2) of the isolated material with that of the natural isomer verified that the former was optically pure (+)-chorismate.

As shown in Figure 1, (+)-chorismate is a poor substrate for the catalytic antibody. The ratio of the initial rates of rearrangement obtained for the (−)- and (+)-isomers, corrected for the spontaneous background reaction, is 38 under the depicted conditions. Extrapolation to lower substrate concentrations (well below K_m for (−)-chorismate) provides an estimate of the enantioselectivity of the catalyst closer to 90:1.

In summary, we have shown that an induced antibody with chorismate mutase activity possesses exquisite enzyme-like specificity. Our findings are significant as they further demonstrate the potential of these tailored catalysts for chiral discrimination on a practical level. Since strain and proximity are the principal catalytic effects antibodies are likely to impart, we are currently targeting other shape-selective reactions, especially sigmatropic rearrangements and Diels–Alder cyclizations, with the expectation that any catalytic antibodies generated will exert precise regio- and stereochemical control over the promoted transformations.

Acknowledgment. We are grateful to Drs. Glenn Berchtold and Robert Padykula for the generous gift of racemic methyl (1β,6β)-5β-[[1-(methoxycarbonyl)ethenyl]oxy]-7-oxabicyclo[4.1.0]hept-3-ene-3-carboxylate. We also thank Stephen Carpenter and Maria-Theresa Auditor for performing some preliminary experiments. This work was supported in part by a Junior Faculty Research Award to D.H. from the American Cancer Society and Grant GM38273 from the National Institutes of Health (D.H.).

Local Structure Evaluation in Solid Organophosphorus Compounds by Double Cross Polarization Carbon-13 Nuclear Magnetic Resonance Spectroscopy[†,‡]

Edward W. Hagaman

Chemistry Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831-6201

Received February 1, 1988

Atom connectivity information that yields molecular structure descriptions is inaccessible in conventional solid-state ^{13}C NMR spectroscopy. The ^{1}H–^{13}C–^{31}P double cross polarization (DCP)/MAS ^{13}C NMR experiment reported here uses the direct dipolar interaction between isolated ^{13}C–^{31}P spin pairs in an organic solid to identify the subset of carbons within a spherical volume element of 0.4 nm radius centered on the ^{31}P atom. These chemical shift-labeled carbons are further delineated by their ^{31}P–^{13}C cross polarization rates which encode ^{31}P–^{13}C internuclear distances. Hence, the experiment reveals the carbon types in the first, second, and third bonding spheres with respect to the phosphorus atom, furnishing a statistical description of the carbon bonding network at this site.

The essence of this experiment is contained in the ^{13}C–^{31}P cross polarization step. The ^{13}C–^{31}P dipolar interaction acts as a selective filter within the molecular framework that restricts the ^{13}C spectrum to the resonances of those carbons that acquire magnetization by transfer from ^{31}P. The experiment is performed in such a way that the ^{13}C signal intensity accrues by the ^{31}P–^{13}C cross polarization rate, $(T_{CP})^{-1}$, and decays by $(^{13}\mathrm{C}T_{1\rho})^{-1}$.[1] The relative magnitude of these rates determines the effective radius of the volume element in which DCP signals can be observed.

