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METALATION REACTIONS
II. PREPARATION OF BIS(TRIMETHYLSILYL)ALLENES FROM ENYNES

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SUMMARY

Dimetalation of 1,4-enynes was carried out with butyllithium in ether at low temperatures. Treatment of the metalated enynes with trimethylsilyl chloride yielded in all cases 1,3-bis(trimethylsilyl)allenes conjugated to a double bond. In one case a bis(trimethylsilyl)-1,3-enyne with one trimethylsilyl group in a vinylic and the other in an allylic position was obtained as an additional product.

Enynes not having aryl substituents gave, after short metalation periods and subsequent silylation, a mixture of monosilyl products in addition to the disilyl derivatives.

RESULTS AND DISCUSSION

Acetylenes undergo metalation and polymetalation by butyllithium at the propargylic position[1,2,3,4]. This can be ascribed to the electron-withdrawing effect[5] of the ethynyl group and to the stabilization of the anion formed[6]. In this work we studied the metalation of 1,4-enynes and the reaction of the anions produced with trimethylsilyl chloride. The starting enynes[7] undergo metalation by butyllithium in ether even at temperatures as low as −100°. This rate enhancement of metalation relative to simple acetylenes is certainly due to the effect of the additional double bond on the propargylic carbon atom. The anion formed from 1-phenyl-4-penten-1-yne (Ia) was treated with trimethylsilyl chloride and the product was distilled and separated by GLC into two components (IIa) and (IIIa) in a ratio of 2/1. The structure assignment (IIa) is supported by the infrared spectrum, which shows an allenic band at 1880 cm^{-1} and two bands characteristic of trimethylsilyl group at 840 and 1245 cm^{-1}. The ultraviolet spectrum with a maximum at 246 mμ and the chemical shifts of the protons of the phenyl group at τ 2.89, vinyl protons $CH{=}CH_2$ at τ 3.84, 4.92 and

$$RC{\equiv}C{-}CH_2{-}CR'{=}CHR'' \quad (I)$$

a: $R=C_6H_5$; $R'=R''=H$
b: $R=C_6H_5$; $R'=CH_3$; $R''=H$
c: $R=C_6H_5$; $R'=H$; $R''=CH_3$
d: $R'=H$; $R=R''=C_6H_5$
e: $R=R'=C_6H_5$; $R''=H$
f: $R=(CH_3)_3C$; $R'=CH_3$; $R''=H$
g: $R=CH_3(CH_2)_5$; $R'=CH_3$; $R''=H$

TABLE 1

SPECTRAL DATA OF DISILYL DERIVATIVES (II) AND (III)

No.	Chemical shifts of protons, τ[a]								Coupling constants J (Hz)	UV λ_{max} (mμ) (ε_{max})	IR ν_{max} (cm^{-1})
	A	B	C	R′		D		R″			
(IIa)	2.89 (m)	9.84(s)	9.85(s)	3.84(q)		5.11 (d)		4.92(d)	$J_{R''D}$ 2, $J_{R'R''}$ 16, $J_{R'D}$ 10	246 (20,000)	1880, 1590, 1245, 840
(IIb)	2.84 (m)	9.78(s)	9.81 (s)	8.14			5.27[b]			246 (28,500)	1880, 1590, 1245, 830–845
(IIc)	2.77 (m)	9.82(s)	9.86(s)	4.12(d)[c]		4.34(q)		8.24(d)	$J_{DR''}$ 4.9, $J_{DR'}$ 15.3	247 (28,000)	1880, 1250, 845
(IId)	2.82 (m)	9.86(s)	9.86(s)		3.46(s)[b]			2.82(m)		290 (28,000)	1880–1888, 1250, 830–855
(IIe)	2.78 (m)	9.78(s)	9.85(s)	2.78(m)			4.98[b]				1880, 1240, 838
(IIg)	7.92–8.20(m)[d]	9.87(s)	9.94(s)	8.22(s)			5.22–5.34			233 (6,410)	1890, 1250, 840
(IIIa)	2.76(m)	9.83(s)	9.94(s)	3.83(t)		7.99(d)			$J_{R'D}$ 8	219 (18,900) 286 (17,800)	2180, 1245, 840
(IIIf)[e]	8.7[illegible] (s) 8.[illegible]8(s)	9.84(s)	9.93(s)		8.17 7.99					255 (9,850)	2190, 2200, 1245, 830–855

