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METALATION REACTIONS—XIV[9]

THE GENERALITY OF THE 1,3-SIGMATROPIC SHIFT OF HYDROGEN IN ALLENYLLITHIUM COMPOUNDS

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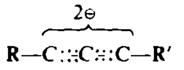
Abstract—Dimetalation of aliphatic 2-alkynes was observed in mild conditions in ether solution. Only 2-butyne has undergone monometalation exclusively. The dilithio compounds of 1- and 2-alkynes were attacked by electrophiles first at the 3-position. A 1,3-sigmatropic shift occurred in the monolithioallenes to give terminal acetylides. Metalation of 3-alkyne gave only a monolithiated compound in the conditions studied.

Polymetalation of terminal[1,2] and internal[3,4,5] acetylenes with butyllithium was achieved recently. The observation,[4,5] that the second proton was abstracted in some cases faster than the first and that both protons were abstracted from the same propargylic carbon was rationalized[4] by the assumed stability of the sesquiacetylenic structure (I) with three sp hybridized carbons and six p-orbitals containing eight electrons. The electron delocalization in the sesquiacetylenic system raised the question of the position of the first attack of an electrophile on the dilithio derivative. It was found[4] that dilithiophenylpropyne (II) was attacked first at the benzylic position by D_2O, MeBr or trimethylchlorosilane and that a 1,3-sigmatropic shift occurred in the formed monolithiated derivative from the terminal to the benzylic position to give a different lithium derivative which reacted to yield the product. The intermediates and product in the reaction of II with D_2O were consecutively III, IV and V. It was of interest to study the generality of polymetalation of acetylenes and the possible sigmatropic rearrangements during the reactions of the lithiated compounds.


$R\text{—}\overbrace{C\vdots\vdots C\vdots\vdots C}^{2\ominus}\text{—}R'$

I

$[PhC\text{—}C\text{—}CH]Li_2$

II

$[PhCD\text{—}C\text{—}CH]Li$

III

$PhCDHC\equiv CLi$

IV

$PhCHDC\equiv CD$

V

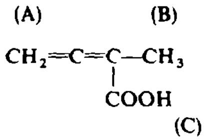
RESULTS

A precipitate was formed during the reaction of BuLi with 2-butyne in ether. This reaction was therefore studied (Fig 1) in THF-d_8 solution. The PMR signal of the methyls disappeared during metalation and a triplet at δ 2·14 ppm and a quartet at δ 1·82 ppm appeared in its place with a coupling constant through five bonds $^5J_{HH}$ 3 Hz. These new signals corresponded to anion VI. The increase in reaction time, amount of catalyst, metalating agent or in temperature did not change this spectrum proving that no polymetalation occurred. Treatment of the metalation product with

FIG 1. The PMR spectrum of VI with n-BuLi in THF-d_8 after 110 min. recorded on Varian HA100 at 1·5°C. The chemical shifts were measured relative to THF. Singlet C is the starting material.

$[\overset{(B)}{CH_3}C\equiv C\overset{(A)}{CH_2}]^-Li^+$

VI



$$\overset{(A)}{CH_2}=C=\underset{\underset{(C)}{COOH}}{C}-\overset{(B)}{CH_3}$$

VII

$\overset{(A)}{CH_3}-C\equiv C-\overset{(B)}{CH_2}\overset{(C)}{COOH}$

VIII

solid CO_2 yielded two acids (VII and VIII) in a 7:1 ratio, characterized by their PMR spectra (Table 1) and analysis.

2-Pentyne reacted smoothly with BuLi (3–4 mole-equivalents) in ether to give a dilithio derivative which yielded the bis (trimethylsilyl) acetylene (IX).

