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^{1}H and ^{13}C NMR Spectra and One-Bond ^{13}C,^{13}C Coupling Constants of (*E*)-2-Alken-4-yn-1-ols, (*E*)-2-Alken-4-yn-1-yl Acetates and (*E*)-2-Alken-4-yn-1-als†

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^{13}C and some selected ^{1}H NMR chemical shifts of conjugated (*E*)-enynes of the type of (*E*)-2-alken-4-yn-1-ols ($RC{\equiv}CCH{=}CHCH_2OH$; R = H, Me, Et, *n*-Pr, *n*-Bu, $SiMe_3$), (*E*)-2-alken-4-yn-1-yl acetates ($RC{\equiv}CCH{=}CHCH_2OAc$; R = H, Me, Et, *n*-Pr, *n*-Bu) and (*E*)-2-alken-4-yn-1-als ($RC{\equiv}CCH{=}CHCH{=}O$; R = Et, *n*-Pr) and of (2*Z*,4*E*)-deca-2,4-dien-6-yne as a conjugated (*Z*,*E*)-dienyne were measured. The unequivocal assignment of the ^{13}C NMR chemical shifts is based on the application of standard techniques such as H,H-COSY, C,H-COSY and APT and, above all, on the investigation of the C,C connectivities by determination of the one-bond ^{13}C,^{13}C coupling constants $^{1}J_{C,C}$. These coupling constants show typical values for the different structural fragments. The effect of increments of the alkyl group on the resonances of the acetylenic carbon atoms are compared with those of the *n*-alkynes. The shift effects observed on going from (*E*)-2-alken-4-yn-1-ols to (*E*)-2-alken-4-yn-1-als are discussed in comparison with results from other classes of compounds. © 1997 John Wiley & Sons, Ltd.

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Keywords: NMR; ^{13}C NMR; $^{1}J(^{13}C,^{13}C)$ coupling constants; (*E*)-2-penten-4-yn-1-ol; (*E*)-2-alken-4-yn-1-ols; (*E*)-2-alken-4-yn-1-yl acetates; (*E*)-2-alken-4-yn-1-als

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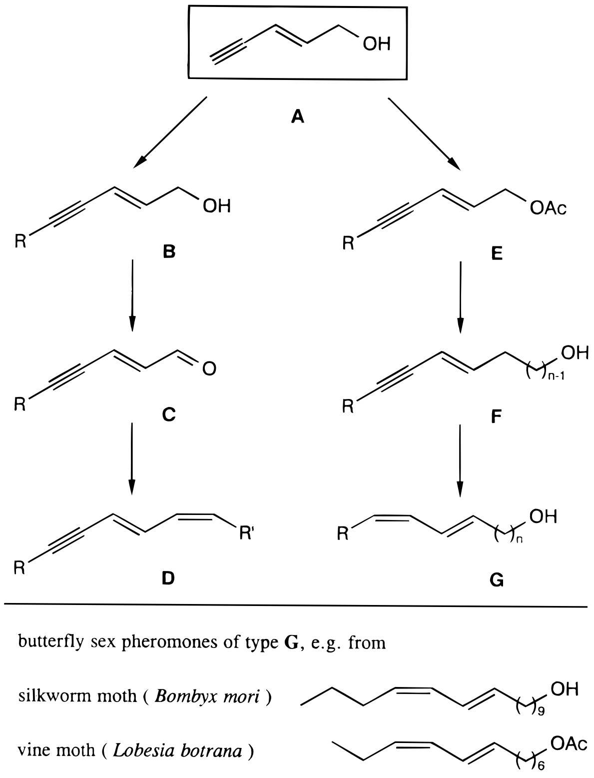
INTRODUCTION

