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CONVENIENT SYNTHESIS OF (TRIPHENYL)GERMYL AND (TRIPHENYL)STANNYL SUBSTITUTED ALLENES

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Summary

Allenyl-germanes and -stannanes, $Ph_3MC(R)=C=CR'R''$ (M = Ge, Sn) can be obtained, generally in excellent yield, through alkylcopper(I)-induced 1,3-substitution of the propargylic chlorides $Ph_3MC{\equiv}CCR'R''Cl$. In the tin series, however transmetallation is the main process when MeCu, $H_2C=CHCu$ or PhCu are used. The allenyl compounds in which R is (trimethylsilyl)ethynyl or 4,4-dimethyl-1,2-pentadienyl can be obtained by using the organozinc compounds instead of the copper(I) compound and using tetrakis(triphenylphosphine)palladium as catalyst.

Introduction

Some time ago, we reported on an efficient synthesis of silylallenes by reaction of 2-propynylic esters of the type $R_3SiC{\equiv}CCR'R''X$ with organocopper(I) compounds [1]. An alternative approach to such silylallenes involves the conversion of $HC{\equiv}CCR'R''X$ by silylcuprate species [2]. Allenes bearing the higher Group IVa elements have received little attention thus far. For instance, reports on allenylgermanes are very rare. The compounds have been prepared by reaction of R_3GeLi with propargylic halides [3] and by reaction of allenylmagnesium halides with R_3GeCl [4], but both the regiochemistry and the chemical yield of the reactions are poor. A more promising approach is the reaction of σ-allenylsilver(I) species with R_3GeCl [5]. The synthesis of allenylstannanes following the R_3SnLi as well as the allenylmagnesium halide route suffers from the same shortcomings mentioned for the germyl case [4,6]. Much better results were obtained in our laboratory by using σ-allenyl silver(I) complexes [5] and the stannylcuprate-induced substitution of 2-propynylic esters [7].

In this paper, the organometal-mediated synthesis of both germyl- and stannyl-allenes from the propargylic chlorides $Ph_3MC{\equiv}CR'R''Cl$ (M = Ge, Sn) is reported.

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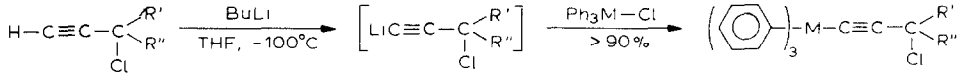
Results and discussion

Synthesis of starting materials

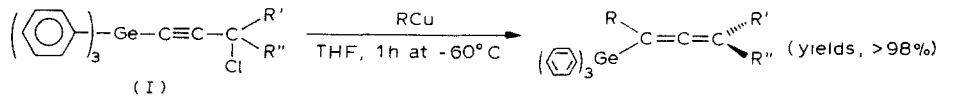
For synthesis of the desired allenes, appropriately substituted propargylic substrates were required. In view of the well known ability of propargylic halides to undergo organocopper(I)-induced S_N2' reactions, it was decided to attempt the preparation of 1-alkynyl-germanes and -stannanes with chlorine in the 3-position. It emerged that these compounds can be readily made in over 90% yields by lithiating propargylic chlorides at $-100\,°C$ in tetrahydrofuran (THF) and then adding Ph_3MCl (M = Ge or Sn). With these compounds available, the second part of the study could be carried out.



