1.67–1.31 (6 H, m, H-7, 2 H-14, 2 H-4′, H-2″ax), 1.28–1.16 (10 H, m, H-7, Me, 2-Me, 5″-Me), 1.14 (6 H, m, Me, 5′-Me), 1.09 (6 H, m, Me, 8-Me), 1.04 (3 H, d, *J* = 7.3 Hz, 4-Me), and 0.86 (3 H, t, *J* = 7.1 Hz, 3 H-15) ppm; ^{13}C ($CDCl_3$) δ 175.7, 139.5, 132.5, 128.8, 127.3, 100.9, and 94.4 ppm; IR (film) 3480, 2930, and 1730 cm^{-1}; FABMS (Li spike) *m/z* 823 (M^+ + Li), 817 (M^+ + 1); FABHRMS calcd for $C_{40}H_{68}LiN_2O_{13}S$ (M^+ + Li) 823.4602, found 823.4623.

10-Aza-10-demethyl-11-deoxyerythromycin A (18).[21] Naphthalene (0.5 g, 3.9 mmol) was dissolved in THF (3.9 mL, 1.0 N) at room temperature, and freshly cut lithium pieces (55 mg, 2 equiv) were added. The mixture was sonicated for 45 min. Portions of this solution of lithium naphthalenide were added dropwise to a solution of the sulfonamide 17 (80 mg, 96 μmol) in THF (1.0 mL, 0.1 N) maintained at −78 °C, until the deep green color of the reagent was no longer quenched. The mixture was allowed to stir for a further 10 min before quenching with aqueous $NaHCO_3$ solution and allowing to warm to room temperature. K_2CO_3 solution was added and the mixture extracted with CH_2Cl_2. The organics were dried over $MgSO_4$, filtered, and concentrated. The residue was crudely chromatographed (95/5 CH_2Cl_2/MeOH; 90/10/1 CH_2Cl_2/MeOH/NH_4OH) to remove naphthalene. The resulting clear oil was dissolved in $CHCl_3$ (2 mL, 0.05 N). Formaldehyde (31 μL of 37% aqueous solution, 4 equiv) was added followed by formic acid (7.3 μL, 2 equiv) and the mixture heated to 60 °C. After 90 min (TLC 90/10/1 CH_2Cl_2/MeOH/NH_4OH) it was cooled to room temperature, diluted with aqueous K_2CO_3 solution, and extracted with CH_2Cl_2. The organics were dried over $MgSO_4$, filtered, and concentrated. The residue was chromatographed (95/5/1–90/10/1 CH_2Cl_2/MeOH/NH_4OH) to give the lactam 18 (21 mg, 31%) as a clear oil (which could be lyophilized from benzene to give a white powder): ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.81 (1 H, d, *J* = 9.1 Hz, NH), 4.78 (1 H, d, *J* = 11.3 Hz, H-13), 4.72 (1 H, d, *J* = 4.5 Hz, H-1″), 4.61 (1 H, d, *J* = 7.2 Hz, H-1′), 4.30 (1 H, d, *J* = 2.9 Hz, H-3), 4.16 (1 H, ddd, *J* = 14.4, 10.5, 1.9 Hz, H-11), 4.06 (1 H, dq, *J* = 9.5, 6.2 Hz, H-5″), 3.90 (1 H, br s, OH), 3.86 (1 H, d, *J* = 5.5 Hz, H-5), 3.56 (1 H, m, H-5′), 3.34 (3 H, s, OMe), 3.30 (1 H, dd, *J* = 10.2, 7.2 Hz, H-2′), 3.01 (1 H, t, *J* = 9.8 Hz, H-4″), 2.66 (1 H, d, *J* = 14.4 Hz, H-11), 2.60–2.40 (3 H, m, H-2, H-8, H-3′), 2.36 (1 H, d, *J* = 15.4 Hz, H-2″eq), 2.30 (6 H, s, NMe_2), 2.17 (1 H, d, *J* = 10.3 Hz, 4″-OH), 2.13 (1 H, d, *J* = 2.0 Hz, 2′-OH), 2.00 (1 H, m, H-14), 1.85 (1 H, dd, *J* = 15.3, 10.5 Hz, H-7), 1.81 (1 H, m, H-4), 1.68 (1 H, br d, *J* = 12.5 Hz, H-4′), 1.62 (1 H, d, *J* = 15.4 Hz, H-7), 1.54 (1 H, dd, *J* = 15.3, 5.0 Hz, H-2″ax), 1.48 (1 H, m, H-14), 1.41 (3 H, d, *J* = 6.4 Hz, 8-Me), 1.32 (3 H, d, *J* = 6.2 Hz, 5″-Me), 1.28–1.18 (13 H, m, H-4′, Me, Me, 2-Me, 5′-Me), 1.13–1.08 (6 H, m, Me, 4-Me), and 0.83 (3 H, t, *J* = 7.3 Hz, 3 H-15) ppm; ^{13}C ($CDCl_3$) δ 178.3, 176.9, 101.9 and 94.9 ppm; IR (film) 3465, 3370, 2970, 2940, 1715, and 1660 cm^{-1}; FABMS (Li spike) *m/z* 711 (M^+ + Li). Anal. Calcd for $C_{35}H_{64}N_2O_{12}$: C, 59.64; H, 9.15; N, 3.97. Found: C, 59.36; H, 9.13; N, 3.78.

