gave the amide, which was crystallized from *n*-hexane to yield the pure product: mp 75–77 °C;[20] MR 0.0.

3β-Benzoyloxy-12,14α-cyclo-12,13-seco-5α-cholest-13(17)-ene (5b). Compound **6b** (500 mg) was added to a mixture of anhydrous 4-toluenesulfonic acid (250 mg) and benzene (125 mL) and refluxed for 5 min. After usual workup the crude residue was chromatographed on silica gel G–Celite–$AgNO_3$ (1:1:0.3). Fractions eluted with petroleum ether gave **5b** (400 mg): oil; NMR δ 1.46 (t, J = 0.7 Hz, C-13 Me), 0.93 (d, J = 7 Hz, C-20 Me), 0.84 (d, J = 6 Hz, C-25 Me_2), 0.8 (s, C-10 Me); mass spectrum (di) *m/e* 490 (M^+), 206, 121. Anal. Calcd for $C_{34}H_{50}O_2$: C, 83.2; H, 10.3. Found: C, 83.4; H, 10.0.

Treatment of 3β-Benzoyloxy-12,14α-cyclo-12,13-seco-5α-cholest-13(17)-ene (5b) with Hydrogen Chloride. The spiro olefin (**5b**;[17] 200 mg) was dissolved in hydrogen chloride saturated ether (20 mL) at −78 °C. The solution was poured instantaneously into a $NaHCO_3$ saturated solution and extracted with diethyl ether; the organic layer was dried (Na_2SO_4) and evaporated in vacuo to give 3β-benzoyloxy-14-chloro-5α,14β,17β*H*-cholestane (**4b**).

Acknowledgments. This research was supported by the Italian Research Council. We thank Professor G. Galli, Institute of Pharmacology and Pharmacognosy, University of Milan, for mass spectra.

Registry No.—**1a,** 2465-00-1; **1b,** 4356-22-3; **2a,** 6562-21-6; **2b,** 6673-65-0; **3a,** 40446-06-8; **3b,** 6673-66-1; **4b,** 66792-81-2; **5b,** 66792-87-8; **6b,** 66808-37-5; **7a,** 66808-38-6; **8a,** 66792-86-7; **8b,** 66792-85-6; **9a,** 66792-84-5; **9b,** 66792-83-4; **9b** methyl ester, 66792-82-3; **10,** 66792-88-9; **10** semicarbazone, 66792-89-0; (*R*)(−)-2,6-dimethylheptanamide, 66792-90-3.

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(16) When the addition was carried out in chloroform on the same compounds, a high yield of **4a** or **4b,** respectively, was obtained only below −50 °C.
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Importance of the Structure of the Phosphorus Functionality in Allowing Dihedral Angle Control of Vicinal ^{13}C–^{31}P Coupling. Carbon-13 NMR Spectra of 7-Substituted Bicyclo[2.2.1]heptane Derivatives[1]

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Carbon-13 NMR spectra were obtained on norbornenes with the 7 position bearing the following substituents: Cl_2P (syn and anti), Me_2P (syn and anti), $Me_2(S)P$ (anti), Me_3P^+ (anti). Norbornanes with 7-Cl_2P and 7-Me_2P were also studied. For the groups $Me_2(S)P$ and Me_3P^+, vicinal C–P coupling was clearly controlled by dihedral angle relations; carbons anti to P were strongly coupled (about 16 Hz), while carbons syn to P showed no coupling. This result is consistent with observations made previously for rigid cyclohexanes bearing these substituents in equatorial or axial positions, respectively. However, the trivalent groups Cl_2P and Me_2P showed no indication of their vicinal coupling (absolute), being minimized at the same dihedral angle; with these groups in either the syn or anti 7 position of norbornene or in the 7 position of norbornane, coupling to the two sets of vicinal carbons differed very little. Again this result is consistent with observations from cyclohexanes and leads to the conclusion that dihedral angle control of vicinal (C–P) coupling is not general in phosphorus chemistry. One-bond ^{13}C–^{31}P coupling was also considered; there was no consistent relation with steric crowding in the compounds studied. Chemical shifts of the phosphorus compounds followed the expected trends, with γ-gauche carbons shifted relatively upfield and anti carbons relatively downfield from the corresponding bicyclo[2.2.1]heptane. Curiously, in *syn*-7-bromonorbornene both types of γ carbon were shifted upfield.