SCHEME 1

Preparation of germylallenes using RCu reagents

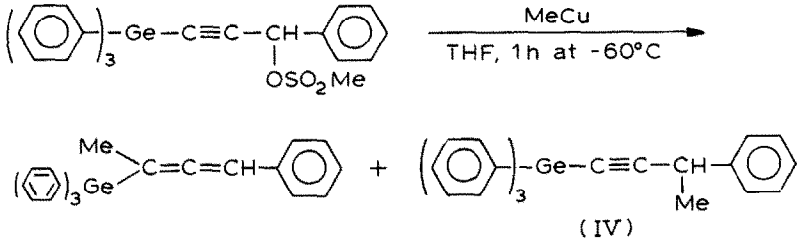
We first prepared RCu reagents by stirring the Grignard compounds RMgCl with an equimolar amount of the THF soluble complex $LiCuBr_2$ for 15 min at $0\,°C$ (R = Me) or at $-60\,°C$ (the other alkyl groups). To the resulting organocopper(I) species was added compound I (1.0 mole equivalent), and the mixture was stirred during 1 h at $-60\,°C$. This procedure worked very well. Thus in all the cases studied (see Scheme 2) nearly quantitative yields of the desired germylallenes III were obtained. In none of the experiments did we detect transmetallation products, indicating that the S_N2' reaction is much faster than attack by R on Ge. The regioselectivity of the reaction is excellent, even when the group R in the RCu reagent is bulky, e.g. t-Bu, and the substituents R' and R'' are both small, e.g. H. A similar preference for a S_N2' instead of a S_N2-type reaction has been observed in our laboratory in the synthesis of 1,1-di-t-butylpropadiene from a 2-propynylic precursor [8].



SCHEME 2

We also attempted the preparation of the chloride $Ph_3GeC{\equiv}CCH(Cl)Ph$, but without success. It was therefore decided to prepare the mesylate instead of the chloride, as 2-propynylic mesylates are generally useful precursors for allenes. Its

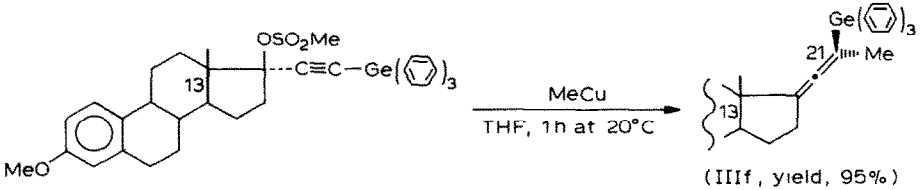
preparation was accomplished by reaction of (triphenylgermyl)ethynyllithium with benzaldehyde and conversion of the resulting alcohol following standard procedures into the mesylate. Treatment of the resulting mesylate with MeCu gave a ca. 95% yield of a mixture of the desired allene and the S_N2-product IV in the ratio 85/15 (Scheme 3).



SCHEME 3

It is conceivable that the lower regioselectivity in this case is due to the mesylate group. However, the reaction given in Scheme 4 proceeds regiospecifically, so that it is more likely to assume that the S_N2 product in Scheme 3 is the result of the high reactivity of the benzylic center in the starting compound.

Scheme 4 shows that the S_N2' reaction in the steroid proceeds in an *anti* fashion.

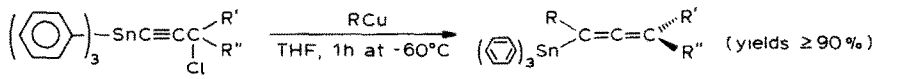


SCHEME 4

This stereochemical outcome is deduced from the $\delta(^{13}CH_3)$-value in the ^1H NMR spectrum, which amounts to 0.24 ppm. This high-field shift is caused by the strong shielding effect exerted by the (triphenyl)germyl group. It agrees well with $\delta(^{13}CH_3)$-values for related silicon [9] and tin [7] substituted allenes.

Preparation of stannylallenes using RCu reagents

For preparation of the stannylallenes, the procedure described for the germylallenes was used. Except for MeCu, when alkylcopper(I) reagents were used, the results were quite similar to those obtained for the germylallenes (Scheme 5). The



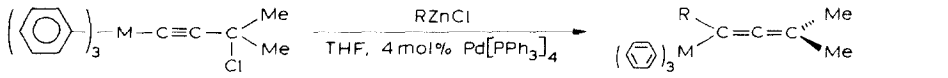
(Va R = Et, R',R'' = H,H, Vb R = Pr, R',R'' = H,H, Vc R = i-Pr, R',R'' = H,H, Vd. R = Bu, R',R'' = H,H, Ve R = t-Bu, R',R'' = H,H, Vf R = Et, R',R'' = Me,H, Vg R = t-Bu, R',R'' = Me,H, Vh R = t-Bu, R', R'' = Me,Me)

