electron acceptors as suggested by the downfield chemical shifts[39] of the p-hydrogens in phenyllithium and diphenylzinc. However, the ^{19}F shifts of the m- and p-fluoro-substituted diphenylmercury indicated[40] a very slight electron donation by the HgC_6H_4F substituent. For boron, confirmation of this acceptance is available from other substituents; thus the group $B(OH)_2$ ($\sigma_R^\circ = +0.227$) is almost the same as BPh_2 ($+0.221$), whereas BCl_2 ($+0.298$) is a stronger acceptor. The BPh_3^- group is probably a resonance donor ($\sigma_R^\circ = -0.129$): it would be expected to be similar to CPh_3 (-0.130).

We are presently studying further organometallic derivatives, particularly benzyl compounds, to determine the significance of metal hyperconjugation.

Experimental Section

Compounds were obtained commercially or prepared by known methods. Purities were checked by gas chromatography or melting point. Tetraphenylphosphonium bromide was prepared from triphenylphosphine and bromobenzene.[41] Tetraphenylstannane, tetra-

phenylgermane, and tetraphenylsilane were kindly supplied by Professor J. C. Maire, Département de chimie organique, Marseille, France (for other compounds of Si, Ge, Sn see ref 28 and 42). Pentaphenylphosphorus, -arsenic, and -antimony were kindly supplied by Dr. D. Hellwinkel and Professor G. Wittig of the Institute für organische chemie der Universität, Heidelberg, Germany. The compounds of type $C_6H_5PHO(OMR_3)$ where M = Si or Ge were kindly donated by Dr. J. F. Brazier, 11 Nouvelle Faculté des Sciences, Toulouse, France.

Spectra were obtained on a Perkin-Elmer 125 spectrophotometer under conditions similar to those previously specified and solvents were purified as before.[43] Intensity area A values quoted are the average of four readings, usually in two separate solutions; reproducibility of $A^{1/2}$ was ± 1 unit. For compounds having more than one benzene ring, the A, ϵ_A, and ϵ values have been divided by the number of benzene rings. We have shown that for mono-[3] and meta-disubstituted compounds[5] the variation of the A values with solvent are generally small, although this does not hold for certain para-disubstituted derivatives.[6] The accuracy of σ_R° values measured by the ir method has been discussed previously and attention drawn to the uncertainties with values <0.1 unit.

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Nuclear Magnetic Resonance Spectroscopy. ^{13}C Spectra of Aliphatic Carboxylic Acids and Carboxylate Anions[1]

R. Hagen and John D. Roberts

Contribution No. 3788 from the Gates and Crellin Laboratories of Chemistry, California Institute of Technology, Pasadena, California 91109. Received January 10, 1969

Abstract: The ^{13}C chemical shifts of each of the carbons of the simple aliphatic carboxylic acids and their corresponding anions from formic to valeric acid have been measured in aqueous solution. Perhaps surprisingly, ionization of an aliphatic acid results in a downfield shift of its carbon resonances. The results have been correlated with other substituent effects, with ^{13}C and H resonances in corresponding hydrocarbons, and with the distance between the carboxylic(ate) group and the carbons undergoing resonance absorption.

Despite the low sensitivity of the ^{13}C nucleus for nmr detection,[2] ^{13}C chemical shifts can be determined quite readily using ^{13}C of natural abundance with the aid of proton decoupling in the digital-frequency-sweep spectrometer previously described,[3] even in fairly dilute (0.5 M) solutions. The purpose of the present work was to determine if the electrostatic perturbation produced by carboxylate groups could be clearly distinguished on ^{13}C chemical shifts. If this were possible, it might have important applications for determining sites of protonation of amine groups or deprotonation of carboxyl groups in peptide chains made up of basic or acidic amino acids.[4] To this end, the ^{13}C chemical

shifts of some continuous-chain carboxylic acids and the corresponding tetramethylammonium carboxylate salts have been determined in aqueous solution and are summarized in Table I.

The chemical shifts shown in Table I were measured against the ^{13}C resonance of tetramethylammonium ion as internal standard at about 30–35° with a precision judged to be ± 0.1 ppm. These were converted to the carbon disulfide scale by adding 137.0 ppm. Positive chemical shifts represent upfield resonances from the carbon disulfide standard. All of the shifts were measured at three concentrations, 0.5, 1.0, and 2.0 M, but only the shifts of the carboxyl carbon were more sensitive than ± 0.1 ppm to concentration and for this reason the small upfield effects of concentration changes are only shown for the carboxyl carbons.