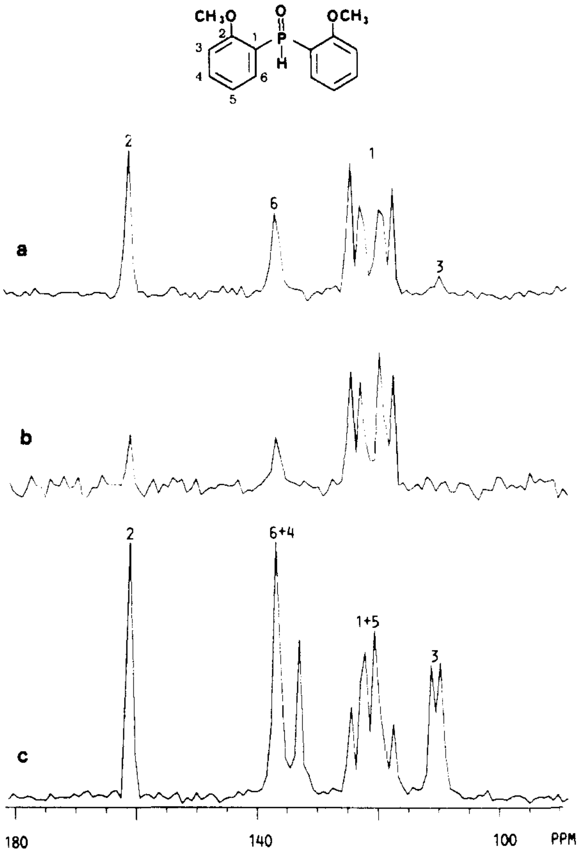


Figure 1. Conventional ^{1}H–^{13}C CP/MAS ^{13}C NMR spectrum (1c) and ^{1}H–^{13}C–^{31}P DCP/MAS ^{13}C NMR spectra (1a,b) of di-ortho-anisylphosphine oxide, **1**. All experiments used a 1 ms ^{1}H–^{13}C cross polarization contact time. DCP spectra 1a and 1b were generated with 15 and 1 ms ^{13}C–^{31}P cross polarization contact times, respectively.

On the basis of measurements of a limited, representative set of organophosphorus compounds, T_{CP} is a few ms for carbons directly bonded to phosphorus ($r < 0.2$ nm) and a few tens to hundreds of ms for carbons two- and three-bonds distant from the ^{31}P atom ($0.2 < r < 0.4$ nm). Typical ^{13}C $T_{1\rho}$ values for diamagnetic organic substances (30–200 ms) allow facile observation of carbons one-, two-, and three-bonds distant from the ^{31}P atom.[2] Schaefer et al. first reported the ^{1}H–^{13}C–^{15}N DCP/MAS NMR experiment as a method to identify carbons directly bonded to nitrogen and to estimate the concentration of ^{15}N–^{13}C bonds in a partially double-labeled solid.[1] The ^{1}H–^{13}C–^{31}P DCP/MAS NMR experiment differs from this seminal experiment by virtue of stronger dipolar coupling between the isolated cross polarization partners, facilitating the identification of carbons within a volume element that extends over several bond lengths.

Figures 1 and 2 illustrate the signal selection criteria of the ^{1}H–^{13}C–^{31}P DCP/MAS ^{13}C NMR experiment. Figure 1c displays the aromatic region of the conventional ^{1}H–^{13}C CP/MAS ^{13}C NMR spectrum of di-ortho anisyl phosphine oxide, **1**, with chemical shift assignments. Figure 1 (parts a and b) shows DCP spectra recorded with 15 and 1 ms ^{13}C–^{31}P cross polarization contact times, respectively. Each reveals resonances from those carbons one-bond removed, C(1), and two-bonds removed, C(2) and C(6), from the ^{31}P atom.[3] These are distinguished quantitatively by their T_{CP}, 2 and 16 ms, respectively, and qualitatively by comparison of signal intensities between the two DCP spectra. A low intensity peak from the resolved C(3), three-bonds distant

---

[†] This paper is dedicated to Clair J. Collins, an exemplary scientific scholar, by the author, protégé, and personal friend.

[‡] Research sponsored by the Division of Chemical Sciences/Office of Basic Energy Sciences, U.S. Department of Energy, under contract DE-AC05-84OR21400 with the Martin Marietta Energy Systems, Inc.

(1) Schaefer, J.; McKay, R. A.; Stejskal, E. O. *J. Magn. Reson.* **1977**, *34*, 443–447. Stejskal, E. O.; Schaefer, J.; McKay, R. A. *J. Magn. Reson.* **1984**, *57*, 471–485.

(2) $T_{1\rho}$ values are rf field dependent. The range quoted here is from a collection of model measurements performed by using 45 KHz rf fields.

(3) Crystal lattice forces lift the symmetry plane appropriate for the rotationally averaged species in solution, making the aromatic rings inequivalent. The two resolved phosphorus-substituted carbon resonances each show $^{1}J_{CP}$ = 102 ± 6 Hz (solution value = 105 Hz).

