JOC Article

Reaction of Electron-Deficient N═N, N═O Double Bonds, Singlet Oxygen, and CC Triple Bonds with Acyloxyketenes or Mesoionic 1,3-Dioxolium-4-olates: Generation of Unstable Mesoionic 1,3-Dioxolium-4-olates from Acyloxyketenes

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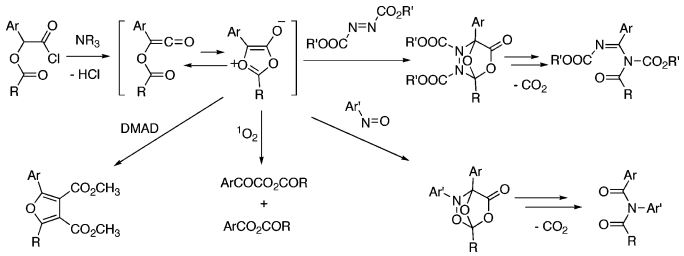
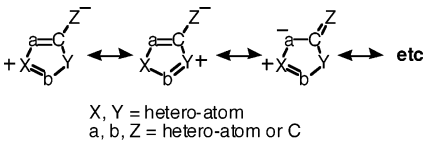


Reactions of azodicarboxylates and nitrosobenzene derivatives with acyloxyketenes generated from dehydrochlorination of α-acyloxyarylacetyl chlorides were carried out to give triacylbenzamidine and *N*-arylimide derivatives, respectively, in good yields. The same compounds were obtained from the reaction with mesoionic 1,3-dioxolium-4-olates generated by $Rh_2(OAc)_4$-catalyzed decomposition of aryldiazoacetic anhydride derivatives. Formation of the same compounds from the different starting materials indicates that their reactions involve the same intermediates. The formation of triacylbenzamidine and *N*-arylimide derivatives is explained by 1,3-dipolar cycloaddition between electron-deficient N═N or N═O bonds and mesoionic 1,3-dioxolium-4-olates following by decarboxylation, ring opening of the resultant carbonyl ylides, and subsequent Mumm rearrangement of the corresponding imidates. The reaction with singlet oxygen composed of more electronegative atoms than N═N and N═O bonds also gave products arising from the singlet oxygen adducts with 1,3-dioxolium-4-olates. The generation of less stable mesoionic 1,3-dioxolium-4-olates from acyloxyketenes was also confirmed by isolation of furandicarboxylates on generation of acyloxyketenes from α-acyloxyarylacetyl chlorides in the presence of reactive dipolarophile dimethyl acetylenedicarboxylate.

Introduction

Since the synthesis of sydonone via intramolecular dehydration of *N*-nitroso-*N*-phenylglycine by Earl and Mackney[1] and the introduction of the concept of mesoionic molecules **1** by Baker and Ollis,[2] preparation and synthetic application of many mesoionic compounds have been reported.[3] Mesoionic compounds **1** cannot be represented by normal covalent structures but by many resonance forms bearing positively and negatively charged atoms.[2]



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Typical mesoionic compounds **2**−**5** composed of nitrogen and oxygen atoms as ring heteroatoms are shown in Scheme 1. Mesoionic compounds contain six ring electrons delocalizing over p-orbitals of carbon atoms and heteroatoms, which suggests a kind of aromaticity. However, the energy level of p-orbitals of an oxygen atom is lower than those of a nitrogen and a carbon atom, and therefore resonance stability of mesoionic systems

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(1) Earl, J. C.; Mackney, A. W. *J. Chem. Soc.* **1935**, 899.

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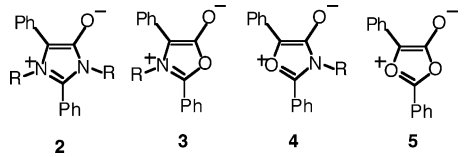
SCHEME 1



containing an oxygen atom should be smaller than those containing nitrogen atoms.

PM3 calculation of heats of hydrogenation $\Delta\Delta H_f$ for some 2,5-diphenyl-substituted mesoionic compounds revealed that $\Delta\Delta H_f$ increases in the order of the 1,3-imidazolium-4-olate **2**,[4] the münchnone **3**,[5] the isomünchnone **4**,[3d,6,7] and the 1,3-dioxolium-4-olate **5**[8,9] and that the resonance stability of 2,5-diphenyl-substituted mesoionic 1,3-dioxolium-4-olate **5** is 26 kcal/mol lower than that of 1,3-imidazolium-4-olate **2** containing two nitrogen atoms. In fact, diphenyl-substituted mesoionic 1,3-imidazolium-4-olates **2**, münchnones **3**, and isomünchnones **4** can be isolated as stable crystals, but 1,3-dioxolium-4-olates **5** cannot be isolated as stable compounds. Consequently, we have been interested in the chemical behaviors of unstable 1,3-dioxolium-4-olates **5**. To produce the 1,3-dioxolium-4-olates we have utilized an intramolecular carbenoid/carbonyl reaction method, which has very often been reported as a traditional method for generation of carbonyl ylides, using aryldiazoacetic anhydride derivatives **6**.