10-Aza-9-deoxo-11-deoxyerythromycin A (5). Protected azalide **20a/b** (160 mg, 0.2 mmol) was dissolved in 1/1 THF/MeOH (4.0 mL, 0.05 N), and KH_2PO_4 (933 mg, 35 equiv) was added. The mixture was cooled to −20 °C and freshly ground 6% sodium amalgam (1.88 g, 25 equiv) was added in one portion. After 45 min an additional 35 equiv of KH_2PO_4 and 25 equiv of amalgam were added. After a further 45 min (TLC 95/5/1 CH_2Cl_2/MeOH/NH_4OH) the mixture was decanted into aqueous K_2CO_3 solution. The amalgam residue was washed several times with EtOAc, decanting into the aqueous mixture. This mixture was partitioned and the aqueous portion reextracted with EtOAc. The combined organics were dried over $MgSO_4$, filtered, and concentrated. The crude residue was dissolved in MeOH (4.0 mL, 0.05 N) and formaldehyde (79 μL of a 37% aqueous solution, 5 equiv) added. Sodium cyanoborohydride (124 mg, 10 equiv) was added in one portion. After 90 min a further 5 equiv of formaldehyde and 10 equiv of the borohydride were added and the mixture stirred for a further 12 h (TLC 95/5/1 CH_2Cl_2/MeOH/NH_4OH). Aqueous K_2CO_3 was added and the mixture extracted with CH_2Cl_2. The organics were dried over $MgSO_4$, filtered, and concentrated. The residue was chromatographed (95/5 CH_2Cl_2/MeOH; 97.5/2.5/0.5–95/5/1 CH_2Cl_2/MeOH/NH_4OH) to give the azalide 5 (80 mg, 58%) as a clear oil (which could be lyophilized from benzene to give a white powder): ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.83 (1 H, dd, *J* = 10.6, 2.6 Hz, H-13), 4.71 (1 H, br d, *J* = 2.7 Hz, H-1″), 4.54 (1 H, d, *J* = 7.3 Hz, H-1′), 4.48 (1 H, br s, H-3), 4.02 (1 H, dq, *J* = 8.7, 6.5 Hz, H-5″), 3.68 (1 H, d, *J* = 5.1 Hz, H-5), 3.56 (1 H, m, H-5′), 3.30 (3 H, s, OMe), 3.27 (1 H, dd, *J* = 12.2, 4.8 Hz, H-2′), 3.04 (1 H, d, *J* = 3.8 Hz, H-4″), 2.79 (1 H, d, *J* = 13.4 Hz, H-11), 2.59 (1 H, dq, *J* = 7.3, 2.2 Hz, H-2), 2.52 (1 H, m, H-3′), 2.33 (3 H, s, −NMe), 2.29 (6 H, s, −NMe_2), 2.28–2.15 (4 H, m, 2 H-9, H-11, H-2″), 1.92 (2 H, m, H-4, H-8), 1.79 (1 H, dd, *J* = 14.2, 4.4 Hz, H-7), 1.65 (1 H, br d, *J* = 11.3 Hz, H-4′), 1.58 (1 H, dd, *J* = 15.0, 4.8 Hz, H-2″), 1.53 (1 H, m, H-14), 1.33 (1 H, m, H-14), 1.25 (3 H, d, *J* = 6.4 Hz, 5″-Me), 1.23–1.15 (17 H, m, H-4, H-7, 2-Me, 6-Me, 12-Me, 5′-Me, 3″-Me), 1.08 (3 H, d, *J* = 7.3 Hz, Me), 1.03 (3 H, d, *J* = 6.6 Hz, Me), and 0.84 (3 H, t, *J* = 7.3 Hz, 3 H-15) ppm; ^{13}C ($CDCl_3$) 176.6, 103.0, and 95.2 ppm; IR (film) 3460, 2975, 2940, and 1730 cm^{-1}; FABMS *m/z* 705 (M^+ + H). Anal. Calcd for $C_{36}H_{68}N_2O_{11}$: C, 61.34; H, 9.72; N, 3.97. Found: C, 61.11; H, 9.81; N, 3.81.

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Supplementary Material Available: Full listings of ^{13}C and IR data for all compounds included in the Experimental Section, ^{1}H NMR spectra for compounds **9**, **17a/b**, and **20a/b**, ^{13}C NMR spectrum for compound **9**, and full data for compounds **16** and **24** (8 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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[21] While the sodium amalgam procedure is perfectly adequate for the desulfonylation an alternative general procedure is also available and is illustrated here.

Molecular Structure of Phosphonium Ylides

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The structures of 12 phosphonium ylides were completely optimized at the HF/6-31G* level. Use of larger basis sets and electron correlation in optimizing the structures of methylenephosphorane and phosphorane cyclopropylide resulted in little geometric change. The phosphonium ylides can be grouped into two classes: (1) nonstabilized ylides and (2) stabilized ylides. All examples of the nonstabilized ylides have nonplanar ylidic carbon geometries, while the stabilized ylides have planar ylidic carbons. These structures are used to support the concept that the dominant resonance structure is the ylide form.

