methylfuran (**2b**) and 9.52 g (0.05 mol) of **1** was allowed to stand at ambient temperature for 21 days; an aliquot was analyzed by ^{1}H NMR periodically. After 11 days integration of starting material and product signals revealed 81% conversion to a single product, and the reaction proceeded no further thereafter. Purification of the reaction mixture by liquid chromatography (pentane) gave 10.02 g (70% yield) of **3b** as a white crystalline solid: mp 69–70 °C; ^{1}H NMR (neat) 6.4 (AB q, J = 5, 2, 2 H), 4.73 (d, J = 4.4, 1 H), 4.17 (d, J = 4.4, 1 H), 1.87 (s, 3 H), 1.5 (s, 3 H). Anal. Calcd for $C_9H_{10}Cl_3NO_3$: C, 37.73; H, 3.52; N, 4.89. Found: C, 37.76; H, 3.56; N, 4.85.

X-ray crystallographic data for 3b ($C_9H_{10}Cl_3N_1O_3$): M_r 254.55; space group $P2_1/n$; Cu radiation, wavelength 1.54184 Å; cell dimensions a = 7.002 (4) Å, b = 20.355 (15) Å, c = 9.389 (5) Å, and β = 106.86 (5)°. The structure was solved by direct methods (program MULTAN) and also by Patterson search method (program VECMAT). Least-squares refinements brought the final discrepancy (R) factor down to 0.0788 for 1208 observed reflections. No significant features in the difference Fourier map were found at this stage. A listing of the structure factors and atomic coordinates has been included in the supplementary material section.

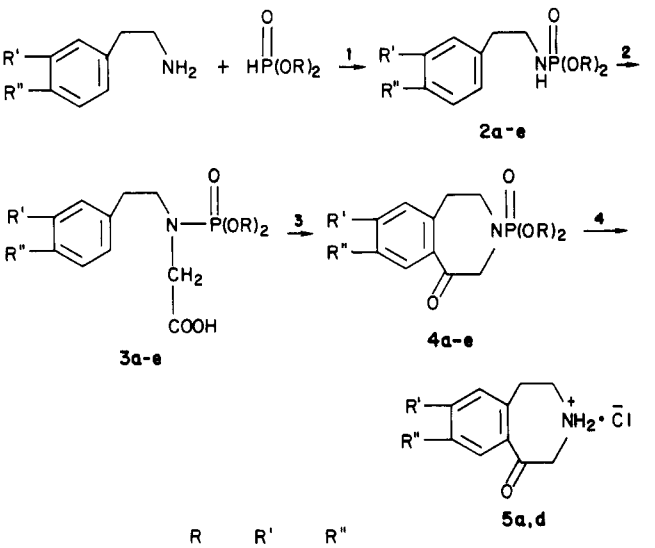
Reaction of 2-Methylfuran with 1. A mixture of 4.10 g (0.05 mol) of 2-methylfuran (**2c**) and 9.52 g (0.05 mol) of **1** was allowed to stand at ambient temperature. After 4 h analysis by ^{1}H NMR revealed a conversion of 83%, and no further conversion to bicyclic products occurred thereafter. A 4:1 ratio of **3c** and **4c** was observed by ^{1}H NMR. **3c**: 6.62 (dd, J = 2, 5, 1 H), 6.28 (d, J = 5, 1 H), 5.12 (m, 1 H), 4.6 (d, J = 4.4, 1 H), 4.47 (dd, J = 4.4, 4.4, 1 H), 1.52 (s, 3 H). **4c**: 6.78 (dd, J = 2, 5, 1 H), 6.15 (d, J = 5, 1 H), 5.12 (m, 1 H), 4.92 (d, J = 4.4, 1 H), 3.68 (d, J = 4.4, 1 H), 1.82 (s, 3 H). Upon standing for longer periods, conversion of the products to a new product was observed. The ^{1}H NMR spectrum of this product was identical with that of **5** obtained below.

