^{31}P and ^{13}C NMR Spectra of 2-Norbornyl Phosphorus Compounds. Karplus Equations for $^3J_{PC}$ in Several P(III) and P(IV) Derivatives[1]

Louis D. Quin,* Michael J. Gallagher, Glen T. Cunkle, and Donald B. Chesnut

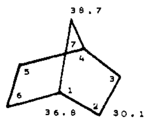
Contribution from the Gross Chemical Laboratory, Duke University, Durham, North Carolina 27706. *Received October 1, 1979*

Abstract: The following phosphorus functions were installed in both exo and endo 2 positions of norbornane: BrClP–, Cl_2P–, $(CH_3)_2P$–, $(CH_3O)_2P$–, $(CH_3)_2P(O)$–, $(CH_3)_2P(S)$–, $(CH_3O)_2P(O)$–, and $(CH_3)_3P^+$–. For the first four, δ ^{31}P values for exo were upfield of those for endo, while the reverse held for the second four. The ordering of $\Delta\delta$ ^{31}P was the same as seen for five of these substituents when equatorial vs. axial on cyclohexane, suggesting a common origin for an effect which must act in opposition to the shielding of steric compression. ^{13}C NMR spectra of exo–endo mixtures were interpreted with the aid of deuterium labeling at C-3 and C-7, and by obtaining spectra at two different frequencies to distinguish coupled signals. $^3J_{PC}$ values for these compounds as well as for *tert*-butylcyclohexyl and 7-norbornyl derivatives allowed least-squares analysis of the dependence on dihedral angle, giving Karplus equations of two distinct types. For P(IV) derivatives, a reasonably symmetrical curve with a minimum near 82–88° was obtained. However, for all P(III) forms, curves of unusual skewed shape were obtained, with ^3J values near $\phi = 0°$ about two to three times those near $\phi = 180°$, and with minima near 105–106°. Best fits of the data required a change in coupling sign near the minima.

Introduction

Because motion about the bonds of the norbornane ring system is limited to a form of pseudorotation[2] where torsion angles in extreme forms do not exceed about 14°, the system is quite useful for the assessment of steric influences on various properties. Among phosphorus compounds, we have already made a series of 7-substituted norbornane and norbornene derivatives and found them of considerable value, first[3] in assessing nonbonded interactions that influence ^{31}P NMR shifts, and also[4] in exploring further the possible control of three-bond ^{31}P–^{13}C coupling by dihedral angle relationships.

In our continuing study of both properties of phosphorus compounds, we have prepared a series of 2-norbornyl derivatives with various phosphorus functions in either the exo or endo positions, with the expectation that new information on ^{31}P shift effects and ^{31}P–^{13}C couplings would result. With regard to the former effect, these two positions offer quite different environments, with steric crowding being provided in the exo by the γ-oriented C-7 and in the endo by C-6. Such crowding effects are well known to produce marked shielding of the ^{13}C nuclei involved, although the exact nature of the interaction remains uncertain.[5] The chemical-shift data[6] for the 2-methyl isomers **2** and **3**, when compared to norbornane (**1**), clearly reveal these effects; the more upfield location of the CH_3 signal for **3** is strongly suggestive of greater steric compression in the endo position, although study of ground-state differences in geometries and steric relations between exo, endo isomers is still in progress[7] and in need of firm experimental measurement of structural parameters. As part of our treatment[3,8] of ^{31}P NMR effects, we view steric crowding of phosphorus by γ carbons to cause the same upfield shift as seen for ^{13}C signals, and on this basis a phosphorus atom in the endo-2-norbornyl position would be predicted to have a signal upfield relative to the exo isomer. However, we have presented evidence for the presence of yet another influence that can be exerted on ^{31}P in certain cyclic systems. Thus, in rigid cyclohexanes, crowding is greater in the axial than in the equatorial position; while some phosphorus functions (H_2P–, Me_2P–) are more shielded when in the axial position, others (Cl_2P–, $(MeO)_2P$–, $Me_2P(S)$–, $Me_2P(O)$–) are more shielded in the less crowded equatorial position.[9] Substituents at the two 2-norbornyl positions have different steric environments than are found at the cyclohexyl positions, and present new opportunities to probe for the structural effect that can cause unexpectedly low-field signals.



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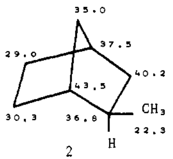

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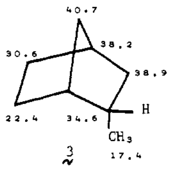

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Dihedral angles associating 2-norbornyl substituents with the ring carbons vary greatly from the exo to the endo isomer. An exo 2 substituent is related to C-6 by a dihedral angle that could approach 180°, but to C-7 by less than 90°. An endo substituent has a dihedral angle close to 40° for C-6 and to 150° for C-7. Both substituents have values around 90° for C-4. Therefore, much new coupling information can be expected from a study of various 2-norbornyl phosphorus compounds. Some P(IV) functions (e.g., phosphine oxide[10] and phosphonate[11]) are known to have $^3J_{PC}$ described by a Karplus-type relationship and have coupling minima near $\phi = 90°$, while P(III) functions (Cl_2P– and Me_2P–), only recently considered,[4] were reported as appearing not to have such a minimum. However, very few data were available for the latter type. The 2-norbornyl system should provide coupling information at critical ϕ values that allow further exploration of the nature of the relation for both types of functions.

Synthesis of 2-Norbornyl Phosphorus Compounds

As outlined in Scheme I, the starting phosphorus compound for the entire series of 2-norbornyl derivatives was the phosphonous dichloride **4**. 2-Norbornylmagnesium chloride reacted smoothly with phosphorus trichloride to provide the expected[9] mixture with a preponderance (2:1) of the exo over the endo isomer. As will be discussed subsequently, their structures were confirmed by ^{13}C NMR spectroscopy, based primarily on well-known steric effects in norbornanes acting at C-6 and C-7. It is frequently necessary in alkylation of PCl_3 to employ the less reactive organocadmium reagent to prevent multiple alkylation, but this proved unnecessary in this case. The exo–endo mixture was not appreciably separated by fractional distillation and was used directly for other syntheses. When 2-norbornylmagnesium bromide was reacted with PCl_3, the major product was the phosphonous bromochloride (**11**) resulting from halogen exchange. It was easily separated from the lower boiling dichloride (**4**) by fractional distillation. These

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Table I. ^{31}P NMR Shifts[a] of the 2-Norbornyl Phosphorus Compounds Prepared and of Some Comparable 4-*tert*-Butylcyclohexyl Derivatives[b]

	2-norbornyl			4-*tert*-butylcyclohexyl		
	endo	exo	Δδ	axial	equatorial	Δδ
Cl_2P	+196.8	+187.5	−9.3	+208.9	+194.6	−14.3
ClBrP	+191.3	+183.9	−7.4			
$(MeO)_2P$	+192.4	+185.3	−7.1	+192.6	+190.0	−2.6
$(MeO)_2PO$	+36.8	+35.6	−1.2			
$Me_3P^+(I^-)$[c]	+29.5	+30.1	+0.6	+30.8	+29.6	−1.2
Me_2PO	+44.5	+45.6	+1.2			
Me_2PS	+40.2	+42.9	+2.7	+43.3	+42.5	−0.8
Me_2P	−47.4	−43.2	+4.2	−54.8	−42.5	+12.3

[a] Positive signs are downfield of H_3PO_4, negative upfield; $CDCl_3$ was used as solvent except where noted. [b] Data taken from ref 9. [c] D_2O/CF_3COOH solvent.

products contained rather small amounts (5–10%) of the endo isomers.

