proton absorption at δ 5.42 and the presence of absorptions for the vinylic protons for the two stereoisomers at δ 4.60 and 4.71. The 4-(1-methylcyclopropyl)-1-methylcyclohexene was characterized by the absence of a vinylic proton absorption at δ 4.72 and the presence of a δ 5.38 ring olefinic proton absorption. The isomeric 4-(1-methylcyclopropyl)-1-methylbicyclo[4.1.0]heptanes exhibited no absorptions in the alkenyl proton region. All of these materials had been characterized earlier by other workers.[11,12]

Analysis of Product Mixtures from Cyclopropanation of 4-Vinylcyclohexene. The wide-range-distilled product mixtures obtained from partial cyclopropanation of 4-vinylcyclohexene under the various conditions were analyzed by capillary GC with a SE-54 column. The retention times at 80 °C for unreacted 4-vinylcyclohexene and its different cyclopropanated products, in minutes from time of injection, were as follows: 4-vinylcyclohexene, 2.7; *cis*- and *trans*-3-cyclopropylnorcaranes, 5.0 (two isomers did not separate); 4-cyclopropylcyclohexene, 5.3; *cis*- and *trans*-3-cyclopropylnorcaranes, 11.3 and 11.5 (partially resolved). The identities of each of the products were established by ^1H NMR examination of pure samples collected by GC from a SE-30 packed column. All of the materials had been characterized earlier by other workers.[13]

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Registry No. **1a**, 138-86-3; **1b**, 100-40-3; **2a**, 60059-22-5; **2b**, 80105-51-7; *cis*-**3a**, 62740-28-7; *trans*-**3a**, 62740-29-8; *cis*-**3b**, 131791-69-0; *trans*-**3b**, 71268-78-5; *cis*-**4a**, 62740-27-6; *trans*-**4a**, 62869-85-6; *cis*-**4b**, 131791-70-3; *trans*-**4b**, 131791-71-4.

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Structure and Inversion Barrier of Phosphirene and 1,2-Dihydrophosphete. An ab Initio Study

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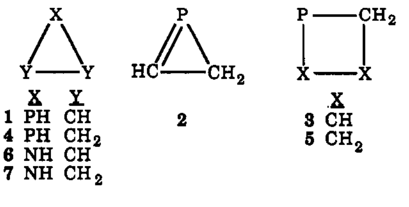
The geometry of 1*H*-phosphirene (**1**), 2*H*-phosphirene (**2**), and 1,2-dihydrophosphete (**3**) were optimized at HF/6-31G*, and single-point calculations at MP2 were performed. The transition structure for inversion at P of 1 and 3 were also optimized (**1pl** and **3pl**). The inversion barrier of 1 and 3 is 92.65 kcal mol^{-1} and 46.62 kcal mol^{-1}, respectively. 1 is not antiaromatic based on the highly pyramidal P atom and no energetic destabilization. Analysis of the electron density distribution and comparison with the inversion barriers of N analogues indicate that the antiaromatic contribution in **1pl** is small.

Small-membered rings have long fascinated organic chemists for their structural simplicity and strained bonds. Small rings incorporating multiple bonds severely test the limits of chemical bonds and ring strain and offer excellent opportunities to evaluate bonding theories. Recently, Regitz[1-3] and Mathey[4-6] have independently developed synthetic strategies for preparing both 1*H*-phosphirene (**1**) and 2*H*-phosphirene (**2**). Of interest is the relative energy of these compounds, particularly in comparison to the nitrogen analogues, since Regitz found that chlorine substituted 2*H*-phospirenes will rearrange to give 1*H*-phosphirenes, contrary to azirenes.[3] The inversion barrier of 1 is of interest since this process goes through a cyclic, planar, formally 4π-electron geometry which may be antiaromatic. Comparison with the inversion barrier of 1*H*-azirine will provide information concerning the effects of pyramidalization and bond lengths on cyclic 4π-electron interactions. Determining the inversion barrier of 1,2-dihydrophosphete (**3**) allows for comparison of the effects of ring size. Following up on our previous theoretical studies of phosphirane **4** and phosphetane **5**,[7] we report here the continuation of our examination of strained-ring organophosphorus systems. Using ab initio calculations, we have determined the geometries of **1**–**3** and the inversion barrier of **1** and **3**. Comparisons of the geometries, energies, and electron density distributions are made with both their saturated and nitrogen analogues.

