	$SiEt_3$	156/0·7	1·5513	35	80·2	8·7	80·3	8·7
p-F	Br	$SiEt_3$	174/2·0	1·5480	60	74·3	7·6	74·3	7·4
p-NO_2[a]	Br	$SiEt_3$	89–91	—	40	67·6	6·7	67·3	6·7
p-OMe[b]	Br	$SiEt_3$	165/0·8	1·5895	30	75·2	8·3	75·5	8·2
H	Br	$GeEt_3$	152/0·5	1·5760	40	67·3	7·1	67·4	7·1
H	Br	$SiMe_3$	120/0·5	1·5672	11	78·8	7·0	78·7	7·1
H	I	$SiMe_3$	120/0·5		7				

[a] The petrol concentrate was chromatographed using ether:petrol (1:4) as eluent. Evaporation of product-rich fractions afforded pale yellow crystals of pure material.

[b] Decompostion occurred during vacuum distillation. The crude distillate was chromatographed and solvent was removed from product-rich fractions to leave analytically pure material.

TABLE 2. PRINCIPAL UV ABSORPTION MAXIMA OF $XC_6H_4(C{\equiv}C)_nMEt_3$ COMPOUNDS IN MeOH

X	n	M	λ_{nm}(log ε)						
H	2	Si	298·5 (4·45)		280·1 (4·51)		264·8 (4·32)		251·0 (3·95)
m-Br	2	Si	298·8 (4·34)		281·6 (4·51)		266·0 (4·32)		252·2 (3·95)
m-Me	2	Si	299·3 (4·42)		281·3 (4·49)		266·0 (4·30)		252·3 (3·95)
p-F	2	Si	297·4 (4·40)		280·0 (4·45)		264·9 (4·28)		251·3 (3·95)
p-NO_2	2	Si	317·5 (4·34)		265·0 (3·40)^{a}				
p-OMe	2	Si	307·0 (4·43)		289·5 (4·46)		274·0 (4·26)		260·0 (3·90)
H	2	Ge	295·9		278·2		263·5		250·0
m-Br	2	Ge	297·0		280·0		265·0		251·4
m-Me	2	Ge	297·0		279·2		264·1		250·9
p-F	2	Ge	294·0		277·6		262·5		249·5
p-NO_2	2	Ge	321·0		266^{a}				
p-OMe	2	Ge	304·5		286·5		271·5		258
H	3	Si	342·9	320·0	300·0	282·2	258·0	245·0	
m-Br	3	Si	343·2	320·7	300·6	283·0	259·0	246·0	
p-F	3	Si	342·9	320·0	300·0	282·6	258·0	245·0	
p-NO_2	3	Si	354·0	333·0	312·0	—	285·0	274·0	
p-OMe	3	Si	349·8	327·1	307·2	288·5	272·0	242·0	
H	3	Ge	329·1	308·2	289·5	273·0	248·0	237·0	
m-Br	3	Ge	330·1	309·2	290·2	274·0	—	—	
p-F	3	Ge	329·1	308·2	289·8	273·6	249·0	236·0	
p-NO_2	3	Ge	345·0	323·0	304·0	—	278·0	267·0	
p-OMe	3	Ge	337·0	316·0	297·0	—	264·0	256·0	

[a] Minimum

TABLE 3. PRINCIPAL UV ABSORPTION MAXIMA OF $XC_6H_4(C{\equiv}C)_nH$ COMPOUNDS IN MeOH

X	n	λ_{nm} (log ε)						
H^{a}	2	283·2 (4·28)		268·1 (4·36)		254·1 (4·18)		242·0 (3·78)
m-Br	2	283·6 (4·26)		269·6 (4·38)		255·2 (4·16)		242·6 (3·90)
m-Me	2	284·4 (4·23)		269·0 (4·34)		255·0 (4·18)		242·6 (3·85)
p-F	2	283·0 (4·23)		267·6 (4·34)		253·8 (4·18)		241·5 (3·95)
p-NO_2	2	307·0 (4·28)		254·0 (3·40)^{b}				
p-OMe	2	294·5 (4·32)		278·0 (4·38)		264·0 (4·18)		
H^{c}	3	329·1	308·2	289·5	273·0	248·0	237·0	
m-Br	3	330·1	309·2	290·2	274·0	—	—	
p-F	3	329·1	308·2	289·8	273·6	249·0	238·0	
p-NO_2	3	345·0	323·0	304·0	—	278·0	267·0	
p-OMe	3	337·1	316·2	297·0	—	264·0	256·0	

[a] Lit.[20] λ_{max} [Ether] nm (log ε): 283 (4·31), 268 (4·43), 254 (4·24), 242 (3·88).

