Metallation Reactions. Part XV.[1] Metallation of Diacetylenes

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Hexa-2,4-diyne was metallated with butyl-lithium and methyl-lithium smoothly to the trilithio-derivative by abstraction of three protons from the same carbon. Prolonged metallation with butyl-lithium led to the tetralithio-compound. A trilithio-derivative was also obtained from octa-2,4-diyne, but octa-3,5-diyne yielded a dilithio-derivative. The two triple bonds of hepta-1,6-diyne were metallated independently to give di-, tri- and tetra-lithio-derivatives. A 1 Hz coupling constant through seven bonds was observed in the monolithiohexadiyne.

THE easy polymetallation of acetylenes with butyl-lithium [2-9] and the preferential abstraction [7,9] of the second propargylic proton from the same carbon as the first one, even when another propargylic carbon was present in the molecule led us to the assumption [6] of the stabilization of the ' sesquiacetylenic ' system composed of three carbons in a linear arrangement and carrying 8 π electrons in 6 orbitals. This assumption seemed to be supported by the n.m.r. spectra of the lithiated compounds.[6]

It was of interest to investigate whether diacetylenes containing two propargylic groups would be polymetallated on the same carbon or whether monometallation of one propargylic carbon would be followed by monometallation of the second.

Metallation of hexa-2,4-diyne with 6 mol. equiv. of butyl-lithium in hexane for 65 h at room temperature and subsequent treatment of the mixture with chlorotrimethylsilane gave the trisilyl derivative (I). The use of 2 mol. equiv. of the metallating agent and a shorter reaction time (16 h) yielded a mixture of (I) and the monosilyl derivative (II). An attempt was made to stop the reaction at the monometallation stage by the use of methyl-lithium in ether, which was found

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[1] Part XIV, J. Klein and J. Y. Becker, *Tetrahedron*, 1972, **28**, 5385.

[2] K. C. Eberly and H. E. Adams, *J. Organometallic Chem.*, 1965, **3**, 165.

[3] R. West, P. A. Carney, and I. C. Mineo, *J. Amer. Chem. Soc.*, 1965, **87**, 3788.

[4] R. West and P. C. Jones, *J. Amer. Chem. Soc.*, 1969, **91**, 6156.

[5] J. E. Mulvaney, T. L. Folk, and D. J. Newton, *J. Org. Chem.*, 1967, **32**, 1674.

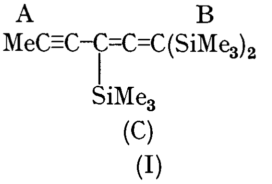
[6] J. Klein and S. Brenner, *J. Amer. Chem. Soc.*, 1969, **91**, 3094.

[7] J. Klein and S. Brenner, *J. Organometallic Chem.*, 1969, **18**, 291.

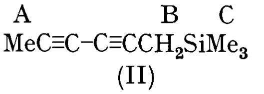
[8] J. Klein and S. Brenner, *Tetrahedron*, 1970, **26**, 5807; *J. Org. Chem.*, 1971, **36**, 1319.

[9] J. Klein and E. Gurfinkel, *J. Org. Chem.*, 1969, **34**, 3952.

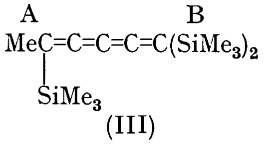
previously to favour monometallation of acetylenes.[10,11] However, even this reagent gave (I) after 16 h of metallation and subsequent silylation. Shorter reaction periods yielded a mixture of starting material, (I), (II), and an additional trisilylcumulene (III) (Table 1). It is of interest that although no (III) was found after long metallation times and very little of it relative to (I) at the beginning, there were metallation periods for which the amount of (III) relative to (I) was appreciable. It appears that complex formation of the intermediate trilithio-derivative (VII), either with methyl-lithium or with the diacetylene caused the silylation to take a different course. Similar effects of complexation on the product distribution were found by us before.[11] * It seems also that the trilithio-compound is formed faster than the monolithio-derivative, but the reaction between the trilithio-compound and two equiv. of diacetylene to give three equiv. of the monolithio-compound, also takes place.