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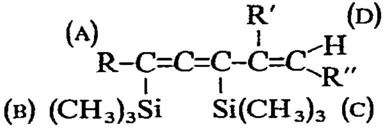
[a] s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet. [b] This is the position of the internal line of the AB doublet. The other line is not apparent in view of the small $\Delta\nu$ between the two vinylic protons. [c] Chemical shifts based on simple AB analysis of the quartet. [d] Chemical shift of the $-CH_2-C=C=$ protons. [e] We have here two isomers, *cis* and *trans*.

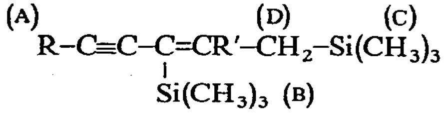
5.11 (one proton each) with coupling constants of 16, 10 and 2 cps and two singlets (each of 9 protons) at τ 9.84 and 9.85 for two trimethylsilyl groups confirm structure (IIa). The structure (IIIa) for the second product was assigned on the strength of the ultraviolet spectrum, which shows a maximum at 289 mμ due to conjugation of the phenyl group with two multiple bonds, and an acetylenic band in the infrared at 2180 cm^{-1}. The NMR spectrum, showing phenyl protons at τ 2.76, one olefinic proton at τ 3.83, two allylic protons at τ 7.99 with a coupling constant of 8 Hz and two singlets of nine protons each of trimethylsilyl groups at τ 9.83 and 9.94, supported this assignment.



$\mathrm{R{-}C(Si(CH_3)_3){=}C{=}C(Si(CH_3)_3){-}C(R'){=}C(H)R''}$

(II)

a: R $=C_6H_5$; R'=R''=H
b: R $=C_6H_5$; R'$=CH_3$; R''=H
c: R $=C_6H_5$; R'=H; R''$=CH_3$
d: R'=H; R=R''$=C_6H_5$
e: R =R'$=C_6H_5$; R''=H
g: R $=CH_3(CH_2)_5$; R'$=CH_3$; R''=H



$\mathrm{R{-}C{\equiv}C{-}C(Si(CH_3)_3){=}CR'{-}CH_2{-}Si(CH_3)_3}$

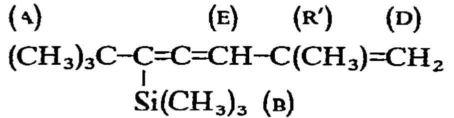
(III)

a: R$=C_6H_5$; R'=H
f: R$=(CH_3)_3C$; R'$=CH_3$

Metalation of 1-phenyl-4-methyl-4-penten-1-yne (Ib) and treatment of the metalation product with trimethylsilyl chloride yielded an allene (IIb), which was characterized by its ultraviolet, infrared and NMR spectra (Table 1).

Similar metalation–silylation reactions were carried out with 1-phenyl-4-hexen-1-yne (Ic), 1,5-diphenyl-4-penten-1-yne (Id) and 1,4-diphenyl-4-penten-1-yne (Ic). The bis(trimethylsilyl)allenes (IIc), (IId) and (IIe) were obtained, as shown by their analysis (Table 5) and spectra (Table 1).

