Communications to the Editor

Infrared Bands from Alkali Ion Motion in Solution

Sir:

Recently, this laboratory discussed the 5-μ infrared spectrum and the electrical conductance of THF solutions of $Na^+Co(CO)_4^-$ in terms of the presence of ion pairs.[1] We wish now to report the observation of infrared bands arising from the motion of the alkali ion in THF solutions of Li^+, Na^+, and K^+ salts of $Co(CO)_4^-$ and of $Mn(CO)_5^-$.

The assignment of a band at 190 cm^{-1} in solutions prepared by shaking Na amalgam with $Co_2(CO)_8$ in THF to a vibration of the Na^+ was first made last June.[2] Subsequently, however, we have found small amounts of $Hg[Co(CO)_4]_2$ present in solutions similarly prepared. Although precautions had been taken to eliminate impurities as a source of the observation in the original experiments (for example, a THF solution of $Co_2(CO)_8$ shaken with Hg did not show the 190-cm^{-1} band), this finding created a special difficulty because $Hg[Co(CO)_4]_2$ was found to have a band at 192 cm^{-1}. Consequently, we felt it necessary to eliminate $Hg[Co(CO)_4]_2$ as a possible source of this band in a more positive manner in order to place this interpretation on a firmer foundation.[3] To this end, $Li^+Co(CO)_4^-$, $Na^+Co(CO)_4^-$, and $K^+Co(CO)_4^-$ solutions in THF were prepared by methods which did not involve the presence of Hg at any stage. These solutions showed the same bands found in the original work. In addition, we also prepared Hg-free THF solutions of $Li^+Mn(CO)_5^-$, $Na^+Mn(CO)_5^-$, and $K^+Mn(CO)_5^-$ and found similar bands. These bands appear at 407, 190, and *ca.* 150 cm^{-1} in the Li^+, Na^+, and K^+ THF solutions of $Co(CO)_4^-$, respectively, with an uncertainty of perhaps 5 cm^{-1} due to the broadness of the bands. The corresponding bands in the $Mn(CO)_5^-$ solutions are seen 20–30 cm^{-1} higher in frequency. Solutions in the concentration range from 0.1 to 0.3 *M* were examined between 800 and 33 cm^{-1} with cell thicknesses between 0.1 and 0.5 mm.

These data indicate that these bands arise from vibration of the alkali ions in these solutions. Moreover, since the initial report,[2] Evans and Lo[4] have reported far-infrared bands in benzene solutions of tetrabutylammonium halides which they attribute to interionic vibrations. The primary significance of these data lies in their direct relation to the force field at the ion and to the structure of the aggregate of which it is a part. Our data suggest a force field dependence upon the cation. The fact that the frequency of a given alkali ion shifts with change in anion, coupled with the expected presence of ion pairs in these solutions,[1] suggest that the vibration takes place in an ion pair or higher aggregate involving the anion. The solvent is also expected to participate in the aggregate, but its role has not yet been established. The details of this work and other measurements now in progress will be reported separately.

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[1] W. F. Edgell, M. T. Yang, and N. Koizumi, *J. Am. Chem. Soc.*, **87**, 2563 (1965).

[2] W. F. Edgell and A. T. Watts, Abstracts, Symposium on Molecular Structure and Spectroscopy, Ohio State University, June 1965, p 85.

[3] The band at 407 cm^{-1} assigned[2] to Li^+ motion in $Li^+Co(CO)_4^-$ appeared near an infrared-inactive mode of the $Co(CO)_4^-$ ion. Thus there was an outside possibility that its origin was in a breakdown of selection rules for the anion and, therefore, the cleanest proof of the correctness of the assignment required direct evidence on solutions of Na^+ salts.

[4] J. C. Evans and G. Y.-S. Lo, *J. Phys. Chem.*, **69**, 3223 (1965).