Table I. Energies of 1–3 Using the 6-31G* Basis Set

compd	E(HF)[a]	rel E[b]	E(MP2)[a]	rel E[b]
1	-418.107 704	0.0	-418.462 482	0.0
1pl	-417.951 072	98.29	-418.314 835	92.65
2	-418.112 186	2.81	-418.482 100	-12.31
3	-457.174 108	0.0	-457.656 699	0.0
3pl	-457.090 647	52.37	-457.582 399	46.62

[a] In atomic units. [b] Relative energy in kilocalories per mole.



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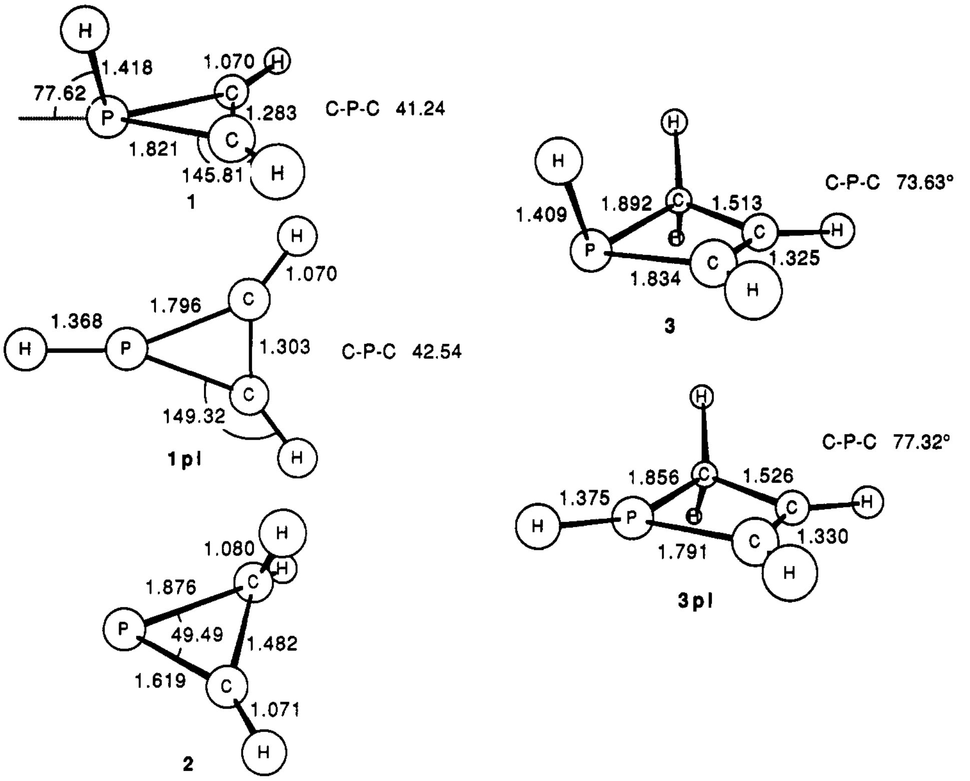

Figure 1. Geometry of 1–3 optimized at HF/6-31G*. All distances are in angstroms and all angles are in degrees.

Computational Methods

The minimum energy geometry of 1–3 were fully optimized, within C_s symmetry, at HF/6-31G* using the standard gradient techniques in GAUSSIAN-86.[8] The optimized geometries of 1–3 are shown in Figure 1 and the total energies are given in Table I. Analytical frequency analysis confirmed these structures to be local minima. Single-point calculations at the MP2/6-31G*//HF/6-31G* level were also performed to assess the importance of electron correlation.

