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Reactions of Phosphites with Nitroalkene Derivatives: Syntheses of β-Keto Phosphonates and α-Cyanoalkylphosphonates

Dae Young Kim* and Dong Young Oh†

Department of Chemistry, Soonchunhyang University, Asan P.O. Box 97, Chungnam 336-600, Korea
†Department of Chemistry, Korea Advanced Institute of Science and Technology, Taejon 305-701, Korea
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The addition of phosphite derivatives **1** to nitroalkenes **2** afforded α-phosphoryl nitronates which, on treatment MCPBA, were converted β-keto phosphonates **3**. A versatile reaction conditions to generate α-phosphoryl nitronates were examined. α-Cyanoalkylphosphonates **6** were prepared from the diethyl trimethylsilyl phosphite (DTSP) **1c** with nitroalkenes **2** and followed by reduction.

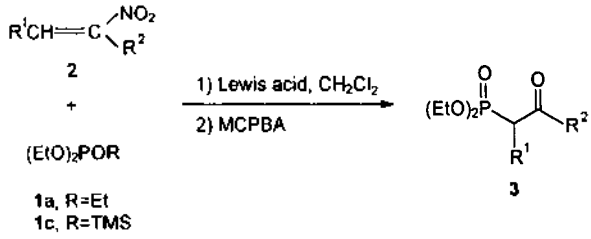
Introduction

Phosphonates are valuable reagents for the construction of carbon-carbon double bonds because their use provides control of olefin regio- and stereoselectivity.[1] β-Keto phosphonates and α-cyanoalkylphosphonates are useful intermediates for homologations of aldehydes and ketones to α, β-unsaturated carbonyl and nitrile compounds *via* the Hornor-Wadsworth-Emmons condensation. Many synthetic approaches for the preparation of β-keto phosphonates have been developed, ranging from the direct Arbuzov reaction of trialkyl phosphites with 1-haloalkyl ketones[2] to the more sophisticated methods using organometallic reagents.[3] They have limitations in terms of the conditions employed, competition from other reactions, and the preparation of starting materials. Recently, β-keto phosphonates were also obtained by either base-induced isomerization of enol phosphates or reaction of ketone enolates with dialkylphosphorochloridite followed by air oxidation.[4] These synthetic methods using n-butyllithium are not convenient in terms of economical cost and safety. Other miscellaneous methods include oxidation of β-hydroxyalkylphosphonates,[5] acylation of 1-(trimethylsilyl)vinylphosphonates,[6] hydrolysis of vinylogous phosphoramides,[7] reaction of 2-(diethoxyphosphinyl)carboxylic acid chlorides with organometallic reagents,[8] the use of (diethoxyphosphoryl)acetonitrile oxides,[9] *via* allenenic intermediates,[10] Pd(0)-catalyzed rearrangement of the 2,3-epoxyalkyl phosphonates,[11] reaction of phosphite with epoxysulfones[12] or chloroepoxide,[13] reaction of silyl enol ethers with phosphite using hypervalent iodine compound,[14] alkylation of β-keto phosphonates,[15] addition of allenicphosphonates with dialkylamines,[16] acylation of triethyl phosphonoacetate[17] or diethyl phosphonoacetic acid.[18] α-Cyanoalkylphosphonates have been obtained by the reaction of triethyl phosphite with 1-bromo-1-nitro-2-phenylethylene[19] and treatment of benzyl cyanide with suitable base and diethyl chlorophosphate.[20]

Our research has focused on the reaction and development of synthetic routes to α-substituted alkylphosphonates,[21] and we have developed the synthetic method from nitroalkene derivatives to β-keto phosphonates[22] and α-cyanoalkylphosphonates.[23] Herein we report the reaction of phosphites with nitroalkene derivatives in more details, providing information on its scopes, mechanisms, and limitations.