$\overset{A}{\mathrm{MeC{\equiv}C}}{-}\underset{\underset{(C)}{\mathrm{SiMe_3}}}{\mathrm{C}}{=}\mathrm{C}{=}\overset{B}{\mathrm{C}}\mathrm{(SiMe_3)_2}$

(I)


$\overset{A}{\mathrm{MeC{\equiv}C}}{-}\mathrm{C{\equiv}C}\overset{B}{\mathrm{CH_2}}\overset{C}{\mathrm{SiMe_3}}$

(II)


$\overset{A}{\mathrm{Me}}\underset{\mathrm{SiMe_3}}{\mathrm{C}}{=}\mathrm{C{=}C{=}C{=}}\mathrm{C}\overset{B}{\mathrm{(SiMe_3)_2}}$

(III)

Table 1

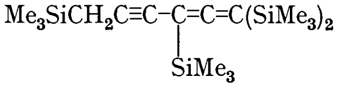
Composition of the metallation ^{a}–silylation product of hexa-2,4-diyne

Compound (%)	Duration of metallation (min)						
	14	38	55	90	180	390	48 h
(II)	8·3	11·9	4·8	2·3	9·1	9·5	
(III)	Trace	3·3	22·7	16·1	12·3	5·2	
(I)	8·2	23·6	33·8	47·6	75·3	83·5	94 [b]
Hexa-2,4-diyne	83·1	60·8	38·6	34·0	3·1	1·7	Trace

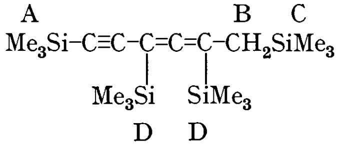
[a] With 1·4M-methyl-lithium in ether. [b] 6% Was unidentified.

The metallation–silylation of hexa-2,4-diyne with two mol. equiv. of methyl-lithium gave a mixture of (I) and (II). No disilyl derivative was found.

A mixture of (I) and a tetrasilyl derivative was obtained by metallation of hexa-2,4-diyne with an excess of butyl-lithium in ether. The yield of the tetrasilyl derivative could be raised by metallation with butyl-lithium in tetrahydrofuran. Two possible structures, (IV) and (V), were considered for the tetrasilyl compound because of the presence of acetylenic and allenic bonds in the i.r. spectrum, but structure (V) was preferred, since the methylene protons appear in the n.m.r. spectrum as an AB quartet, due to their diastereotopic environment, or restricted rotation.

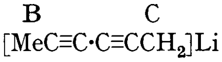

$\mathrm{Me_3SiCH_2C{\equiv}C{-}\underset{SiMe_3}{C}{=}C{=}C(SiMe_3)_2}$

(IV)

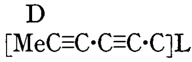

$\overset{A}{\mathrm{Me_3Si}}{-}\mathrm{C{\equiv}C}{-}\underset{\underset{D}{\mathrm{Me_3Si}}}{\mathrm{C}}{=}\mathrm{C}{=}\underset{\underset{D}{\mathrm{SiMe_3}}}{\mathrm{C}}{-}\overset{B}{\mathrm{CH_2}}\overset{C}{\mathrm{SiMe_3}}$

(V)

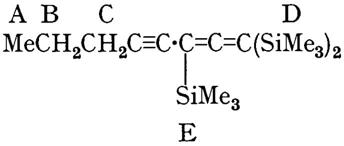
The n.m.r. spectrum of the metallated compounds was also recorded in $(C_2D_5)_2O$. The monolithio-derivative (VI) showed a quartet (2H) at δ 2·73 and a triplet (3H) at 1·86 with a remarkable coupling constant through seven bonds of *ca.* 1 Hz. The methyl protons of the trilithio-derivative (VII) appeared as a singlet at δ 0·13. The signal for (VII) disappears after having grown in intensity to a certain point, due to precipitation of the compound, but reappears on addition of the starting compound. Again, complex formation between (VII) and the diacetylene could be invoked to explain this phenomenon.