The differences in chemical shifts between corresponding carbons in the carboxylic acids studied in this

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(3) F. J. Weigert and J. D. Roberts, *J. Amer. Chem. Soc.*, 89, 2967 (1967).
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Table I. ¹³C Chemical Shifts[a] of Carboxylic Acids and Tetramethylammonium Carboxylate Salts in Aqueous Solution at 15.1 MHz Relative to ¹³CS₂

	Carboxyl 0.5 M	1.0 M	2.0 M	α	β	γ	δ
Formic acid[b]	26.5	26.5	26.7				
Acetic acid[b]	15.6	15.7	16.0	171.7			
Propionic acid[b]	12.4	12.6	12.9	165.0	183.8		
Butyric acid[b]	13.2	13.4	13.9	156.5	174.3	179.4	
Valeric acid[b]	13.1			158.7	165.8	170.8	179.3
Formate ion	21.4	21.6	21.8				
Acetate ion	11.1	11.4	11.8	168.8			
Propionate ion	7.7	7.9	8.4	161.5	182.0		
Butyrate ion	8.5	8.8	9.4	152.6	172.9	178.9	
Valerate ion	8.4			154.8	164.1	170.2	179.1

[a] In parts per million (ppm). [b] All solutions of the acids were equimolal in tetramethylammonium chloride. The shifts agree reasonably well (average deviation ±0.6 ppm) with those reported by E. Lippmaa and T. Pehk, *Kemian Teollisuus*, **12**, 1001 (1967), when account is taken of the differences in the conditions of taking the spectra (neat liquid *vs.* aqueous solutions).

Table II. ¹³C Chemical-Shift Increments of Carboxylic and Carboxylate Groups[a,b]

Compound	C-α	C-β	C-γ	C-δ
Acetic acid	−23.5			
Propionic acid	−22.2	−3.4		
Butyric acid	−21.0	−2.7	+2.0	
Valeric acid	−21.2	−2.3	+2.7	−0.6
Acetate ion	−26.3			
Propionate ion	−25.7	−5.2		
Butyrate ion	−24.9	−4.1	+1.4	
Valerate ion	−25.1	−4.0	+2.1	−0.8

[a] In parts per million (ppm). [b] The increments were calculated by subtracting the chemical shifts of the unsubstituted hydrocarbons[7,8] from those observed for 0.5 M aqueous solutions of the acids or tetramethylammonium salts. For this purpose, the hydrocarbon shifts were converted to carbon disulfide reference by the relation $\delta_{CS_2} = \delta_{C_6H_6} + 64.4$ ppm which applies to the calibration mixture described in the Experimental Section.

carbons of the substituted hydrocarbon. The validity of this procedure in the present case with the very large difference in environment in which the shifts are measured is questionable. However, the results (Table II) show that the substituent effects of carboxylic and carboxylate groups follow trends very much like those produced by hydroxyl, amino, acetyl, chlorine, and bromine (but not iodine).[8,9] The increments for α, β, and δ carbons are negative while those for γ carbons are positive. As expected, the effect of carboxylic and carboxylate groups falls off rapidly with increasing chain length. Also, the effect of adding carbons to the chain on the shifts of the α and β carbons becomes smaller with increasing chain length.

The variations of the shielding of carbons α to most substituent groups are apparently dominated by the

Table III. Changes in ¹³C and Proton Chemical Shifts on Ionization of Aliphatic Carboxylic Acids

Acid	¹³C increment, ppms[a] COOH	α	β	γ	δ	¹H increment, ppm[a] HCO₂	α	β	γ	δ
Formic	−5.1					−0.22				
Acetic	−4.5	−2.8					+0.22			
Propionic	−4.7	−3.5	−1.8				+0.22	+0.03		
Butyric	−4.7	−3.9	−1.4	−0.6			+0.20	+0.03	+0.02	
Valeric	−4.7	−3.9	−1.7	−0.6	−0.2		+0.21			0.00

[a] For 0.5 M solutions, the values are positive if an *upfield* shift of the resonance occurs on ionization.

work and the respective tetramethylammonium carboxylate salts are seen in Table I to be quite small (6 ppm at the carboxylic carbon). Concentration effects on ¹³C resonances are often of comparable magnitude[5,6] but, as already mentioned, the ¹³C chemical shifts of carboxylic acids and their salts seem rather insensitive to concentration. The changes in the carboxylic carbon resonances which do occur with concentration are larger for the higher carboxylic acids and their salts. This is perhaps as would be expected for a smaller degree of solvation of the carboxylic function of the larger molecules by water.

