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METALATION REACTIONS—VIII

METALATION OF 1,4-ENYNES AND PROTONATION OF THEIR ANIONS

J. KLEIN and S. BRENNER
Department of Organic Chemistry, The Hebrew University, Jerusalem, Israel

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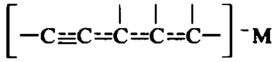
Abstract—A series of 1,4-enynes was prepared and the compounds metalated with butyllithium in ether. The formation of the mono- and dilithio derivatives was studied by PMR and UV. Protonation of the dilithio compounds gave vinylallenes, 1,3- and 1,4-enynes. Isomerisation of the 1,4-enynes in DMSO using dimsylsodium gave vinylacetylenes from compounds containing a terminal double bond and vinylallenes from those with an internal double bond. The sequence of the H—D exchange of the various protons was also studied.

BASE catalysed isomerisation of acetylenes are known and have been studied extensively.[1-8] In the isomerisation of 1,4-enynes it has been shown that the products are conjugated vinylallenes.[9-12] Conjugated vinylacetylenes were obtained in a system containing a propargylic hydroxy group.[13] Carbanions were assumed to be intermediates in these reactions, but the formation of the anions was not studied directly.

Acetylenes have a lower enthalphy than allenes[14] and it is possible that the vinylallenes obtained could be due to the slower isomerisation of these compounds relative to the 1,4-enynes. An effective catalyst system such as methylsulfinyl carbanion in DMSO was therefore used in this study to throw light on the reaction. The advantage of this catalyst is that after proton abstraction, it gives a neutral species which does not form H-bonds. The probability of various additional processes proceeding by internal return or conducted tour mechanism[15-17] during the isomerisation is therefore reduced in this system. Deuterated DMSO was used to indicate the positions of kinetic protonation, since three positions of protonation 1,3 and 5 are available in the intermediate pentenynlic anion (I) giving a vinylallene, a 1,4- or 1,3-enyne respectively.

I 

$$\left[-\mathrm{C}\equiv\mathrm{C}\mathrel{=\!=}\overset{|}{\mathrm{C}}\mathrel{=\!=}\overset{|}{\mathrm{C}}\mathrel{=\!=}\overset{|}{\mathrm{C}}-\right]^{-}\mathrm{M}^{+}$$

Metalation of the enynes and protonation by H_2O of the pentenynyllithium compounds formed was also studied to compare the results of these protonation processes with the catalysis under different conditions.

The enynes (IIa-k) were prepared by a modification[18] of the condensation of the corresponding acetylenemagnesium halide with appropriate allyl halides[19] in the presence of copper (I) chloride.

The IR spectra of II show a weak band corresponding to C≡C stretching at 2225–2250 cm^{-1} and the double bond stretching band at 1640–1655 cm^{-1}. The ≡C—H stretching band appears at 3070 cm^{-1}, but is obscured in compounds containing a phenyl group. The *trans* configuration of IIc and IId is supported by their bands at 970 and 965 cm^{-1} respectively.

The PMR spectra of II (Table 1) show a propargylic allylic methylene. The assignment of signals in compounds containing three vinylic protons was based on the rules,[20] that attribute the sequence of the signals of these protons from higher to lower fields as *trans*, *cis* and vicinal to the methylene group. This assignment is supported by the double resonance on irradiation of the propargylic methylene group and by the coupling constants. The vinylic signal at the highest field of the compounds IIb, IIg, IIh and IIk was assigned to the proton *trans* to the Me group, as previously found.[21]

The UV spectra of II are recorded in Table 2. The spectra of several acetylenes are given for reference and the extinction of the compounds II not containing a Ph group is also recorded at 230 nm, but no maximum appears in their spectra. There is no evidence of interaction between the double bond and phenylacetylene group, but introduction of a Me group on the double bond as in IIb and IIc has a small hyperchromic effect on the 1,4-enyne system. An interesting difference is observed

TABLE 1. THE PMR SPECTRA OF THE 1,4-ENYNES II[a]