From a study[2] of the effect of phosphorus functions on the ^{13}C NMR spectra of the cyclohexane ring came an indication that three-bond ^{13}C–^{31}P coupling was under steric control in a Karplus-like relation for tetravalent phosphorus functions (e.g., $Me_2(S)P$ and Me_3P^+) but not for some trivalent functions (e.g., Cl_2P and Me_2P). To illustrate, ^{31}P coupling to ring carbons 3 and 5 was 13 Hz when $Me_2(S)P$ was placed in the equatorial position of 4-*tert*-butylcyclohexane (dihedral angle about 180°), but only 4 Hz when in the axial position (dihedral angle about 60°), strongly suggestive of a Karplus effect. On the other hand, Cl_2P similarly placed gave $^3J_{PC}$ values of 11 and 9 Hz, respectively, and Me_2P gave values of 11 and 8 Hz. However, uncertainty about dihedral angles in the axially substituted cyclohexanes, which might be capable of distortion to skew-boat conformations, left the situation unclear. We also[3] encountered cases among some phosphorinane derivatives (**1–4**) where a dihedral angle control of vicinal coupling was suggested. Thus, two $^3J_{PC}$ path-

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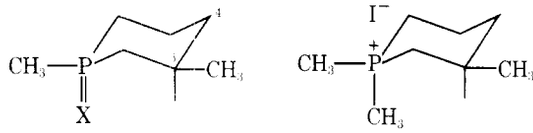
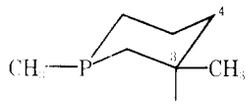
ways exist in 3-methyl derivatives, but that to the ring carbon (C-4) is mediated by a small dihedral angle (60° for an ideal chair) while that to CH_3 by a large angle (180°). In compounds **1, 2,** and **3,** $^3J_{PC}$ was small (6–7 Hz) for C-4 and large for CH_3



1, X = O
2, X = S

3

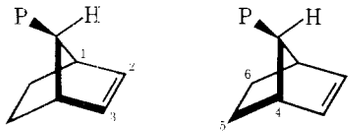


4

(16–18 Hz). In this series, the phosphine (**4**) also showed an apparent steric dependence for coupling (~0 Hz to C-4 and 5 Hz to CH_3).

We have now prepared a group of 7-substituted bicyclo[2.2.1]heptane derivatives partly to clarify this apparent inconsistency of steric control of ^{13}C–^{31}P coupling. This ring system is characterized by considerable rigidity and thus dihedral angles can be reasonably evaluated. In this paper, we will show unequivocally that the covalent character of the phosphorus atom does indeed have a commanding influence in allowing a normal Karplus relation to exist. These bicyclic compounds have other ^{13}C NMR spectral features of interest, and their ^{31}P NMR spectra, which are reported elsewhere,[4] are also of significance.

A sizable literature is developing on the existence of Karplus-like relations between $^3J_{PC}$ and dihedral angle. Such relations seem well established for phosphine oxides[5] and phosphonates.[6] However, our own previous studies[2,3] appear to be the only ones concerned with phosphine sulfides and phosphonium salts, as well as with trivalent functions. 7-Substituted bicyclo[2.2.1]heptane derivatives are of value in such studies because two different coupling paths with widely divergent dihedral angles are present, as shown below for the unsaturated system:

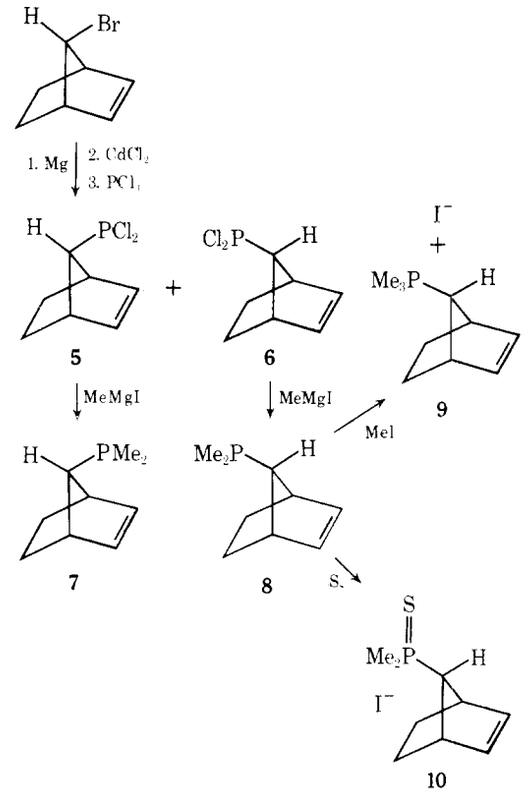


Dihedral angles are known[7] from X-ray analysis of *anti*-7-norbornenyl *p*-bromobenzoate to be 164° for PCCC-3 and 57° for PCCC-5. Angles in solution cannot deviate much from these values. Therefore, $^3J_{PC}$ should differ drastically to C-2,3 or C-5,6 if a normal Karplus relation prevails. The same effects would, of course, be present in *syn*-7-norbornene derivatives, and for norbornanes as well. Examples of each ring type are included in the present study.

Synthesis. The starting compound for all of our synthetic work was *syn*-7-bromonorbornene, which was prepared by the method of Kwart and Kaplan.[8] The Grignard reagent from this bromide was converted to the cadmium derivative[9] for alkylation of PCl_3. This reaction gave a low yield (16%) of a mixture of *syn*-7- (**5,** 20%) and *anti*-7-norbornenylphosphonous dichloride (**6,** 80%). The mixture was not separated but was used directly in the next reaction, that with methylmagnesium iodide (Scheme I). The mixture of phosphines **7** and **8** was then reacted with methyl iodide or sulfur. The products after purification were further enriched in the anti structures (**9** and **10,** respectively) and it was not possible to observe definite spectra for the minor isomers.

That the major isomer from the alkylation of PCl_3 had the

Scheme I



anti structure was readily apparent from the ^{13}C NMR spectrum. This spectrum will be discussed in detail subsequently, where it will be seen that the steric crowding of Cl_2P with the syn methylenes (C-5,6) caused their ^{13}C shifts to be substantially upfield of the minor isomer. Other reactions (e.g., carbonation[10]) of Grignard reagents derived from 7-halonorbornenes likewise give mostly anti products.

Hydrogenation of *syn*-7-bromonorbornene gave 7-bromonorbornane,[8] and this was converted to the phosphonous dichloride **11** and the phosphine **12** (Scheme II). The last reaction gave a product containing small but spectrally significant amounts of other products which were not easily removed by distillation. Usable spectral data for **12** nevertheless were collected on this crude product.

^{13}C NMR Spectra of 7-Substituted Norbornenes. Since the synthetic method led, as already noted, to considerably more of the anti isomers (**6, 8, 9, 10**) than of the syn, spectral data were more readily collected for the anti series of compounds, and they form the basis of most of the ^{13}C NMR study. Assignment of peaks in the spectra of both anti and syn isomers was straightforward and requires no comment. Data appear in Table I.