$[\overset{B}{\mathrm{Me}}\mathrm{C{\equiv}C{\cdot}C{\equiv}C}\overset{C}{\mathrm{CH_2}}]\mathrm{Li}$

(VI)


$[\mathrm{MeC{\equiv}C{\cdot}C{\equiv}C{\cdot}}\overset{D}{\mathrm{C}}]\mathrm{Li_3}$

(VII)


$\overset{A}{\mathrm{Me}}\overset{B}{\mathrm{CH_2}}\overset{C}{\mathrm{CH_2}}\mathrm{C{\equiv}C{\cdot}}\underset{\underset{E}{\mathrm{SiMe_3}}}{\mathrm{C}}{=}\mathrm{C{=}C}\overset{D}{\mathrm{(SiMe_3)_2}}$

(VIII)

Metallation of octa-2,4-diyne with 5 mol. equiv. of

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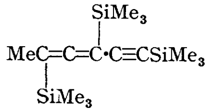
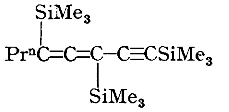
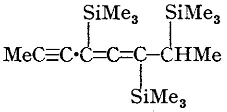
* Other structures could be assigned to (I), (VIII), and (XXIII), *e.g.* (IA), (VIIIA), and (XXIIIA) respectively. We prefer, however, the assignment we made on the following grounds.


$\mathrm{Me\underset{SiMe_3}{C}{=}C{=}\overset{SiMe_3}{C}{\cdot}C{\equiv}CSiMe_3}$

(IA)


$\mathrm{Pr^n\overset{SiMe_3}{C}{=}C{=}\underset{SiMe_3}{C}{-}C{\equiv}CSiMe_3}$

(VIIIA)


$\mathrm{MeC{\equiv}C{\cdot}\overset{SiMe_3}{C}{=}C{=}\overset{SiMe_3}{C}{-}\underset{SiMe_3}{C}HMe}$

(XXIIIA)

Compound (I) undergoes a reaction with $AgNO_3$ in aqueous alcohol to give hexa-2,4-diyne. A similar reaction was obtained with $PhC(SiMe_3){=}C{=}C(SiMe_3)_2$ which gave benzylacetylene but not with $PhC(SiMe_3){=}C{=}C(SiMe_3)Me$ showing that two silyl groups are necessary on the same carbon to give this reaction. This eliminates (IA). By analogy we assumed that silylation occurs on the carbons of the triple bond vicinal to the metallated propargylic position. In compounds (I) and (VII), only two and not three different silyl groups were observed even on expanding the n.m.r. spectrum. In (XXIII), however, three such groups appeared.

[10] J. Klein, S. Brenner, and A. Medlik, *Israel J. Chem.*, 1971, **9**, 177.

[11] J. Y. Becker, S. Brenner, and J. Klein, *Israel J. Chem.*, in the press.

methyl-lithium or butyl-lithium in ether and subsequent treatment with chlorotrimethylsilane gave a mixture of products, containing the trisilyl derivative (VIII) even after short reaction periods. The amount of (VIII) in the product was 85% after 23 h metallation with butyl-lithium.

The abstraction of the third proton of the methyl group in 2,4-diynes show that the remaining proton in the intermediate dilithio-derivative, $[MeC{\equiv}C{\cdot}C{\equiv}CCH]Li_2$, is still acidic and is abstracted rapidly by the metallating agent. This acidity is similar to that of an ethynyl proton and it is not decreased essentially by the presence of two charges in the adjoining unsaturated system.

