Tetrahedron. Vol 32, pp 115 to 120 Pergamon Press 1976 Printed in Great Britain

CARBON-13 CHEMICAL SHIFTS OF SOME PROPARGYL ALCOHOL DERIVATIVES

M. T. W. HEARN*
Dyson Perrins Laboratory, Oxford OX1 3QY

(*Received in UK* 4 *August* 1975; *Accepted for publication* 19 *August* 1975)

Abstract—The natural abundance ^{13}C chemical shifts of a range of propargyl alcohol derivatives have been determined and individual resonances assigned. The shielding effects of the triple bond and hydroxyl group on neighbouring carbons have been characterised. The observed trends for these compounds are compared to those of alkyl or allyl alcohols.

INTRODUCTION

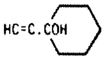
With the rapid expansion of the number of publications dealing with ^{13}C magnetic resonance during the past few years, it is now possible to define the chemical shift range of a particular type of C atom and establish broad guidelines for substituent chemical effects. The chemical shifts of ^{13}C nuclei in most organic compounds generally occur within a range of *ca.* 200 ppm from TMS with the position of the resonance signal roughly following the hybridisation sequence $sp^3 \rightarrow sp \rightarrow sp^2$ with increasing movement to lower field, and the electronegativity of adjacent nuclei. Substituent effects at directly bonded and more distant carbons in monosubstituted compounds can generally be rationalised in terms of contributions from inductive, bond or charge delocalisation and steric effects.[1]

Using derived sets of substitution parameters from a number of compound types, it has been possible to estimate the chemical shifts of other related carbon nuclei. Such estimates obviously have a useful role in assignments. Good quantitative correlations have been found with alkyl groups but, in general, the predicted values only qualitatively agree with the observed resonances of carbons in compounds with several interacting substituents, particularly if these can participate in mesomeric effects. The assignment of peaks in heavily functionalised compounds with a large number of quaternary carbons can thus prove difficult if data from closely related compounds containing similarly substituted carbons are not available.

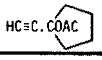
As part of a programme to establish ^{13}C NMR as a spectroscopic aid for structure elucidation and biosynthesis in natural polyacetylenes,[2,3] the chemical shifts of carbons of a variety of acetylenic alcohols and derivatives have been determined. Although ^{13}C data is now available for a range of acetylenic compounds,[4-9] conspicuously absent from the growing volume is detailed information on acetylenic alcohols. Fragmentary data have been reported[9] previously for the ^{13}C shifts of the sp-hybridised carbons of propargyl alcohol and several related ethynyl carbinols measured using the adiabatic, rapid-passage technique. Compared to the present instrumental methods, the precision of this technique is considerably lower (experimental uncertainty *ca.* 0·5 ppm compared to *ca.* 0·1 ppm) and not sufficiently sensitive to reveal subtle long-range substituent chemical shift effects at remote sites of a complex molecule. In this paper, ^{13}C data, which were obtained using pulsed FT techniques for a range of acetylenic alcohols (**1-28**), are presented and discussed in terms of substituent and conformational effects. The compounds used in this study cover a wide range of substituent types and permit an assessment of the importance of substituent hybridisation on carbinyl and acetylenic shifts. The results amplify the additivity correlations generated for allyl[10] and alkyl[11] alcohols.

Ethynyl Alcohols* (1 - 20)

1. $H\overset{1}{C}\equiv\overset{2}{C}.\overset{3}{C}H_2OH$
2. $HC\equiv C.CHOH.CH_3$
3. $HC\equiv C.CHOH.CH_2CH_3$
4. $HC\equiv C.COH.(CH_3)_2$
5. $HC\equiv C.COH.(CH_3)CH_2CH_3$
6. $HC\equiv C.CHOH.CH(CH_3)_2$
7. $HC\equiv C.CHOH.CH(C_6H_5)_2$
8. $HC\equiv C.CHOH.CH=CH_2$
9. $HC\equiv C.CHOH.CH\overset{t}{=}CHCH_3$
10. $HC\equiv C.CHOH.CH\overset{t}{=}CHC_6H_5$
11. $HC\equiv C.CHOH.C_6H_5$
12. $HC\equiv C.COH(C_6H_5)CH_3$
13. $HC\equiv C.CHOH.C\equiv CH$
14. $HC\equiv C.CHOH.C\equiv C.CHOH.C\equiv CH$
15. $HC\equiv C.CH=CH_2OH$
16. $HC\equiv C.CH(OEt)_2$
17. $HC\equiv C.CH_2CH_2OH$

18. 

