acetamidine **18** was extracted with chloroform and after evaporation of the solvent the residue was chromatographed on a column of alumina (eluent benzene).

A stirred suspension of **18** (0.2 g) and lead tetraacetate (0.8 g) in 20 ml of anhydrous benzene was refluxed for 20 min. The hot solution was filtered and cooled and 20 ml of 30% aqueous sodium hydroxide was added. The product was extracted with chloroform, the solvent evaporated, and the separated compound **2c** purified by chromatography on alumina (eluent chloroform).

Acknowledgment. The authors wish to thank Professor M. Tisler for his comments and helpful discussions concerning the manuscript of this article.

Registry No.—**5a**, 874-40-8; **5b**, 875-84-3; **5c**, 19542-10-0; **5d**, 877-27-0; **9** (R = H), 23160-99-8; **9** (R = Me), 54557-76-5; **10a**, 28735-23-1; **10b**, 28735-26-4; **10c**, 19542-09-7; **11**, 61140-00-9; **12**, 61140-01-0; **13**, 61140-02-1; **13** HCl, 61140-03-2; **14a** HCl, 21126-64-7; **15a**, 1120-99-6; **15b**, 18915-36-1; **15c**, 17584-12-2; phosphorus pentasulfide, 1314-80-3; 3,7-dimethyl-7,8-dihydro-*s*-triazolo[4,3-*b*]-*as*-triazine, 61140-04-3; 6,7-dimethyl-7,8-dihydro-*s*-triazolo[4,3-*b*]-*as*-triazine, 61140-05-4; ethanedial, 107-22-2; 2-oxopropanal, 78-98-8; 2,3-butanedione, 431-03-8; 3-chloro-*s*-triazolo, 6818-99-1; chloroacetone, 78-95-5; *N*,*N*-dimethylformamide, 68-12-1; acetamide, 60-35-5; 3-formylamino-*as*-triazine, 61140-06-5.

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Phosphorus-Containing Cyclohexanes. Stereochemical Analysis of *cis*- and *trans*-2-Phenyl-2-oxo-5-*tert*-butyl-1,3,2-dithiaphosphorinanes

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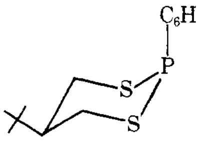
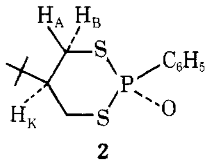
Assignments of configuration to *cis*- and *trans*-2-phenyl-2-oxo-5-*tert*-butyl-1,3,2-dithiaphosphorinanes (**2** and **3**) were accomplished through analysis of ^{1}H NMR spectral data and an LIS study with Eu(fod)$_3$. Cis diastereomer **2** was found to be conformationally heterogeneous with a considerable contribution made to the conformational equilibrium by the twist-boat conformer **4c**; the other major conformer was the chair structure with equatorial *tert*-butyl and axial phenyl groups. Complexation of **2** with Eu(fod)$_3$ had no significant influence on the conformational distribution. Trans diastereomer **3** adopted essentially one chair conformation with equatorial *tert*-butyl and phenyl substituents.

Although substituents attached to carbon or nitrogen atoms in saturated six-membered rings usually prefer an equatorial orientation, the same groups display this tendency to a much weaker degree when attached to other atoms such as sulfur,[1] phosphorus,[2-4] selenium,[5a] and arsenic;[5b] in fact, axial preferences are often encountered. This conformational novelty has stimulated much interest and study,[6] especially with regard to diverse phosphorus-containing cyclohexane systems.[2-4,7]

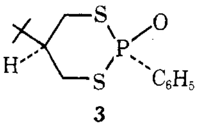
Previously, we reported[4a] that the more stable isomer (85% at 200 °C; ca. 97% at 25 °C) of 2-phenyl-5-*tert*-butyl-1,3,2-dithiaphosphorinane (**1**) possesses a cis configuration with the *P*-phenyl group axially disposed. In order to further support the stereochemical assignment, we converted **1** stereospecifically to cis 2-oxo derivative **2** and synthesized the trans diastereomer **3** for comparison. Stereochemical information on these compounds was obtained by ^{1}H NMR spectroscopy and ^{1}H NMR lanthanide-induced shift (LIS) studies. Our results, which yielded configurational assignments for **2** and **3**, as well as an analysis of their conformational behavior, are presented in this article.