(*E*)-2-Penten-4-yn-1-ol (**A**) can be synthesized isomerically pure from epichlorohydrin and sodium acetylide in liquid ammonia.[1,2] This stereochemically defined high functionalized compound has been used in the syntheses of natural products, e.g. eicosanoides.[3] We designed syntheses of olefinic natural products, such as butterfly sex pheromones, derived from **A** (Scheme 1). **A**, protected as the tetrahydropyranyl ether (THP ether), is easily alkylated and can be transferred into the (*E*)-2-alken-4-yn-1-ols **B** and (*E*)-2-alken-4-yn-1-yl acetates **E**. The alcohols **B** were oxidized with pyridinium dichromate (PDC)[4] to the (*E*)-2-alken-4-yn-1-als **C**. These aldehydes yield, by Wittig olefination, the (*Z*,*E*)-dienynes **D**, which can serve as interesting precursors for conjugated trienes. The acetates **E** should be transformable by a stereo- and regioselective chain lengthening[5,6] to the (*E*)-alkenynols **F** and allow, by hydrogenation, e.g. the synthesis of conjugated (*E*,*Z*)-dienpheromones of the type **G**. To this class of compounds belong the



Scheme 1.

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† Dedicated to Professor Dr Reiner Radeglia, Bundesanstalt für Materialforschung und prüfung (BAM), Berlin, on the occasion of his 60th birthday.

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pheromones of the vine moth (*Lobesia botrana*)[7] and of the silkworm moth (*Bombyx mori*), the latter being the first structurally elucidated pheromone.[8,9] In spite of the considerable synthetic potential of (*E*)-2-penten-4-yn-1-ol and its derivatives, apart from one report[10] no ^{13}C NMR data are known.

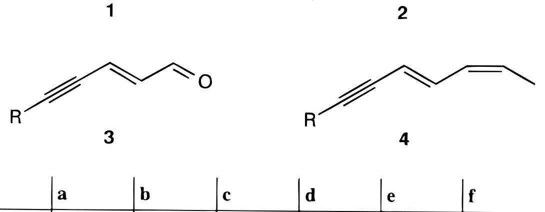
RESULTS AND DISCUSSION

Continuing our investigations on pheromone syntheses[11] and NMR studies of pheromones and other olefinic natural products,[12,13] cycloolefins[14,15] and alkynols,[16] we measured and assigned unequivocally the ^{13}C NMR spectra of the (*E*)-2-alken-4-yn-1-ols **1a–f**, (*E*)-2-alken-4-yn-1-yl acetates **2a–e**, (*E*)-2-alken-4-yn-1-als **3c** and **d** and (2*Z*,4*E*)-deca-2,4-dien-6-yne (Scheme 2, Table 1).

The ^{13}C NMR chemical shift assignment of the CH_2O (**1**, **2**), ester (**2**) and carbonyl signals (**3**) is completely unproblematic. Olefinic carbon atoms can be easily assigned by C,H shift correlation spectra (**2d** and **e**, **3d**) caused by the clear distinction of the olefinic protons through their different coupling patterns.

For this reason, the ^1H NMR parameters of some selected compounds were measured (Table 2), viz. the alcohols **1a** and **b**, the acetates **2a** and **b** and the aldehyde **3c**. In **1** and **2**, the ^1H NMR signals at about 6.2 ppm (dt) correspond to the 2-H position and those at about 5.7 ppm yield from the 3-H position. Compound **3c** shows a double doublet at 6.4 ppm (2-H) and a multiplet at 6.66 ppm (3-H). The vicinal $^1H,^1H$ coupling constant $^3J_{2,3}$ with values of around 15.9 Hz is typical for (*E*)-olefins.[12–15,17] An allylic coupling $^4J_{1,3}$ could be observed in some cases only. The long-range couplings $^4J_{3,5}$ (**1**) and $^5J_{3,6}$ (**2**, **3**) through the triple bond gave values of about 2 Hz. This is in a good agreement with values from other acetylenes.[18]

