(22) A cis ring juncture would be expected to shield C-4 by a decreased β effect of N_b in one conformation or an added γ effect from C-7 in another conformation.

(23) *Cf.* B. Birdsall, N. J. M. Birdsall, and J. Feeney, *J. Chem. Soc., Chem. Commun.*, 316 (1972).

(24) The scheme is founded on the theoretical analysis $J_R = J_{CH}\Delta f / \gamma^{H_2}/2\pi$ (J_R = residual splitting constant, J_{CH} = natural ^{13}C–^{1}H coupling constant, Δf = distance of ^{1}H frequency from applied radiation frequency in hertz, $\gamma^{H_2}/2\pi$ = decoupling field strength): R.

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Nuclear Magnetic Resonance Spectroscopy. Carbon-13 Chemical Shifts of Chlorinated Organic Compounds[1a]

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The ^{13}C chemical shifts of a variety of perchlorocarbons, their hydrogen-substituted derivatives, and chlorocarbon ketones have been determined and assigned to specific carbons by high-resolution nuclear magnetic resonance spectroscopy. The assignment of ^{13}C resonances for these substances was often aided by ^{13}C–^{1}H couplings and Overhauser enhancements observed in the carbon spectra of the hydrogen-substituted derivatives. Correlations between ^{13}C chemical shifts and structure were found for simple molecules and these correlations appear to provide the possibility of reasonable structural assignments for complex perchlorocarbons.

Chlorocarbon chemistry is growing in interest and importance,[2] and because the number of techniques for structural analysis of this type of substance is limited, we have investigated the degree to which ^{13}C nmr (cmr) spectra might be useful in this difficult area.

Detection and interpretation of the cmr resonances of chlorocarbons is substantially harder than for hydrocarbons of corresponding structures because of the absence of Overhauser enhancement of the ^{13}C signals associated with proton decoupling and the lack of spin–spin splitting information, as can be obtained for hydrocarbons by off-resonance decoupling. Nonetheless, we have been able to find correlations between ^{13}C chemical shifts and structural features for chlorocarbons and it is possible that cmr spectra may, in the long run, prove nearly as useful in the chlorocarbon area as ^{19}F spectra have been in the study of fluorocarbon structures.

Experimental Section

Chlorocarbons. *cis*- and *trans*-1,2-dichloroethylene, trichloroethylene, tetrachloroethylene, 1,1,1-trichloroethane, hexachloroethane, hexachloropropene, 1,1-difluorohexachloropropane, 1,1,1-trifluoropentachloropropane, hexachlorobutadiene, and hexachlorocyclopentadiene were commercial samples. All of the other chlorocarbons used in this study were generously provided by Professor R. West (University of Wisconsin) and Dr. V. Mark (Hooker Research Center).

Cmr Spectra. Cmr spectra were obtained for ^{13}C in natural abundance using a Varian DFS-60 spectrometer[3] operating at 15.08 MHz. For the hydrogen- and fluorine-substituted chlorocarbons, cmr spectra were determined both with and without proton or fluorine noise decoupling.[4] The preferred solvent was chloroform, which provides resonances for a proton field-frequency lock and internal ^{13}C reference. However, dioxane, cyclohexane, benzene, or tetrachloroethylene were sometimes used. Sweep rates of 40 Hz sec^{-1} or less were employed, which allowed the use of a high radiofrequency power level without saturation of the ^{13}C resonances.[5] The chemical shifts were reproducible to ±1.0 ppm. This variation in chemical shift with solvent, while relatively large, is not so large as to vitiate the structural correlations to be described later. Chemical shifts measured relative to internal standard were corrected to carbon disulfide as internal reference by the relation $\delta_C^{CS_2} = \delta_C^{INT} + N$, where N is 165.8 ppm for cyclohexane, 126.2 ppm for dioxane, 115.4 ppm for chloroforms, 64.6 ppm for benzene, and 71.0 ppm for tetrachloroethylene in a 1:1

tetrachloroethylene–dioxane mixture. Coupling constants and line widths are believed accurate to ±3 Hz. All chemical shifts obtained in this study are presented in Tables I–III. If it is desired that the shifts be referenced to tetramethylsilane (TMS), they can be corrected by the relation $\delta_C^{TMS} = 192.8 - \delta_C^{CS_2}$.

Results and Discussion

Assignments. The bulk of the compounds we have investigated are perchloroalkenes and cycloalkenes which are available in considerable profusion.[2] For these compounds, it is easy to distinguish between the resonances of the double-bond carbons, which fall between 50 and 75 ppm, and those of the single-bond carbons, which come between 90 and 120 ppm. It is interesting that the 50–75-ppm range of the alkenic carbon resonances for perchloroalkenes is not substantially different from the 40–80-ppm range of the corresponding resonances of ordinary alkenes,[6] although the alkane carbons of the perchlorocarbons are shifted some 50 ppm downfield relative to hydrocarbons by the substituent effect of the chlorines.

With the start provided by the differences between double-bonded and single-bonded carbons and taking advantage of symmetry or spin–spin splittings where present, it is possible to assign unambiguously the resonances of many of the compounds shown in Table I, which is arranged to highlight the structural features of each compound for future comparisons. The resonances of the more complicated compounds were assigned (where possible) so as to be consistent with the general pattern of correlation of chemical shifts with structures, as will be discussed below.

A. Single-Bonded Carbon Chemical Shifts. The data of Table I show that the chemical shift of a single-bonded carbon is strongly influenced by the nature of the directly bonded atoms. The single-bonded carbons are here classified as trichloromethyl (CCl_3), dichloromethylene (CCl_2), or chloromethine (CCl). Each class is then subdivided according to the number of directly attached double-bonded or single-bonded carbons. The chemical shift of each subgroup falls within a relatively narrow range, as illustrated in Figure 1.

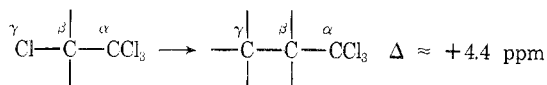**1. The CCl_3 Carbon.** Chemical shifts for trichlorometh-
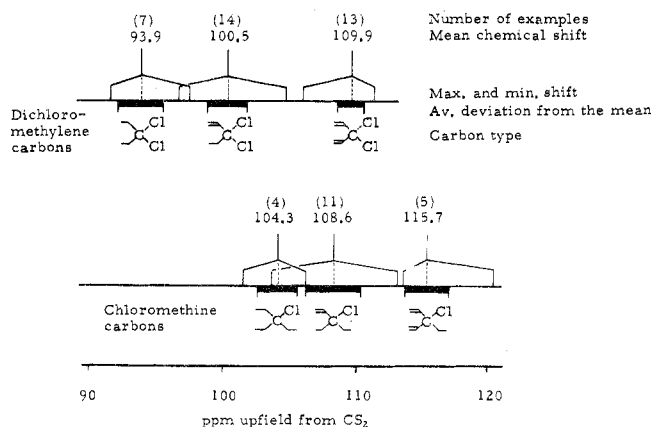
Figure 1. Correlation of ¹³C chemical shifts of dichloromethylene and chloromethine carbons in fully chlorinated compounds, with degree of substitution. The number of examples is shown in parentheses along with the position of the mean chemical shift of each structural type. The observed range of shifts is shown by the light lines, while the heavy bars are centered on the means and cover the range of average deviation.

yl carbons of five compounds are given in Table IV. The resonances for compounds **6** and **7** were assigned by virtue of the shift change on substitution of a fluorine atom by chlorine and by the ¹³C–¹⁹F coupling constant, both of which diminish with increase in the number of intervening bonds. The two signals were assigned for octachloropropane (**8**) on the basis of the expected intensity ratio 2:1. Further confirmation for these assignments is given by the chlorocarbon hydrides, **49** and **50**, from the one-bond ¹³C–¹H coupling constant, and the cmr-shift change produced by substitution of a chlorine for a hydrogen, which diminishes with an increase in the intervening number of bonds.