The Conformational Preference of the Cyclopropyl Substituent in Triarylmethyl Cations

Sir:

The ability of the cyclopropyl group to interact with an adjacent center of unsaturation is well documented.[1] Much recent work has been directed toward gaining an understanding of this interaction and its geometric requirements. A large number of nmr data[2] have been interpreted in terms of the postulate that maximum interaction between the cyclopropyl group and an adjacent p orbital occurs when the plane of the three-membered ring is parallel to the axis of the p orbital, *i.e.*, the bisected conformation A (Figure 1). Recent ultraviolet studies on a series of arylcyclopropanes, on the other hand, showed no evidence for a dependence of conjugation on geometry.[3]

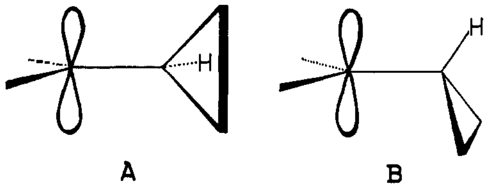

Figure 1.

Carbinol I, mp 99.5–100°, was prepared[4] in 57% yield by the reaction of the lithium reagent of *p*-bromophenylcyclopropane with diethyl carbonate. Carbinol I was converted to the corresponding carbonium ion II in trifluoroacetic acid solution and could be recovered in high yield upon basifying the solution. The results of the analysis of the nmr spectra of the cyclopropyl

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[1] M. Y. Lukina, *Russ. Chem. Rev.*, 419 (1962).

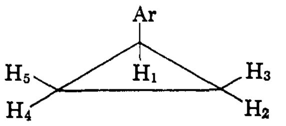
[2] (a) C. U. Pittman, Jr., and G. Olah, *J. Am. Chem. Soc.*, **87**, 2998 (1965); **87**, 5123 (1965); (b) G. L. Closs and H. B. Klinger, *ibid.*, **87**, 3265 (1965); (c) N. C. Deno, H. G. Richey, J. S. Liu, D. N. Lincoln, and J. O. Turner, *ibid.*, **87**, 4533 (1965).

[3] A. L. Goodman and R. H. Eastman, *ibid.*, **86**, 908 (1964).

[4] Satisfactory elemental analyses were obtained for all new compounds.

protons as a five-spin system, using the iterative computer program of Swalen and Reilly,[5] are listed in Table I. The listed parameters closely reproduce the experimental spectra (average deviations between calculated and observed line frequencies for I and II are 0.07 and 0.13 cps, respectively). Essentially identical spectra were obtained for II as the tetrafluoroborate salt in methylene chloride. For comparison, Table I also lists spectral parameters for III[6] and IV, the *p*-isopropyl analogs.

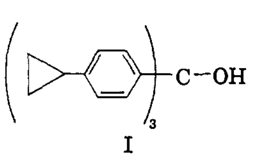
Table I. Nuclear Magnetic Resonance Spectral Parameters[a]



	I	II	III	IV	V	VI
ω_1	−1.835	−2.246			−1.65	−2.07
ω_2	−0.903	−1.461			−0.96	−1.38
ω_3	−0.634	−1.161			−0.49	−0.84
J_{12}	8.40	8.25			8.3	9.1
J_{13}	5.05	4.80			6.1	6.5
J_{23}	−4.48	−4.88			−4.5	−4.9
J_{24}	9.31	9.05			9.3	9.1
J_{25}	6.31	6.89			6.3	6.9
J_{35}	9.36	9.78			9.4	9.8
ω, isopropyl methine			−2.88	−3.28		
ω, isopropyl methyl			−1.22	−1.47		
ω, aromatic protons	−7.02[b]	−7.54	−7.15	−7.74[b]	−6.88	−7.33
ω, aromatic methyls					−2.33	−2.65

[a] Chemical shift values (ω) are in parts per million from internal TMS. Coupling constants (J) are in cycles per second. Spectra of the carbinols were obtained from 15 wt % solutions in CH_2Cl_2. Carbonium ion spectra were obtained from 15 wt % solutions in trifluoroacetic acid containing 30% trifluoroacetic anhydride by volume. All spectra were run at room temperature. Line frequencies were measured by the side-band technique. [b] Center of A_2B_2 quartet.

