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(37) (a) It is of interest to note that according to the ^{13}C SCS (C_4) in system **1** [or para ^{19}F SCS in system **1** (ref 2 and 3)] the electron-withdrawing effect of the weak polar CN σ bond (X = NCH_3, Table III) is similar in magnitude but opposite in sign to the electronic effect of the weak polar CSi σ bond (X = $Si(CH_3)_2$ which is now accepted as being due to hyperconjugative electron donation. (b) M. Bullpitt, W. Kitching, D. Doddrell, and W. Adcock, *J. Org. Chem.*, accepted for publication. (c) P. Beltrame, P. L. Beltrame, P. Caramella, G. Cellerino, and R. Fantechi, *Tetrahedron Lett.*, 3543 (1975).
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The Palladium(II)-Catalyzed Olefin Carbonylation Reaction. IV. Carbon-13 Nuclear Magnetic Resonance Analysis of the Reaction Products

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Carbon-13 NMR spectra of the acyclic and alicyclic diester and β-methoxy ester products from the palladium(II)-catalyzed olefin carbonylation reaction are reported. Substituent effects were derived for the carbons of an alkyl chain containing two carbomethoxyl functions which demonstrate the importance of the steric environment on carbon-13 chemical shifts.

Carbon-13 nuclear magnetic resonance spectrometry (^{13}C NMR) is one of the most powerful techniques available for the study of the structure of organic molecules. This usefulness is based, in part, on empirical correlations of carbon-13 shieldings and molecular structure.[2,3] In general, the effects of various substituents on the ^{13}C shieldings of neighboring carbons are found to be additive within families of compounds. Consequently, the positions of ^{13}C absorptions for related compounds may often be predicted with good precision in a wide variety of systems and can be valuable for signal assignments in the analysis of complex spectra.

Generally, ^{13}C shielding parameter sets have been derived from the results for a series of monosubstituted compounds, while the combined effects in di- and polysubstituted systems, with few exceptions,[4,5] have not been studied in detail. In this paper, we report the results of a ^{13}C NMR study of a series of acyclic and alicyclic diesters and β-methoxy esters obtained from the transition metal catalyzed carbonylation reaction of olefins.[5,6]

Experimental Section

All diesters and β-methoxy esters were obtained from the palladium(II)-catalyzed carbonylation reaction of olefins.[6,7] Isolation and purification of the individual products were effected by preparative vapor phase chromatography. The carbon-13 nuclear magnetic resonance spectra (^{13}C NMR) were measured on a Bruker HX-90E pulse Fourier transform NMR spectrometer equipped with an SPX high-power amplifier, a broad band decoupler, and a Model B-NC 12 computer. The spectrometer was operated at 22.63 MHz with a 4-μs pulse duration (flip angle 30°), a 2-s pulse repetition time, and an acquisition time of 0.819 s. Because of the small amounts of material available in most cases, the sample was placed in a 5-mm sample tube held concentrically inside the standard 10-mm sample tube and surrounded by deuterium oxide. In this way the sample was concentrated and a greater portion of computer memory was allotted to sample instead of deuteriochloroform. Spectra were taken on neat or chloroform-*d* solutions and were calibrated with tetramethylsilane as the internal reference. Several spectra taken on neat and 50% solutions in chloroform-*d* solutions of the same compound showed no solvent shift effects. Multiplicities and couplings were obtained directly from undecoupled spectra. Chemical shift assignments are based on multiplicities and the general pattern of shielding effects of substituents.[2,3]

Results and Discussion

The carbon-13 chemical shift data for the acyclic diester products obtained from the palladium(II)–copper(II)-catalyzed carbonylation of selected α-olefins[6,7] are listed in Table I. The assignment of individual signals in the spectra of the diesters is unambiguous and is based on off-resonance decoupling experiments and on the general pattern of shielding effects of substituents (vide infra). The aliphatic carbons of the diester molecules studied absorb over a wide range, 10.7–58.9 ppm. The methoxyl carbons of the ester functions are slightly deshielded with respect to methanol ($\sim$+2.3 ppm) absorbing at an average value of 51.6 ± 0.4 ppm. Interestingly, in only two cases were the chemical shifts of two nonequivalent methoxyl functions in the same molecule not accidentally overlapping.

Absorptions which were assigned to the carbonyl function ranged from 169.3 to 177.0 ppm. The lower field values were observed for malonic esters while the higher field values were obtained from adipic esters. The data, in addition, suggest that a terminal carboxyl carbon is shielded compared to an internal carboxyl carbon by an average of 2.5 ppm. This is probably the result of a slight deshielding influence that an additional β-carbon–carbon bond exerts at the internal carboxyl carbon.