Methylation of the 2:1 isomer mixture of the phosphonous dichloride (**4a,b**) was best accomplished by addition *to it* of methylmagnesium bromide; the more common reverse procedure gave negligible yields. The resulting phosphine mixture (**5a,b**) was then readily converted to the phosphine oxide (**6a,b**), phosphine sulfide (**7a,b**), and phosphonium salt (**8a,b**) by conventional procedures. In all products, the ratio of exo to endo changed only slightly from the starting 2:1 value. The ratio was also maintained when a deficiency (67%) of methyl iodide was used in the quaternization of the phosphine mixture, implying that the reaction proceeded with rather similar rates for each isomer. Quaternization of the corresponding amine has recently[7a] been shown to proceed about 20 times faster with the exo isomer.

Ester derivatives were prepared by reaction of the 2:1 isomer mixture of the phosphonous dichloride with methanol and triethylamine; the resulting phosphonite (**9a,b**) was then cleanly oxidized with *m*-chloroperbenzoic acid to the phosphonate (**10a,b**). Ester **10a** is the only member of the series to have been reported previously,[12] having been derived from norbornene by peroxide-catalyzed reaction with dimethyl phosphonate. Spectral properties matched well those that were reported. Again there was little departure from the 2:1 isomer ratio.

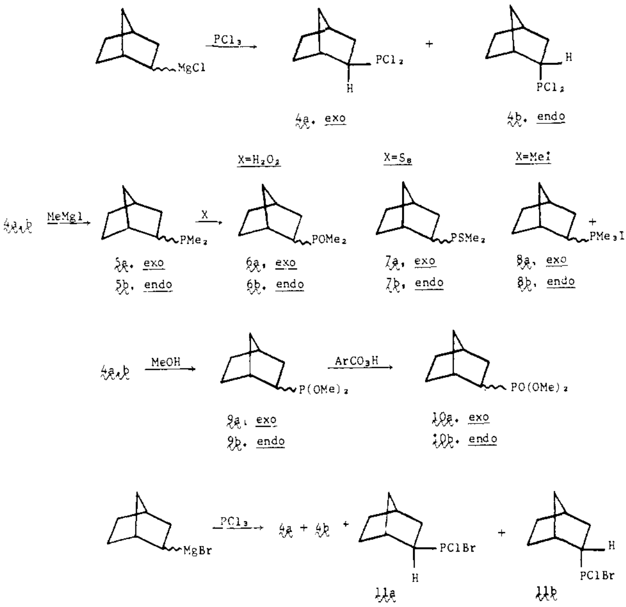
Pure samples (by ^{13}C NMR) of the exo isomers of the phosphine (**5a**) and its oxide (**6a**), sulfide (**7a**), and methiodide (**8a**) were obtained by using the sample of *exo*-2-norbornylphosphonous dichloride (**4a**) prepared by fractional distillation of the **4a**–**11** mixture.

To aid in the assignment of ^{13}C NMR signals, deuterio derivatives of the above compounds were also prepared. This was accomplished by using the mixture of *exo*-3-deuterio-*exo*-2-chloronorbornane (**12**) and *syn*-7-deuterio-*exo*-2-chloronorbornane (**13**) that results from addition of DCl to norbornene.[13] By ^{13}C NMR, the product was a nearly 1:1 mixture of isomers; other techniques[13] suggest a product mixture of 60% **12** and 34% **13**, along with 6% of *exo*-5-deuterio-*exo*-2-norbornyl chloride, formed under similar conditions. The 1:1 mixture behaved spectroscopically as a single compound with both C-3 and C-7 containing 75% H–25% D, since all other C atoms gave identical chemical shifts. The presence of deuterium also reduces the C-3 and C-7 signals in intensity by the partial loss of nuclear Overhauser enhancement. The new set of 1:1:1 signals from D–C coupling was of low intensity and not always visible. The **12**–**13** mixture was used directly in the Grignard reaction to prepare the deuterated form of **4a,b** and then all other derivatives shown in Scheme I.

^{31}P NMR Spectra

Data for the various 2-norbornyl compounds are presented in Table I. Mixtures of exo and endo isomers were used in the determinations, but the greater intensity (2:1) of the former signal always provided unambiguous assignment of the two.

Scheme I



The data present the same challenge of interpretation as was encountered in the cyclohexane system; for some substituents (Me_2P–, $Me_2P(O)$–, $Me_2P(S)$–, Me_3P^+–), the greater crowding of the endo position causes the signal for these isomers to appear upfield of that of the exo isomers, but for others (Cl_2P–, ClBrP–, $(MeO)_2P$–, $(MeO)_2PO$–) the less crowded isomers are those that resonate in the upfield direction. Clearly a second nonbonded interaction or structural influence is present whose magnitude is dependent upon the nature of the phosphorus function. It either acts to cause enhanced shielding in the exo isomers or deshielding in the endo isomers, in the latter case in opposition to the shielding of steric compression. The notion of this interaction must depend on subtle molecular differences related to parameters such as bond and torsion angles, bond lengths, etc. For the rigid cyclohexane derivatives, an attempt to account for the second effect by an analysis of the structural differences between axial and equatorial isomers has led[3] to two empirical suggestions, both implicating the phosphorus atom and a C–H bond in the β position (C-2,6) to phosphorus: (1) Moving the P atom from the axial to the equatorial position sacrifices two β-CH bonds anti to P; if this structural feature had been involved in a deshielding of axial P, then its loss would account for the shielding effect noted for some substituents as they are placed in the equatorial position. (2) There is an increase from two to four gauche β-CH bonds on moving from axial to equatorial; if closer proximity (smaller average torsion angles) to these bonds is associated with increased shielding, then the upfield shift of the equatorial po-

Table II. ^{13}C NMR Data for 2-Norbornanes with P(IV) Substituents[a]