19. 

20. 

*For Table 1, the carbons are numbered from left to right as shown.

Alkynyl Alcohols* (21 - 28)

21. $\overset{1}{C}H_3.\overset{2}{C}\equiv\overset{3}{C}.\overset{4}{C}H_2OH$
22. $CH_2OH.C\equiv C.CH_2OH$
23. $CH_3.C\equiv C.COH(CH_3)_2$
24. $CH_3.CHOH.C\equiv C.CHOH.CH_3$
25. $CH_3CH_2CH_2.C\equiv C.CHOH.CH_3$
26. $Br.C\equiv C.CH_2OH$
27. $EtO.C\equiv C.COH(CH_3)_2$
28. $TMS.C\equiv C.CH_2CH_2OH$

* For Table 2, the carbons are numbered from left to right as shown.

RESULTS AND DISCUSSION

The ^{13}C resonances of the sp-hybridised carbons of the 1-yn-3-ols were generally observed in the range 70–90 ppm downfield from TMS, whilst the hydroxylic carbon ^{13}C resonances were found in the range 50–70 ppm. The assignment of resonances to particular atoms is a refractory problem with NMR spectra of complex molecules. Procedures which are now common[1] in ^{13}C NMR—proton noise and off-resonance decoupling, intensity data, the application of chemical shift theory and parameters—were used for the present assignments. These procedures readily permit the various types of carbons to be distinguished. The ^{13}C chemical shifts for a number of ethynyl alcohols (**1-20**) are given in Table 1 and alkynyl alcohols (**21-28**) in Table 2. For comparison, the

Table 1. ^{13}C chemical shifts of HC≡C·C(OH)R·R′ in ppm downfield from TMS

Compound	C_1*	C_2	C_3	C_4	C_5	C_6	C_7	C_8	C_9	
(1)	73.8	82.0	50.4							
(1)$^{ref\ \#9}$	74.2	82.3	-							
(2)	72.0	85.8	57.7	24.0						
(3)	72.9	84.9	63.3	30.6	9.4					
(4)	70.2	88.8	64.9	31.2					3-CH_3	31.2
(4)$^{ref\ \#9}$	70.3	88.1	-	-						
(5)	71.3	87.7	68.5	36.3	9.0				3-CH_3	29.1
(5)$^{ref\ \#9}$	69.1	88.4	-	-	-				-	
(6)	73.5	83.7	67.4	34.2	18.2				4-CH_3	17.3
(7)	75.1	83.4	64.7	57.3	140.0	128.3	128.8	126.8	C'_1	140.5
(8)	74.6	82.8	62.6	136.6	116.7					
(9)	74.0	83.6	62.2	129.9	128.6	17.4				
(10)	74.7	82.9	62.4	128.6	127.5	135.8	126.7	128.4		131.9
(11)	74.9	83.6	63.6	139.9	126.6	128.3	128.3			
(12)	73.1	87.2	69.7	33.1	144.9	124.9	128.2	127.6		
(13)	72.9	80.4	50.9	80.4	72.9					
(14)	72.8	80.5	51.2	81.0						
(15)	78.2	81.8	108.9	143.7	62.1					
(16)	73.5	79.2	91.0	60.9	15.1					
(17)	70.5	80.7	22.9	60.7						
(18)	72.2	87.8	68.6	39.7	25.1	25.1				
(19)	74.3	83.6	75.0	36.9	22.4	25.1	CH_3	21.7, CO	168.9	
(20)	73.2	84.3	80.1	40.4	23.3		CH_3	21.6, CO	169.2	

* The carbons are numbered as indicated in the text.