1-Phenylpenta-1,3-diyne was metallated with methyl-lithium in ether with a view to separating the successive stages of metallation. Protonation or treatment with deuterium oxide of the reaction mixture after 1 h of reaction gave 45% starting material, 25% of the allenes (IX) or (X) respectively and 15% of (XI), the product of addition of methyl-lithium to a triple bond. The enyne (XI) did not contain a vinylic deuterium atom, even when the reaction mixture was treated with deuterium oxide. The vinylic proton in (XI) entered the molecule before water addition by abstraction of a proton or hydrogen atom from the solvent or the diacetylene by the intermediate lithium derivative (XII) or radical (XIII). Protonation of the metallation product after 4 h yielded starting material (6%), (XI) (33%), but not the allene (IX). The remainder of the product consisted of polymeric material. Silylation of the metallation product after 4 h yielded (XI) and the trisilyl derivative (XIV). Similar results were obtained after 15 h of metallation. Silylation gave 17% (XI), 35% (XIV), and polymeric material. The amount of polymeric material (80%) was much higher in the protonation product, which contained also 17% (XI). Polymerization of the trilithio-derivative (XV) occurred therefore, to a higher extent during protonation than during silylation.

A B C

$PhC{\equiv}CCH{=}C{=}CH_2$

(IX)

$PhC{\equiv}CCD{=}C{=}CH_2$

(X)

A B C

$PhC{=}CCH{=}CMe_2$

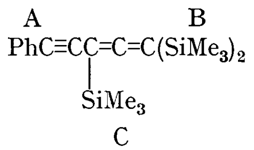
(XI)

$PhC{\equiv}C{\cdot}CLi{=}CMe_2$

(XII)

$PhC{\equiv}C\dot{C}{=}CMe_2$

(XIII)



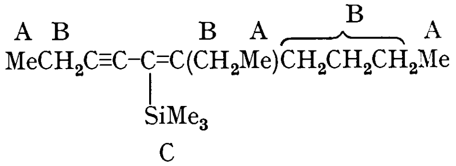
$$\overset{A}{PhC{\equiv}C}\underset{\underset{C}{SiMe_3}}{C}{=}C{=}\overset{B}{C(SiMe_3)_2}$$

(XIV)

Metallation of 1-phenylpenta-1,3-diyne with butyl-lithium in ether (4 mol. equiv.) and subsequent silylation gave also the trisilyl derivative (XIV) as expected from the same intermediate (XV). Protonation with water of the metallation products, after 1 h, yielded a mixture that contained, according to the n.m.r. spectra, 30% (XVIII) and 36% (XIX) (no starting material remained). These two compounds derived from the trilithio-derivative (XV), because by treatment of the same metallation mixture with deuterium oxide it gave (XX) and (XXI), respectively. No polymerisation was observed, even after 4 h of metallation with butyl-lithium in ether.

$[PhC{\equiv}C{\cdot}C{\equiv}CC]Li_3$

(XV)



$$\overset{A}{Me}\overset{B}{CH_2}C{\equiv}C{-}\underset{\underset{C}{SiMe_3}}{C}{=}C(\overset{B}{CH_2}\overset{A}{Me})\overbrace{CH_2CH_2CH_2}^{B}\overset{A}{Me}$$

(XVI), (XVII)

A B C D

$PhCH{=}C{=}CH{\cdot}C{\equiv}CH$

(XVIII)

A B C

$PhCH_2C{\equiv}C{\cdot}C{\equiv}CH$

(XIX)

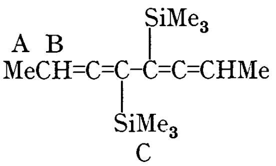
$PhCD{=}C{=}CD{\cdot}C{\equiv}CD$

(XX)

$PhCD_2C{\equiv}C{\cdot}C{\equiv}CD$

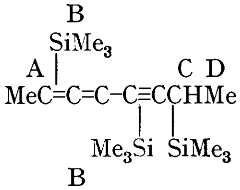
(XXI)