2-Methyl-5-[2-nitro-1-(trichloromethyl)ethyl]furan (5). A chloroform solution of the crude mixture of **3c**, **4c**, and starting materials obtained above was treated at room temperature with 3 drops of trifluoroacetic acid. The solution turned dark immediately. After standing overnight the solution was washed with aqueous sodium bicarbonate solution, dried over anhydrous sodium sulfate, filtered, and evaporated to give a dark oil. The product was purified by evaporative distillation to give 5.0 g of **5** as a yellow oil which slowly solidified: mp 26–27 °C; ^{1}H NMR ($CDCl_3$) 6.38 (d, J = 4, 1 H), 5.93 (b, 1 H), 5.47–4.43 (m, 3 H), 2.1 (s, 3 H). Anal. Calcd for $C_8H_8Cl_3NO_3$: C, 35.26, H, 2.96, N, 5.24. Found: C, 35.34, H, 2.98, N, 5.12.

Registry No. 1, 763-16-6; **2a**, 110-00-9; **2b**, 625-86-5; **2c**, 534-22-5; **3a**, 92315-06-5; **3b**, 92315-07-6; **3c**, 92315-08-7; **4a**, 92418-53-6; **4c**, 92418-54-7; **5**, 92315-09-8.

Supplementary Material Available: Tables of X-ray crystallographic atomic coordinates for dimethylfuran adduct **3b** (4 pages). Ordering information is given on any current masthead page.

Scheme I[a]



	R	R'	R"
a	CH_3	-OCH_2O-	
b	C_2H_5	-OCH_2O-	
c	*i*-Pr	-OCH_2O-	
d	*i*-Pr	OCH_3	OC_2H_5
e	*n*-Bu	-OCH_2O-	

[a] 1. CCl_4, $(C_2H_5)_3N$; 2. NaH, $ClCH_2COOH$ in THF; 3. $SnCl_4$, $(CF_3CO)_2O$; 4. HCl(g) in THF.

Phosphoryl as a Novel Amino Protecting Group for Friedel–Crafts Acylation of *N*-[2-(3,4-Dialkoxyphenyl)ethyl]glycine

Yu-Fen Zhao,* She-Kang Xi, Ai-Teng Song, and Gai-Jiao Ji

Institute of Chemistry, Academia Sinica, Beijing, China

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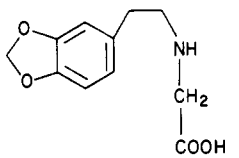
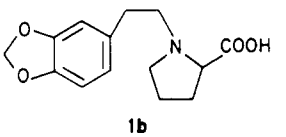
The family Cephalotaxaceae contains so far only one known genus with eight species and possibly two to three varieties mostly native to China.[1] Some ester alkaloids of cephalotaxus have shown significant activity in a variety of experimental leukemia systems. This has stimulated many groups in the world to develop total syntheses of these alkaloids.[2] Some of the promising starting materials for synthesis of the parent cephalotaxine are *N*-[2-[3,4-(methylenedioxy)phenyl]ethyl]glycine (**1a**) and *N*-[2-[3,4-(methylenedioxy)phenyl]ethyl]proline (**1b**). However,



1a



1b

under acid-catalyzed conditions these compounds failed to give Friedel–Crafts acylation products.[3,4] This is due to the basicity of the nitrogen causing decarbonylation. Use of the tosyl group has had some success in intramolecular condensation of some *N*-homopiperonylglycine derivatives.[4,5] Still, there is substantial decarbonylation. Also, the deprotection of the sulfonyl group was complicated and often unsuccessful.[4,6]

Recently, we showed a successful use of the diisopropoxyphosphinyl group as an amino protecting group in the intramolecular acylation reaction of the glycine derivatives.[7] In this paper, we report that the dimethoxy-, diethoxy-, and di-*n*-butoxyphosphinyl groups are also good amino protecting groups for the Lewis acid catalyzed

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0022-3263/84/1949-4549$01.50/0

Table I. Physical and Spectral Data of the Glycine Derivatives and Their Cyclization Products

compd	IR (C=O), cm^{-1}	NMR,[a] δ (J, Hz)	mp, °C	yield,[d] %
3a	1735	3.85 (13.0)	*b*	21
3b	1735	3.80 (12.5)	*c*	62
3c	1730	3.80 (13.0)	93–94	85
3d	1730	3.76 (12.0)	83–85	81
3e	1730	3.80 (12.5)	*b*	*e*
4a	1670	3.90 (11.0)	128–129	44 (74)[f]
4b	1670	3.91 (12.5)	92–93	34 (56)[f]
4c	1670	3.91 (11.0)	154–156	73 (77)[f,g]
4d	1670	3.92 (10.5)	92–94	60
4e	1675	3.91 (10.0)	73–75	16

[a] Chemical shifts of PNCH_2COOH or PNCH_2C=O. [b] Semisolid, purified by reversed phase column chromatrography. [c] Semisolid, purified by silica gel column chromatography. [d] For the solid, the yields are after recrystallization. [e] From ^{1}H NMR, the crude product was pure and the yield was almost quantitative. [f] Crude yield of product which had pure ^{1}H NMR spectra. [g] Compounds **4a–d** and **5a,d** have correct analyses within ±0.4% for C, H, N.