The signal at 95.6 ppm for chlorocarbon **21** is assigned to the CCl₃ carbon, because the signal at 115.2 ppm is logically assigned to C-5 in order to be consistent with the shift of 119.7 ppm for C-5 in chlorocarbon **37**. Finally, the signal due to the CCl₃ carbon (C-6) in chlorocarbon **22** is at 104.7 ppm, which is consistent with the assignments for the three CCl₂ carbons (C-3, C-4, C-5) as shown below.

An examination of Table IV shows that the atoms at both the β and γ positions can influence the trichloromethyl carbon shift. Thus, the trichloromethyl carbon chemical shift is readily correlated with the hybridization of the β-carbon atom and the number of γ-chlorine and carbon atoms. An increase in the shielding at the trichloromethyl carbon of about 4.4 ppm is observed for each γ-chlorine atom that is replaced by a carbon atom.

A similar upfield shift is observed for the structural change
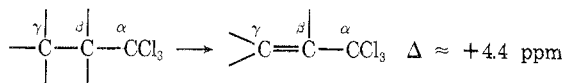
2. The CCl₂ and CCl Carbons. Chemical shifts for dichloromethylene and chloromethine carbons are presented in Table V. These shifts are classified according to the type of β and γ atoms, and are arranged in subclasses according to the number of β sp²- and sp³-hybridized carbons.

Here, as noted for the CCl₃ carbon, an upfield shift of 5–8 ppm is associated with each change of a β sp³ carbon

to β sp² carbon atom. A β chlorine atom is more deshielding than a β carbon by 8–10 ppm. There does not appear to be a consistent correlation for the γ atom shift. It is observed that the chemical shifts of the CCl₂ and CCl carbons fall within narrow limits for each subgroup of β carbon atoms and there is relatively little overlap between the subgroups for the dichloromethylene carbon, or between the subgroups for the chloromethine carbon shifts. However, there is considerable overlap in the chemical-shift ranges between the subgroups for the two different classes (CCl₂ or CCl) of carbon. While this is a potential limitation to the analysis of complex structures, most of the compounds studied here have sufficiently few sp³ carbons that their resonances can usually be assigned by comparison with the chemical shifts predicted from the semiempirical correlations shown in Figure 1.

Chlorocarbons **22**, **30**, and **44** are cyclopentenyl structures, and the number of lines in the cmr spectra is consistent with an unsymmetrical 1- or 3-cyclopentenyl derivative, represented as isomers **a** and **b**.

Predicted chemical shifts, ppm

	R
22a	**22b**	R = CCl₃
30a	**30b**	R = CCl═CCl₂
44a	**44b**	R = 1-cyclopentenyl
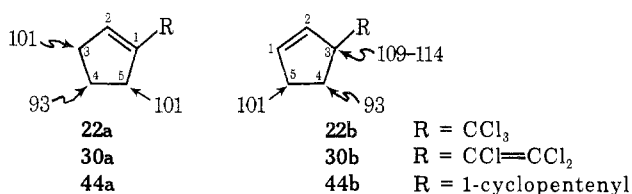
The observed resonances (see Table I) are most consistent with isomers **22a**, **30a**, and **44a**. For compound **22**, the sp³ carbon resonance at 104.7 ppm is assigned to the trichloromethyl carbon. The nature of the substituent R appears to have no significant effect on the sp³ carbon chemical shifts for these compounds.

The molecular formula (C₁₀Cl₁₀) for chlorocarbon **41** suggests six double-bond equivalents. In the observed cmr spectrum, there are three sp³ and two sp² carbon signals, all of equal intensity. We consider two possible structures, **41a** and **41b**.

For structure **41b**, the quaternary carbon (C-1) resonance would be predicted to be at about 119 ppm (the chloromethine carbon resonances with one β sp² carbon and two β sp³ carbons should come at about 109 ppm, plus an additional 10 ppm for the substitution of the β chlorine by a β sp³ carbon). The chemical shift for C-5 in structure **41b** should be 90–95 ppm, consistent with the observed chemical shift for C-7 in norbornene derivatives. Thus, structure **41b** is not in agreement with the observed shifts of 107.2, 112.0, and 101.6 ppm. The chemical shifts predicted for structure **41a**, on the other hand, are in reasonable agreement with experiment (109, 109, and 104 ppm for C-1, C-4, and C-5, respectively). Structure **41a** has subsequently been proved to be correct.[7]

The cmr spectra of the chlorocarbons **32** and **33** (isomeric bicyclo[3.3.0]octatrienes, C₈Cl₈) show eight signals. The chemical shifts predicted for four possible structures, a–d, of these isomers are as shown. The predicted shifts for a are in close agreement with those observed for **32**, with the signals at 110.4 and 106.2 ppm assigned to C-3 and C-8, respectively.[8] The shifts predicted for b are consistent with signals at 115.7 and 100.4 ppm for **33**.

Table I: ^{13}C Chemical Shifts of Chlorocarbons[a]

Structure		Formula	C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-8	C-9	C-10
	1	C_2Cl_4	75.4									
	2	$C_2Cl_4F_2$	72.6[b] [308, 35]									
	3	C_2Cl_6	87.5									
	4	C_3Cl_4	70.0		130.4							
	5	C_3Cl_6	65.5	60.7	99.9							
	6	$C_3Cl_6F_2$	64.7 [307]	95.8 [27.5]	92.6							
	7	$C_3Cl_5F_3$	71.6 [287]	100.3 [32]	93.3							
	8	C_3Cl_8	91.4[c]	89.8[c]								
	9	C_4Cl_6	(65.5	66.1)								
	10	$C_4Cl_4F_4$	78.8[c,f] [300, 15]		104.4[c] [15]							
	11	C_4Cl_6	58.7		100.7							
	12	C_4Cl_{10}	(89.9	89.3)								
	13	$C_5Cl_2F_6$	90.1[b,g] [7, 24]	87.6[b,g] [262, 24]	65.0[b] [28]							
	14	C_5Cl_6	(60.8	61.8)			110.6					
	15	C_5Br_6	(62.8	70.0)			135.7					
	16	C_5Cl_8	57.6		99.9	93.4						
	17	C_6Cl_6	61.4	75.0			55.6	62.0				
	18	C_6Cl_6	(56.7	61.3)[d]			83.3[d]					
	19	C_6Cl_8	59.8	103.3			65.5					
	20	C_6Cl_8	(55.2)		57.1			(56.0)				
	21	C_6Cl_8	(59.8	62.1)			115.2	95.6				
	22	C_6Cl_{10}	(50.8	55.9)	99.6*	92.2	101.1*	104.7				

No.	Formula	1	2	3	4	5	6	7	8	9
23	C₆Cl₄F₄	82.4 [257, 28]	66.6 [30]	60.4				60.4)		
24	C₇Cl₈	113.9	(55.3	59.4)	104.9	110.8	(59.4	79.7		
25	C₇Cl₈	106.8	55.4					75.0		
26	C₇Cl₈	(54.3	59.7	62.0	64.6*)	110.6	65.9*	74.2		
27	C₇Cl₈	(54.7	57.2	58.3	64.7*)	110.6	64.7*	107.6		
28	C₇Cl₈	(57.7	58.1	63.0)				97.6		
29	C₇Cl₁₀	113.4	(53.0	60.6)	102.0	106.4	97.6	75.0		
30	C₇Cl₁₀	52.4	58.0	99.9	92.4	101.0	64.3			
31	C₇Cl₁₈	105.4 / 104.1ᵉ	55.7 / 54.5ᵉ			95.4 / 94.2ᵉ		95.4 / 94.2ᵉ		
32	C₈Cl₈	(52.0	53.0)	110.4	(57.7	59.6	65.1	65.3)	106.2	
33	C₈Cl₈	115.7	(46.6	57.5	60.5	60.7	65.9	67.8)	100.4	
34	C₈Cl₁₀	103.8	56.3	59.3	100.4					
35	C₈Cl₁₀	(54.8	56.0)	96.8	94.9	113.9	(56.4	58.3)	111.6	
36	C₉Cl₁₀	(50.0	57.6	58.1	62.7)	110.2	65.0*	74.5**	66.0*	75.3**
37	C₁₀Cl₁₀	(60.8	61.8)			119.7				
38	C₁₀Cl₁₀	(51.8	61.1	64.3	67.0)	110.5				
39	C₁₀Cl₁₀	(54.3	54.5	60.4	64.7)	109.4				

