from 30% to 50% EtOAc in hexane): ^{1}H NMR δ 7.55–7.27 (m, 5), 4.30–3.94 (m, 6), 3.57–3.51 (m, 1), 1.35–1.13 (m, 9); ^{31}P NMR +19.4; EIMS, *m/z* (relative intensity) 300 (M^+, 4), 254 (6), 199 (10), 196 (22), 172 (15), 118 (100), 109 (25), 91 (78), 79 (27); HRMS, calcd for $C_{14}H_{21}O_5P$ 300.1126, found 300.1122.

Ethyl α-(Diisopropoxyphosphinyl)phenylacetate (23b). Ethyl phenylacetate (**22**, 821 mg, 5.0 mmol) was treated sequentially with LDA (1.1 equiv in 15 mL of THF), HMPA (1.0 mL, 5.7 mmol), diisopropyl phosphorochloridate (1.00 mL, 5.5 mmol), and LDA (2.2 equiv) according to the general procedure. Purification by gradient radial chromatography (silica, 10% to 50% EtOAc in hexane) gave compound **23b** (154 mg, 9.4%): ^{1}H NMR δ 7.53 (d, 2, *J* = 7.8 Hz), 7.35–7.26 (m, 3), 4.70–4.56 (m, 2), 4.26–4.15 (m, 3), 1.30–1.24 (m, 15); ^{31}P NMR +17.5; EIMS, *m/z* (relative intensity) 328 (M^+, 5), 286 (5), 244 (7), 199 (12), 164 (22), 118 (100), 107 (25), 91 (34), 90 (34), 79 (28). Anal. Calcd for $C_{16}H_{25}O_5P$: C, 58.53; H, 7.67. Found: C, 58.26; H, 7.66.

Isopropyl α-(Diethoxyphosphinyl)propionate (28). In accordance with the general procedure, isopropyl propionate (**27**, 580 mg, 5.0 mmol) was added to a solution of LDA (1.2 equiv) in THF (15 mL) at −78 °C. The resulting enolate was treated sequentially with HMPA (0.99 mL, 5.7 mmol), diethyl phosphorochloridate (0.83 mL, 5.7 mmol), and LDA (2.2 equiv). Standard workup and purification by column chromatography gave compound **28** (252 mg, 29%): ^{1}H NMR δ 5.19–4.92 (m, 1), 4.32–3.99 (m, 4), 3.01 (dq, 1, J_{HP} = 23.4 Hz, *J* = 7.3 Hz), 1.57–1.11 (m, 15): ^{31}P NMR +24.6; EIMS, *m/z* (relative abundance) 252 (M^+, 2), 210 (30), 193 (100), 165 (70), 137 (49), 109 (51), 99 (18), 81 (36). Anal. Calcd for $C_{10}H_{21}O_5P$: C, 47.62; H, 8.39. Found: C, 47.80; H, 8.54.

***tert*-Butyl α-(Diethoxyphosphinyl)propionate (30).** *tert*-Butyl propionate (**29**, 650 mg, 5.0 mmol) was added to a solution of LDA in THF (5.5 mmol in 15 mL) at −78 °C, and the resulting enolate was treated sequentially with HMPA (1.0 mL, 5.7 mmol), diethyl phosphorochloridate (0.83 mL, 5.7 mmol), and LDA (2.2 equiv) as in the general procedure. Standard workup and purification by column chromatography gave compound **30** (359 mg, 27%): ^{1}H NMR and EIMS data identical with previous data;[20] ^{31}P NMR +24.9.

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[4 + 2] Cycloadditions between 2*H*-Phospholes and Alkenes. Synthesis and Properties of 1-Phosphanorbornenes

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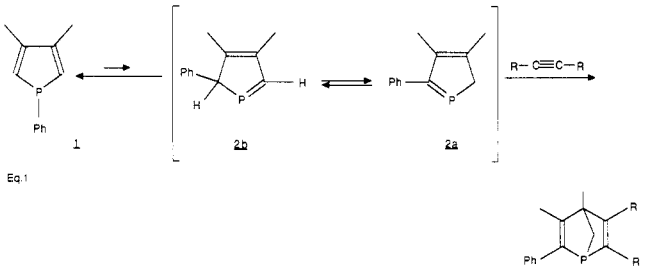
2*H*-Phospholes, obtained by isomerization of 1*H*-phospholes at ca. 150 °C, achieve [4 + 2] cycloadditions with disubstituted alkenes to yield 1-phosphanorbornenes. In the case of symmetrical (*E*)-alkenes, α-exo,β-endo compounds are formed predominantly or even exclusively. Spectral assignments of these compounds are checked by an X-ray structure determination. The 1-phosphanorbornenes formed by reacting 2*H*-phospholes and (*Z*)-alkenes undergo an epimerization and then give the same products as (*E*)-alkenes do. The study of the evolution of the reaction mixture shows that the [4 + 2] cycloaddition should proceed via a concerted mechanism followed by a cleavage of the newly formed P–C single bond. Regioselectivity of nonsymmetrical alkenes is controlled by the steric hindrance of the phosphole moiety. The transient phosphadiene exhibits a rather high reactivity toward dienophiles and the presence of an alcoholic function does not disturb the cycloaddition.

