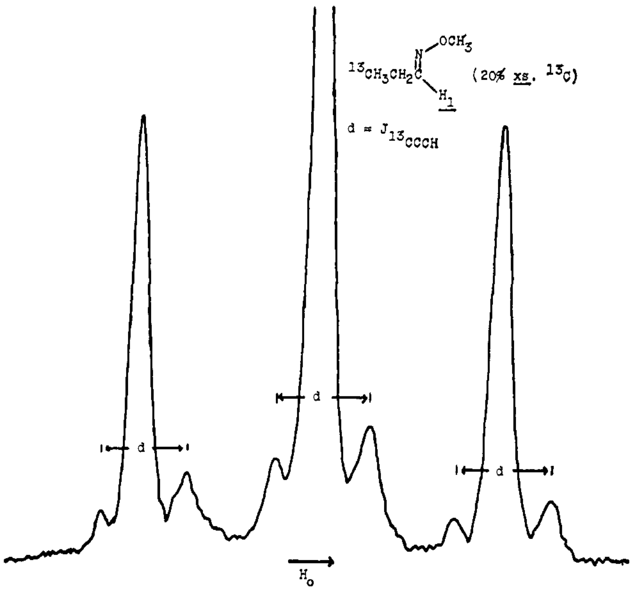
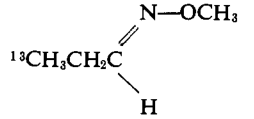


Figure 1.

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⟩	
	 $^{13}CH_3CH_2C(=N-OCH_3)H$		
			%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.

---

(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.

Gerasimos J. Karabatsos[8], Chester E. Orzech, Jr., Nelson Hsi[9]
Department of Chemistry, Michigan State University
East Lansing, Michigan

Received February 3, 1966

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] $\rho_{C-H} = 0.20J_{^{13}C-H}$ (ρ_{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]

---

(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).

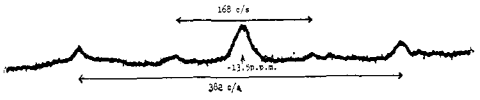


Figure 1.

The question of ^{13}C-H coupling involving a positively charged carbon atom is of particular interest.

In a previous paper[9] we briefly reported that $^{1}J_{^{13}C-H}$ for $(CH_3)_2{}^{13}CH^+$ is 382 cps. This would imply more than 75% s character for the carbon atomic orbital used in the ^{13}C-H bond and would not be compatible with the suggested sp^2 hybridization at the ^{13}C atom.

It of course could be argued that the symmetry environment of the positively charged carbon atom being different from that of the uncharged carbon atom does not allow any more the application of simple linear relationships. On the other hand the exceptional value of $J_{^{13}C-H}$ observed for the isopropyl cation clearly indicated the need for a more detailed investigation of proton-$^{13}C^+$ spin-spin coupling constants in carbonium ions.

Using improved methods to generate stable carbonium ions in strongly acidic solutions the proton-$^{13}C^+$ spin-spin coupling in $(CH_3)_2{}^{13}CH^+$ has now been reinvestigated and the investigation also extended to $(C_6H_5)_2{}^{13}CH^+$. The ions were generated from the corresponding ^{13}C-enriched chlorides (Merck Sharp and Dohme, Ltd., Montreal, Canada) with antimony pentafluoride (neat at +2° in the case of the isopropyl and in SO_2-SbF_5 solvent at −60° in the case of the benzyhydryl system). Table I summarizes the observed ^{13}C-proton coupling constants (obtained from ^{13}C satellite bands of enriched samples on a Varian Model A-60 spectrometer equipped with a variable temperature probe).