The assignment of the C≡C signals without any comparable data is only possible for the terminal acetylenes **1a** and **2a**, caused by their significantly more intensive signals for C-5 atoms in contrast to the C-4 position. Methods such as HMBC based on the selective use of long-range C,H couplings are not suitable to yield unequivocal information in these conjugated compounds with their widely varying long-range relations. For this reason we determined the carbon–carbon connectivities from the one-bond $^{13}C,^{13}C$ couplings. The high solubility and the high purity of the substances allowed the measurement of the $^{13}C,^{13}C$ coupling constants directly from the ^{13}C satellites. In this way, the determination of all $^1J_{C,C}$ coupling constants was possible in one experiment only; the use of INADEQUATE techniques[19] was not necessary, because they were expected not to give complete information in a single experiment because of the substantial differences in the $^1J_{C,C}$ coupling constants of the compounds investigated. The observation of the ^{13}C satellites was prevented only in a few cases by impurities or signal overlap. In most cases these measurements were carried out in acetone-d_6, in order to exclude the overlapping of acetylene signals with the $CDCl_3$ signal at 77 ppm. Decisive for the evaluation was an unequivocal assignment of the CH_2O and CHO signals, respectively, in position 1 as the starting point. $^1J_{C,C}$ coupling constants were measured for **1b**, **d** and **f**, **2b** and **c**, **3c** and **d** and **4d** (Table 1). The wide range of $^1J_{C,C}$ values reflects the large bandwith of carbon atoms in different bonding situations. The $^1J_{C,C}$ couplings show typical values for different structural fragments and vary in only narrow limits. They depend, as is well known, on the hybridization and the particular bonding type of the coupling carbon atoms (Table 3)[19–24] (for comprehensive reviews on one-bond coupling constants, see Refs 25 and 26). The olefinic carbon atoms are coupled with 70–75 Hz through the double bond, the olefinic and the acetylenic carbon atoms with 84–92 Hz through the single bond and the sp-hybridized carbon atoms with 177–181 Hz through the triple bond. The significantly smaller value of 136.3 Hz for the trimethylsilylacetylene **1f** is typical for such structures caused by the dependence of the coupling constant in C≡C fragments on the product of electronegativities of the substituents[22] (for a review on NMR parameter of acetylenes, see Ref. 27).



	a	b	c	d	e	f
R	H	Me	Et	*n*-Pr	*n*-Bu	$SiMe_3$

Scheme 2.

The assignment of the very closely spaced ethyl signals of **1c**, **2c** and **3c** was carried out using the APT technique. The *n*-propyl and *n*-butyl signals of **2d** and **e** and **3d** and the olefinic carbon atoms of the (*Z*)-double bond in **4d** were assigned by H,H- and C,H-COSY spectra.

The αC–δC increments (C-5 position) and α′C–δ′C increments (C-4 position) describe the influence of the alkyl substituents on the ^{13}C NMR chemical shifts of the acetylenic carbon atoms in **1** and **2**, respectively (for the mean values of the rows **1a–e** and **2a–e** see Table 4). Examples are given for **1d** and **2c**:

1d: $\delta(^{13}C\text{-}5) = 77.91 + \alpha C + \beta C + \gamma C = 91.03$ ppm (exp.: 90.91 ppm);

2c: $\delta(^{13}C\text{-}4) = 80.75 + \alpha' C + \beta' C = 76.93$ ppm (exp.: 77.03 ppm).

A comparison with the corresponding increments for *n*-alkynes[28] shows that in the conjugated (*E*)-enynes **1** and **2** the acetylenic alkyl substituted carbon atoms (C-5) are more strongly and the neighbouring acetylenic carbon atoms (C-4) are weakly influenced (Table 4).