Table II lists the changes in chemical shifts observed on going from carbinols I and III to cations II and IV, respectively. The methine hydrogen resonance in IV is shifted downfield 24.0 cps from its position in III, while the methyl protons shift downfield only 14.9 cps. The reverse order is noted for cation II. In this case the cyclopropyl methine signal is shifted downfield 24.7 cps (relative to its position in I), while the methylene proton signals experience a downfield shift of about 32 cps. This chemical shift behavior in II is consistent with the operation of a type of charge delocalization involving the cyclopropyl group which places more positive charge on the β-carbon atoms than on the α-carbons of the ring.[7] Similar conclusions regarding charge distributions in cyclopropylcarbonium ions have been made on the basis of nmr studies of other cyclopropylcarbonium ions.[2a,c]



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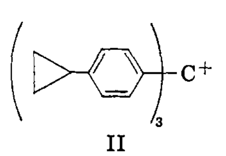

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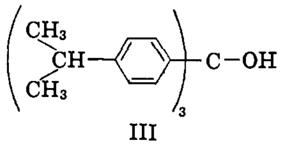

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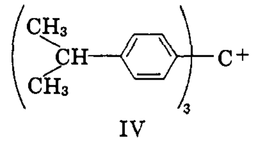

IV

Table II. Chemical Shift Differences between Carbinol and Carbonium Ion[a]

Proton	ω(I) − ω(II)	ω(III) − ω(IV)	ω(V) − ω(VI)
H_1	24.7		25.4
H_2	33.5		25 1
H_3	31.7		21.3
Isopropyl methine		24.0	
Isopropyl methyl		14.9	

[a] Values are in cycles per second. Spectra were run at 60.0 Mc.

The most graphic evidence for the bisected geometry, A, for cyclopropylcarbonium ions is to be seen in the nonequivalence of the methyl groups of the cyclopropyldimethylcarbonium ion reported by Pittman and Olah.[2a] This geometry, favored[2,11,12] for several cyclopropylcarbonium ions, is predicted from a consideration of the Walsh[8] model for the cyclopropane ring to maximize the interaction with an adjacent p orbital.[13]

The synthesis of V (mp 177.5–179°) provides a model in which steric interactions with the *o*-methyl groups constrain the cyclopropyl substituents to a geometry similar to B. (The *cis*-methylene hydrogens on the cyclopropyl ring are estimated from Dreiding models to be no more than 1.4 A from the methyl hydrogens in the bisected conformation A, *vs.* 2.5 A in conformation B. The sum of the van der Waals radii is 2.4 A.) The population of bisected conformations must be much less in VI than in II. The observation that the methylene protons of V are deshielded by *ca.* 23 cps on going to VI, when compared with the corresponding value of 32 cps for I going to II, suggests that while A may be the favored conformation for charge delocalization, conformation B is much more favorable than has hitherto been supposed. The electron-releasing effect of the methyl substituents would decrease the positive

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(5) J. D. Swalen and C. A. Reilly, *J. Chem. Phys.*, 37, 21 (1962).

(6) N. C. Deno, J. J. Jaruzelski, and A. Schriesheim, *J. Org. Chem.*, 37, 21 (1962).

(7) Theoretical treatments[8,9] indicate that the orbital which carbon uses to bond to hydrogen in cyclopropane is nearly sp^2 hybridized, as in aromatic hydrocarbons. We therefore feel some justification in calculating the fraction of positive charge residing on the six cyclopropyl β-carbon atoms in II by applying the 10 ppm/unit charge proportionality constant derived by Fraenkel, *et al.*,[10] to the observed 0.5 ppm downfield shift of the methylene protons in II. This treatment suggests that 5% of the total unit positive charge is found on each β-methylene group (30% on all six), a result which is reasonable but cannot be regarded as established.

(8) A. D. Walsh, *Trans. Faraday Soc.*, **45**, 179 (1949).

(9) C. A. Coulson and W. E. Moffitt, *Phil. Mag.*, 40, 1 (1949).