The presence of a phenyl group in (I) is not necessary for metalation. Thus 2,6,6-trimethyl-1-hepten-4-yne (If) was metalated more slowly than (Ia)–(Ie) and gave, on treatment with trimethylsilyl chloride, a mixture of five products. The three main components of the mixture, 1, 2 and 3 (in the order of increasing retention times in GLC), were in a ratio 15/35/50. Components 1 and 2 were monosilanes (elemental analysis and NMR). The infrared spectrum of component 1 showed the presence of an allenic group and NMR revealed one vinyl proton at τ 4.99, two protons of a $=CH_2$ group at τ 5.15, an allylic methyl at τ 8.19, $(CH_3)_3C$ at τ 8.32 and $(CH_3)_3Si$ at τ 9.82. Structure (IV) was therefore assigned to component 1. Formula (V) was attributed to component 2, since it, too, contained one vinyl proton, an allylic methyl



$\mathrm{(CH_3)_3C{-}C(Si(CH_3)_3){=}C{=}CH{-}C(CH_3){=}CH_2}$

(IV)

(A) (E) (R') (D) (B)
$\mathrm{(CH_3)_3C{-}C{\equiv}C{-}CH{=}C(CH_3){-}CH_2{-}Si(CH_3)_3}$

(V)

TABLE 2

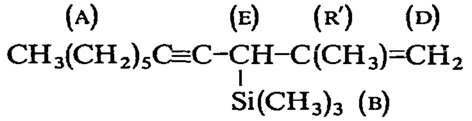
SPECTRAL DATA OF THE MONOSILYL DERIVATIVES

No.	Chemical shifts of protons, τ[a]					IR ν_{max} (cm^{-1})
	A	B	E	R′	D	
(IV)	8.92 (s)	9.82 (s)	4.99	8.19 (s)	5.15[b]	1930, 1247, 840
(V)[c]	8.79 (s)	9.96 (s)	4.96	8.23–8.30 (m)		2200, 1248, 840–875
(VI)	7.74 (m)[d]	9.91 (s)	8.24		5.01[b]	2205, 1249, 842–872
(VII)	7.72 (m)	9.93 (s)	5.07	8.2	8.44[e]	2205, 2160, 1249, 845–860

[a] s, singlet; m, multiplet. [b] This is the position of the internal line of the AB doublet. The other line is not apparent in view of the small $\Delta\nu$ between the two vinylic protons. [c] λ_{max} in UV at 240 mμ (ε_{max} 23,000). [d] Chemical shift of the $-CH_2-C{=}C$ protons. [e] Together with the $(CH_2)_4$ multiplet.

and methylene group (Table 2). Component 3 was shown by NMR to be a mixture of the *cis* and *trans* isomers of (IIIf). This spectrum consisted of three pairs of singlets. The signals in each pair had the same ratio (by integration). The NMR spectra of each isomer showed $(CH_3)_3C$, $(CH_3)_3Si$ and a five-proton signal for $=C-CH_3$ and $=C-CH_2-Si\lessgtr$ groups. These signals were at τ 8.76, 9.84 and 8.17 for one isomer and at τ 8.88, 9.93 and 7.99 for the other.

A similar reaction occurred with 2-methyl-1-undecene-4-yne (Ig). Long metalation times and subsequent treatment with trimethylsilyl chloride gave in good yield a product that consisted almost exclusively of the bis(trimethylsilyl)allene (IIg), a structure supported by its analysis and spectral properties (Table 1). Shorter reaction periods gave a mixture of five components 4, 5, 6, 7 and 8, in a ratio of 8/32/30/11/9 as found by GLC. The structure of these components was studied only partially. Preparative GLC yielded four fractions, the first one containing components 4 and 5. Component 5 was shown to be (IIg). The second fraction consisted of the component 6 and exhibited in the NMR spectrum one trimethylsilyl group at τ 9.91, two vinylic protons at τ 5.01 and four allylic protons at τ 8.25 attributed to $=C-CH_3$ and $=C-Si\lessgtr$. All these data supported the structure (VI) for component 6. The third fraction contained component 7 as the only one. Structure (VII) was assigned to component 7 on the force of its NMR spectrum, showing one trimethylsilyl group at τ 9.93, an allylic methyl group at τ 8.2, one vinylic proton at τ 5.07 a $CH_2-C\equiv$ at τ 7.72, a terminal methyl at τ 9.09 and all the remaining protons between τ 8.35 and 8.94. The fourth fraction contained component 8, which appeared to be a bis(trimethylsilyl) derivative (by NMR).