We observed in preliminary experiment that $Rh_2(OAc)_4$-catalyzed decomposition of aryldiazoacetic anhydride derivatives **6** in the presence of a strongly reactive dipolarophile such as *trans*-1,2-dibenzoylethylene, *N*-phenylmaleimide, or DMAD gave 1,3-dipolar cycloadducts **8** of 1,3-dioxolium-4-olates **5** with olefinic dipolarophiles or furandicarboxylates **9** with acetylenic dipolarophiles in good yields, respectively.[8−10] However, 1,3-dioxolium-4-olates **5** do not react with slightly less reactive dipolarophiles such as dimethyl benzylidenemalonate or dimethyl *p*-nitrobenzylidenemalonate.[10] And also we observed that as soon as 5-*p*-nitrophenyl-1,3-dioxolium-4-olates **5** were formed, the solution turned red and then the red color of **5** faded instantly. These phenomena suggest that the generated 1,3-dioxolium-4-olates **5** are rapidly converted to acyloxyketenes. We confirmed rapid ring opening of **5** to acyloxyketene **7** by isolation of [2+2] ketene adducts **10** with ketenophiles such as dihydrofuran or carbodiimides in high yields.[11] Fast conversion of 1,3-dioxolium-4-olates **5** to acyloxyketene **7** is supported by PM3 calculation of their heats of formation, indicating that acyloxyketenes **7** are ca. 9 kcal/mol more stable than the corresponding 1,3-dioxolium-4-olates **5**.[11]

TABLE 1. Isolated Yields of Triacylbenzamidines 13a−h

13	substrate	Ar	R	R′	yield/%
13a	**11a**	C_6H_5	CH_3	C_2H_5	80[a]
13b	**11a**	C_6H_5	CH_3	CH_3	71[a]
13c	**11b**	*p*-$NO_2C_6H_4$	*p*-$CH_3OC_6H_4$	C_2H_5	53[a]
13d	**11b**	*p*-$NO_2C_6H_4$	*p*-$CH_3OC_6H_4$	CH_3	60[a]
13e	**6a**	*p*-$NO_2C_6H_4$	CH_3	C_2H_5	86[b]
13f	**6a**	*p*-$NO_2C_6H_4$	CH_3	CH_3	95[b]
13c	**6b**	*p*-$NO_2C_6H_4$	*p*-$CH_3OC_6H_4$	C_2H_5	81[b]
13d	**6b**	*p*-$NO_2C_6H_4$	*p*-$CH_3OC_6H_4$	CH_3	92[b]
13g	**6c**	*p*-$NO_2C_6H_4$	*p*-ClC_6H_4	C_2H_5	70[b]
13h	**6c**	*p*-$NO_2C_6H_4$	*p*-ClC_6H_4	CH_3	45[b]

[a] Isolated yields of amidines **13** in the reaction between azodicarboxylates **12** and acyloxyketenes **7** from acyloxyacetyl chlorides **11**. [b] Isolated yields of amidines **13** by $Rh_2(OAc)_4$-catalyzed decomposition of diazoacetic anhydrides **6** in the presence of **12**.

We would like to report novel facts that formation of acyloxyketene **7** by dehydrochlorination of acyloxyarylacetyl chloride **11** in the presence of very reactive dipolarophiles such as azodicarboxylates, nitroso compounds, singlet oxygen, or dimethyl acetylenedicarboxylate gave products arising from 1,3-dipolar cycloadducts of 1,3-dioxolium-4-olates **5** with dipolarophiles.

Results and Discussion

Dehydrochlorination of α-Acyloxyarylacetyl Chloride in the Presence of Azodicarboxylates. A benzene solution of *i*-Pr_2NEt was added dropwise to a benzene solution of α-acetoxyphenylacetyl chloride **11a** and 1.1 equiv of diethyl azodi-

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(12) Hamaguchi, M.; Tomida, N.; Mochizuki, E.; Oshima, T. *Tetrahedron Lett*. **2005**, *46*, 1259. Crystallographic data for compound **13a** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC 254325. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax +44(0)-1223−33603.3; e-mail deposit@ccdc.cam.ac.uk).