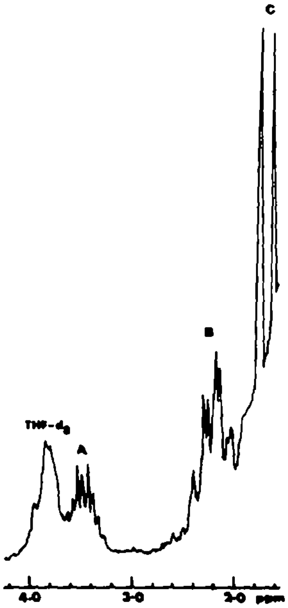
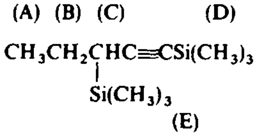


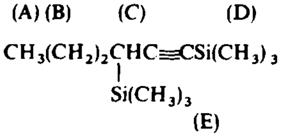
FIG 2. The PMR spectrum of XXII in n-BuLi/THF-d_8 solution after 30 min., at room temp. The chemical shifts were measured relative to the low field component of the THF signal.

Metalation of 2-hexyne with 4 moles of BuLi in ether at room temperature and addition of excess of trimethylchlorosilane, after 30 hr, gave two products in a 4:1 ratio. The main product was characterized as the disilyl derivative (X). Treatment of the metalation product with MeBr and subsequent work up with H_2O or D_2O gave



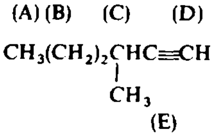
$\overset{(A)}{CH_3}\overset{(B)}{CH_2}\underset{\underset{(E)}{Si(CH_3)_3}}{\overset{(C)}{CH}}C{\equiv}C\overset{(D)}{Si(CH_3)_3}$

IX



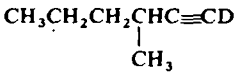
$\overset{(A)}{CH_3}\overset{(B)}{(CH_2)_2}\underset{\underset{(E)}{Si(CH_3)_3}}{\overset{(C)}{CH}}C{\equiv}C\overset{(D)}{Si(CH_3)_3}$

X



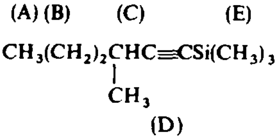
$\overset{(A)}{CH_3}\overset{(B)}{(CH_2)_2}\underset{\underset{(E)}{CH_3}}{\overset{(C)}{CH}}C{\equiv}\overset{(D)}{CH}$

XI



$CH_3CH_2CH_2\underset{CH_3}{CH}C{\equiv}CD$

XII

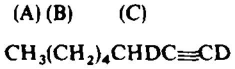


$\overset{(A)}{CH_3}\overset{(B)}{(CH_2)_2}\underset{\underset{(D)}{CH_3}}{\overset{(C)}{CH}}C{\equiv}C\overset{(E)}{Si(CH_3)_3}$

XIII

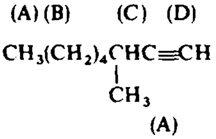
XI or XII, respectively. When the product of reaction with MeBr was treated with trimethylchlorosilane, before the addition of H_2O, XIII was formed.

Similarly, metalation of 2-octyne with 4 moles of BuLi for 18 hr, at room temperature, gave after addition of H_2O or D_2O, 1-octyne or its dideutero derivative (XIV), respectively. Treatment of the metalation product with MeBr and then H_2O yielded



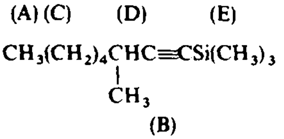
$\overset{(A)}{CH_3}\overset{(B)}{(CH_2)_4}\overset{(C)}{CHD}C{\equiv}CD$

XIV



$\overset{(A)}{CH_3}\overset{(B)}{(CH_2)_4}\underset{\underset{(A)}{CH_3}}{\overset{(C)}{CH}}C{\equiv}\overset{(D)}{CH}$

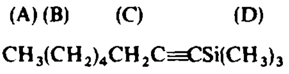
XV



$\overset{(A)}{CH_3}\overset{(C)}{(CH_2)_4}\underset{\underset{(B)}{CH_3}}{\overset{(D)}{CH}}C{\equiv}C\overset{(E)}{Si(CH_3)_3}$