Introduction

Bicyclic systems with phosphorus at the bridgehead have been known for a long time[1-3] but their synthesis is so long and tedious and the overall yields are so low that the study of their properties has remained limited. In such a context, the discovery in our laboratory of a very simple one-step synthesis of 1-phosphanorbornadienes from phospholes and alkynes[4,5] opens interesting new perspectives. The key feature underlying this synthesis is the appearance, above ca. 150 °C, of an equilibrium between 1-phenyl-1*H*-phospholes such as **1** and 2-phenyl-2*H*- or -5*H*-phospholes such as **2a,b** via the superimposition of [1,5] phenyl and hydrogen sigmatropic shifts (eq 1).



Since this initial discovery, Regitz has been able to synthesize stable 2*H*-phospholes[6] but no further extension of the chemistry of these species has yet appeared in the literature. We report here on the reaction of the transient 2*H*-phospholes with alkenes with some emphasis on the stereochemistry of these [4 + 2] cycloadditions.

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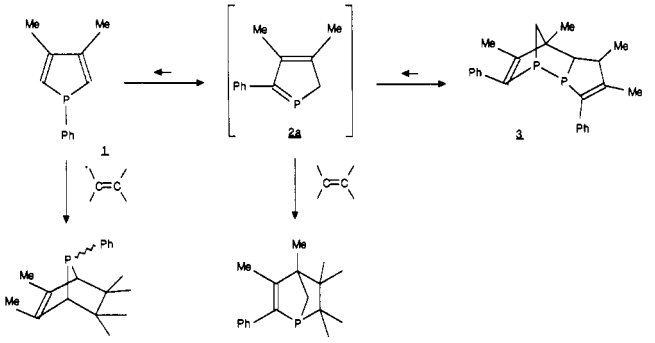
0022-3263/89/1954-4754$01.50/0

Scheme I. Possible Reaction Paths in the Alkene + Phosphole System



Results and Discussion

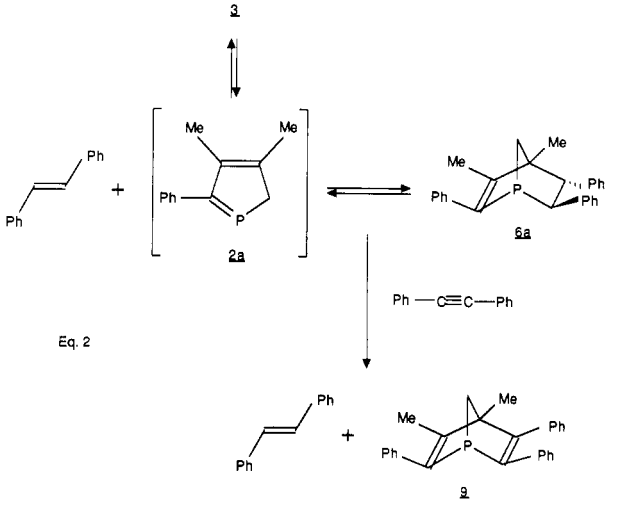
All our experiments have been performed with the readily available 1-phenyl-3,4-dimethylphosphole (1).[7] In order to reduce the number of possible isomers, we have first selected symmetrical alkenes with various steric and electronic properties. In each case, *E* and *Z* isomers were submitted to the same reaction conditions. A nonsymmetrical alkene was added to this series in order to generalize the main observations (see Scheme II).

2*H*-Phospholes are far more reactive than 1*H*-phospholes as conjugated dienes. When the equilibrium depicted in eq 1 becomes operative, alkenes preferentially react with 2*H*-phospholes. At lower temperature, however, when no 2*H*-phosphole is present in the reaction medium, alkenes, especially the activated ones, may react with 1*H*-phospholes to give 7-phosphanorbornenes.[8] This is the reason why we prefer to add the activated alkenes just before reaching the temperature of isomerization. The formation of the 7-phosphanorbornene byproducts is easily detected by the appearance of a signal at low field (ca. 110 ppm) in the ^{31}P NMR spectra of the crude reaction mixtures. This problem is especially important in the case of dimethyl maleate. Another side product may appear when the alkene is a poor dienophile (e.g., stilbene). In such a case, the transiently formed 2*H*-phosphole may react with itself to give the already described dimer **3**.[9] The formation of **3** is easily monitored via its characteristic ^{31}P NMR spectrum (AB: δ_A −31 ppm; δ_B +35 ppm; ^1J(A–B) = 198 Hz). The three possible paths are summarized in Scheme I.