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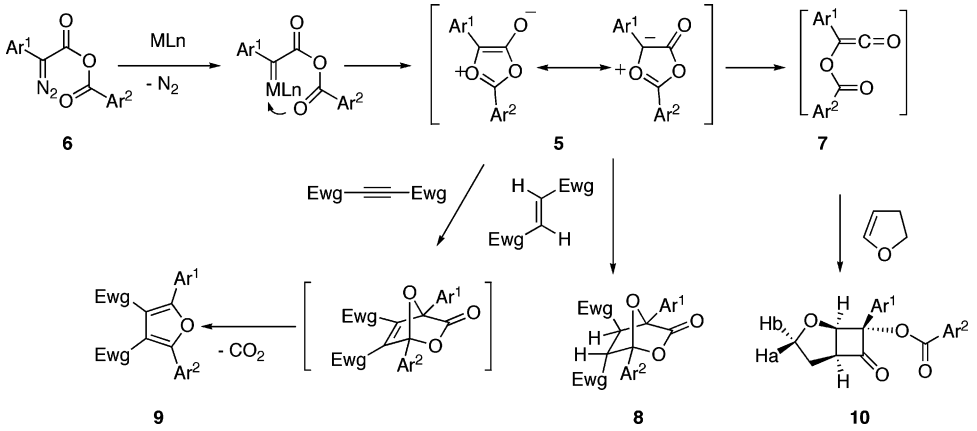
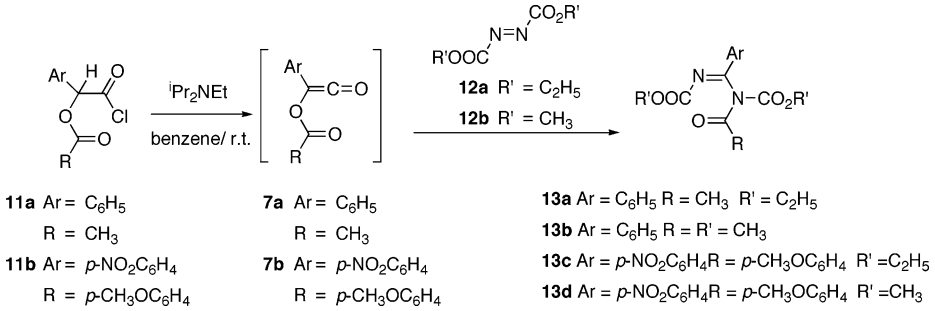
SCHEME 2



SCHEME 3



carboxylate **12a** (DEAD) at room temperature and the mixture was stirred for 2 h. Workup of the reaction mixture gave white crystals (80%), ^{1}H NMR and IR spectra of which showed the presence of nonequivalent ethyl groups and exhibited two ester groups at 1759 and 1716 cm^{-1}, respectively. Its structure was determined to be triacylbenzamidine derivative **13a** ($R' = C_2H_5$) by X-ray crystallographic analysis.[12]

Reaction of **11a** with dimethyl azodicarboxylate **12b** under the same condition gave **13b** in good yield. Furthermore, dehydrochlorination of α-anisoyloxy-*p*-nitrophenylacetyl chloride **11b** in the presence of DEAD **12a** or dimethyl azodicarboxylate **12b** gave triacylbenzamidine derivatives **13c** or **13d**, respectively, as shown in Scheme 3 and Table 1.

Formation of triacylbenzamidine derivatives **13** cannot be rationalized by direct reaction between acyloxyketenes **7** and azodicarboxylates **12**.

To clarify a process from acyloxyketenes **7** and azodicarboxylates **12** to triacylbenzamidines **13**, $Rh_2(OAc)_4$-catalyzed decomposition of aryldiazoacetic anhydrides **6** in the presence of azodicarboxylates was carried out. Intramolecular carbenoid/carbonyl reaction has very often been reported as a traditional method for generation of carbonyl ylides.[13] $Rh_2(OAc)_4$-catalyzed decomposition of aryldiazoacetic anhydrides **6** should initially form carbonyl ylides, namely, mesoionic 1,3-dioxolium-4-olates **5** have been confirmed by our studies.[8,9]