Friedel–Crafts acrylation reaction; the deprotection of these phosphoryl groups can be achieved under very mild conditions.

Results and Discussion

When we applied the literature method[8] to *N*-[2-[3,4-(methylenedioxy)phenyl]ethyl]-*N*-(dialkoxyphosphinyl)-glycine (**3**) by treating *N*-(dialkoxyphosphinyl)glycine with *β*-[3,4-(methylenedioxy)phenyl]ethyl iodide, the expected compound could not be isolated. Instead, [(3,4-methylenedioxy)phenyl]ethylene was isolated in quantative yield. Therefore, a new synthetic approach was developed (Scheme I). The *N*-alkyl dialkyl phosphoramidates **2a–e**, which were synthesized by phosphorylation of the amines,[9] were directly alkylated with chloroacetic acid in THF to give **3a–e**. This alkylation step not only prevents the side reaction but also shortens the synthetic path as compared to the case where ethyl chloroacetate was used as the alkylation reagent. The *N*-homopiperonyl-*N*-(dialkoxyphosphinyl)glycines **3b–e** were isolated in good yield. The exception was the dimethyl compound **3a**, which was obtained in 21% yield accompanied with the *N*-homopiperonylglycine hydrochloride salt, a result of the removal of the phosphoryl group after alkylation. This is because the dimethyl phosphoramidate group is more sensitive to the acid medium than the corresponding diethyl and diisopropyl ones.[6] Friedel–Crafts reaction of **3a–e** catalyzed by stannic chloride and trifluoroacetic anhydride gave *N*-(dialkoxyphosphinyl)tetrahydro-3-benzazepin-1-ones **4a–e** (Table I). These are unprecedented examples which demonstrated that the P–N bonds persisted during the Lewis acid catalyzed reactions. It should be pointed out that for a successful intramolecular Friedel–Crafts acylation, it is essential to have an activated benzene ring system.[7]

For each of the crude Friedel–Crafts reactions, HPLC chromatography showed that the ketone is the only product and that there is no decarbonylation (Table II).

All of the compounds **4a–e** can be quantitatively transformed into the keto amine hydrochloride salt after standing in hydrogen chloride saturated THF solution at 20 °C. This deprotection procedure[10] has the merits of simplicity and economy as compared to the corresponding sulfonyl derivatives.[4]

Table II. HPLC Data[a]

compd	t_R, min	compd	t_R, min
4a	4.3	**4e**	8.8
4b	4.7	**3a**	3.7
4c	6.0	**5a**	10.2

[a] Column, 5-um ODS-C_{18} (7.7 mm ǂ 10 cm); solvent, 80% methanol in water; detector, 254 nm; flow rate, 1 mL/min.

As an amino protecting group for the glycine derivatives, the phosphoryl is quite different from the corresponding acetyl and sulfonyl ones. Thus, under the same treatment by trifluoroacetic anhydride and stannic chloride, the *N*-acetyl compound was completely decarbonylated; the *N*-sulfonyl one had some decarbonylation, while the *N*-phosphoryl one gave no decarbonylation side products at all.[4,5,7] Thus, for the dual purpose of protection of the amino group, the phosphoryl group is the best among these three, perhaps associated with the nature of delocalization of the nitrogen lone pair electrons. This rationalization can be further supported by Weinstein's report[3] that a pyrrole ring π system served this function. On the other hand, too strong an electron withdrawing group such as the trifluoroacetyl group shifted the glycine derivatives to a completely different reaction path.[5,11] This principle is important in the design of protecting reagents.