Enyne	(R)[b]	(A)	(R')	(B)	(R'')	Coupling Constants Hz
IIa	2·91 (m)	6·92 (d, d)	3·65–4·56 (m) 4·15[c]	4·73 (q)	4·94 (q)	$J_{AR}5$; $J_{R'R''}10$ $J_{R'B}17{\cdot}2$; $J_{BR''}2{\cdot}5$
IIb	2·87 (m)	6·98 (s)	8·21 (s)	5·2 (d)	4·98 (d)	
IIc	2·76 (m)	6·94 (d, d)	4·0 ———	——— 4·9 (m)	8·34 (d, d)	$J_{AR'}$ 5: $J_{BR''}$ 5·5
IId	2·76 (m)	6·8 (d, d)	3·92 (se)	3·32 (d)	2·76 (m)	$J_{AR'}6$; $J_{R'B}16$; $J_{AB}1{\cdot}5$
IIe	2·65 (m)	6·42 (t)	2·64 (m)	4·45 (m)	4·45 (m)	$J_{AB}1{\cdot}5$ $J_{AR''}1{\cdot}5$
IIf	8·8 (s)	7·13 (d)	3·80–4·48 (m)	4·71 (q)	4·94 (q)	$J_{AR'}6$; $J_{R'R''}$ 10 $J_{R'B}16$; $J_{BR''}$ 2·4
IIg	8·8 (s)	7·20 (s)	8·23 (s)	5·22 (m)	5·04 (m)	
IIh	9·11 (t)[f] 8·45–8·85 (m) 7·78–8·13 (m)	7·24 (s)	8·26 (s)	5·3[d]	5·12[d]	
IIi	9·09 (t)[f] 8·34–8·84 (m) 7·66–8·06 (m)	7·14 (m)	3·94–4·52 (m)	4·77 (m)	4·98 (m)	$J_{R'R''}$ 10; $J_{R'B}16$
IIj	9·08 (t)[f] 8·34–8·82 (m) 7·67–8·03 (m)	7·16 (m)	3·88–4·50 (m)	4·77 (m)	4·98 (m)	$J_{R'R}10$; $J_{R'B}16$
IIk	9·07 (t)[f] 8·33–8·80 (m) 7·63–8·07 (m)	7·19 (s)	8·23 (s)	5·23[d]	5·05[d]	

[a] In CCl_4 solution using TMS as internal standard (in τ units).

[b] For R = Ph the position of the central peak is given.

[c] From spin decoupling experiment.

[d] Broad band.

[e] An unclear spectrum of this compound was reported (Ref 45).

[f] First line: Me; second line: aliphatic methylene groups; third line: propagylic methylene group.

TABLE 2. UV SPECTRA[a] OF 1,4-ENYNES II AND ACETYLENES

	λ_{max} nm (ε)
$C_6H_5C\equiv CH$	235(19,600); 241(15,200)s; 246(17,900); 264(430); 271(420); 278(340); 282(180)
$C_6H_5C\equiv CCH_3$	238(23,000); 244(19,000)s; 249(23,000); 266(560); 273(590); 279(410)
$C_6H_5C\equiv CCH_2CH_3$	241(20,000); 247(16,500)s; 252(20,000); 267(560); 274(590); 281(390)
IIa	240(21,000); 250(19,000); 264(650)s; 272(580); 279(420)
IIb	239(17,500); 251(18,000); 266(1800)s; 272(1850)s; 279(2000); 294(1500)
IIc	239(17,500); 244(15,000)s; 251(17,000); 266(2150)s; 272(2750); 279(1900); 289(2000)
IId	239(25,000)s; 254(31,000); 293(1800); 305(450); 327(310)
IIe	240(60,000); 251(57,000); 272(1410); 279(950); 306(420); 326(280)s
$HC\equiv C(CH_2)_3-CH_3$	212(810); 230(160)r
$CH_3CH_2C\equiv CCH_2CH_3$	220(280); 230(250)r; 235(200)s; 246(120)s
IIf	223(73); 229(72)
IIg	230(210)
IIh	224(150); 230(140)r
IIi	230(74)r
IIj	230(125)r
IIk	230(125)

[a] In ethanol; s – shoulder; r – extinction reported for reference, not at a maximum.