1



2



3

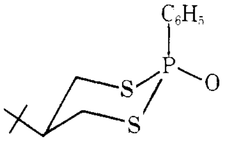
Results and Discussion

Oxidation of **1** with hydrogen peroxide[8] (presumably stereospecific with retention[9]) afforded a single diastereomer (mp 105–106 °C); there was no evidence for the presence of the other possible isomer. Spectral and analytical data were consistent with **2**. The 100-MHz ^{1}H NMR spectrum of **2** exhibited a complex AA′BB′KX (X = ^{31}P) pattern which was treated as an A_2B_2KX approximation[10] to provide the parameters presented in Table I.[11] The nearly identical, middling values of J_{AK} and J_{BK} (e.g., 7.2 and 5.9 Hz) suggest that **2** is a mixture of conformational isomers in solution (CDCl$_3$ and C$_6$D$_6$); the axial and equatorial orientations of H$_A$, H$_B$, and H$_K$ are interchanged, thereby averaging the ^{1}H NMR spectral parameters. This observation can be accommodated by a mixture of chair conformers (**4a** and **4b**), a twist-boat form (**4c**), or an equilibrium mixture of chair and boat forms.

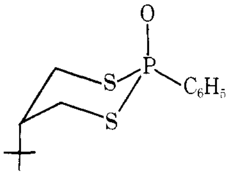
Table I. ^{1}H Nmr Data at 100 MHz for 2 and 3[a]

Compd	δH_K	$\delta H_A{}^f$	$\delta H_B{}^f$	δt-Bu	J_{AK}	J_{BK}	J_{AX}	J_{BX}	$J_{AX} + J_{BX}$
2[b]	2.07	2.97	3.29	0.96	7.3	5.9	14.2	22.2	36.5
2[c,d]	1.63	2.59	2.94	0.55	7.2	6.0	14.5	22.5	37.0
3[b]	2.01	3.45	3.20	1.01	9.4	3.5	12.7	19.9	32.6
3[e]	1.66	3.13	2.64	0.56	9.6	3.5	11.6	19.6	31.2

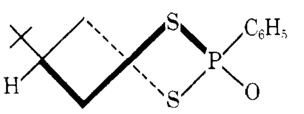
[a] Chemical shifts are reported in parts per million downfield from Me_4Si. J values are in hertz. J_{AB} was 14.0 ± 0.5 Hz. Spectral data were obtained at 100 MHz, except as noted. [b] Measured in $CDCl_3$. [c] Measured in C_6D_6. [d] The parameters defining the A_2B_2KX pattern were used as input for the LAOCN3 NMR program. The computed spectrum agreed well with the experimental spectrum (21 lines) with iteration. [e] Recorded at 60 MHz. [f] A reversal in the relative order of the chemical shifts of H_A and H_B is observed.



4a



4b



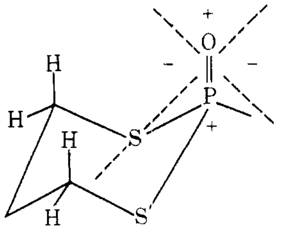
4c

Evidently, the expected axial preference of an oxygen on phosphorus vs. a phenyl group[12] competes effectively with the equatorial preference of the 5-*tert*-butyl group; the result is a mixture of conformers **4a, 4b,** and/or **4c.**

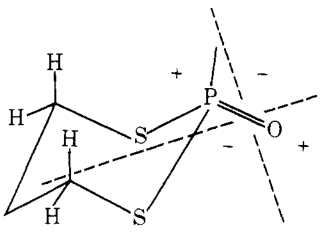
Condensation of 2-*tert*-butyl-1,3-propanedithiol with phenylphosphonic dichloride gave mostly the other possible stereoisomer **3** (mp 141.5–142.5 °C). The 100-MHz ^{1}H NMR spectrum of **3** revealed an AA′BB′KX (X = ^{31}P) pattern which provided the parameters in Table I when approximated as an A_2B_2KX spin system. The large J_{AK} (9.7–10.0 Hz, $H_{4,6\text{-axial}}$–$H_{5\text{-axial}}$ coupling) and small J_{BK} (3.6–3.8 Hz, $H_{4,6\text{-equat}}$–$H_{5\text{-axial}}$ coupling) are typical for a highly biased equilibrium favoring a chair conformer with the *tert*-butyl group equatorial. This analysis is consistent with the $^3J_{PSCH}$ values for **3** (Table I).[11b] Given the aforementioned axial preference of the phosphoryl group against the phenyl group,[12] the conformational bias for **3** suggests that **3** has the trans configuration.