The data reveal in a striking way that a Karplus relation is most definitely in effect in the case of the phosphine sulfide (**10**) and the phosphonium salt (**9**). The $^3J_{PC}$ values to C-2,3, where the dihedral angles are large (164°[7]), are 15.9 and 16.5

Scheme II

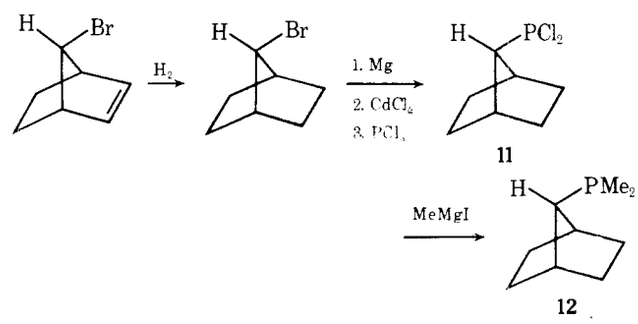
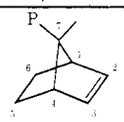
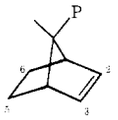
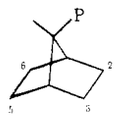
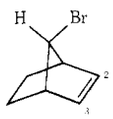
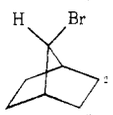
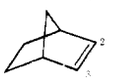
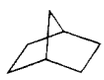


Table I. ^{13}C NMR Spectral Data

	P =					
	registry no.	C-1,4	C-2,3	C-5,6	C-7	P-CH_3
			A. 			
Cl_2P	66793-02-0	44.0 (14.6)	136.6 (6.2)	22.1 (9.7)	71.2 (47.6)	
Me_2P	66793-03-1	44.1 (11.0)	137.3 (6.1)	22.8 (8.6)	64.5 (12.2)	13.1 (12.8)
$Me_2(S)P$	66793-04-2	43.7 (0)	138.5 (15.9)	22.8 (0)	58.6 (44.6)	21.8 (54.3)
$Me_3P^+(I)$	66793-05-3	43.5 (0)	137.7 (16.5)	23.8 (0)	52.5 (40.9)	10.2 (53.1)
			B. 			
Cl_2P	66793-06-4	*a*	134.8 (6.7)	25.5 (<1)	76.7 (40.3)	
Me_2P	66793-07-5	*a*	133.9 (3.7)	24.3 (2.6)	66.8 (6.1)	14.2 (12.6)
			C. 			
Cl_2P	66793-08-6	42.2 (13.4)	27.5 (10.4)	31.5 (6.1)	65.4 (45.8)	
Me_2P	66793-09-7	39.4 (12)	27.6 (10)	31.7 (7)	54.9 (11)	17.1 (14)
			D. Miscellaneous			
	20047-65-8	44.3	132.8	22.7	66.0	
	13237-88-2	42.8	27.5	27.5	58.5	
		41.8[b]	135.2[b]	24.6[b]	48.5[b]	
		36.1[b]	29.6[b]	29.6[b]	38.3[b]	

[a] Not clearly observed on spectrum. [b] Data of J. B. Stothers, C. T. Tan, and K. C. Teo, *Can. J. Chem.*, **51**, 2893 (1973).

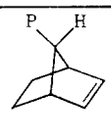
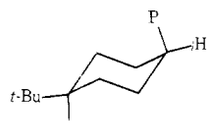
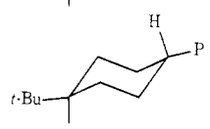
Hz, respectively, which are quite close to those reported[2] for equatorial substitution on the cyclohexane ring. On the other hand, no ^{31}P coupling was observed for C-5,6, where the dihedral angle should be about 57°.[7] This is near the angle (65°) of minimum coupling reported[11] for three-bond ^{13}C–^{13}C coupling in carboxylic acids in rigid systems. These results therefore provide confirmation of a small dihedral angle in the 1-axially substituted 4-*tert*-butylcyclohexanes where $^3J_{PC}$ is only about 4 Hz. This is a conformationally significant point, for it shows that the chair shape is largely retained in these cyclohexanes and that a skew-boat conformation, which would have quite large dihedral angles to C-3,5 (153–169°[2]), is not adopted.