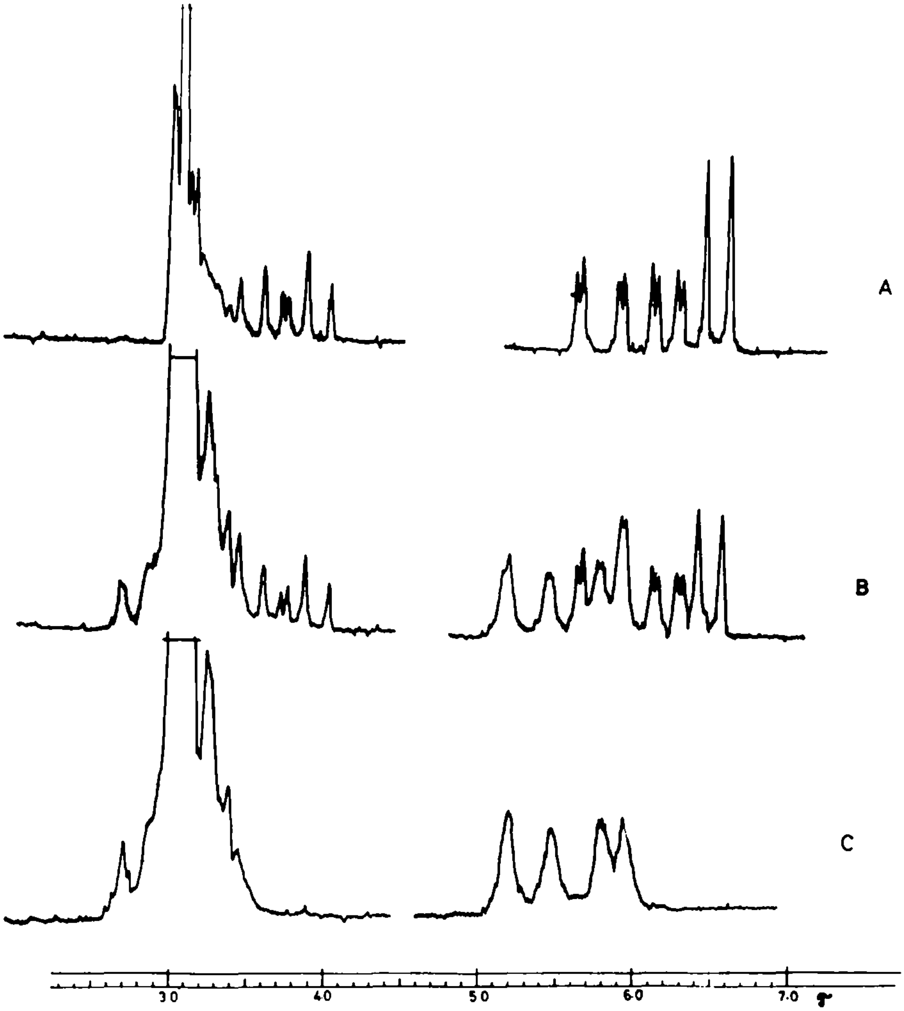


FIG 1. NMR spectrum of a solution formed by addition at −90° of 100 mg of IIa to 1 ml of 3·0 F butyllithium in deuterated ether. The spectrum was recorded at 38°: (A) 3 min after the addition of IIa (monoanion IIIa); (B) 30 min after the addition of IIa; (C) 120 min after the addition of IIa (dianion IVa).

TABLE 3

Compound	Monolithium derivative		Dilithium derivative	
	λ max (nm)	ε max	λ max (nm)	ε max
IIa	399	10,000	426	9,000
IIb	402	15,000	428	10,000
IIc	382	9,000	405	6,000
IId	474	42,000	503	33,000
IIe	431	16,000	374	13,000

between the spectra of IIe and IId. The first compound has a head to tail arrangement of the phenylacetylene and styrene chromophores and shows large extinctions at 240 and 251 nm, that are approximately the sum of extinctions of the two chromophores, whereas the two chromophores of IId are in a head to head arrangement and the corresponding extinctions are not enhanced significantly relative to the compounds containing one Ph group only.

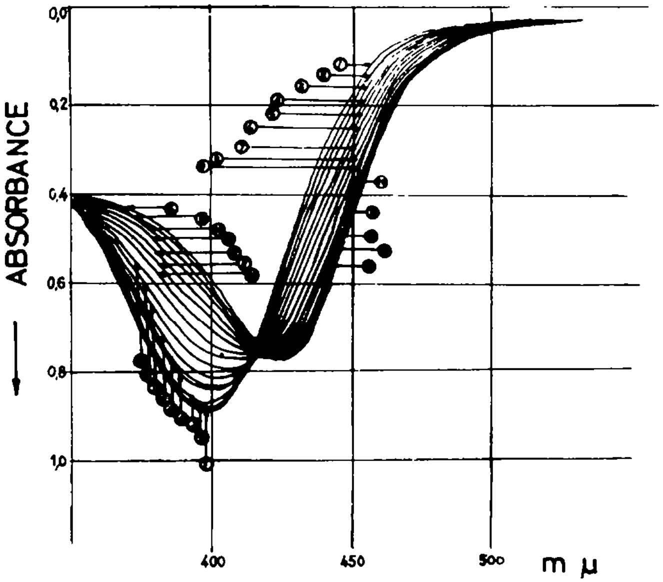


FIG 2. Absorption spectra on metalation of IIa at 25° in ether. Initial concentrations: IIa: $8 \cdot 8 \times 10^{-5}$ M. Butyllithium: 0·053 F.