The downfield shift of the axial 4,6 protons (H_A) relative to the equatorial 4,6 protons (H_B) in **3** (Table I) can be explained by a predominant axial disposition of the phosphoryl group. This reversal in the relative order of the chemical shifts of H_A and H_B (cf. **2** and **3**) is similar to that reported for *cis*- and *trans*-2-oxo-5-*tert*-butyl-1,3,2-dioxaphosphorinanes.[2,13,14] Deshielding of protons in proximity to a phosphoryl group, as in **3**, is apparently a general phenomenon[15] and is analogous to the action of the sulfinyl moiety in cyclic sulfites.[16]

In an axial position, the P=O bond exerts a deshielding influence on *both* sets of 4,6 protons and, conversely, in an equatorial position it exerts a shielding influence (see diagram below). In either circumstance, it is the axial set of 4,6 protons which senses a greater effect, because of proximity in the case of an axial P=O, and directionality in the other case. A conformational equilibrium between chair structures or a twist form would naturally tend to average this effect. In **3** the axial protons resonate at a lower field than the equatorial protons and at a lower field than either set of 4,6 protons in **2** (same solvent for comparison). This qualitative result agrees with a predominantly axial P=O bond in **3.** On the contrary, the axial 4,6 protons in **2** resonate at a higher field than the equatorial protons, which indicates a fair amount of the equatorial phosphoryl conformation **4a** and strongly militates against a significant contribution from **4b.** The shielding of H_A in **2** may be reinforced by the axial phenyl group in **4a.**[17] The tentative inference is that stereoisomer **2** is chiefly composed of a fairly balanced mixture of **4a** and **4c,** to the virtual exclusion of **4b.**



first case—axial P=O



second case—equatorial P=O

The oxygen of the phosphoryl group in **2** and **3** provides a handle for obtaining additional structural information by complexation of it with lanthanide shift reagents, the use of which in the evaluation of molecular spatial arrangements is well established.[19] Tris(1,1,1,2,2,3,3-heptafluoro-7,7-dimethyl-4,6-octanedionato)europium (III), $Eu(fod)_3$, was employed[20] and the induced proton shifts were monitored. Upon treatment of a solution of **3** with incremental amounts of $Eu(fod)_3$ all protons experienced the usual accompanying downfield shift as the shift reagent complexed the strongly basic phosphoryl oxygen.[21] A plot of the chemical shifts of H_A, H_B, and H_K vs. added $Eu(fod)_3$ (Figure 1) demonstrates that the axial 4,6 protons (H_A) were deshielded to a much greater extent than H_B and H_K. This can only be consistent with a predominantly axial position of the phosphoryl group, which brings the Eu complex in proximity with the syn-axial protons. Analogous results and conclusions have been reported for *trans*-2-methyl-2-oxo-5-*tert*-butyl-1,3,2-dioxaphosphorinane[13] and related compounds.[14b,15b,19e-g]

Treatment of **2** with incremental amounts of $Eu(fod)_3$ also caused downfield shifts of the three sets of 4,6 and 5 protons (Figure 1) but in this case all sets were deshielded to approximately the same degree. In fact, the 4,6 protons were shifted about the same extent as the equatorial protons in **3** (see sensitivity values in Table II). Apparently, the chair conformer with an axial P=O (**4b**) must not make an appreciable contribution to the conformational profile of **2,** otherwise the contiguity of the europium atom to H_A should have induced a greater average deshielding for this pair of protons, as for **3.** Thus, cis diastereomer **2** exists in a conformation or conformations in which the remote 4,6 protons (H_A and H_B) are located at similar average distances from the phosphoryl oxygen. This condition is satisfied by the flexible twist form **4c** or possibly a mixture of **4c** and chair form **4a.** The relatively large chemical shift differences for H_A and H_B, Δ_{AB}, suggest the latter interpretation since pseudorotation in flexible forms usually averages chemical shifts to a greater extent.[22] The ^{1}H NMR data for the LIS studies are collected in Table II.