SCHEME 5

yields of the allenes, V, were generally excellent ($\geqslant 90\%$) and either none or only small amounts of compounds due to transmetallation were observed. We were initially very sceptical about the feasibility of this approach to stannylallenes, as we knew from other work that 1-alkynyltriphenylstannanes are very easily transmetallated by RCu species to give copper(I) alkynylides and Ph_3SnR [9]. Attack of RCu on germane in 1-alkynyltriphenylgermanes is much slower, and with silicon we have never observed it. This parallels literature data on the transmetallation of $R_3MC{\equiv}C$ by alkyllithiums [10]. In our case, the S_N2' reaction is apparently so fast that the competing attack on tin in II is completely excluded. However, the choice of R is crucial. Thus, transmetallation of II was the main process ($> 95\%$) when R was methyl, vinyl and phenyl. There is thus a subtle balance between the S_N2'-reaction and transmetallation of II on treatment with organocopper(I) reagents.

Conversion of I and II by RZnCl, using $Pd[PPh_3]_4$ as the catalyst

The $Pd[PPh_3]_4$-promoted substitution of 2-propynylic halides and esters by organozinc compounds was recently reported [11]. The reaction gives allenes of high purity in high yield. We wondered whether this approach would also be suitable for synthesis of germyl- and stannyl-allenes bearing an unsaturated substituent in the α-position, since the method was especially suitable for introduction of unsaturated substituents [11]. The results of this study are shown in Scheme 6. Treatment of I and II (R′,R″ = Me,Me) with (trimethylsilyl)ethynylzinc chloride in THF at 40 °C, with 4 mol% of $Ph[PPh_3]_4$ as catalyst, furnished the desired allenes IIIh and Vi in about 98% yield. Similarly the conjugated diallene Vj was obtained in 70% yield by reaction of stannyl compound II with 4,4-dimethyl-1,2-pentadienylzinc chloride at 40 °C in THF. The zinc compound is readily prepared from 4,4-dimethyl-1,2-pentadiene by lithiation with n-butyllithium followed by addition of zinc chloride.



(I, II)

(IIIh M = Ge, R = $Me_3SiC{\equiv}C$,
Vi M = Sn, R = $Me_3SiC{\equiv}C$,
Vj M = Sn, R = t-BuCH=C=CH–)

SCHEME 6

The organozinc/$Pd[PPh_3]_4$ method thus seems to be very effective for preparation of germyl- and stannyl-allenes (and no doubt, also silylallenes) with unsaturated groups R. The chemistry of these interesting allenes will be explored.

Experimental

All operations with organometallic reagents were carried out under dry nitrogen. The products were analyzed by NMR (Varian EM-390 and CFT-20 spectrometers) and IR spectroscopy.

1. General procedure for the preparation of I and II

The propargylic chlorides I and II are prepared by adding cautiously, n-butyllithium (0.010 mol, 1.5 *M* solution in n-hexane) at −100 °C to a stirred solution of

the propargylic chloride (0.010 mol) in THF (25 ml), followed, after 10 min, by Ph_3MCl (0.010 mol; M = Ge or Sn). The mixture is stirred during 0.5 h at −60 °C and then allowed to warm to room temperature. The mixture is poured into saturated aqueous ammonium chloride (150 ml) and the product is extracted with ether/pentane (v/v 50/50, 3 × 50 ml). The combined extracts are washed with water (3 × 50 ml) and dried with $MgSO_4$. The solvent is evaporated in vacuo and the residue used without further purification (yields ⩾ 90%).

2. General procedure for the preparation of RCu

To a stirred suspension of CuBr (0.010 mol) in THF (25 ml) a solution of dry lithium bromide (0.010 mol) in THF (5 ml) is added at 20 °C. The homogeneous solution is cooled to 0 °C (R = Me, Ph) or −60 °C (R = alkyl, H_2C=CH) and a solution of RMgX (0.010 mol; X = Cl: R = alkyl: X = Br: R = H_2C=CH and Ph) in THF (10–15 ml) is added dropwise. The mixture is then stirred for 15 min at 0 and −60 °C, respectively, and used directly.