The trivalent phosphorus functions Cl_2P and Me_2P, on the other hand, show no semblance of a normal Karplus relation. Coupling to C-5,6, which should be minimal in such a relation, is even larger than that to C-2,3. This, of course, confirms the observation made previously for these groups as substituents on cyclohexanes[2] and results in the conclusion that the nature of the phosphorus functionality does play a controlling role in determining if stereodependence of three-bond coupling will prevail. Stereodependence of two-bond coupling is also determined by the phosphorus function,[12] but here no strong relation exists for the tetracovalent functions of phosphorus, and it is the trivalent state that exhibits the steric control. Also, a recent observation of two substantially different $^3J_{PC}$ values for 1,6-diphosphatriptycene, where the dihedral angles involved are the same, suggests that an influence on ^3J may arise from orientation of the lone pair orbital.[13]

The two trivalent derivatives in the syn series (**5** and **7**) show the same absence of a minimum for $^3J_{PC}$ to the carbon(5,6) related by small dihedral angle, thus establishing that the situation holds for both sp^3 and sp^2 carbon. (It will be seen in the next section that the norbornyl derivatives also fail to have the Karplus minimum.)

Chemical shift differences in an isomer pair at the carbons γ oriented to phosphorus were of immediate value in assigning their structures. Thus, it is known[14] from studies of other 7-substituted norbornenes that relative to norbornene itself the 1,3-interactions between a 7-substituent syn to a CH_2 group (C-5,6) cause these ring carbons to be upfield shifted. The same effect is observed for the other isomer but at the sp^2 carbons. Such upfield shifts, routinely observed for carbons with a γ-gauche oriented substituent, have commonly been explained by the operation of steric compression, although the effect is not yet fully understood and may have a more complex origin.[15] Indeed, upfield shifts of a smaller magnitude are sometimes experienced for carbon in the γ-antiperiplanar

Table II. Comparison of α Effects and $^1J_{PC}$ for Phosphorus Compounds[a]

	Cl_2P		Me_2P		$Me_2(S)P$		Me_3P^+	
	α	^1J	α	^1J	α	^1J	α	^1J
	22.7	47.6	16.0	12.2	10.1	44.6	4.0	40.9
	21.6	44	12.3	10	9.0	51	1.5	48
	20.7	45	11.6	9	13.5	53	4.4	51
$CH_3CH_2CH_2CH_2P$	29.7	44	19.4	12	21.4	54		

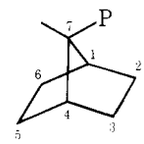
[a] Cyclohexyl data of ref 2 are used; the α effect was determined by subtracting the value for cyclohexane (δ 27.7) from the C-1 chemical shifts. Butyl data are given in ref 17.

relation.[16] The operation of the γ-gauche interaction in the isomeric phosphonous dichlorides **5** and **6**, and in their corresponding dimethyl derivatives **7** and **8**, is clearly evident, and allows the assignment of their structure. For one dichloride and its dimethyl derivative, C-5,6 are upfield by about 2 ppm of the value for norbornene, and these compounds are assigned the anti structures **6** and **8**, respectively. For the other pair, it is C-2,3 which are upfield shifted, and these compounds are assigned the syn structures **5** and **7**. Support for these assignments comes from the chemical shifts of C-7; the 1,3 interaction between the C-7 substituent and the CH_2 groups of the anti isomers is greater than that involving the sp^2 carbon of the syn isomers, and the C-7 chemical shifts for the anti isomers are considerably upfield of the syn isomers (Cl_2P, 5.5 ppm; Me_2P 2.3 ppm). Coupling information also is applicable to the structure assignments. As already noted, the three-bond P–C coupling in the sulfide (**10**) and the salt (**9**) is dependent on the dihedral angle, and only the anti assignment to these compounds allows the Karplus-like relation expected from the earlier cyclohexane studies[2] to prevail.