Another interesting aspect of these data is the occurrence of magnetic nonequivalence. Thus, the ^{13}C NMR data for the *dl* and meso diastereoisomers of dimethyl 2,3-dimethylbutanedioate (**1** and **2**, respectively) demonstrate the effect of the presence of two asymmetric centers in the molecule. All carbons, including the ester carbonyl and methoxyl, have different chemical shifts for the two diastereomers. Carbon-13 NMR is therefore useful for detecting mixtures of diastereomers. In all, three diesters studied were found to be diastereomeric mixtures. These spectra were somewhat unusual in that several carbons which might be expected to give two signals were accidentally equivalent while in other cases carbons two or three bonds removed from the asymmetric center were nonequivalent.

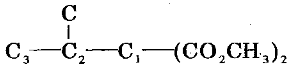
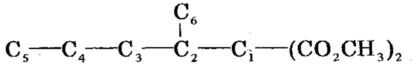
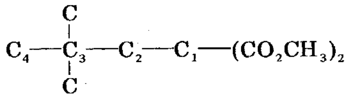
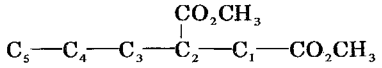
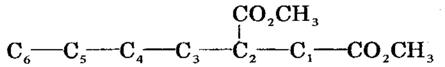
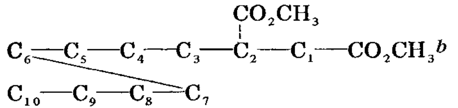
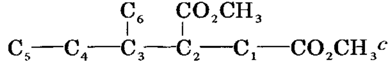
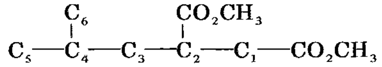
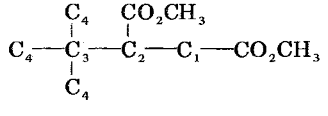
The substituent effects for the linear diesters given in Table I were determined by two methods. The change in chemical shift with respect to the parent alkane, $\Delta\delta = \delta_{obsd} - \delta_{RH}$, is given in parentheses. A second comparison was determined by calculating the chemical shift difference of the diester and the corresponding hydrocarbon wherein methyl groups take the place of ester functions. These calculations, $\Delta\delta = \delta_{obsd} - \delta_{RCH_3}$, are given in brackets. Thus the chemical shift of dimethyl *n*-propylsuccinate was compared with those of pentane and 3-methylhexane, respectively. The chemical shift data for the parent and methyl-substituted hydrocarbons were taken directly from the literature.[8,9] Positive values in Table I indicate downfield shifts while negative values indicate upfield shifts.

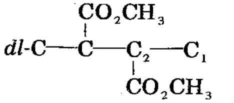
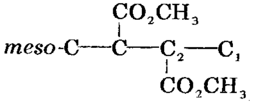
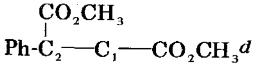
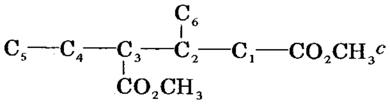
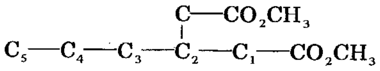
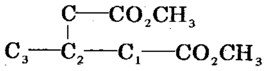
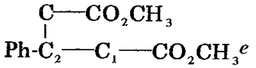
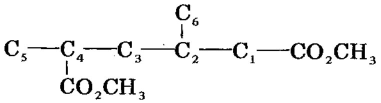
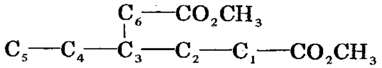
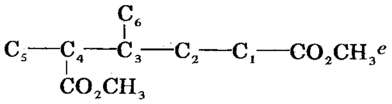
The substituent effects of the carbomethoxyl group derived from a series of terminal aliphatic monoesters by comparison with the parent alkane are α, +20; β, +3; γ, −2.5; δ, +0.8.[3,10] When compared with the methyl-substituted parent alkane, the effects are determined as α, +11.35; β, −6.90; γ, −0.10.[11] The shielding effects derived from the branched dimethyl esters in this study are complicated, however, by the fact that the observed change in chemical shift is usually the result of not one, but two substituents. The data suggest that these shielding effects are quite dependent upon steric and conformational differences. Although the general trends are qualitatively similar for all compounds studied, often large quantitative differences occur which are dependent upon substitution at or near a particular carbon. For instance, comparison of the $\delta_{obsd} - \delta_{RH}$ values for a carbon $\alpha\beta$ to two ester groups (i.e., for succinic esters) demonstrates that the terminal carbons are more highly deshielded than the internal carbons. An average substituent effect of 21.7 ± 0.9 was the value for terminal carbons (C1) and 17.7 ± 1.6 for internal carbons (C2). For all acyclic diesters studied, the average deshielding effect for a terminally substituted carbomethoxyl group averaged 4.0 ppm larger than the corresponding effect of an internal ester substituent. The average deshielding at a carbon $\alpha\beta$ to two carbomethoxyl groups calculated for 16 carbon atoms by comparison with the parent alkane was 19.5 ppm with a standard deviation of 2.2 ppm. Thus computation of diester shielding effects in this manner is subject to rather large errors.