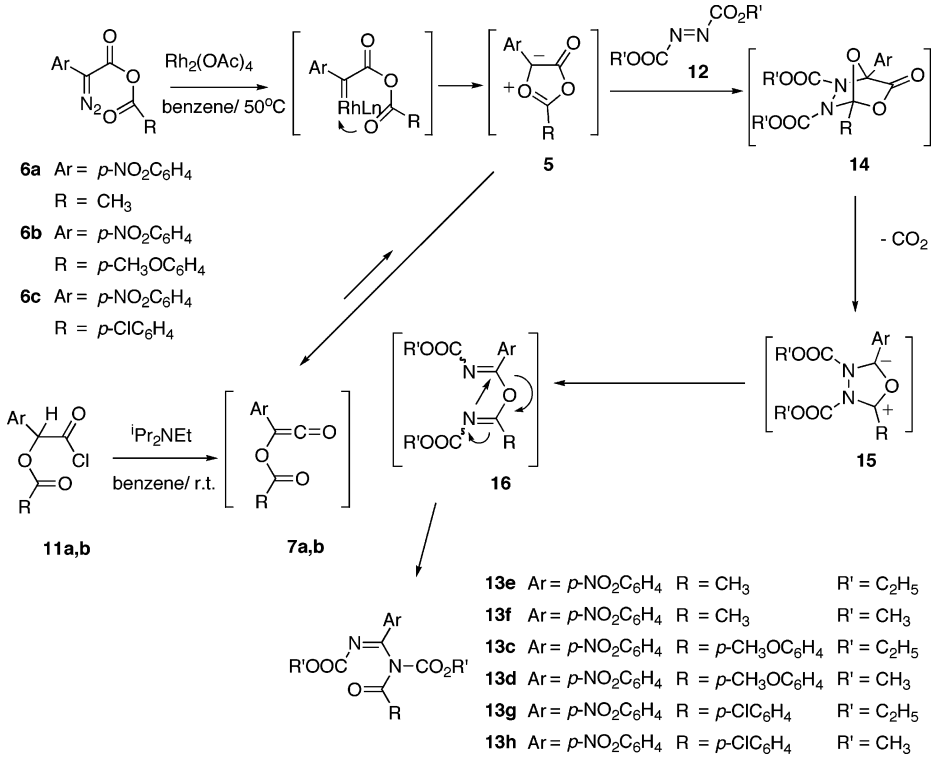
TABLE 2. Isolated Yields of *N*-Arylimides 21

21	substrate	Ar	R	X	yield/%
21a	**11a**	C_6H_5	CH_3	H	84[a]
21b	**11a**	C_6H_5	CH_3	CN	67[a]
21c	**11b**	*p*-$NO_2C_6H_4$	*p*-$CH_3OC_6H_4$	H	52[a]
21d	**11b**	*p*-$NO_2C_6H_4$	*p*-$CH_3OC_6H_4$	CN	45[a]
21e	**6a**	*p*-$NO_2C_6H_4$	CH_3	H	84[b]
21f	**6a**	*p*-$NO_2C_6H_4$	CH_3	CN	95[b]
21c	**6b**	*p*-$NO_2C_6H_4$	*p*-$CH_3OC_6H_4$	H	84[b]
21d	**6b**	*p*-$NO_2C_6H_4$	*p*-$CH_3OC_6H_4$	CN	95[b]
21g	**6c**	*p*-$NO_2C_6H_4$	*p*-ClC_6H_4	H	81[b]
21h	**6c**	*p*-$NO_2C_6H_4$	*p*-ClC_6H_4	CN	60[b]

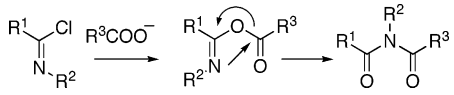
[a] Isolated yields of *N*-arylimides **21** in the reaction between nitrosobenzenes **20** and acyloxyketenes **7** from acyloxyacetyl chlorides **11**. [b] Isolated yields of *N*-arylimides by $Rh_2(OAc)_4$-catalyzed decomposition of diazoacetic anhydrides **6** in the presence of **20**.

$Rh_2(OAc)_4$-Catalyzed Decomposition of Aryldiazoacetic Anhydrides 6 in the Presence of Azodicarboxylates 12. A benzene solution of acetic *p*-nitrophenyldiazoacetic anhydride **6a**, 1.1 equiv of diethyl azodicarboxylate **12a** (DEAD) and a catalytic amount of $Rh_2(OAc)_4$ was heated at 50 °C for 2 h. Column chromatography of the reaction mixture gave colorless needles in the yield of 86%. The product from **6a** showed quite similar IR and NMR spectra to that of the triacylbenzamidine **13a**. The NMR and IR spectra showed the presence of nonequivalent ethyl esters and exhibited two ester groups at 1759 and 1734 cm^{-1}, respectively, which exclude imidoyl imidate **16e**, indicating the same triacylbenzamidine structure **13e**. $Rh_2(OAc)_4$-catalyzed decomposition of *p*-anisic *p*-nitrophenyldiazoacetic anhydride **6b** in the presence of azodicarboxylates **12a**,**b** gave triacylbenzamidine derivatives **13c**,**d**, which are identical with the products obtained from the reaction of **12a**,**b** with the acyloxyketene **7b** from the dehydrochlorination of **11b**, as shown in Scheme 4 and Table 1. The reaction of *p*-chlorobenzoic *p*-nitrophenyldiazoacetic anhydride **6c** in the presence of azodicarboxylates **12a**,**b** gave the corresponding triacylamidine derivatives **13g** and **13h**, respectively (Table 1). It is noteworthy that the same compounds **13c**,**d** were isolated from the different starting compounds, α-*p*-anisoyloxyl-*p*-nitrophenylacetyl chloride **11b** and *p*-anisic *p*-nitrophenyldiazoacetic anhydride **6b**.