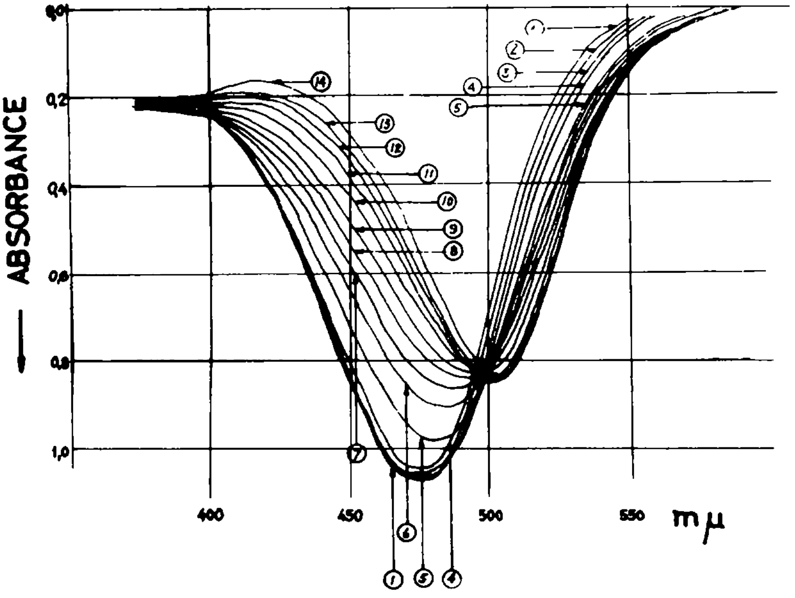


FIG 3. Absorption spectra on metalation of IId at 25° in ether. Initial concentrations: IId: $2 \cdot 25 \times 10^{-5}$ M. Butyllithium: 0·053 F.

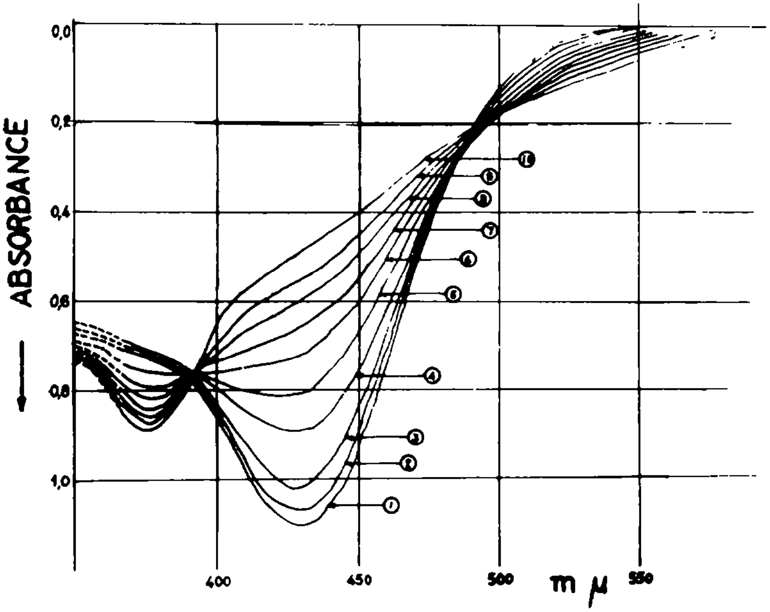
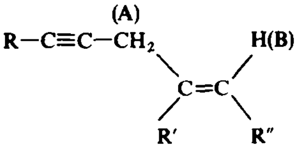


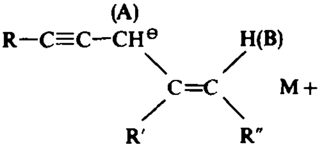
Fig 4. Absorption spectra on metalation of IIe at 25° in ether. Initial concentrations: IIe: $6{\cdot}9 \times 10^{-5}$ M. Butyllithium: 0·053 F.

The metalation of the enynes II with butyllithium in ether solution is fast and can be observed in the PMR spectrum of the solution.[22] Fig 1 shows the spectrum of the mixture of IIa and butyllithium in ether-d_{10}. The monoanion IIa, but no starting materials, is observed after 3 min and after 2 hr the dianion IVa only is found in the solution. A discussion of the PMR spectra of these compounds was published[22] in a preliminary communication.

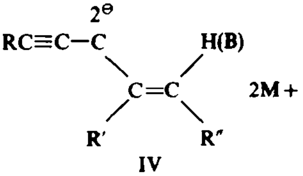
The formation of the anions (III and IV) can be observed in dilute solutions by their UV and visible spectra. The enynes II were added directly to an excess of a solution of butyllithium in ether in the measuring cell of a UV spectrophotometer and the spectra of the solution were recorded at varying intervals (Figs 2, 3 and 4). Instantaneously after mixing of the components a strong absorption peak was formed at a region where the starting materials did not absorb. The intensity of this band then decreased and a new band was formed. The new band corresponded to that of the dianion IV, since the same absorption band was obtained on dilution of a solution containing IV, as determined by PMR.[22] The first band therefore belonged to the monoanion III.[22] The isosbestic points in the figures support the occurrence of a transformation of one species into another without interfering reactions under the conditions studied. The results obtained for a series of enynes (IIa–e) are given in Table 3. The transformation of the mono into the dilithium derivatives is accompanied in all compounds, except one, by a bathochromic shift of 23–29 nm. A hypsochromic shift of the main band was observed in one of the compounds (IIe) studied. The presence of a Ph substituent on the even-numbered carbon atom apparently introduces a profound perturbation into the system. It seems however that an absorption band, although of low intensity, is present at higher wavelength as shown by the appearance of a second isosbestic point