Optimization of the geometry of 1 restricted to C_{2v} symmetry led to the planar structure **1pl**, which is the transition structure (confirmed by having one imaginary frequency) for inversion at phosphorus. Since our previous calculation of the inversion barrier of phosphetane and Laane's[9,10] determination of the inversion barrier of 3-phospholene indicated a transition structure with a planar ring, we optimized the geometry of 3 restricted to C_s symmetry. This resulted in the planar structure **3pl**, which was then confirmed to be a transition structure by frequency analysis. Both of these structures are shown in Figure 1. The structures, energies, and inversion barriers of azirine **6** and aziridine **7** were obtained by Alcami, Paz, and Yanez.[11] These calculations were performed at the same calculational level as employed in this work.

The topological electron density analysis was performed using EXTREME.[12] Chemical information from the topological method is derived primarily from the critical points.[13,14] Critical points occur where the gradient of the electron density vanishes, i.e. $\nabla\rho = 0$.[15] Critical points are found at nuclei, between bonded atoms and in the center of rings and cages. The value of the density at the bond critical point ($\rho(r_c)$) correlates with the bond length and bond order.[16,17] The ellipticity ϵ indicates the degree of noncylindrical distribution of the density about the bond; the greater the value, the more the density is oriented in a particular direction.[18] For example, the ellipticity at a C–C bond point is nearly zero since the bond is primarily of σ symmetry, while the ellipticity at a C=C bond point is large, indicating the density is concentrated in the π direction over the in-plane direction. By tracing the gradient of the density from the bond critical point to the neighboring nuclei, the bond path is obtained, corresponding to the ridge of maximum density between the bonded nuclei.[19] The length of the bond path (r_{path}) is longer than the internuclear separation (r), unless symmetry demands they be equivalent, and the quantity R measures the ratio of r_{path} to r.

Results

The parent 1*H*-phosphirene is unknown but 1,2,3-triphenylphosphirene (**8**)[5] and 1-chloro-2-phenyl-3-*tert*-butylphosphirene (**9**)[20] have been prepared and their crystal structures determined. The C–P and C–C bond lengths in **8** are 1.820 and 1.299 Å, respectively, and the C–P–C angle is 41.8°. The C–P and C–C bond lengths in **9** are

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1.784 and 1.303 Å, respectively, and the C–P–C angle is 42.9°. A previous calculational study of phosphirene assumed the experimental geometry of **8**.[21] The calculated C–P and C–C distances in **1** are 1.821 and 1.283 Å with C–P–C angle of 41.2°, in remarkable agreement with the experimental structures, especially considering the differences in substituents and phases.

The angle formed between the P–H bond and the phosphirene ring plane in **1** is 77.62°, indicating that P is highly pyramidal. The comparable angle in **8** and **9** is 70.79° and 75.0°, both slightly smaller than the parent, probably in order to reduce the repulsion between the phenyl ring and the phosphirene ring. For comparison, the corresponding angle in azirine **6** has been calculated at HF/6-31G* to be 69.1°.[11] As expected, phosphorus is more pyramidal than nitrogen, presumably leading to a less destabilizing lone-pair π-bond interaction in **1** than in **6**.

The transition state for inversion of P in **1** is shown in Figure 1 and is labeled **1pl**. As anticipated, the structure belongs to the C_{2v} point group. Analytical frequency analysis finds only one imaginary frequency (1988*i* cm^{-1}), and this mode involves the H bonded to P moving through the molecular plane. The planar P atom uses greater s-character to form bonds, reflected in the shorter C–P and P–H bonds in **1pl** than in **1**. The C–C bond stretches during the inversion process. The inversion barrier is calculated to be 98.29 kcal mol^{-1} at HF/6-31G*. Inclusion of electron correlation effects through MP2 reduces the barrier to 92.65 kcal mol^{-1} (MP2/6-31G*//HF/6-31G*). Correlation does reduce the barrier, and one should, therefore, take care in estimating the true barrier since higher order effects might prove important. However, the qualitative trends discussed below should not be effected by this relatively small energetic correction.