Shielding effect calculations based on the chemical shift difference $\delta_{obsd} - \delta_{RCH_3}$, however, were found to give more consistent results. Substituent effects calculated by this method are listed in Table II. In general, the standard deviation is within 1.0 ppm or less of the average value for a given disubstitution pattern. Comparison with the parent alkane yields a substituent effect in which two bulky ester functions have replaced two hydrogens. This method gives satisfactory results for terminal monoesters but leads to large deviations for the branched diesters. The reliability of the calculations in which the carbomethoxyl groups have replaced methyl groups is probably based upon conformational and rotational restrictions of the diester which are more closely related to those of the dimethyl-substituted alkane (RCH_3) than to those of the parent alkane (RH). The enhanced accuracy of this method is therefore probably the result of a greater accountability for steric perturbations.

The importance of the steric environment on ^{13}C shielding effects at a particular carbon is often reflected in these data. For instance, the $\beta\gamma$ substituent effect is determined for all such carbons to be −4.6 ± 1.7 ppm. A $\beta\gamma$ carbon occurs in both succinic and glutaric esters and as either a secondary or tertiary carbon. When the secondary $\beta\gamma$ carbons are separated from the tertiary $\beta\gamma$ carbons to generate

Table I. Carbon-13 Chemical Shifts in Diesters[a]

Registry no.		Chemical shift, ppm							
		C1	C2	C3	C4	C5	C6	Ester CH_3	Carbonyl(s)
51122-91-9		58.9 (+34.6) [+24.9]	29.0 (+3.8) [−5.0]	20.4 (−3.9) [+1.2]				52.2	169.3
39520-20-2		57.8 (+35.3) [+25.0]	33.4 (+5.6) [−5.1]	36.9 (−4.9) [+0.2]	20.1 (−0.6) [−0.6]	14.0 (−0.1) [0.0]	17.1 (−5.5) [+2.0]	52.0	169.5
58219-43-5		48.8 (+29.9) [+23.1]	42.1 (+5.6) [+11.2]	30.5 (+0.2) [−0.4]	29.2 (+0.5) [−0.7]			52.3	170.3
23143-72-8		36.2 (+22.5) [+6.7]	41.5 (+18.9) [+7.5]	34.6 (+0.1) [−4.4]	20.6 (−2.0) [+0.4]	14.0 (+0.3) [+0.1]		51.4	172.1,175.0
4136-86-1		36.0 (+22.1) [+6.3]	41.3 (+18.4) [+6.6]	31.7 (−0.3) [−4.8]	29.2 (−2.8) [−0.5]	22.5 (−0.4) [−0.8]	13.8 (−0.1) [−0.3]	51.6	172.3,175.3
56425-00-4		35.9 (+21.8)	41.3 (+18.3)	29.4 (−3.0)	27.0 (−2.9)	29.5 (−0.8)	29.5 (−0.8)	51.7	172.5,175.5
58219-44-6 58219-55-9		33.6 31.5 (+22.3) (+20.2) [+6.0] [+5.7]	45.8 45.6 (+16.5) (+16.3) [+6.3] [+7.1]	37.2 36.6 (+0.5) (−0.1) [−2.3] [−1.9]	27.4 27.1 (−1.9) (−2.2) [−0.2] [+1.3]	11.8 (+0.5) [0.0]	16.4 15.9 (−2.2) (−2.7) [+0.6] [+2.1]	51.5	172.8,174.8
58219-45-7		36.4 (+22.3) [+6.5]	39.6 (+18.9) [+7.5]	41.6 (−0.2) [−5.0]	26.2 (−1.6) [+0.8]	22.8 (+0.3) [−0.4]	22.3 (−0.2) [+0.1]	51.4	171.9,175.2
58219-46-8		32.6 (+14.1) [+8.2]	51.6 (+15.1) [+6.2]	32.6 (+2.3) [−0.4]	27.8 (−0.9) [+0.7]			51.2	173.0,174.6