The question of the nature of the bonding in phosphonium ylides involves the relative contribution of the two resonance structures A, the *ylide* form, and B, the *ylene* form.[1] The short P-C distance (1.66–1.70 Å) of most ylides

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A B

and the fact that the ylidic carbon of many ylides is planar led to the early support of the ylene form.[2-12]

In the past decade, a close reevaluation of the structure and spectroscopic properties resulted in support of the ylide structure. The majority of ylides that have been examined by X-ray crystallography have substituents on the ylidic carbon that act to delocalize the carbanion via resonance.[5-12] A planar carbanion maximizes the resonance delocalization. Schmidbaur's group has recently reported two important crystal structures. The first was of triphenylphosphorane cyclopropylide $Ph_3P{=}C(CH_2)_2$, which has, as its most unusual feature, the cyclopropyl group bent out of plane by 58°.[13] Second, a reinvestigation of the crystal structure of triphenylmethylenephosphorane $Ph_3P{=}CH_2$ revealed that the methylene plane is bent 28° out of plane.[4] Nonstabilized ylides prefer a nonplanar carbon environment, due to the carbanionic character. Schlosser[14] has confirmed this nonplanar carbanion in ^{13}C NMR experiments of a variety of nonstabilized ylides.

Computational chemistry has also contributed to this discussion, but in a limited role. Due to computational limitations, most theoretical studies have been restricted to the parent phosphonium ylide, methylenephosphorane $H_3P{=}CH_2$ (1). Early EHT[15] calculations supported the ylide form, as did ab initio calculations[16,17] using small basis sets. However, more recent calculations using at least split-valence basis sets augmented with polarization functions give a nonplanar carbanion with the HOMO comprised of primarily a carbon p-orbital.[18-22] Schaefer and co-workers[23] have reproduced the large out-of-plane bending in phosphorane cyclopropylide, concluding that the nonplanar structure is electronic in origin.

In this paper, we examine the molecular structure of a series of phosphonium ylides by completely optimizing the geometries at the HF/6-31G* level. We evaluate the proper basis set and computational level needed to produce reasonable agreement with experiment. The nonstabilized ylides all have nonplanar ylidic carbons, and we estimate the energy needed to enforce planarity. Two stabilized ylides are reported and have planar structures. These results are in complete agreement with recent experimental studies.

Computational Method

The geometries of 1–12 were completely optimized at the HF/6-31G* level using the standard routines in GAUSSIAN-90.[24] These structures are shown in Figure 1. All structures were confirmed to be local minima by analytical frequency analysis.[25] To assess the role of basis set size and electron correlation, 1 and 7 were reoptimized using larger basis sets and/or calculational methods incorporating correlation (MP2 and CISD). The resultant geometries of 1 and 7 are listed in Tables I and II, respectively, and a summary of the important geometric parameters of 1–12 at HF/6-31G* are listed in Table III.

We optimized the geometry of a number of the ylides with various restrictions. The energy associated with pyramidalization of the ylidic carbon can be estimated using the energy of the structure containing a planar carbon (referred to as the "planar" structure). Rotational barriers about the P=C bond were obtained by comparing the energies of the planar structure with the energy of the structure having a planar ylidic carbon with one of its substituents eclipsing one of the P—H (or P—C) bonds. This we call the "eclipsed" structure. Newman projections along the C—P bond (carbon in front) of these three forms of 1 are shown in Figure 2.

Results

(1) Basis Set and Electron Correlation Effects. In order to obtain reasonable geometries of the phosphonium ylides, one must satisfactorily choose an appropriate basis set and computation level. Since the critical question concerning the ylides is the relative participation of the ylide vs ylene contribution, the chosen computational method must not arbitrarily favor one resonance form over the other. Since the ylide form involves formally charged centers, the basis set must be able to handle these atoms. The ylene form requires a basis set that can describe pentavalent phosphorus. If the phosphonium ylides are best described by some mixture of these two forms, electron correlation may be necessary to allow for the proper mixture of configurations to describe them.

Previous studies have addressed some of these concerns. Many early calculations employed basis sets having diffuse functions on carbon to adequately describe the formal carbanion in the ylide.[18-20] Schaefer[23] has argued that diffuse functions are not essential since the neighboring phosphonium center will be able to offer its functions to offset the carbanion.

Geometry optimization using basis sets lacking polarization functions produce structures having an abnormally long P—C distance.[26] Polarization functions on P alone give a too short P—C distance.[17] Polarization functions

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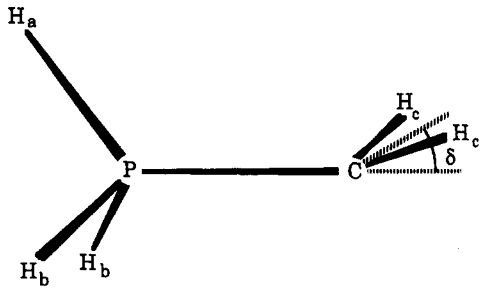
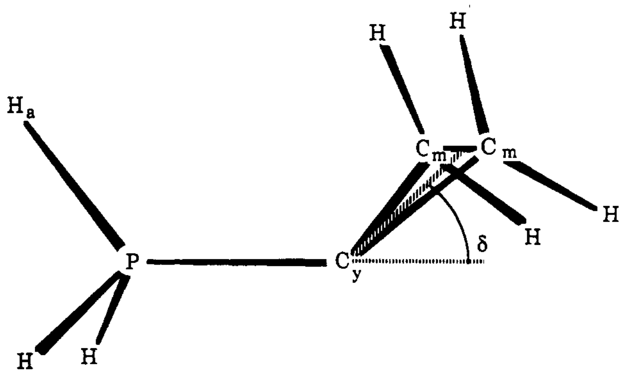
Table I. Optimized Geometric Parameters^{a} of $H_3P{=}CH_2$ at Various Computational Levels