Substituted 2*H*-phosphirenes have only recently been reported,[3] and no structural data is known. The HF/6-31G* optimized structure of **2** is shown in Figure 1. The P=C bond is 1.619 Å, significantly shorter than a typical P–C double bond (1.64–1.67 Å). The calculated P–C bond length is 1.876 Å, about 0.01 Å longer than the typical P–C single bond.

Doxsee, Shen, and Knobler[22] recently reported the synthesis of a number of substituted 1,2-dihydrophosphetes, one of which (1,3,4-triphenyl-1,2-dihydrophosphete, **10**) was characterized by an X-ray crystal structure. The bond lengths and angles in **10** are P-C2, 1.821 Å; C2–C3, 1.366 Å; C3–C4, 1.517 Å; P–C4, 1.886 Å; C2–P–C4, 74.0°; P–C2–C3, 95.5°; C2–C3–C4, 101.3°; and P–C4–C3, 88.0°. The calculated HF/6-31G* geometry of **3** is given in Figure 1. The calculated structure is in remarkable agreement with the structure of **10**, considering the differences in substituents. As expected, the ring of **3** is not planar, but is nearly so; the C4–P–C2–C3 dihedral angle is only 4.13°. The H bonded to P lies 76.26° out of the C4–P–C2 plane, indicating that P is nearly as pyramidal in **3** as in **1**. The corresponding angle in **10** (the amount the phenyl ring lies above the C4–P–C2 plane) is 71.7°, which is slightly smaller than in the parent compound, due primarily to steric effects.

Inversion of P in phosphetane and 3-phospholene is accompanied by the ring becoming planar. We located the transition structure for inversion of **3** by assuming C_s symmetry. The resulting structure is shown in Figure 1 and was confirmed by having one and only one imaginary frequency (1169*i*). The imaginary frequency corresponds with the motion of the H through the ring plane. Similar to inversion of **1**, the C–P and P–H bonds shrink and the C–C bonds lengthen during the inversion of **3**. The inversion barrier is 52.37 kcal mol^{-1} at HF/6-31G*//HF/6-31G*; inclusion of electron correlation reduces the barrier to 46.62 kcal mol^{-1} at MP2.

Table II. Topological Parameters of 1–3 at HF/6-31G*//HF/6-31G*

	point	$\rho(r_c)^a$	ϵ^a	$r_{\text{path}}{}^b$	R^c
1	P–C	0.1397	0.5718	1.8510	1.63
	C=C	0.3761	0.2982	1.2911	0.64
	ring	0.1280			
1pl	P–C	0.1435	0.0671	1.8243	2.12
	C=C	0.3689	0.4411	1.3070	0.28
	ring	0.1254			
2	P–C	0.1345	1.7614	1.8920	0.84
	P=C	0.1858	0.2612	1.6356	1.02
	C–C	0.2630	0.2079	1.4889	0.49
	ring	0.1339			
3	P–C2	0.1554	0.1509	1.8424	0.45
	P–C4	0.1493	0.1602	1.8982	0.35
	C2=C3	0.3624	0.4359	1.3264	0.08
	C3–C4	0.2622	0.0280	1.5142	0.10
	ring	0.0714			
3pl	P–C2	0.1599	0.6792	1.8052	0.79
	P–C4	0.1522	0.5554	1.8732	0.91
	C2=C3	0.3568	0.4775	1.3299	0.02
	C3–C4	0.2549	0.0410	1.5303	0.27
	ring	0.0680			

[a] Values in atomic units. [b] Distances in angstroms. [c] Defined as $((r_{\text{path}} - r) - 1.0)*100$.