The strong deshielding of the sp-hybridized carbon atoms by the trimethylsilyl group (**1a** → **1f**; α, 17.05; β, 21.54) is in a good agreement with the system HC≡CH/HC≡CSiMe$_3$ (α, 18.2; β, 21.2)[27] and the (*E*)-isomers HC≡CCH=CHMe/Me$_3$SiC≡CCH=CHMe (α, 16.4; β, 21.5).[29]

The transition from the alcohol **1c** to the α,β-unsaturated aldehyde **3c** results in hardly any changes on carbon atom C-2 but, as expected, in strong deshielding

Table 1. ^{13}C NMR chemical shifts of compounds 1a–f, 2a–e, 3c and d and 4d (ppm, in $CDCl_3$) and one-bond ^{13}C,^{13}C coupling constants (Hz) of 1b, d and f, 2b and c, 3c and d and 4d (1b and 4d in $CDCl_3$, 1d and f, 2b and c and 3c and d in acetone-d_6)

						Chemical shifts (ppm)						
Compound	R	1	2	3	4	5	6	7	8	9	10	Others
1a	H	62.10	143.66	108.80	81.52	77.91						
1b	Me	62.16	140.12	110.57	77.44	86.25	3.80					
1c	Et	62.32	140.12	110.69	77.60	92.16	12.78	13.58				
1d	*n*-Pr	62.55	140.13	110.91	78.41	90.91	21.99	21.17	13.32			
1e	*n*-Bu	61.86	139.93	110.43	78.17	90.40	18.57	30.41	21.53	13.08		
1f	$SiMe_3$	62.30	142.93	110.00	103.06[a]	94.96[b]						−0.23 ($SiMe_3$)[c]
2a	H	63.32	138.11	111.79	80.75	78.63						170.07; 20.45 (OAc)
2b	Me	63.77	134.59	113.99	76.90	87.33	3.84					170.13; 20.45 (OAc)
2c	Et	63.74	134.50	113.99	77.03	93.06	12.67	13.40				170.03; 20.37 (OAc)
2d	*n*-Pr	63.91	134.54	114.19	77.91	91.87	21.11	21.87	13.25			170.27; 20.57 (OAc)
2e	*n*-Bu	63.88	134.48	114.17	77.73	91.96	18.78	30.46	21.71	13.33		170.20; 20.53 (OAc)
3c	Et	192.75	138.35	133.17	76.70	107.59	13.03	12.58				
3d	*n*-Pr	193.18	138.67	133.64	77.75	106.84	21.40	21.66	13.17			
4d	*n*-Pr	13.11	127.43	128.79	135.09	111.32	80.01	92.31	21.35	22.06	13.16	

						^{13}C,^{13}C coupling constants (Hz)						
	R	1	2	3	4	5	6	7	8	9	10	Others
1b	Me	46.5	46.2; 74.5	74.4; 90.4	90.1; 180.1	180.3; 68.4	68.5					
1d	*n*-Pr	46.1	46.1; 74.5	74.5; 90.1	90.1; 176.8	176.8; 66.4	—[d]	—[d]	34.8			
1f	$SiMe_3$	45.6	45.7; 74.1	73.9; 84.6	83.5; 136.3	136.3						
2b	Me	48.4	48.4; 74.6	74.7; 90.6	90.5; 180.6	180.8; 68.3	68.2					59.5 (OAc)
2c	Et	48.4	48.2; 74.6	74.6; 90.3	90.3; 177.3	177.4; 67.0	67.0; —[d]	—[d]				59.5 (OAc)
3c	Et	53.4	53.4; 70.4	70.3; 91.3	91.2; 177.8	177.8; 65.8	66.0; 37.0	37.0				
3d	*n*-Pr	53.4	53.4; 70.4	70.4; 91.2	91.2; 177.6	177.6; 65.7	65.7; 37.4	—[d]	34.9			
4d	*n*-Pr	42.3	42.2; —[d]	—[d]; 56.0	56.4; 73.5	73.5; 91.5	91.5; 176.7	176.7; 67.3	67.3; —[d]	—[d]; 35.0	35.0	

[a] $^2J_{4,\,Si}$: 16.5 Hz.
[b] $^1J_{5,\,Si}$: 85.0 Hz.
[c] $^1J_{Me,\,Si}$: 56.3 Hz.
[d] Not observed.