level	P=C	P—H_a	P—H_b	C—H_c	H_a—P—C	H_b—P—C	H_c—C—P	H_b—P—C—H_a	H_c—C—P—H_a	δ
HF/3-21G^{b}	1.728	1.437	1.404	1.072	128.7		119.8			25.4
HF/D-21G*^{c}	1.649	1.414	1.391	1.072	126.6	113.5	120.3	120.5		10.6
HF/DZ+P+d(C)^{d}	1.672	1.402		1.071	118.0		119.0			10.0
HF/DZ+P+d(C)^{e}	1.675	1.414	1.389	1.076	127.7	112.1	118.4			23.7
HF/DZ+P+d(C)^{f}	1.668		1.401	1.075	118.6	117.7	119.2			10.8
HF/6-31G*^{g}	1.6665	1.4158	1.3897	1.0750	128.42	112.23	118.15	121.11	75.58	24.96
HF/6-31+G*	1.6723	1.4136	1.3890	1.0752	127.50	112.26	118.44	120.95	76.49	23.34
HF/6-31G**	1.6662	1.4186	1.3922	1.0746	128.12	112.30	118.04	121.84	75.79	24.74
HF/6-31+G**	1.6719	1.4162	1.3915	1.0746	127.19	112.31	118.37	120.89	76.83	22.87
HF/6-311+G**	1.6691	1.4209	1.3949	1.0751	127.06	112.34	117.97	120.82	75.54	25.18
MP2/6-31G*^{f}	1.6736	1.4402	1.4044	1.0836	130.60	111.49	116.84	121.17	72.53	30.70
MP2/6-31+G*	1.6805	1.4365	1.4029	1.0849	129.57	111.51	117.10	121.11	73.13	29.56
MP2/6-31G**	1.6721	1.4287	1.3948	1.0785	130.56	111.46	116.53	121.11	72.22	31.45
MP2/6-31+G**	1.6790	1.4251	1.3938	1.0798	129.46	111.49	116.80	121.02	72.82	30.32
MP2/6-311+G**	1.6769	1.4305	1.398	1.0842	129.2	111.66	116.38	121.04	71.91	32.05
CISD/6-31G*	1.6711	1.4379	1.4036	1.0821	130.14	111.68	117.3	121.25	73.42	28.94

[a] All distances in Å and all angles in deg. [b] See ref 26. [c] See ref 22. [d] DZ+P with diffuse functions on carbon. See ref 18. [e] DZ+P with diffuse functions on carbon. See ref 20. [f] DZ+P with diffuse functions on carbon. See ref 19. [g] See ref 21.

Table II. Optimized Geometric Parameters of $H_3P{=}C(CH_2)_2$ at Various Computational Levels



level	P—C	P—H_a	C_y—C_a	C_m—$C_{m'}$	P—C—C	H_a—P—C_y	C—C_y—C	δ
HF/6-31G*	1.6716	1.4211	1.4913	1.5030	130.13	129.19	60.52	41.8
HF/6-31+G*	1.6777	1.4212	1.4933	1.5046	129.02	127.90	60.50	43.2
HF/DZ+P^{a}	1.682	1.413	1.504	1.528	127.6	129.0	61.1	44.9
MP2/6-31G*	1.6771	1.4494	1.4971	1.5076	127.81	131.16	60.46	44.8

[a] See ref 23.

on both P and C are necessary.

No systematic study of the effect of electron correlation on the structure of ylides has been reported. Detailed examination of the role of the basis sets on the structure of ylides is also lacking. To address these questions, we have completely optimized the structure of methylenephosphorane 1 using a variety of basis sets and computational levels. These optimized geometries are listed in Table I.

The most critical features in the structure of methylenephosphorane are the P—C distance and the degree of pyramidalization at carbon. We obtain this latter value by measuring the angle δ formed by the bisector of the R—C—R angle and the projection of the P—C vector (see Tables I and II). Unfortunately, there are no experimental values for this compound. The X-ray structure of triphenylmethylenephosphorane has been carefully detailed.[4] The P—C distance is 1.692 Å, and δ is 28°. The electron diffraction study of trimethylmethylenephosphorane was solved assuming a planar carbanion and results in a P—C distance of 1.640 Å.[27]

Improvement of the basis set beyond 6-31G* results in very little change in the molecular structure. Diffuse functions lengthen the P—C bond slightly. Other structural parameters, including δ, are insensitive to basis set