The values of the various quantities obtained via the topological electron density analysis are listed in Table II. Typical values of ρ(P–C) and ρ(P–C) are 0.15 and 0.19 e au^{-3}, respectively. The values for the P–C critical points in the phosphirenes are smaller than normal, reflecting not the short P–C internuclear distances, but rather the long P–C bond paths (1.851 Å in **1** and 1.892 Å in **2**). The values at the other P–C critical points are all normal. The density at the P–C bond point increases upon inversion for both **1** and **3**, corresponding to the shortening bond during inversion. The P–C bonds are quite bent in **1** and **2**, indicated by large *R*, and relatively unbent in **3**, reflecting the greater strain in the smaller rings. Inversion leads to an extremely bent P–C bond in **1pl** and added bending of all bonds in **3pl**.

Discussion

Our calculations indicate that **2** is more stable than its isomer **1** by 12.3 kcal mol^{-1} at MP2/6-31G*//HF/6-31G*, though this is reduced to 10.6 kcal mol^{-1} with the inclusion of zero-point energy corrections. Regitz[3] has noted that chlorinated analogues of **2** spontaneously rearrange to the corresponding analogue of **1**, contrary to what is predicted from our calculations of the parent isomers. To preliminarily explore the effects of substituents, we have optimized the fluoro- and chloro-substituted analogues of **1** and **2**. At MP2/6-31G*//HF/6-31G*, **Fl-1** is 21.9 kcal mol^{-1} lower in energy than **Fl-2** and **Cl-1** is 10.5 kcal mol^{-1} below **Cl-2**. These calculations are in agreement with the experimental ordering. Apparently, the halogen substituents invert the stability of these ring systems.

Regitz commented that the stability of **1** over **2** could only be understood if **1** has "no antiaromatic character".[3] The concept of antiaromaticity was introduced to explain the difficulty in preparing stable cyclic 4p-electron systems.[23] There is no clear definition of aromaticity itself,

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but rather properties associated with aromaticity; antiaromaticity is even less well defined.[24] Breslow opts to define an antiaromatic system as "one in which electron delocalization considerably raises the energy".[25] However, this energetic destabilization must be quantified in reference to some system. As noted by Breslow[25,26] and Bauld,[27] a satisfactory reference is difficult to derive. For 1, a reference requires the P lone pair to not interact in a cyclic arrangement with the double bond, such as vinyl phosphine. However, 1 is a strained ring, and no model can be obtained that will completely decouple ring strain energy (RSE) from the antiaromatic resonance energy. One option is offered in eq 1, which gives a reaction energy of -21.0 kcal mol^{-1}. However, eq 1 tacitly assumes that the RSE of 1 is equal to the RSE of 4, which, of course, is impossible. If one assumes that the difference in RSE between 1 and 4 is the same as the difference between cyclopropene and cyclopropane (26 kcal mol^{-1}), the resonance energy of 1 is actually stabilizing. An alternative approach compares the energy of 1 with 6, eq 2. The energy of this reaction is -22.2 kcal mol^{-1}, indicating that 1 is much more stable than azirine, and thus must be less antiaromatic.

$\Delta H = -21.0$ kcal mol^{-1} Eq 1

Eq 2

4 6 1 7

$\Delta H = -22.2$ kcal mol^{-1}

Further information concerning the antiaromatic character of 1 is its structure, particularly the pyramidal P atom. Pyramidalization reduces the interaction between the lone pair and π-bond electrons, minimizing the 4π antiaromaticity. The published crystal structures confirm this, and our structure also shows a highly pyramidal P atom. The degree of pyramidalization is greater in 1 than in the nitrogen analogue 6, suggesting that the former is less antiaromatic. This is also supported by the longer C–P bond (1.821 Å) than C–N bond (1.490 Å), which again decreases the lone-pair–π-electron interaction. Therefore, there is no structural, energetic, or chemical evidence to suggest any antiaromatic character in 1.