All the diacetylenes studied above contained at least one propargylic methyl group. The methylene of an ethyl group in the propargylic position of acetylenes is known to be metallated[11] much slower than the propargylic methyl. The metallation of octa-3,5-diyne was therefore investigated. Metallation of this compound with butyl-lithium in hexane gave addition products and treatment of the product with chlorotrimethylsilane gave two isomeric monosilyl compounds (XVI) and (XVII) containing a butyl group. Even metallation with butyl-lithium in ether gave (XVI) and (XVII) after silylation. However, the same reaction in tetrahydrofuran (5 mol. equiv.) for 40 h at —10°, yielded a disilyl (XXII) and trisilyl derivative (XXIII),* in a 3 : 1 ratio, which were products of di and tri-metallation.



$$\overset{A}{Me}\overset{B}{CH}{=}C{=}\overset{SiMe_3}{C}{-}\underset{\underset{C}{SiMe_3}}{C}{=}C{=}CHMe$$

(XXII)



$$\overset{A}{Me}C{=}C{=}\overset{\overset{B}{SiMe_3}}{C}{-}\underset{\underset{B}{Me_3Si}}{C}{\equiv}\overset{C}{C}\underset{SiMe_3}{\overset{D}{C}}HMe$$

(XXIII)

It is of interest, that this was the only internal diacetylene from which the product of dimetallation was isolated, and it constituted the main product of the reaction. In addition, dimetallation occurred by monometallation at each propargylic position and not at one carbon exclusively, as above or as in the monoacetylenes[9] where the triple bond was linked to alkyls higher than methyl. The slowing down of the metallation by the presence of an ethyl instead of a propargylic methyl group made the

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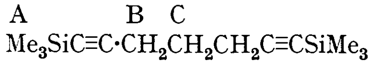
* See footnote on p. 600.

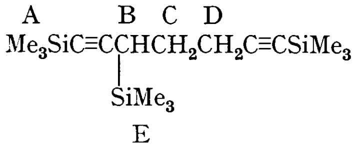
reaction on the second propargylic carbon, which is activated here by an additional triple bond, faster than dimetallation on the same carbon.

The importance of solvents in activating differentially two kinds of reactions with butyl-lithium is illustrated in the dramatic change that takes place on changing hexane or even ether to tetrahydrofuran. This seemingly unimportant change transforms the course of the reaction from exclusive addition to the triple bond to exclusive propargylic metallation.

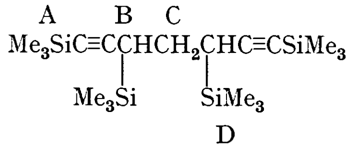
Finally, metallation of hepta-1,6-diyne with the triple bonds separated by three methylenes, was also studied. The reaction of this compound with 4 mol. equiv. of methyl-lithium in ether for 4 h gave after silylation the disilyl derivative (XXIV). Metallation with 5 mol. equiv. of butyl-lithium in ether for 48 h yielded (XXIV),


$\overset{A}{Me_3Si}C\equiv C{\cdot}\overset{B}{CH_2}\overset{C}{CH_2}CH_2C\equiv CSiMe_3$

(XXIV)


$\overset{A}{Me_3Si}C\equiv C\overset{B}{C}H(\underset{E}{SiMe_3})\overset{C}{CH_2}\overset{D}{CH_2}C\equiv CSiMe_3$

(XXV)


$\overset{A}{Me_3Si}C\equiv C\overset{B}{C}H(Me_3Si)\overset{C}{CH_2}CH(\underset{D}{SiMe_3})C\equiv CSiMe_3$

(XXVI)

the trisilyl (XXV), and tetrasilyl derivative (XXVI) in a 2 : 6 : 1 ratio. This course of reaction is similar to that of terminal monoacetylenes[1] which give dimetallation and where attack on the dimetallated compound yielded terminal acetylenes and substitution at the propargylic position. The two triple bonds react independently and in a similar manner, but tri- and tetra-metallation are slowed down relative to terminal monoacetylenes by the presence of the two charges. No isomerization and interaction between the triple bonds were found as observed in different conditions.[12]

The acceleration of metallation of the conjugated diynes relative to monoacetylenes[1] could be ascribed both to the inductive and resonance effects that the second group exerts on the reaction. The σ^*,[13,14] σ_m,[15,16] and σ_p[15,16] values of the ethynyl group were found to be 1·43, 0·205, and 0·233, respectively.