Table 2. ^{1}H NMR chemical shifts (ppm) and selected ^{1}H,^{1}H coupling constants (Hz) of compounds 1a and b, 2a and b and 3c

Compound	1	2	3	5	6	7	Others	$^3J_{1,2}$	$^4J_{1,3}$	$^3J_{2,3}$	$^4J_{3,5}$ or $^5J_{3,6}$
1a[a]	4.16 (d)	6.32 (dt)	5.72 (dd)	2.94 (d)			3.44 (s, OH)	4.7		16.0	1.7
1b[a]	4.09 (d)	6.10 (dt)	5.65 (m)		1.93 (d)		3.77 (s, OH)	4.9		15.9	2.3
2a[b]	4.60 (dd)	6.25 (dt)	5.77 (m)	3.33 (d)			2.04 (s, OAc)	5.6	1.5	16.0	2.1
2b[b]	4.56 (dd)	6.06 (dt)	5.74 (m)		1.94 (d)		2.04 (s, OAc)	6.1	0.8	15.8	2.2
3c[a]	9.53 (d)	6.36 (dd)	6.66 (m)		2.40 (dq)	1.20 (t)		7.8		15.8	2.1

[a] $CDCl_3$.
[b] Acetone-d_6.

of the β-carbon atom C-3 of about 22.5 ppm, which is in a good agreement with the pairs allyl alcohol/acrolein and (*E*,*E*)-hexa-2,4-dien-1-ol/(*E*,*E*)-hexa-2,4-dien-1-al (Table 5). An adjacent carbon–carbon triple bond deshields C-3 by only 9.3 ppm, which is significantly smaller (see, for example, the pair propargyl alcohol/propargyl aldehyde). In this connection, it is surprising that on transition from **1c** to the aldehyde **3c** (the latter constitutes a vinylogous propargyl aldehyde),

Table 3. Dependence of ^{13}C,^{13}C coupling constants $^1J_{C,C}$ (Hz) on the hybridization of the carbon atoms and the different bond types in compounds 1–4

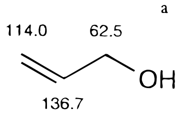
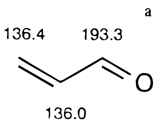
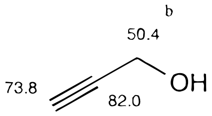
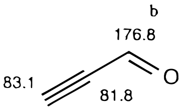
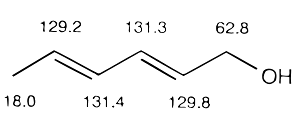
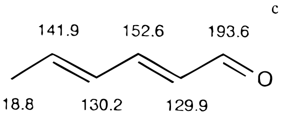
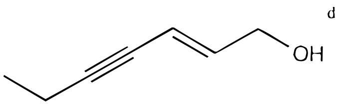
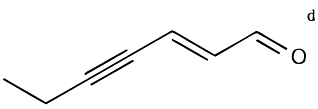
Hybridization	Bond type	$^1J_{C,C}$ (Hz)
C_{sp^3}–C_{sp^3}	$—CH_2CH_2—$	35–37
C_{sp^2}–C_{sp^3}	$=CHCH_2—$	42
	$=CHCH_2O—$	46–48
	$CH_3CO_2—$	59.5
C_{sp^2}–C_{sp^2}	$=CHCH=O$	53
	$=CHCH=$	56
	$—CH=CH—$	70–75
C_{sp}–C_{sp^3}	$\equiv CCH_2—$	66–68
C_{sp}–C_{sp^2}	$\equiv CCH=$	84–92
C_{sp}–C_{sp}	$—C\equiv C—$	177–181
	$—C\equiv CSiMe_3$	136.3