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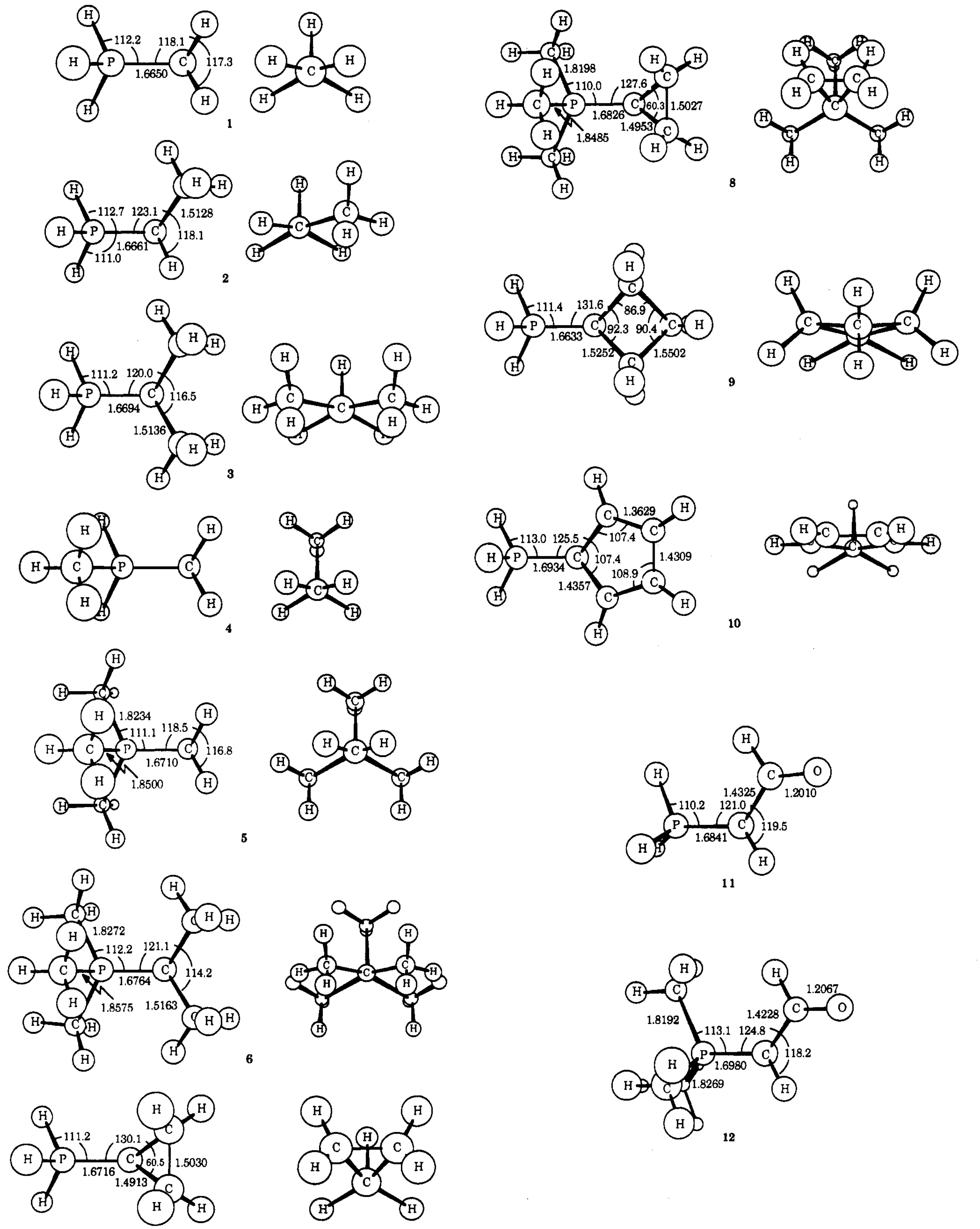


Figure 1. Optimized geometries of 1–12 at HF/6-31G*. All distances are in Å, and all angles are in deg.

changes. Inclusion of electron correlation through MP2 results in a larger change in the geometry than modification of the basis set, but still the effect is small. As expected, bond distances lengthen with correlation, but the P—C bond stretches by an average of only 0.007 Å to about 1.68 Å. A more significant effect of correlation is a more pyramidalized carbanion: $\delta \approx 30°$. Both of these parameters agree remarkably well with Schmidbaur's[4] X-ray structure of triphenylmethylenephosphorane.

A more limited set of comparisons of the effect of basis set and correlation on the structure of phosphonium cyclopropylide 7 is given in Table II. Here again we see

Table III. Energy and Some Geometric Parameters of 1-12 at HF/6-31G*

compd	energy[a]	P=C[b]	P—C—X[c]	X—C—X′[c]	sum[d]	δ[e]
H_3P=CH_2 (1)	-381.392339	1.6665	118.15	117.29	353.59	24.96
H_3P=CHMe (2)	-420.422516	1.6661	123.07 (C) 114.85 (H)	118.13	356.05	
H_3P=CMe_2 (3)	-459.454162	1.6694	120.00	116.48	356.48	18.20
MeH_2P=CH_2 (4)	-420.441135	1.6637	118.92	117.69	355.53	20.81
Me_3P=CH_2 (5)	-498.537653	1.6710	118.47	116.76	353.70	24.59
Me_3P=CMe_2 (6)	-576.594976	1.6764	121.08	114.25	356.41	18.01
H_3P=$C(CH_2)_2$ (7)	-458.246281	1.6716	130.13	60.52	320.78	41.79
Me_3P=$C(CH_2)_2$ (8)	-575.392424	1.6826	127.59	60.33	315.51	45.12
H_3P=$C(CH_2)_3$ (9)	-497.288853	1.6633	131.62	92.28	355.52	16.55
H_3P=$C(CH)_4$ (10)	-534.024749	1.6934	125.55	107.41	358.51	10.85
H_3P=CHCHO (11)	-494.139953	1.6841	120.98 (C) 119.52 (H)	119.50	360.00	0.00
Me_3P=CHCHO (12)	-611.289316	1.6980	124.85 (C) 117.00 (H)	118.15	360.00	0.00

[a] In au. [b] In Å. [c] In deg. [d] Sume of the angles (deg) about the ylidic carbon. [e] Out-of-plane bending (deg). See Figure 3.