[b] Minimum.

[c] Lit.[7] λ_{max} [Ether]: 328, 307, 288·5, 272, 256(sh), 248·5, 243, 237, 220.

EXPERIMENTAL

General procedures. M.ps and b.ps are uncorrected. Petrol refers to light petroleum. Du Pont Grade H alumina was used for column chromatography. UV spectral profiles were recorded on a Unicam SP800 and wavelengths and extinction coefficients of absorption maxima were checked manually on a SP500 instrument. Spectra of aryl-butadiynes (III) and -hexatriynes (IV) were obtained by adding conc NaOHaq

(2 drops) to a standard soln of the silyl-substituted aryl-butadiyne or -hexatriyne in methanol. A 5% dilution factor was involved in this technique. Solns of III or IV in petrol were obtained by direct extraction from $MeOH-H_2O$ mixtures. Solns in DMF were prepared by diluting petrol solns with DMF followed by removal of petrol under reduced pressure.

Bromoethynyl(triethyl)silane(II)

(a) Ethynyl(triethyl)silane (20 g, 0·14 mole) was added to EtMgBr (0·15 mole) in ether (400 ml). The mixture was subsequently boiled under reflux for 1 hr, then cooled and maintained at −45° whilst Br_2 (26 g, 0·16 mole) was added slowly. The mixture was than allowed to attain room temp and was poured into H_2O. Organic products were extracted with ether and the ether layer was dried (Na_2SO_4) and distilled to give II (55%) b.p. 50°/1·5 mm, n_D^{25} 1·4793 (Found: C, 43·7; H, 7·0. $C_8H_{15}BrSi$ requires: C, 43·8; H, 6·9%).

(b) A soln of $(CH_2Br)_2$ (37 g, 0·21 mole) in THF (150 ml) was added dropwise to Mg turnings (5 g) in THF (50 ml). When spontaneous refluxing ceased and all the Mg had dissolved, $PhSO_2Cl$ (35 g, 0·2 mole) was added and the mixture gently boiled under reflux for 15 min. The THF soln of $PhSO_2Br$ thus obtained was added to $Et_3SiC{\equiv}CMgBr$ (0·15 mole) prepared according to method (a). This mixture was boiled under reflux for30 min, then cooled and poured into H_2O. Working up by the same procedure, culminating in distillation, gave $Et_3SiC{\equiv}CH$ (*ca* 1 g) followed by II (60%).

Iodoethynyl(triethyl)silane

A soln of I_2 (30 g) in ether (200 ml) was added to $Et_3SiC{\equiv}CMgBr$ (0·1 mole) in ether (100 ml). The mixture was set aside at room temp for 2 hr then poured into H_2O. The organic layer was separated, dried (Na_2SO_4) and distilled to give $Et_3SiC{\equiv}CI$ (40%) b.p. 68°/1·5 mm, n_D^{20} 1·5270 (lit.[17] b.p. 117–120°/0·4 mm, n_D^{20} 1·5270).

Bromo- and iodo-ethynyl(trimethyl)silane

The procedures described by Buchert and Zeil[21] were followed. An ether soln of $Me_3SiC{\equiv}CMgBr$ (prepd from $Me_3SiC{\equiv}CH$ and EtMgBr) was treated with Br_2 (one equiv) to give $Me_3SiC{\equiv}CBr$ (49%) b.p. 55°/55 mm, n_D^{25} 1·4597 (lit.[21] b.p. 48°/50 mm, n_D^{20} 1·4612) or with I_2 (one equiv) to give $Me_3SiC{\equiv}CI$ (38%) b.p. 50°/14 mm, n_D^{25} 1·5184 (lit.[21] b.p. 53°/15 mm, n_D^{20} 1·5109). [For an improved synthesis of this compound see ref. 17].

Bromoethynyl(triethyl)germane

A soln of $Me_3SiC{\equiv}CH$[22] (19·8 g, 0·20 mole) in THF (30 ml) was added to EtMgBr (0·15 mole) in THF (100 ml). The mixture was boiled under reflux for 2 hr then Et_3GeBr (24 g, 0·1 mole) was added and the reflux was maintained for a further 3 hr. Following treatment with H_2O and drying (Na_2SO_4), the organic layer was fractionated to give the compound, $Et_3GeC{\equiv}CSiMe_3$ (95%) b.p. 98°/20 mm, n_D^{25} 1·4470 (Found: C, 51·4; H, 9·3. $C_{11}H_{24}GeSi$ requires: C, 51·4; H, 9·4%).