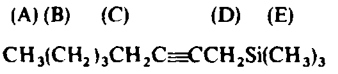
XVI

3-methyloct-1-yne (XV) and a small amount of an additional product which was not identified. Addition of trimethylchlorosilane to the product of reaction with MeBr before decomposition with H_2O, yielded XVI. Reaction of the metalated 2-octyne with trimethylchlorosilane gave three products (XVII,[11] XVIII and XIX). The ratio



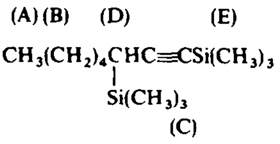
$\overset{(A)}{CH_3}\overset{(B)}{(CH_2)_4}\overset{(C)}{CH_2}C{\equiv}C\overset{(D)}{Si(CH_3)_3}$

XVII



$\overset{(A)}{CH_3}\overset{(B)}{(CH_2)_3}\overset{(C)}{CH_2}C{\equiv}C\overset{(D)}{CH_2}\overset{(E)}{Si(CH_3)_3}$

XVIII



$\overset{(A)}{CH_3}\overset{(B)}{(CH_2)_4}\underset{\underset{(C)}{Si(CH_3)_3}}{\overset{(D)}{CH}}C{\equiv}C\overset{(E)}{Si(CH_3)_3}$

XIX

of XVII, XVIII and XIX changed with the duration of metalation, and after four, six, eight and twenty hr was 1:2·5:3·3 then 2·2:1:7·2 then 1:0·1:1·2 and 1:0:8·4, respectively.

Metalation of 2-octyne with MeLi in THF gave a monolithio derivative (XX) that was silylated to XVIII. An interesting rearrangement of XX to the lithium derivative

$[CH_3(CH_2)_4C{\equiv}CCH_2]Li$
XX

$[CH_3(CH_2)_5C{\equiv}C]Li$
XXI

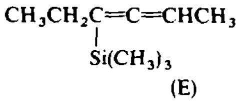
of 1-octyne (XXI) occurred on leaving the solution at room temperature over 20 hr as evidenced by the formation of XVII on silylation. This rearrangement occurred in the absence of starting material and was therefore intramolecular. After 5 days of metalation and consecutive silylation we observed 10% of the disilyl derivative XIX, 40% of XVIII and 50% of the rearranged monosilyl derivative (XVII).

The influence of shifting the triple bond away from the end of the molecule and to the 3-position on the course of metalation was investigated in the case of 3-hexyne. The reaction of this compound with BuLi (4 moles) in THF-d_8 for 3 hr formed the monolithiated product (XXII), characterized by its PMR spectrum (Fig 2, Table 1),

$[CH_3CH_2C{\equiv}C\overset{\ominus}{C}HCH_3]Li^{\oplus}$
(D) (B) (A) (C)
XXII

$CH_3CH_2CD{=}C{=}CHCH_3$
XXIII

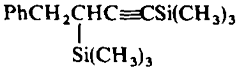
(A) (C) (B) (E) (D)
$CH_3CH_2CH{=}C{=}CHCH_3$
XXIV

(A) (B) (C) (D)

$CH_3CH_2\underset{\substack{|\\ Si(CH_3)_3}}{C}{=}C{=}CHCH_3$
(E)
XXV

which exhibited the methine multiplet at δ 3·42 ppm, the adjoining Me as a doublet at δ 1·62 ppm and the methylene as an octet at δ 2·16 ppm. Treatment of this compound with D_2O gave XXIII. Metalation in ether was much slower. Treatment of the mixture after 70 hr with H_2O gave hexa-2,3-diene (XXIV)[10] and reaction of the product of metalation with trimethylchlorosilane yielded XXV.