The actual results of our various experiments are collected in Scheme II. In each reaction, the major isomer has been isolated and fully analyzed after purification. Attempts to separate the minor isomer failed in each case and the characterization was performed on the mixture of isomers using various isomeric ratios. All these compounds are very air-sensitive and it is more convenient to oxidize them by oxygen or sulfur to handle or analyze them easily.

Each cycloaddition leads to a major isomer with the substituent α to phosphorus in the exo position. This may be due to the steric hindrance caused by the phenyl group of the phosphole moiety. Nonstereoselective [4 + 2] cycloadditions were observed when (*Z*)-alkenes were allowed to react with phosphole **2a**. No similar epimerization has been detected when dimethyl maleate and dimethyl fumarate were allowed to react with pentachlorocyclopentadiene at the same temperature,[10] and more severe conditions are required for stilbene isomerization upon reaction with hexachlorocyclopentadiene.[11] This phenomenon is not dependent on the concentration of the reagents. Formation of **5a** is detected by ^{31}P NMR as soon as equilibrium (eq 1) is operative. In the case of *cis*-stilbene, **7b,c** first appear and then are transformed into **6a** after a short delay. This finding means that the [4 + 2] cycloaddition of (*Z*)-alkenes with phosphole **2a** proceeds via a concerted mechanism and then is followed by the reversible cleavage (probably homolytic) of the newly formed P–C bond allowing the isomerization (see scheme III).

This reversible cleavage is the first step of a nonconcerted retro-Diels–Alder reaction giving back the 2*H*-phosphole **2a**. Indeed, when tolan is added at 150 °C to the mixture resulting from the reaction of *trans*-stilbene with **1** (mainly containing the 2*H*-phosphole dimer **3** and the phosphanorbornene **6a**), both **3** and **6a** disappear and the phosphanorbornadiene **9**[4] is formed (eq 2).

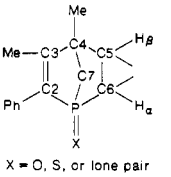


Eq. 2

Table I. ^{13}C NMR Spectral Data of Various 1-Phosphanorbornene Oxides and Sulfides[a]

compd	C3	C4	C5	C6	C7	Me(1)	Me(2)
4*	155.9	55	42.6	43.6	47	14.8	20
	(17.6)		(27.5)	(45)	(70)	(13.6)	(19)
5a*	155.5	54.3	42	43.2	46	14.2	19.2
	(17.8)		(27.4)	(43.9)	(69.4)	(13.6)	(19.1)
6a*	155.2	61.0	42.2	46.6	48.8	15.5	19.6
	(16.6)	(4.4)	(27.1)	(57.3)	(65.5)	(13.1)	(18.2)
8a*	155.1	60.7	50.1	46.7	52.5	15.8	19.4
	(14.1)		(20)	(45.8)	(54)	(12)	(16.6)

[a] δ in ppm ($CDCl_3$), J(P–C) in hertz; Carbon numbering as follows:



X = O, S, or lone pair

Table II. ^1H NMR Spectral Data of Protons H_α and H_β

	H_α	H_β	$^3J(H_\alpha–H_\beta)$	$^2J(P–H_\alpha)$
4a	3.04	3.21	5.42	
5a	3.06	3.26	5.4	
6a	3.02	3.37	6.7	
7b	4.30	3.54	10.7	5.1
7c	3.12	3.65	9.95	3.4
8a*	2.50–2.60	2.98	6.1	