EXPERIMENTAL

Hexa-2,4-diyne, octa-2,4-diyne, octa-3,5-diyne, and hepta-1,6-diyne were commercial products (Farchan Res. Lab.). 1-Phenylpenta-1,3-diyne was prepared by isomerisation of 1-phenylpenta-1,4-diyne.[17]

Metallation with Butyl-lithium.—A solution of butyl-lithium in hexane (Foote) was estimated by titration with butan-2-ol in xylene with 1,10-phenanthroline as indicator.[18] A measured amount of this solution was introduced into a flask with a side arm closed with a rubber cap and equipped with a **T** stopcock and an argon atmosphere at room temperature. The substrate was added slowly with a syringe and left for the desired period. When other solvents were used as reaction medium (anhydrous ether or tetrahydrofuran), the hexane was evaporated *in vacuo* and an equivalent amount of the desired solvent added. When tetrahydrofuran was used, the temperature of the metallation mixture was kept below 0 °C during the reaction.

TABLE 2

U.v. and i.r. spectra

Compound	$\lambda_{max.}$/nm (ε)	$\nu_{max.}$/cm^{-1}
(I)	252, (13,800), 240 (13,200), 232 (11,700)	845, 1255, 1910, 2130
(III)	249 (15,000)	845, 1255, 1900
(V)	253 (12,600), 242 (13,300), 233 (11,800)	845, 1255, 1900, 2130
(VIII)	255 (14,800), 243 (14,400), 234 (13,000)	840, 1250, 1908, 2120
(XI)	293, 276, 261, 250	1600, 1650, 2200
(XIV)	252 (11,200)	845, 1255, 1900, 2145
(XVI), (XVII)	235 (9200)	845, 1255, 1620, 2160w
(XXII)	287 (10,800), 273 (11,800), 259 (8600), 246 (5800)	845, 1250, 1915vw
(XXIII)	250 (1180), 234 (1480)	840, 1250, 1910, 2180
(XXIV)	292 (340)	840, 1250, 2180
(XXV)	302 (680)	840, 1250, 2130, 2160, 2180
(XXVI)	307 (560), 256 (360)	840, 1250, 2120, 2160

TABLE 3

Analytical data *

Compound	Formula	Calculated (%)		Found (%)	
		C	H	C	H
(I)	$C_{15}H_{30}Si_3$	61·2	10·2	61·1	10·05
(II)	$C_9H_{14}Si$	72·0	9·35	70·85	8·55
(III)	$C_{15}H_{30}Si_3$	61·2	10·2	61·8	10·15
(V)	$C_{18}H_{38}Si_4$	59·0	10·4	58·2	9·8
(VIII)	$C_{17}H_{34}Si_3$	63·35	10·6	63·15	10·8
(XI)	$C_{12}H_{12}$	92·3	7·7	92·0	7·8
(XXII)	$C_{14}H_{26}Si_2$	67·2	10·4	68·05	9·65
(XXIV)	$C_{13}H_{24}Si_2$	66·1	10·1	65·85	10·15
(XXV)	$C_{16}H_{32}Si_3$	62·35	10·4	62·5	10·2
(XXVI)	$C_{19}H_{40}Si_4$	60·0	10·5	61·0	10·35

* Analysis of silicon compounds are often inaccurate (ref. 19). The analyses of products (XIV), (XVI), (XVII), and (XXIII) were not accurate. Compound (XIV) backfired during the analysis. Structural assignments were based on spectroscopic evidence only.