Table 2. ^{13}C chemical shifts of R—C≡C·(OH)R·R′ in ppm downfield from TMS

Compound	C_1*	C_2	C_3	C_4	C_5	C_6	C_7
(21)	3.6	81.6	77.7	50.4			
(22)	50.3	83.7	83.7	50.3			
(23)	3.5	77.9	84.4	65.2	31.6		
(24)	24.1	57.8	85.6				
(25)	13.5	22.1	20.7	82.6	84.3	58.4	24.7
(26)	45.7	78.2	51.5				
(27)	14.3	74.3	91.3	43.3	65.1	32.1	
(28)	84.0	103.9	24.5	61.4			

* The carbons are numbered as indicated in the text.

few previously reported chemical shifts for simple acetylenic alcohols are also included. The substantial differences which are evident between the spectra obtained by the rapid dispersion and the absorption modes appear in several instances to be greater than the experimental uncertainty of the two methods and may possibly be due to solvent-solute interactions or like effects. The earlier data were derived mainly from carbon disulphide solutions, while solutions in deuterochloroform were used in the present study.

In order to differentiate the effects of an OH group, the triple bond or additional substituents on the ^{13}C shift of a particular nucleus, it is useful to consider the various contributions made to the total shielding constant. The paramagnetic term, which is influenced by inductive, resonance and steric effects, has been shown to be dominant for most ^{13}C chemical shifts although contributions from the diamagnetic term are not insignificant. With the acetylenic alcohols, the inductive effect of the OH group would be anticipated to fall off very rapidly after the α-carbon and be independent of the conformation. The possible role of heteroatom mediated resonance effects on the shieldings of the acetylenic carbons can be inferred from the data but cannot currently be determined for the attached hydroxylic carbon. Steric effects, which have been shown to be very important in various kinds of hydrocarbons, are also expected to be sensitive to the conformational features present in the alkynols with the greatest response more evident in the crowded compounds, e.g. 4-methyl-pent-1-yn-3-ol, at carbon nuclei β,γ-displaced from the point of substitution. Anisotropic contributions of the triple bond would also be expected to play an important role in the shielding of the immediately adjacent carbon nuclei.

The individual contribution which each of these terms make to the observed shielding composite can be assessed by comparison of the shift data with those of alkynes and alkyl alcohols. In view of the respective triple bond, carbinyl or substituent character of the various carbon nuclei, the chemical shifts of the ynols (**1**-**28**) can be readily divided into three sets and discussed in these terms.