A terminal acetylene, 4-phenylbut-1-yne[6] was also submitted to metalation with BuLi in ether for 14 hr. Reaction of the product of metalation with D_2O gave 4-phenyl-1,3-d_2-but-1-yne (XXVI) and treatment with trimethylchlorosilane yielded XXVII and XXVIII in an 8:1 ratio, proving the formation of a dilithio derivative during metalation, as found before in the case of 1-butyne.[2]

$PhCH_2CHDC{\equiv}CD$
XXVI


$PhCH_2\underset{\substack{|\\ Si(CH_3)_3}}{C}HC{\equiv}CSi(CH_3)_3$
XXVII

$PhCH_2CH_2C{\equiv}CSi(CH_3)_3$
XXVIII

$[CH_3CH_2CH{\cdot}C{\equiv}C]Li_2$
XXIX

TABLE 1. PMR AND IR SPECTRA

Compound	Protons, δ ppm A	B	C	D	E	coupling constants H_z	ν_{max} (cm^{-1})
VII	1·87 t	5·11 q	9·70 s			J_{AB} 3	1700, 1945, 1970, 3430
VI	2·14 q	1·82 t				J_{AB} 3	
VIII	1·85 t	3·23 q	9·70 s			J_{AB} 2·5	
IX	1·25 m	1·70 m	*	0·30 s	0·25 s		840, 1250, 2160
X	1·05 t	1·60 m	*	0·18 s	0·13 s		845, 1255, 2160
XI	0·90 m	1·41 m	2·15 m	1·80 d	0·90 m		3305
XIII	0·98 t	1·41 m	2·26 m	1·11 d	0·16 s		845, 1255, 2180
XIV	0·95 t	1·38 m	2·13 m				
XV	0·93 t	1·37 m	2·16 m	1·83 d			2100 (vw), 3310
XVI	1·01 t	1·07 d	1·38 m	2·13 m	0·18 s		840, 1250, 2170
XVII	0·96 t	1·48 m	2·26 m	0·11 s			850, 1260, 2185 (st)
XVIII	0·96 m	1·45 m	2·21 m	*	0·06 s		860, 1260, 2230 (vw)
XIX	1·05 t	1·55 m	0·11 s	*	0·16 s		850, 1260, 2160 (st)
XXII	3·42 m	2·16 (oct).	1·62 d	**		J_{BD} 7 J_{AB} 3 J_{AC} 6	
XXIV	1·03 t	5·17 m	2·07 m	1·70 d,d	5·17 m	J_{AC} 7 J_{BD} 5 J_{ED} 4·5	875, 1970
XXV	0·98 t	2·06 m	4·91 m	1·77 d	0·10 s		845, 1255, 1920, 1940
XXVII	7·20 m	2·73 d,d	1·93 d,d	0·07 s			845, 1250, 1900, 2170
XXVIII	7·21 m	2·85 t	2·50 t	0·11 s			845, 1255, 2180

st—strong, w—weak, vw—very weak, s—singlet, t—triplet, d—doublet, m—multiplet, q—quartet

* hidden by other protons

** hidden by the protons of n-BuLi

1-Pentyne was metalated easily to the same dilithio derivative (XXIX) as that obtained from 2-pentyne. It was characterized by the PMR signal of the methine proton appearing as a triplet at δ 2·16 ppm. Dimetalated 1-pentyne yielded with trimethylchlorosilane the same disilyl derivative (IX) as that obtained from dimetalated 2-pentyne.

TABLE 2. ANALYTICAL DATA

Compound	Formula	Calculated (%) C	Calculated (%) H	Found (%) C	Found (%) H
VII	$C_5H_6O_2$	61·22	6·12	60·92	5·81
IX	$C_{11}H_{24}Si_2$	62·26	11·32	62·49	11·50
X	$C_{12}H_{26}Si_2$	63·71	11·50	64·28	11·95
XIII	$C_{10}H_{20}Si$	71·42	11·90	72·22	11·50
XVI	$C_{12}H_{24}Si$	73·10	12·70	73·20	12·40
XVII	$C_{11}H_{22}Si$	72·52	12·08	72·02	11·90
XIX	$C_{14}H_{30}Si_2$	66·14	11·81	65·87	11·67
XXVII	$C_{16}H_{26}Si_2$	70·07	9·48	70·10	9·48
XXVIII	$C_{13}H_{18}Si$	72·27	8·90	72·07	9·08

Metalation of 1-octyne with 4 moles BuLi in ether, for 35 hr, at room temperature, gave after silylation with trimethylchlorosilane, the same disilyl derivative (XIX) which was obtained from dimetalated 2-octyne.