$$\overset{(A)}{CH_3(CH_2)_5}C{\equiv}C-\underset{\displaystyle Si(CH_3)_3\ (B)}{\overset{(E)}{CH}}-\overset{(R')}{C(CH_3)}{=}\overset{(D)}{CH_2}$$

(VI)

$$\overset{(A)}{CH_3(CH_2)_5}C{\equiv}C-\overset{(E)}{CH}{=}\overset{(R')}{C(CH_3)}-\overset{(D)}{CH_2}-Si(CH_3)_3\ (B)$$

(VII)

These results prove that: (*a*) dimetalation occurred in compounds lacking a phenyl group and that (*b*) a proton was abstracted exclusively from the central carbon of the monoanion $\equiv C{-}\bar{C}H{-}C{<}$. This occurs although an additional propargylic methylene group is present in the molecule, and in spite of the charge on the carbon from which this proton is abstracted. The selective abstraction of the second proton can be attributed to the special stability of the system (X). A reaction path is conceivable involving, in a consecutive series, a monolithium derivative of (I), a monosilyl-monolithium compound and finally the disilyl derivative. All these reactions would have to occur in the mixture of (I), butyllithium and trimethylsilyl chloride. Transmetalations were observed after the addition of water to triphenylmethyllithium in DMSO[8].

The metalation of (Ib) was therefore studied by NMR (Fig. 1) and (Table 3).

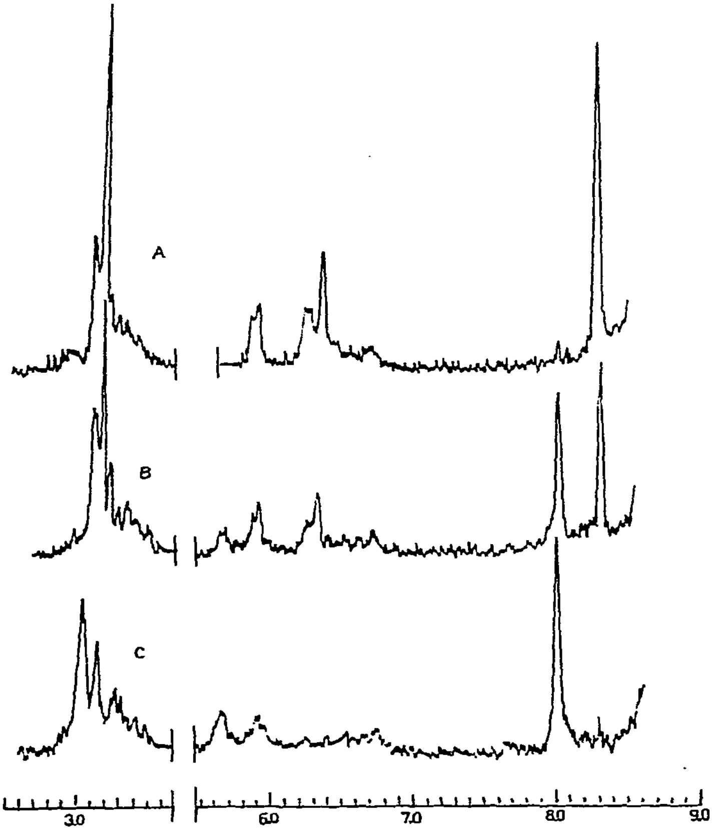
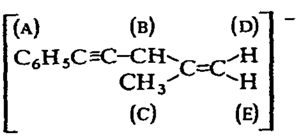
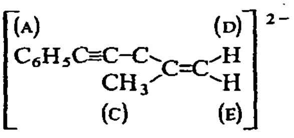


Fig. 1. NMR spectrum of a solution formed by addition at −90° of 100 mg (Ib) to 1 ml of 3.0 *M* butyllithium in deuterated ether. The spectrum was recorded at 38°. A: 3 min after the addition of (Ib) [monoanion (VIII)]; B: 30 min after the addition of (Ib); C: 120 min after the addition of (Ib) [dianion (IX)].