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Table I (Continued)

Structure	Formula	C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-8	C-9	C-10
	$C_{10}Cl_{10}$	(49.9	54.9	55.9	59.4)	109.7	(61.9	62.9	64.5	66.5)	110.4
	$C_{10}Cl_{10}$	112.0*	(59.1	64.1)	107.2*	101.6					
	$C_{10}Cl_{12}$	109.0*	(51.5	57.4)	109.5*	104.0	106.1	94.9	(54.1	60.9	99.5
	$C_{10}Cl_{12}$	107.5*	(52.7	54.3)	108.6*	105.2	106.4	87.4	(56.4	58.7	97.5
	$C_{10}Cl_{14}$	(48.3	61.8)	99.7*	91.6	100.7*					

a The 13C chemical shifts are in parts per million upfield from CS2 and, unless otherwise stated, were measured from internal chloroform as solvent; the asterisks denote pairs of resonances which have been assigned to be consistent with other data; however, there is a possibility that the assignments could be interchanged; the parentheses enclose values of double-bonded carbon resonances which could not be specifically assigned; the brackets contain the 13C–19F coupling constants in hertz. b Measured from internal cyclohexane as solvent. c Measured from internal dioxane as solvent. d Measured from internal chloroform in 1:1 chloroform–dioxane as solvent. e Measured from internal tetrachloroethylene in 1:1 C2Cl4–dioxane as solvent. f Large Overhauser enhancement in 19F noise-decoupled cmr spectrum. g Small Overhauser enhancement in 19F noise-decoupled cmr spectrum.

Table II: 13C Chemical Shifts of Chlorocarbon Hydrides[a]

Structure	Formula	C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-8	C-9	C-10
	$C_2Cl_2H_2$	72.3 [206, 32.5]									
	$C_2Cl_2H_2$	72.6 [208, ~1]									
	C_2Cl_3H	76.0 [200.5]	67.4 [8]								
	$C_2Cl_3H_3$	132.8 [134]	82.9 [5]								
	C_3Cl_7H	117.8^b [186]	93.5^b	91.3^b							
	C_3Cl_7H	96.9^b	113.8^b [166]								
	C_4Cl_5H	69.4*	72.7 [169.8]	(69.1*	63.0)						
	$C_5Cl_4H_2$	67.6^g [8]	64.6 [4.4]			145.7^f [136]					
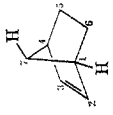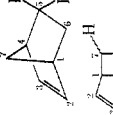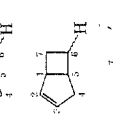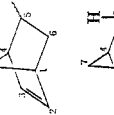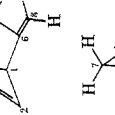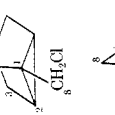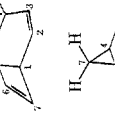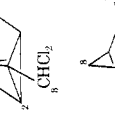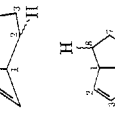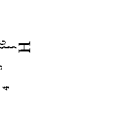
No.	Formula							
53	C_5Cl_7H	56.9	—	105.9[g]	115.2[f] [162]	—	—	—
54	$C_6Cl_5H_3$	(58.1)	65.4	—	—	122.9[g]	—	—
55	$C_7Cl_4H_6$	155.5[c,f] [135]	153.5[c,f] [135]	—	69.0	69.0	168.7[f] [113]	176.1[c,e,f] [130]
56	$C_7Cl_6H_2$	111.6	57.3[g]	64.8[f] [179.5]	128.8[f] [164.5]	115.1[g]	58.6)[c]	61.2)
57	$C_7Cl_6H_2$	109.1[g] [10]	55.0	—	—	51.7[f] [191.5, 4.5]	(58.1	76.5
58	$C_7Cl_6FH_3$	111.1[c] (1H, 19F [20])	(59.8	62.9)[c]	114.6[c]	149.9[c,f] [142] [23]	97.4[f] [174] [204]	91.9
59	$C_7Cl_7H_3$	112.0[c] (1H, 19F [20])	60.3	61.9	110.7	129.7[f] [163] [15]	100.9[f] [170] [216]	94.4
60	$C_7Cl_7H_3$	109.7[c]	61.6[c]	60.3[c]	115.0[c]	147.6[f] [143]	131.5[f] [163]	91.8
61	$C_7Cl_8H_2$	110.3	60.3	—	—	128.1[f] [166]	—	93.8
62	$C_7Cl_8H_2$	111.3	58.0	—	—	131.2[f] [168]	—	93.8
63	$C_7Cl_8H_2$	111.6	(58.6)	59.5)	110.8	123.8[f] [167]	126.1[f] [169]	93.2
64	$C_7Cl_8H_2$	133.2[g]	153.2[f] [191]	128.8[f] [164]	114.6[g]	98.9*	135.1[g]	101.1*
65	$C_7Cl_8H_2$	129.4[c,a,*] [166]	(58.5	61.4[c]	111.6[c]	98.0[c]	101.7[c]	128.6[c,a,*] [165]

Table II (Continued)

Structure	Formula	C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-8	C-9	C-10
66	$C_7Cl_8H_2$	$123.7^{c,g,*}$ [165]	(61.0	$59.8)^c$	105.2^c	95.8^c	100.4^c	$122.4^{c,g,*}$ [165]			
67	$C_7Cl_8H_2$	$104.9^{c,*}$	58.6^c	59.4^c	115.7^c	$138.1^{c,f}$ [145]	$105.3^{c,*}$	92.5^c			
68	$C_7Cl_9H_2$	119.8^g	55.0	60.3	101.2	111.5^g	128.9^f [168]	128.9^f [168]			
69	C_7Cl_9H	113.1	54.7	59.2	100.9	111.7^g	122.5^f [161.5]	105.4^g			
70	C_7Cl_9H	105.1	(56.9	59.6)	110.9^g	119.6^f [167.6]	101.3^g	94.3			
71	$C_8Cl_6H_4$	108.7^c	62.1^c	60.6^c	114.7^c	$152.1^{c,f}$ [140]	52.5^c	91.2^c	$81.4^{c,f}$ [160]		
72	$C_8Cl_8H_4$	154.9^c / 154.6^d	131.5^c / 131.4^d	99.7^c [6] / 99.2^d	116.5^c / 116.2^d			$150.9^{c,f}$ [147] / $150.9^{d,f}$	$154.9^{c,f}$ [154] / $154.6^{d,f}$		
73	C_8Cl_9H	110.8	63.7 [8]	61.9 [6]	127.1^f [164]	111.6^g [7]	(59.7	56.2)	93.8		
74	$C_8Cl_9H_3$	149.6^c / 149.3^d	131.5^c / 131.9^d	99.9^c / 99.6^d	116.6^c / 116.3^d			$153.3^{c,f}$ [145] / $153.3^{d,f}$	$126.9^{c,f}$ [180] / $126.5^{d,f}$		
75	$C_8Cl_{10}H_2$	112.3^f	122.3^f [159]	102.1^g [5]			60.8		92.6		
76	$C_8Cl_{10}H_2$	111.6^g	58.0	58.0	98.8	107.3^g	$118.7^{f,*}$	99.9	$119.7^{f,*}$		