Acetylenic carbons. The chemical shifts of sp-hybridised carbons in simple alkynes[4] extend over a range of 25 ppm from 65 ppm. In alk-1-ynes the terminal sp-carbon is generally found near δ 68·5 and the interior sp-carbon *ca.* δ 85·0. From Table 1, it is evident the terminal sp-carbon C_1 in ethynyl alcohols is again at higher field than the substituted sp-carbon C_2 although the shift difference between them is smaller in magnitude than for monoyne hydrocarbons. The hydroxymethyl group has the expected deshielding effect on the bonded sp-hybridised carbon but the value is approximately half that shown for α-CH_2OH effects operating at sp^2 or sp^3 centres, e.g. *ca.* 10 ppm compared to *ca.* 17·4 ppm in prop-2-en-1-ols[10] or 20 ppm in alkyl alcohols.[11] A second reason for the convergence in the resonance positions can be found by comparing the chemical shifts of the acetylenic alcohols with the corresponding alkyne, saturated alcohol and alkane. This reveals that the γ-effect of the hydroxylic group (γ^{π}_{OH}) in alk-1-yn-3-ols operating via the π bond at the ethynyl carbon C_1[†] is positive, i.e. deshielding by *ca.* 6·5 ppm, while the β-effect at the interior sp-hybridised carbon C_2[†] (β^{σ}_{OH}) is also deshielding. In alkyl alcohols, a different pattern is seen[11] with the γ^{σ}_{OH}-effect shielding (*ca.* $-5{\cdot}0$ ppm) and the β^{σ}_{OH}-effect strongly deshielding (*ca.* 10 ppm). The γ^{σ}_{OH}-effect in saturated acyclic systems is primarily a steric effect operating through space rather than through the bonds of the molecule and arises predominantly from interaction in *gauche* rotamers. As will be discussed in a subsequent section, the γ^{σ}_{OH}-effect which is transmitted to the sp^3 hybridised substituent carbons appears unperturbed in the ynols from that seen in comparable acyclic saturated alcohols. The two γ^{π}_{OH}- and γ^{σ}_{OH}-effects present in propargylic alcohol derivatives thus exhibit distinct shielding roles. It is difficult to accommodate this reversal with the earlier conclusion[12] that γ-effects are predominantly steric in nature. Furthermore, the magnitude of the γ^{π}_{OH}-effect in primary acetylenic alcohols (*ca.* 6·5 ppm) is considerably larger than the corresponding $\gamma^{\pi}_{CH_3}$-effect (*ca.* 0·6 ppm) seen[4] in linear alkynes which is also deshielding in nature. In propynol, as well as in the other acetylenic alcohols, the spatial arrangement which the oxygen atom bears to the β- and γ-removed sp-hybridised carbon nuclei is completely different to that found in the fully tetrahedronal acyclic alcohol situation. By virtue of the triple bond, the acetylenic carbons are in a constrained arrangement in which the distal acetylenic carbon C_1 and the OH group cannot be involved in *gauche* interactions. Striking dissimilarities also exist between corresponding propynyl and allyl compounds. In allyl derivatives,[10] the β-olefinic carbon shieldings differ only slightly from those in the corresponding alkene, indicating that the intervening methylene group effectively insulates the β-carbon from the inductive effects of polar substituents. The fact that the β-acetylenic carbons in the mono-ynols do not follow this pattern (divergencies of *ca.* 5 ppm relative to the alkyne were observed) suggest that additional effects must be considered to accommodate these differences. The nuclear screening constant of a sp-hybridised nucleus is very sensitive to the electronic environment of the nucleus and responds significantly to inductive, conjugative or charge perturbative changes in the local electronic distribution. An important factor would appear to be the polarity of the bonds at that, and neighbouring, nuclei. Since the γ^{π}-effects of the OH or Me group in allyl alcohols or alkenes are both shielding, and of the same sign and magnitude as observed for the γ^{σ}-effect of alkanes, the large deshielding γ^{π}_{OH}-effect in acetylenic alcohols may possibly arise more from anisotropic contributions of the heteroatom rather than from sterically induced perturbations. It would be interesting, in this regard, to compare the chemical shifts of an analogously structured set of compounds to the 1-yn-3-ols in which the OH group is replaced by a Me. Unfortunately, no experimental data are available for this comparison. However, values for the chemical shifts of the acetylenic carbons in branched alkynes and hence 1-yn-3-ols can be calculated with additivity parameters established for linear alkynes[4] and the predicted value for ethyne (δ 72·8). Thus in the 1-yn-3-ols, the chemical shift of the terminal sp-hybridised carbon can be expressed as a function of the number of β^{π}, γ^{π}, δ^{π}..... effects present in the molecule and related to the corresponding branched Me compound by the appropriate shift correction,[11] $\delta_c^{OH}(\gamma) = \delta_c^{CH_3}(\gamma) + 1{\cdot}7$. Using these estimates, an insight can be gained into the relative importance of the steric and electronic effects of the OH group on the proximal and distal acetylenic carbon shieldings. As can be seen by comparing the observed and calculated shift values for some alkyl substituted acetylenic alcohols (Table 3), the observed downfield shifts of the distal carbon C_1 are considerably divergent from those predicted by steric polarisation. It is obvious other factors must significantly contribute to the shieldings of the acetylenic carbons in these compounds. Although the observed deshielding by the γ^{π}_{OH}-effect must be caused by electron withdrawal

Table 3. Calculated and observed chemical shifts for the acetylenic carbons in some prop-1-yn-3-ols

Compound	Carbon	Calculated	Observed	Difference
(1)	C_1	66.4	73.8	7.4
	C_2	86.3	82.0	-4.3
(2)	C_1	67.0	72.0	5.0
	C_2	91.5	85.8	-5.7
(3)	C_1	67.4	72.9	5.5
	C_2	89.9	84.9	-5.0
(4)	C_1	67.6	70.3	2.7
	C_2	89.2	88.1	-1.2
(5)	C_1	68.0	71.3	3.3
	C_2	88.1	87.7	-0.4
(6)	C_1	68.6	73.5	4.9
	C_2	88.3	83.7	-4.6

Shifts calculated according to the relationships,

$\delta C_1 = 72.8 + \beta_C^{\pi} + m\delta_C^{\pi} + n\gamma_C^{\pi} + \ldots\ldots -1.7$

$\delta_{C2} = 72.8 + \alpha_C^{\sigma} + a\beta_C^{\sigma} + b\delta_C^{\sigma} + \ldots\ldots +0.5$ where the coefficients a,b .....m,n..... of the substitution parameters will be 0,1......