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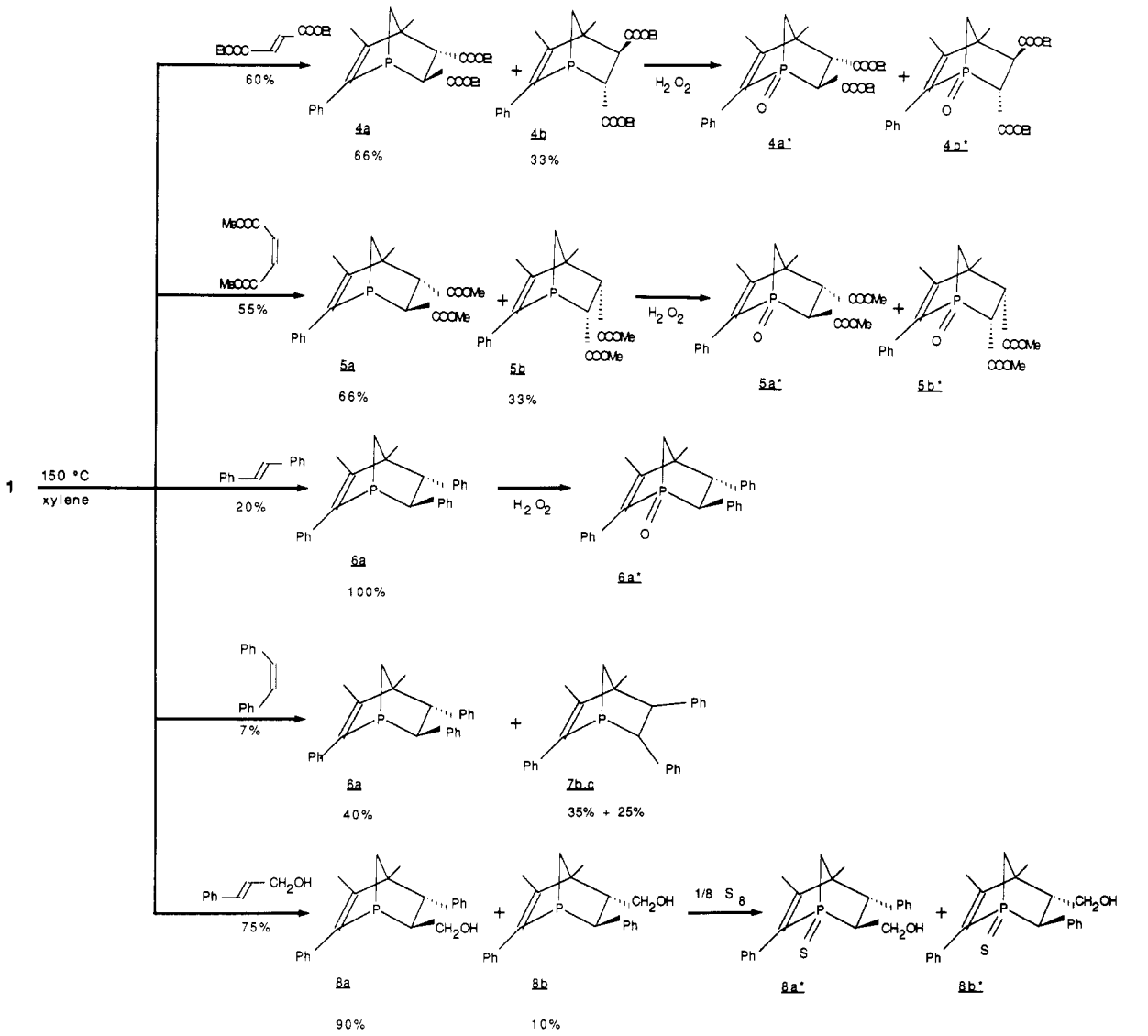
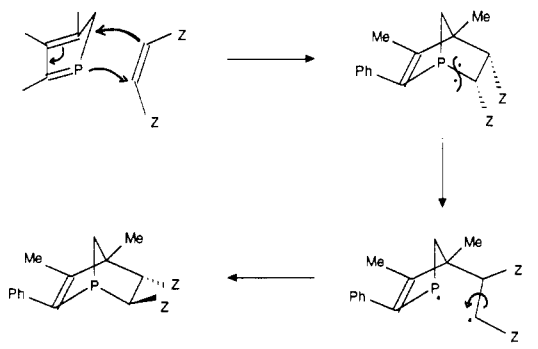
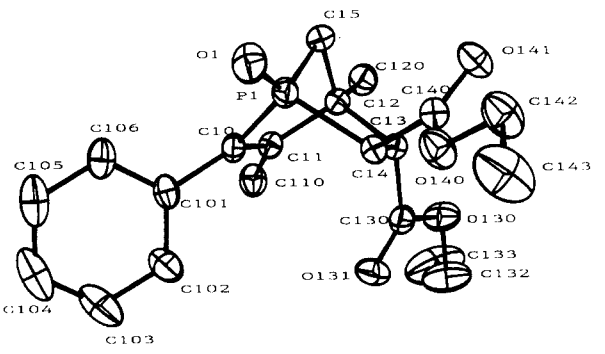
Scheme II. Reaction of Various Alkenes with Transient 2-Phenyl-3,4-dimethyl-5*H*-phosphole (2a) (Product Ratios in %) (Overall Yield)