Results and Discussion

Synthesis of β-Keto Phosphonates 3. The nitro group is particularly versatile in synthesis since it may be transformed into legion of diverse functionality.[24] It can be readily converted to a carbonyl substituent in the classical Nef reaction.[25] The nitroalkenes are synthetic equivalent of the carbonyl α-cations.[26] Addition of phosphites to nitroalkenes affords α-phosphoryl nitronates in the presence of Lewis acid. These nitronates are converted into β-keto phosphonates under Nef reaction conditions. The addition reaction required one equivalent of Lewis acid and the order of reactivity of Lewis acids was $TiCl_4$>$SnCl_4$>$ZnCl_2$ (Table 1, entries 1-3). Therefore, we performed the addition of triethyl phosphite **1a** with nitroalkenes **2** in the presence of $TiCl_4$ and followed by the Nef reaction with *m*-chloroperbenzoic acid (MCPBA). In general, the Nef reaction often involves either acidic or strongly basic condition. However, the reaction of triethyl phosphite and nitroalkene in the presence of $TiCl_4$ followed by hydrolysis with water gave a β-keto phosphonate with trace amounts. Fortunately,



Scheme 1.

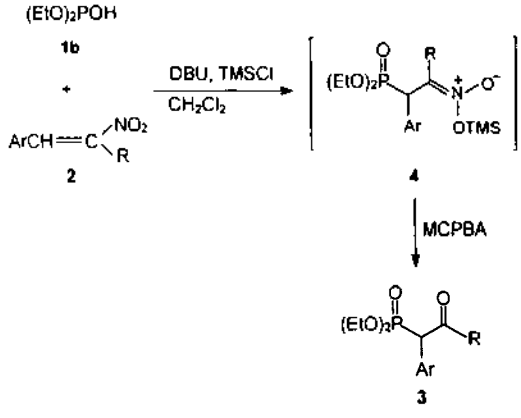
oxidative cleavage of α-phosphoryl nitronates with MCPBA afforded β-keto phosphonates **3** in good yields under mild conditions. Treatment of diethyl trimethylsilyl phosphite (DTSP)[27] **1c**, instead of triethyl phosphite **1a** with nitroalkene **2a** gave the similar results (Table 1, entries 1 and 4). The reduced yields were obtained when the substituents of nitroalkenes **2** were alkyl groups (Table 1, entries 10-11). The present synthetic route provides a convenient preparation of β-keto phosphonates **3** from nitroalkenes **2** and triethyl phosphite **1a** under acidic conditions.

In the presence of DBU and chlorotrimethylsilane (TMSCl), addition of diethyl phosphite (**1b**) to nitoalkenes **2** at room temperature affords α-phosphoryl nitronates **4** which, on treatment with MCPBA, were smoothly converted into 1-aryl-2-oxoalkylphosphonates **3** in good yields (Table 2). In this reaction, the Nef reaction proceeded smoothly at room temperature in the presence of MCPBA

Table 1. Preparation of β-keto phosphonates **3**

Entry	R	R^1	R^2	Lewis	Yield[a] (%)
1	Et	Ph	Me	$TiCl_4$	**3a**, 92
2	Et	Ph	Me	$SnCl_4$	**3a**, 80
3	Et	Ph	Me	$ZnCl_2$	**3a**, 23
4	TMS	Ph	Me	$TiCl_4$	**3a**, 87
5	Et	Ph	Et	$TiCl_4$	**3b**, 78
6	Et	*p*-OMe, C_6H_4	Me	$TiCl_4$	**3c**, 93
7	Et	*p*-OMe, C_6H_4	Et	$TiCl_4$	**3d**, 81
8	Et	*p*-Cl, C_6H_4	Me	$TiCl_4$	**3e**, 84
9	Et	*p*-Cl, C_6H_4	Et	$TiCl_4$	**3f**, 72
10	Et	H	Et	$TiCl_4$	**3g**, 22
11	Et	$-(CH_2)_4-$		$TiCl_4$	**3h**, 31

[a] Isolated yields are based on nitroalkenes **2**.



Scheme 2.

