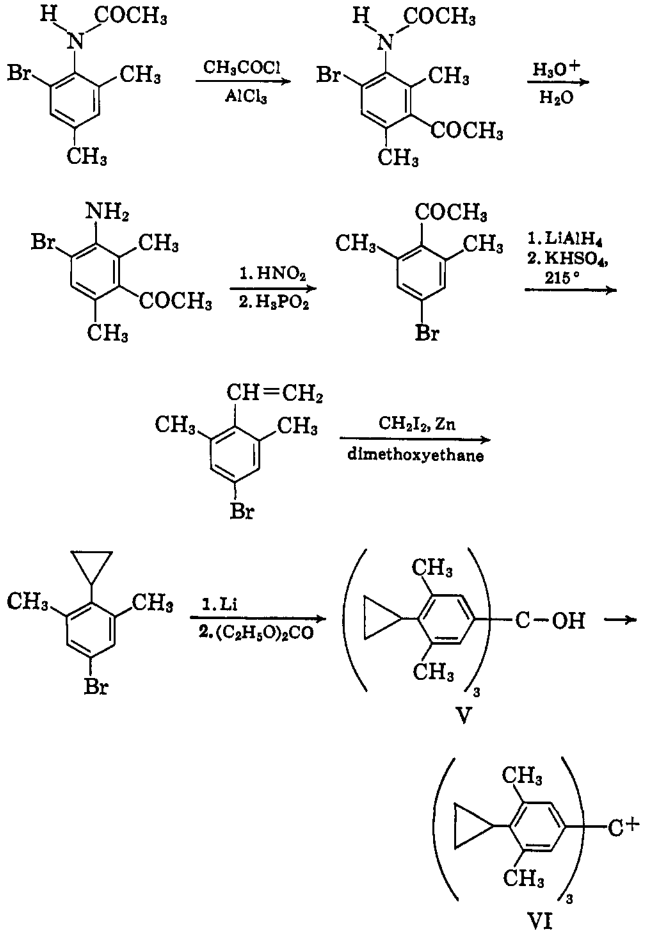
charge on the ring of VI, relative to II, and hence the electron demand on the cyclopropyl ring. An assessment of the contribution of this effect to the difference in 23 (for V going to VI) and 32 cps (for I going to II) must await a more detailed analysis.



It has been pointed out[2c] that nmr spectroscopy cannot be used to distinguish between conformer A, on the one hand, and two rapidly equilibrating ions with bicyclobutonium[14] geometries. A comparison of the downfield shift values (Table II) for the methine protons in II, IV, and VI suggests the presence of little positive charge on the methine carbons attributable to bicyclobutonium type interactions in II and VI. This result does not, of course, rule out the possibility that greater electron demand, as in the unsubstituted cyclopropylcarbinyl system, could make the less symmetrical geometry of the bicyclobutonium ion the more favorable one.[14a]

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(14) R. H. Mazur, W. N. White, D. A. Semenow, C. C. Lee, M. S. Silver, and J. D. Roberts, *J. Am. Chem. Soc.*, **81**, 4390 (1959).

(14a) NOTE ADDED IN PROOF. The downfield shifts, observed on going from carbinol to carbonium ion, for the protons at the *para* positions of triphenylcarbinol, VII (66.8 cps), and 3,3′,3″,5,5′,5″-hexamethyltriphenylcarbinol, VIII (65.2 cps), are similar enough to render unlikely any argument explaining the smaller downfield shift observed for the methylene protons of V on going to VI (compared with I going to II) in terms of lesser electron demand in the methylated rings of VI. The conclusion that steric inhibition of resonance is an important factor in explaining the properties of VI receives further support in the observation of nearly identical basicities for V ($pK_{R^+}$ = −6.5), III (−6.5), and VIII (−6.5), while I (−4.9) is appreciably more basic than VII (−6.6). The definition of $pK_{R^+}$ and values for I, III, and VII are taken from N. C. Deno and A. Schriesheim, *J. Am. Chem. Soc.*, **77**, 3051 (1955).

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(15) Dow Chemical Company Fellow, 1963–1964; Archer Daniels Midland Company Fellow, 1965–1966.

(16) Fellow of the Alfred P. Sloan Foundation.

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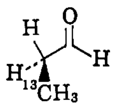
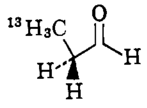
## Proton–Carbon-13 Spin–Spin Coupling. VII. The Relative Magnitudes of *trans* and *gauche* $J_{^{13}CCCH}$

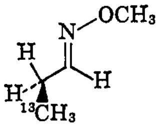
*Sir:*

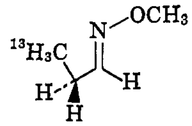
The question of the relative contributions of various factors to the spin–spin coupling between directly bonded and nonbonded proton and $^{13}C$ has received extensive attention in the past few years. For directly bonded proton and $^{13}C$ the theoretically predicted dominant contribution to $J_{^{13}CH}$ by the Fermi contact term has been experimentally supported by its dependence on the carbon 2s orbital hybridization. The anticipated similarities, however, between vicinal proton–proton and vicinal proton–$^{13}C$ couplings have often been masked by the extreme sensitivity of the vicinal $J_{^{13}CCCH}$ to factors that frequently reverse its predicted dependence on carbon orbital hybridization.[1] The possibility of using this coupling as a probe to study rotational isomerism[2] prompts us to report results on the relative magnitudes of *trans* and *gauche* proton–$^{13}C$ couplings.