Scheme III. Proposed Mechanism for 1-Phosphanorbornene Isomerizations



Scheme IV. ORTEP Representation of One Enantiomer of 4a* Showing the 50% Probability Ellipsoids and the Numbering Scheme Used



^{13}C NMR is an efficient tool for the detection of the 1-phosphanorbornene skeleton (see Table I). However, the full determination of the stereochemistry needs additional ^{1}H and ^{31}P NMR spectra. $^{3}J(H_\alpha-H_\beta)$ coupling constants between 5 and 7 Hz were observed when $H_\alpha-C_6$ and $H_\beta-C_5$ are in the endo,exo configuration, but $^{3}J(H_\alpha-H_\beta)$ coupling greater than 9.5 Hz is found when H_α and H_β are eclipsed (see Table II). The stereochemical assignment of H_α depends on the value of the $^{2}J(P-H_\alpha)$ coupling in $1\lambda^3$-phosphanorbornenes. This value is close to 0 Hz when H_α is in the endo position with a maximum of $H_\alpha-C-P$ lone pair dihedral angle. On the contrary, exo H_α exhibits larger coupling constants with phosphorus (ca. 5 Hz). A single-crystal X-ray structure determination was carried out on compound **4a*** to confirm the NMR stereochemical assignments (see Scheme IV). A comparison of selected bond lengths and angles with 1-phosphanorbornane[2] and 1-phosphanorbornadienes[4,5] is done in Table III.

Scheme V. Selectivity of the Reaction

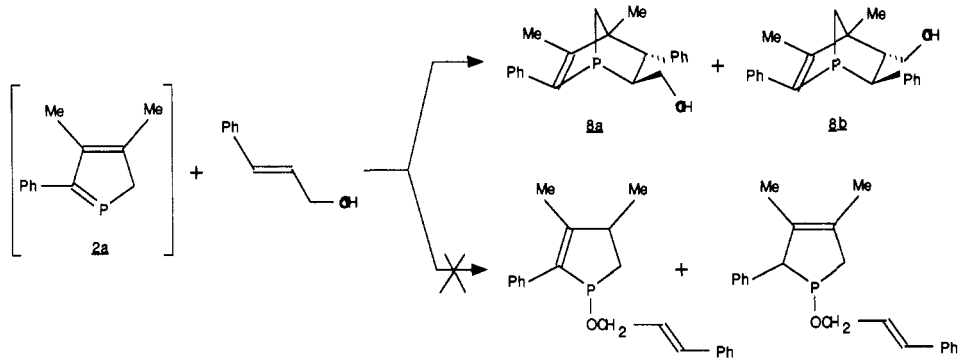
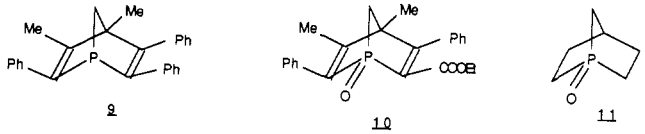


Table III. Selected Bond Lengths and Angles in 1-Phosphanorbornane,[2] 1-Phosphanorbornadienes,[4,5] and 1-Phosphanorbornene[a]



	9	10	4a*	11
		Bond Lengths		
P–O		1.476	1.474	1.487
P–C2	1.869	1.819	1.799	1.779
P–C6	1.869	1.816	1.858	1.779
P–C7	1.835	1.806	1.795	1.792
		Bond Angles		
C2PC6	96.1	100.8	99.8	99.8
C2PC7	85.5	90.1	92.6	94.4
C6PC7	85.5	90.6	91.7	94.4

[a] Bond lengths are given in angstroms and angles in degrees.

A nonsymmetrical alkene such as cinnamyl alcohol shows how the regioselectivity of the cycloaddition is dependent on steric effects. Thus compound **8a** is almost only formed with the two phenyl groups localized as far as possible. No formation of the dimer **3** is observed and high yields are obtained (ca. 80%). This reaction gives also an indication on the reactivity of the transient 2*H*-phosphole. It appears to be more reactive as a diene toward the C=C double bond than as a P=C double bond toward the alcohol functionality. Indeed, no addition of the alcohol onto the P=C double bond was put in evidence[4] (see Scheme V).

This series of reactions offers an easy route to functionalized bicyclic compounds with phosphorus at the bridgehead. The possible control of the stereo- and regioselectivity plus the good yields encourage us to study the chemical properties of these species.