The chemical shifts of the carbons of a continuous-chain hydrocarbon are not the same and in order to evaluate the effect of substituents such as carboxylic and carboxylate groups it is customary to subtract the shifts of the carbons of the hydrocarbons[5,7] from respective

electronegativity of the substituent.[5,8,10−12] The carboxylate group is expected to be substantially less electronegative than the carboxylic group and one would therefore expect an upfield shift of the α (and other) carbons on ionization of a carboxylic acid. However, this is exactly the opposite of what is observed, although an upfield shift is generally observed for the corresponding proton resonances[13,14] (see Table III).

The general importance of the second-order paramagnetic effect on carbon resonances and its smaller degree of importance on proton resonances suggests

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(13) M. van Gorkom, *Tetrahedron Letters*, 5433 (1966).
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that perhaps the expected diamagnetic shift occurs for both kinds of nuclei. However, for the carbon resonances this would be overlaid by a downfield shift corresponding to the paramagnetic term in the Ramsey shielding expression which is larger when there are lower lying excited states for the electrons surrounding the nuclei. This idea does not receive experimental support from the absorption spectra of acetic acid and sodium acetate in aqueous solution, each of which has about the same absorption maximum, although acetate ion has the larger extinction coefficient.[15]

The rate of falloff of the chemical shift with distance along the chain as a function of substituent is of special interest. There are problems in making comparisons along these lines with aliphatic compounds carrying different substituent groups because of the possibilities of differences in conformations. We have chosen here to consider the changes in ^{13}C chemical shifts which occur on ionization of valeric acid at the α, β, γ, and δ carbons. If we consider the negative charge of the carboxylate anion to be centered between the carboxylate oxygens and take the carbon chain to be in the staggered extended conformation, then the falloff of β, γ, and δ chemical shifts relative to the α chemical shift is reasonably close to what would be expected for a r^{-3}

dependence, in accord with the undocumented prediction of van Gorkom.[13]

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Ionic Reactions in Bicyclic Systems. VIII. Acetolysis of syn- and anti-7-Chloro-exo-norbornyl p-Toluenesulfonates[1]

Harlan L. Goering and Michael J. Degani

Contribution from the Department of Chemistry, The University of Wisconsin, Madison, Wisconsin 53706. Received February 15, 1969

Abstract: Acetolysis of syn- (I-OTs) and anti-7-chloro-exo-norbornyl p-toluenesulfonate (II-OTs) has been reinvestigated. Ion-pair return associated with solvolysis results in isomerization of I-OTs to II-OTs; at 70% solvolysis of I-OTs the composition of the unsolvolyzed ester is about 70% I-OTs and 30% II-OTs. Isomerization in the opposite direction is unimportant. The I-OTs → II-OTs isomerization involves a 6,2-hydride shift and migration of the anion from C_2 to C_6. This transformation is intramolecular (very little exchange with p-toluenesulfonate ion) and evidently involves internal return. Intermediates generated from I-OTs and II-OTs undergo 6,2-hydride shifts in competition with solvent capture.

In an earlier investigation[2] it was observed that 6,2-hydride shifts are involved in acetolysis of syn- (I-OTs) and anti-7-chloro-exo-norbornyl p-toluenesulfonate (II-OTs). Both esters give mixtures of syn- and anti-7-chloro-exo-norbornyl acetate (I-OAc and
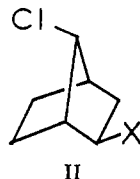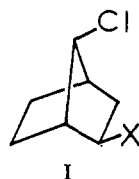
II-OAc). Formation of the anti product from the syn substrate, and vice versa, requires a 6,2-hydride shift and exo capture at C_6. It was also observed that 6,2 shifts are apparently associated with ion-pair return (presumably internal return[3]) as well as with solvent capture; infrared analysis of the unsolvolyzed ester indicated that I-OTs and II-OTs are interconverted during solvolysis. As illustrated by III, this isomerization involves migration of the anion from C_2 to C_6 as well as a 6,2-hydride shift. We were particularly interested in this isomerization in connection with our

(1) This research was supported by the National Science Foundation (GP-6555X) and the Air Force Office of Scientific Research (AFOSR-847-67).

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(3) The 7-chloronorbornyl p-toluenesulfonates, I-OTs and II-OTs, are considerably less reactive than the parent exo-norbornyl p-toluenesulfonate and consequently would not be expected to show a special salt effect. Thus, presumably only internal return is involved in these systems. See S. Winstein, *et al.*, *ibid.*, 78, 2784 (1956); 80, 169, 459 (1958); 83, 885 (1961).