sible for the chemical shift has a strong directional character. The coupling constant of the α- and β-hydrogens (8.2 sec.$^{-1}$) is the value expected for the case in which the hydrogens on adjacent carbons are close to being completely eclipsed. Only a single value of the coupling constant is obtained from a first-order consideration of the spectrum. Bothner-By[18] has found that the coupling constants for the cis- and trans- α- and β-protons will appear to approach that for a single coupling constant if

$$\frac{J_{\alpha\alpha'} + J_{\beta\beta'}}{J_{\alpha\beta} - J_{\alpha\beta'}} >> 1$$

and this will probably be the case here.

In complete contrast to cyclobutanone, the chemical shifts of the α- and β-hydrogens of cyclopentanone are almost the same (differing by only 2.4 cycles at 60 mc.), and the coupling constant must be very small. The spectrum consists of only two peaks of approximately equal intensity. For the A_2B_2 case, if the coupling constant were equal to or larger than the chemical shift, the spectrum would be much more complex than that observed. Thus the coupling constant must be much smaller than 2.4 sec.$^{-1}$. This seems unreasonable in view of the results which have been obtained with other compounds. Also, it is strange that the α- and β-hydrogens are almost equally shielded.

The spectra of the other cycloalkanones are about what one might expect. The chemical shift for the α-hydrogens with respect to the corresponding saturated hydrocarbon is about the same for the 6-, 7- and 8-membered ring ketones, and in each case the resonance band is rather broad. The far ring protons give bands with half-widths of 9 and 6 cycles for the 6- and 7-membered rings, respectively. However, the band for cyclooctanone is very broad, and there is a suggestion of it being in two parts with chemical shifts of 8.19 and 8.50, respectively. The former band has a half-width of about 25 sec.$^{-1}$, and the half-width of the latter is about 10 sec.$^{-1}$. It can be seen that there is far less regularity in the spectra of the ketones than there was with the alkenes.

Experimental

Materials.—Except for cyclopropene, cyclobutane and cyclobutene, which were prepared by standard procedures, all of the compounds used were commercial samples. All compounds were analyzed by vapor phase chromatography, and if an impurity was found, the compound was purified by preparative scale vapor phase chromatography.

Instruments.—The infrared spectra were determined using a Perkin-Elmer model 21 spectrometer equipped with a calcium fluoride prism. It was calibrated using polystyrene and water vapor. The ultraviolet spectra were obtained using a Cary model 14 spectrometer. The n.m.r. spectra were obtained using a Varian spectrometer with a radio frequency of 60 mc.

Spin–Spin Coupling Constants between Non-bonded C13 and Protons in Some C13-Labeled Compounds

By Gerasimos J. Karabatsos

Spin–spin coupling constants between C13 and protons separated by one, two or three bonds have been measured in twelve compounds possessing either the isopropyl or the t-butyl group and labeled with C13 at specific carbon atoms. In diisopropyl ketone-carbonyl-C13, isobutyric acid-carbonyl-C13 and methyl isobutyrate-carbonyl-C13 the C13-proton coupling constants do not decrease monotonically with the number of bonds separating the two nuclei; $J_{C^{13}-C-H}$ corresponds to 80% $J_{C^{13}-C-C-H}$ in the ketone and 97% in the acid and ester; $J_{C^{13}-C-C-H}$ is found to vary over a range of 53% (5.8 c.p.s. in methyl isobutyrate-carbonyl-C13 to 3.8 c.p.s. in isobutyl alcohol-1-C13). In compounds possessing the isopropyl group $J_{C^{13}-C-C-H}$ has values in the range of 70–80% of the corresponding $J_{H-C-C-H}$; the two constants undergo changes which are, qualitatively, directly proportional to each other. The smallest spin–spin coupling constant between C13 and proton was found to be (3.5 c.p.s.) in the system C13–O–C–H of the methyl esters.