We now turn our attention to the inversion barriers of 1 and 3. The transition structure for inversion are planar. The barriers are 92.65 kcal mol^{-1} for 1 and 46.62 kcal mol^{-1} for 3. For comparison, the inversion barrier at MP2/6-31G*//HF/6-31G* of 4 and 5 are 69.35 and 43.35 kcal mol^{-1}, respectively. The inversion barrier of phosphine and trimethylphosphine is 31.8 and 22.0 kcal mol^{-1}, respectively.[28] The estimated barrier[9] of 3-phospholene is about 16 kcal mol^{-1}. As expected, strain in the three- and four-membered rings does increase the inversion barrier.

The relative barrier heights for 4 and 5 has been explained in terms of the geometric restrictions imposed at P in the three-membered ring and the loss of stabilization energy associated with surface delocalization of electron density in the three-membered ring.[29] The latter effect is similar in spirit to Dewar's concept of σ-aromaticity,[30,31] which would stabilize three-membered rings relative to four-membered rings. Both of these effects should apply to 1 and 3 along with the possibility that **1pl** is antiaromatic which would further increase the inversion barrier of 1 relative to 3, which does not have a cyclic π-system.

Table III. Calculated Inversion Barriers (kcal mol^{-1})

compd	E(HF)	E(MP2)
1	98.29	92.65
3	52.37	46.62
4[a]	73.18	69.35
5[a]	46.45	43.35
6[b]	45.59	46.26
7[b]	19.40	19.93

[a] See ref 7. [b] See ref 11.

Surface delocalization is evidenced by little difference in ρ between the bond critical point and the ring critical point, and the ellipticity at the bond critical point is large with the major axis in the ring plane. Surface delocalization is present in 1. Electron density at the ring critical point is 92% the value at the P–C bond point. The major axis at the P–C bond point defined by the ellipticity is in the plane. The major axis at the C═C point is perpendicular to the plane, corresponding to the p-bond; however, the ellipticity is markedly smaller than usual, due to build up of density in the ring plane. On the other hand, there is no surface delocalization in 3: density at the ring point is less than half that in the bonds and all major axes are directed perpendicular to the ring.

The surface delocalization is depleted during inversion of 1. The density at the ring point of **1pl** is 87% that at the P–C bond point. The P–C bond paths are bent further outward in **1pl** than in 1. The major axes at all bond points in **1pl** point perpendicular to the ring and the ϵ at the C═C point is standard. Neither 3 nor **3pl** display any surface delocalization.

Thus, some of the difference (46.03 kcal mol^{-1}) in the inversion barriers of 1 and 3 is due to both the increased geometric restrictions at P and the loss of surface delocalization of the former. Quantifying this is difficult. The difference in the barrier heights of 4 and 5 is 26.00 kcal mol^{-1}, and this energy difference is due to geometric and surface delocalization effects. However, 1 should have greater geometric restrictions toward inversion than 4 (the former has a smaller C–P–C angle), and since the inversion barriers of 3 and 5 are similar, we expect that somewhat more than 26 kcal mol^{-1} are derived from these two effects. Nevertheless, it is reasonable to assume that some amount of the difference between the barriers of 1 and 3 and 4 and 5 ($46.03 - 26.00 = 20.03$ kcal mol^{-1}) can be attributed to the antiaromaticity of **1pl**.

To better address the antiaromatic character of **1pl**, we will compare the inversion barriers of the P systems with N analogues. The calculated inversion barrier of a number of related three- and four-membered heterocycles are given in Table III. The inversion barrier of 6 is 46.26 kcal mol^{-1}, significantly smaller than for 1, but this is primarily due to the greater pyramidal nature of P and the more dramatic hybridization changes that P must undergo.[7]

A more appropriate comparison is the difference in inversion barriers between the saturated and unsaturated rings. The barrier in 1 is 23.30 kcal mol^{-1} greater than in 4. The difference in the inversion barriers of 1*H*-azirine 6 and aziridine 7 is 26.4 kcal mol^{-1}.[11] Again, these values reflect both differences in geometrical restrictions placed

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on the heteroatom and the effect of antiaromaticity, but quantifying the energetic consequence of each is difficult (and arbitrary). Nonetheless, the difference for N is larger than for P, suggesting less antiaromaticity in the latter.