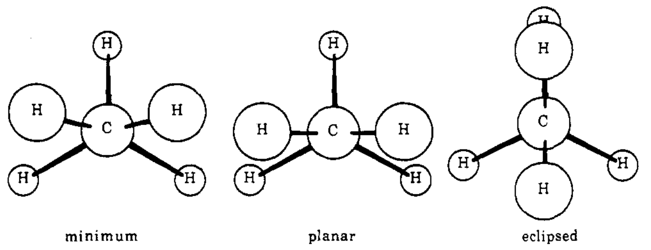


Figure 2. Newman projections along the P—C bond (carbon in front) of the three conformations of 1.

minor geometrical changes with variation of these basis sets. Since the ylidic carbon is likely to carry a large negative charge in 7, diffuse functions may be important. However, addition of diffuse functions lengthens the P—C bond only 0.0061 Å and makes the carbanion slightly more pyramidal. The effects on the geometry of 7 due to correlation are similar to the methylenephosphorane case. Bonds lengthen a small fraction and δ increases by a handful of degrees.

Thus, we can conclude that the HF/6-31G* level produces a geometry that is exceptionally similar to the geometry obtained with much more expensive methods. The only caveat is that the HF/6-31G* structures may slightly *underestimate* carbanion pyramidalization.

(2) Geometries of the Phosphonium Ylides 1-12. Phosphonium ylides can be broadly cast into two categories: (1) ylides having no stabilizing groups on the ylidic carbon and (2) ylides stabilized by one or more substituents on the ylidic carbon. These stabilizing substituents generally can conjugate with the P—C π-bond or delocalize the carbanion. We have examined a few examples of each type. Compounds 1-9 are nonstabilized ylides and 10-12 are stabilized ylides. A summary of the most pertinent geometric data for these compounds are listed in Table III, and further information is given in Figure 1 and the supplementary material.

The P—C distance in the nonstabilized ylides having only H substituents on P (1-3, 7, and 9) is relatively constant, varying from 1.6633 Å (9) to 1.6716 Å (7). Replacement of H with methyl groups on P generally lengthens the P—C bond, with the longest being 1.6826 Å in 8. The P—C distance in the stabilized ylides is longer (1.6934 Å (10), 1.6841 Å (11), and 1.6980 Å (12)) than in the nonstabilized ylides.

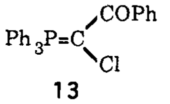
All of the nonstabilized ylides possess pyramidalized ylidic carbons. As was pointed out in the earlier section, HF/6-31G* geometries may slightly underestimate the value of δ. Nevertheless, the value of δ ranges from 16.55° in 9 to 45.12° in 8. Another method for gauging the pyramidal nature is the sum of the angles about C. A planar atom will have the angle sum equal to 360°. Since we cannot define a unique bisector of the H—C—C angle in 2 to obtain δ, its angle sum of 356.05° suggests that the ylidic carbanion is about as pyramidal as the carbon in 3.

All of the nonstabilized ylides that do not have a cyclopropyl ring have δs around 20-25°. The ring strain associated with the cyclopropyl ring forces the ylidic carbon to be very pyramidal. Our values are quite similar to the earlier theoretical work.[23] The X-ray structure[4] of triphenylphosphonium cyclopropylide shows similar features as well—the P—C distance is 1.696 Å and δ 58°—but both are somewhat larger than the theoretical values of 7. We optimized the structure of 8 to obtain some estimate of the effect of having P substituents larger than simply hydrogens. This trimethyl derivative has a longer P—C distance and a larger δ than the parent, about midway between the values of 7 and the X-ray structure.

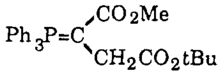
The carbon in phosphonium cyclobutylide 9 is pyramidal, with δ 16.6°. The X-ray crystal structure[3] of triphenylphosphonium cyclobutylide also shows a pyramidal carbon, with δ 19°. The P=C distance is 1.6633 Å in 9 and 1.668 Å in the experiment, while the angles in the four-membered ring in the two structures differ by less than 1°. The calculated structure is in excellent agreement with the crystal structure.

The degree of pyramidalization in the stabilized ylides is much smaller than in the nonstabilized ylides. 11 and 12 optimize to C_s symmetry, which demands a planar carbon. X-ray crystal structures of a number of stabilized ylides containing α-carbonyl groups all show an ylidic carbon that is very nearly planar.[5-8,10-12] The value of δ for 10 is 10.85° with an angle sum of 358.51°. For comparison, the angle sum in the X-ray structure of triphenylphosphonium cyclopentadienylide is 358°.[9]

The substituents in the stabilized ylides act to delocalize the electrons of the π-bond of the ylene or the carbanion of the ylide. This should manifest itself in structural features. In 11 and 12, the C_{ylide}—C_α distance should be shorter than a normal C—C bond and the C—O distance should be long. The C—C and C—O distances in the optimized structure are 1.4325 and 1.2010 Å in 11 and 1.4228 and 1.2067 Å in 12, in agreement with the above expectation. The C_{ylide}—C_α distances in the crystal structure of 13[6] and 14[11] are 1.361 and 1.415 Å and the

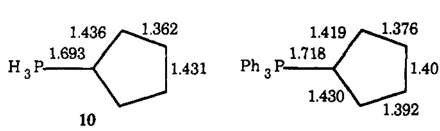

$Ph_3P{=}C(COPh)(Cl)$

13


$Ph_3P{=}C(CO_2Me)(CH_2CO_2tBu)$

14

C—O distances are 1.301 and 1.221 Å, respectively. In 10,



10

Figure 3. Comparisons of the geometries of **10** and the X-ray structure of triphenylphosphorane cyclopentadienylide. All distances are in Å.