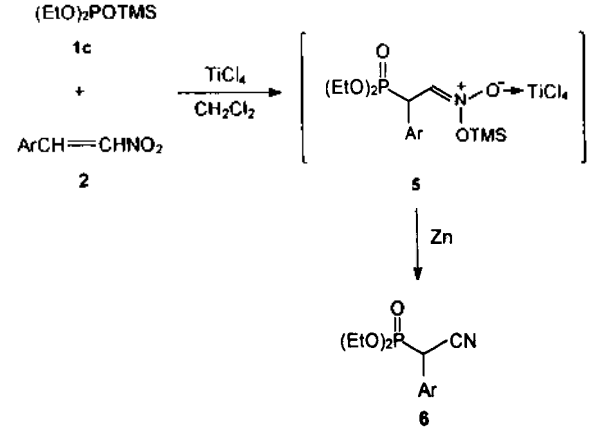
Table 2. Preparation of β-keto phosphonates **3** under basic conditions

No	Ar	R	Yield[a] (%)
3a	Ph	Me	85
3b	Ph	Et	87
3c	*p*-OMe, C_6H_4	Me	81
3d	*p*-OMe, C_6H_4	Et	84
3e	*p*-Cl, C_6H_4	Me	71
3f	*p*-Cl, C_6H_4	Et	65

[a] Isolated yields are based on nitroalkenes **2**.

in CH_2Cl_2. The Nef reaction step was crucial for obtaining the desired carbonyl compounds **3**. We found that treatment of aqueous HCl solution instead of MCPBA to α-phosphoryl nitronates **4** affords β-keto phosphonates **3** in trace amount. Present procedure provides a preparation of β-keto phosphonates **3** from the reaction of nitroalkene **2** with diethyl phosphite **1b** under basic conditions.

Synthesis of α-Cyanoalkylphosphonates 6. In the presence of $TiCl_4$, DTSP **1c** react smoothly with β-nitrostyrenes **2** to give α-phosphory nitronate **5**. Subsequent addition of zinc dust to the reaction mixture produce low valent titanium from $TiCl_4$,[28] which then converts α-phosphoryl nitronates **5** to 1-aryl-1-cyanomethylphosphonates **6**. Products are purified by Kugelrohr distillation (Table 3). The present reaction offers a new synthetic route to α-cyanoalkylphosphonates **6** a successful use of titanium compound as Lewis acid and reductant in a simple one-pot procedure.



Scheme 3.

Table 3. Preparation of cyclic α-cyanoalkylphosphonates **6**

No	Ar	Yield[a] (%)	bp (°C/mmHg)	^{31}P NMR[b]
6a	Ph	86	144-148/0.3	14.49
6b	*p*-OMe, C_6H_4	88	159-163/0.3	14.69
6c	*o*-OMe, C_6H_4	74	160-164/0.3	14.10
6d	*p*-Cl, C_6H_4	85	149-151/0.4	13.89
6e	*o*-Cl, C_6H_4	81	143-146/0.3	10.15
6f	*p*-Me, C_6H_4	91	144-149/0.3	15.02

[a] Isolated yields by Kugelrohr distillation. [b] The conversion of positive ^{31}P NMR signals to down field from H_3PO_4 is used.

In conclusion, this study has shown that it is possible to prepare β-keto phosphonates **3** and α-cyanoalkylphosphonates **6** from the reaction of phosphite **1** with nitroalkene **2** derivatives. The reaction of phosphite **1** with nitroalkenes **2** may involve the initial formation of α-phosphoryl nitronates and a subsequent the Nef reaction or reduction. These reactions described here represent convenient and novel methods for the preparation of β-keto phosphonates **3** and α-cyanoalkylphosphonates **6**.