Experimental Section

All reactions were performed under argon. NMR spectra were recorded on multinuclear WP 80 SY and AC 200 SY Bruker spectrometers operating at 80.13 and 200.13 (^{1}H), 20.15 and 50.32 (^{13}C), and 32.44 (^{31}P) MHz; chemical shifts are in ppm downfield from internal TMS (^{1}H and ^{13}C) and external 85% H_3PO_4 (^{31}P), and coupling constants are in hertz. Mass spectra were recorded on a Shimadzu GC-MS QP 1000 instrument at 70 eV under electronic impact. Elemental analyses were performed by the Service Central de Microanalyse du CNRS, France. Silica gel (70–230 mesh) was used for chromatographic separations. All commercially available reagents were used as received from the suppliers.

General Procedure for the Synthesis of 1-Phosphanorbornene Oxides. 2-Phenyl-3,4-dimethyl-5-*endo*,6-*exo*-bis(ethoxycarbonyl)-1-phosphabicyclo[2.2.1]hept-2-ene *P*-Oxide (4a*). Diethyl fumarate (4.5 mL, 27.5 mmol) was added at 120 °C to a stirred solution of 1 (5 mL, 26.6 mmol) in 4 mL of xylene. Refluxing xylene was required for 3 h. The mixture was allowed to cool down. (It was possible to purify $1\lambda_3$-phosphanorbornenes by using hexane/dichloromethane (80:20) as eluent for a rapid chromatography on silica gel. These compounds are air-sensitive and must be rapidly analyzed). At room temperature 50 mL of 3% H_2O_2 and 15 mL of xylene were added and vigourously stirred for 3 h. Then the reaction mixture was poured into a cooled 10% aqueous solution of sodium thiosulfate. The crude product was extracted with CH_2Cl_2, washed with water, and dried ($MgSO_4$). The solvent was removed, leaving a yellow oil that was chromatographed with hexane/ethyl acetate (40:60) as eluent. **4a*** was first eluted and then a mixture of **4a*** and **4b***. Pure **4a*** (25%) gave colorless crystals in pentane (mp = 108–109 °C). Overall yield of **4a*** + **4b*** was 55%.

4a*: ^{1}H NMR ($CDCl_3$) δ 1.30 (t, ^3J(H–H) = 7.2 Hz, 6 H, CH_3(ester) × 2), 1.62 (s, 3 H, Me), 1.87 (d, ^4J(P–H) = 2.7 Hz, 3 H, Me), 2.0–2.48 (m, $^2J(H_\alpha–H_\beta)$ = 11 Hz, $^2J(P–H_\alpha)$ = 11 Hz, $^2J(P–H_\beta)$ = 10 Hz, 2 H, CH_2), 3.36–3.56 (m, 2 H, H_α–H_β), 4.18 (q, ^3J(H–H) = 7.2 Hz, 2 H, CH_2 ester), 4.27 (q, ^3J(H–H) = 7.2 Hz, 2 H, CH_2 ester), 7.27–7.38 ppm (m, 5 H, Ph); ^{13}C NMR ($CDCl_3$) δ 14.1 (s, C H_3 (ester) × 2), 14.8 (d, ^3J(P–C) = 13.6 Hz, Me), 20 (d, ^3J(P–C) = 19 Hz, Me), 42.6 (d, ^2J(P–C) = 27.5 Hz, C5), 43.6 (d, ^1J(P–C) = 45 Hz, C6), 47 (d, ^1J(P–C) = 70 Hz, C7), 55 (s, C4), 61.4 (s, OCH_2), 62.1 (s, OCH_2), 127.8–131.6 (m, Ph + C2), 155.9 (d, ^2J(P–C) = 17.6 Hz, C3), 170 (s, >C=O), 170.8 ppm (s, >C=O); ^{31}P{^{1}H} NMR ($CDCl_3$) δ 51.9 ppm; MS, *m/z* (relative intensity) 376 (M, 20), 204 (M – diethyl fumarate, 100). Anal. Calcd for $C_{20}H_{25}O_5P$: C, 63.52; H, 6.69. Found: C, 64.02; H, 6.44.