Table IV. Pyramidalization and Rotational Barriers (kcal mol^{-1}) at HF/6-31G*

compd	$E_{\text{pyramidal}}$	E_{rotation}
$H_3P{=}CH_2$ (1)	0.87	0.13
$H_3P{=}CMe_2$ (3)	0.99	1.00
$Me_3P{=}CH_2$ (5)	0.70	0.22
$Me_3P{=}CMe_2$ (6)	0.85	−0.02
$H_3P{=}C(CH_2)_2$ (7)	3.97	0.32
$Me_3P{=}C(CH_2)_2$ (8)	4.15	

full delocalization of the carbanion into the cyclopentadienyl ring would lead to identical C—C bonds in the ring. In Figure 3 we compare the C—C distances of **10** with the experimental[9] distances of $Ph_3P{=}C(CH)_4$. Both compounds display bond alternation, but the distances do reflect a move toward an average of the C—C and C=C distances.

(3) Pyramidalization Energy and P=C Rotational Barriers. Pyramidalization energy is defined as the energy of the planar form less the energy of the local minimum structure that has a pyramidal ylidic carbon. The rotational barrier is defined as the energy difference of the planar and eclipsed forms. The values of these energies for a few of the ylides are listed in Table IV.

The pyramidalization energy for **1**, **3**, **5**, and **6** are less than 1 kcal mol^{-1}, reflecting a shallow potential energy surface for inversion at the ylidic carbon. A flat surface for pyramidalization at the ylidic carbon has been invoked by Schmidbaur[4] and Schlosser[14] to explain crystallographic and NMR experiments. The pyramidalization energies of the cyclopropylides **7** and **8** are larger, about 4 kcal mol^{-1}.

The rotational barrier about the P=C has been investigated for **1** at a number of computational levels. Absar[28] estimated the difference in energy of the planar and eclipsed forms at HF/DZ using fixed geometries as 0.003 kcal mol^{-1}. Lischka[18] estimated the difference between the pyramidal and eclipsed form as 0.13 kcal mol^{-1}, and Eades, Gassman, and Dixon[19] estimated the barrier as 0.2 kcal mol^{-1}. Schaefer[29] optimized the actual transition state for rotation about the P=C bond in **7** (not our assumed planar eclipsed form); it lies 5.8 kcal mol^{-1} above the ground state. Our results for some of the phosphonium ylides are given in Table IV. We find the energy difference between the ground state and the eclipsed form of **1** is about 1 kcal mol^{-1}. The rotational barriers for all the ylides are very small. Allen[30] has pointed out that low rotational barriers are anticipated for systems having near local C_{3v} symmetry about P.

Discussion

The HF/6-31G* method produces phosphonium ylide geometries that are remarkably similar to experiment. The recent high-resolution X-ray crystal structure of triphenylmethylenephosphorane found two molecules in the unit cell, with P=C distances of 1.697 and 1.688 Å. This can best be compared with **5**, where the P=C distance is 1.6710 Å. For most phosphonium ylides, one of the phosphorus substituents bisects the plane formed by the ylidic carbon and its substituents, and this plane bends toward the unique P substituent. The distance between P and this unique substituent is longer than the distances to the other two substituents, and it forms a larger angle to the P=C bond than the other two substituents. In one of the molecules of triphenylmethylenephosphorane, the P—C distance to the unique phenyl ring is 1.837 Å, about 0.02 Å longer than the other P—C distances. The C—P=C angle formed by the unique phenyl ring is 117.8°, while the other two angles are 112.8° and 109.9°. In our calculated structure of **5**, the P—C distance to the bisecting methyl group is 1.8500 Å and the other P—C distance is 1.8234 Å. The C—P=C angle formed to the bisecting methyl is 122.85° and the angle to the other methyls is 111.08°. These angles about P indicate a tetrahedral environment and does not support the dsp^3 hybridization of P necessary in the *ylene*.

All of our calculated structures, except for **11** and **12**, follow this same pattern. The bisecting P substituent interacts with the carbanion lone pair, leading to the long bond and the large angle. The carbon substituents bend toward the bisecting phosphorus substituent.

When conjugating groups are absent from the ylidic carbon, these nonstabilized ylides have nonplanar ylidic carbon environments. Previous theoretical studies on the unsubstituted phosphonium ylide **1** have shown a nonplanar geometry. Our work includes a number of examples of methyl-substituted ylides, and all of these are nonplanar. Concern that larger groups might affect the geometry are unwarranted. Increasing steric bulk about the phosphonium center (compare **1** vs **5**), carbanionic center (compare **1** vs **3**), or both (compare **1** with **6**) does slightly decrease the pyramidalization at carbon, but not to planarity. These calculations completely agree with the recent X-ray studies showing nonstabilized ylides with pyramidal ylidic carbon centers. This geometry strongly suggests that the *ylide* form A is the dominant resonance structure in describing the phosphonium ylides.