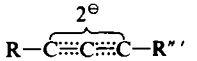
II



III

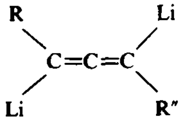


IV

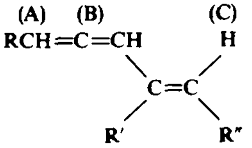


$$R{-}\overbrace{C\cdots C\cdots C}^{2\ominus}{-}R''$$

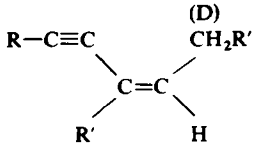
V



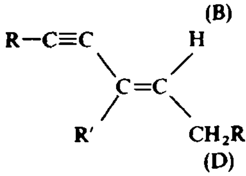
VI



VII



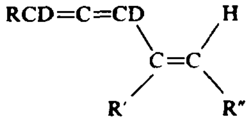
VIII



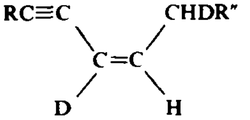
IX

$R{-}C{\equiv}CCD_2CR'{=}CHR''$

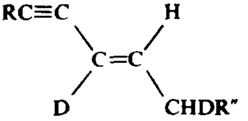
X



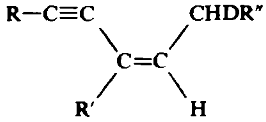
XI



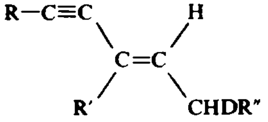
XII



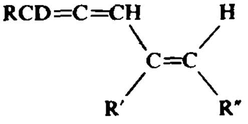
XIII



XIV



XV



XVI

a: R = Ph; R' = R'' = H
b: R = Ph; R' = CH_3; R'' = H
c: R = Ph; R = H; R'' = CH_3
d: R = R'' = Ph; R' = H
e: R = R' = Ph; R'' = H
f: R = Me_3C; R' = R'' = H
g: R = Me_3C; R' = Me; R'' = H
h: R = $CH_3(CH_2)_5$; R' = Me; R'' = H
i: R = $CH_3(CH_2)_5$; R' = R'' = H
j: R = $CH_3(CH_2)_3$; R' = R'' = H
k: R = $CH_3(CH_2)_3$; R' = Me; R'' =

in this case. A Ph group in the terminal position [IId] causes a bathochromic shift of 70 nm in the mono- and di-lithium derivatives relative to the parent compound (IIa). A Me group in the 4-position has no appreciable effect on the spectra, but a terminal one causes an appreciable hypsochromic shift (17 nm) in the monoanion and this is even higher in the dianion. This effect of a Me substituent on the spectra of allylic anions has been observed before.[23]

There is some doubt whether the bathochromic shift on dianion formation reflects the real difference between the absorption of the mono- and di-anions. Shifts of similar magnitude have been found before by changing the temperature[24] the counterion,[24–26] the solvents[27] or by specific solvation[28–30] and formation of various solvated species.[25] The solvation and dissociation of the mono- and di-lithium derivatives may be different. However, the constancy of the shift in different systems including compound IId which contains an additional conjugated Ph group and where the charge dispersal and solvation is probably different, seems to indicate that there is a difference between the spectra of the mono- and di-anions. This conclusion is in agreement with the known spectrum of phenyllithium[23] where a bathochromic shift relative to benzene was found for the π–π^* transition.

The structure of the dianions (IV) has been discussed[22] in connection with their PMR spectra which indicate a larger electron localization in the three atom segment of IV, not containing the vinyl group, than in the same segment of the monoanion III. "Extended acetylene" structure V with four bonds in one straight line was attributed to IV. Such a geometry probably permits better overlap between orbitals on adjacent carbons and formation of stronger bonds thus causing the localization of the charges in the extended acetylene segment. Recently, West[31] has found strong bands at 1870 and 1770 cm^{-1} in the IR spectrum of dilithio- and trilithiopropyne respectively, which seem to indicate an allenic structure (VI) for these compounds or at least the presence of compounds of such structure in the polylithioacetylenes. It is possible that the free ions have structure V, whereas the undissociated compound assumes the allenic geometry due to the partial covalent character of the C-Li bond.