Experimental

General. ^{1}H and ^{13}C NMR spectra were recorded on a Varian FT-80A and Bruker AC 200 spectrometer using tetramethylsilane as an internal standard. ^{31}P NMR spectra obtained on a Varian FT-80A spectrometer at 29.95 MHz. Chemical shifts were related to 85% H_3PO_4 as an external standard. Chemical shifts are measured in part per million (δ) and coupling constants, *J*, are reported in Hz. Multiplicity was simplified such as s=singlet, bs=broad singlet, d=doublet, t=triplet, dq=double quartet, and m=multiplet. Infrared spectra were measured on a Perkin-Elmer 283B. Mass spectra were determined with a Hewlett-Packard 5985A through electron impact ionization method. Methylene chloride was refluxed and distilled from phosphorus pentoxide. Column chromatography was performed on Merck silica gel 60 (230-400 mesh). The nitroalkenes[29] and α-nitro epoxides[30] were prepared as reported previously.

Synthesis of β-Keto Phosphonates 3 under Acidic Conditions. To a stirred solution of nitroalkenes **2** (1 mmol) in methylene chloride (8 mL) was added dropwise $TiCl_4$ (0.11 mL, 1 mmol) at − 78 °C. After being stirred at − 78 °C for 10 min, triethyl phosphite **1a** (0.19 mL, 1.1 mmol) was added dropwise and the reaction mixture was stirred at − 78 °C for 30 min. After being warmed to 0 °C, MCPBA (0.414 g, 1.2 mmol, 50% purity) in methylene chloride (5 mL) was added to the reaction mixture. The resulting solution was left for 1 h to reach room temperature. It was washed with 1 M Na_2SO_3, saturated aqueous $NaHCO_3$, and water and then dried ($MgSO_4$) and evaporated to leave a crude oil. This was purified by flash chromatography on silica gel (diethyl ether).

Synthesis of β-Keto Phosphonates 3 under Basic Conditions. To a stirred solution of diethyl phosphite (**1b**, 0.166 g, 1.2 mmol) and the nitroalkene **2** (1.0 mmol) in methylene dichloride (5 mL) was added dropwise DBU (0.198 g, 1.3 mmol) at 0 °C. After 20 min, chlorotrimethylsilane (0.19 mL, 1.5 mmol) was added dropwise to the reaction mixture. The mixture was stirred at room temperature for 1 h after which a solution of MCPBA (0.259 g, 1.5 mmol) in methylene dichloride (5 mL) was added dropwise to it at 0 °C. The resulting solution was left for 1 h to reach room temperature. It was then washed with aqueous Na_2SO_3 (1 M, 20 mL), HCl (1 M, 20 mL), saturated aqueous $NaHCO_3$ (20 mL) and water (20 mL) and then dried ($MgSO_4$) and evaporated to leave a crude oil. This was purified by flash chromatography on silica gel (diethyl ether).

Diethyl 1-phenyl-2-oxopropylphosphonate (3a). ^{1}H NMR ($CDCl_3$, 80 MHz) δ 0.92-1.50 (m, 6H), 2.44 (s, 3H), 3.8-4.6 (m, 5H), 7.23-7.7 (m, 5H); IR ($CHCl_3$) 3460, 2958, 2910, 1569, 1255, 1050-1022 cm $^{-1}$; Mass (m/z) 270 (M^+, 2.5%), 255 (12.3) 227 (100).

Diethyl 1-phenyl-2-oxobutylphosphonate (3b). ^{1}H NMR ($CDCl_3$, 80 MHz) δ 0.84-1.34 (m, 9H), 2.60-3.0 (m, 2H), 3.70-4.20 (m, 4H), 4.23 (d, *J*=25.2 Hz), 7.26-7.47 (m, 5H); IR (neat) 3470, 2984, 1653, 1576, 1253, 1052-1025, 966 cm $^{-1}$; Mass (m/z) 284 (M^+, 3.1%), 269 (5.4), 241 (61.1), 136 (100).

Diethyl 1-(*p*-methoxyphenyl)-2-oxopropylphosphonate (3c). ^{1}H NMR ($CDCl_3$, 80 MHz) δ 1.20 (dt, 6H, *J*=6.9, 9.0 Hz), 2.41 (s, 3H), 3.91 (s, 3H), 3.90-4.20 (m, 4H), 4.26 (d, *J*=26.5), 6.80-7.60 (m, 4H); IR (neat) 3450, 2984, 2911, 1603, 1569, 1260, 1087-1020 cm^{-1}; Mass (m/z) 300 (M^+, 0.5%), 285 (16.0), 257 (100).