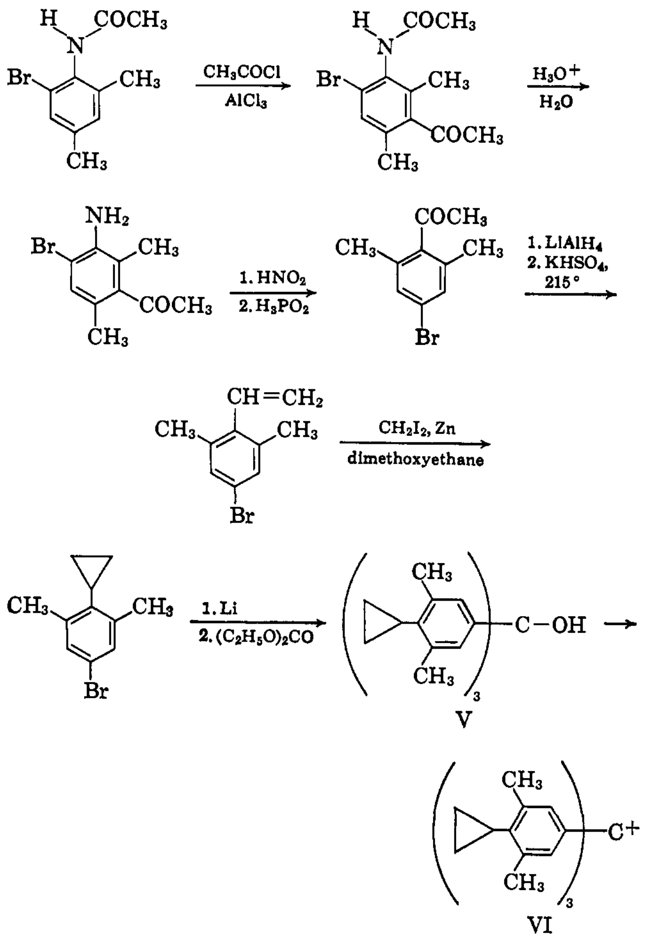
(10) G. Fraenkel, R. E. Carter, A. McLachlan, and J. H. Richards, *J. Am. Chem. Soc.*, **82**, 5846 (1960).

(11) N. C. Deno, *Progr. Phys. Org. Chem.*, 2, 150 (1964).

(12) N. C. Deno, J. S. Liu, J. O. Turner, D. N. Lincoln, and R. E. Fruit, Jr., *J. Am. Chem. Soc.*, **87**, 3000 (1965).

(13) Extended Hückel MO calculations of Hoffman indicate an appreciable energy minimum for the analogous conformation of cyclopropanecarboxaldehyde: R. Hoffman, *Tetrahedron Letters*, 3819 (1965). This has been shown experimentally by L. S. Bartell, B. L. Carroll, and J. P. Guillory, *ibid.*, 705 (1964).

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]

Acknowledgment. This research was supported in part by a grant from the U. S. Public Health Service, USPHGM-12296.

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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 ($\mathrm{p}K_{\mathrm{R}^+}$ = −6.5), III (−6.5), and VIII (−6.5), while I (−4.9) is appreciably more basic than VII (−6.6). The definition of $\mathrm{p}K_{\mathrm{R}^+}$ and values for I, III, and VII are taken from N. C. Deno and A. Schriesheim, *J. Am. Chem. Soc.*, 77, 3051 (1955).

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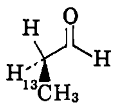
Proton–Carbon-13 Spin–Spin Coupling. VII. The Relative Magnitudes of *trans* and *gauche* $J_{^{13}\mathrm{CCCH}}$

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 $J_{^{13}\mathrm{CH}}$ 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 $J_{^{13}\mathrm{CCCH}}$ 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 $J_{^{13}\mathrm{CCCH}}$ on dihedral angle were analogous to that of vicinal proton–proton coupling,[3,4] *trans* $J_{^{13}\mathrm{CCCH}}$ 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 $\Delta H°(\mathrm{I} \rightarrow \mathrm{II}) = -800$ cal/mole and $\Delta H°(\mathrm{I'} \rightarrow \mathrm{II'}) = +390$ cal/mole, if *trans* $J_{^{13}\mathrm{CCCH}}$ 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.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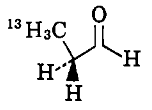
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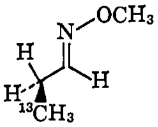
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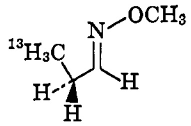
II′

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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.