		C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-8	C-9	C-10
77	$C_9Cl_6H_4$	109.9^b	60.9^b			53.5^b		90.9^b	84.2^{b,f} [163]		
78	$C_{10}Cl_8H_4$	115.8^{g,*}	(60.1^g [10]	60.6 [10]	116.6^{g,*}	112.2	103.2	133.1^f [146]	(55.9	60.1^g [10]	145.1^f [138]
79	$C_{10}Cl_{10}H_2$	110.3^{g,*}	(60.9^g [7]	63.0^g [6]	110.9^{g,*}	110.5	106.4	113.8^f [161]	58.2	57.9^g	127.8^f [168]
80	$C_7Br_2Cl_6H_2$	120.1^g	(55.6	59.6	101.3	110.8^g	139.6^{f,*} [170]	141.6^{f,*} [170]			
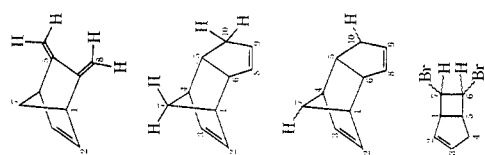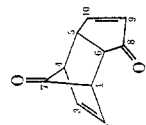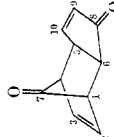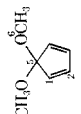
[a] See footnote a, Table I; square brackets contain the ¹³C–¹H coupling constants in hertz. [b] Measured from internal benzene as solvent. [c] Measured from internal dioxane as solvent. [e] Measured from internal cyclohexane as solvent. [d] Measured from internal benzene as solvent. [e] Only the two center lines of the expected quartet were observed. [f] Large Overhauser enhancement in proton-decoupled cmr spectrum. [g] Small Overhauser enhancement in proton-decoupled cmr spectrum.

Table III: ¹³C Chemical Shifts of Chlorocarbon Ketones[a]

	Structure	Formula	C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-8	C-9	C-10
81		C_3Cl_6O	102.6	17.3								
82		C_4Cl_4O	18.8	58.7	26.0	103.0						
83		$C_5Cl_4O_2$	13.3	44.1			122.5					
84		C_5Cl_6O	14.7	61.8	35.7	102.4	105.4					
85		C_5Cl_6O	10.0	116.4	56.0							
86		$C_5Cl_6O_2$	10.6	105.4			125.7					
87		$C_5Cl_4O_5S$	17.0	56.2	38.1	90.2	95.5					

Table III *(Continued)*

No.	Formula									
88	C_6Cl_6O	17.2[b]	49.1	(57.7	64.3	66.4)	116.0			
89	C_7Cl_6O	119.0	10.8	60.8*	36.0	117.0	56.7	61.3*		
90	C_8Cl_6O	(48.5)	22.8	52.1	60.7	66.1)	106.1	(67.4	69.3)	
91	$C_{10}Cl_8O_2$	121.7	56.0			14.2				
92	$C_{10}Cl_8O_2$	122.3	10.9	55.6	34.1	116.9				
93	$C_{10}Cl_8O_2$	122.1[e]	11.3[e]	54.7[e]	37.2[e]	114.3[e]				
94	$C_{10}Cl_8O_2$	119.8	(61.3	115.6	114.8	117.8	13.2*	12.0*	(53.4)	36.8
95	$C_{10}Cl_{10}O$	111.3	(56.1	108.5*	108.6*	117.0	94.7	12.3	(55.1)	36.5
96	$C_7Cl_4H_6O$	(63.8	64.3)		88.3	141.2				
97	C_7Cl_7HO	120.9[g]	7.8	57.2	34.7	114.7	105.0	125.7[f] [162.5]		
98	$C_8Cl_5H_3O$	119.9*	9.4	85.6	21.4	119.3*	(58.0	59.0)	131.4 [150]	

[a] See footnote *a* and *e–g*, Table I. [b] Measured from internal dioxane as solvent.

Table IV
[13]C Chemical Shifts[a] for the Trichloromethyl Carbon

$$R_\gamma^2—\overset{R_\gamma^1}{\underset{R_\gamma^3}{C_\beta}}—\overset{*}{C}_\alpha Cl_3$$

Compd	Carbon	C_β	R^1	R^2	R^3	*CCl₃, ppm	Δppm
3	1, 2	sp³	Cl	Cl	Cl	87.5	
							3.9
8	1, 3	sp³	C	Cl	Cl	91.4	
							4.2
21	6	sp³	C	C	Cl	95.6	
							4.3
5	3	sp²	C=		Cl	99.9	
							4.8
22	6	sp²	C=		C	104.7	

[a] See footnote *a*, Table I.

Predicted chemical shifts, ppm
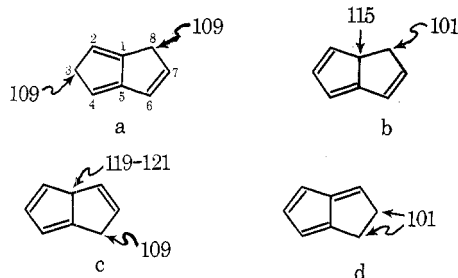
The cmr spectra of **34** and **35** (isomeric bicyclo[3.3.0]octadienes, C₈Cl₁₀) show two and four sp³ carbon resonances, respectively. Of the set of possible structures e–j, **34** has the symmetrical structure e or f, with e being more consistent with the shifts of 100.4 and 103.8 ppm. Chlorocarbon **35** must have one of the unsymmetrical structures g–j, and the predicted shifts for g are in best agreement with the observed shifts. Thus, the observed resonances are assigned to C-5 at 113.9 ppm, C-8 at 111.6 ppm, C-3 at 96.8 ppm, and C-4 at 94.9 ppm.

Predicted chemical shifts, ppm
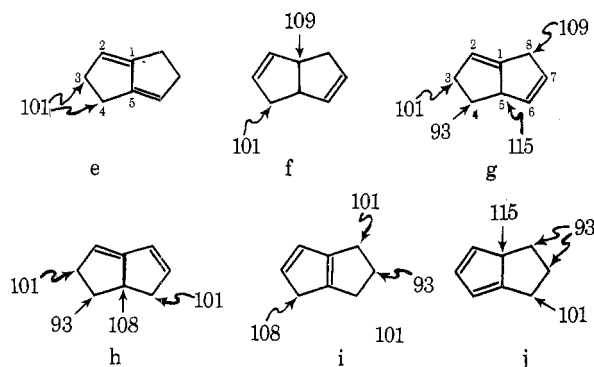
The C-7 resonances for octachloro- (**25**) and hexachloro-5,6-dihydronorbornadiene (**57**) are at 79.7 and 76.5 ppm, respectively, and appear abnormally deshielded for dichloromethylene carbons. The C-7 resonance for the parent hydrocarbon, norbornadiene, has also been observed at low field.[9] These low-field shifts may be due to extra ring strain in the dienes as compared to norbornene derivatives.

The cmr spectrum of **64** shows examples of the resonances due to dichloromethylene carbons (C-5 and C-7) with a β cyclopropyl group which are assigned at 98.9 and 101.1 ppm, respectively. These resonances are only slight-

Table V
[13]C Chemical Shifts[a] for Dichloromethylene and Chloromethine Carbons

	Compd	Carbon	*CCl₂, ppm[b]	R^1	R^2	R^3
	44	4	91.6	Cl		
	22	4	92.2	Cl		
	30	4	92.4	Cl		
	16	4	93.4	Cl		
	35	4	94.9	C		
	31	5, 6	95.4	C		
	29	6, 7	97.6	C		
	35	3	96.8	Cl	Cl	
	22	3	99.6 (101.1)	Cl	Cl	
	44	3	99.7 (100.7)	Cl	Cl	
	30	3	99.9	Cl	Cl	
	16	3, 5	99.9	Cl	Cl	
	11	3, 4	100.7	Cl	Cl	
	43	10	97.5	Cl	C	
	42	10	99.5	Cl	C	
	29	4	102.0	Cl	C	
	24	4	104.9	Cl	C	
	44	5	100.7 (99.7)	C	Cl	
	30	5	101.0	C	Cl	
	22	5	101.1 (99.6)	C	Cl	
	19	2, 3	103.3	C	Cl	
	28	7	107.6	Cl		
	40	10	110.4	Cl		
	32	3	110.4	Cl		
	38	5	110.5	Cl		
	14	5	110.6	Cl		
	26	5	110.6	Cl		
	32	8	106.2	C		
	39	5	109.4	C		
	40	5	109.7	C		
	36	5	110.2	C		
	27	5	110.6	C		
	20	2, 5	110.7	C		
	35	8	111.6	C		
	29	5	106.4	C	Cl	Cl
	42	5	104.0	C	C	Cl
	43	5	105.2	C	C	Cl
	41	5	101.6	C	C	C
	24	5	110.8	C	Cl	
	29	1	113.4	C	Cl	
	34	1	103.8	C	Cl	
	42	1	109.0 (109.5)	C	Cl	
	42	4	109.5 (109.0)	C	Cl	
	43	1	107.5 (108.6)	C	Cl	
	43	4	108.6 (107.5)	C	Cl	
	42	6	106.1	C	C	
	43	6	106.4	C	C	
	41	1	112.0 (107.2)	C	C	
	41	4	107.2 (112.0)	C	C	
	21	5	115.2	Cl	Cl	
	35	5	113.9	C	Cl	
	33	1	115.7	C	Cl	
	24	1	113.9	C	C	
	37	5	119.7	C	C	

