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^{13}C NMR SPECTRA OF ALLENES

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Allenes are very interesting compounds in ^{13}C NMR spectroscopy because of the extremely low field shift of the central allenic carbon reported by Friedel *et al.*[1] ($\delta^{13}C$ = -15 ppm relative to CS_2). As far as we know no more ^{13}C NMR data on allenes have been reported.

With an independent MO theory of diamagnetism Pople[2] calculated $\delta^{13}C$ = +35 ppm relative to CS_2 for the central carbon atom. Ditchfield *et al.*[3] using *ab initio* MO theory with a basis of contracted Gaussian functions calculated $\delta^{13}C$ = +5.8 ppm from CS_2.

In view of the obvious lack of ^{13}C NMR data on allenes and the unique applicability of this technique to the study of charge distribution in these otherwise rather "inaccessible" molecules, we found it worthwhile to communicate some of our preliminary results.

Proton noise decoupled ^{13}C NMR spectra were measured at 25.16 MHz on neat liquids (unless stated otherwise) at probe temperature on Varian HA-100 and XL-100/15 NMR spectrometers. Results are given in tables I and II.

For a given alkyl substituent there is a fair linear relationship between the number of these substituents and δC_β of the allenes. Considered as a constitutive property[4], a methyl group contributes +3.3 ppm to C_β while an ethyl group contributes +4.8 ppm. The group contribution of a S-alkyl substituent is 7 ± 2 ppm. To estimate the group contributions of other substituents more allenes are being measured.

Table I. ^{13}C chemical shifts of polysubstituted allenes $R_1R_2C_\alpha{=}C_\beta{=}C_\gamma R_3R_4$.

substituents				^{13}C chemical shifts (ppm)^{a}			
R_1	R_2	R_3	R_4	δC_α	δC_β	δC_γ	δR
H	H	CH_3	CH_3	121.6	-13.6	100.3	174.2(CH_3)
CH_3	H	CH_3	H	108.3^{b}	-13.4^{b}	108.3^{b}	
CH_3	CH_3	CH_3	CH_3	101.1	- 6.5	101.1	173.0(CH_3)
C_2H_5	H	C_2H_5	H	100.5	-10.3	100.5	171.6(CH_2) 180.5(CH_3)
H	CH_3	SCH_3	H	103.4^{c}	- 8.3^{c}	100.6^{c}	178.8(CH_3) 178.5(SCH_3)
H	H	CH_3	SCH_3	113.6	- 9.9	93.8	174.3(CH_3) 178.0(SCH_3)
H	H	C_2H_5	SCH_3	111.5^{c}	- 9.3^{c}	86.5^{c}	
H	H	i-C_3H_7	SCH_3	111.9	- 8.2	81.5	171.4(CH_3) 161.0(CH) 178.2(SCH_3)
H	H	CH_3	SC_2H_5	114.7	-10.3	95.8	173.8(CH_3) 166.9(CH_2) 178.9(CH_3-CH_2S)
H	H	i-C_3H_7	SC_2H_5	112.9	- 8.2	83.7	171.5(CH_3) 161.0(CH) 167.0(CH_2)
C_6H_5	C_6H_5	C_6H_5	C_6H_5	80.1^{d}	-15.8^{d}	80.1^{d}	56.3(C_1) 65.3(C_p) 64.3, 64.4(C_o , C_m)

a: δ-values in ppm (±0.1 ppm) relative to CS_2 external were measured directly (HA-100 spectra) or indirectly (XL-100/15 spectra, internal ^{2}H lock), or were obtained by converting the literature data to this standard.

b: ^{b} ref. 1.

c: 40% $^{v}/v$ solution in CCl_4/acetone-d_6 2:1, at about 40°C.

d: saturated solution in $CHCl_3$.

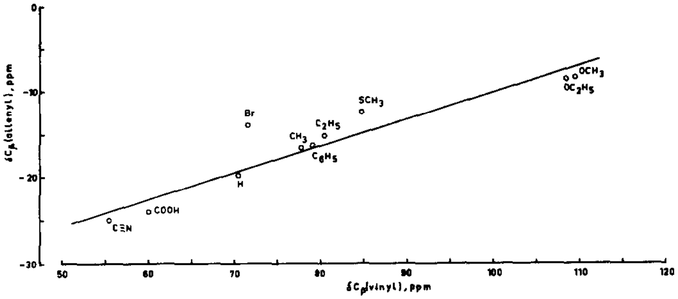
Table II. ^{13}C chemical shifts^{a} of monosubstituted allenes and corresponding alkenes.