C	-$PO(OMe)_2$[b] exo	-$PO(OMe)_2$[b] endo	-$POMe_2$[b] exo	-$POMe_2$[b] endo	-$PSMe_2$[b] exo	-$PSMe_2$[b] endo	-P^+Me_3[c] exo	-P^+Me_3[c] exo[d]	-P^+Me_3[c] endo[d]
1	38.1 (s)	38.9 (1.8)	37.7 (3.7)	39.1 (s)	38.4 (s)	40.0 (1.9)	38.1 (s)	40.8 (s)	e
2	37.8 (143.4)	f	42.8 (71.2)	41.8 (75.0)	44.5 (54.0)	42.9 (56.4)	35.8 (50.6)	39.1 (50.6)	g
3	31.9 (4.5)	30.9 (s)	31.3 (3.4)	29.7 (s)	32.4 (3.7)	30.5 (s)	32.1 (4.8)	34.8 (4.8)	33.6 (s)
4	36.3 (4.1)	37.2 (2.8)	36.3 (2.3)	f	36.4 (3.7)	37.5 (5.5)	36.4 (3.2)	39.4 (3.6)	f
5	28.5 (s)	29.2 (s)	28.4 (s)	29.3 (s)	28.4 (s)	28.9 (s)	27.4 (s)	30.0 (s)	31.5 (5)
6	31.8 (18.5)	25.4 (5.5)	32.1 (14.3)	25.1 (5.1)	32.4 (14.3)	24.3 (6.5)	31.9 (14.0)	34.8 (14.7)	28.4 (7.1)
7	37.1 (s)	40.7 (19.3)	37.3 (s)	41.4 (14.4)	36.9 (s)	41.9 (12.9)	37.7 (s)	40.4 (s)	42.9 (15.3)
CH_3	52.5 (5.5)	52.4 (7)	15.2 (67.4)	17.1 (68.9)	20.0 (54.3)	22.2 (56.0)	8.1 (54.3)	9.6 (55.4)	11.2 (55.2)
		51.7 (8)	14.7 (66.8)	16.4 (69.0)	19.7 (53.7)	20.9 (56.0)			

[a] Chemical shifts downfield from $Me_4Si = 0$. Assignments that are underlined were confirmed at 15.0 MHz with deuterated derivatives. Values in parentheses are $^{31}P-^{13}C$ coupling constants in hertz. Solvent was $CDCl_3$ excepted as noted. [b] Data reported were obtained at 67.89 MHz; spectra were also run at 15.0 MHz. [c] Obtained at 15.0 MHz only. [d] Solvent: $CF_3COOH-D_2O$. [e] Upfield half only is visible (40.1). [f] Not clearly observed. [g] Upfield half only is visible (37.1).

Table III. ^{13}C NMR Data for 2-Norbornanes with P(III) Substituents[a]

C	-PCl_2[b] exo	-PCl_2[b] endo	-PMe_2[b,c] exo	-PMe_2[b,c] endo	-$PClBr$[d] exo	-$PClBr$[d] endo	-$P(OMe)_2$[d,e] exo	-$P(OMe)_2$[d,e] endo
1	38.5 (17.3)	39.4 (12.3)	38.2 (14.8)	38.0 (8.5)	39.7 (17.6)	f	g	h
2	54.5 (46.5)	53.4 (44.0)	44.2 (8.5)	43.3 (6.3)	53.1 (50.6)	51.9 (48.2)	44.3 (19.5)	42.7 (16.5)
3	33.1 (14.8)	33.3 (28.0)[i]	33.7 (11.0)	33.8 (18.3)[i]	35.4 (14.7)	f	30.4 (13.5)	f
4	j	f	35.7 (3.5)	f	37.1 (1.2)[k]	f	g	g
5	28.4 (s)	29.5 (s)	28.2 (s)	28.9 (s)	28.3 (1.2)	29.7 (s)	29.5 (s)	29.6 (s)
6	31.2 (7.5)	24.8 (28.0)	30.7 (6.3)	23.9 (22.8)	32.2 (10.2)	24.1 (26.7)	31.5 (7.5)	25.8 (24.0)
7	j	40.5 (3.5)	36.0 (2.3)	39.5 (3.5)	37.1 (9.2)[k]	40.6 (3.6)	g	40.7 (3.0)

[a] Chemical shifts downfield from $Me_4Si = 0$. Assignments that are underlined were confirmed at 15.0 MHz with deuterated derivatives. Values in parentheses are $^{31}P-^{13}C$ coupling constants in hertz. Solvent: $CDCl_3$. [b] Data reported were obtained at 25.03 MHz; spectra were also run at 15.0 MHz. [c] Exo CH_3: 10.7 (13.3) and 13.7 ppm (14.8). Endo CH_3: 12.0 (12.5) with other doublet better resolved at 15.0 MHz, 11.9 (11.6) and 12.8 ppm (11.6). [d] Obtained at 15.0 MHz only. [e] Unresolved signals for OCH_3 at 53.0–54.4 ppm. [f] Not observed. [g] Present in unresolved cluster at 36.8–38.0 ppm. [h] Downfield half at 38.7 ppm; upfield half overlapped. [i] Upfield half not visible; assumed to overlap with upfield half of exo C-3. [j] C-4 and C-7 better resolved at 15.0 MHz, giving C-4 37.0 (s), C-7 37.0 ppm (4.7). [k] Tentative assignment.

sition is explained. If either of these explanations has any validity, then a counterpart geometrical situation might be sought in the 2-norbornyl system that would explain the differing ^{31}P shift effects at the exo and endo positions. Indeed, there is such a similarity; while there is no anti C–H bond to consider in this system, there is a pronounced difference in the torsion angle relating the β-CH (at C-1) to P in the two isomers. For the exo isomer, this angle is only 39.0°, a value calculated[14] from X-ray structural data recently published[15] for *exo-N*-(2-norbornyl)benzamide, while for the endo hydrogen of this compound the value is 84.2°. We are therefore led to propose that the upfield shifts sometimes seen for exo substituents are possibly the result of greater proximity to this β-CH bond at C-1, just as relatively upfield shifts sometimes seen for equatorial cyclohexane substituents may result from gauche CH bonds. Considerable work, both experimental and theoretical, is required to show if this purely empirical observation has any value in the explanation of a very peculiar NMR effect.

A particular phosphorus functional group will have its own tendency to respond to the two chemical-shift effects. Our work (see $\Delta\delta$ values in Table I) so far suggests that the effect of steric compression consistently dominates for Me_2P– while the "second" effect strongly dominates for Cl_2P–. For some other groups ($Me_2P(S)$–, Me_3P^+–), the effects are more balanced, and smaller differences exist between isomers. Indeed, in these cases the balance can lie on either side, as is seen in, e.g., the $Me_2P(S)$– group responding more to steric compression in the 2-norbornyl system (exo +42.9, endo +40.2) and more to the "second" effect in the cyclohexane system (axial +43.3, equatorial +42.5). Differences of these magnitudes are rather trivial, however, and do not by themselves deserve much attention.

Regardless of the origin of the "second effect" acting on ^{31}P NMR shifts, it has to be accepted from our results with two different cyclic systems as being quite real and of importance in the development of a comprehensive theory of structure–spectra relations. The presence of the effect in other types of compounds will be sought in future work.