[a] See footnote *a*, Table I. [b] Parentheses enclose assignments which may be interchanged.

ly affected by hydrogen substitution at C-2 and C-3, as will be shown later. It appears (see Table V) that a β sp² carbon and cyclopropyl carbon have a similar effect upon the dichloromethylene carbon shift. This observation is borne out by resonances of C-3 and C-5 for **72** and **74** which come at 99.7 and 99.9 ppm, respectively.

3. The CH Group. Substitution of hydrogen for chlorine in the perchlorocarbons can aid in assignment of the resonances by giving [13]C–[1]H couplings, and by producing recognizable shifts of the carbons relative to the parent compound. Thus, there is a large upfield shift for the carbon directly attached to hydrogen compared to the parent perchlorocarbon, while the carbons β to the CH group experi-

Table VI
^{13}C Chemical-Shift Changes between Perchlorocarbons and Chlorocarbon Hydrides

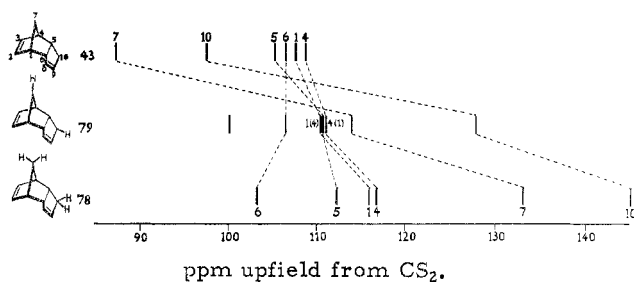| Carbon	—Perchlorocarbon to monohydro derivative—				——Monohydro to vicinal dihydro derivative——					Monohydro to gem-dihydro derivative		
	70–31	53–16	69–29	79–43	68–69	60–67	61–70	62–70	63–70	67–70	78–79	72–74
1	γ −0.3		γ −0.3	β +2.8	β +6.7	β +4.8	β +5.2	β +6.2	β +6.5	γ −0.2	β +5.5	β +5.3
3		β +6.0										
4	β +5.5	α +21.8	γ −1.1	$\beta + \gamma$ +2.3	+0.3	−0.7	−0.6	+0.4	−0.1	β +4.8	$\beta + \gamma$ +5.7	
5	α +24.2		β +5.3	$\beta + \gamma$ +5.3	γ −0.2	β +9.5	β +8.5	β +11.6	β +4.2	α +18.5	$\beta + \gamma$ +1.7	
6	β +5.9		α +24.9	$\gamma + \gamma$ 0.0	β +6.4	α +26.2	α +26.8	α +29.9	α +24.8	β +4.0	$\gamma + \gamma$ −3.2	γ 0.0
7	γ −1.1		β +7.8	α +26.4	α +23.5	γ −0.7	γ −0.5	γ 0.5	γ −1.1	γ −1.8	α +19.3	γ −2.4
8												α +28.0
10				α +30.3							α +17.3	

Figure 2. Variation in ^{13}C chemical shifts for successive substitution by hydrogen in *endo*-perchlorocyclopentadiene dimer.
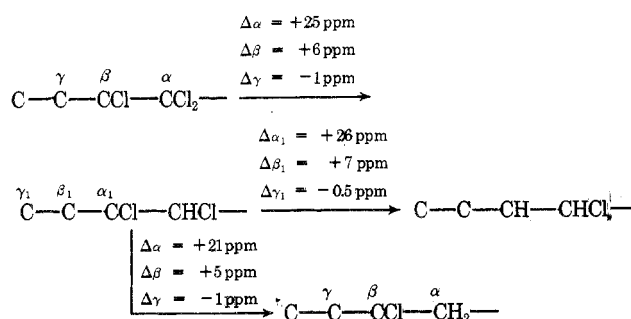
ence a smaller upfield shift. The one-bond ^{13}C–^{1}H coupling further aids in assignment and the directly bonded carbon resonance shows substantial Overhauser enhancement for proton-decoupled spectra. The β carbon usually has only a small Overhauser enhancement and sometimes an observable, but small, two-bond ^{13}C–C–^{1}H coupling.

The six sp^3 carbon resonances of the exo and endo isomers of hexachlorocyclopentadiene dimer (42 and 43) were assigned with the aid of the cmr spectra of the *endo*-7,10-dihydro and *endo*-7,7,10,10-tetrahydro derivatives 78 and 79. The chemical-shift assignments for compounds 43, 78, and 79 are summarized in Figure 2 (see also Table VI). The C-7 and C-10 resonances are readily identified by the large upfield shift (17–30 ppm) for the introduction of each hydrogen, and by the enhanced signal intensity in proton-decoupled spectra. The C-1, C-4, and C-5 resonances are identified by much smaller upfield shifts (2–6 ppm) for each proton introduced at C-7 or C-10, and small Overhauser enhancements. The γ carbon (C-6) is but little affected by substitution of chlorine by hydrogen and, for compound 78, actually experiences a small downfield shift. The signal at 105.2 ppm in 43 is assigned to C-5 (predicted shift 104 ppm) while the signals at 107.5 and 108.6 ppm are assigned to C-1 and C-4 in general agreement with other bridgehead carbon assignments in other norbornene derivatives. Assignments for the exo isomer 42 were made in a corresponding way.

The five sp^3 carbon resonances of decachlorobicyclo-[3.2.0]heptene (29) are in reasonable agreement with the predicted shifts. Analysis of the cmr spectra of the 6-hydro (69), 6,7-dihydro (68), and 6,7-dibromo-6,7-dihydro (80) derivatives allows a fairly definite set of assignments for compound 29. The variations in chemical shifts for this group of compounds are summarized in Figure 3 (see also Table VI). High-field resonances and Overhauser enhancements indicate those carbons with directly bonded

protons (C-6 for 69, and C-6 and C-7 for 68). The resonances due to C-5 and C-7 of 69 and C-1 and C-5 of 68 are identified by an upfield shift (6–8 ppm relative to 29) and small Overhauser enhancements. The signal due to C-4 is least affected by hydrogen substitution at C-6 and C-7, and for 69 and 68, a small downfield shift (−1.1 ppm) is observed. The mode of synthesis of 69 suggests the hydrogen to be either at C-6 or C-7, and having the hydrogen at C-6 is more consistent with the cmr data. The highest field resonance (113.4 ppm) for 29 can only be the C-1, and if the hydrogen in 69 were at C-7, an upfield shift for the C-1 resonance would be expected, but is not observed.