If the dependence of $J_{^{13}CCCH}$ on dihedral angle were analogous to that of vicinal proton–proton coupling,[3,4] *trans* $J_{^{13}CCCH}$ would be greater than *gauche*. Propionaldehyde-3-$^{13}C$ and its oxime O-methyl ether are suitable models for cogent information on this subject, because the relative populations of unlabeled I and II,[5] and I′ and II′,[6] have been calculated as a function of temperature. Since $\Delta H°(I \rightarrow II) = -800$ cal/mole and $\Delta H°(I' \rightarrow II') = +390$ cal/mole, if *trans* $J_{^{13}CCCH}$ were greater than *gauche*, temperature increase would decrease the coupling of propionaldehyde-3-$^{13}C$ and increase that of propionaldehyde-3-$^{13}C$ oxime O-methyl ether.


I


II


I′


II′

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(1) G. J. Karabatsos and C. E. Orzech, Jr., *J. Am. Chem. Soc.*, **87**, 560 (1965).

(2) G. J. Karabatsos, N. Hsi, and C. E. Orzech, Jr., unpublished results.

(3) M. Karplus, *J. Chem. Phys.*, 30, 11 (1959).

(4) M. Karplus, *J. Am. Chem. Soc.*, **85**, 2870 (1963).

(5) G. J. Karabatsos and N. Hsi, *ibid.*, **87**, 2864 (1965).

(6) G. J. Karabatsos and N. Hsi, *ibid.*, in press.

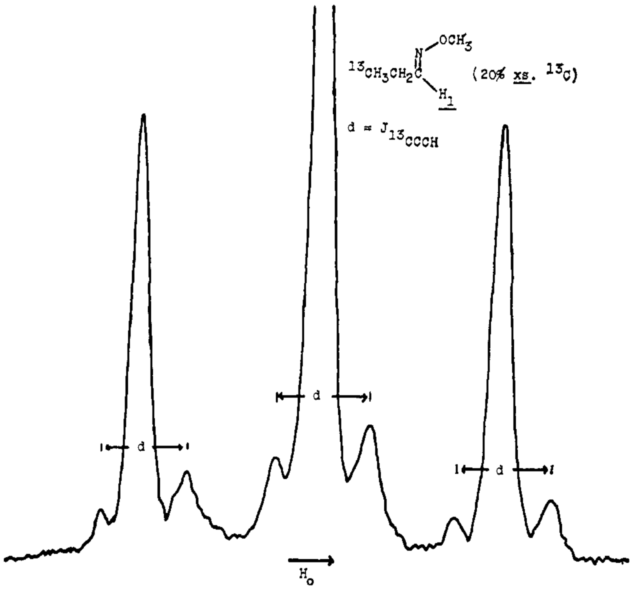
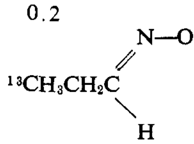


Figure 1.

Propionaldehyde-3-$^{13}C$ oxime O-methyl ether was prepared[6] from propionaldehyde-3-$^{13}C$ which had been prepared by passing 1-propanol-3-$^{13}C$ over hot copper metal. The 1-propanol-3-$^{13}C$ was synthesized by allowing 20% excess $^{13}C$ methylmagnesium iodide to react with ethylene oxide.

In Table I we have summarized all pertinent information obtained from first-order spectral analysis. The $J_{^{13}CCCH}$ values of the aldehyde are averages of several measurements in neat solution with an accuracy of ±0.05 cps. Those of the oxime ether, taken in 40% carbon tetrachloride solution, are less accurate on account of peak overlap (Figure 1) that results from incomplete washout[6,7] of $J_{HCN}$. The *trans* and *gauche* $J_{^{13}CCCH}$ were calculated from linear plots of per cent II and II′ *vs.* the experimentally measured corresponding coupling constants. Both had the same, presumably positive, sign.