2-Phenyl-3,4-dimethyl-5-*endo*,6-*exo*-bis(methoxycarbonyl)-1-phosphabicyclo[2.2.1]hept-2-ene *P*-oxide (5a*): white crystals mp = 109–110 °C (yield 20%); ^{1}H NMR ($CDCl_3$) δ 1.62 (s, 3 H, Me), 1.85 (d, ^4J(P–H) = 2.7 Hz, 3 H, Me), 2.02–2.46 (m, $^2J(H_\alpha–H_\beta)$ = 12.0 Hz, ^2J(P–H) = 10 Hz, 2 H, CH_2), 3.6 3.8 (m, 2 H, H_α–H_β), 3.72 (s, 3 H, OCH_3), 3.80 (s, 3 H, OCH_3), 7.2–7.5 ppm (m, 5 H, Ph); ^{13}C NMR ($CDCl_3$) δ 14.1 (d, ^3J(P–C) = 13.6 Hz, Me), 19.2 (d, ^3J(P–C) = 19.1 Hz, Me), 42 (d, ^2J(P–C) = 27.4 Hz, C5), 43.2 (d, ^1J(P–C) = 43.9 Hz, C6), 46 (d, ^1J(P–C) = 69.4 Hz, C7), 51.1 (s, OCH_3), 52.2 (s, OCH_3), 54.3 (s, C4), 127.2–132.6 (m, Ph + C2), 155.5 (d, ^2J(P–C) = 17.8 Hz, C3), 169.6 (d, J(P–C) = Hz, >C=O) 170.5 ppm (d, J(P–C)= 18.8 Hz, >C=O); ^{31}P{^{1}H} NMR ($CDCl_3$) δ 51.9 ppm; MS, *m/z* (relative intensity) 349 (M, 10), 205 (M–dimethyl maleate, 100): Anal. Calcd for $C_{18}H_{21}O_5P$: C, 62.07; H, 6.07. Found: C, 62.21; H, 5.82.

2,5-*endo*,6-*exo*-Triphenyl-3,4-dimethyl-1-phosphabicyclo[2.2.1]hept-2-ene *P*-oxide (6a*): yellow crystals (yield 18%); ^{1}H NMR ($CDCl_3$) δ 1.32 (s, 3 H, Me), 1.58 (d, ^4J(P–H) = 2.5 Hz, 3 H, Me), 1.84–2.32 (m, ^2J(P–H) = 9.8 Hz, 2 H, CH_2), 3.29 (d, ^3J(H–H) = 6.6 Hz, 1 H, H_α), 3.71 (d, ^3J(H–H) = 6.6 Hz, 1 H, H_β), 7.12–7.5 ppm (m, 15 H, Ph × 3); ^{13}C NMR ($CDCl_3$) δ 15.5 (d, ^3J(P–C) = 13.1 Hz, Me), 19.6 (d, ^3J(P–C) = 18.2 Hz, Me), 44.1 (d, ^2J(P–C) = 27.1 Hz, C5), 46.5 (d, ^1J(P–C) = 57.3 Hz, C6), 48.8 (d, ^1J(P–C) = 65.5 Hz, C7), 61.0 (d, ^2J(P–C) = 4.4 Hz, C4), 126.6–138.2 (m, Ph × 3 + C2), 155.2 ppm (d, ^2J(P–C) = 16.6 Hz, C3); ^{31}P{^{1}H} NMR ($CDCl_3$) δ 51.9 ppm; MS, *m/s* (relative intensity) 384 (M, 25), 204 (M – stilbene, 100).

2,5-*endo*-Diphenyl-3,4-dimethyl-6-*exo*-(hydroxymethyl)-1-phosphabicyclo[2.2.1]hept-2-ene *P*-Sulfide (8a*). Cinnamyl alcohol (3.6 mL, 29.9 mmol) was added at 120 °C to

a stirred solution of 1 (5 mL, 26.6 mmol) in 4 mL of xylene. Refluxing xylene was required for 3 h. The resulting mixture was then allowed to cool down and when the temperature was ca. 100 °C, 900 mg of S_8 (29 mmol) were added. Solvent was removed, leaving a yellow oil that was chromatographed with hexane/dichloromethane (20:80) as eluent. **8a*** was first eluted and, then, a mixture of **8a*** + **8b***. Pure **8a*** was crystallized in hexane (white crystals, mp = 156–158 °C); yield 50%. Overall yield of **8a*** + **8b*** was 75%.

8a*: ^{1}H NMR ($CDCl_3$) δ 1.26 (s, 3 H, Me), 1.48 (d, ^4J(P–H) = 2.4 Hz, Me), 2.0 (s, 1 H, OH), 2.12–2.29 (m, 2 H, CH_2), 2.5–2.6 (m 1 H, H_α), 2.98 (d, $^3J(H_\alpha–H_\beta)$ = 6.1 Hz, 1 H, H_β), 3.8–4.2 (m, 2 H, CH_2OH), 7.06–7.45 ppm (m, 10 H, Ph × 2); ^{13}C NMR ($CDCl_3$) δ 15.8 (d, ^3J(P–C) = 12 Hz, Me), 19.4 (d, ^3J(P–C) = 16.6 Hz, Me), 46.7 (d, ^1J(P–C) = 45.8 Hz, C6), 50.1 (d, ^2J(P–C) = 20 Hz, C5), 52.5 (d, ^1J(P–C) = 54 Hz, C7), 54.4 (s, OCH_2 or C4), 60.7 (s, C4 or OCH_2), 126.0–138.0 (m, Ph × 2 + C2), 155.1 ppm (d, ^2J(P–C) = 14.1 Hz, C3); ^{31}P{^{1}H} NMR ($CDCl_3$) δ 55.3 ppm; MS, *m/z* (relative intensity) 354 (M, 30), 220 (M – cinnamyl alcohol, 100).