Table VI shows the chemical-shift variations for substitution of chlorine by hydrogen in chlorocarbons. The average chemical-shift changes at the α, β, and γ carbons for substitution by a single proton are approximately +25, +6, and −1 ppm, respectively. Substitution by a second proton to yield a vicinal dihydro derivative results in similar average α, β, and γ carbon shift increments. For substitution by a second proton to yield a geminal dihydro derivative, the average α, β, and γ carbon shift increments are +21, +5, and −1 ppm, respectively.

$$\Delta\alpha = +25 \text{ ppm}$$
$$\Delta\beta = +6 \text{ ppm}$$
$$\begin{matrix} \gamma & \beta & \alpha \\ \end{matrix} \quad \Delta\gamma = -1 \text{ ppm}$$
$$C—C—CCl—CCl_2— \longrightarrow$$

$$\Delta\alpha_1 = +26 \text{ ppm}$$
$$\Delta\beta_1 = +7 \text{ ppm}$$
$$\begin{matrix} \gamma_1 & \beta_1 & \alpha_1 \\ \end{matrix} \quad \Delta\gamma_1 = -0.5 \text{ ppm}$$
$$C—C—CCl—CHCl— \longrightarrow C—C—CH—CHCl—$$

$$\Delta\alpha = +21 \text{ ppm}$$
$$\Delta\beta = +5 \text{ ppm}$$
$$\Delta\gamma = -1 \text{ ppm} \quad \begin{matrix} \gamma & \beta & \alpha \\ \end{matrix}$$
$$\longrightarrow C—C—CCl—CH_2—$$

In a study of norbornene hydrocarbons, sterically induced shifts have been attributed to the C-7, C-5, and C-6 carbons.[9a] The C-7 chemical-shift variations with hydrogen substitution at C-5 and C-6 for the chloronorbornenes do not appear due to steric factors, but correlate well with the number rather than with configuration (exo or endo) of the hydrogens at C-5 and C-6, with an additive downfield "γ-shift parameter" at C-7 for each hydrogen. The chemical-shift change at C-7 per exocyclic double bond is −1.3 ppm for the change from 67 to 71, and −2 ppm for the change from 31 to 77.

B. The sp^2 Carbon Chemical Shifts. The sp^2 alkenic carbon resonances occur in the range 50–75 ppm. However, certain assignments are generally only possible for

Table VII
13C Chemical Shifts of Some Alkenic Carbons in Perchlorocyclopentenes[a]

Compd		sp² carbon shift		Δδ	Mean sp² carbon shift
	16	C-1	57.6		
	20	C-3	57.1	−0.5	
	53	C-1	56.9	−0.7	
	22	C-1	50.8	−6.8	53.4
		C-2	55.9	−1.7	
	30	C-1	52.4	−5.2	55.2
		C-2	58.0	+0.4	
	44	C-1	48.3	−9.3	55.0
		C-2	61.8	+4.2	

[a] See footnote *a*, Table I.

ppm upfield from CS_2.
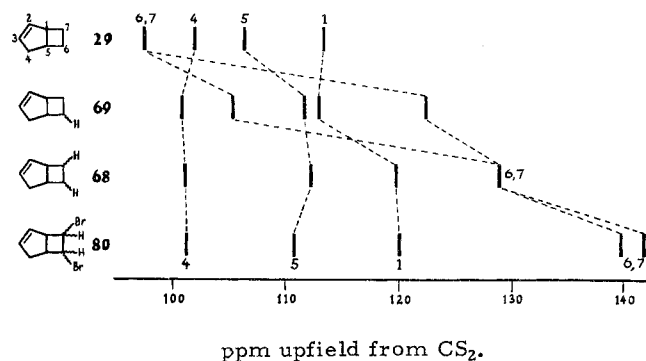
Figure 3. Variation in 13C chemical shifts for successive substitution by hydrogen in perchlorobicyclo[3.2.0]hept-2-ene.

Table VIII
13C Chemical Shifts of Alkenic Carbons in Perchlorocycloalkenes[a]

Compd		sp² carbon shift		Mean	
	16	C-1	57.6		
	29	C-2	53.0	56.8	
		C-3	60.6		
	69	C-2	54.7	56.9	
		C-3	59.2		
	68	C-2	55.0	57.6	
		C-3	60.3		
	80	C-2	55.6	57.6	Average = 57.4 ppm
		C-3	59.6		
	24	C-2	55.3	57.4	
		C-3	59.4		
	34	C-2	56.3	57.8	
		C-3	59.3		
	76	C-2	58.0	58.0	
			58.0		
	22	C-1	50.8	53.4	
		C-2	55.9		
	30	C-1	52.4	55.2	Average = 54.5 ppm
		C-2	58.0		
	44	C-1	48.3	55.0	
		C-2	61.8		
	11	C-1	58.7		
	24	C-6	(59.4)	59.9	Average = 59.4 ppm
		C-7	(60.4)		
	56	C-6	(58.1)	59.7	
		C-7	(61.2)		

[a] See footnote *a*, Table I.

simple molecules. For more complex molecules, the only helpful data involve comparisons with model compounds and with sp² carbon resonances for hydrocarbons. For this reason, the sp² carbon resonances assigned in Table I seem reasonable and internally consistent; however, these assignments cannot be considered unequivocal. In general, sp² carbon chemical shifts in hydrocarbons do not appear sensitive to conjugation.[10] Similar effects are observed here for the sp² alkenic carbon resonances in the chlorocarbons. For hydrocarbons, replacement of a vinylic proton by carbon results in deshielding of the α sp² carbon resonance and shielding of the β sp² carbon resonance.[11] For chlorocarbons, there is a corresponding deshielding change of the α sp² carbon shift on replacement of chlorine by carbon. The β sp² carbon seems to be erratic in experiencing a smaller shielding or deshielding effect.

The data in Tables VII and VIII give a mean value of the sp² alkenic carbon shift in a five-membered ring of 57.4 ± 0.5 ppm, when chlorine is the only substituent. A carbon substituent at an alkenic carbon in the chlorocyclopentenes causes a larger chemical-shift difference between the two sp² carbon resonances, but the mean shift is nearly constant at 54.5 ppm.

The position of the vinyl substituent for the perchlorovinylcyclopentadienes, **26, 27,** and **36,** does not seem to be deducible from the cmr chemical-shift data. However, the relatively constant chemical shifts of 64–65 and 74–75

ppm observed for some sp² carbon resonances in chlorocarbons **26, 27, 30,** and **36** suggest that these resonances be assigned to the sp² carbons of the vinyl substituents themselves.

The number of resonances in the cmr spectrum of the divinyl derivative **36** indicates unsymmetrical substitution (1,2- or 1,3-divinyl). There is no compelling evidence to assign the higher field resonance (74–75 ppm) to the terminal sp² carbon, except by comparison with the sp² carbons in unsaturated hydrocarbons.[9]

The resonances for the sp² carbons in the chloronorbornenes are tentatively assigned in Table IX. The sp² carbon resonances for the exo 5,6-dihydro derivative **61** are shielded relative to those for the endo derivative **62.** The measurable three-bond 13C–1H couplings were used to assign the sp² carbon resonances of chlorocarbons **60, 67,** and 71 (see below).

C. 13C–1H Coupling Constants. As mentioned previously, the 13C–1H coupling constants in chlorocarbon hydrides provide an additional tool for the cmr spectral analysis. The observed coupling constants are summarized in Table X. The one-bond 13C–1H coupling constants for sp³-hybridized carbons carrying one proton are about the same whether the carbon is attached to chlorine or to ei-

Table IX
¹³C Chemical Shifts^a for C-2, and C-3, C-7 in Some Chlorinated Norbornenes

	31	70	62	61	63	67	60	71	77	25	57
C-7	95.4	94.3	93.8	93.8	93.2	92.5	91.8	91.2	90.9	79.7	76.5
Δδ/H^b		-1.1	-0.8	-0.8	-1.1	-1.4	-1.2				-1.6
C-2	55.7	56.9	58.0	60.3	58.6	58.6	61.6	62.1	60.9	55.4	55.0
C-3	55.7	59.6	58.0	60.3	59.5	59.4	60.3	60.6	60.9	55.4	55.0

^{a} See footnote a, Table I; also Figure 4. Where C-2 and C-3 are not identical by symmetry, the assignments are tentative.
^{b} The C-7 shift relative to C-7 in compound **31** for the norbornenes, and C-7 in compound **25** for the norbornadiene, divided by the number of protons at C-5 and C-6.