Diethyl 1-(*p*-methoxyphenyl)-2-oxobutylphosphonate (3d). ^{1}H NMR ($CDCl_3$, 80 MHz) δ 0.92-1.35 (m, 9H), 2.60-3.0 (m, 2H), 3.77 (s, 3H), 3.60-4.20 (m, 4H), 4.21 (d, *J*=25.2 Hz), 6.80-7.0 (m, 2H), 7.20-7.50 (m, 2H); IR (neat) 3480, 2982, 1610, 1576, 1253, 1051-1025, 969 cm $^{-1}$; Mass (m/z) 314 (M^+, 1.6%), 299 (10.4), 261, 166 (100).

Diethyl 1-(*p*-chlorophenyl)-2-oxopropylphosphonate (3e). ^{1}H NMR ($CDCl_3$, 80 MHz) δ 0.92-1.33 (m, 6H), 2.40 (s, 3H), 3.90 (s, 3H), 3.82-4.20 (m, 4H), 4.22 (d, *J*=26.3 Hz), 0.81-7.59 (m, 4H); IR (neat) 3450, 2985, 2910, 1576, 1256, 1050-1017 cm^{-1}; Mass (m/z) 304 (M^+, 4.5%), 289, 261, 156 (100).

Diethyl 1-(*p*-chlorophenyl)-2-oxobutylphosphonate (3f). ^{1}H NMR ($CDCl_3$, 80 MHz) δ 0.92-1.35 (m, 9H), 2.60-3.0 (m, 2H), 3.80-4.20 (m, 4H), 4.20 (d, *J*=25.1 Hz), 7.26-7.41 (m, 4H); IR (neat) 3470, 2983, 1576, 1252 (P=O), 1051-1017, 967 cm^{-1}; Mass (m/z) 318 (M^+, 2.5%), 303, 275 (100), 170.

Diethyl 2-oxobutylphosphonate (3g). ^{1}H NMR ($CDCl_3$, 200 MHz) δ 1.07 (t, 3H, *J*=7.2 Hz), 1.34 (t, 6H, *J*=7.0), 2.65 (q, 2H, *J*=7.3), 3.08 (d, 2H, *J*=22.8), 4.07-4.23 (m, 4H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 7.54, 16.27 (d, *J*=5.95), 37.35, 42.12 (d, 127.42), 62.50 (d, *J*=6.24); IR (neat) 2990, 1710, 1255, 1036, 970 cm^{-1}; Mass (m/z) 204 (M^+, 13%), 180 (5), 179 (100), 163 (5), 152 (21), 151 (33), 135 (12), 109 (36).

2-(Diethoxyphosphinyl)cyclohexanone (3h). ^{1} NMR ($CDCl_3$, 200 MHz) δ 1.36 (t, 6H, *J*=7.1 Hz), 1.5-2.6 (dt, 1H, *J*=23.1, 5,3), 3.9-4.4 (m, 4H); IR (neat) 2900 (aliphatic C-H), 1680 (C=O), 1240 (P=O), 900, 1010 (P-O) cm^{-1}; Mass (m/z) 234 (M^+, 7.2%), 206 (17), 178 (16), 150 (21), 138 (25), 111 (26), 84 (100).

Synthesis of α-Cyanoalkylphosphonates 6. To a stirred solution of β-nitrostyrene **2** (2.1 mmol) in methylene chloride under nitrogen at − 40 °C was slowly added titanium(IV) chloride (0.22 mL, 2 mmol). After 10 min of stirred at − 40 °C, diethyl trimethylsilyl phosphite **1c** (421 mg, 2 mmol) was added into the reaction mixture. The resulting solution was left to slowly return to room temperature. After disappearance of β-nitrostyrene (*ca.* 2 h), zinc dust (261 mg, 4 mmol) was added and resulting mixture was stirred for another hour. The reaction was quenched by adding aqueous $NaHCO_3$ and diethyl ether. The suspension was then filtered through a Celite pad. The filtrate was extracted with diethyl ether. The organic layer separated, dried over $MgSO_4$, and evaporated to leave a thin yellow oil. The product was purified by Kugelrohr dis-

tillation.