Metallation with Methyl-lithium.—A measured solution of methyl-lithium in ether (1·4M) prepared from methyl bromide and lithium was cooled to −20 °C under argon in

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[12] D. A. Ben-Efraim and F. Sondheimer, *Tetrahedron*, 1969, **25**, 2837.

[13] T. L. Brown, *Chem. Rev.*, 1958, **58**, 595.

[14] R. W. Taft, jun., in 'Steric Effects in Organic Chemistry,' ed. M. S. Newman, Wiley, New York, 1956.

[15] M. Charton, *J. Org. Chem.*, 1965, **30**, 552; M. Charton and H. Meislid, *J. Amer. Chem. Soc.*, 1958, **80**, 5940.

[16] J. A. Landgrebe and R. H. Rynbrandt, *J. Org. Chem.*, 1966, **31**, 2585.

[17] H. Taniguchi, I. M. Mathai, and S. I. Miller, *Organic Syntheses*, 1970, **50**, 97.

[18] S. C. Watson and J. F. Eastham, *J. Organometallic Chem.*, 1967, **9**, 165.

[19] R. West and G. A. Gornowicz, *J. Amer. Chem. Soc.*, 1971, **93**, 1714, 1720.

TABLE 4

^{1}H N.m.r. spectra (δ values)

Compound	Protons					Coupling constants (Hz)
	A	B	C	D	E	
(I)	1·71(s)	0·10(s)	0·15(s)			
(II)	1·58(q)	1·93(t)	0·16(s)			J_{AB}^{1}
(III)	1·93(s)	0·11(s)	0·07(s)			
(V)	0·16(s)	1·23(d), 1·37(d)	0·10(s)	0·13(s)		J_{AB}^{14}
(VI)		1·86(t)	2·73(q)			J_{BC}^{1}
(VII)				0·13(s)		
(VIII)	1·01(t)	1·53(m)	1·93(t)	0·13(s)	0·17(s)	
(IX)	7·30(m)	5·58(t)	5·0(d)			J_{BC}^{6}
(XI)	7·24(m)	5·41(m)	1·89(d)			J_{BC}^{6}
(XIV)	7·23(m)	0·17(s)	0·27(s)			
(XVI), (XVII)	0·90—1·26(m)	1·86—2·43(m)	0·07(s)			
(XVIII)	7·16(m)	6·37(dd)	5·71(dd)	2·83(dd)		J_{BC}^{6}, J_{BD}^{1}, $J_{CD}^{2\cdot5}$
(XIX)	7·16(m)	3·52(d)	2·0(t)			J_{BC}^{3}
(XXII)	1·97(d)	6·07(q)	0·17(s)			J_{AB}^{6}
(XXIII)	1·71(s)	0·14(s)	1·83(q)	1·23(d)	0·11(s)	J_{CD}^{7}
(XXIV)	0·07(s)	2·90(t)	1·87(quint)			J_{BC}^{7}
(XXV)	0·12(s)	2·43(m)	1·81(m)	1·68(m)	0·10(s)	
(XXVI)	0·11(s)	1·80 Octet of an AA′BB′ system		0·08(s)		

the same apparatus as described above. A solution of the substrate in anhydrous ether was added slowly with a syringe. The solution was then brought to room temperature during 30 min and left for the desired interval of time.

Silylation.—The metallation mixture was cooled to −70 °C and a solution of chlorotrimethylsilane was added slowly with a syringe. The mixture was left overnight at room temperature and then poured on ice. The phases were separated and the organic layer submitted to g.l.c.

Protonation.—Water or deuterium oxide was added slowly with a syringe to the cooled metallation mixture and then separated in a manner similar to the reaction with chlorotrimethylsilane.

Separations of the products were performed by g.l.c. on a 2 m × ¼ in column of 20% SE-30 on Chromosorb W. Compounds (XVIII) and (XIX) were not separated and were identified in their mixture by their n.m.r. spectra.

All the n.m.r. spectra were recorded at room temperature on a Varian T60 instrument.

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