Protonation of IVa was carried out by three procedures: (a) slow addition of water to the ether solution of IVa at low temperatures (b) dropwise addition of the solution of IVa from a syringe to ice and (c) addition of precooled methanol to the solution of IVa at $-50°$. All these procedures gave similar results, namely 3–9% IIa, 50–56% of the vinylallene (VIIa), 27–30% of a mixture of approximately equal amounts of the *cis* and *trans* conjugated enynes (VIIIa and IXa) and 11–15% of addition products. Deuteration of IVa by addition of D_2O gave similar amounts of dideuterated products (Xa, XIa, XIIa and XIIIa), thus proving that the dianion is the species protonated. No appreciable interconversion between the products occurred during protonation, as evidenced by the similar results obtained by the various procedures and also by the absence of isomerisations of the least stable isomer (IIa) on treating it with lithium hydroxide under similar conditions.

It can therefore be assumed that the compounds obtained on protonation of IVa are the kinetically formed products. Only the vinylallene VIIa could have been formed by first step protonation at the carbon near the Ph group. The three other products (IIa, VIIIa and IXa) are the product of a first step protonation at the 3 or 5 positions. This course of reaction is different from the silylation of the dianions IV inferred to proceed first at the 1-position.[32] Also the protonation dilithio-1-phenylpropyne first occurred at the carbon near to the phenyl.[33] It appears therefore that the position of attack on IV depends on the reagent.

Treatment of IVb with water gave 15% IIb, 55% VIIb and 30% VIIIb and IXb. Protonation of IVg in a similar manner gave no IIg, 60% VIIg and 40% VIIIg and IXg; the last reaction is out of line since it seems to favour protonation near the bulky t-Bu group.

The protonation of the monolithio derivatives (III) was not studied, since these compounds were always accompanied by large amounts of IV, even when equimolar amounts of butyllithium were used for metalataion of II.

The isomerisation of II in DMSO was carried out using catalytic amounts of a solution of methylsulfinyl carbanion.[34] The isomerisation was followed by PMR. Vinylallenes (VII) and in some cases vinylacetylenes (VIII and IX) were formed very rapidly and after a few minutes no starting material was observed. A subsequent transformation was then observed in most cases which led to the disappearance of the allenes VII and formation of vinylacetylenes. After 15 min no further change in the spectrum occurred, even when the solution was left for 24 hr. The final products of isomerisation are recorded in Table 4. PMR spectra of the vinylallenes are recorded in Table 5, and the PMR and UV spectra of the conjugated enynes in Table 6. These spectra determine unequivocally the structure of the products.

TABLE 4. PRODUCTS OF ISOMERIZATION OF II IN DMSO SOLUTION

Starting material	Final product
IIa	VIIIa (60%); IXa (40%)
IIb	VIIIb
IIc	VIIc
IId	VIId
IIf	VIIIf
IIg	VIIIg
IIh	VIIIh (60%), IXh (40%)

TABLE 5. PMR SPECTRA OF VINYLALLENES

Compound	Chemical shifts[a] τ					Coupling constants Hz
	R	A, B	R′	C	R″	
VIIa[c, d]	2·78 (m)[b]	3·8[b]	3·65 (m)	4·71 (q)	4·95 (q)	$J_{R'C}$17 $J_{R'R''}$10 $J_{CR'}$ 1·5
VIIb[d]	2·88 (m)[b]	3·76 (s)	8·26 (s)	5·18	5·09	$J_{CR'}$4·5
VIIc	2·81 (m)[b]	3·59		4·66 (m)[f]	8·33 (d)	$J_{CR'}$ 6·0
VIId	2·74 (m)[b]	3·30		3·67 (m)[f]	2·74 (m)[b]	
VIIf	9·13 (t)[e] 8·66 (m) 7·99 (m)	4·25 (m) A 4·74 (d) B	8·27 (s)	5·33	5·23	J_{AB}7·0 $J_{CR'}$ 5·0
VIIg	8·95 (s)	4·06 (d) 4·62 (d)	8·15–8·32 (m)	5·22	5·14	J_{AB}6·6

[a] In DMSO, using TMS as internal standard.

[b] Position of the main peak.

[c] This spectrum was analyzed with the aid of XIa.

[d] ν_{max} 1930 cm^{-1}.

[e] Downwards: methyl, aliphatic methylenes and allylic methylene.

[f] No separate assignment to the protons was possible.

