Tetrahedron Letters No. 21 pp 2139 - 2140, 1972. Pergamon Press. Printed in Great Britain.

LONG-RANGE CARBON-CARBON COUPLING CONSTANTS IN ENRICHED COMPOUNDS. ^{13}C-1 LABELED CARBOXYLIC ACIDS AND CARBOXYLATE ESTERS

James L. Marshall and Arthur M. Ihrig
Department of Chemistry, North Texas State University
Denton, Texas 76203

(Received in USA 2 March 1972; received in UK for publication 18 April 1972)

Recently we made the observation[1] that $^{3}\underline{J}_{C-C}$ values were somewhat greater than $^{2}\underline{J}_{C-C}$ values in ^{13}C-7 labeled benzene derivatives. To see if this remarkable phenomenon was unique to this system, or whether it was of a more general nature, we decided to synthesize and study ^{13}C-labeled aliphatic carboxylic acids and esters. Accordingly, ^{13}C-1 butanoic and pentanoic acids and ^{13}C-1 ethyl butanoate were synthesized in the usual manner[1] and studied by cmr as before.[1] The recorded parameters are listed in Table I. The signals for C_2-C_5 of all entries in Table I were identified by comparison[2] with previously determined parameters for the acids.[3] The two remaining signals in the spectrum of ethyl butanoate were assigned as the ethyl carbons (1' and 2'), with the 2'-carbon at higher field. The chemical shift parameters of natural abundance methyl butanoate supported these assignments: consistent with previously published additivity relationships,[2] the 1'-carbon signal of ethyl butanoate was 9 ppm downfield from the 1'-carbon signal of methyl butanoate.

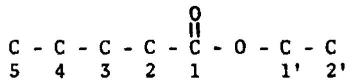
The most remarkable observation from Table I is the similarity of the $\underline{J}_{C-C}$ values to those of the previously studied aromatic system.[1] Foremost, again the $^{3}\underline{J}_{C-C}$ values ($\underline{J}_{14}$) are larger than the $^{2}\underline{J}_{C-C}$ values ($\underline{J}_{13}$), and in magnitude these values are quite similar to those in the aromatic system. It is tempting to speculate that geometry is of little importance in determining the value of $^{3}\underline{J}_{C-C}$, but until the effect of hybridization is understood, no conclusion is warranted. To help distinguish between the effects of hybridization and geometry, we are currently investigating labeled alicyclic systems.

Other observations from Table I are noteworthy. Concerning the carbon-carbon spin-spin coupling transmitted through the oxygen atom, the two-bonded coupling constant $^{2}\underline{J}_{C-O-C}$ is virtually identical to that in methyl benzoate (2.6 Hz)[1] and in dimethyl ether (2.4 Hz).[4] This coupling constant $^{2}\underline{J}_{11'}$ is also about the same as the longer-range coupling constant $^{3}\underline{J}_{12'}$, demonstrating that $^{3}\underline{J}_{C-C}$ values are not really attenuated over $^{2}\underline{J}_{C-C}$ values even when the spin-spin coupling is transmitted through a heteroatom.

We gratefully acknowledge financial support from the Robert A. Welch Foundation, Grant No. B-325, and from North Texas State University Faculty Research.

Table I.

Carbon Chemical Shift and Carbon-Carbon Coupling Constant Values of 1-Labeled Carboxylate Systems



$$\overset{\displaystyle O}{\overset{\|}{}}$$
$$\underset{5}{C} - \underset{4}{C} - \underset{3}{C} - \underset{2}{C} - \underset{1}{\overset{\overset{O}{\|}}{C}} - O - \underset{1'}{C} - \underset{2'}{C}$$

	Chemical Shifts, ppm[a]						Coupling Constants, Hz					
	δ_5	δ_4	δ_3	δ_2	δ_1'	δ_2'	J_{15}	J_{14}	J_{13}	J_{12}	J_{11}'	J_{12}'
$CH_3CH_2CH_2CH_2{}^{13}CO_2H$	+13.7	+4.7	-0.2	-6.9	--	--	<0.3[b]	3.5	1.7	55.3[d]	---	---
$CH_3CH_2CH_2{}^{13}CO_2H$	--	+14.0	+9.0	-8.8	--	--	--	3.6	1.8	55.4[d]	---	---
$CH_3CH_2CH_2{}^{13}CO_2CH_2CH_3$	--	+13.9	+8.6	-9.0	-33.0	-13.0	--	3.5	1.9	57.9[d]	2.5	2.3
$(CH_3CH_2CH_2CO_2CH_3)$[c]	--	+14.0	+8.6	-8.9	-24.0	--						

---

[a] Referenced to internal cyclohexane. [b] No splitting, but slight broadening observed. [c] Natural abundance material studied to obtain chemical shifts only as a check for correct assignments for $CH_3CH_2CH_2CO_2CH_2CH_3$. [d] The J_{12} values for acetic acid and ethyl acetate have previously been reported to be, respectively, 56.7 and 58.8 Hz [G. E. Maciel et al., J. Mag. Res., **1**, 41 (1969)].

REFERENCES

1. A. M. Ihrig and J. L. Marshall, J. Amer. Chem. Soc., **94**, 1756 (1972).
2. D. M. Grant and E. G. Paul, ibid, **86**, 2984 (1964).
3. W. J. Horsley and H. Sternlicht, ibid, **90**, 3738 (1968).
4. H. Dreeskamp, K. Hildenbrand, and G. Pfisterer, Mol. Phys., **17**, 429 (1969).