29913-52-8	 $dl\text{-}C-\overset{CO_2CH_3}{C}-\underset{CO_2CH_3}{C_2}-C_1$	13.6 (+0.6) [−5.6]	41.7 (+16.9) [+7.7]					51.6	175.5
29800-12-2	 $meso\text{-}C-\overset{CO_2CH_3}{C}-\underset{CO_2CH_3}{C_2}-C_1$	14.9 (+1.9) [−4.3]	42.6 (+17.8) [+8.6]					51.7	175.0
15463-92-0	 $Ph\text{-}\overset{CO_2CH_3}{C_2}-C_1-CO_2CH_3{}^d$	37.7 (+20.9)	47.1 (+17.8)					51.8 52.3	171.9,173.4
36162-68-2 58267-04-2	 $C_5-C_4-\underset{CO_2CH_3}{C_3}-\overset{C_6}{C_2}-C_1-CO_2CH_3{}^c$	39.3 39.0 (+16.8) (+16.5) [+11.7] [+13.2]	32.4 (+4.6) [−7.1] [−6.1]	52.5 52.2 (+10.7) (+10.4) [+13.0] [+13.7]	22.8 22.4 (+2.1) (+1.7) [−4.8] [−3.4]	12.1 (−2.0) [+0.3]	17.6 17.1 (−5.0) (−4.5) [+1.8] [+3.3]	51.3 51.1	173.1,175.4 175.1
58219-47-9	 $C_5-C_4-C_3-\overset{C-CO_2CH_3}{C_2}-C_1-CO_2CH_3$	38.7 (+16.1) [+13.1]	32.2 (+4.4) [−8.4]	36.7 (−5.1) [+1.3]	20.0 (−0.7) [0.0]	14.0 (0.1) [−0.1]		51.3	172.9
19013-37-7	 $C_3-\overset{C-CO_2CH_3}{C_2}-C_1-CO_2CH_3$	40.6 (+16.3) [+11.2]	27.7 (+2.5) [−9.1]	20.0 (−4.3) [+1.3]				51.3	172.6
19006-47-4	 $Ph\text{-}\overset{C-CO_2CH_3}{C_2}-C_1-CO_2CH_3{}^e$	38.3 (+14.1)	40.4 (+1.5)					51.5	172.0
4819-15-2	 $C_5-\underset{CO_2CH_3}{C_4}-C_3-\overset{C_6}{C_2}-C_1-CO_2CH_3$	41.6 (+19.1) [+11.7]	28.6 (+0.8) [−3.5]	40.9 (−0.9) [−5.7]	37.5 (+16.8) [+12.1]	17.3 (+3.2) [−5.4]	19.7 (−2.9) [+0.7]	51.2	173.0,177.0
26933-03-9	 $C_5-C_4-\overset{C_6-CO_2CH_3}{C_3}-C_2-C_1-CO_2CH_3$	31.5 (+20.2) [+11.5]	28.5 (−0.8) [−6.9]	36.0 (−0.7) [−4.6]	26.0 (−3.1) [+0.6]	10.7 (−0.6) [+0.1]	38.2 (+19.2) [+12.6]	51.5	173.5,174.1
58219-48-0	 $C_5-\underset{CO_2CH_3}{C_4}-\overset{C_6}{C_3}-C_2-C_1-CO_2CH_3{}^e$	32.0 31.8 (+20.7) (+20.5) [+11.3] [+11.1]	29.9 28.9 (+0.6) (−0.4) [−6.7] [−7.8]	35.7 35.2 (−1.0) (−1.5) [−2.8] [−3.3]	44.4 44.1 (+15.1) (+14.8) [+11.6] [+11.3]	14.0 12.4 (+2.7) (+1.1) [−4.9] [−6.5]	16.8 15.8 (−1.8) (−3.1) [+1.7] [+0.7]	51.4	173.7,176.4 176.3

[a] δ_C, parts per million from Me_4Si, $\Delta\delta = (\delta_{obsd} - \delta_{RH})$ in parentheses, $\Delta\delta = (\delta_{obsd} - \delta_{RCH_3})$ in brackets. [b] δ_C = 29.4, C = 32.0, C = 22.8, and C = 12.2. [c] Diastereomeric mixture. [d] δ_C aromatic = 127.8, 128.9, and 137.8. [e] δ_C aromatic = 127.0, 127.2, 128.7, and 142.7.

Table II. Carbon-13 Shielding Effects in Linear Diesters[a]

Substitution	Shielding effect	No. of measurements	Standard deviation
$\alpha\alpha$	+25.0	2	0.1
$\alpha\beta$	+6.9	14	0.9
$\alpha\gamma$	+12.7	6	1.0
$\alpha\delta$	+11.5	7	0.3
$\beta\beta$	−7.4	7	2.3
$\beta\gamma^b$	−4.6	15	1.7
$\beta\gamma'$	−5.7	9	1.2
$\beta\gamma''$	−3.1	6	1.0
$\beta\delta$	−4.1	2	1.0
$\beta\epsilon$	−5.6	3	0.8
$\gamma\gamma^b$	+1.5	6	1.0
$\gamma\delta$	+0.7	11	0.6
$\gamma\epsilon$	+0.3	1	
$\delta\delta$	0.0	1	
$\delta\epsilon$	−0.3	7	0.4
$\epsilon\epsilon$	−0.1	1	

[a] A carbon α to two ester functions is referred to as $\alpha\alpha$, a carbon α to one ester function and β to another is referred to as $\alpha\beta$, etc. [b] Substituent effects in which a *tert*-butyl group is involved are not included in these calculations.