Spin–spin coupling constants between C13 and proton directly bonded to each other have been measured in compounds of C13 natural abundance, either from C13 or proton resonance n.m.r. studies, and some interesting correlations have been made.[1] No evaluation of such constants has been made when C13 and hydrogen are separated by more than one bond.[2] The possibility of using proton n.m.r. for ascertaining the position of C13 in specific atoms of products during mechanistic studies[3] led to the examination of the proton n.m.r.

spectra of various C13-labeled compounds, available from such studies. This paper records various C13-proton spin–spin coupling constants together with some qualitative correlations.

Results and Discussion

All C13-labeled compounds whose proton n.m.r. spectra are reported in this paper contain either the isopropyl or the t-butyl group.[4] The excess C13 content in the compounds varied from about 65% (diisopropyl ketone) to about 15% (dimethylacetic acid and its derivatives). Table I summarizes the measured spin–spin coupling constants between C13 and hydrogen, each value being the average of twelve measurements.

(1) (a) P. C. Lauterbur, J. Chem. Phys., **26**, 217 (1957); (b) A. D. Cohen, N. Sheppard and J. J. Turner, Proc. Chem. Soc., 118 (1958); (c) N. Sheppard and J. J. Turner, Proc. Roy. Soc. (London), **A252**, 506 (1959); (d) N. Sheppard and J. J. Turner, Mol. Phys., **3**, 168 (1960); (e) J. N. Shoolery, J. Chem. Phys., **31**, 1427 (1959); (f) N. Muller and D. E. Prichard, ibid., **31**, 768, 1471 (1959); (g) G. V. D. Tiers, ibid., **64**, 373 (1960); (h) E. B. Whipple, J. H. Goldstein and W. E. Stewart, J. Am. Chem. Soc., **81**, 4761 (1959).

(2) J. N. Shoolery has measured such constants in methylacetylene (private communication).

(3) For an example see G. J. Karabatsos and J. D. Graham, J. Am. Chem. Soc., **82**, 5250 (1960).

(4) The author is indebted to Professor P. D. Bartlett for his encouragement in pursuing this work. Some of the compounds, namely diisopropyl ketone and its derivatives, dimethylacetic acid and trimethylacetic acid, were synthesized in his laboratories.

Inspection of the data (Table I) reveals certain interesting features, the most striking of all being the fact that $J_{C^{13}-C-H}$ is smaller than $J_{C^{13}-C-C-H}$ in the case of diisopropyl ketone and to a smaller extent in dimethylacetic acid and its methyl esters. (The difference in the last two cases is practically within experimental error.) Such anomalous spin–spin coupling constants—J's do not decrease monotonically with the number of bonds separating the interacting nuclei—involving magnetic nuclei other than C^{13} have been observed and recorded in the literature. In the case of lead tetraethyl[5] J_{CH_2-Pb} (42 c.p.s.) is about one-third of J_{CH_3-Pb} (142 c.p.s.). Similar constants have been obtained with diethylmercury,[6] di-n-propylmercury and di-isopropylmercury,[6b] the last compound having the values: $J_{Hg-C-H} = 78$ c.p.s. and $J_{Hg-C-C-H} = 126$ c.p.s. Further examples of such anomalous constants, involving chemical systems structurally unrelated to those of the compounds under discussion, are the cases of proton–fluorine interactions in cyclobutene derivatives[7] and fluorine–fluorine interactions in perfluorodimethylethylamine.[8]