TABLE 6. SPECTRA OF VINYLACETYLENES

Compound	Chemical shifts[a] τ				Coupling constants Hz	cm^{-1} λ_{max} nm (ε)
	R	A	B	C		
IXa	2·82 (m)[b]	4·45 (d)	3·88 (oct)	8·20 (d)	J_{AB}16 J_{BC}6	2185–2190, 950 (s) 272(23,000) 287(18,500)
VIIIa	2·82 (m)[b]	4·43 (d)	4·07 (oct)	8·09 (d)	J_{AC}10 J_{BC}6·5	2185–2190 272(23,000) 287(18,500)
VIIIb	2·83 (m)[b]	4·65 (s)	8·07 (s)	8·00 (s)		2195 277(22,000) 294(18,500)
VIIIf	9·11 (t)[c] 8·63 (m) 7·74 (m)	4·91 (s)	8·19 (s)	8·26 (s)		2200 232(8400)
VIIIg	8·76 (s)	4·84 (s)	8·15 ——	8·32		
IXh	8·78 (s)	4·61 (q)	4·01 (oct)	8·23 (q)	J_{AB}16 J_{BC}6·5 J_{AC}1·5	2200, 955 (m)
VIIIh	8·76 (s)	4·58 (q)	4·12 (oct)	8·19 (q)	J_{AC}10 J_{BC}6·5 J_{AB}1·2	2200

[a] In CCl_4, using TMS as internal standard.

[b] Main peak.

[c] Downwards: Signals of methyl, aliphatic methylenes, propargylic methylene.

Conjugated enynes were formed as final products in almost all cases. In two cases, where no terminal methylene group was present, only vinylallenes VIIc and VIId were produced. It is possible that VIId is not isomerised, since conjugation with phenyl would then be lost. We do not know whether the unchanged vinylallene VIIc is the most stable isomer or whether much more stringent conditions have to be used to isomerize VIIc to VIIIc and IXc. It is clear however, that the presence of a terminal methylene either provides the driving force for isomerisation by the difference of energy between a terminal and internal double bond or enhances the rate of proton abstraction by the stabilization of the intermediate anion which is larger on a methylene than on a methine group.

The *cis* enynes VIIIa and VIIIh were obtained in larger amounts than their *trans* isomers (ration 3:2). This fact reflects the greater stability of *cis*-allylic anions.[35, 36]

It is of interest that isomerisation of IIi did not give undec-1-en-3-yne by abstraction of the allenic proton at the 3 and protonation at the 5 position. It seems therefore that the abstraction of the allenic proton from the carbon away from the vinyl group is much faster.

The isomerisation of II was also studied in DMSO-d_6 uding the catalyst[34] prepared in the same solvent. The products were analysed by GLC and PMR. Integration of the signals has permitted us to evaluate the extent of exchange of each kind of proton.

TABLE 7. ANALYSES OF PRODUCTS OF THE REACTIONS

$RC{\equiv}CMgB + XCH_2{\cdot}C(R') = CHR'' \rightarrow II$

Compound	X	Yield %	b.p. (mm)	Analyses found	Analyses calc.	Ref.[a]
IIa	Br	64	60° (0·3)	C = 92·89 H = 7·30	C = 92·96 H = 7·04	19, 41, 43
IIb	Cl	60	80–82° (0·3)	C = 92·94 H = 7·60	C = 92·31 H = 7·69	41
IIc	Cl	64	80° (0·3)	C = 92·44 H = 7·65	C = 92·31 H = 7·69	
IId	Br	39	160–165° (1)	[b]		
IIc	Br	22[c]	140° (0·8)	C = 93·34 H = 6·14	C = 93·58 H = 6·42	
IIf	Br	40	99–100°	C = 88·33 H = 11·47	C = 88·52 H = 11·48	44
IIg	Br	35	50° (20)	C = 88·55 H = 11·80	C = 88·23 H = 11·77	
IIh	Cl	65	70° (0·3)	C = 87·70 H = 12·25	C = 87·80 H = 12·20	
IIi	Br	60	190–194°	C = 87·71 H = 11·76	C = 88·00 H = 12·00	
IIj	Br	42	145°	C = 88·43 H = 11·43	C = 88·50 H = 11·50	19, 43
IIk	Cl	40	65–68° (20)	C = 88·07 H = 11·68	C = 88·22 H = 11·78	

[a] For known compoupds.

[b] Traces of cinnamyl bromide did not permit to obtain a correct analysis.

[c] Solidifies on trituration with hexane, m.p. 54°.

Isomerisation of IIa in DMSO-d_6 yielded XIVa and XVa, containing approximately 45% of XIIa and XIIIa. The latter compounds were probably formed by partial exchange of the allenic protons in XVIa or the methylene protons in IIa before isomerisation to the conjugated enynes.