SCHEME 4

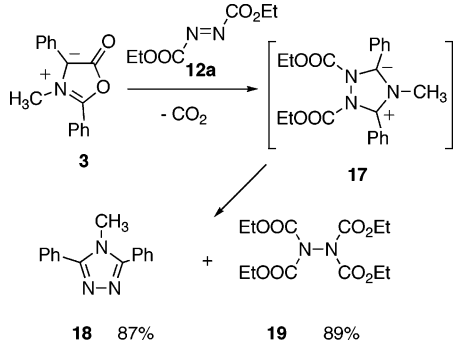


SCHEME 5



Formation of the same triacylbenzamidines **13** from different starting materials **11** and **6** must involve the common intermediates. The formation of triacylbenzamidines **13** is rationalized by common intermediates 1,3-dioxolium-4-olates **5**, which undergo 1,3-dipolar cycloaddition with the electron-deficient N═N bond and subsequent elimination of carbon dioxide from the resultant cycloadducts **14** to give cyclic carbonyl ylides **15**. The carbonyl ylides **15** undergo ring opening with cleavage of the N−N bond to provide imidoyl imidates **16**. Furthermore, imidoyl imidates **16** undergo Mumm rearrangement (Scheme 5),[14] well-known as a favorable rearrangement of acyl imidates to imides, to yield the final products, triacylbenzamidine derivatives **13** (Scheme 4). The $Rh_2(OAc)_4$-catalyzed process of aryldiazoacetic anhydrides **6** to the intermediate 1,3-dioxolium-4-olates **5** can be easily understood by intramolecular carbenoid/carbonyl reaction. However, ring closure of the acyloxyketene **7** to unstable 1,3-dioxolium-4-olate **5** requires ca. 9 kcal/mol, which can be easily obtained at the reaction temperature. Therefore, acyloxyketene **7** generated by dehydrochlorination of acid chloride **11** can cyclize to 1,3-dioxolium-4-olate **5** unless any trapping reagents of the ketene are present. However, an ca. 9 kcal/mol energy difference between **5** and **7** means that **5** is in very low concentration in the equilibrium state between **5** and **7** ([**5**]/[**7**] = ca. 10^{-6}). Good yields of **13** from the reaction with 1,3-dioxolium-4-olates **5** in very low concentration suggest that the electron-deficient N═N bonds are strongly reactive dipolarophiles toward **5**.

SCHEME 6



However, it is noteworthy that the related mesoionic compound, the aza-analogue of **5**, münchnone **3** bearing a lactone moiety reacted with DEAD to afford quite different products **18** and **19** in good yields (Scheme 6).[15]

Dehydrochlorination of α-Acyloxyarylacetyl Chloride in the Presence of Nitrosobenzenes. We realized that the electron-deficient N═N bonds are strongly reactive dipolarophiles toward 1,3-dioxolium-4-olates. It prompted us to react acyloxyketenes or 1,3-dioxolium-4-olates with nitrosobenzene derivatives **20** because the N═O bond containing a more electronegative oxygen atom seems to be more electrophilic than azodicarboxylates.

A benzene solution of *i*-Pr_2NEt was added dropwise to a benzene solution of α-acetoxyphenylacetyl chloride **11a** and 1.1 equiv of nitrosobenzene **20a** and the mixture was stirred overnight. Workup of the reaction mixture gave white crystals (84%), which were determined to be *N*-acetyl-*N*-phenylbenza-

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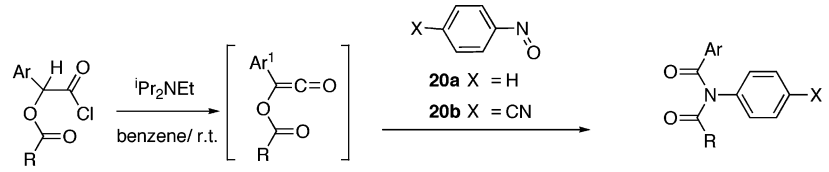
SCHEME 7