In view of the substantial amount of twist form apparently present in **2,** the following summation obtains. The unfavorable disposition of the groups on phosphorus in **2** (axial phenyl

Table II. ^{1}H NMR Eu(fod)$_3$-Shift Data for 2 and 3[a]

Compd[b]	Mg Eu(fod)$_3$	νt-Bu	νH_A	νH_B	νH_K	J_{AK}	J_{BK}	J_{AX}	J_{BX}	Δ_{AB}
2	0	42.2	162.8	181.2	106.0	7.4	6.3	14.5	21.7	18.5
	10	46.0	186.9	213.3	123.0					26.3
	20	56.5	205.5	237.9	137.8					32.4
	25	60.0	216.2	252.4	145.2					36.2
	35	66.6	236.2	278.2	161.0					42.1
	40	69.0	243.4	288.0	166.8	7.0	6.5	15.0	24.0	44.6
		48.5[c]	145.9[c]	193.4[c]	110.1[c]					
3	0	45.0	199.4	174.0	107.5	9.8	3.7	12.1	20.2	25.4
	10	60.0	275.2	203.8	139.0					71.4
	20	73.7	346.0	230.0	167.5					116.0
	25	78.3	371.0	239.0	178.0	10.8	3.0	12.8	21.0	132.0
		96.5[c]	497.1[c]	188.3[c]	204.2[c]					

[a] The LIS study was carried out at 60 MHz. Coupling constants are in hertz and have an estimated error of ≤±0.5 Hz. The proton frequencies are reported in hertz downfield from Me$_4$Si. $\Delta_{AB} = \nu_A - \nu_B$. J_{AB} varied between 13.7 and 14.2 Hz. [b] Solutions were 0.155 M in 1:1 CCl$_4$–C$_6$D$_6$. [c] Sensitivity given in proton shift (Hz) per molar equivalent of Eu(fod)$_3$.

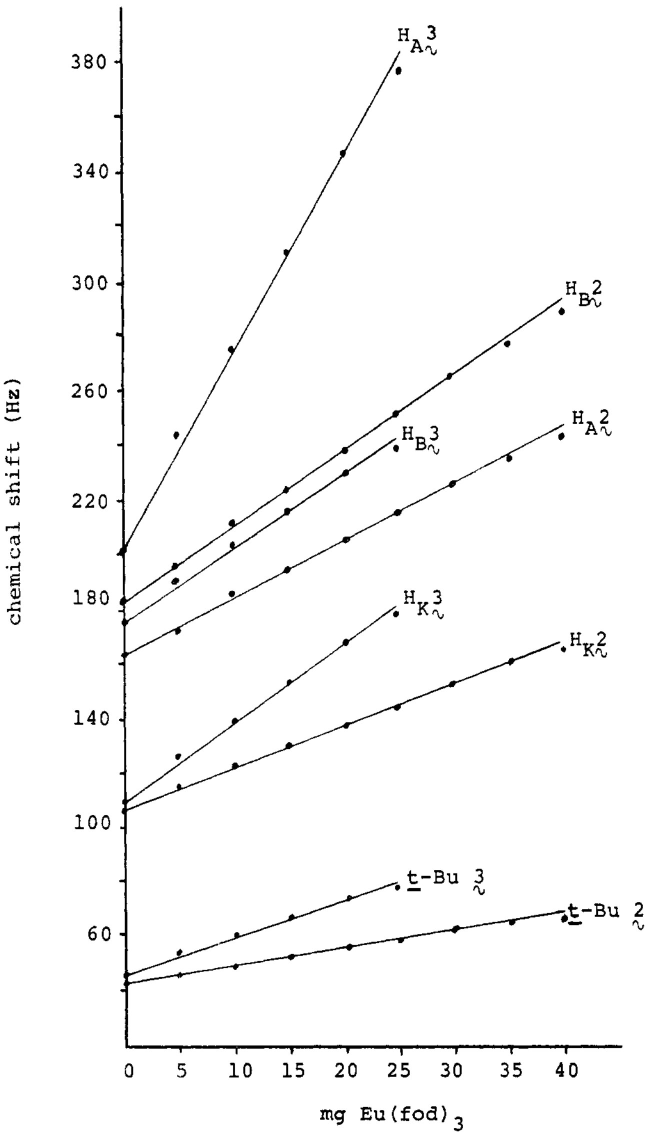


Figure 1. Induced chemical-shift changes upon incremental addition of Eu(fod)$_3$ to solutions of **2** and **3**.

and equatorial phosphoryl) is enough to force the molecule to adopt a necessarily low energy (perhaps as low as ca. 0.5 kcal/mol) twist conformer[23] to a large extent with the virtual exclusion of any axial phosphoryl–axial *tert*-butyl form. The low energy twist conformation is in agreement with the results of Bentrude and co-workers on 1,3,2-dioxaphosphorinane derivatives.[2,24]