^{13}C NMR Spectra

Since the materials available for this study were mixtures of the endo and exo isomers, and most of the carbons are spin coupled to ^{31}P, the ^{13}C NMR spectra were quite complex and required great care in interpretation. The difference in concentration of the isomers allows easy recognition of their particular signals in the array; major difficulties arose from partial or complete overlapping of signals at the routinely used 15.0 MHz. In several cases this problem was solved by operation at the higher frequencies of 25.03 or 67.89 MHz; comparison of two spectra at the different frequencies for a given mixture usually made it possible to obtain unambiguous assignments. The data for only the higher frequencies, giving the best resolution, are provided in Table II for the P(IV) compounds and in Table III for the P(III) compounds; values generally differed insignificantly from those at lower field. Another technique useful in the recognition of certain signals is that of specific deuterium labeling. As discussed in the Synthesis section, deuterium can be placed at each of the 3 or 7 positions, and these carbons become recognizable from the diminution of the resonance signal remaining for the C–H form. This technique was especially useful for the exo series, since these signals were always the most intense and any diminution by the D effect was quite obvious. The weaker endo signals were not as noticeably affected, unless the signal was a more intense singlet. In Tables II and III are noted those signals that gave obvious intensity reduction when the deuterio analogues were separately examined. The distinction of C-3 is especially important, since the only other ^{13}C NMR study[11a] of a 2-norbornyl phosphorus compound (the exo phosphonate) made an assignment to C-3 that we initially questioned and will subsequently show to require revision.

Aiding in the recognition of signals also is the magnitude of the ^{31}P–^{13}C coupling. From a study of alkyl derivatives of a variety of phosphorus functional groups,[16] parameters were available for one- and two-bond couplings, and for the most part the signal assignments in the 2-norbornyl series resulted in comparable values. Three-bond coupling is under strong steric control, however, and can vary widely. This important point is discussed in the next section; following recognition of the relations for the various phosphorus functions it then becomes possible to use ^3J to confirm signal assignments.

The body of literature on other types of 2-norbornyl derivatives[6,17] provides an excellent framework for discussing relative effects of phosphorus functions at particular carbons; some interesting peculiarities associated with these functionalities occurred, as is evident in the following summary of assignments.

C-1 and C-4. These bridgehead carbons in 2-norbornyl derivatives are generally easily distinguishable by the deshielding β effect of the 2 substituent, causing C-1 to fall several parts per million downfield of C-4. This effect was maintained in all of the phosphorus compounds, even though the β effects of some of the functionalities when located on alkyl chains are known[16] to be quite small (and sometimes even negative). Coupling phenomena were especially helpful in the P(III) series; ^2J values are generally large (10–20 Hz) and should be similar at both C-1 and C-3. Since the latter is firmly established with the deuterated compounds, the assignment of C-1 becomes unambiguous. C-4, on the other hand, has small three-bond coupling (1–4 Hz), since its dihedral angle relation to ^{31}P in either the exo or endo position places it near the minimum in the Karplus plot for P(III) derivatives (vide infra). For P(IV) compounds, two-bond coupling to C-1 and C-3 is small or negligible,[16] in contrast to the P(III) compounds, and values for the norbornyl compounds all fell in the range 0–2 Hz. This makes recognition of C-4 less obvious, since its coupling is also small (3–4 Hz). However, since definite β shielding occurred at the firmly established C-3, and since C-1 is similarly situated, the usual assignment holds of C-1 being more downfield than C-4.

C-2. Each phosphorus function has its own α effect and $^1J_{PC}$ value,[16] and these make recognition of C-2 a simple matter. Without exception, the more crowded endo isomer has the more upfield signal, as is true for nonphosphorus substituents.[6,17] In all of the P(III) compounds the exo isomer had a slightly larger value for $^1J_{PC}$ than did the endo isomer, but this relation is not present consistently for the P(IV) compounds.

C-3. This carbon, appearing at δ 30.1 in norbornane,[6] was found in the δ 29.5–35.4 range in the phosphorus derivatives, and had the expected[16] small $^2J_{PC}$ values for P(IV) and large $^2J_{PC}$ values for P(III). In several cases, it was unambiguously recognized by examining the deuterated compounds. The P(IV) derivatives all had C-3 at a more downfield position (1–2 ppm) in the exo isomer, as is true for other types of norbornane derivatives, but curiously in the P(III) series this steric influence on the β effect was absent and the chemical shifts were nearly identical for an isomer pair.

C-5. 2-Substituents have only weak effects at C-5, which generally has a chemical shift of 29–30 ppm.[6,17] The phosphorus substituents were not exceptional, providing shifts of 27.4–29.7. Exo isomers have C-5 at slightly lower field than endo, and this generality was also observed. Most of the C-5 signals were singlets, since four bonds separate this atom from ^{31}P. However, *exo*-PClBr did show weak (1–2 Hz) coupling.

C-6. The antiperiplanar relation of C-6 to an exo 2 substituent has been utilized by Eliel et al.[18] in their study of the general shielding that accompanies this atomic array. The shielding is pronounced only when the substituent is a second-row element, however, and we have shown elsewhere that equatorial phosphorus substituents on the cyclohexane ring do exhibit the effect at C-3,5, but by the expected modest amount.[19] However, our 2-norbornyl derivatives, without exception, fail to show the effect, and the chemical shifts at C-6 are all downfield by 1–2 ppm of the value for norbornane itself. The endo 2 substituents, on the other hand, cause a dramatic upfield shift (routinely about 8 ppm) of C-6 because of the γ_{gauche} orientation. Striking differences occurred in the three-bond coupling between the P(III) and P(IV) compounds; for the former, $^3J_{PC}$ was larger for the endo isomers and small for the exo isomers, while just the opposite was observed for the P(IV) series. The explanation will be seen to lie in the remarkably different shapes of the Karplus curves for the two classes of functionalities (vide infra).

C-7. Chemical shifts for C-7 were generally in the range found for other 2-norbornyl compounds. In the exo series, C-7 is shifted upfield from the norbornane value of δ 38.7 by about 2–3 ppm owing to the steric crowding, and the phosphorus substituents agreed with this generality. Similarly, endo substitution generally causes downfield shifts of C-7 by 2–3 ppm, which were reproduced in the phosphorus compounds. Again the steric control of three-bond P–C coupling led to strikingly different effects at C-7; for P(IV), singlets were observed for exo substitution and strongly coupled doublets (13–19 Hz) for endo substitution, while for P(III) there was generally only weak coupling from either location of the P substituent.

CH$_3$. Since the 2 position is chiral, two methyl groups attached to a phosphorus atom are nonequivalent, and for the functions Me$_2$P–, Me$_2$P(O)–, and Me$_2$P(S)– separate doublets are seen for each methyl of both exo and endo isomers. The effect is also present for the two methoxy carbons of the (MeO)$_2$P(O)– and (MeO)$_2$P– functions, although the peak separation is much smaller and a distinct four-line pattern was only observable for *endo*-(MeO)$_2$P(O). Separate ^{1}H NMR signals were also observed for the diastereotopic methyls.

The phosphonate spectrum requires special consideration, for our interpretation differs considerably from that of Buchanan and Benezra.[11a] Thus, we invert the C-3 and C-5 assignments, but we do so with the confidence in our C-3 assignment provided by the deuterated derivative. Furthermore, the revision places the chemical shift of C-5 in line with all other C-5 values reported for 2-norbornanes, and reduces its four-bond ^{31}P coupling to the more reasonable 0–1-Hz range, rather than the 5.9-Hz value required by the previous assignment. We also have reversed the C-1, C-4 assignments; the phosphonate group has a confirmed β-deshielding effect of 1.7 ppm at C-3 and it will therefore also deshield β-oriented C-1 relative to C-4. Our assignment shows the β effect at C-1 to be 1.8 ppm.