It should also be noted that cyclopropenyl anion does not have a transition structure that corresponds to direct inversion of the anionic carbon. Rather, this C_{2v} structure is a hilltop, pocessing two imaginary frequencies.[32] We have also noted this behavior for the inversion of diazirinyl anion.[33] These planar 4π-electron structures are apparently extremely unstable, most likely from their antiaromatic nature, and are decidedly different from **1pl**. The C_{2v} structure **1pl** is a true transition structure, implying that it is less antiaromatic than cyclopropyl anion or diazirinyl anion.

Conclusions

1*H*-Phosphirene 1 is not antiaromatic. The P atom is pyramidal and two reasonable approaches to access the energy effect of the electron delocalization suggest no destabilization. The long P–C bonds coupled with the pyramidal P effectively reduce the interaction of the P lone pair with the π-electrons to nil. The inversion barrier of 1 is quite large, though only a small part of this can be attributed to antiaromaticity in the planar transition structure. Certainly, this planar transition structure is less antiaromatic that the planar form of 1*H*-azirine.

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Supplementary Material Available: Full geometries and energies of 1–3 (4 pages). Ordering information is given on any current masthead page.

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Synthesis of α-Aminocyclobutanones by the Photolytic Reaction of Chromium–Aminocarbene Complexes with Olefins

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Photolysis of chromium–(*N*-phenylamino)carbene complexes in the presence of cyclohexadiene, cyclopentadiene, and dihydropyran produced bicyclic cyclobutanones in modest yields.

Introduction

Inter-[1] and intramolecular[2] [2+2] cycloaddition reactions of ketenes with olefins to produce cyclobutanones[3] have been extensively developed. Reactions of this type involving electron-rich alkoxy- or aminoketenes are considerably less common, and in the case of aminoketenes, the nitrogen atom was always substituted with an electron-withdrawing acyl group.[4] Recently Brady[5] reported the cycloaddition of a few *N*-(aryl/alkyl)amino)ketenes, generated from *N*-arylglycine salts and tosyl chloride, to cyclopentadiene and cyclooctene, to produce modest yields of α-aminocyclobutanones. Concurrent with this, work in our laboratories had shown that photolysis of chromium–alkoxy- and –aminocarbene complexes produced reactive intermediates having ketene-like reactivity[6] and that photolysis of chromium–alkoxycarbene complexes in the presence of olefins efficiently produced α-alkoxycyclobutanones.[7] The availability of a wide variety of chromium–aminocarbene complexes by the reaction of amides with $Cr(CO)_5^{2-}$ [8] coupled with the ability to generate under very mild conditions (visible light irradiation through Pyrex, Et_2O solvent, no added base) species behaving like aminoketenes provided the opportunity to examine the photochemical reaction of these complexes with olefins to produce α-aminocyclobutanones. The results of these studies are presented below.

Results and Discussion

Photolysis of a variety of chromium–aminocarbene complexes with imines produces β-lactams[9] and with alcohols produces α-amino esters[10] in excellent yield, indicative of a ketene-like reactivity pattern of this class of reactions. In contrast, photolysis of (dimethylamino)-carbene complex 1 in the presence of an excess of cyclopentadiene resulted in no reaction. Starting carbene 1 was recovered unchanged after 48 h of irradiation, notwithstanding the fact that the same carbene converted to β-lactams in 12 h when photolyzed with imines[11] (eq 1). The inherent basicity of the dimethylamino group may seriously reduce the electrophilicity of the ketene carbonyl

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