The phosphorus substituents give the expected downfield shifts at C-7 relative to norbornene. These α effects were of very similar magnitude to those seen for substitution on cyclohexane.[2] The one-bond ^{13}C–^{31}P coupling was also similar, in spite of the fact that the hybridization at C-7 of the bicyclic compounds differs from that of a cyclohexane carbon. More s character is diverted into the exocyclic bonds of the bicyclics to allow for the contraction of the internal bond (C_1–C_7–C_4 is 96° in *anti*-7-norbornenyl *p*-bromobenzoate[7]), but there is no clear trend in the data to show relevance to P–C coupling. Thus, in the anti series, the two trivalent groups have slightly enhanced J_{PC} values, as would be expected from increased s character, but the tetravalent functions had slightly smaller values. Inconsistencies also were present when an open-chain model[17] was used for comparison. Data that illustrate these divergencies are collected in Table II. The absence of a clear relation between ring strain and ^{13}C–^{13}C coupling has also been noted for COOH bonded to various strained cyclic carbons.[11]

For the two phosphorus compounds in the syn series, values for $^1J_{PC}$ are smaller by several hertz than they are in the anti series. Recent reports[6b,6c,18] have noted that $^1J_{PC}$ for phosphonates is slightly smaller in sterically congested structures, but in the trivalent phosphorus derivatives of the norbornenes (and in the cyclohexanes as well; see Table II), the opposite is seen to be true, since steric crowding is obviously smaller in the syn than in the anti series. It is therefore premature to draw any broad conclusions about the influence of steric congestion on the magnitude of $^1J_{PC}$. Thus, a proposal[19] that bond angles increase to relieve steric congestion, and that this angle effect is to be associated with increased $^1J_{PC}$, must be viewed with caution, for it is not a general phenomenon.

^{13}C NMR Spectra of the 7-Norbornyl System. The two



11, P = Cl_2P
12, P = Me_2P

norbornyl derivatives **11** and **12** gave ^{13}C NMR spectra that were easily assigned (Table I). The steric crowding of C-2,3 caused these carbons to resonate several ppm to higher field than comparable carbons in norbornane (for **11**, 2.1; for **12**, 2.0 ppm). This has been observed for 7-COOH[11] and 7-CH_3[14] norbornanes. Also seen in these latter two compounds is a downfield shift for C-5,6 (1.4 and 2.1 ppm, respectively) relative to norbornane, and this effect is reproduced in the phosphorus compounds ([[= [/9: [2= 2/[PPM(/ The net effect is to create for these compounds a considerable difference between CH_2 groups syn and anti to the 7-substituent. There are exceptions to this situation, however; it has been reported that 7-OH causes upfield shifts of equal magnitude at both C-2,3 and C-5,6,[20] and we have found that this is true also for 7-bromonorbornane.[21] This curious effect was also noted in our work with *syn*-7-bromonorbornene; both the crowded sp^2 carbons as well as the uncrowded CH_2 groups were shielded (2.4 and 1.9 ppm, respectively) relative to norbornene, whereas for *syn*-7-methylnorbornene[14] and the two phosphorus compounds **5** and **7**, deshielding occurs at the CH_2 groups. There is obviously a danger in assuming for the 7-substituted bicyclo[2.2.1]heptane system that the usual consistency in the direction of substituent effects prevails without exception.

The expectation that $^3J_{PC}$ for **11** and **12** would fail to show minima in the usual Karplus region was realized. In fact, for both compounds the value for $^3J_{PC\text{-}5,6}$, where the dihedral angle is large, was considerably smaller than that for $^3J_{PC\text{-}2,3}$. These two compounds are important to our argument that the trivalent groups Cl_2P and Me_2P (and possibly others) are not generally to be associated with the usual Karplus control of $^3J_{PC}$; here both coupling pathways are to carbons of sp^3 hybridization, whereas our previous examples depended on structures with mixed sp^2 and sp^3 carbons. It is possible that a minimum in the absolute three-bond coupling occurs at

some quite different dihedral angle than is encountered for the tetravalent functions. At present, however, no experimental data are available that bear on this point.