Table 4. Alkyl group increments for the calculation of ^{13}C NMR chemical shifts of the acetylenic carbon atoms in the conjugated (*E*)-enynes 1 and 2 compared with these of *n*-alkynes (ppm)

Increment	Value[a]	Ref. 28	Increment	Value[b]	Ref. 28
αC	8.52	6.93	α′C	−3.97	−5.69
βC	5.82	4.75	β′C	0.15	2.32
γC	−1.22	−0.13	γ′C	0.85	−1.31
δC	−0.21	0.51	δ′C	−0.21	0.56

[a] For sp-hybridized carbon atoms substituted with the alkyl group: basic value δ(^{13}C-5) in **1a** and **2a**, respectively.
[b] For the neighbouring sp-hybridized carbon atoms: basic value δ(^{13}C-4) in **1a** and **2a**, respectively.

Table 5. ^{13}C NMR chemical shift effects Δδ (ppm) during the transition from alcohol to the corresponding aldehyde

				Δδ		
		1	2	3	4	5
[a] 	[a] 	130.8	−0.7	22.4		
[b] 	[b] 	126.4	−0.2	9.3		
[c] 	[c] 	130.8	0.1	21.3	−1.2	12.7
[d] 	[d] 	129.0	−1.8	22.5	−0.9	15.4

[a] Ref. 30.
[b] Ref. 10.
[c] Ref. 31.
[d] Table 1.

the more distant acetylenic carbon atom C-5 is significantly more deshielded. Here this effect is even slightly stronger than for (*E*,*E*)-hexa-2,4-dien-1-ol/(*E*,*E*)-hexa-2,4-dien-1-al.

EXPERIMENTAL

The NMR spectra were recorded on a ARX 300 spectrometer (Bruker). All samples were dissolved as 0.5 m solutions in $CDCl_3$. For the measurement of the ^{13}C satellites highly concentrated solutions in acetone-d_6 or $CDCl_3$ were used. For observing the ^{13}C satellites, the number of scans necessary was about 4000. The 2D spectra were acquired using the standard Bruker software. Typical parameters were as follows: (i) for COSY-45: sweep width 2000 Hz, 1K data points in F_2, 128 experiments in F_1 (eight scans, four dummy scans), relaxation delay 1.2 s; (ii) for HMQC; sweep width in F_1 10.5 kHz and in F_2 2030 Hz, 1K data points in F_2, 128 experiments in F_1 (eight scans, four dummy scans), relaxation delay 1.2 s, delay for inversion recovery 630 ms, zero filling, 1K data points in F_2 and 256 data points in F_1, filter function square sine-bell in both dimensions. The pulse widths (90°) for all experiments were 12.5 ms (^1H) and 11.3 ms (^{13}C).

Compound **1** was synthesized by reaction of sodium acetylide with epichlorohydrin in liquid ammonia.[1,2] First **1a** was converted into its tetrahydropyranyl ether by reaction with 3,4-dihydro-2*H*-pyran, then metalated with sodium amide in liquid ammonia and subsequently alkylated with the corresponding alkyl halide (MeI, EtBr, *n*-PrBr, *n*-BuBr). To prepare the alcohols **1b–e**, the THP group was cleaved by hydrolysis or by reaction with acetyl chloride–acetic acid. Compound **2a** was obtained by acetylation of the THP ether of **1a** with acetyl chloride–acetic acid. The synthesis of the silyl compound **1f** followed the synthesis of 3-trimethylsilylpropargyl alcohol[32] by metalation of **1a** with butyllithium in diethyl ether, reaction with trimethylchlorosilane and subsequent hydrolysis. The aldehydes **3c** and **d** were prepared by oxidation of the alcohols **1c** and **d**, respectively, with pyridinium dichromate in DMF.[4] (2*Z*,4*E*)-Deca-2,4-dien-6-yne (**4d**) was synthesized by the Wittig reaction, starting from **3d** and ethyltriphenylphosphonium bromide using the silazide method.[33]

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