TABLE I

SPIN-SPIN COUPLING CONSTANTS (C.P.S.) BETWEEN C^{13} AND HYDROGEN

Compound	$(J_{C^{13}-H})^a$	$(J_{C^{13}-C-H})^b$	$(J_{C^{13}-C-C-H})^b$	$(J_{C^{13}-O-C-H})^b$
$\overset{O}{\overset{\|\|}{(CH_3)_2CHCCH(CH_3)_2}}$ (13)		4.1	5.1	
$\overset{OH}{\overset{\|}{(CH_3)_2CHCHCH(CH_3)_2}}$ (13)	136		4.5	
$(CH_3)_2CHCH_2CH(CH_3)_2$ (13)			~4.8	
$(CH_3)_3CCO_2H$ (13)			4.2	
$(CH_3)_3CCO_2CH_3$ (13)			4.4	3.5
$(CH_3)_3CCO_2{}^-$ (13)			4.4	
$(CH_3)_3CCH_2OH$ (13)	132		4.8	
$(CH_3)_3CCD_2OH$ (13)			4.8	
$(CH_3)_2CHCO_2H$ (13)		5.2	5.4	
$(CH_3)_2CHCO-O_2CH_3$ (13)		5.6	5.8	3.5
$(CH_3)_2CHCH_2OH$ (13)	140		3.8	
$(CH_3)_2CHCD_2OH$ (13)			3.8	

^{a} Values are precise to ±2 c.p.s. ^{b} Values are precise to ±0.1 c.p.s.

The factors causing $J_{C^{13}-C-H}$ to be smaller than $J_{C^{13}-C-C-H}$ are not clear at all. Furthermore, the limited number of examples reported here prevents any empirical correlations from being made, although it appears from the relative magnitudes of the two J's in the three compounds reported that a considerable variation in $J_{C^{13}-C-H}$ may exist; per-
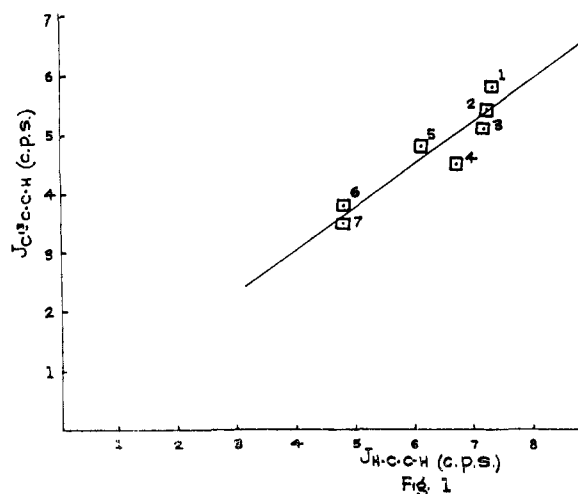
(5) E. B. Baker, J. Chem. Phys., 26, 960 (1957).

(6) (a) P. T. Narasimhan and M. T. Rogers, J. Am. Chem. Soc., 82, 34 (1960); (b) R. E. Dessy, T. J. Flautt, H. H. Jaffé and G. F. Reynolds, J. Chem. Phys., 30, 1422 (1959).

(7) M. Sharts and J. D. Roberts, J. Am. Chem. Soc., 79, 1308 (1957).

(8) A. Saika and H. S. Gutowsky, ibid., 78, 4818 (1956).

Fig. 1.—Relationship between $J_{C^{13}C-C-H}$ and $J_{H-C-C-H}$ in compounds possessing the isopropyl group: 1, $(CH_3)_2$-$\overset{13}{C}HCO_2CH_3$; 2, $(CH_3)_2CHCO_2H$; 3, $(CH_3)_2CHCOCH(CH_3)_2$; 4, $(CH_3)_2CHCH(OH)CH(CH_3)_2$; 5, $(CH_3)_2CHCH_2CH(CH_3)_2$; 6,$(CH_3)_2CHCH_2OH$; 7, values represent $J_{C^{13}-O-C-H}$ from $(CH_3)_2CHCO_2CH_3$ and $J_{H-O-C-H}$ from CH_3CH_2OH; latter value taken from J. T. Arnold, Phys. Rev. 102, 136 (1956).

haps in these cases $J_{C^{13}-C-H}$ is abnormally small. The possibility that the C^{13}C–H angle might be important, as in the case of gem-hydrogens,[9] cannot be definitely excluded, although there is no reason to suspect that the contact electron-spin interaction term is the dominant one.