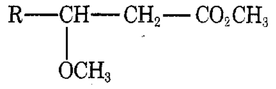
two new parameters, $\beta\gamma'$ and $\beta\gamma''$, the standard deviation is reduced to 1.2 and 1.0 ppm, respectively. A significant standard deviation (2.3 ppm) is observed also for the $\beta\beta$ carbons. Although this substitution pattern occurs for malonic and glutaric esters, no single substitution difference is readily apparent which simply explains the large range in values derived for this substituent effect. Another example of the importance of steric effects is related to the shielding effects calculated from compounds containing a *tert*-butyl group. Nearly all carbons in these molecules showed deviation from generally observable behavior. Often the deviation was so large that the substituent effect was excluded from the calculations of standard substituent effects (Table II).

There are several significant features to the correlations listed in Table II. All diester shielding effects are based upon a comparison with the shielding effects of two methyl groups. The data demonstrate that a carbon α to an ester function is strongly deshielded compared with the methyl analogue. Slight deshielding is also observed for a γ carbon while a significant shielding effect at the β carbon is noted. The effects at the δ and ϵ carbons are quite small. Another aspect of these shielding correlations concerns additivity relationships. Interestingly, the diester ^{13}C shielding effects when calculated in this manner cannot be reduced to simple mono-substituent relationships. Thus, from the $\alpha\alpha$ relationship a value of 12.5 ppm ($\alpha\alpha/2 = \alpha$) may be established for a single α-substituent effect. Using the relationship $\alpha\beta - \alpha = \beta$, then yields a β-substituent effect of −5.6 ppm. A $\beta\beta$ shielding effect ($2\beta = \beta$) of −11.2 is therefore calculated from this relationship which is compared to an observed value of −7.4 ppm. Therefore, when derived by comparison with the dimethyl-substituted alkane, the ^{13}C shielding of two ester functions must be considered as a unit effect rather than as the summation of two separate effects.

The shielding effects given in Table II can be used to predict the chemical shifts of carbons in other diester molecules. The chemical shifts for the appropriate dimethyl-substituted compound are obtained, the relative position of each carbon to the two ester functions is determined, and the shielding effect value is added to the chemical shift of the carbons of the parent compound. If the shifts for the methyl-substituted material are unavailable, an estimate may be obtained by empirical correlations.[8] Thus, the chemical shifts for the ten aliphatic carbons of dimethyl octylsuccinate were determined as shown in Table III. Significantly, the calculated value for each carbon is within 0.9 ppm of the observed value.

In order to test the accuracy of this method, the chemical shifts for 93 carbons from 15 diester molecules were derived by addition of appropriate parameters (Table II) to the calculated chemical shift[8] for each appropriate carbon of the dimethyl-substituted alkane. The standard error of estimation for a calculated chemical shift for the diesters was 1.0 ppm. The agreement between the computed values using this method and the experimental values was excellent. In 81% of the cases, the difference between experimental and predicted values was less than 1.0 ppm. In 87% of the cases, the difference between predicted and experimental values was less than 1.5 ppm and less than 2.0 ppm for 93% of the cases. Importantly, deviations greater than 2.0 ppm were often the result of large deviation in the computation of the chemical shift of the alkane.

The ^{13}C chemical shift and shielding effect data for nine β-methoxy esters are given in Table IV. Assignments are based upon off-resonance decoupling experiments and are consistent with the general pattern of substituent effects. Of the aliphatic backbone, those carbons α (C2) to the methoxyl function absorb the farthest downfield, 79.5 ± 2.9 ppm. The chemical shift of C2 of the β-methoxy esters is extremely dependent upon the nature of its alkyl substituent, R.

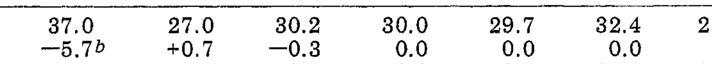


$$\mathrm{R{-}\underset{\displaystyle OCH_3}{\underset{|}{CH}}{-}CH_2{-}CO_2CH_3}$$

The chemical shift determined from the isomeric 3-methoxyheptanotes is 78.2 ppm for R = *n*-butyl, 81.6 ppm for R = *sec*-butyl, 86.3 ppm for R = *tert*-butyl, and 76.4 ppm for R = isobutyl. These results demonstrate the deshielding effect of β-methyl substituents (R = *sec*-butyl and *tert*-butyl) and the shielding effect of γ-methyl substituent (R = isobutyl). Interestingly, however, methyl substitution at C1 (Table IV) has little effect on chemical shift.