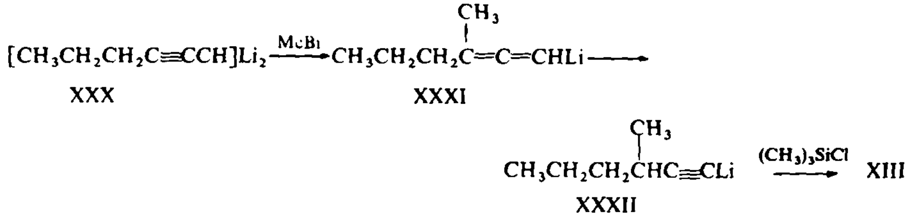
DISCUSSION

Metalation of 2-alkynes with BuLi proceeds smoothly in mild conditions in ether solution to the dilithiated derivative. This procedure is much milder than the previously used[1, 2] heating with BuLi in hexane solution. We have no sufficiently supported explanation for the absence of dimetalation in the case of 2-butyne. Complex formation[9] might be responsible for this behaviour.

3-Hexyne formed a monometalated compound. This is probably a kinetic effect due to the introduction of a Me in place of H on the metalated carbon. Me is metalated much faster than methylene and a 50-fold decrease in proton exchange in the side-chain was observed by introduction of a Me on the side-chain of toluene.[7]

The 1-alkynes studied were also dimetalated by BuLi in mild conditions. The abstraction of an additional proton necessary for reaching the sesquiacetylenic structure was probably slowed down by the two negative charges already present in the molecule.

The dilithiated derivatives of 1- and 2-alkynes reacted first at the 3-position as shown particularly by the methylation. It seems, however, that the structure of the dilithiated 2-alkyne is not the same for the various acetylenes. One possible structure for dilithio derivative of 2-hexyne is XXX and of 2-oxtyne is XXXIII, similar to II



(1) $[CH_3CH_2CH_2C{\equiv}CCH]Li_2 \xrightarrow{MeBr} CH_3CH_2CH_2C(CH_3){=}C{=}CHLi \longrightarrow$

XXX XXXI

$CH_3CH_2CH_2CH(CH_3)C{\equiv}CLi \xrightarrow{(CH_3)_3SiCl}$ XIII

XXXII

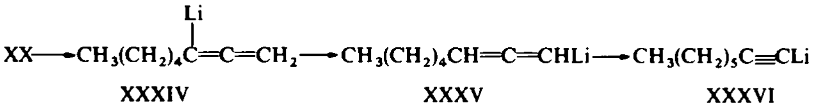
(2) $$[CH_3(CH_2)_4C{\equiv}CCH]Li_2 \xrightarrow{D_2O} CH_3(CH_2)_4CD{=}C{=}CHLi \longrightarrow CH_3(CH_2)_4CDHC{\equiv}CLi \xrightarrow{D_2O} \text{XXVI}$$

XXXIII

where no rearrangement occurred during the metalation. Alkylation (1) and deuteration (2) would then proceed in a manner similar to that of II with a 1,3-hydrogen shift in the monolithium derivative formed after the first step of the reaction with the electrophiles.

In the discussion above we assumed a mechanism for the rearrangement of the lithiated derivatives by analogy to that in the case of 1-phenyl-1-propyne, where the dilithiated compound II was identified spectroscopically before the reaction with electrophiles.

However, the obtention of XVII in the metalation-silylation of 2-octyne, suggested another possibility (3) which consists of a hydrogen shift in a different monolithiated compound, namely XXXIV, obtained in the first step of metalation (propargylmetallic compounds are known to exist in the allenic form). This compound has probably undergone two consecutive sigmatropic hydrogen shifts (XXXV and XXXVI) and the last compound gave either the monosilyl compound XVII on reaction with trimethylchlorosilane or the dilithio derivative (XXXVII) on further metalation. The disilyl derivative XIX could have been obtained either from XXXIII or from XXXVII.