The case is extreme when considering the cyclopropylides **7** and **8**. Previous calculations by Schaefer[23] on **7** indicate a very large δ value. Since the only crystal structure of a cyclopropylide[13] has large groups on phosphorus, we examined the trimethyl derivative **8** to explore the role of sterics in the bending at the carbanion. The value of δ is 45.1° in **8** and 41.8° in **7**. The methyl groups cause a larger distortion from planarity than hydrogen. This probably arises from the ability of methyl groups to better stabilize the positive charge on P than H. When P carries a smaller positive charge, it is less capable of stabilizing the carbanion, which consequently becomes more pyramidal. Since the phenyl group is better at stabilizing positive charge than the methyl groups, the out-of-plane bending in triphenylphosphonium cyclopropylide is larger than **8**. This effect, along with increased steric interactions, also explains the longer P—C bond in the methyl-substituted ylides compared with their hydrogen analogues. The smaller positive charge on P due to the methyl substituents leads to less electrostatic attraction toward the carbanion and a longer bond. The lengthening of the P—C distance with methyl substitution is found in the stabilized ylides as well: 1.6841 Å in **11** and 1.6980 Å in **12**.

The large bending in **7** and **8** arises from the strain of the three-membered ring. Maximum stabilization of the carbanion by the phosphonium center occurs when the

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anion resides in a carbon p orbital, which requires sp^2 hybridization on carbon. However, in 7 and 8, the three-membered ring cannot readily accommodate an sp^2 center, which would require a wide interior angle. The molecules adopt a pyramidal center that minimizes ring strain energy. The strain in the four-membered ring is apparently smaller; the value of δ in **9** is only 16.5°. The triphenyl derivative of **9**, as found in the X-ray structure,[3] also has a nonplanar carbon.

Nonstabilized carbanions are pyramidal species. At HF/6-31G*, the value of δ for methyl anion ($^-CH_3$) and isopropyl anion ($CH_3{}^-CHCH_3$) is 71.22° and 61.34°, respectively. In these species, the anionic lone pair occupies an sp^3 hybrid orbital to minimize the lone pair–bond pair repulsions. The nonstabilized ylides are not as pyramidal as these carbanions. The energetic consequence of nonplanar ylides is about 1 kcal mol^{-1} (4 kcal mol^{-1} for the cyclopropylides). In comparison, the planar form of methyl anion is 12.98 kcal mol^{-1} above the pyramidal ground state, and the planar form of the isopropyl anion is 10.68 kcal mol^{-1} higher in energy than its pyramidal ground state. These results suggest that a full negative charge is not bourn on the ylidic carbon and that phosphorus acts to polarize the carbanion. This conclusion is supported by previous theoretical studies that find a large negative charge on carbon and a HOMO that is primarily formed from the carbon p orbital with some small density spread toward the phosphorus.[18,19,26,28]

The three stabilized ylides examined here, **10**–**12**, differ from the others in that they have a planar or nearly planar ylidic carbon. This might indicate a strong role for the *ylene* structure. However, since the *ylene* structure plays a minor role in describing the nonstabilized ylides, it is unlikely that the *ylene* form will strongly participate in these stabilized ylides, where substituents will act to withdraw charge from carbon.

Geometric evidence for the withdrawal of carbanionic charge through the π-system into the carbon substituents is substantial. The C_{ylide}—C_α distance in **10** is 1.4357 Å, shorter than a typical C—C single bond. The formal C=C is 1.3629 Å and the other C—C distance is 1.4309 Å, reflecting delocalization of the π electrons about the ring. The ylidic carbon is not planar, but is very nearly so. These geometric features are also present in the X-ray structure[9] of triphenylphosphonium cyclopentadienylide.

Similarly, the C_{ylide}—C_α distance in **11** is short, only 1.4325 Å, and is even shorter in **12**: 1.4228 Å. The C—O distances are at the high end of the normal range of carbonyl distances. The ylidic carbon in **11** and **12** is planar, optimal for the carbanion to delocalize into the carbonyl group. X-ray structures of ylides that have α-carbonyl groups show a shortened C_{ylide}—C_α bond and a planar carbon.

While this delocalization might suggest the participation of the *ylene* form in the stabilized ylides, there is overwhelming evidence against any sizable contribution of the *ylene* even for the stabilized ylides. The HOMO of **11** is composed primarily of the p_z orbitals of the ylidic carbon and oxygen, with a smaller component from P. The angles about P are close to tetrahedral values and definitely do not reflect the dsp^3 hybridization needed in the ylene. Schlosser[14] and Albright[31] have used the ^{13}C NMR shifts of a variety of stabilized ylides to discount the ylene participation. The X-ray structures[5–12] of all stabilized ylides show tetrahedral P centers, planar ylidic carbons, short C_{ylide}—C_α and long C=O distances.

In summary, our calculations are completely consistent with the experimental structures of both stabilized and nonstabilized ylides. The nature of the electronic distribution in phosphonium ylides is best described by the *ylide* resonance structure.

Supplementary Material Available: Optimized geometries in the form of Z-matrices at the HF/6-31G* level (8 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of this journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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