A similar isomerisation of IIb gave a mixture of XIVb + XVb (55%) and XIIb + XIIIb (45%). The vinylic proton in XIVb and XVb is then also exchanged after an additional few minutes giving XIIb and XIIIb. This reaction did not occur by abstraction of a proton from a Me with formation of pentenynylic anion since the anion should be protonated on the terminal carbon preferentially, as it was at the beginning of the isomerisation. From the two other possible mechanisms, direct exchange of the vinylic proton or a base catalyzed addition and elimination e.g. of the solvent to the double bond, the latter is preferred since the exchange is accompanied by the equilibration of XIVb and XIVc initially obtained in unequal quantities. Prolonged exposure of the enynes XIIb and XIIIb to the catalyst (24 hr) exchanges almost all protons of the Me groups.

During isomerisation of IIc in DMSO-d_6, the vinylallene XVIc was formed first. The second allenic proton was then exchanged rapidly to give XIc. Similarly, the vinylallenes (XVId and XId) were obtained consecutively from IId. The vinylic proton near the Ph group was also exchanged during this treatment, thus proving that the reaction is reversible under these conditions and the vinylallene is the most stable isomer.

An isomerisation without H–D exchange was found in IIh, and gave in DMSO-d_6 the vinylacetylenes (VIIIh and IXh) in a 3:2 ratio. A possible explanation for this behaviour is the insolubility of IIh in DMSO; the reaction proceeds then in the bulk of IIh, after abstraction of one proton from the substrate. The protons are then transferred from one molecule of IIh to another. Similar proton transfers between molecules and their conjugate anions in DMSO solution have been recorded.[8, 37, 38]

In conclusion, the following sequence can be inferred for the isomerisation of 1,4-enynes in DMSO with methylsulfinyl carbanion as catalyst. The carbanion formed by proton abstraction from the propargylic–allylic methylene group is protonated at the extremities of the system (1 and 5 positions) giving vinylallenes and vinylacetylenes. In some cases, deuterium was also introduced partly at the 3 position, showing that protonation also occurrs at this position in these cases. The vinylallene was then isomerised further to the vinylacetylene in all cases with a terminal olefin methylene group (in II). The vinylallene can also exchange both allenic protons with deuterium. H–D base catalysed exchange of the vinylic protons on the carbon vicinal to the acetylene group of the vinylacetylenes was also observed as a slower process. Finally, no triple bond migration with formation of a terminal conjugated enyne system was observed, due to the different kinetic acidity of the two allenic protons.

EXPERIMENTAL

The terminal acetylenes used were commercial products (Farchan Ltd.).

Preparation of 1,4-*enynes*. The reaction sequence was performed under argon in a flask fitted with a dropping funnel, a reflux condenser and a magnetic stirrer. EtMgBr was prepared from Mg and EtBr in THF, dried by refluxing over CaH_2 and redistilled. The soln was then heated to 50–60° and the 1-alkyne (equimolar amount) added dropwise. The mixture was left for 1 hr after the evolution of gas stopped. 0·2 g of copper (I) chloride was then added and the mixture stirred for an additional 30 min. The allylic halide (equimolar amount) dissolved in THF was then added dropwise. The soln was kept at 50–60° during this addition and during 3 hr of subsequent stirring, then cooled and poured on ice and acidified with H_2SO_4. The products were extracted with ether and the ether layer washed with $NaHCO_3$ aq and water, then dried and distilled. The b.ps and analyses of the products are given in Table 8. These products should be kept under N_2 in dark bottles.

Butyllithium in hexane (Foote Co.) was titrated with 1 M BuOH in xylene, using 1,10-phenanthroline as an indicator.[39] For solns in ether, benzylamine was used as an indicator.[40]

Solutions of butyllithium in ether-d_{10}. A flask fitted with a rubber-capped injection port and connected through a 3-way stopcock to a vacuum line was purged with N_2, then evacuated. A soln of BuLi in hexane was then added and the flask immersed in a water bath and the solvent pumped off until a stable low pressure was obtained. The flask was then cooled to −50°, N_2 introduced and ether injected.

The PMR spectra were taken in a rubber capped tube which was flushed with N_2. The BuLi soln approximately 3·0 F was injected into the tube and cooled to −90°. 100 μl of II were then injected, the tube was removed from the bath and the spectra were measured at 36°.

The formation of the anions was followed in the UV by injecting the appropriate amount of a solution of II to a 0·05 F soln of BuLi in ether at room temp and the spectrum recorded in intervals of a few min at first and subsequently at longer intervals. The extinction recorded in Table 3 is based on the assumption that all of the enyne is converted to III and at the end to IV.

Isomerisation of II. To a soln of II in 10 ml DMSO two drops of the catalyst[34] were added and the soln left for a period of several seconds to several minutes. Water was then added and the product extracted with ether. The ether soln was washed several times with water. The products were analysed and separated on a 3 m × $\frac{1}{4}$′ column of polydiethylene glycol succinate 20% on Chromosorb P.

The isomerisation in DMSO-d_6 was carried out in small amounts in NMR tubes.

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