[†] The acetylenic carbons in the β- and γ-orientation to the OH group have been designated for convenience the proximal and distal carbons; with other substituents the usual α,β relationship is used.

from the nucleus of interest the origins of this effect remain poorly understood. Further research into the mechanism of this effect is required before definite conclusions can be drawn.

In common with linear alkynes, successive replacement of the methylene protons in propargyl alcohol by Me groups results in the deshielding of the α-acetylenic carbon by *ca.* 3 ppm and the shielding of the β-carbon by *ca.* 2 ppm. Further homologation of the alkyl substituents results in shielding effects roughly in accordance with additivity parameters seen in alkyl substituted olefinic and acetylenic hydrocarbons.

When the substituent is a sp^2-hybridised group, e.g. as in 3-phenyl-prop-1-yn-3-ol (**11**) both the α- and β-acetylenic carbons are moved to slightly lower field than in the prototype. It is also interesting to compare the relative shielding effects of an ethyl, vinyl and ethynyl group in the same position. For example, in pent-1-yn-3-ol (**3**) the α- and β-acetylenic resonances are shifted by − 0·9 and 2·9 ppm relative to the parent alcohol whereas in pent-4-en-1-yn-3-ol (**8**) they are 0·8 and 0·8 ppm and in penta-1-4-diyn-3-ol (**13**) − 0·9 and − 1·5 ppm respectively. The only difference between these three compounds is the successive change in hybridisation of the substituent.

In disubstituted mono-ynols (Table 2), the second alkyl substituent reinforces the downfield shifts of the acetylenic carbons. Some additional insight regarding the effect of a hydroxymethyl or a Me group upon the neighbouring carbon nuclei is available from the data for the symmetrical yndiols and related hydrocarbons. In the spectra of hex-3-yn-2,5-diol (**24**), for example, the sp-hybridised carbons are downfield by *ca.* 4·5 ppm from their position in the corresponding hex-3-yne. The difference is even larger (8·9 ppm downfield) between but-2-yn-1,4-diol (**22**) and but-2-ynol (**21**). Substituents with dominant + M effects are known to cause polarisation of the triple bond. The pronounced shielding of the β-acetylenic carbon in these compounds, e.g. in the ethoxypropynol (**27**), can be rationalised in terms of the significant contribution to the resonance hybrid by such forms as $-\bar{C}{=}C{=}\bar{X}$.

Carbinol carbons. The large inductive perturbation of an OH group on the resonances of the directly attached carbon has been recognised for many years. In a detailed study of the ^{13}C shifts of acyclic and alicyclic alcohols, Roberts *et al.* established[11] a linear relationship existed between carbon chemical shifts in alcohols and analogously constituted hydrocarbons. For saturated primary alcohols, the difference in the net inductive shift (the average of the downfield inductive and upfield resonance effect) between an OH and a Me group at the α-carbon was found to be *ca.* 48·3 ppm. Furthermore, striking regularities in the ^{13}C shifts were observed on systematic substitution of a Me group for a proton at the α carbon with attenuation of the downfield shift of *ca.* 7 ppm/Me group. As anticipated, the shift data presented in the Tables 1 and 2 show a similar set of downfield shifts for Me substitution at the hydroxylic and more distant carbons. However, compared to the corresponding saturated alcohol, the resonances of the hydroxylic carbon are invariable at higher field. One of the most prominant features in the ^{13}C spectra of simple alkynes[4,7] is the diamagnetic shift of *ca.* 10 ppm induced at the attached carbon by the alkyne linkage relative to the corresponding alkyl group. In the ynols an identical effect operates with the triple bond shielding the hydroxylic carbon by *ca.* 11 ppm. The effect of a triple bond at the neighbouring α-position also appears to be broadly independent of the electronegativity or substitution pattern of the α-carbon. The observed resonances of the carbinyl carbons thus broadly follow the expected shift additivity for the various substituents in the simple alkyl substituted prop-1-yn-3-ols.