Finally, we emphasize that only absolute values for $^3J_{PC}$, as obtained in the routine practice of NMR spectroscopy, are considered in this paper; sign determinations have not been made. However, it seems quite unlikely for a sign difference to exist for a pair of syn and anti (or cis and trans[2]) isomers that have nearly the same absolute values for ^3J, and for the present we are ignoring a sign change as a possible explanation for the apparent absence of a Karplus minimum in the absolute values for the trivalent derivatives. Nevertheless, while very little work has been done on the signs of three-bond C–P coupling, it is known that in phosphines the sign may be either positive (in aromatic derivatives[13,22]) or negative (in acetylenic derivatives[23]). In the study of acetylenic compounds,[23] it was noted that the sign for the tetravalent derivatives was the opposite of that for the trivalent derivatives and that for the two types of phosphorus functions different degrees of importance had to be attributed to the several factors usually considered in the coupling mechanism (Fermi contact, spin dipolar, and orbital terms). A difference in coupling mechanism would seem to offer a possible explanation for the variability in dihedral angle control of $^3J_{PC}$ as noted in the present study.

Experimental Section

General. Proton-decoupled Fourier transform ^{13}C NMR spectra were obtained with a JEOL FX-60 Spectrometer at 15 MHz. All samples were run in $CDCl_3$ solution. Analyses were performed by MHW Laboratories, Garden City, Mich. All reactions involving phosphorus compounds were conducted under nitrogen. Melting points are corrected; boiling points are uncorrected.

***syn*-7-Bromonorbornene.** This compound was prepared by the procedure of Kwart and Kaplan,[8] which involves first the addition of bromine to norbornene to form 2,7-dibromonorbornene, and then dehydrohalogenation with potassium *tert*-butoxide. The product had bp 42 °C (3.2 mm) (lit.[8] bp 68–70 °C (13 mm). Its ^{13}C NMR spectrum is given in Table I.

7-Norbornenylphosphonous Dichloride (*syn*- 5 and *anti*-6). The Grignard reagent was prepared from 4.86 g (0.20 mol) of magnesium and 17.3 g (0.10 mol) of *syn*-7-bromonorbornene in 100 mL of anhydrous ether. The reaction was initiated with methyl iodide. To the refluxing dark solution was added 18.3 g (0.10 mol) of cadmium chloride (dried at 110 °C) in small portions from a reservoir attached by Gooch tubing. The mixture was cooled to room temperature and the precipitate of metallic halides removed by filtration in a nitrogen atmosphere. The filtrate containing the organocadmium reagent was added dropwise to a solution of 27.0 g (0.20 mol) of phosphorus trichloride in 500 mL of anhydrous ether at −78 °C. A voluminous precipitate formed and was removed by filtration under nitrogen after the mixture was warmed to room temperature. The mixture was distilled through a short Vigreaux column and the fraction boiling at 75–78 °C (3 mm) was collected as product (2.3 g, 16.4%). The ^{31}P NMR spectrum, to be discussed in detail elsewhere,[4] had signals for the anti isomer (**6**) at δ +190.9 (80%) and the syn (**5**) at δ +199.7 (20%). The ^{13}C NMR spectrum is given in Table I. The ^1H NMR ($CDCl_3$) spectrum only showed separate signals for the isomers in the vinyl region (anti, δ 6.2 (m, 79%); syn, δ 6.1 (m, 21%)); others were δ 1.2 (m, 2 H, *endo*-H-5,6), 1.8 (m, 2 H, *exo*-H-5,6), 2.6 (m, 1 H, H-7), 3.5 (m, 2 H, H-1,4).