Aqueous 3M NaOH (50 ml) was added to a vigorously stirred soln of $Et_3GeC{\equiv}CSiMe_3$ (8·6 g, 0·03 mole) in MeOH (250 ml) thermostatted at 30°. After 4 min the mixture was neutralized with 2M HCl, organic products were extracted with petrol and the petrol extracts were dried and distilled to give $(Me_3Si)_2O$ followed by $Et_3GeC{\equiv}CH$ (93%) b.p. 75°/70 mm, n_D^{25} 1·4460 (lit.[23] b.p. 70–71°/65 mm, n_D^{20} 1·4485).

A soln of $PhSO_2Br$ (0·04 mole) in THF (40 ml) prepared as described was added to $Et_3GeC{\equiv}CMgBr$ [prepared from $Et_3GeC{\equiv}CH$ (0·035 mole) and EtMgBr (0·04 mole) in THF]. The mixture was boiled under reflux for 15 min, then cooled and poured into ice. Organic products were extracted with ether and the ether layer was separated, dried and distilled to give $Et_3GeC{\equiv}CBr$ (60%) b.p. 77°/2 mm, n_D^{25} 1·4960 (Found: C, 36·5; H, 5·7. $C_8H_{15}BrGe$ requires: C, 36·4; H, 5·7%).

Oxidative coupling procedures

(a) *1-Phenyl-4-triethylsilylbutadiyne*, $C_6H_5(C{\equiv}C)_2SiEt_3$. A soln of II (23 g, 0·105 mole) in DMF (25 ml) was added dropwise during 15 min to a rapidly stirred mixture of $PhC{\equiv}CH$ (10·2 g, 0·1 mole) $NH_2OH.HCl$ (1·0 g), CuCl (0·2 g) and $EtNH_2$ (7·5 g, 0·16 mole) in DMF (120 ml) maintained at 25°. The resulting soln was stirred for a further 30 min at room temp and any blue colouration which developed was discharged by addition of further small quantities of $NH_2OH.HCl$. The mixture, which finally turned red, was acidified with 2M HCl, organic products were extracted with petrol and the petrol extracts were dried (Na_2SO_4). Volatile products and solvent were removed by distillation at atmo pressure and the residue was fractionated to give $Ph(C{\equiv}C)_2SiEt_3$ (50%) b.p. 132°/0·55 mm, n_D^{25} 1·5785 (Found: C, 79·7; H, 8·4. $C_{16}H_{20}Si$ requires C, 79·9; H, 8·4%).

The ether extract obtained from a similar reaction (0·02 mole scale), in which $Et_3SiC{\equiv}CI$ was used in place of II, was washed with aqueous $Na_2S_2O_3$ and dried. Distillation gave a forerun [identified by g.l.p.c. comparison with an authentic sample as $Et_3Si(C{\equiv}C)_2SiEt_3$] followed by $Ph(C{\equiv}C)_2SiEt_3$ (11%) b.p. 132°/0·55 mm, n_D^{25} 1·5785.

(b) *1-Aryl-4-triethylsilylbutadiynes* $XC_6H_4(C{\equiv}C)_2SiEt_3$. Other $XC_6H_4(C{\equiv}C)_2SiEt_3$ compounds (X = *m*-Br, —Me; *p*-F, —NO_2, —OMe) were prepared on a *ca* 0·03–0·06 mole scale in a similar way, care being taken to maintain the ratio of $EtNH_2$, DMF, CuCl and reactants. Physical constants and UV data for all compounds are given in Table 1 and 2 respectively.

(c) *1-Aryl-4-triethylgermylbutadiynes*, $XC_6H_4(C{\equiv}C)_2GeEt_3$. A 5 mmole scale coupling between $PhC{\equiv}CH$ and $Et_3GeC{\equiv}CBr$ gave $Ph(C{\equiv}C)_2GeEt_3$ (*cf* Tables 1 and 2). The petroleum concentrate obtained from an analogous coupling involving $p\text{-}NO_2C_6H_4C{\equiv}CH$ was chromatographed using ether: petrol (1:4) as eluent, to yield pure solutions of $p\text{-}NO_2C_6H_4(C{\equiv}C)_2GeEt_3$ (Table 2).