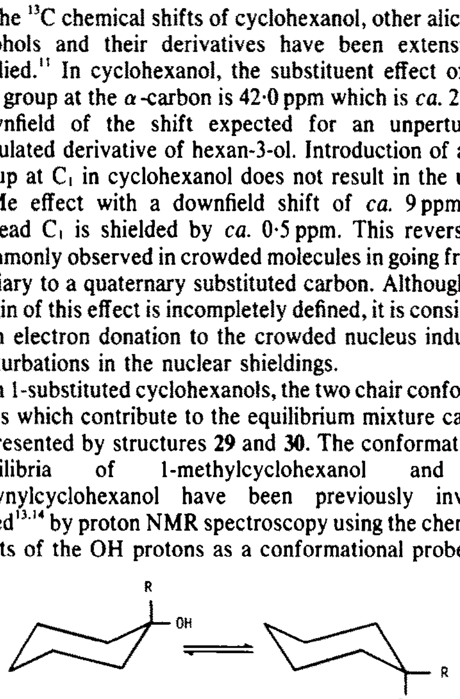
In olefinic compounds, e.g. allyl alcohols,[10] the small downfield shift observed for the α-carbons caused by the double bond is often outweighed by steric compression effects which are shielding in nature. This results in the chemical shift of a carbon bonded to a double bond being similar to the analogous carbon in the saturated system, e.g. the hydroxymethyl carbon in allyl and propyl alcohol are 63·3 and 63·9 ppm respectively. With this point in mind the similarity of the shifts of the hydroxymethyl carbon in the enynols and the ynols, e.g. pent-4-en-1-yn-3-ol (**8**) and pent-1-yn-3-ol (**3**) is readily explainable. More remote replacements of H atoms on the β olefinic carbon with other substituents, e.g. methyl in hex-*trans*-4-en-1-yn-3-ol (**9**) or phenyl in 5-phenylpent-4-en-1-yn-3-ol (**10**) have little effect on the carbon shifts.

Substituent carbons. The substituent carbons in a β, γ, δ orientation to the geminal hydroxylic and acetylenic groups will experience a composite shielding effect. The magnitudes of the induced shifts at these more distant carbons are expected to bear some relationship to the individual shift parameter of these two groups. The data in the Tables for the substituent carbons do, in fact, show similarities to the anticipated shifts. For example, there are indications of some additive relationship for shifts induced at the β, γ, δ carbons in the alkyl substituted propynols particularly for the sign if not the absolute magnitude of the shielding, e.g. the predicted shifts for the C_3, C_4 and C_5 carbons of pent-1-yn-3-ol (**3**) from those found in pentane are 25·0, 6·1 and − 4·4 ppm respectively whilst the observed shifts are 28·8, 8·0 and − 4·3 ppm respectively for these same carbons. As mentioned in the previous section, the γ_{OH}^{g}-effect evident in several compounds is qualitatively analogous to that found from saturated alcohol data, i.e. the effect is weakly shielding by *ca.* 3·0 ppm. In the disubstituted alcohols, alkyl substituents attached to the distal acetylenic carbon have only small conformational or electronic interactions with the proximal substituents as can be seen by comparing the Me shifts in 2-methylbut-1-yn-3-ol (**4**) and 2-menthylpent-3-yn-2-ol (**23**) or other related pairs. This also applies for polar substituents which exhibit mesomerically dominated electron donation, e.g. Br, OCH_2CH_3. Furthermore, the distal substituents show shift effects generally unperturbed from the corresponding alkyne, i.e. the effect of a hydroxymethyl or similar group when transmitted through the π-bonds of the triple bond to carbons removed further than the γ-position is very small. In compounds with the triple bond and the OH group separated by two intervening carbons, e.g. the alcohols (**15, 17, 28**), the chemical shifts of the acetylenic carbons resemble more closely the parent alkyne.

From the above discussion with the acyclic compounds there are some striking regularities in shift trends. If these trends show the same level of qualitative agreement with those anticipated from electronic and conformational considerations as is the case with saturated alcohols, then extension to alicyclic acetylenic alcohols should reveal comparable regularities. The data for the alicyclic compounds (**18-20**) do, in fact, show this. Thus, the chemical shifts of the acetylenic α- and β-carbons and the carbinyl carbon in 1-ethynylcyclohexanol are very similar to those found in the tertiary acyclic alcohols. The effect of an OH and an ethynyl group at C_1 on the ring β, γ, δ-carbons is readily demonstrated by examining the ring carbon shieldings in related compounds including 1-methylcyclohexanol. The shift differences, relative to cyclohexane, for this series of compounds are found in Table 4.