By employing the europium-shift technique the configurational assignments for the title stereoisomers have been bolstered. Moreover, important conformational information has been obtained on one of the isomers, namely **2**, which is conformationally heterogeneous. It is noteworthy that the conformational equilibrium is not altered by complexation of **2** with Eu(fod)$_3$ as evidenced by the nearly identical vicinal H–H coupling constants with and without added Eu(fod)$_3$ (see Table II). Both $^3J_{PSCH}$ values follow suit, although they are observed to increase slightly with increasing Eu(fod)$_3$ concentration.[25] This conformational consistency with the addition of shift reagent is in harsh contrast to observations of Bentrude and co-workers with the *cis*-2-oxo-1,3,2-dioxaphosphorinanes,[14b,19e] in which complexation generally caused a concomitant displacement in the conformational equilibria.

Phosphorus-31 chemical shifts were measured for **2** and **3**. The values of −55.1 and −47.3 ppm for the cis and trans isomers, respectively, illustrate that the different configurations engender a large (8 ppm) difference in δ^{31}P. The resonance of trans isomer **3** at higher field than cis isomer **2** is opposite to the order of resonance for pairs of (corresponding[26]) cis/trans isomers of 5-*tert*-butyl-1,3,2-dioxaphosphorinanes,[19e] 5-*tert*-butyl-2-oxo-1,3,2-dioxaphosphorinanes,[19e] 1-methyl-4-*tert*-butyl-4-phosphoranol,[3d] and 2-phenyl-5-methyl-1,3,2-dithiaphosphorinanes.[4b] The meaning of this result is not clear at this point, but the anomalous chemical shift order may be attributable to a large proportion of twist boat conformer present in **2** in solution. Additional ^{31}P NMR data for other 2-oxo-1,3,2-dithiaphosphorinane derivatives is required to illuminate this problem.

Conclusion

Assignment of the cis configuration to **2**, through analysis of ^{1}H NMR spectral and europium-shift data for **2** and **3**, supports the cis assignment advanced for **1**,[4a,b] with its axial phenyl substituent. By extension, the suggestion of an axial preference for a variety of P substituents (CH$_3$, C$_2$H$_5$, OCH$_3$, Cl, C$_6$H$_5$) in the 1,3,2-dithiaphosphorinanes is reinforced.[4a,b] Cis diastereomer **2** is conformationally heterogeneous in solution and the twist-boat conformation is populated to a considerable extent. Complexation of **2** with the europium-shift reagent Eu(fod)$_3$ had a negligible effect on the conformational equilibrium.[27]

Experimental Section

All melting points (determined on a Mel-Temp hot-stage apparatus) and boiling points are uncorrected. Infrared spectra were recorded on a Perkin-Elmer Model 457 spectrophotometer. Proton nuclear magnetic resonance spectra were obtained on Varian A-60 and HA-100 spectrometers. Chemical shifts are reported in parts per million downfield from tetramethylsilane (internal reference); coupling constants are reported in hertz. Proton decoupling was achieved on the HA-100 instrument; europium-shift studies were carried out at 60 MHz. Phosphorus-31 NMR spectra were recorded at 40.5 MHz on a HA-100 spectrometer using a reference capillary containing 85% H_3PO_4. The spectra were calibrated by the sideband technique.[28] The ^{31}P chemical shifts are an average of at least two scans and have a standard deviation of about ±0.3 ppm. Analyses of ^1H NMR spectra were performed using a modified version of the LAOCN3 NMR program;[29] calculated spectra were plotted by assigning a Lorentzian line shape.[30] Determination of the chemical shifts of A and B protons of AB patterns was performed by utilizing the following equation: $\Delta\nu_{AB} = \sqrt{(\nu_1 - \nu_4)(\nu_2 - \nu_3)}$.[31]

Mass spectra were recorded on a Perkin-Elmer Hitachi RMU-6 mass spectrometer at an electron energy of 70 eV. Microanalyses were performed by Alfred Bernhardt Mikroanalytisches Laboratorium, West Germany. Molecular weight determinations (osmometry in benzene) were made by Schwartzkopf Microanalytical Laboratories, Woodside, N.Y.