Dihedral Angle Control of Vicinal P–C Coupling

Previous workers[11] have noted for phosphonates that there is a definite relation between the magnitude of three-bond ^{31}P–^{13}C coupling ($^3J_{PC}$) and the dihedral angle (ϕ) relating these atoms. From one study[11e] there resulted a Karplus curve showing maxima for J at $\phi = 0$ and 180°, with the usual minimum at $\phi = 90°$ ($J \sim 0$ Hz). Similarly, an apparent Karplus relation exists for $^3J_{PC}$ in phosphine oxides.[10] Our previous studies on rigid cyclohexyl[19] and 7-norbornyl[4] phosphorus compounds had indicated that two other P(IV) functions (Me$_2$P(S)– and Me$_3$P$^+$–) probably had similar Karplus curves, but that some P(III) functions (Cl$_2$P– and Me$_2$P–) either failed to show this relation or had a curve with a minimum quite displaced from the usual 90°. The new 2-norbornyl phosphorus compounds provide an abundance of coupling data

Table IV. Dihedral Angles and Absolute Three-Bond Coupling Constants[a] for Various Phosphorus Functions

ϕ, deg	$PO(OMe)_2$	$P(O)Me_2$	$PSMe_2$	$^{+}PMe_3$	PCl_2	PMe_2	$P(OMe)_2$
40[b]	5.4	6.2	6.6	7.1	26.9	22.7	24.0
57[c]					10.4	10	
67[d]			4	4	9	8	7
86[e]	0	0	0	0	4.7	1.8	
122[f]	3.9	3.1	3.6	3.2	0	4.4	
120[g]			4.8				
150[h]	19.5	13.5	13.4	15.3	3.6	3.6	3.0
164[i]					6.1	7	
167[j]	18.3	14.7	14.6	14.7	8.0	6.6	7.5
174[k]			13	15	11	11	9

[a] For consistency, all values for 2-norbornanes are taken from the 15.0-MHz spectra. [b] C-6 in *endo*-2-norbornanes.[11e] [c] C-2,3 in 7-norbornanes.[18] [d] C-3,5 in *cis*-4-cyclohexanes.[21] [e] C-7 in *exo*-2-norbornanes.[14,15] [f] C-4 in *exo*-2-norbornanes.[14,15] [g] C-4 in *endo*-2-norbornanes.[11e] [h] C-7 in *endo*-2-norbornanes.[11e] [i] C-5,6 in 7-norbornanes.[18] [j] C-6 in *exo*-2-norbornanes.[14,15] [k] C-3,5 in *trans*-4-cyclohexanes.[21]

Table V. Least-Squares Values of the Parameters (Hz) in the Generalized Karplus Equation $^{3}J = A \cos^2 \phi + B \cos \phi + C$

	A	B	C	rms error[a]	$\phi_{\min}$,[b] deg
		A. P(IV) Class			
$PO(OMe)_2$	17.3	−4.7	−0.9	2.1	82
$PO(Me)_2$	14.8	−2.0	−0.7	1.0	86
$PS(Me)_2$	12.6	−1.2	0.8	1.3	87
$P^{+}(Me)_3$	14.3	−1.3	0.5	1.6	88
		B. P(III) Class			
$P(OMe)_2$	27.2	15.2	−3.4	0.5	106
PCl_2	28.5	15.5	−3.4	2.2	106
$P(Me)_2$	26.1	13.9	−3.4	1.4	105

[a] The root-mean-square error between calculated and observed coupling values. [b] The dihedral angle between 0 and 180° at which J has its algebraic minimum. The ^{3}J values for 0° are presumed positive.

for all of these functions, and, if it is assumed that the coupling constants are reasonably independent of strain in the particular carbon framework involved, then these new data along with our earlier data[4,19] allow definition of the Karplus relation for three-bond coupling of these functions. A major difficulty is in the choice of dihedral angles; surprisingly little structural work has been done in the norbornane system, and no ϕ values are published for an atom attached to the 2 position as related to C-4, C-6, or C-7. Previous workers[11a,e] studying $^{3}J_{PC}$ used values derived from molecular models, and we have done this also for the endo system using Prentice-Hall framework models. However, the recently published[15] X-ray analysis of *exo*-*N*-(2-norbornyl)benzamide includes coordinates that allow the calculation[14] of the required dihedral angles. With the exception of C-6, these values agree with those derived from models; C-6 has a smaller ϕ value (164°) than the 180° assumed from models.[11a,e] The smaller value, as will be seen, is more in line with the trend in coupling constants. For 7-norbornyl derivatives, ϕ for C-2 and C-5 were taken from the X-ray data of *anti*-7-norbornenyl *p*-bromobenzoate,[20] in the absence of data for a saturated norbornane. Published X-ray data for *cis*- and *trans*-4-*tert*-butylcyclohexyl *p*-toluenesulfonate allowed calculation[21] of the dihedral angles relating an axial and an equatorial substituent to C-3,5. The various angles used are summarized in Table IV, along with pertinent coupling data.

The phosphorus–carbon vicinal coupling constants may be analyzed in terms of the generalized Karplus relation[22] which relates the coupling constant J to the dihedral angle in the four-atom fragment involved. The phosphorus data were subject to a three-parameter least-squares analysis to give a best fit to the Karplus equation, and the pertinent parameters so derived are exhibited in Table V along with the root-mean-square error which measures the goodness of fit of the data to the Karplus model. The error values and the plotted data indicate a reasonably good fit to the theoretically based functional dependence on the dihedral angle ϕ. In addition, from the least-squares derived equation one may calculate the values of ϕ at which extrema are predicted; extrema are to be found at values of $\phi = 0$ and 180° and in the intervening region at the point $\phi_{\min}$ ($\cos \phi_{\min} = -B/2A$) indicated in Table V.

Karplus plots for proton–proton vicinal couplings usually exhibit minima at 90°. Similar behavior for carbon–carbon vicinal couplings has been exhibited by Marshall and Miiller[23] in a study of aliphatic carboxylic acids in which by a least-squares procedure we estimate $\phi_{\min}$ to be 82°. Heavier atoms show a similar dependence on the dihedral angle, as, for example, the data of Doddrell and co-workers[24] on tin–carbon vicinal couplings where $\phi_{\min}$ is approximately 86°. The data in Table V for the P(IV) compounds are quite in line with these results. The Karplus parameters for these four phosphorus compounds are similar and yield $\phi_{\min}$ values ranging from 82 to 88°. Figure 1 shows the observed data and the least-squares curve for the $PSMe_2$– group as an example of the P(IV) case. For the phosphonate group, our 2-norbornyl values fall reasonably close (0–2 Hz) to the published Karplus curve[11e] based on other types of phosphonates, except that our 150° value was significantly higher than would be expected from this curve (19.5 vs. 13 Hz).