Table X
One-Bond ¹³C–¹H Coupling Constants for Chlorocarbon Hydrides

Compd	Carbon	$^1J(^{13}C-^1H)$, Hz	
75	2, 4	159	
79	7	161	
69	6	161.5	
53	4	162	
60	6	163	
64	3	164	
73	4	164	
56	4	164.5	
65	7	165	sp³ carbon R—C—H R = Cl or C
66	1	165	(with C above and C below the central C)
50	2	166	
61	5, 6	166	Mean $^1J(^{13}C-^1H) = 165 \pm 6$ Hz
66	7	165	
63	5(6)	167	
70	5	167.6	
62	5, 6	168	
68	6, 7	168	
79	10	168	
63	6(5)	169	
80	6, 7	170	
52	5	136	
78	10	138	
71	5	140	sp³ carbon (CH₂ with two H)
60	5	143	
67	5	145	
74	7	145	
78	7	146	Mean $^1J(^{13}C-^1H) = 142 \pm 5$ Hz
72	7	147	
Ethylene		157^c	
71	8	160	sp² carbon =C (with two H)
Vinyl chloride	2	160–161^c	
77	8, 9	163	
Vinylidene chloride	2	166^c	Mean $^1J(^{13}C-^1H) = 161 \pm 5$ Hz
1,2,3,4-Tetrachlorobenzene	5	171.9^a	
2,4,6-Trichloroaniline	3	170.1^a	
1,3,5-Trichlorobenzene	6	172.2^a	sp² carbon C—H
2,3,5,6-Tetrachloronitrobenzene	4	175.0^a	
56	3	179.5	Mean $^1J(^{13}C-^1H) = 174 \pm 6$ Hz
[57	5, 6	191.5]^b	
Vinyl chloride	1	195.0^c	sp² carbon =C (with H and Cl)
47	1	200.5	
45		206	
46		208	Mean $^1J(^{13}C-^1H) = 202 \pm 7$ Hz
64	2	191	sp³ carbon (cyclopropyl) Mean $^1J(^{13}C-^1H) = 191$ Hz

^{a} J. Goldstein and G. S. Reddy, *J. Chem. Phys.*, **36**, 2644 (1962). ^{b} Not included in the mean value. ^{c} G. Govil, *J. Chem. Soc. A*, 1420 (1967).

ther sp² or sp³ carbons. The average value of this type of coupling was 165 ± 6 Hz. The *gem*-dihydro carbons show an average value $^1J(^{13}C-^1H) = 142 \pm 5$ Hz. The difference between the average values for the coupling constants at these two carbon types is 24 Hz, which compares with the differences in $^1J(^{13}C-^1H)$ of 28–31 Hz for chloromethanes.[12] The larger coupling constant (191 Hz) for the cyclopropyl derivative **64** is consistent with the increased

value for $^1J(^{13}C-^1H)$ in the cyclopropane hydrocarbon.[13]

The one-bond sp^2 carbon-proton coupling constants fall into three distinct classes. Cyclic double-bond sp^2 carbons ($^1J(^{13}C-^1H)$ = 174 ± 6 Hz), terminal double-bond sp^2 carbons bonded to one proton $^1J(^{13}C-^1H)$ = 202 ± 7 Hz), and terminal double-bond sp^2 carbons bonded to two protons ($^1J(^{13}C-^1H)$ = 161 ± 5 Hz). These couplings are comparable to one-bond sp^2 carbon-proton coupling constants in hydrocarbons;[14] thus, the terminal sp^2 carbon of styrene has $^1J(^{13}C-^1H)$ = 161 Hz,[13a] and the sp^2 carbons of cyclohexene have $^1J(^{13}C-^1H)$ = 170 Hz.[15]

Chlorocarbon **51** is a monohydro derivative of hexachlorobutadiene. It is not possible to assign the proton to C-1 or C-2 from chemical-shift data alone; however, $^1J(^{13}C-^1H)$ = 169.8 Hz seems incompatible with the proton at C-1, but is reasonable for the proton at C-2 (see Table X). The observed coupling constant $^1J(^{13}C-^1H)$ = 191.5 Hz for hexachloro-5,6-dihydronorbornadiene (**57**) is larger than expected, possibly because ring strain produces greater s character in the alkenic C(-H) orbitals which should be reflected[16] in an increased $^1J(^{13}C-^1H)$.

Figure 4 shows the sp^2 carbon resonances observed for chlorocarbon hydrides **60**, **67**, and **71**. The broader of the resonances in the proton-decoupled spectra is assigned to C-3 for both **67** and **71**. This assignment is subject to the assumption that the three-bond $^{13}C-^1H$ coupling constant is not zero, while a four-bond coupling is not observable. The spectra shown in Figure 4 were measured at 20 Hz sec^{-1} sweep rate, and, while the three-bond couplings are not resolved, the participating sp^2 carbon resonances are measurably broader. The partial resolution of the three-bond $^{13}C-^1H$ coupling at the sp^2 carbons for **60** was reproducible, although the assignments are not conclusive because of the rapid sweep rates employed.

D. Chlorocarbon Ketones. The cmr chemical-shift data for the chlorocarbon ketones are summarized in Table III. Carbonyl carbon resonances are observed at 9-23 ppm, and other sp^2- and sp^3-hybridized carbon resonances are observed in the usual regions, as previously discussed.

1. The sp^3 Carbon Chemical Shifts. It is possible to correlate the chemical shifts of a carbon (the β' carbon) directly bonded to a carbonyl carbon with that of a carbon (the β carbon) directly bonded to a dichloromethylene carbon (see Table XI).[17]

The assignments of the resonances for C-1 and C-5 of the ketone **89** were made with the aid of the substituent chemical-shift parameters in Table XI, in conjunction with the assignments shown in Table I for **24**. For chlorocarbon ketone **98**, the chemical shifts for C-1 and C-5 are very similar (119.9 and 119.3 ppm) and, for ketone **89**, the corresponding shifts are C-1 and C-5, 119.3 and 117.0, respectively. If the C-4 methoxy substituent of ketone **98** has a shielding effect at C-5, with negligible effect at C-1, then there is further evidence for the assignment of C-1 of **89** to the resonance at 119.0 ppm. For this reason, the C-1 resonance is assigned to higher field than the C-5 resonance in **92** and **93**, and the C-6 resonance to higher field than the C-5 resonance in **94** and **95**.

The diketone **94** has been assigned as the endo (rather than exo) isomer on the basis of the better correlation between the observed chemical shifts and the shifts predicted from *endo*-perchlorocyclopentadiene dimer **43**, with the substituent chemical-shift parameters presented in Table XI. The indication that ketone **95** is the exo isomer is the greater similarity between the C-7 chemical shift for the ketone and *exo*- (rather than *endo*-) perchlorocyclopentadiene dimer **42**.

2. The sp^2 Carbon Chemical Shifts. The alkenic sp^2
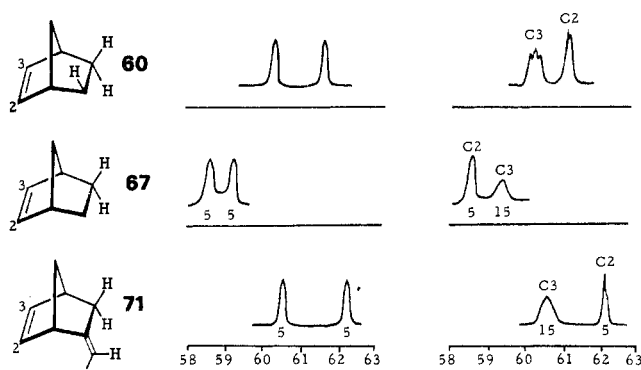
Figure 4. Schematic proton-coupled (right) and -decoupled (left) ^{13}C spectra of **60**, **67**, and **71** at 15.0 MHz. The numbers directly under the peaks are approximate line widths at half-height.

carbon resonances in the β' and γ' unsaturated ketones[17] are observed at ~34 and 55-60 ppm. The lower field signal is assigned to the γ' alkenic carbon by analogy with the corresponding hydrocarbon ketones.[18] The deshielding effect of the methoxy substituent on the C-4 resonance of **98** (compare with **89**) is also consistent with ^{13}C shifts in hydrocarbon β',γ' unsaturated ketones.[18] In many cases, the β' alkenic carbon resonance cannot be distinguished from other alkenic carbon resonances in the same molecule. However, the low-field alkenic carbon resonance (ca. 34 ppm) and carbonyl carbon resonance (9-23 ppm) readily characterize a β',γ' unsaturated chlorocarbon ketone.