0002-7863/88/1510-5594$01.50/0 © 1988 American Chemical Society

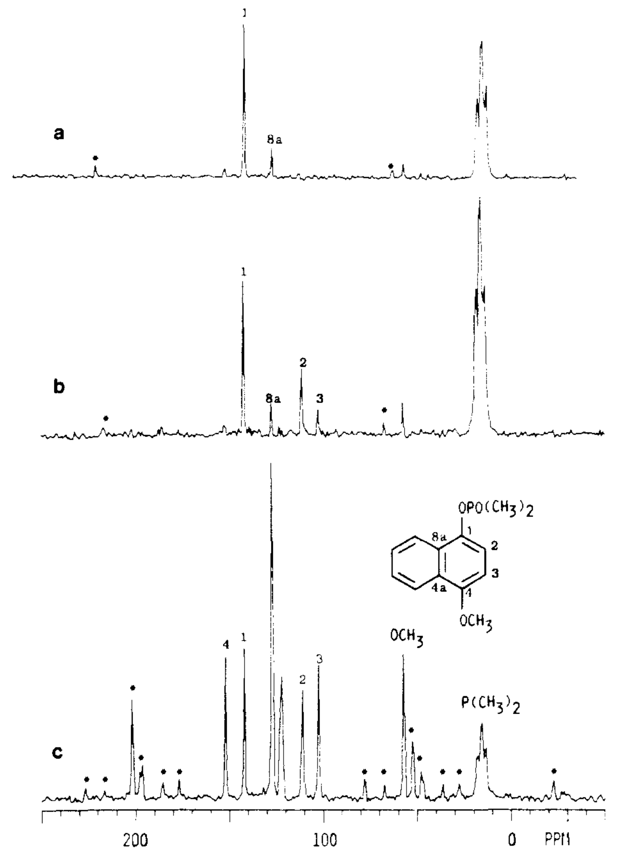


Figure 2. $^1H-^{13}C-^{31}P$ DCP/MAS ^{13}C NMR spectra (2a,b) and $^1H-^{13}C$ CP/MAS ^{13}C NMR spectrum (2c) of (4-methoxy-1-naphthyl)dimethylphosphinate, **2**. Assignments are indicated on the spectra; * identifies spinning sidebands (MAS = 4 ± 0.05 KHz). The dipolar dephased DCP spectrum, 2a, was generated by using a 40 μs dephasing interval.

from the ^{31}P atom, appears in the long contact time spectrum, Figure 1a.

Figure 2 (parts a–c) depicts spectra of (4-methoxy-1-naphthyl)dimethylphosphinate, **2**. Figure 2c is the conventional $^1H-^{13}C$ CP/MAS ^{13}C NMR spectrum, with assignments. Figure 2b, the DCP spectrum, reveals all aromatic carbons two- and three-bonds distant from the ^{31}P atom. The strong two-bond interaction, $r_{P-C(1)}$ = 0.267 nm, yields the intense resonance at 145 ppm (note the signal discrimination between the two oxygenated aromatic carbons). The X-ray crystal structure of **2** reveals that the phosphorus atom lies roughly in the plane defined by the aromatic carbons and trans to the bridgehead carbon.[4] This conformation maximizes the difference in the three bond internuclear distances, $r_{P-C(2)}$ = 0.313 nm and $r_{P-C(8a)}$ = 0.391 nm, and is reflected in the relative intensities, i.e., cross polarization rates, of the resonances of these centers.[5] One of three aromatic carbons four-bonds removed from the phosphorus atom, C(3), is represented in the spectrum but is too distant (0.454 nm) to account for the observed intensity in the spectrum. The X-ray data reveal an intermolecular $^{31}P-^{13}C(3)$ contact at a comparable internuclear distance, 0.482 nm. In fact, the C(3) intensity in the spectrum is the sum of both inter- and intramolecular contributions.

A DCP signal from the methoxyl carbon of **2** is evident in Figure 2b. This signal, as intense as that from C(8a), arises entirely from a $^{13}C-^{31}P$ intermolecular interaction developed over the uncharacteristically short internuclear distance of 0.387 nm. Hence, weak DCP resonances from intermolecular $^{31}P-^{13}C$ cross polarization are observed and can be comparable in strength to signals which arise from intramolecular interactions across three bonds. With this caveat in mind, the $^1H-^{13}C-^{31}P$ DCP/MAS ^{13}C NMR experiment is principally an intramolecular probe. Figure 2a depicts the application of the dipolar dephasing technique[6] in editing the DCP spectrum of **2**. This spectrum retains solely the nonprotonated C(1) and C(8a) resonances in the aromatic region.