3. Preparation of RZnCl

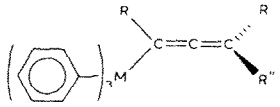
The organozinc chlorides RZnCl are prepared by adding, n-butyllithium (0.010 mol, 1.5 *M* solution in n-hexane at −60 °C to a stirred solution of (trimethylsilyl)acetylene (0.010 mol) or t-butylallene (0.010 mol) in THF (25 ml), followed, after 10 min for R = $Me_3SiC{\equiv}C$ and 1 h for R = t-BuCH=C=CH, by a solution of $ZnCl_2$ (0.010 mol) in THF (10 ml). The mixture is then stirred for an additional period of 15 min at −20 °C and then used as such.

4. General procedure for the preparation of allenes III and V using RCu reagents

(a). The allenes III and V are prepared by adding the propargylic halide I or II (0.010 mol) at −60°C to the RCu compound (0.010 mol, see under *2*). The mixture is stirred for 1 h at −60°C then poured into saturated aqueous ammonium chloride (200 ml) containing NaCN (1 g). The product is extracted with ether/pentane (v/v 50/50, 3 × 50 ml). The combined extracts are washed with water (3 × 150 ml) and dried with $MgSO_4$. The solvent is stripped off in vacuo and the residue crystallized from methanol or purified by column chromatography (neutral Al_2O_3 containing 5% water, n-hexane as the eluent).

(b). Allene IIIf is obtained by a modified procedure. To a solution of $Ph_3GeC{\equiv}CLi$ (0.005 mol) in THF (20 ml) (obtained by adding cautiously a 1.5 *M* solution of n-butyllithium (0.005 mol) in hexane at −60°C to $Ph_3GeC{\equiv}CH$ (0.005 mol) in THF (25 ml) followed by stirring the mixture for 30 min at −30°C) oestron methyl ether (0.005 mol) is added at −30°C. The mixture is then stirred for 50 h at 20°C. The alcohol is isolated by pouring the mixture into saturated aqueous NH_4Cl (200 ml) and extracting with CH_2Cl_2 (3 × 50 ml). Washing the combined extracts with water and drying with $MgSO_4$ followed by evaporation of the solvent, gives the required alcohol in quantitative yield. Without further purification the alcohol (0.005 mol) is then dissolved in THF (20 ml) containing LiBr (0.01 mol). n-Butyllithium (0.005 mol; 1.5 *M* solution in n-hexane) is carefully added at −60°C and the mixture stirred for 30 min at this temperature. Subsequently methanesulfonyl chloride (0.005 mol) is added all at once, and the mixture is stirred for 30 min at −60°C. The solution is then added to MeCu (0.01 mol; prepared as indicated under *2* in THF (20 ml)), and the mixture is stirred for 2 h at 0°C. Work-up is carried out in the usual way.

Physical constants and characteristic spectroscopic data for allenes III and V obtained in this manner are listed below (purity $\geqslant 95\%$, unless otherwise stated; yields $\geqslant 90\%$).



(III M = Ge, V M = Sn)

Compound IIIa: R = Et, R',R'' = H,H. M.p. 91–92°C. IR (NaCl): 1931 (C=C=C) cm^{-1}. ^1H NMR (CCl_4, TMS): δ 7.10–7.60 (m, 15H, aromatic protons), 4.40 (t, 2H, $=CH_2$), 2.07 (tq, 2H, CH_2–CH_3), 1.01 (t, 3H, CH_2–CH_3) ppm.

Compound IIIb: R = i-Pr, R',R'' = H,H. M.p. 75–76°C. IR (NaCl): 1930 (C=C=C) cm^{-1}. ^1H NMR (CCl_4, TMS): δ 7.20–7.60 (m, 15H, aromatic protons), 4.42 (d, 2H, $=CH_2$), 2.22 (m, 1H, $CHMe_2$), 0.99 (d, 6H, $C(CH_3)_2$) ppm.

Compound IIIc: R = t-Bu, R',R'' = Me,H. M.p. 93–94°C. IR (NaCl): 1929 (C=C=C) cm^{-1}. ^1H NMR (CCl_4, TMS): δ 7.10–7.70 (m, 15H, aromatic protons), 4.68 (q, 1H, =C=CH), 1.40 (d, 3H, =C–CH_3), 1.00 (s, 9H, $C(CH_3)_3$) ppm.