All reactions involving trivalent phosphorus compounds were conducted under an atmosphere of dry nitrogen. Phenylphosphonic dichloride (phenyldichlorophosphine oxide) was obtained as a free sample from Stauffer Chemical Co. (Specialties), New York, N.Y. Triethylamine was distilled from potassium hydroxide and stored over molecular sieves (3A). Europium $(fod)_3$ was purchased from Pierce Chemical Co., Rockford, Ill., and was stored in a desiccator.

2-*tert*-Butyl-1,3-propanedithiol. This compound was prepared according to the procedure of Eliel and Hutchins.[22] Distillation afforded the product in 60% yield, bp 53–55 °C (0.75–0.85 mm) [lit.[22] bp 40 °C (0.04 mm)], $n^{25}D$ 1.5095. GLC analysis indicated the material to be ca. 94% pure. An improved procedure is now available.[22b]

2-Phenyl-5-*tert*-butyl-1,3,2-dithiaphosphorinane (1). In a 300-ml flask was placed 100 ml of dry ether and triethylamine (8.1 g, 0.080 mol). The flask was fitted with a drying-tube-protected condenser, nitrogen inlet, and two dropping funnels. A magnetic stirring bar was placed in the flask and the contents were cooled to ca. 0 °C in an ice bath. In one funnel was placed 2-*tert*-butyl-1,3-propanedithiol (3.3 g, 0.020 mol) and 40 ml of dry ether; the other was charged with phenyldichlorophosphine (3.6 g, 0.020 mol) and 40 ml of dry ether. Both solutions were added slowly and synchronously to the cold, stirred solution. After addition, the contents were stirred for 1 h while being allowed to warm to ambient temperature. The mixture was filtered and the residue was rinsed with dry ether. The total filtrate was stripped at reduced pressure, leaving an almost colorless oil which solidified on standing in vacuo. The solid was fractionally sublimed (80 °C, 0.0006 mm) and product was collected in portions as indicated in Table III.

A sample of fraction 5 was slowly recrystallized from 70% ethanol to afford shiny, opalescent leaflets, mp 94–95 °C (sharp), which turned out to be pure **1**. Fractions 1, 2, 6, and 7 were combined with the sublimation residue and distilled: bp 159–163 °C (0.08 mm); mp 69–90.5 °C; cis/trans isomer ratio 85/15; IR (KBr) ν_{max} 3070, 3050, 2965, 2930, 2870, 1498, 1473, 1440, 1375, 1230, 1090, 860, 810, 755, 705 cm^{-1}; MS *m/e* (rel abundance) 270 (100, M$^+$).

Anal. Calcd for $C_{13}H_{19}PS_2$: C, 57.74; H, 7.08; P, 11.46. Found: C, 57.66; H, 6.92; P, 11.56.

Stereospecific Oxidation of 1 with 3% Aqueous Hydrogen Peroxide. Phosphine **1** (81 mg, 0.30 mmol) was combined with 1 ml of 3% H_2O_2 and 2 ml of CH_2Cl_2 under an atmosphere of nitrogen. The mixture was stirred for 12 h at ambient temperature. The CH_2Cl_2 solution was separated by pipet and the solvent was evaporated. The resultant colorless oil crystallized upon treatment with *n*-pentane. The white solid was recrystallized by adding enough ether to dissolve it warm and then cooling to 0 °C. The yield of long, gleaming needles, mp 105–106 °C, was 68 mg. Concentration and cooling of the mother liquor yielded another 10 mg, for a total yield of 78 mg (91%). This material proved to be **2**, IR (KBr) ν_{max} (P=O) 1202 cm^{-1}. Sublimation furnished an analytical sample. Mol wt (osmometry in benzene): calcd, 286; found, 279.

Anal. Calcd for $C_{13}H_{19}OPS_2$: C, 54.52; H, 6.69. Found: C, 54.36; H, 6.84.

Table III

Fraction	Yield, g	Mp, °C
1	0.360	
12	0.23	
3	1.22	84.5–91.5
4	0.56	84–91
5	0.90	84–90.5
6	0.68	76–90
7	0.18	
	4.13	