The absorptions assigned to the methoxyl of the ester group averaged 51.2 ± 0.2 ppm and were little changed from similar carbons of the linear diesters. The ether methoxyl carbons for the aliphatic compounds studied absorbed

Table III. Calculation of ^{13}C Chemical Shifts for Dimethyl Octylsuccinate

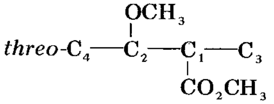
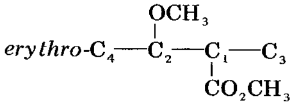
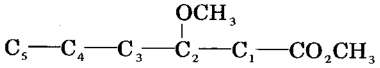
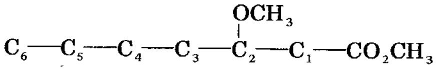
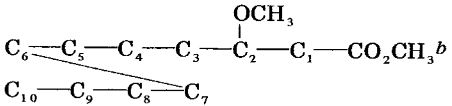
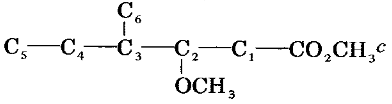
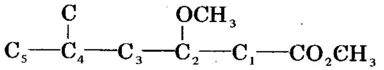
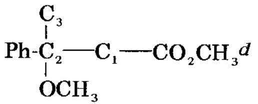
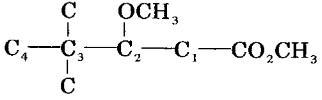


$$\mathrm{H_3CO_2C{-}C_1{-}\overset{\displaystyle CO_2CH_3}{\overset{|}{C_2}}{-}C_3{-}C_4{-}C_5{-}C_6{-}C_7{-}C_8{-}C_9{-}C_{10}}$$

	C1	C2	C3	C4	C5	C6	C7	C8	C9	C10
RCH_3[a]	29.6	34.6	37.0	27.0	30.2	30.0	29.7	32.4	22.7	13.9
Substituent effect	+6.9	+6.9	−5.7[b]	+0.7	−0.3	0.0	0.0	0.0	0.0	0.0
Calculated	36.5	41.5	31.3	27.7	29.9	30.0	29.7	32.4	22.7	13.9
Observed	35.9	41.3	29.4	27.0	29.5	29.5	29.4	32.0	22.8	14.2
Difference	−0.6	−0.2	−1.9	−0.7	−0.4	−0.5	−0.3	−0.4	+0.1	+0.4

[a] Calculated chemical shifts[8]. [b] $\beta\gamma'$ substituent effect.

Table IV. Carbon-13 Chemical Shifts in β-Methoxy Esters[a]

Registry no.		Chemical shift, ppm								
		C1	C2	C3	C4	C5	C6	Ether CH_3	Ester CH_3	C=O
39788-67-5	 *threo*-$C_4-C_2(OCH_3)-C_1(CO_2CH_3)-C_3$	45.4 (+20.6) [+11.4]	78.4 (+53.6) [+44.4]	12.1 (−0.9) [−7.1]	15.7 (+2.7) [−3.5]			56.5	51.3	175.2
39788-68-6	 *erythro*-$C_4-C_2(OCH_3)-C_1(CO_2CH_3)-C_3$	45.8 (+21.0) [+11.8]	78.2 (+53.4) [+44.2]	12.5 (−0.5) [−6.7]	16.9 (+3.9) [−2.3]			56.5	51.3	175.2
54905-29-2	 $C_5-C_4-C_3-C_2(OCH_3)-C_1-CO_2CH_3$	39.6 (+25.9) [+10.1]	78.1 (+55.5) [+43.8]	37.1 (+2.6) [−1.9]	18.8 (−3.8) [−1.4]	14.2 (+0.5) [+0.3]		56.8	51.1	171.8
51664-88-1	 $C_6-C_5-C_4-C_3-C_2(OCH_3)-C_1-CO_2CH_3$	39.6 (+25.7) [+9.9]	78.2 (+55.3) [+43.5]	34.4 (+2.4) [−2.1]	27.8 (−4.2) [−1.9]	23.2 (+0.3) [−0.1]	14.1 (+0.2) [0.0]	56.8	51.1	171.6
58219-49-1	 $C_{10}-C_9-C_8-C_7$, $C_6-C_5-C_4-C_3-C_2(OCH_3)-C_1-CO_2CH_3$[b]	39.5 (+25.4)	78.1 (+55.5)	34.4 (+2.0)	25.4 (−4.5)	29.8 (−0.5)	29.8 (−0.4)	56.9	51.3	172.0
58219-50-4 58219-51-5	 $C_5-C_4-C_3(C_6)-C_2(OCH_3)-C_1-CO_2CH_3$[c]	36.7 36.0 (+25.4) (+24.7) [+9.1] [+10.2]	81.7 81.5 (+52.4) (+52.2) [+42.2] [+43.0]	38.7 37.9 (+2.0) (+1.2) [−0.8] [−0.6]	25.6 (−3.7) [−2.0] [−0.2]	12.2 (+0.9) [−0.4]	14.3 (−4.3) [−1.5] [+0.5]	57.7 57.3	51.1	172.1 172.0
58219-52-6	 $C_5-C_4(C)-C_3-C_2(OCH_3)-C_1-CO_2CH_3$	39.6 (+25.5) [+9.7]	76.4 (+55.7) [+44.3]	44.2 (+2.4) [−2.4]	25.0 (−2.8) [−0.4]	23.4 22.5 (+0.9) (0.0) [0.2] [0.3]		56.7	51.1	171.5
58219-53-7	 $Ph-C_2(C_3)(OCH_3)-C_1-CO_2CH_3$[d]	47.6 (+23.4)	77.7 (+38.8)	23.0 (−1.2)				50.5	51.3	170.7
58219-54-8	 $C_4-C_3(C)(C)-C_2(OCH_3)-C_1-CO_2CH_3$	36.2 (+17.7) [+11.8]	86.3 (+49.8) [+40.9]	35.7 (+5.4) [+2.7]	25.9 (−2.8) [−1.2]			60.2	51.6	173.5