Another feature of the data (Table I) is the considerable variation (5.8–3.8 c.p.s.) observed in the spin–spin coupling constants between C^{13} and hydrogen separated by three bonds ($J_{C^{13}-C-C-H}$). In the case of the acids and their methyl esters substitution of a hydrogen for a methyl group increases $J_{C^{13}-C-C-H}$ by 30%, a fact which is practically reversed in the corresponding alcohols. It was observed during determinations of $J_{C^{13}-C-C-H}$ in compounds containing the isopropyl group that the corresponding $J_{H-C-C-H}$ in the same compounds was always larger by about 20-30%. A summary of various $J_{H-C-C-H}$ in isopropyl groups and the calculated percentage $J_{C^{13}-C-C-H}$ to $J_{H-C-C-H}$ ratios are given in Table II. A plot of $J_{H-C-C-H}$ versus $J_{C^{13}-C-C-H}$ is shown in Fig. 1.

It was interesting to find (Fig. 1) that in compounds possessing system I numerical changes in $J_{H-C-C-H}$ and $J_{C^{13}-C-C-H}$ appear to occur in the same direction, and the two J's to be related to each

$$\begin{array}{c} CH_3 \diagdown \quad \diagup H \\ C \\ \diagup \quad \diagdown \\ CH_3 \quad C^{13} \\ I \end{array}$$
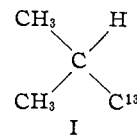
other, at least qualitatively. linearly. The significance and meaning of this observation is debat-

(9) H. S. Gutowsky, M. Karplus and D. M. Grant, J. Chem. Phys., 31, 1278 (1959).

able. Certainly, the possibility that this correlation might be only a fortuitous coincidence void of any physical significance—the number of compounds examined is small—cannot be excluded. If, however, the correlation is real, one might suggest that for system I either the contact electron-spin term in C^{13} is a dominant one undergoing changes which are proportional to those in the corresponding term in proton, or/and changes of other terms, e.g., electron-orbital term, in C^{13} parallel those of the contact electron–spin term in proton.

Finally, it was interesting to observe that substitution of an atom of oxygen for an atom of carbon (methyl esters of C^{13}-carbonyl labeled acids) results in considerable decrease of C^{13}–proton coupling constant (Table I, $J_{C^{13}O-C-H} < J_{C^{13}C-C-H}$).

TABLE II

PROTON SPIN–SPIN COUPLING CONSTANTS (C.P.S.) IN ISOPROPYL GROUPS

Compound	$J_{H-C-C-H}$	$\dfrac{J_{C_{13}C-C-H}}{J_{H-C-C-H}} \times 100$
$(CH_3)_2CHCCH(CH_3)_2$ (with O= above carbonyl)	7.2	71
$(CH_3)_2CHC(OH)HCH(CH_3)_2$	6.7	67
$(CH_3)_2CHCH_2CH(CH_3)_2$	6.1	79
$(CH_3)_2CHCO_2H$	7.2	75
$(CH_3)_2CHCO_2CH_3$	7.3	79
$(CH_3)_2CHCH_2OH$	4.8	79
$(CH_3)_3CH^a$	5.0	
$(CH_3)_3CHCH(CH_3)_2{}^a$	5.5	
$(CH_3)_2CHCH_2CH_2CH_3{}^a$	5.2	
$(CH_3)_2CHOH^b$	6.1	
$(CH_3)_2CHBr^b$	6.4	
$(CH_3)_2CHNH_2{}^b$	6.1	

^{a} Taken from J. A. Pople, W. G. Schneider and H. J. Bernstein, "High-Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N.Y., 1959, pp. 236–237. ^{b} Taken from A. A. Bothner-by, C. Naar-Colin and B. L. Shapiro, "NMR Spectra and Structure Correlations," Vol. II, Harvard University, 1958.