The elucidation of the carbon bonding network around phosphorus centers in solids by $^1H-^{13}C-^{31}P$ DCP/MAS ^{13}C NMR is a new capability that has broad potential for applications in structure determination and reaction site identification in phosphorus derivatized solids.

---

[4] Hagaman, E. W.; Brown, G. M., unpublished results.

[5] For $^{13}C-^{31}P$ cross polarization contact times $\ll T_{CP}$, the ratio of integrated signal intensities and the ratio of rates, $(T_{CP})^{-1}$, are equivalent. In the present case, with contact time $< T_{CP}$, the argument is qualitatively but not rigorously correct.

[6] Opella, S. J.; Frey, M. H. *J. Am. Chem. Soc.* **1979**, *101*, 5854–5856.

Pyridine Ylide Formation by Capture of Phenylchlorocarbene and *tert*-Butylchlorocarbene. Reaction Rates of an Alkylchlorocarbene by Laser Flash Photolysis

James E. Jackson,* N. Soundararajan,* and
Matthew S. Platz*

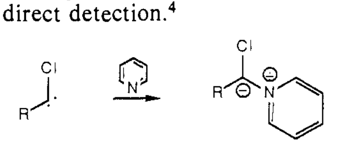
Department of Chemistry, The Ohio State University
120 West 18th Avenue, Columbus, Ohio 43210

Michael T. H. Liu*

Department of Chemistry, University of Prince Edward
Island, Charlottetown, P.E.I., Canada

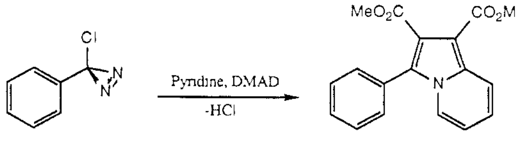
Received March 21, 1988

Fluorenylidene and the naphthylcarbenes are intercepted by acetone or acetonitrile to give ylides which are easily detected by *l*aser *f*lash *p*hotolysis (LFP).[1] Phenylchlorocarbene does not react at a measurable rate with these quenchers to form ylides[2] although its *p*-Cl, *p*-CF_3, and *p*-nitro derivatives react with acetone to form carbonyl ylides.[3] We herein report that phenylchlorocarbene (**2a**) and *tert*-butylchlorocarbene (**2b**) react with pyridine to give ylides **1a,b** which serve as ideal kinetic probes of carbene dynamics. This permits measurements of the first absolute rate constants of an "invisible" alkylchlorocarbene, which lacks a suitable chromophore for its direct detection.[4]



2a: R = Ph
b: R = t-Bu

1



3a

4

---

[1] (a) Barcus, R. L.; Hadel, L. M.; Johnston, L. J.; Platz, M. S.; Savino, T. G.; Scaiano, J. C. *J. Am. Chem. Soc.* **1986**, *108*, 3928. (b) Griller, D.; Hadel, L. M.; Nazran, A. S.; Platz, M. S.; Wong, P. C.; Savino, T. G.; Scaiano, J. C. *J. Am. Chem. Soc.* **1984**, *106*, 2227.

[2] Soundararajan, N.; Jackson, J. E.; Platz, M. S., unpublished research at Ohio State University.

[3] Soundararajan, N.; Jackson, J. E.; Platz, M. S.; Liu, M. T. H. *Tetrahedron Lett.*, in press.

[4] A similar strategy of ylide trapping has been used to monitor the dynamics of methylene. (a) Turro, N. J.; Cha, Y.; Gould, I. R. *J. Am. Chem. Soc.* **1987**, *109*, 2101. (b) Turro, N. J.; Cha, Y.; Gould, I. R.; Padwa, A.; Gasdaska, J. R.; Tomas, M. *J. Org. Chem.* **1985**, *50*, 4417.

0002-7863/88/1510-5595$01.50/0