Diethyl 1-phenyl-1-cyanomethylphosphonate (6a). ^{1}H NMR ($CDCl_3$, 80 MHz) δ 1.20 (t, 6H, *J*=7.3 Hz), 4.01 (m, 4H), 4.31 (d, 1H, *J*=26.0), 7.37 (s, 5H); IR ($CDCl_3$) 2250, 1260, 1020 cm^{-1}; Mass (m/z) 253 (M^+, 18.5%), 117 (92.9), 109 (100).

Diethyl 1-(*p*-methoxyphenyl)-1-cyanomethylphosphonate (6b). ^{1}H NMR ($CDCl_3$, 80 MHz) δ 1.21 (t, 6H, *J*=7.2 Hz), 3.78 (s, 3H), 4.0 (m, 4H), 4.30 (d, 1H, *J*= 26.0), 6.80-7.70 (m, 4H); IR ($CDCl_3$) 2245, 1260, 1035 cm^{-1}; Mass (m/z) 283 (M^+, 14.5%), 147 (90.1), 109 (100).

Diethyl 1-(*o*-methoxyphenyl)-1-cyanomethylphosphonate (6c). ^{1}H NMR ($CDCl_3$, 80 MHz) δ 1.20 (t, 6H, *J*=7.3 Hz), 3.75 (s, 3H), 4.04 (m, 4H), 4.35 (d, 1H, *J*= 25.5), 6.85-7.70 (m, 4H); IR ($CDCl_3$) 2240, 1260, 1030-1010 cm^{-1}; Mass (m/z) 283 (M^+, 11.5%), 147 (100), 109 (94.1).

Diethyl 1-(*p*-chlorophenyl)-1-cyanomethylphosphonate (6d). ^{1}H NMR ($CDCl_3$, 80 MHz) δ 1.20 (t, 6H, *J*=7.3 Hz), 4.06 (m, 4H), 4.35 (d, 1H, *J*=25.8), 7.15-7.55 (m, 4H); IR ($CDCl_3$) 2260, 1260, 1040-1010 cm^{-1}; Mass (m/z) 287 (M^+, 6.8%), 152 (11.0), 151 (32.4), 150 (28.8), 109 (100).

Diethyl 1-(*o*-chlorophenyl)-1-cyanomethylphosphonate (6e). ^{1}H NMR ($CDCl_3$, 80 MHz) δ 1.20 (t, 6H, *J*=7.2 Hz), 4.12 (m, 4H), 4.70 (d, 1H, *J*=26.3), 7.10-7.55 (m, 4H); IR ($CDCl_3$) 2230, 1260, 1030-1010 cm^{-1}; Mass (m/z) 287 (M^+, 4.2%), 151 (31.4), 150 (28.8), 109 (100).

Diethyl 1-(*p*-tolyl)-1-cyanomethylphosphonate (6f). ^{1}H NMR ($CDCl_3$, 80 MHz) δ 1.20 (t, 6H, *J*=7.2 Hz), 2.21 (s, 3H), 3.98 (4m, H), 4.30 (d, 1H, *J*=25.3), 7.10-7.55 (m, 4H); IR ($CDCl_3$) 2250, 1260, 1020 cm^{-1}; Mass (m/z) 267 (M^+, 20.7%), 131 (100), 109 (97.6).