[a] δ_C, parts per million from Me_4Si, $\Delta\delta = (\delta_{obsd} - \delta_{RH})$ in parentheses, $\Delta\delta = (\delta_{obsd} - \delta_{RCH_3})$ in brackets. [b] δ C = 29.4, C = 32.1, C = 22.8, and C = 14.1. [c] Diastereomeric mixture. [d] δ_C aromatic = 126.2, 127.4, 128.3, and 143.8.

an average of 57.3 ± 1.2 ppm. The slight deshielding effect of δ methyl substituents is observed for R = *sec*- and *tert*-butyl and a very large shielding effect is noted for a γ-phenyl (50.5 ppm).

The ^{13}C shielding data for the β-methoxy esters are summarized in Table V. Again, because of consistency, the substituent effects were calculated by comparison with the methyl-substituted alkane. The results predictably demonstrate the very large deshielding effect at the carbon α to an oxygen (C2). In fact the ether group causes a 36.7-ppm larger downfield shift than does a carbomethoxyl group. Similarly, the deshielding effect of a β ether oxygen is 3.4 ppm larger than that of a carbomethoxyl group.

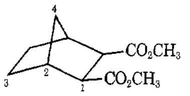
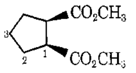
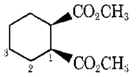
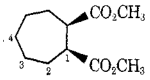
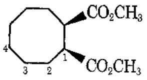
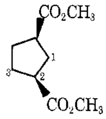
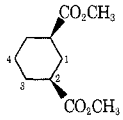
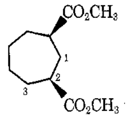
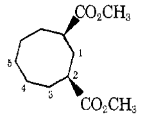
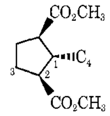
Carbon-13 chemical shift and shielding data for the series of alicyclic diesters and β-methoxy esters obtained from the transition metal catalyzed olefin carbonylation reaction are summarized in Tables VI and VII, respectively. The assignment of individual signals is straightforward and is based on the general pattern of shielding effects, decoupling experiments, and, in certain cases, relative peak in-

Table V. Carbon-13 Shielding Effects in β-Methoxy Esters

Carbon[a]	Shielding	Deviation
α	+10.3	1.0
β	+43.6	0.8
γ	−1.9	1.0

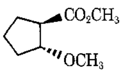
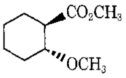
[a] Position relative to the ester function.

Table VI. Carbon-13 Chemical Shifts in Cyclic Diesters[a]

		Chemical shift, ppm						
Registry no.		C1	C2	C3	C4	C5	Ester CH_3	Car-bonyl(s)
35436-52-3		51.3 (+21.2)	40.2 (+3.4)	28.9 (−1.2)	36.0 (−2.7)		51.7	173.1
4841-91-2		47.4 (+20.9) [+10.0]	29.1 (+2.6) [−3.9]	24.3 (−2.2) [+1.3]			51.4	174.1
1687-29-2		42.7 (+14.9) [+7.7]	26.4 (−1.4) [−5.7]	24.0 (−3.8) [−0.3]			51.5	173.9
38312-27-5		46.1 (+16.1)	28.3 (−1.1)	26.5 (−2.9)	28.7 (−0.7)		51.4	174.5
54905-31-6		44.2 (+16.4)	26.4 (−1.4)	26.4 (−1.4)	27.1 (−0.6)		51.6	175.0
39590-04-0		33.8 (+7.3) [−10.9]	44.2 (+17.7) [+9.1]	29.5 (+3.0) [−4.5]			51.5	175.3
6998-82-9		31.3 (+3.5) [−14.0]	42.6 (+14.8) [+9.2]	28.6 (+0.8) [−7.4]	25.0 (−2.8) [−2.0]		51.6	175.3
54905-30-5		33.7 (+4.3)	44.3 (+15.0)	31.6 (+2.2)	26.2 (−3.2)		51.4	176.0
54905-32-7		30.5 (+2.7)	43.6 (+15.8)	29.6 (+1.8)	24.1 (−3.7)	26.8 (−1.0)	51.6	176.8
54339-19-4		43.2 (+7.8)	51.9 (+16.5)	29.0 (+3.2)	18.5 (−2.4)		51.5	175.1

[a] δ_C, parts per million from Me_4Si, $\Delta\delta = (\delta_{obsd} - \delta_{RH})$ in parentheses, $\Delta\delta = (\delta_{obsd} - \delta_{RCH_3})$ in brackets.