(VIII)



(IX)

$[R{-}C{\equiv}C{\equiv}C{-}R']^{2-}$

(X)

TABLE 3

NMR DATA OF (Ib) AND ITS METALATION PRODUCTS (VIII) AND (IX)

No.	Chemical shifts of protons, τ[a]					Coupling constants (Hz)
	A[b]	B	C	D	E	
(Ib)	2.63 (m)	6.88 (s)	8.15 (s)	5.11 (d)	4.89 (d)	J_{DE} 3
(VIII)	3.12 (m)	6.37 (s)	8.30 (s)	6.26[c]	5.89 (d)	J_{DE} 3
(IX)	3.07–3.18 (m)		7.99 (s)	5.89[c]	5.60[c]	

[a] s, singlet; d, doublet; m, multiplet. [b] Position of the main peak. [c] Broad peak.

A proton was abstracted very rapidly from (Ib) by butyllithium in ether and the first spectrum recorded was that of the monoanion (VIII) (upper trace). This spectrum still showed two vinylic protons, proving that none of them was abstracted by butyllithium. The chemical shift of these protons is upfield to that of (Ib), showing that the formed negative charge is delocalized onto the carbon to which they are attached. However, the change in the chemical shift of these vinylic protons on the transformation of (Ib) to (VIII) is less than in other similar anions, *e.g.* pentadienyllithium[9] or phenylallylsodium[10] derivatives, indicating a weaker charge delocalization in systems containing a triple bond. Proton (B) is shifted to lower field on the formation of (VIII), due to a change of hybridization of the carbon to which it is linked.

The monoanion (VIII) reacted with excess butyllithium. A second proton was abstracted from (Ib), (VIII) was converted first partly (centre trace) and then totally to the dianion (IX) (lower trace of Fig. 1). Two terminal vinyl protons are present in this dianion, as revealed by their chemical shifts and the same coupling between these protons in the starting material (Ib) the monoanion (VIII) and the dianion (IX). The second proton was therefore abstracted from the same carbon as the first one. The downfield shift of the vinylic protons on the transformation of (VIII) to (IX) is unusual. It was expected that the introduction of a second negative charge in the same system would cause a larger delocalization of the charges due to electron repulsion. The charge withdrawal from the terminal olefinic carbon was actually observed. The phenyl protons did not change their chemical shift after the introduction of the second charge.

The downfield shift of the vinylic protons on formation of (IX) is not an expression of an anisotropy effect due to a conformational change, since both protons of the vinylic group undergo a similar downfield shift. These results indicate a strong localization of the electrons is the $-C_3^{2-}-$ segment leading to an effective withdrawal of charge from the vinyl group on transformation of the monoanion (VIII) into the dianion (IX). This localization of charge is due apparently to the formation of strong bonds in a two four-electron three centered system in a molecule that has the structure (X), which we call an extended acetylene[7] (or sesquiacetylene) in which three consecutive carbons are *sp* hybridized. Similar spectra of mono- and di-anions were observed on metalation of other enynes (Ia)–(Ie)[6].

Two factors, electronic and steric, seem to govern the position of the attack of trimethylsilyl chloride on the dianion. This attack occurs in all cases except one on the carbons of the $[-C{\equiv}C{\equiv}C-]^{2-}$ segment where most of the charge is concentrated. In the case of (Ia) an additional product (IIIa) was obtained, and its formation may be attributed to the lack of substituents at positions 1 and 2. Therefore, the dianion of (Ia) has the charge delocalized towards the C_1 carbon atom to a greater extent than the other anions. The steric hindrance is also less for attack at this position. Steric effects are particularly important in the case of (If), which yielded almost exclusively the enyne (IIIf) as the disilyl derivative. Attack at the carbon adjacent to the tert-butyl group seems to be prohibited. The two silyl groups are never found on the same carbon. This is possibly a result of steric hindrance by the first group or of the electronic structure of the monosilyl-monolithium derivative formed in the first step. The predominant or even exclusive formation of disilyl derivatives with both silyl groups on the allenic group in the case of unhindered substrates probably has reasons similar to those for the formation of dilithium derivatives where the two metal atoms are probably symmetrically distributed on the C=C=C segment. This pattern of formation of single products is not followed for the monosilyl derivatives, where mixtures were obtained. It seems that this a consequence of a greater delocalization of charge in the mono- then in the di-anion[6].