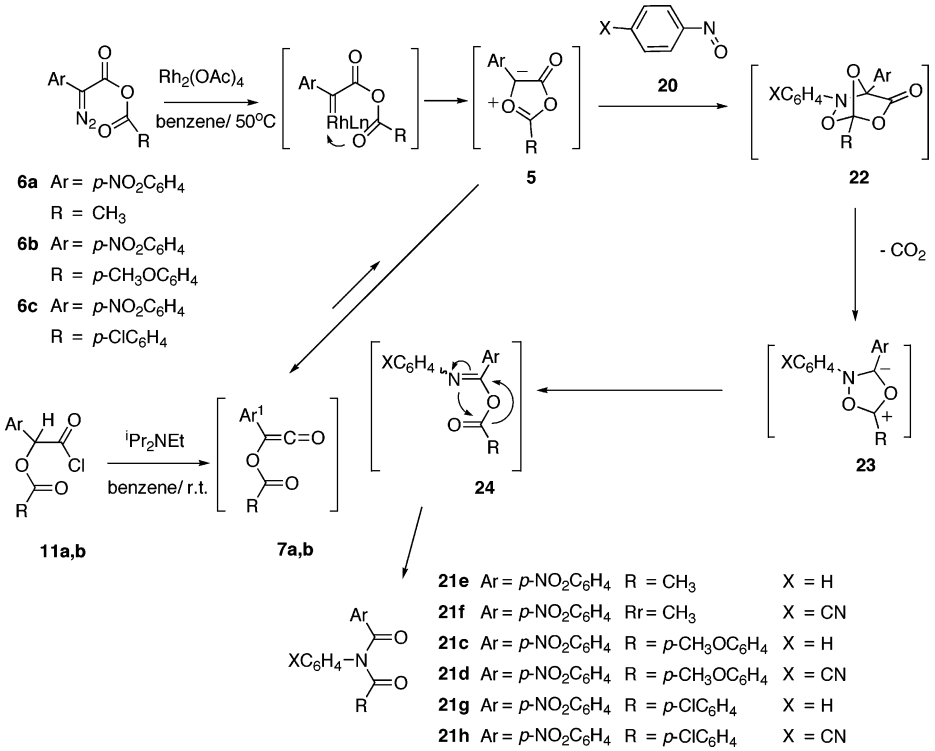


11a Ar = C_6H_5 R = CH_3
11b Ar = *p*-$NO_2C_6H_4$ R = *p*-$CH_3OC_6H_4$

7a Ar = C_6H_5 R = CH_3
7b Ar = *p*-$NO_2C_6H_4$ R = *p*-$CH_3OC_6H_4$

21a Ar = C_6H_5 R = CH_3 X = H
21b Ar = C_6H_5 R = CH_3 X = CN
21c Ar = *p*-$NO_2C_6H_4$ R = *p*-$CH_3OC_6H_4$ X = H
21d Ar = *p*-$NO_2C_6H_4$ R = *p*-$CH_3OC_6H_4$ X = CN

SCHEME 8



6a Ar = *p*-$NO_2C_6H_4$ R = CH_3
6b Ar = *p*-$NO_2C_6H_4$ R = *p*-$CH_3OC_6H_4$
6c Ar = *p*-$NO_2C_6H_4$ R = *p*-ClC_6H_4

5 **22** **23** **24**

11a,b **7a,b**

21e Ar = *p*-$NO_2C_6H_4$ R = CH_3 X = H
21f Ar = *p*-$NO_2C_6H_4$ Rr = CH_3 X = CN
21c Ar = *p*-$NO_2C_6H_4$ R = *p*-$CH_3OC_6H_4$ X = H
21d Ar = *p*-$NO_2C_6H_4$ R = *p*-$CH_3OC_6H_4$ X = CN
21g Ar = *p*-$NO_2C_6H_4$ R = *p*-ClC_6H_4 X = H
21h Ar = *p*-$NO_2C_6H_4$ R = *p*-ClC_6H_4 X = CN

mide **21a** by direct comparison with an authentic sample prepared independently by using Mumm rearrangement as outlined in Scheme 5.

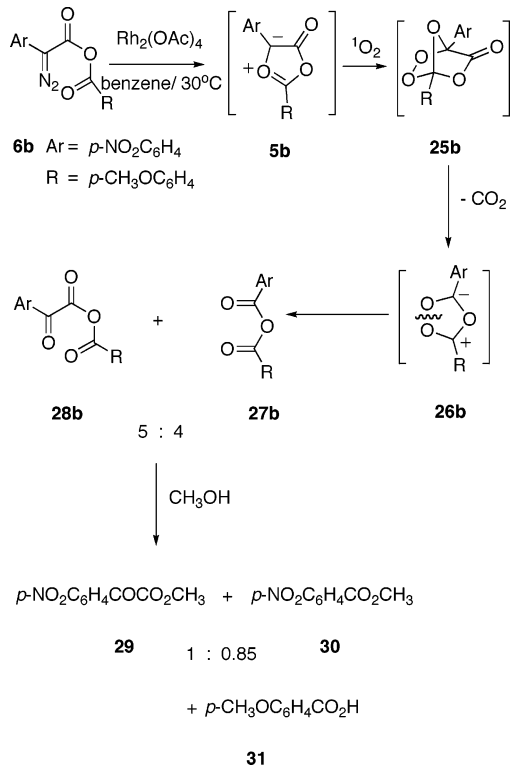
The dehydrochlorination of **11b** with nitrosobenzenes **20a**,**b** gave the corresponding *N*-arylimide derivatives **21c**,**d** in moderate yields (Table 2).