Compound IIId: R = Et, R',R'' = Me,Me. M.p. 74–75°C. IR (NaCl): 1938 (C=C=C) cm^{-1}. ^1H NMR (CCl_4, TMS): δ 7.15–7.65 (m, 15H, aromatic protons), 2.06 (q, 2H, CH_2CH_3), 1.53 (s, 6H, $=C(CH_3)_2$), 0.98 (t, 3H, CH_2CH_3) ppm.

Compound IIIe: R = t-Bu, R',R'' = Me,Me. M.p. 92–93°C. IR(NaCl): 1933 (C=C=C) cm^{-1}. ^1H NMR (CCl_4, TMS): δ 7.10–7.65 (m, 15H, aromatic protons), 1.40 (s, 6H, $=C(CH_3)_2$), 1.00 (s, 9H, $C(CH_3)_3$) ppm.

Compound IIIf: R = Me, R',R'' = steroid skeleton. M.p. 85–86°C. ^1H NMR (CCl_4, TMS): δ 7.20–7.60 (m, 15H, aromatic protons belonging to the (triphenyl)germyl group), 7.05 (d, 1H, A-ring proton), 6.40–6.62 (m, 2H, A-ring protons), 3.68 (s, 3H, OCH_3), 1.87 (s, 3H, 21-Me), 1.0–2.9 (m, 15H, B/C/D-ring protons), 0.24 (s, 3H, 13-Me) ppm. $[\alpha]_D^{20} + 113.0°$ (CH_2Cl_2).

Compound Va: R = Et, R'R'' = H,H. M.p. 75–76°C. IR (NaCl): 1930 (C=C=C) cm^{-1}. ^1H NMR (CCl_4, TMS): δ 7.10–7.65 (m, 15H, aromatic protons), 4.35 (t, 2H, $=CH_2$), 2.26 (tq, 2H, CH_2), 1.10 (t, 3H, CH_3) ppm. ^{13}C NMR ($CDCl_3$, TMS): δ 206.7 (=C=) ppm.

Compound Vb: R = n-Pr, R',R'' = H,H. n_D^{20} 1.6193. IR (NaCl): 1930 (C=C=C) cm^{-1}. ^1H NMR (CCl_4, TMS): δ 7.20–7.65 (m, 15H, aromatic protons), 4.30 (t, 2H, $=CH_2$), 2.18 (m, 2H, CH_2–C=), 1.35–1.80 (m, 2H, CH_2), 0.86 (t, 3H, CH_3) ppm. ^{13}C NMR ($CDCl_3$, TMS): δ 207.0 (=C=) ppm. The compound probably contained some Ph_3Sn-n-C_3H_7 ($\simeq 10\%$).

Compound Vc: R = i-Pr, R',R'' = H,H. M.p. 56–57°C. IR (NaCl): 1930 (C=C=C) cm^{-1}. ^1H NMR (CCl_4, TMS): δ 7.10–7.65 (m, 15H, aromatic protons), 4.33 (d, 2H, $=CH_2$), 2.41 (m, 1H, $CHMe_2$), 1.07 (d, 6H, $(CH_3)_2C$) ppm. ^{13}C NMR ($CDCl_3$, TMS): δ 205.7 (=C=) ppm.

Compound Vd: R = n-Bu, R',R'' = H,H. n_D^{20} 1.6119. IR (NaCl): 1925 (C=C=C) cm^{-1}. ^1H NMR (CCl_4, TMS): δ 7.10–7.60 (m, 15H, aromatic protons), 4.29 (t, 2H, $=CH_2$), 2.19 (m, 2H, CH_2–C=), 1.10–1.70 (m, 4H, $2 \times CH_2$), 0.78 (t, 3H, CH_3) ppm. ^{13}C NMR ($CDCl_3$, TMS): δ 207.0 (=C=) ppm. The compound probably contained some Ph_3Sn-n-C_4H_9 ($\simeq 10\%$).

Compound Ve: R = t-Bu, R',R'' = H,H. M.p. 82–83°C. IR (NaCl): 1920 (C=C=C) cm^{-1}. ^1H NMR (CCl_4, TMS): δ 7.10–7.70 (m, 15H, aromatic protons), 4.30 (s, 2H, $=CH_2$), 1.10 (s, 9H, t-Bu) ppm. ^{13}C NMR ($CDCl_3$, TMS): δ 204.9 (=C=) ppm.