Experimental

Preparation of C^{13}-Labeled Compounds. a. Diisopropyl Ketone and its Derivatives.—Preparation of 2,4-dimethyl-3-pentanone-3-C^{13} and 2,4-dimethylpentane-3-C^{13} will be described elsewhere. Preparation of 2,4-dimethyl-3-pentanol-3-C^{13} has been recorded.[10]

b. Trimethylacetic acid-1-C^{13} and dimethylacetic acid-1-C^{13} were isolated as by-products from the addition of carbon dioxide-C^{13} to t-butyllithium and isopropyllithium, respectively, at $-60°$, during synthesis of di-t-butyl ketone and diisopropyl ketone. Their infrared spectra (carbonyl frequency) have been discussed.[11]

c. Methyl Dimethylacetate-1-C^{13} and Methyl Trimethylacetate-1-C^{13}.—One gram of C^{13}-carbonyl labeled acid was dissolved in anhydrous ether (10 ml.) and diazomethane[12] was added until the yellow color persisted. The ether was evaporated through a small fractionating column. Practically quantitative yields of the esters were obtained.

d. C^{13} and Deuterium Labeled Alcohols.—The deuterated and undeuterated C^{13}-labeled isobutyl and neopentyl alcohols were prepared by reduction of the corresponding acids in ether solutions with lithium aluminum deuteride and lithium aluminum hydride. Vapor phase chromatography and infrared spectroscopy were used to ascertain purity of all samples.

Measurements.—All spectra were taken with a model V4250A Varian Associates high resolution n.m.r. spectrometer, at 60 Mc., with the exception of those of diisopropyl ketone and diisopropylmethane which were measured at 40 Mc. Thin-walled Wilmad Glass Co. tubes were used in taking the spectra; no sample degassing was applied. Trimethylacetic acid (10% solution in carbon tetrachloride) and its anion (10% solution in dilute aqueous potassium hydroxide) were the only compounds whose spectra were taken in solution. Spin–spin coupling constants were measured using the standard side band technique,[13] the frequency counter being employed.

(10) G. J. Karabatsos, J. Org. Chem., 25, 1409 (1960).

(11) G. J. Karabatsos, ibid., 25, 315 (1960).

(12) F. Arndt, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1948, p. 165.

(13) J. T. Arnold and M. E. Packard, J. Chem. Phys., 19, 1608 (1951).

Molecule-induced Homolytic Decompositions. I. Oxygen-18 Labeling Studies on the Reaction Yielding Cyclohexyl Acetate from Cyclohexene and Acetyl Peroxide[1]

BY J. C. MARTIN AND E. H. DREW

The decomposition of acetyl peroxide in cyclohexene solution gives a small amount ($\sim$10%) of cyclohexyl acetate. This has been attributed[2] to a mechanism involving an addition of free acetoxy radicals to cyclohexene. To test the hypothesis that this product results instead from the operation of a molecule-induced decomposition in which cyclohexene attacks acetyl peroxide, we used O^{18}-tracer techniques to determine the disposition of the label in cyclohexyl acetate from the decomposition of carbonyl-labeled peroxide. The finding of 58% of the label in the carbonyl oxygen of the product acetate (42% in the saturated oxygen) serves to rule out the possibility that all of the product results from a process involving acetoxy radical. The demonstration of a dependence of labeling specificity on the availability of hydrogen atom donor molecules serves to confirm the postulated mechanism (mechanism II).

It has recently been shown[3,4] that suitable neighboring groups can bring about an anchimeric[5]

acceleration of the homolytic cleavage of oxygen–oxygen bonds similar to the well-known accelerating effect of neighboring nucleophilic groups in

(1) Presented before the Division of Organic Chemistry at the 137th Meeting of the American Chemical Society, Cleveland, Ohio, April, 1960.

(2) H. J. Shine and J. R. Slagle, J. Am. Chem. Soc., 81, 6309 (1959).

(3) J. C. Martin and W. G. Bentrude, Chemistry & Industry, 192 (1959); complete report in preparation.

(4) J. E. Leffler, R. D. Faulkner and C. C. Petropoulos, J. Am. Chem. Soc., 80, 5435 (1958).

(5) S. Winstein, C. R. Lindegren, H. Marshall and L. Ingraham, ibid., 75, 147 (1955).