Conclusions

Because of its effective dual protecting ability for the amino group and the simplicity of the deprotection procedure, the phosphoryl group is superior to the sulfonyl and acetyl groups as a general amino protecting group for organic synthesis. Also, it is worthwhile to note that the P–N bonds in the phosphoryl derivatives are relatively stable to organic and Lewis acids.[6]

Experimental Section

Methods. ^{1}H NMR spectra were taken on a Cameca-RMN 250 MHz spectrometer and chemical shifts are expressed in ppm relative to an internal Me_4Si standard in $CDCl_3$ unless otherwise indicated. IR spectra were measured as KBr plates or film on an NaCl cell on a Shimadzu 430 spectrometer. Mass spectra were taken on a AEI-50 spectrometer. Melting points were uncorrected. HPLC was performed on a Shimadzu LC-2 instrument. Elemental analyses were performed by the Analytical Laboratory, Institute of Chemistry, Academia Sinica, Beijing, China.

Preparation of *N*-[2-(3,4-Dialkoxyphenyl)ethyl]-*N*-(dialkoxyphosphinyl)glycines 3a–e. Preparation of **3c**[7] as the general procedure. To an ice-cold solution of **2c** (16.45 g, 0.05 mol) in 150 mL of THF was added 10.0 g (0.25 mol) of NaH (60% oil dispersion) slowly by portions under the protection of nitrogen. Then a solution of 10.65 g (0.11 mol) of chloroacetic acid in 50 mL of THF was added dropwise to the above grey suspension within 30 min. The mixture was allowed to stir overnight, and the temperature was raised to room temperature. To the suspension trace water was added to decompose the excess NaH. The solvent THF was removed with a rotary evaporator. The residue was treated with 6 N HCl to pH 2 and then extracted with chloroform. The organic layer was washed with water, dried with anhydrous magnesium sulfate, filtered, and evaporated. The residue was recrystallized from chloroform–*n*-hexane, giving 16.5 g (85%) of colorless crystal: mp 93–4 °C; IR (max) (chloroform) 1730, 1245, 1015 cm^{-1}.

Preparation of *N*-[2-[3,4-(Methylenedioxy)phenyl]-ethyl]-*N*-(dimethoxyphosphinyl)glycine (3a).[7] Compound

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was prepared by the general procedure described for **3c**. After workup, an oily residue was obtained. It was purified on an ODS-C_{16} (30–75 μm) column eluted with aqueous methanol to give **3a** in 21% yield; IR 1730, 1240, 1030 cm^{-1}.

Preparation of *N*-[2-[3,4-(Methylenedioxy)phenyl]-ethyl]-*N*-(diethylphosphoryl)glycine (3b). By the general procedure, 3.0 g of **2b** was treated with 2 g (60% oil dispersion) of NaH and then with 2 g of chloroacetic acid. After regular workup, the residue oil was purified on a silica gel column eluted by *n*-hexane/ethanol [3/2 (v/v)]. The compound **3b** (2.23 g) was obtained in 62% yield as a semisolid: IR 1735, 1247, 1020 cm^{-1}; ^1H NMR δ 1.28 (6 H, m), 2.70 (2 H, t), 3.17 (2 H, t), 3.80 (2 H, d, J = 12.5 Hz), 4.05 (4 H, m), 5.84 (2 H, s), 6.58 (3 H, m), 9.70 (1 H, br). Anal. Calcd for $C_{15}H_{22}NO_7P$: C, 50.14; H, 6.17; N, 3.90. Found: C, 50.16; H, 6.64; N, 3.88.

Preparation of *N*-[2-(3-Methoxy-4-ethoxyphenyl)-ethyl]-*N*-(diisopropoxyphosphinyl)glycine (3d).[7] The compound was synthesized from 17.9 g of **2d** in a similar manner as described above. The compound **3d** (17.0 g) was obtained as colorless crystal, mp 83–5 °C, in 81% yield; IR 1730, 1230, 986 cm^{-1}.