Compound Vf: R = Et, R',R'' = Me,H. M.p. 58–59°C. IR (NaCl): 1940 (C=C=C) cm^{-1}. ^1H NMR (CCl_4, TMS): δ 7.20–7.70 (m, 15H, aromatic protons), 4.73 (qt, 1H, =CH), 2.22 (dq, 2H, CH_2–C=), 1.55 (d, 3H, CH_3C=), 1.03 (t, 3H, CH_3) ppm. ^{13}C NMR ($CDCl_3$, TMS): δ 205.4 (=C=) ppm.

Compound Vg: R = t-Bu, R',R'' = Me,H. M.p. 96–97°C. IR (NaCl): 1930 (C=C=C) cm^{-1}. ^1H NMR ($CDCl_3$, TMS): δ 7.15–7.70 (m, 15H, aromatic protons), 4.70 (q, 1H, =CH), 1.48 (d, 3H, CH_3–C=), 1.07 (s, 9H, t-Bu) ppm. ^{13}C NMR ($CDCl_3$, TMS): δ 203.4 (=C=) ppm.

Compound Vh: R = t-Bu, R',R'' = Me,Me. M.p. 78–79°C. IR (NaCl): 1940 (C=C=C) cm^{-1}. ^1H NMR (CCl_4 TMS): δ 7.15–7.65 (m, 15H, aromatic protons), 1.50 (s, 6H, $=C(CH_3)_2$), 1.07 (s, 9H, t-Bu) ppm. ^{13}C NMR ($CDCl_3$ TMS): δ 202.1 (=C=) ppm.

5. General procedure for the preparation of allenes III and V using RZnCl reagents

A solution of $Pd(PPh_3)_4$ in THF (0.0004 mol, as a 0.02 *M* solution) is added to a stirred solution of RZnCl (0.010 mol) in THF (35 ml) at −20°C followed by halide I or II (0.010 mol). The mixture is stirred for 2 h at 40°C then poured into a saturated aqueous NH_4Cl (200 ml). The product is extracted with pentane (3 × 50 ml) isolated, and purified as described under **4.** (Yields: 98% in case of IIIh, 98% in case of Vi; and 70% in case of Vj; purity ⩾ 95%).

Physical constants and characteristic spectroscopic data for allenes III, and V are the following.

Compound IIIh: R = $Me_3SiC{\equiv}C$, R',R'' = Me,Me. M.p. 96–97°C. IR (NaCl): 2135 (C≡C), 1938 (C=C=C) cm^{-1}. ^1H NMR (CCl_4, TMS): δ 7.25–7.68 (m, 15H, aromatic protons), 1.47 (s, 6H, $(CH_3)_2C$=) −0.03 (s, 9H, $(CH_3)_3Si$) ppm. ^{13}C NMR ($CDCl_3$, TMS): δ 212.7 (=C=) ppm.

Compound Vi: R = $Me_3SiC{\equiv}C$, R',R'' = Me, Me. n_D^{20} 1.6062. IR (NaCl): 2128 (C≡C), 1925 (C=C=C) cm^{-1}. ^1H NMR (CCl_4, TMS): δ 7.20–7.80 (m, 15H, aromatic protons), 1.53 (s, 6H, $(CH_3)_2C$=), 0.10 (s, 9H, $(CH_3)_3Si$) ppm. ^{13}C NMR ($CDCl_3$, TMS): δ 211.8 (=C=) ppm.

Compound Vj: R = t-BuCH=C=CH, R'R'' = Me,Me. M.p. 103–104°C. IR (NaCl): 1944 (C=C=C) cm^{-1}. ^1H NMR (CCl_4, TMS): δ 7.20–7.70 (m, 15H, aromatic protons), 5.99 (d, 1H, =CH), 4.86 (d, 1H, =CH), 1.53 (s, 3H, CH_3-C=), 1.42 (s, 3H, CH_3–C=), 0.66 (s, 9H, t-Bu) ppm. ^{13}C NMR ($CDCl_3$, TMS): δ 207.3 and 203.5 (2 × =C=) ppm.

Acknowledgement

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