Dimethyl(7-norbornenyl)phosphine (*syn*-7, and *anti*-8) and Methiodide (9). A mixture of phosphonous dichlorides **5** and **6** (14.4 g, 0.078 mol) was added dropwise to the Grignard reagent prepared from 6.08 g (0.25 mol) of magnesium turnings and 35.3 g (0.25 mol) of methyl iodide in 300 mL of ether. Gentle reflux was permitted. At the end of the reaction, a saturated solution of ammonium chloride was added. Layers were then separated and the ether layer was dried ($MgSO_4$). Distillation left an oil that was fractionated with a Vigreaux column. After three distillations, the fraction (2.4 g, 20%) of bp 48–52 °C (2.5 mm) was taken as product. The ^{13}C NMR spectrum (Table I) showed that the anti isomer accounted for about 80% of the product. Analysis was performed on the methiodide (**9**), prepared in benzene solution and recrystallized from benzene–chloroform, mp 270–273 °C dec. The ^{13}C NMR spectrum of **9** is given in Table I. The only signal attributable to the syn isomer was that of the methyl carbon (δ 12.5 ($^1J_{PC}$ = 53.7 Hz)). The analysis of **9** follows.

Anal. Calcd for $C_{10}H_{18}IP$: C, 40.54; H, 6.08. Found: C, 40.30; H, 6.06.

Dimethyl(*anti*-7-norbornenyl)phosphine Sulfide (10). A mixture of 2.8 g (0.018 mol) of phosphine **8** prepared as above and 3.0 g of sulfur in 200 mL of benzene was refluxed for 4 h. The mixture was cooled to room temperature and excess sulfur was removed by filtration. After four recrystallizations from ethanol–water, the product (**10**) had mp 133–135 °C. The ^{13}C NMR spectrum obtained on this sample was only that of the anti isomer; ^{31}P NMR analysis[4] did reveal that a few percent of the syn isomer was still present.

Anal. Calcd for $C_9H_{15}PS$: C, 58.06; H, 8.06. Found: C, 57.89; H, 8.26.

7-Bromonorbornane. *Syn*-7-bromonorbornene was hydrogenated as first described by Kwart and Kaplan,[8] using a PtO_2 catalyst at 50 psi. Occasionally hydrogen uptake was incomplete; the sample was distilled and again subjected to the hydrogenation. The product had bp 40 °C (3 mm) (lit.[8] bp 70–72.5 °C (15 mm)); its ^{13}C NMR spectrum is recorded in Table I.

7-Norbornylphosphonous Dichloride (11). The Grignard reagent was prepared from 35.0 g (0.20 mol) of 7-bromonorbornane and 4.86 g (0.20 mol) of magnesium turnings in 200 mL of ether. Initiation of the reaction by methyl iodide was required. The cadmium reagent was then prepared by the slow addition, at reflux, of 18.3 g (0.10 mol) of anhydrous cadmium chloride. The solution from removal of precipitated metallic halides was added to a solution of 54 g (0.39 mol) of phosphorus trichloride in 300 mL of ether at −78 °C. After solids had been removed by filtration, the solution was fractionally distilled (Vigreaux column) twice and the product (11) collected at 80–85 °C (4.0 mm), yield 12.7 g (32%). The ^{13}C NMR spectrum is given in Table I.

Dimethyl(7-norbornyl)phosphine (12). To the Grignard reagent prepared from methyl iodide (21.3 g, 0.15 mol) and 3.63 g (0.15 mol) of magnesium in ether was added 10.0 g (0.05 mol) of 7-norbornylphosphonous dichloride (**11**). After addition of saturated ammonium chloride solution, layers were separated; the ether layer was dried ($MgSO_4$) and distilled. Product (**12**) was collected at 48–52 °C (2.5 mm), yield 6.3 g. The sample was difficult to purify; its ^{13}C NMR spectrum was obtained on the crude product (Table I).

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