Table VII. Carbon-13 Chemical Shifts in Cyclic β-Methoxy Esters[a]

		Chemical shift, ppm								
Registry no.		C1	C2	C3	C4	C5	C6	Ether CH_3	Ester CH_3	C=O
54108-60-0		50.3 (+23.8) [+7.8]	85.6 (+59.1) [+43.1]	32.1 (+5.6) [−2.8]	23.5 (−3.0) [+0.3]	28.7 (+2.2) [−6.2]		57.0	51.8	175.9
13640-66-9		50.2 (+22.4) [+10.1]	80.2 (52.4) [+40.1]	30.2 (+2.4) [−6.4]	24.2 (−3.6) [−3.2]	25.0 (−2.8) [−2.4]	28.8 (+1.0) [−7.8]	56.3	51.2	175.1

[a] δ_C, parts per million from Me_4Si, $\Delta\delta = (\delta_{obsd} - \delta_{RH})$ in parentheses, $\Delta\delta = (\delta_{obsd} - \delta_{RCH_3})$ in brackets.

tensities. The absorptions assigned to the carbons of the functional groups are generally similar to the chemical shift ranges for the acyclic systems. The methoxyl group of the ester functions absorbs at an average value of 51.5 ± 0.2 ppm and the ether methoxyl at 56.6 ± 0.5 ppm. Analogously, the absorptions of the carbonyl function for the 1,2-diesters were observed at slightly lower field (174.1 ppm average) than those of the 1,3-diesters (175.9 ppm average).

The shielding results for the alicyclic diesters and methoxy esters also follow the general trends established from the acyclic derivatives, although comparisons with the dimethyl-substituted alkanes can only be made for the cyclopentane and cyclohexane derivatives. Large deviations from predicted values based on acyclic substituent effects may result from conformational effects, intramolecular interactions, and variations in C–C–H and C–C–CO_2R bond angles, all of which are interrelated. The limited amount of information available does not allow a determination of the importance of each of these contributions at the present time.

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Multiple Regression Analysis of Carbon-13 Chemical Shifts and Carbon-13 Proton Coupling Constants in Ortho-Substituted Aromatics

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Carbon-13 proton coupling constants for off-ring C–H bonds in eight ortho-substituted aromatic systems have been correlated with the divided substituent constants σ_I and σ_R^0. The correlations are in general good and the parameters of the regression equation reveal predominant control by the inductive effect. The influences of hydrogen bonding, steric inhibition of resonance, size of the substituent, and van der Waals forces are discussed. Carbon-13 chemical shifts for off-ring carbons in seven ortho-substituted aromatic systems have also been correlated with σ_I and σ_R^0 but in only a few systems are the correlations good. Attempts to improve the correlations through removal of hydrogen-bonding substituents, variation of σ_R^0 for substituents with possible steric inhibition of resonance, and addition of van der Waals radii, the Q parameter, and $\langle E^2 \rangle$ to the regression equation are discussed.

The analysis of the chemical and physical properties of ortho-substituted aromatics is potentially exceedingly complex. In addition to the conventional "through-the-ring" electronic effects, there is the possibility of interaction of the substituent with the ortho site through its electrical field, by van der Waals forces, hydrogen bonding, or dative bonding, or by steric inhibition of resonance as well as other steric effects, to mention just the more easily categorized effects and omitting, obviously, solvation effects. Consequently, it is not surprising that such systems have generally resisted analysis with the Hammett equation. While no one set of ortho-substituent constants has been found to be generally applicable, Charton has correlated reactivities and properties of many ortho-substituted systems with the divided substituent constants σ_I and σ_R^0.[1]

The present study is an attempt to determine what substituent constants or other empirical parameters will correlate successfully with ^{13}C chemical shifts and ^{13}C–^{1}H coupling constants of off-ring carbons in ortho-substituted benzene derivatives. Since theoretical analyses of ^{13}C–^{1}H coupling constants point to a heavy dependence upon hybridization and effective nuclear charge,[2] it might be anticipated that correlations with inductive and resonance effects would be successful. Carbon-13 chemical shifts, however, appear to be sensitive to a greater number of factors, such as neighbor anisotropy effects, many of which are still poorly understood.[3]

Experimental Section

Compounds. Most compounds were obtained commercially or prepared by standard procedures. Several, however, were previously unknown. Methyl *o*-fluorophenyl sulfide, bp 51–55 °C (1.7 mm) (Anal. Calcd for C_7H_7FS: C, 59.12; H, 4.97. Found: C, 59.26; H, 5.04), was prepared by methylation of the thiophenol with methyl iodide. *N,N*-Dimethyl-*o*-trifluoromethylaniline, bp 93 °C (17 mm) (Anal. Calcd for $C_9H_{10}F_3N$: C, 57.14; H, 5.33. Found: C, 56.85; H, 5.33), was obtained by methylation of *o*-trifluoromethylaniline