The P(III) compounds, however, represent a different and a new result. In the initial analysis of the Me_2P– compound, the presumption of all positive J values (based on the alternation of sign with intervening atoms suggested by the Hund's rule picture[25]) led to a fit which was adequate but which suggested that with a reinterpretation of the signs of several of the data points a better fit might be obtained. In particular, if the signs of the coupling constants for the 86 and 122° points are made negative relative to the other values, a much better fit of the Karplus relation is obtained. Figure 2 illustrates this case, showing the experimental data along with the two least-squares curves calculated for the two different sets of sign choices. Furthermore, the parameters of the fits obtained in this latter case are in close agreement with those of the $(MeO)_2P$– curve where inspection of the data indicates that there is no possible ambiguity of sign choice for that particular group. A similar analysis of the Cl_2P– data suggests that the 86° J value in that compound may also be negative relative to the others; while the goodness of fit as measured by root mean square error values of the two possible curves for this species is essentially the same, the assignment of a negative J value to the 86° point in the Cl_2P– case again yields Karplus parameters which are in virtual agreement with the $(MeO)_2P$– and Me_2P– cases. The resulting similar Karplus parameters for the three examples of the P(III) class suggest strongly that the assignment of relatively negative coupling constants to the 86 and 102° cases is quite reasonable. Indeed, the similarities of the Karplus parameters within each of the two chemically

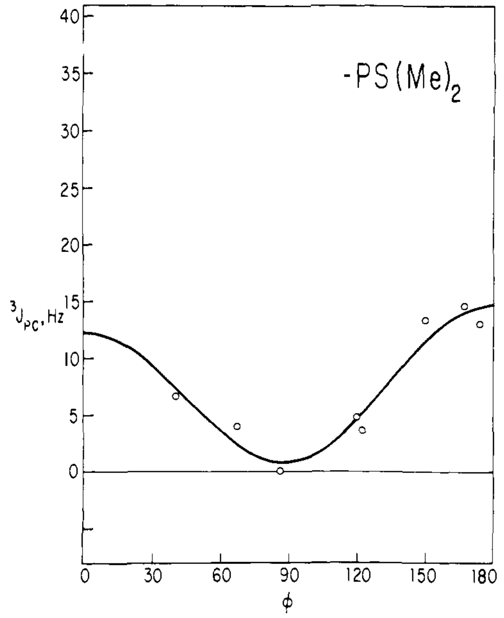


Figure 1. A plot of $^3J_{PC}$ (Hz) for the P(IV) group -PS(Me)$_2$ as a function of the dihedral angle ϕ (deg). The curve represents the least-squares fit to the general Karplus relation based on the experimental data shown.

different classifications of P(IV) and P(III) phosphorus would seem to be physically very plausible. The current interpretation explains what was previously[4] taken to be an apparent lack of a Karplus relation for the Cl_2P- compounds; with the unusual shape and minimum, the relation does not become apparent with only a few data points.

Negative three-bond coupling constants are not theoretically forbidden, although they do appear to be rare in the current literature. In addition, for the P(III) class here the dihedral angle of approximately 106° at which the coupling constant has its minimum algebraic value is a new observation. One can note from the generalized Karplus function that ϕ_{min} will be less than 90° if the quantity $B/2A$ is negative and of absolute value less than unity, and will be greater than 90° if $B/2A$ is positive and less than one. In the former case $J(180°) > J(0°)$ is predicted while in the latter $J(0°) > J(180°)$ is expected. The experimental data presented here exhibit the appropriate but different behavior in each separate class (P(III) and P(IV)), lending additional support to our analysis.

The general theoretical expression for the dependence on the dihedral angle of vicinal coupling constants is not simple even in the approximate valence bond treatment due originally to Karplus.[22,26] Reasonable simplifying assumptions reduce the analytical complexity of the theoretical expression, but there remains the need to determine the angular dependence of a series of nontrivial quantum mechanical exchange integrals. Hecht[27] gives explicit expressions for the necessary integrals in the case of proton–proton vicinal couplings which illustrate the general dependence upon cos ϕ and its square. Theoretical evaluation of these integrals by Hecht, however, leads to a vicinal coupling for this case which shows *no* minimum between 0 and 180° as opposed to the situation realized experimentally.

The chemical picture is also nontrivial. Not only does it appear important as to class of phosphorus being considered (P(III) or P(IV)), but also additional stereochemical effects would appear to be present. Sorenson and Jakobson[28] report that the proximity and orientation of the phosphorus lone pair electrons very strongly influence three-bond ^{13}C–^{31}P couplings in 1,6-diphosphatriptycene at different carbons which have the same ϕ value. In studies on nitrogen–proton couplings over two and three bonds, Wasylishen and Schaefer[29] (see also the review by Wasylishen[30]) suggest that observed phosphorus–proton coupling constants in P(III) phosphorus compounds are dependent on lone-pair orientation in a manner analogous to the corresponding nitrogen–proton coupling case. The theoretical INDO calculations of $^3J_{NH}$ in ethylamine by Wasylishen and Schaefer seem pertinent and are most interesting in that the HCCN dihedral angle dependence in what they designate as the eclipsed conformation (eclipsed amino protons and adjacent methylene protons) resembles the normal vicinal coupling as exhibited in this work by the results of the P(IV) class, while the staggered conformer (lone pair trans to the methyl group) strongly resembles the results of the P(III) class, including the shift of algebraic minimum to about 100° from about 80° and a change of sign near the minimum. The protonated species ($H_3N^+CH_2CH_3$) results resemble those of the P(IV) class for both conformations. Study of molecular models of the phosphorus compounds used in the current investigation suggests that in all cases steric effects would dictate a preference for the gauche arrangement of the lone pair relative to the carbon which is the next nearest neighbor to the phosphorus, an arrangement closer to the eclipsed arrangement of Wasylishen and Schaefer than to the staggered arrangement. Unfortunately, no calculations were carried out for the gauche conformation, this conformation along with the trans arrangement being expected to be energetically preferred. A crucial question that needs resolution is whether or not the theoretical results of Wasylishen and Schaefer are due primarily to the lone-pair orientation or to a staggered vs. eclipsed effect; until this matter is resolved it will be difficult to make a definitive statement on the relationship between their calculated results and our experimental ones. Additional theoretical calculations in this area are clearly indicated. Despite the many complexities, however, the analysis of the present data would seem to indicate clearly that the vicinal ^{31}P–^{13}C spin–spin couplings in the P(III) class of phosphorus compounds represent a new situation.

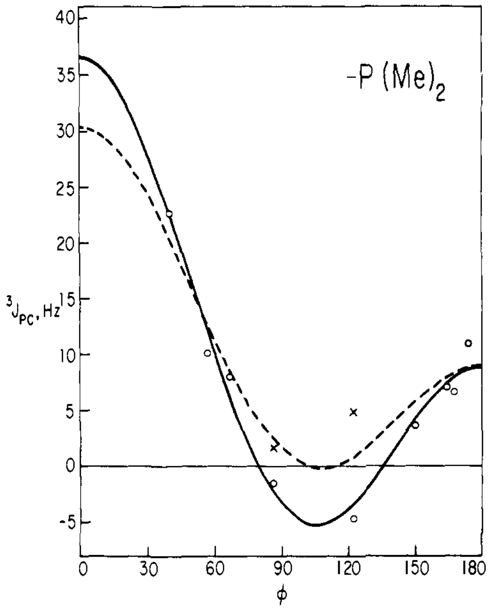


Figure 2. A plot of $^3J_{PC}$ (Hz) for the P(III) group -P(Me)$_2$ as a function of the dihedral angle ϕ (deg). The solid curve represents the least-squares fit to the general Karplus relation based on the experimental data (open circles) in which the 86 and 122° J values are presumed negative, while the dashed curve is a similar fit using positive values for J for the 86 and 122° data (shown as crosses).