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[4+4] Cyclodimer of *tert*-Butyl 9-Anthroate and Furan and [4+4] Cyclodimers of Alkyl 9-Anthroate

Taehee Noh*, Heejun Lim, Daekyun Kim, and Kyungmoon Jeon

Department of Chemistry Education, Seoul National University, Seoul 151-742, Korea
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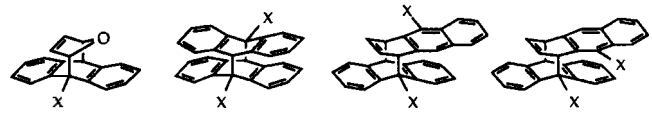
Irradiation of *tert*-butyl 9-anthroate and furan through a Uranium glass filter gave the [4+4] cyclodimer (21.8%) of *tert*-butyl 9-anthroate and furan and the 1,4-10',9' cyclodimer (4.2%) of *tert*-butyl 9-anthroate as well as the 9,10-10',9' cyclodimer (65.7%) of *tert*-butyl 9-anthroate. The [4+4] cyclodimer of *tert*-butyl 9-anthroate and furan was found to be thermally dissociated into their unit components with the activation enthalpy of 35.6 kcal/mole and the activation entropy of 7.6 eu, and photochemically dissociated to produce excited *tert*-butyl 9-anthroate. Quantum yields for the photodissociation to *tert*-butyl 9-anthroate and the formation of excited *tert*-butyl 9-anthroate in cyclohexane at room temperature were determined to be 0.56 and 0.19, respectively. The 1,4-10',9' cyclodimer of *tert*-butyl 9-anthroate in DMF was thermally dissociated into *tert*-butyl 9-anthroate with the activation enthalpy of 34.8 kcal/mole and the activation entropy of 16.4 eu. Upon irradiation, the [4+4] cyclodimers of *tert*-butyl 9-anthroate and the [4+4] cyclodimers of methyl 9-anthroate were quantitatively dissociated. However, no adiabatic photoreversion was observed from any of the cyclodimers. Quantum yields for the photodissociation in cyclohexane at room temperature were measured and compared.

Introduction

Since the first dimer of an aromatic compound, the 9,10-10',9' anthracene cyclodimer, was discovered over a hundred years ago, many arene-arene dimers have been synthesized.[1] Recently, synthesis of energy-rich cyclodimers and investigation of their properties have been carried out for studying unusual chemical behaviors such as adiabatic photodissociation and chemiluminescence.[2] Adiabatic photodissociation has been reported in some anthracene-benzene dimers,[3,4] naphthalene-benzene dimers,[5-7] anthracene-naphthalene dimers,[8] and dibenzenes.[9] The photoreversion of [4+4] anthracene-benzene cyclodimer was found to be one of the most efficient adiabatic processes. However, the synthesis of the cyclodimers has been accomplished by multistep strategies,[2-4] because benzene itself does not add photochemically to the anthracene ring. Therefore, the extension of its chemistry to the derivatives is rather limited. Recently, we studied the photolysis and the thermolysis of [4+4] anthracene-furan cyclodimers,[10] which can be prepared from direct irradiation of anthracenes and furan. Although the efficiency of adiabaticity is relatively low, the photoreversion of [4+4] anthracene-furan cyclodimers was found to produce excited anthracenes. In addition, we found the first example of intermolecular photodimerization of *meso*-substituted anthracene involving the 1, 4, 9', and 10' positions of the anthracene rings in the irradiation of methyl 9-anthroate.[11] In this paper, we report the photoreaction of *tert*-butyl 9-anthroate (**1**) and furan, and the properties of [4+4] cyclodimer (**2**) of **1** and furan and [4+4] cyclodimers (**5-9**) of alkyl 9-anthroate.



2 X = $CO_2C(CH_3)_3$ **5** X = $CO_2C(CH_3)_3$ **7** X = $CO_2C(CH_3)_3$ **9** X = CO_2CH_3
3 X = CO_2CH_3 **6** X = CO_2CH_3 **8** X = CO_2CH_3
4 X = CN

Results and Discussion

The irradiation of **1** in the presence of excess furan with a medium-pressure mercury lamp through a Uranium glass filter gave three products, one of which was the desired [4+