$Rh_2(OAc)_4$-Catalyzed Decomposition of Aryldiazoacetic Anhydrides 6 in the Presence of Nitrosobenzenes. To confirm that formation of imides from the reaction of nitrosobenzenes with acyloxyketenes proceeds in a similar mechanism to the formation of triacylbenzamidines **13** from the reaction of azodicarboxylates, $Rh_2(OAc)_4$-catalyzed decomposition of aryldiazoacetic anhydrides **6** in the presence of nitrosobenzenes was carried out. A benzene solution of acetic *p*-nitrophenyldiazoacetic anhydride **6a**, 1.1 equiv of nitrosobenzene **20a**, and a catalytic amount of $Rh_2(OAc)_4$ were heated at 50 °C for 1 h. Column chromatography of the reaction mixture gave *N*-acetyl-*N*-phenyl-*p*-nitrobenzamide **21e** as a crystal in a yield of 84%. $Rh_2(OAc)_4$-catalyzed decomposition of *p*-anisic *p*-nitrophenyldiazoacetic anhydride **6b** in the presence of nitrosobenzenes **20a**,**b** gave *N*-arylimide derivatives **21c**,**d** that are identical with the products from the reaction of **20a**,**b** with the acyloxyketene **7b** from the dehydrochlorination of **11b**, as shown in Scheme 7 and Table 2. The reaction of *p*-chlorobenzoic *p*-nitrophenyldiazoacetic anhydride **6c** in the presence of nitrosobenzenes **20a**,**b** gave the corresponding *N*-arylimide derivatives **21g** and **21h**, respectively (Table 2). These results indicate that formation of *N*-arylimides from the reaction of acyloxyketenes with nitrosobenzenes proceeds in a similar mechanism to the reaction of azodicarboxylates with α-acyloxyarylketenes; 1,3-dipolar cycloaddition between common intermediary 1,3-dioxolium-4-olates **5** isomerized from α-acyloxyarylketenes and nitrosobenzenes followed by decarboxylation of the 1,3-cycloadducts **22** giving carbonyl ylides **23**, which undergo ring-opening to acyl imidates **24** and then Mumm rearrangement (Scheme 8).

Reaction of 1,3-Dioxolium-4-olate 5b with Singlet Oxygen. Electron-deficient azo compounds and nitrosobenzenes showed higher reactivities toward 1,3-dioxolium-4-olates than acyloxyketenes. It prompted us to carry out the reaction of singlet oxygen composed of more electronegative atoms than their hetero double bonds.

$Rh_2(OAc)_4$-catalyzed decomposition of *p*-anisic *p*-nitrophenyldiazoacetic anhydride **6b** was carried out in the presence of 9,10-diphenylanthracene as a sensitizer with bubbling oxygen under irradiation of a tungsten lamp.

SCHEME 9



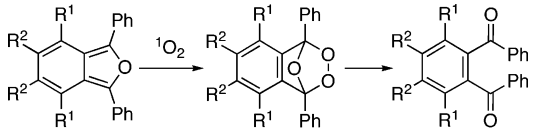
The NMR of the reaction mixture showed formation of two products in a ratio of ca. 5:4, both of which bear a *p*-nitrobenzoyl and a *p*-anisoyl group. The minor product was determined to be *p*-nitrobenzoic *p*-anisic anhydride **27b** by comparison with an authentic sample prepared from *p*-anisoyl chloride and *p*-nitrobenzoate. The structure of the major product **28b** was determined by methanolysis of the reaction mixture. On stirring the reaction mixture in methanol overnight followed by washing the ether solution with aqueous sodium bicarbonate solution, the NMR spectrum of the ether extract showed methyl *p*-nitrobenzoylformate **29** and methyl *p*-nitrobenzoate **30** in a ratio of ca. 1:0.85. *p*-Anisic acid **31** was obtained by acidification of aqueous solution. Formation of unsymmetrical anhydride **27b** can be rationalized by decarboxylation of the singlet oxygen addition product **25b** followed by ring opening of the resultant carbonyl ylide **26b**. *p*-Anisic *p*-nitrobenzoylformic anhydride **28b** may be formed from the singlet oxygen adduct **25b**, although a detailed mechanism is not clear.