Conformational Control of $^2J_{PC}$ in P(III) Compounds

The endo P(III) compounds show a sensitivity in their two-bond coupling to ^{31}P that appears related to the population of the rotameric forms about the P–C bond. It is known from several studies of both heterocyclic[31,32] and acyclic[33–36] phosphines that ^2J is controlled by the dihedral angle relating the lone-pair orbital on P to β carbons, with a small angle associated with large coupling. The steric crowding in the endo 2 position may well cause the preferred population of rotameric forms such as **12**, with P substituents projecting away from the ring framework. Such forms could place the lone-pair orbital closer to C-3 than to C-1, causing $^2J_{PC\text{-}3} > {}^2J_{PC\text{-}1}$. Data for both -PMe$_2$ (C$_1$, 8.5; C-3, 18.3 Hz) and -PCl$_2$ (C$_1$, 12.3; C-3, 28.0 Hz but tentative owing to peak overlap) show ^2J differences suggesting the operation of this effect. The effect is known to be absent or much less pronounced in P(IV) compounds, supporting the concept of a role for the lone pair, and this is true also in the 2-norbornyl series. The spectra for the less congested exo P(III) compounds do not show the large ^2J differences at C-1 and C-3, and both values fall between those seen for the endo series. A similar preference for a less crowded rotameric form has been postulated[32] in a phosphorinane to explain the larger ^2J value for methyl of an axial *P*-ethyl group than for an equatorial group. Most acyclic phosphines and phosphonous dichlorides show only average $^2J_{PC}$ values at room temperature.[33–36]

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Conclusions

The rigid 2-norbornyl framework has provided the expected new insight into steric influences that operate on both ^{13}C and ^{31}P NMR spectral properties. Of special importance is the clarification provided to the nature of the dihedral angle control of three-bond ^{13}C–^{31}P coupling. Combined with data from other rigid systems, the new information has definitely established that, for P(IV) functions in general, a rather ordinary plot of ^3J vs. ϕ is obtained, but that for P(III) functions the ^3J maxima at 0 and 180° are greatly different (about 35 and 10 Hz, respectively). Furthermore, the minimum, with an inversion of coupling sign, occurs at about 15° higher than the usual value of 90°. Knowledge of these relations can be useful in establishing stereochemical features of new substances. The origin of the unique shape of the P(III) plot is tentatively associated with the presence of the lone pair on phosphorus, through the adoption of preferred conformations. If correct, this view would require considerable caution in applying the Karplus plots from the present study to new systems where different conformations may be preferred.

Two-bond ^{13}C–^{31}P coupling of P(III) forms is also known to be under steric control, and the 2-norbornyl system has provided new examples of this phenomenon. Of particular importance is the observation that in the more crowded endo isomer the phosphorus substituent can preferentially populate a conformation that causes pronounced differences in $^2J_{PC}$ to two different pathways.

Less well understood at present, but of considerable value for empirically based interpretations, is the confirmation provided by the 2-norbornyl system of a definite conformational influence other than that of steric compression that is felt on ^{31}P chemical shifts. The concept of upfield shifting resulting from compressing ^{31}P with γ-related carbons is valid only for nonpolar P(III) functions such as P(CH$_3$)$_2$ or PH$_2$. Polar P(III) functions (especially PCl$_2$ and P(OR)$_2$), and to a smaller extent P(IV) groups, are more influenced by a totally different effect that acts in the opposite direction. The cases so far known can be correlated with an increase in number or proximity of ^{31}P to β-CH bonds, but this relation is strictly empirical at this time. Regardless of origin, the effect is real and demands care in the use of steric explanations for the order of ^{31}P NMR shifts in related structures.

Experimental Section

General. Melting points were taken on a Mel-Temp apparatus and are corrected; boiling points are uncorrected. ^{13}C NMR FT ^{1}H-decoupled spectra were obtained at 15 MHz with a JEOL FX-60 spectrometer, at 25.03 MHz with a Bruker HFX-10 spectrometer, and at 67.89 MHz with the Bruker HX-270 spectrometer of the Australian National NMR Centre. ^{31}P NMR spectra (FT, ^{1}H decoupled) were obtained on a Bruker HFX-10 system at 36.43 MHz; 85% H$_3$PO$_4$ was used as external reference, with positive signs downfield, negative upfield. *exo*-2-Bromonorbornane was purchased from Aldrich Chemical Co. 2-Chloronorbornane was prepared by adding anhydrous HCl to norbornene;[32] the same procedure was used for the reaction with DCl to provide a 1:1 mixture[13] of *exo*-3-deuterio-*exo*-2-chloronorbornane and *syn*-7-deuterio-*exo*-2-chloronorbornane. Elemental analyses were performed by MHW Laboratories, Phoenix, Ariz. Mass spectral analyses were conducted at the Mass Spectrometry Research Center, Research Triangle Institute of North Carolina. All reactions and handling of P(III) compounds were conducted under nitrogen.

Synthesis and Separation of a Mixture of *exo*-2-Norbornylphosphonous Dichloride (4a) and *exo*-2-Norbornylphosphonous Bromide Chloride (11). The Grignard reagent prepared from *exo*-2-bromonorbornane (35 g, 0.20 mol) and magnesium (4.9 g, 0.20 g-atom) in diethyl ether (200 mL) was decanted into a pressure-equalizing dropping funnel and added dropwise to a stirred solution of PCl$_3$ (31 g, 0.23 mol) in the same solvent at −30 to −40 °C. No reaction was apparent initially but a precipitate, white at first but turning yellow, began to form as the temperature was allowed to rise. At −10 °C the dry ice–2-propanol bath was removed and the mixture stirred at ambient temperature for 1 h. The mixture was filtered through Celite and the solvent removed under vacuum to give the crude product as a yellow oil (40.3 g). The mixture was fractionated through a Teflon spinning-band column to give two main fractions: (a) phosphonous dichloride **4a** (6.4 g, 16%, bp 109–119 °C, almost entirely at 115 °C (14 mm)) and (b) phosphonous bromide chloride **11** (15.5 g, 32%, bp 145–147 °C (14 mm)). Identity of the fractions was confirmed by high-resolution mass spectrometry: fraction (a), *m/e* 195.9987 (calcd for C$_7$H$_{11}$PCl$_2$, *m/e* 195.9976); fraction (b), *m/e* 239.9469 (calcd for C$_7$H$_{11}$PBrCl, 239.9471). ^{31}P NMR analysis (Table I) showed that each fraction consisted of about 90–95% exo and 5–10% endo isomers. ^{13}C NMR spectra of **11a,b** are given in Table III.