$$(3)\quad \mathrm{XX} \longrightarrow \underset{\mathrm{XXXIV}}{\mathrm{CH_3(CH_2)_4\overset{Li}{C}{=}C{=}CH_2}} \longrightarrow \underset{\mathrm{XXXV}}{\mathrm{CH_3(CH_2)_4CH{=}C{=}CHLi}} \longrightarrow \underset{\mathrm{XXXVI}}{\mathrm{CH_3(CH_2)_5C{\equiv}CLi}}$$

The rearrangement of the monolithio derivative of 2-octyne to the lithio-derivative of 1-octyne, and the obtention of identical dilithio compounds starting with 1- and 2-pentyne show that the formation of identical products from electrophilic reactions of dimetalated 1- and 2-alkynes can proceed by two ways. One possibility is a rearrangement by a 1,3-hydrogen shift of the monolithio allenic compound formed in

$$\underset{\mathrm{XXXVII}}{\mathrm{CH_3(CH_2)_4CHLiC{\equiv}CLi}}$$

the first step of the reaction of the unrearranged dilithio-2-alkyne with an electrophile according to (1) or (2). The reaction can however take also another route (3) where rearrangement by a 1,3-hydrogen shift in the monolithio derivative of 2-alkyne occurs during the metalation leading to similar mono and then dilithio derivatives starting either with 1- or 2-alkynes. The first mechanism was observed with 1-phenylpropyne and the second one with 2-pentyne and possibly 2-octyne.

It seems therefore, that the 1,3-shift in the allenyl-lithium compounds is a general phenomenon and not only limited to the phenyl containing acetylene.[5] Such a 1,3-migration of hydrogen is forbidden in allylic systems but is apparently allowed in an allenic derivative, since allenes are Möbius systems.[8]

The course taken by the reaction depends probably much on the rate of the abstraction of the second proton. When this rate is large as in 1-phenylpropyne then the isomerization of the initially formed terminal propargyl or other allenyl lithium derivatives to the terminal lithium acetylide (Scheme 3) does not occur since this is a relatively slow reaction as found for monolithio-2-octyne (XX). Rearrangement occurs then by the scheme (1) in the allenyllithium compound formed in the first step of the reaction of the unrearranged dilithiated 2-alkyne with an electrophile. However, slow dimetalation as in the case of 2-pentyne favours an isomerization by scheme (3) leading to the same dilithio derivatives starting with 1- or 2-alkyne.

EXPERIMENTAL

All 1- and 2-alkynes used were commercial products (Farchan Res. Lab.). 1-phenyl-3-butyne was prepared by a known procedure.[6]

Solutions of n-BuLi in ether were prepared by evaporating the solvent *in vac.* from a hexane soln. of BuLi (Foote) and by dissolving the residue in ether. The concentration of BuLi in ether was found by titration with sec-BuOH in xylene using benzylamine as indicator.[12]

MeLi solns. were prepared from MeBr and Li metal in ether. The concentration was found by a double titration with HCl and NaOH (phenolphthalein).

Metalations were carried out by addition of the hydrocarbon slowly, with a syringe, to a cooled (– 30°) soln. of BuLi (or MeLi) in ether, under argon and the mixture left to reach room temp. PMR spectra of the anions were recorded at room temp and lower, on Varian T60 or HA100.

Silylation. The metalation mixture was cooled to − 70° and excess trimethylchlorosilane added slowly (syringe). The mixture was left overnight at room temp, then poured on ice. The layers were separated and the organic phase submitted to GLC.

Protonation. H_2O or D_2O was added slowly (syringe) to the cooled metalation mixture which was separated in a manner similar to the reaction with trimethylchlorosilane.

Alkylation. A cooled soln. of MeBr in ether was added in excess to the cooled (− 60°) metalation mixture. The mixture was allowed to reach room temp and then poured on ice or cooled again and reacted with trimethylchlorosilane as above.

Separation of the products were performed by a GLC on a 2m × $\frac{1}{4}$′ column of SE-30 15% on Chromosorb W. We could not separate VII from VIII and elementary analysis was performed on the mixture of the two acids (m.p. 110–123°).

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