(d) *1-Phenyl-4-trimethylsilylbutadiyne*, $Ph(C{\equiv}C)_2SiMe_3$. A series of couplings were carried out on a 5 mmole scale between $PhC{\equiv}CH$ and $Me_3SiC{\equiv}CBr$ in which the quantity of $EtNH_2$ used was gradually reduced from 8 to 0·1 mmole. Working up by the established procedure culminating in fractional distillation gave $PhC{\equiv}CH$ followed by the coupled product, $Ph(C{\equiv}C)_2SiMe_3$ in varying amounts (*cf* Table 1); UV λ_{max}(EtOH) nm (log ε): 298·5 (4·4), 280 (4·5), 264·8 (4·3), 251 (3·95). In reactions with low $EtNH_2$ concns, $BrC{\equiv}CSiMe_3$ was also isolated (identified by g.l.p.c. comparative retention time with authentic sample). Similar couplings in which $Me_3SiC{\equiv}CI$ was used in place of $Me_3SiC{\equiv}CBr$ also lead to recovery of $PhC{\equiv}CH$ together with traces of $Ph(C{\equiv}C)_2SiMe_3$ (Table 1, and of $Me_3Si(C{\equiv}C)_2SiMe_3$ (g.l.p.c. comparison with authentic sample).[24]

(e) *1-Aryl-6-triethylsilylhexatriynes*, $XC_6H_4(C{\equiv}C)_3SiEt_3$. A 0·046 mole scale coupling between $Ph(C{\equiv}C)_2H$ and II by the established method gave an oil, upon evaporation of dried petroleum extracts, which extensively decomposed upon attempted distillation under high vacuum. This oil was therefore purified by chromatography using petrol as eluent. UV spectral data for the pure material thus obtained, and for other 1-aryl-6-triethylsilylhexatriynes similarly prepared, are given in Table 2.

Generation of aryl-butadiynes(III) *and -hexatriynes*(IV) *from their triethylsilyl-precursors*

In a typical reaction, a soln of $Ph(C{\equiv}C)_2SiEt_3$ (0·10 g, 0·43 mmole) in MeOH (5 ml) was thermostatted at 25° and aqueous 5M NaOH (0·25 ml) was added. After 5 min the mixture was acidified with 2M HCl and organic products were extracted with petrol. The petrol extract was washed with H_2O, then dried (Na_2SO_4) and concentrated under reduced pressure. Chromatography using petrol as eluent gave initial silanol-rich fractions followed by solns of pure $Ph(C{\equiv}C)_2H$. Fractions rich in the diyne were concentrated under reduced pressure and the resulting oil was dissolved in MeOH and identified by its UV spectrum. Detailed UV spectra of this and of other $XC_6H_4(C{\equiv}C)_nH$ compounds ($n = 2$, III; $n = 3$, IV) similarly prepared are given in Table 3.

Preparation of arylbutadiynyl- and arylhexatriynyl-triethylgermanes by the Grignard Procedure.

(i) A petrol soln (10 ml) of $Ph(C{\equiv}C)_2H$ (8·0 g, 0·033 mole) was added with stirring to EtMgBr (0·05 mole) in ether (30 ml) and THF (30 ml). The mixture was boiled under reflux for 2 hr then Et_3GeBr (8·2 g, 0·033 mole) was added and refluxing was continued for a further 45 min. Treatment with H_2O followed by extraction of organic products with ether, drying of the ether extracts (Na_2SO_4) and distillation gave $Ph(C{\equiv}C)_2GeEt_3$ (53%) b.p. 152°/0·5 mm, n_D^{25} 1·5760 (Found: C, 67·3; H, 7·0. $C_{16}H_{20}Ge$ requires: C, 67·4; H, 7·1%).

Other $XC_6H_4(C{\equiv}C)_2GeEt_3$ compounds prepared in this way could not be purified by distillation and analytically pure products were obtained by chromatography using petrol as eluent followed by removal of solvent from appropriate fractions under reduced pressure. Details are as follows: X, n_D^{25}, Yield, analytical data: *p*-F, 1·5725, 60% (Found: C, 63·7; H, 6·6. $C_{16}H_{19}FGe$ requires: C, 63·4; H, 6·3%); *m*-Me, 1·5830, 70% (Found: C, 68·6; H, 7·4, $C_{17}H_{22}Ge$ requires: C, 68·4; H, 7·4%). Other $XC_6H_4(C{\equiv}C)_2GeEt_3$ compounds (X = *m*-Br, *p*-OMe) similarly prepared on *ca* 0·1 mmole scale were characterised solely by UV spectroscopy (*cf* Table 2).

(ii) A freshly eluted soln containing $Ph(C{\equiv}C)_3H$ (0·1 mmole estimated by spectroscopy) was added to EtMgBr (0·1 mmole) in ether (20 ml). The mixture was boiled under reflux for 1 hr, then Et_3GeBr (2·4 g, 0·01 mole) was added and refluxing was continued for 1 hr. Working up by the established procedure involving concn of ether extracts and chromatography to remove traces of Et_3GeOH gave petrol solutions of pure $Ph(C{\equiv}C)_3GeEt_3$. The UV spectra of this and of other $XC_6H_4(C{\equiv}C)_3GeEt_3$ compounds similarly prepared are given in Table 2.

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