Ketone **90** is an isomer of hexachloro-2-oxobicyclo[3.3.0]octatriene with the possible structures **90a-e**.

Predicted chemical shifts, ppm
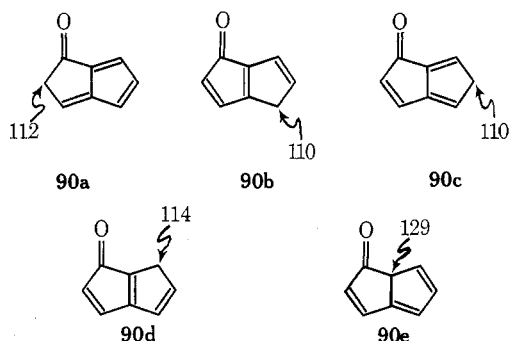
The cmr spectrum of chlorocarbon ketone **90** does not show a low-field alkenic carbon resonance characteristic of a β',γ' unsaturated ketone. The sp^3 carbon resonance is observed at 106.1 ppm. On the basis of the predicted chemical shifts for the sp^3 carbon resonance, structure **90b** or **90c** seems most reasonable for **90**. In the absence of a better correlation for sp^2 carbon chemical shifts in conjugated systems, it is not possible to assign a more specific structure to ketone **90**.

There are four possible structures (**a-d**) for the isomeric diketones **92** and **93**, and the cmr chemical-shift data do not, at this time, permit one to distinguish between them.
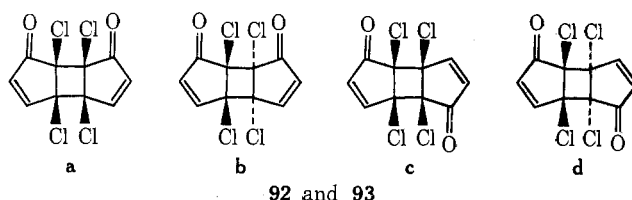
92 and 93

Registry No.—1, 127-18-4; 2, 76-12-0; 3, 67-72-1; 4, 6262-42-6; 5, 1888-71-7; 6, 661-96-1; 7, 1652-89-7; 8, 594-90-1; 9, 87-68-3; 10, 336-50-5; 11, 6130-82-1; 12, 6820-74-2; 13, 706-79-6; 14, 77-47-4; 15,

Table XI
Comparison of ¹³C Chemical Shifts of Carbons Adjacent to a Carbonyl and a Dichloromethylene Group

```
        O                                            O
     * ‖                                         ‖  *
—CCl₂—C—  ⟶  —C—C—              —CCl₂—C—C—  ⟶  —C—C—C—
```

Carbon	Δδ, ppm	Carbon	Δδ, ppm
C-1 (81)–C-1 (8)	+11.2	C-4 (84)–C-3 (16)	+2.5
C-2 (85)–C-3 (16)	+16.5		
C-5 (84)–C-4 (16)	+12.0		
[C-5 (83)–C-4 (16)]/2ᵃ	+14.5		
[C-5 (86)–C-4 (16)]/2ᵃ	+16.1		

ᵃ An additive effect is assumed for the two carbonyl groups in compounds **83** and **86**.

14310-17-9; **16**, 706-78-5; **17**, 6317-25-5; **18**, 1128-20-7; **19**, 1680-65-5; **20**, 3424-05-3; **21**, 6928-57-0; **22**, 50565-48-5; **23**, 50565-49-6; **24**, 34004-45-0; **25**, 15725-07-2; **26**, 50565-47-4; **28**, 21703-93-5; **29**, 50565-50-9; **30**, 50565-51-0; **31**, 2626-30-4; **32**, 27376-18-7; **33**, 37820-33-0; **34**, 50558-31-1; **35**, 50558-34-4; **36**, 50479-39-5; **37**, 2227-17-0; **38**, 27425-40-7; **39**, 27425-42-9; **40**, 27425-41-8; **41**, 33234-21-8; **42**, 2626-29-1; **43**, 27425-43-0; **44**, 27396-27-6; **45**, 156-59-2; **46**, 156-60-5; **47**, 79-01-6; **48**, 71-55-6; **49**, 594-89-8; **50**, 3849-33-0; **51**, 21400-41-9; **52**, 695-77-2; **53**, 50565-55-4; **54**, 16177-47-2; **55**, 50565-56-5; **56**, 50565-57-6; **57**, 3389-71-7; **58**, 14446-77-6; **59**, 50565-58-7; **60**, 2440-02-0; **61**, 2439-87-4; **62**, 38672-05-8; **63**, 2439-88-5; **64**, 50565-59-8; **65**, 28021-60-5; **66**, 26770-94-5; **67**, 50565-60-1; **68**, 50565-61-2; **69**, 50565-62-3; **70**, 35960-34-0; **71**, 4659-42-1; **72**, 50565-63-4; **73**, 50565-64-5; **74**, 50565-65-6; **75**, 50565-66-7; **76**, 50479-40-8; **77**, 6914-86-9; **78**, 50565-67-8; **79**, 29272-51-3; **80**, 50565-68-9; **81**, 116-16-5; **82**, 3200-96-2; **83**, 15743-13-2; **84**, 2514-52-5; **85**, 15743-12-1; **86**; 50565-69-0; **87**, 50565-70-3; **88**, 21306-21-8; **89**, 23326-66-1; **90**, 50565-71-4; **91**, 50565-72-5; **92**, 50565-73-6; **94**, 50565-74-7; **95**, 50565-75-8; **96**, 2207-27-4; **97**, 50565-76-9; **98**, 50479-41-9.

References and Notes

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(5) Care should be taken in interpreting integrated signal intensities which might be obtained for cmr spectra measured by the CAT technique with fairly rapid sweeps and high power levels. Under these conditions (which tend to optimize the signal to noise ratios for a given total time of observation), we have found very substantial and disturbing deviations from the predicted integrals on sam-

ples of known structure. After considerable hassling over the source of the difficulty, it was finally traced to the relatively long relaxation times of carbon in chlorocarbons which, with rapid sweeps, may not permit return of the equilibrium magnetization between sweeps. We have been able to show with the aid of a program for numerical integration of the Bloch equations developed here by Donald W. Roberts, somewhat along the lines of that described by R. Ernst and W. A. Anderson, *Rev. Sci. Instrum.*, **36**, 1696 (1965), that the first in a rapid series of sweeps gives normal integrals, but further sweeps do not, and, after three or four sweeps, a quasi-equilibrium is set up, which leads to an overall accumulation of signal intensities which may give up to 100% errors in relative signal integrals.

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Spectral Comparison of Steric Inhibition of Resonance in Some Hindered p-Arylacetophenones as Neutrals and as Gaseous Ions

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The infrared and ultraviolet absorption spectra of a series of p-phenylacetophenones substituted ortho to the aryl–aryl bond indicate steric inhibition of interaction between the rings by the substituent. The mass spectra, within error limits established earlier for multiple substitution, indicate that steric inhibition of resonance is not important in the ions.

The remarkable correlation of ion intensities in the mass spectra of acylbenzenes with Hammett σ constants[1] is probably the result of a correlation of onset potentials for formation of the pertinent ions unobscured by the various factors which cannot be correlated by such constants and which apparently are unimportant in the acylbenz-