Preparation of *N*-[2-[3,4-(Methylenedioxy)phenyl]-ethyl]-*N*-(di-*n*-butoxyphosphinyl)glycine (3e). The compound **2e** (10.7 g), in 90 mL of THF, was treated with 6 g (60%) of NaH and then 6.4 g of chloroacetic acid. After regular workup, **3e** (13.0 g) was obtained as a semisolid. An analytical sample was purified on an ODS-C_{16} (30–75 μm) column eluted with aqueous methanol: IR (max) 1730, 1245, 1035 cm^{-1}; ^1H NMR δ 0.93 (6 H, m), 1.38 (4 H, m), 1.62 (4 H, m), 2.70 (2 H, m), 3.18 (2 H, m), 3.80 (2 H, d, J = 12.0 Hz), 4.0 (4 H, m), 5.86 (2 H, s), 6.60 (3 H, m), 11.08 (1 H, br). Anal. Calcd for $C_{19}H_{30}NO_7P$: C, 54.94; H, 7.23; N, 3.37. Found: C, 54.33; H, 7.45; N, 3.16.

Preparation of 2,3,4,5-Tetrahydro-7,8-(methylenedioxy)-*N*-(diisopropoxyphosphinyl)-3-benzazepin-1-one (4c).[7] The general procedure for the synthesis of **4a–e** was as follows. To a solution of 1.11 g (0.0020 mol) of **3c** in 30 mL of dry chloroform was added 0.80 mL (0.0057 mol) of trifluoroacetic anhydride under a gentle stream of nitrogen and with stirring. After 20 min, the mixture was cooled in an ice bath. A total of 1.0 mL (0.0087 mol) of stannic chloride was introduced with a hyperdermic syringe over 10 min. The mixture was stirred at 15 °C for 4 h. The resultant mixture was poured into a mixture of crushed ice and 6 N HCl. The chloroform layer was seperated, and the aqueous layer was extracted with chloroform. The organic solution was combined, washed with water, dilute sodium bicarbonate solution, and then water, and then dried by $MgSO_4$ and evaporated. Pale yellow crystals of **4c** [0.81 g (77%)] were obtained. An analytical sample was prepared by recrystallization from methanol/water, giving crystals as colorless needles; mp 154–6 °C (73%); IR 1670, 1250, 980 cm^{-1}.

Preparation of 2,3,4,5-Tetrahydro-7,8-(methylenedioxy)-*N*-(dimethoxyphosphinyl)-3-benzazepin-1-one (4a). Following the general procedure, 0.311 g of **3a** was treated with 0.6 mL of trifluoroacetic anhydride and 0.7 mL of $SnCl_4$ at 0 °C for 2 h and then at 5 °C for 12 h. After regular workup, 0.23 g (74%) of **4a** were obtained. Recrystallization from ether gave 0.135 g (44%) of colorless crystals: mp 128–9 °C; IR 1670, 1240, 1030 cm^{-1}; ^1H NMR δ 2.93 (2 H, t), 3.40 (8 H, m), 3.90 (2 H, d, J = 11 Hz), 5.97 (2 H, s), 6.61 (1 H, s), 7.17 (1 H, s). Anal. Calcd for $C_{13}H_{16}NO_6P$: C, 49.84; H, 5.11; N, 4.47. Found: C, 50.07; H, 5.18; N, 4.48. MS, M^+ 313 (100), M + 1 (17.2), 298 (4.9) 285 (13.6), 270 (4.9), 254 (2.2), 188 (44), 176 (52.3).

Preparation of 2,3,4,5-Tetrahydro-7,8-(methylenedioxy)-*N*-(diethoxyphosphinyl)-3-benzazepin-1-one (4b). Following the general procedure, 0.718 g of **3b** was treated with 1.2 mL of trifluoroacetic anhydride and 1.3 mL of $SnCl_4$ in 20 mL of $CHCl_3$. After workup, 0.38 g (56%) of light yellow solid was obtained. Recrystallization from ether gave 0.23 g (34%) of **4b** as colorless crystals: mp 92–3 °C; IR 1670, 1240, 1030 cm^{-1}; ^1H NMR δ 1.16 (6 H, m), 2.93 (2 H, m), 3.44 (2 H, m), 3.65 (2 H, m), 3.84 (2 H, m), 3.91 (2 H, d, J = 12.5 Hz), 5.97 (2 H, s), 6.62 (1 H, s), 7.17 (1 H, s). Anal. Calcd for $C_{15}H_{20}NO_6P$: C, 52.79; H, 5.87; N, 4.11. Found: C, 52.54; H, 5.76; N, 3.91.