Table I

| $t$, °C | $J_{HCCH}$, (cps) | $J_{^{13}CCCH}$, cps | II, % |
|---|---|---|---|
| | $^{13}CH_3CH_2CHO$ | | |
| −35 | 1.00 | 2.65 | 75.0 |
| −25 | 1.15 | 2.50 | 70.5 |
| 0 | 1.22 | 2.45 | 69.0 |
| 15 | 1.30 | 2.40 | 66.5 |
| 38 | 1.32 | 2.35 | 65.5 |
| 45 | 1.35 | 2.30 | 65.0 |
| $J_t$ | 7.2 | ⟨3.5⟩ | |
| $J_g$ | 0.2 | ⟨0.2⟩ | |
| |  $^{13}CH_3CH_2C(H)=N-OCH_3$ | | |
| | | | %II′ |
| −30 | 5.92 | 2.65 | 23.0 |
| −15 | 5.90 | 2.75 | 23.5 |
| 0 | 5.87 | 2.80 | 24.0 |
| 15 | 5.85 | 2.80 | 25.0 |
| 40 | 5.80 | 2.90 | 26.0 |
| 50 | 5.75 | 3.00 | 27.0 |
| $J_t$ | 10.9 | ⟨7.8⟩ | |
| $J_g$ | 2.8 | ⟨0.7⟩ | |

The results clearly bring out the similarity between vicinal proton–proton and vicinal proton–$^{13}C$ couplings and support the prediction that *trans* $J_{^{13}CCCH}$ is greater than *gauche*.

**Acknowledgment.** We thank the United States Atomic Energy Commission for financial support under Grant COO-1189-18.

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(7) B. L. Shapiro, S. J. Ebersole, and R. M. Kopehik, *J. Mol. Spectry.*, **11** (4), 326 (1963).

(8) Fellow of the Alfred P. Sloan Foundation.

(9) Lubrizol Fellow, 1964–1965.

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*Received February 3, 1966*

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## Stable Carbonium Ions. XXIII.[1] Proton–$^{13}C^+$ Spin–Spin Coupling in Carbonium Ions[1]

*Sir:*

Numerous investigations have been directed toward elucidation of the factors affecting proton–$^{13}C$ coupling.[2,3] The general linearity between $^1J_{^{13}C-H}$ and fractional s character of the $^{13}C$ hybrid atomic orbital has led to the conclusion that the Fermi contact term is essentially the sole contributor to the coupling, as suggested from the valence bond theory.[4] It was noted that $^1J_{^{13}C-H}$ values correlate well with the hybridization of the C–H bond,[5] $\rho_{C-H} = 0.20J_{^{13}C-H}$ ($\rho_{C-H}$ = percentage s character in bonding C orbital). Additivity relations of substituent effects on $^1J_{^{13}C-H}$ in substituted methanes[6] and formyl compounds[7] have been discovered. Deviations from the additivity relations have been observed and empirical corrections have been suggested.[8] Recently the validity of s characters calculated from experimental $J_{^{13}C-H}$ data has been questioned.[3]

The stability of carbonium ions in strongly acidic solvent systems ($SbF_5$, $SbF_5$–$SO_2$, $SbF_5$–$FSO_3H$–$SO_2$) has enabled their spectroscopic (nmr, infrared, ultraviolet) investigation.[9,10] The nuclear magnetic resonance investigations centered mainly on proton resonance, although $^{13}C$ resonance investigations of some ions (like the trimethyl- and triphenylcarbonium ions) were also reported.[9,11]

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(1) Part XXII: G. A. Olah and C. U. Pittman, Jr., *J. Am. Chem. Soc.*, in press.

(2) For summaries see J. B. Stothers, *Quart. Rev.* (London), **19**, 144 (1965); D. M. Grant, *Ann. Rev. Phys. Chem.*, **15**, 489 (1964).

(3) G. J. Karabatsos and Ch. E. Orzech, Jr., *J. Am. Chem. Soc.*, **86**, 3574 (1964); **87**, 560 (1965); D. M. Grant and W. M. Lichtman, *ibid.*, **87**, 3994 (1965); K. Wiberg, *et al.*, *Tetrahedron*, **21**, 2794 (1965).

(4) M. Karplus and D. Grant, *Proc. Natl. Acad. Sci. U. S.*, **45**, 1269 (1959).

(5) N. Muller and D. E. Pritchard, *J. Chem. Phys.*, **31**, 768, 1471 (1959); N. Muller, *ibid.*, **36**, 359 (1962).

(6) E. R. Malinowski, *J. Am. Chem. Soc.*, **83**, 4479 (1961).

(7) E. R. Malinowski, L. Z. Pollara, and J. P. Larmann, *ibid.*, **84**, 2649 (1962).

(8) A. W. Douglas, *J. Chem. Phys.*, **40**, 2413 (1964).

(9) G. A. Olah, E. B. Baker, J. C. Evans, W. S. Tolgyesi, J. S. McIntyre, and I. J. Bastien, *J. Am. Chem. Soc.*, **86**, 1360 (1964).

(10) G. A. Olah, M. B. Comisarow, C. U. Pittman, Jr., and C. A. Cupas, *ibid.*, **87**, 2997 (1965).

(11) G. A. Olah, E. B. Baker, and M. B. Comisarow, *ibid.*, **86**, 2165 (1964).