Table I. Proton-^{13}C Spin-Spin Coupling Constants of Secondary Carbonium Ions and Their Parent Hydrocarbons

	$^{1}J_{^{13}C-H}$, cps	Calcd s character, %	State of hybridization
$(CH_3)_2{}^{13}CH_2$	128	25.6	sp^3
$(CH_3)_2{}^{13}CH^+SbF_5Cl^-$	168	33.6	sp^2
$(C_6H_5)_2{}^{13}CH_2$	126	25.2	sp^3
$(C_6H_5)_2{}^{13}CH^+SbF_5Cl^-$	164	32.8	sp^2

Normally direct one-bond ^{13}C-X coupling interactions are well observable (~±1 cps) from ^{13}C satellite spectra. The observation of the couplings in the case of carbonium ions, however, represents difficulties. Figure 1 shows the low-field part of the proton spectrum of the $(CH_3)_2{}^{13}CH^+$ ion obtained on the high-resolution nmr spectrograph of Baker and Burd.[12] The 382 cps proton-^{13}C coupling constant reported from this spectrum[9] was based on the observations of the assumed ^{13}C satellite bonds. On reinvestigation of the system with improved technique of preparation of the ion it was now found (Figure 2) that the upfield "satellite band" (191 cps from CH$^+$) is not a ^{13}C satellite but is due to a small amount of Brønsted acid impurity in the antimony pentafluoride. This was not recognized in previous work. Inspection of Figure 1 explains the reason. There is a low-field peak centered at −191 cps from CH$^+$, mistakenly considered the parent ^{13}C satellite band. The identity of this peak is not established but is considered due to an impurity. The same low-field peak is, however, substantially reduced in intensity in the improved system shown in Figure 2. Addition of water, producing conjugate acid, increases the upfield peak, but has no effect on the low-field peak. The proton-^{13}C coupling of 168 cps is hardly observable in Figure 1, but is apparent in Figure 2 (all bands were checked to be not spinning side bands).

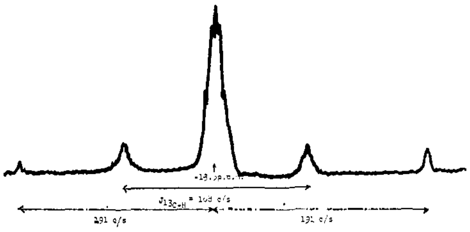


Figure 2.

Having obtained proton-^{13}C spin-spin coupling constants for the $(CH_3)_2{}^{13}CH^+$ and $(C_6H_5)_2{}^{13}CH^+$ ions it is possible now to state that the linearity between $J_{^{13}C-H}$ and fractional s character of the ^{13}C hybrid atomic orbital is also valid in the case of positively charged carbon atoms. The s character observed is in excellent agreement with the suggested sp^2 hybridization of the involved carbonium ions.[13]

Acknowledgment. This work was supported by the National Science Foundation.

---

(12) E. B. Baker and L. W. Burd, *Rev. Sci. Instr.*, **28**, 313 (1957); **34**, 238 (1963).

(13) Note Added in Proof. We recently also observed the proton-^{13}C coupling in a primary carbonium ion: the 2,4-di-*t*-butyl-6-methylphenylcarbonium ion $^{1}J_{^{13}C-H}$ is 169 cps, which corresponds to 33.8% s character.

(14) National Science Foundation predoctoral fellow.

George A. Olah, Melvin B. Comisarow[14]
Department of Chemistry
Western Reserve University, Cleveland, Ohio

Received January 15, 1966

The Identification of the P_2H_2 Molecule in the Pyrolysis of Diphosphine

Sir:

The known hydrides of phosphorus consist of PH, PH_3, P_2H_4, and some solids which are not well characterized.[1,2] This note reports the production of a new hydride of phosphorus, P_2H_2, by the pyrolytic decomposition of diphosphine, P_2H_4, and its identification by mass spectrometry.

Diphosphine, prepared by hydrolyzing calcium phosphide and purified by trap-to-trap distillation,[2] was pyrolyzed in a 1-mm i.d., 3-cm long, electrically heated, tubular flow reactor of quartz construction. The diphosphine was pumped through the reactor at a pressure

---

(1) J. R. Van Wazer, "Phosphorus and Its Compounds," Vol. 1, Interscience Publishers, Inc., New York, N. Y., 1958.

(2) E. C. Evers and E. H. Street, Jr., *J. Am. Chem. Soc.*, **78**, 5726 (1956).