EXPERIMENTAL SECTION

General procedure for metalation of (Ia)–(Ie)

A solution of butyllithium in hexane (Foote) (40 ml 1.6 *M*) was poured into a 3-necked flask, fitted with a dropping funned, nitrogen inlet and a low temperature thermometer. The solvent was evaporated in vac., 40 ml of dry ether was then added. The solution was cooled to −100° and a solution of 2 g of (I) in 10 ml dry ether was added dropwise. The temperature of the solution was kept at −90° during the addition and for 30 min thereafter and was then allowed to rise during 3 h to −70°. At this time a solution of 10 g of trimethylsilyl chloride in 30 ml dry ether was added during 45 min at −70°, causing the disappearance of the deep red coloration that was observed after the addition of (I). The reaction mixture was left overnight at room temperature, cooled in an ice bath and treated slowly with 100 ml of cold water. The two layers formed were separated and the ethereal solution dried on $MgSO_4$ and distilled. The products of metalation of (Ia)–(Ie) after subsequent treatment with trimethylsilyl chloride are recorded in Table 4.

TABLE 4

RESULTS OF REACTIONS OF DIMETALATED ENYNES WITH TRIMETHYLSILYL CHLORIDE

Starting compounds (g)	B.p. (°C/mm)	Products weight (g)	Composition
(Ia) 2	100–110/1	3.4	(IIa)/(IIIa) = 63/37
(Ib) 2	85–100/0.4	2.4	(IIb)/impur. = 89/11
(Ic) 2	87–99/0.4	2.6	(IIc)/impur. = 90/10
(Id) 2	165–175/1	2.3	(IId) = 100%
(Ie) 1[a]		0.5	
(If) 2	100–110/20	2.0	(IIIf)/(IV)/(V) = 50/10/35
(Ig) 2	90–1000/1	3.0	(IIg) > 90%

[a] Analysed by NMR, UV and IR only.

The products were analysed and preparatively separated on a 2 m × $\frac{1}{4}'$ column of 10% polydiethyleneglycol succinate (stabilized) on Chromosorb P.

In the case of 2,6,6-trimethyl-1-hepten-4-yne (If) the solution in butyllithium was allowed to reach room temperature slowly and left for 8 h at this temperature, then cooled again to −60° and treated with trimethylsilyl chloride.

2-Methyl-1-undecen-4-yne (Ig) was left for 16 h at room temperature and then treated as above, yielding the disilyl derivative (IIg). When the metalation with butyllithium was carried out at −70°, then the temperature was allowed to reach 0° and trimethylsilyl chloride was applied, a mixture of mono- and disilyl derivatives was obtained. This mixture was separated at 150° on a 4 m × $\frac{1}{4}'$ column of 10% Carbowax 20M on Chromosorb P.

TABLE 5

ANALYTICAL DATA OF THE SYNTHESIZED COMPOUNDS

Compound	Calcd.		Found	
	C	H	C	H
(IIa)	71.4	9.0	71.25	9.03
(IIb)	72.0	9.33	72.13	9.22
(IIc)	72.0	9.33	72.31	9.34
(IId)	76.3	8.29	76.62	8.08
(IIg)	70.13	11.69	70.0	11.32
(IIIa)	71.4	9.0	72.07	8.93
(IIIf)	68.6	11.44	68.78	11.10
(V)	75.0	11.54	74.95	10.73

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