Reaction of 2-*tert*-Butyl-1,3-propanedithiol with Phenyldichlorophosphine Oxide. In the manner described for the preparation of **1**, 2-*tert*-butyl-1,3-propanedithiol (0.82 g, 5.0 mmol) in dry ether (20 ml) and phenyldichlorophosphine oxide (0.98 g, 5.0 mmol) in dry ether (20 ml) were added slowly to an ice-cooled solution of triethylamine (2.02 g, 0.020 mol) in dry ether (20 ml). After addition, the reaction mixture was stirred for 3 h at ambient temperature and then filtered. the filter cake was washed with 25 ml of dry ether–THF (1:1). The cooled filtrate deposited a white solid which was filtered off; it weighed 35 mg and had mp 137–140 °C. To the clean filtrate was added 20 ml of *n*-pentane and the solution was cooled to 0 °C and filtered, giving 40 mg of solid, mp 137–139 °C. The filtrate was concentrated and minute, prismatic needles separated from solution; these were filtered off with the assistance of an ice-cold mixture of ether–pentane (2:1). This crop weighed 0.371 g and had mp 134–138 °C. A fourth fraction was obtained, 0.256 g, mp 86–91 °C. A portion of the third crop was recrystallized from hexane–ethyl acetate (1:1) as colorless, clear, elongated prisms (very slow) or prismatic needles (faster). The first subcrop had mp 141–142.5 °C; the second had mp 140–141.5 °C. The first-crop material proved to be pure **3**, IR (KBr) ν_{max} (P=O) 1195 cm^{-1}. Mol wt (osmometry in benzene): calcd, 286; found 283.

Anal. Calcd for $C_{13}H_{19}OPS_2$: C, 54.52; H, 6.69. Found: C, 54.39; H, 6.62.

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Registry No.—*cis*-**1**, 61009-66-3; *trans*-**1**, 61009-67-4; **2**, 61009-68-5; **3**, 61009-69-6; 2-*tert*-butyl-1,3-propanedithiol, 24330-57-2; phenyldichlorophosphine, 644-97-3; phenyldichlorophosphine oxide, 824-72-6.

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(25) There is precedent for an increase in ^{31}P–H coupling constants in phosphoryl compounds upon complexation with transition metals.[21a]

(26) The cis/trans designation *may vary from compound to compound. In the* discussion, we are comparing compounds correspondent by their alkyl/phenyl or alkyl/alkyl substitution.

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Preparation, Stereochemistry, and Nuclear Magnetic Resonance Spectroscopy of Methyl 1,3-Dimethyl-2-oxocyclohexaneacetates and Related Derivatives

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The two diastereomeric methyl 1,3-dimethyl-2-oxocyclohexaneacetates, **9b** and **10b**, as well as the related epimeric derivatives (**2–7**) have been prepared and their stereochemistry rigorously established via chemical correlation with the previously known enone **8**. During the correlation, oxidative cleavage of a variety of carbon–carbon double bonds was effected with $RuO_4/NaIO_4$ without concomitant epimerization either at incipient or remote ketone functionalities. Finally, the stereochemical assignments, in accord with the 60- and 220-MHz NMR spectral data, require reversal of the assignment previously made by Muller and Jeger[5] for diastereomers of **7**.

During the course of our studies on the thermal[1] and acid-catalyzed[2] decomposition of β,γ-unsaturated diazo ketones, we required an efficient approach to authentic samples of both diastereomers of methyl 1,3-dimethyl-2-oxocyclohexaneacetate (**1**). In this report we wish to document the preparation and rigorous stereochemical assignment of these esters as well as the related epimeric derivatives (**2–7**). Our stereochemical assignment involves a chemical correlation of **1–7** with the well-known enone (**8**) prepared first by the Marshall group[3] and improved several years later by Caine and co-workers.[4] Interestingly, the diastereomers of **7** were recently isolated and their structures defined employing NMR criteria.[5] The present chemical interrelationships require the reversal of these assignments. Finally, we note the synthetic utility of $RuO_4/NaIO_4$ in aqueous acetone for the oxidative cleavage of olefinic bonds without concomitant epimerization either at incipient or remote carbonyl functionalities.[6]

Our synthetic approach to the diastereomers of **1** involves the facile monoalkylation of 2,6-dimethylcyclohexanone with allyl bromide, utilizing lithium diisopropylamide as the base.[7] The resultant epimeric ketones **9a** and **10a**, produced in equal amounts, were each fully characterized after separation via vapor phase chromatography (VPC). Subsequent oxidation[6] of **9a** and **10a** with $RuO_4/NaIO_4$ in aqueous acetone followed by diazomethane esterification of the resultant acids provided **9b** and **10b**, the desired diastereomers of **1**. In each case, oxidation yielded only a single γ-keto ester, demonstrating that the oxidation conditions do not result in equilibration. On the