***exo*- (4a) and *endo*- (4b) 2-Norbornylphosphonous Dichloride.** The Grignard reagent was prepared by adding 38.1 g (0.29 mol) of 2-chloronorbornane in 70 mL of anhydrous ether to 7.1 g (0.29 mol) of magnesium turnings (activated by washing with HCl) in 40 mL of ether. A crystal of iodine was added on occasions where the reaction was slow to start. When all of the magnesium had reacted, the liquid was decanted from a small amount of insolubles and then added dropwise to a solution of 39.8 g (0.29 mol) of phosphorus trichloride in 120 mL of ether. The temperature was maintained at −40 °C during the addition, and then allowed to rise to 25 °C, where it was held for 2 h. The mixture was filtered and the liquid distilled to give 36.8 g (64%) of product at 115–120 °C (22 mm). ^{31}P NMR analysis (Table I) showed the mixture to consist of 67% **4a** and 33% **4b**; for ^{13}C NMR spectra see Table III.

***exo*- (5a) and *endo*- (5b) 2-Norbornyldimethylphosphine.** A 9.1-g sample (0.046 mol) of the 2:1 **4a,b** mixture in 50 mL of anhydrous ether at 0 °C was treated dropwise (syringe) with 31.2 mL (0.094 mol) of commercial 3 M methylmagnesium bromide. The mixture was stirred for 1 h at 0 °C and then 1.5 h at 25 °C, after which it was quenched with a saturated NH$_4$Cl solution and extracted with ether. The organic phase was dried (MgSO$_4$) and evaporated to give 5.2 g (72%) of crude product. By ^{31}P NMR (Table I), the mixture consisted of 63% **5a** and 37% **5b**; for ^{13}C NMR see Table III. The great sensitivity of the product to air oxidation required its immediate use, without purification, for the preparation of various derivatives.

The 95% exo–5% endo mixture of the phosphonous dichlorides was similarly reacted to give a product of nearly isomer-pure **5a**: ^{1}H NMR δ 0.88 and 1.02 (both d, $^2J_{PH}$ = 2 Hz, of equal intensity, diastereotopic CH$_3$ groups).

***exo*- (7a) and *endo*- (7b) 2-Norbornyldimethylphosphine Sulfide.** An isomer mixture was prepared by reacting 1.5 g (9.6 mmol) of the 63%

5a–37% **5b** mixture with 0.3 g (9.6 mmol) of sulfur in 20 mL of benzene. Evaporation of solvent left a white solid that was recrystallized from CH_3OH; ^{31}P NMR analysis (Table I) showed the composition to be 60% **7a** and 40% **7b**. For ^{13}C NMR see Table II.

Anal. Calcd for $C_9H_{17}PS$: C, 57.45; H, 9.04. Found: C, 57.13; H, 9.55.

A pure sample of **7a** was obtained by subjecting the 95% pure sample of phosphine **5a** to the same procedure. Recrystallization from ethyl acetate gave a sample of mp 149–151 °C; ^{1}H NMR δ 1.62 and 1.75 (both d, $^2J_{PH}$ = 13 Hz, equal intensity diastereotopic CH_3).

Anal. Found: C, 57.40; H, 9.40.

***exo*- (6a) and *endo*- (7a) 2-Norbornyldimethylphosphine Oxide.** The 63% **5a**–37% **5b** mixture of phosphines (2.5 g, 16 mmol) in 30 mL of chloroform was shaken vigorously with 30 mL of 5% hydrogen peroxide. The chloroform layer was decanted and combined with chloroform extracts of the aqueous layer. Evaporation left a pale yellow solid mixture of **6a,b**, which was used directly for ^{31}P (Table I) and ^{13}C NMR (Table II). A sample of 95% **5a** was oxidized by exposure to the atmosphere, leaving a solid which, recrystallized from cyclohexane, formed needles: mp 124–125 °C; ^{1}H NMR δ 1.33 and 1.45 (both d, $^2J_{PH}$ = 12 Hz, diastereotopic CH_3).

Anal. Calcd for $C_9H_{17}OP$: C, 62.8; H, 9.9. Found: C, 61.6; H, 10.0.

Exo (9a) and Endo (9b) Isomers of Dimethyl 2-Norbornylphosphonite. The 67% exo (**4a**)–33% endo (**4b**) phosphonous dichloride mixture (10.6 g, 0.054 mol) in 200 mL of ether was dropped into a cold (−10 °C) solution of 3.5 g (0.108 mol) of absolute ethanol and 11.0 g (0.108 mol) of anhydrous triethylamine in 400 mL of ether. The amine salt that precipitated was filtered off, and the filtrate was concentrated and distilled at 62–64 °C (0.6–0.8 mm) to afford 4.3 g (42%) of a 2:1 mixture (^{31}P NMR analysis, Table I) of **9a,b**; for ^{13}C NMR see Table III.

Exo (10a) and Endo (10b) Isomers of Dimethyl 2-Norbornylphosphonate. The 2:1 mixture of phosphonite isomers prepared above (1.8 g, 9.6 mmol) in 15 mL of dry CH_2Cl_2 at 0 °C was treated with a solution of 2.0 g (10 mmol) of *m*-chloroperbenzoic acid in 10 mL of CH_2Cl_2 over a 15-min period. The mixture was stirred for 1 h at 0 °C and then poured into 25 mL of saturated $NaHCO_3$ solution. The CH_2Cl_2 layer was saved, and combined with the CH_2Cl_2 solution from 24-h continuous extraction of the aqueous layer. Evaporation left 2.1 g of an oil contaminated with *m*-chlorobenzoic acid. This was removed by dissolving the product in 5% NaOH and continuously extracting with $CHCl_3$ to recover the phosphonate. After drying ($MgSO_4$) and distillation (Kugelrohr, 110 °C (0.05 mm)) there was obtained 1.2 g (61%) of the isomers **10a,b** (2:1); for ^{31}P NMR see Table I. The ^{13}C NMR spectrum (Table II) contained the major set of signals corresponding well in δ and J_{PC} to values reported previously.[11a]

Exo (8a) and Endo (8b) Isomers of 2-Norbornyltrimethylphosphonium Iodide. The 63% **5a**–37% **5b** phosphine mixture (0.7 g, 4.5 mmol) in 20 mL of benzene was treated with 0.6 g (4.5 mmol) of methyl iodide. The precipitated isomeric salt mixture (54% **5a**, 46% **5b**) was used directly for ^{31}P (Table I) and ^{13}C (Table II) NMR analysis. The salt similarly prepared from 95% **5a** was recrystallized by dissolving it in boiling chloroform containing 1% methanol and adding ethyl acetate to initiate crystallization: mp 275–278 °C; ^{1}H NMR δ 1.84 (d, $^2J_{PH}$ = 14 Hz, CH_3).

Anal. Calcd for $C_{10}H_{20}IP$: C, 40.3; H, 6.7. Found: C, 40.0; H, 6.6.

References and Notes

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