Preparation of 2,3,4,5-Tetrahydro-7-methoxy-8-ethoxy-*N*-(diisopropoxyphosphinyl)-3-benzazepin-1-one (4d).[7] Compound **4d** was prepared according to the method for the synthesis of **4c**. The crude product was recrystallized from ethyl ether, giving colorless needles: mp 92–4 °C (60%); IR 1670, 1250, 980 cm^{-1}.

Preparation of 2,3,4,5-Tetrahydro-7,8-(methylenedioxy)-*N*-(di-*n*-butoxyphosphinyl)-3-benzazepin-1-one (4e). **3e** (1.16 g) was treated with 1.8 mL of trifluoroacetic anhydride and 2.2 mL of $SnCl_4$ at 15 °C for 4 h and then at 5 °C for 24 h. After workup, the product was recrystallized from $CHCl_3$/*n*-hexane, giving 0.17 g (16%) of colorless crystals: mp 73–5 °C; IR 1675, 1240, 1030, 990 cm^{-1}; ^1H NMR δ 0.87 (6 H, m), 1.26 (4 H, m), 1.47 (4 H, m), 2.92 (2 H, t), 3.43 (2 H, m), 3.55 (2 H, m), 3.75 (2 H, m), 3.91 (2 H, d, J = 10.0 Hz), 5.97 (2 H, s), 6.63 (1 H, s), 7.17 (1 H, s). Anal. Calcd for $C_{19}H_{28}NO_6P$: C, 57.43; H, 7.05; N, 3.52. Found: C, 57.65; H, 7.15; N, 3.39.

Keto Amine–HCl Salt 5a. A solution of 0.245 g of **4c** in 10 mL of dry THF was saturated with dried HCl(g). After being kept overnight at 20 °C, the precipitate was filtered and washed with ether, giving 0.136 g (85%) of **5a** as colorless crystals. Compound **4a** (0.028 g), after the same treatment, gave 0.016 g of **5a** (77%). Compound **4b** (0.023 g) gave 0.013 g (78%) of **5a**. Compound **4e** (0.030 g) gave 0.014 g (75%) of **5a**. All these salts have the same IR: 1650, 1560, 2350–2800 cm^{-1}. ^1H NMR in trifluoroacetic acid: 3.31 (2 H, t), 3.80 (2 H, t), 4.46 (2 H, s), 6.09 (2 H, s), 6.82 (1 H, s), 7.26 (1 H, s).

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Registry No. **2a**, 87261-13-0; **2b**, 92269-46-0; **2c**, 87212-43-9; **2d**, 87212-42-8; **2e**, 92241-51-5; **3a**, 87212-45-1; **3b**, 92241-52-6; **3c**, 87212-49-5; **3d**, 87212-48-4; **3e**, 92241-53-7; **4a**, 89815-74-7; **4b**, 92241-54-8; **4c**, 87212-50-8; **4d**, 87212-53-1; **4e**, 92241-55-9; **5a**, 87212-52-0; chloroacetic acid, 79-11-8.

An Extremely Facile Carbon Epimerization

Stephen L. Buchwalter[1]

Department of Chemistry, Harvard University, Cambridge, Massachusetts 02138

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In connection with studies of the methylenecyclopropane rearrangement,[2] optically active *trans*-2,3-dicyanomethylenecyclopropane (1) was prepared. Attempts to measure the optical rotation of **1** in methanol led to the discovery of the rapid epimerization reported herein. The polarimeter reading was observed to decrease rapidly with time, leading to the pseudo-first-order plot shown in Figure 1. Similar behavior was observed in distilled water but not in benzene, chloroform, or acetonitrile. When **1** was dissolved in methanol that had previously been saturated with sodium bicarbonate, no optical rotation was observed. Liquid chromatography of the product mixtures showed the presence of **1** and a more polar material, later identified as the cis isomer **2**. Epimerization of **1** in methanol-*O-d* led to considerable diminution of protium on the ring carbons as shown by NMR.

The latter experiment rules out an alternative mechanism involving reversible ring-opening. Also in contradiction to that possibility is the known[2] overwhelming thermodynamic preference for the rearranged methylenecyclopropanedinitriles, ((*Z*)- and (*E*)-2-cyanocyclopropylidene)acetonitrile (**3** and **4**). If ring-opening

(1) Current address: Texaco, Inc., P.O. Box 509, Beacon, NY 12508.
(2) Buchwalter, S. L. *Tetrahedron*, accepted for publication.

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