	$X\text{-}C_{\alpha}H{=}C_{\beta}{=}C_{\gamma}H_2$				$X\text{-}C_{\alpha}H{=}C_{\beta}H_2$	
substituent X	δC_{α}	δC_{β}	δC_{γ}	δX	δC_{α}	δC_{β}
H	118.9^{b}	-19.8^{b}	118.9^{b}		70.4^{c}	70.4^{c}
CH_3	109.3^{d}	-16.7^{d}	119.6^{d}		57.5^{c}	77.8^{c}
C_2H_5	102.0^{d}	-15.2^{d}	118.4^{d}		53.0^{c}	80.4^{c}
SCH_3	103.7	-12.4	112.4	178.7	59.4^{e}	84.8^{e}
SC_2H_5^{e}	105.2	-13.2	112.8			
OCH_3	70.6	- 8.3	103.4	138.5	40.5^{f}	109.6^{f}
OC_2H_5	72.0	- 8.6	104.1	129.6(CH_2) 179.4(CH_3)	39.7^{f}	108.5^{f}
C_6H_5	99.2	-16.6	115.0		54.9^{e}	79.1^{e}
Br	121.0	-13.9	109.9		78.1^{c}	71.6^{c}
COOH	105.6^{g}	-24.0^{g}	113.7^{g}	21.4^{g}	64.0^{c}	60.0^{c}
CN	113.2	-25.0	126.5	80.2	85.5^{c}	55.4^{c}
CH_2SCH_3	105.1	-16.8	117.6	160.4(CH_2) 178.9(CH_3)		

a: see Table I note ^{a}. b: 40% $^{v}/v$ solution CCl_4/acetone-d_6 2:1, at -50°C.
c: ref. 5. d: ref. 1. e: see Table I note ^{c}. f: ref. 6. g: saturated solution in $CHCl_3$.

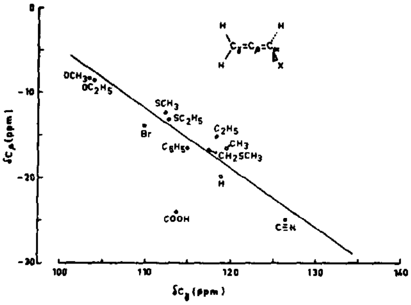
Fig. 1

Plot of δC_{β} for monosubstituted allenyl compounds against δC_{β} for the corresponding vinyl compounds.



Symmetry requires that no interaction occurs between the two perpendicular π-systems in allenes. In fact these π-systems are not isolated between C_{α} and C_{β} or C_{β} and C_{γ}, but they extend into the $C_{\gamma}H_2$ or $C_{\alpha}HX$ fragment respectively, because these fragments contain orbitals which have the correct π-symmetry for interaction. However, if we neglect for the moment this extension of the π-systems, we may compare the δC_{β} of monosubstituted allenes with the δC_{β} of the corresponding vinyl compounds (Table II, Fig. 1). Although Fig. 1 shows a quite appreciable scatter, the linear correlation indicates a parallelism in these chemical shifts, but, in view of the slope of about 0.35, the vinyl C -atom is much more sensitive to the substituent effect than the allenic C_β -atom is. Clearly the termination of both π -systems at C_β is an oversimplification.

Fig. 2.
Plot of δC_β against δC_γ
in monosubstituted allenes.



When, for each allenic compound of Table II, δC_β is plotted against δC_γ , a linear relation appears (Fig. 2). The slope of approximately -0.7 reflects the presence of a reverse relation between δC_β and δC_γ in these compounds. The following explanation may account for these observations. An electron donation from substituent X into the "extended" $C_\alpha C_\beta C_\gamma HH$ π -system, resulting in an increased shielding at C_β , leaves the substituent X somewhat electron deficient. This deficit may result in a "back donation" to substituent X from C_γ and C_β , via the "extended" $C_\gamma C_\beta C_\alpha HX$ π -system. Hence an electron donation into the $C_\alpha C_\beta$ fragment, similar to the donation in the vinyl compounds, is accompanied by an electron withdrawal from the $C_\beta C_\gamma$ part of the molecule and vice versa.

We are extending this work to a larger series of substituted allenes and to cumulenes with three to five double bonds.

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