The ^{13}C chemical shifts of cyclohexanol, other alicyclic alcohols and their derivatives have been extensively studied.[11] In cyclohexanol, the substituent effect of the OH group at the α-carbon is 42·0 ppm which is *ca.* 2 ppm downfield of the shift expected for an unperturbed annulated derivative of hexan-3-ol. Introduction of a Me group at C_1 in cyclohexanol does not result in the usual α-Me effect with a downfield shift of *ca.* 9 ppm but instead C_1 is shielded by *ca.* 0·5 ppm. This reversal is commonly observed in crowded molecules in going from a tertiary to a quaternary substituted carbon. Although the origin of this effect is incompletely defined, it is consistent with electron donation to the crowded nucleus inducing perturbations in the nuclear shieldings.

In 1-substituted cyclohexanols, the two chair conformations which contribute to the equilibrium mixture can be represented by structures **29** and **30**. The conformational equilibria of 1-methylcyclohexanol and 1-ethynylcyclohexanol have been previously investigated[13,14] by proton NMR spectroscopy using the chemical shifts of the OH protons as a conformational probe.



29 **30**

These studies associated with results from acid catalysed equilibration indicated that 1-methylcyclohexanol prefers to exist predominantly as the conformer with the Me group equatorial with a free energy difference, i.e. conformational energy $-\Delta G°$, between the two chair forms of *ca.* 0·24 kcal/mole. Subsequently, this conclusion has been questioned[15] in view of the ^{13}C shift of the carbinyl carbon of 1-methylcyclohexanol which is intermediate between the values for the *cis*- and *trans*-4-t-butyl isomers. This suggests that there are approximately equal populations of each conformer in solution. In 1-ethyl-cyclohexanol, on the other hand, the conformational preference of the ethynyl group is considerably smaller than that of the hydroxy group (*ca.* 0·60 kcal/mole less) and this compound is expected[16] to be primarily in the form in which the ethynyl group is axial. As can be seen in Table 4, the constant shielding of C_4 by *ca.* 2·7 ppm relative to cyclohexane in both the acetylenic alcohol (**18**) and its acetate (**19**) is consistent with this interpretation as are the relative shift differences of the β- and γ-ring carbons when compared to analogously structured alkylcyclohexanols. Further research with conformationally rigid 1-ethynylcyclohexanols to provide a comparison with the 1-Me compound is under investigation. Acetylation attenuates the downfield shift of the OH group at the α-carbon in 1-ethynylcyclohexanol by *ca.* 2·1 ppm. The magnitude of this shift is similar to the value observed[17,18] for other aliphatic acetates.

CONCLUSIONS

By comparison with the alkane and alkyne shielding, it is apparent that in alk-1-yn-3-ols the pronounced downfield shift of the carbinyl carbon relative to the corresponding carbon in an alkane is a composite of the deshielding inductive effect of the OH group and the shielding anisotropic effect of the triple bond. Successive replacement of the carbinyl protons by alkyl or olefinic groups attenuates the downfield shift. These individual α-effects are thus comparable to those seen in alkyl or allyl alcohols and unsubstituted alkynes. A small β^{σ}_{OH} deshielding effect is seen operating at the proximal sp-hybridised carbon. The reduced magnitude compared to that found for the same effect in alkyl alcohols suggests the β^{σ}_{OH}-effect is poorly transmitted to a sp-hybridised carbon. For the secondary and tertiary alcohols, β^{σ}-effects of both the OH group and the triple bond can be seen operating. In contrast to other systems, a dehsielding contribution (γ^{π}_{OH}) at the distal sp-hybridised carbon induced by the OH group is found. This fact appears to argue against the γ^{π}_{OH}-effect operating at a sp-hybridised nucleus being predominantly steric in nature as is the case for sp^3- or sp^2-hybridised nuclei. Concordant with previous studies, the steric interaction of the OH group with the substituent carbons appears to be slightly greater than that predicted for a Me group in the analogously structured alkyne. If allowances are made for this difference, the chemical shifts of the γ, δ-carbon nuclei roughly follow the pattern for branched derivatives of alkanes.

EXPERIMENTAL

Materials. All of the alcohols and derivatives employed in this study are known compounds and were obtained as commercial samples or prepared by published procedures. In all cases the compounds were purified immediately prior to use and their physical properties agreed well with literature values. Proton spectra were recorded to ensure that the samples employed for ^{13}C spectra were of high purity.