X-ray Structure Determination for 4a*. Crystals of **4a*** were obtained by slow diffusion of pentane into a dichloromethane solution of the compound. Data were collected at 18 ± 1° on an Enraf Nonius CAD 4 diffractometer. The crystal structure was solved and refined by using the Enraf Nonius supplied SDP package. The compound crystallizes in space group *P*-1, a = 7.434 (1) Å, b = 16.129 (2) Å, c = 17.509 (2) Å, α = 79.03 (1)°, β = 77.74 (1)°, γ = 76.67 (1)°, v = 1974.13 (54) Å^3; Z = 4; d_{calcd} = 1.266 g/cm^3; Mo K_α radiation (λ = 0.71013 Å) graphite monochromator; μ = 1.6 cm; $F(000)$ = 800. The asymmetric unit contains two independent molecules, corresponding to the *R* and *S* enantiomers. A total of 6909 unique reflections were recorded in the range 2° ≤ 2θ ≤ 50° of which 3422 were considered as unobserved ($F^2 < 3\sigma(F^2)$), leaving 3487 for solution and refinement. The structure was solved by direct methods, yielding a solution for 13 atoms. The hydrogen atoms were introduced as fixed contributors in the final stages of refinement while using anisotropic temperature factors for all other atoms. A non-Poisson weighting scheme was applied with a *p* factor equal to 0.08. The final *R* factors were R = 0.040, R_W = 0.056, G.O.F. = 1.17.

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Supplementary Material Available: Tables of atomic coordinates, thermal parameters, bond lengths, and bond angles for **4a*** (7 pages); structure factor tables for **4*** (19 pages). Ordering information is given on any current masthead page.

Correlations of Stereochemistry and Heteroatom Configurations with ^{17}O Chemical Shifts in Substituted 1-Hetera-4-cyclohexanones

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The ^{17}O chemical shifts for the oxygen atom of the carbonyl group [C=^{17}O] have been measured for several substituted 1-hetera-4-cyclohexanones and selected 3,7-diheterabicyclo[3.3.1]nonan-9-ones in D_3CCN/H_3CCN at 70 °C. The heteroatoms included N, O, S, Se, and P. Sharp trends in shielding and deshielding for C=^{17}O were observed with substituents at various positions. For example, deshielding effects are detected when phenyl or methyl groups are present at the 2,6-positions (α to the C=O). Increased deshielding was observed in the case of *trans*-2,6-diphenyl analogues as compared with the *cis*-2,6-diphenyl analogues. A *shielding* effect was seen when methyl groups were present at the 3,5-positions (β to the C=O). Negligible changes in C=^{17}O chemical shifts occurred in 1-aza and 1-oxa analogues as compared with cyclohexanone. In contrast, the sulfur, selenium, and phosphorus analogues showed a significant *downfield* shift for C=^{17}O as compared to cyclohexanone. For certain 3,7-diheterabicyclo[3.3.1]nonan-9-ones, a *shielding* effect on the C=^{17}O resonance was seen which was reminiscent of the effect elicited with substituents at the 3,5-positions (α to the C=O) in the 1-hetera-4-cyclohexanones. Interestingly, the related system tropinone, as compared to that in *N*-methyl-4-piperidinone, showed a *deshielding* for C=^{17}O which was quite similar to that found in 2,6-substituted (β to the C=O) 1-hetera-4-cyclohexanones compared to the corresponding parent 1-hetera-4-cyclohexanone. This suggests that the piperidinone ring in tropinone exists in a chair form in D_3CCN/H_3CCN at 70 °C.

Introduction

The use of ^{17}O NMR spectroscopy as a method to diagnose a variety of structural problems in oxygen-containing, organic systems is increasing rapidly.[1-4] In recent years, Boykin and co-workers[5-10] have shown that correlations exist between ^{17}O chemical shifts and an internal torsion angle [or perhaps van der Waals interactions] for aromatic nitro compounds,[5] acetophenones,[6] 3-substituted phthalic anhydrides,[7] aromatic carboxylic acids and derivatives,[8] certain aryl ketones,[9] and multisubstituted phthalimides.[10] Crandall and co-workers[11] reported C=^{17}O chemical shifts for several substituted cyclohexanones and indicated that substituent effects depended upon the di-

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