Spectra. The ^{13}C spectra were determined for 25% (v/v) solns in $CDCl_3$ containing *ca.* 5% (v/v) TMS using a Bruker HFX 90 multinuclear spectrometer operating at 22·63 MHz. The spectra were obtained by storing the free induction decays produced by a series of 10 μs r.f. pulses in a Fabritek 1074 computer of average transients. The interferograms which resulted were then Fourier transformed by a Digital PDP 81 computer. The sample temperature was ambient at *ca.* 30°. The data recorded are in ppm

Table 4. ^{13}C shift differences between 1-ethynylcyclohexanol and related compound relative to cyclohexane†

Compound	C_1	C_2	C_3	C_4	C_5	C_6
Cyclohexanol*	42.0	8.0	-3.1	-1.6	-3.1	8.0
1-methylcyclohexanol*	41.5	12.2	-4.7	-1.5	-4.7	12.2
1-ethynylcyclohexanol	40.8	11.9	-2.7	-2.7	-2.7	11.9
1-ethynylcyclohexanyl acetate	47.2	9.1	-5.4	-2.7	-5.4	9.1

* The carbinyl carbons of these compounds shift to δ53.4 and δ81.2 respectively on acetylation.

† Negative values imply upfield shifts. Data converted using $\delta_C^{C_6H_{12}}$ 27.8.

downfield from the carbon resonances of the internal tetramethylsilane and are though to be accurate to ±0·1 ppm. Proton off-resonance decoupled spectra, and smaller sweep width were also used for assignment of resonances.

Acknowledgements—I.C.I. (U.K.) and the Medical Research Council of New Zealand are thanked for their support and Prof. Sir Ewart Jones for his encouragement.

REFERENCES

[1] For compendia of ^{13}C chemical shifts and substituted parameters see J. B. Stothers *Carbon-13 NMR Spectroscopy.* Academic Press, New York (1972); G. C. Levy and G. L. Nelson, *Carbon-13 Nuclear Magnetic Resonance for Organic Chemistry.* Wiley-Interscience, New York (1972).

[2] M. T. W. Hearn and J. L. Turner, *J. Chem. Soc.* Perkin II, Paper No. 5/1201 (1975).

[3] M. T. W. Hearn, *J. Mag. Resonance* Paper No. 6–69 (1975).

[4] D. E. Dorman, M. Jautelat and J. D. Roberts, *J. Org. Chem.* **38**, 1026 (1973), and refs therein.

[5] R. Zeisberg and F. Bohlmann, *Chem. Ber.* **107**, 3800 (1974).

[6] D. Rosenberg and W. Drenth, *Tetrahedron* **27**, 3893 (1971).

[7] M. T. W. Hearn, *J. Chem. Soc.* Perkin II. Paper No. 5/746 (1975).

[8] J. W. Emsley, J. Feeney and L. H. Sutcliffe, *High Resolution Nuclear Magnetic Resonance Spectroscopy,* Vol. 2, p. 1001. Pergamon, London (1966).

[9] P. C. Lanterbur, *Determination of Organic Structures by Physical Methods* (Edited by F. C. Nached and W. D. Phillips) Chap. 7. Academic Press, New York (1967).

[10] H. Brouwer and J. B. Stothers, *Can. J. Chem.* **50**, 1361 (1972).

[11] J. D. Roberts, F. J. Weigert, J. I. Kroschwitz and H. J. Reich, *J. Am. Chem. Soc.* **92**, 1338 (1970).

[12] D. E. Dorman, M. Jautelat and J. D. Roberts, *J. Org. Chem.* **36**, 2757 (1971).

[13] J. J. Uebel and H. W. Goodwin, *J. Org. Chem.* **33**, 3317 (1968).

[14] N. L. Allinger and C. D. Liang, *Ibid.* **33**, 3319 (1968).

[15] G. W. Buchanan and M. Gordon, unpublished observations.

[16] R. J. Ouellette, *J. Am. Chem. Soc.* **86**, 3089 (1964).

[17] M. Christl, H. J. Reich and J. D. Roberts, *Ibid.* **93**, 3463 (1971).

[18] G. W. Buchanan and J. B. Stothers, *Can. J. Chem.* **47**, 3605 (1969).