TABLE 3. Yields of Dimethyl Furandicarboxylates 35 in the Reaction of α-Acyloxyarylketenes 7 and Aryldiazoacetic Anhydrides 6

35	substrate	Ar	R	yield/%
35a	**11a**	C_6H_5	CH_3	64[a]
35c	**11c**	*p*-$NO_2C_6H_4$	*p*-$CH_3OC_6H_4$	40[a]
35d	**11d**	*p*-$NO_2C_6H_4$	*p*-$CH_3C_6H_4$	44[a]
35e	**11e**	*p*-$CH_3C_6H_4$	CH_3	48[a]
35f	**11f**	C_6H_5	C_6H_5	29[a]
35g	**6a**	*p*-$NO_2C_6H_4$	CH_3	80[b]
35c	**6b**	*p*-$NO_2C_6H_4$	*p*-$CH_3OC_6H_4$	88[b]
35h	**6c**	*p*-$NO_2C_6H_4$	*p*-ClC_6H_4	95[b]

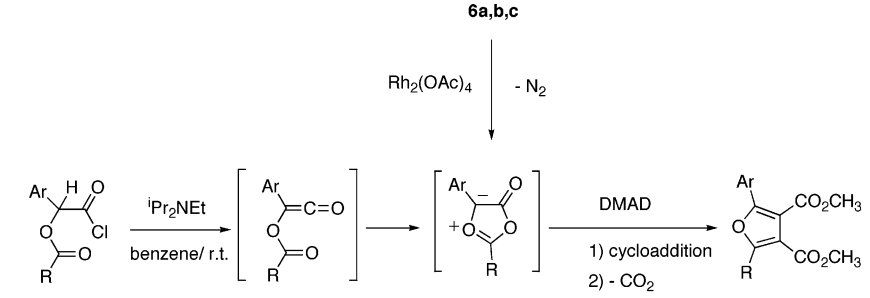
[a] Isolated yields of furans **35** in the reaction between DMAD and acyloxyketenes **7** from acyloxyacetyl chlorides **11**. [b] Isolated yields of furans **35** by $Rh_2(OAc)_4$-catalyzed decomposition of diazoacetic anhydrides **6** in the presence of DMAD.

A very similar reaction has been observed in photooxydation of isobenzofurans **32**, in which *o*-dibenzoylbenzenes **34** are formed via singlet oxygen addition products **33**.[16]



Dehydrochlorination of α-Acyloxyarylacetyl Chloride in the Presence of Dimethyl Acetylenedicarboxylate (DMAD). It was revealed that double bonds composed of electronegative atoms such as Ewg-N═N-Ewg, ArN═O, and ^1O═O can react with 1,3-dioxolium-4-olates **5** in a very low concentration in equilibrium state between **5** and **7** to give final products in good yields. This prompted us to carry out the reaction of DMAD, well-known as strongly reactive acetylenic dipolarophile, with acyloxyketenes. A benzene solution of 1.1 equiv of *i*-$PrNEt_2$ was added dropwise to a benzene solution of α-acetoxyphenylacetyl chloride **11a** and 2 equiv of DMAD and the solution was stirred for 2 h at room temperature. Workup of the reaction

SCHEME 10



11a Ar = C_6H_5 R = CH_3
11c Ar = *p*-$NO_2C_6H_4$ R = *p*-$CH_3OC_6H_4$
11d Ar = *p*-$NO_2C_6H_4$ R = *p*-$CH_3C_6H_4$
11e Ar = *p*-$CH_3C_6H_4$ R = CH_3
11f Ar = C_6H_5 R = C_6H_5

35a Ar = C_6H_5 R = CH_3
35c Ar = *p*-$NO_2C_6H_4$ R = *p*-$CH_3OC_6H_4$
35d Ar = *p*-$NO_2C_6H_4$ R = *p*-$CH_3C_6H_4$
35e Ar = *p*-$CH_3C_6H_4$ R = CH_3
35f Ar = C_6H_5 R = C_6H_5
35g Ar = *p*-$NO_2C_6H_4$ R = CH_3
35h Ar = *p*-$NO_2C_6H_4$ R = *p*-ClC_6H_4

mixture gave dimethyl 2-methyl-5-phenylfuran-3,4-dicarboxylate **35a** as white crystals (64%). Similarly, dehydrochlorination of α-acyloxyarylacetyl chlorides **11c**,**d**,**e**,**f** by addition of *i*-Pr_2-NEt in the presence of DMAD gave furandicarboxylates **35c**,**d**,**e**,**f** in good or moderate yields as shown in Table 3 and Scheme 10.

Berk and his co-workers obtained furandicarboxylate **35a** in 32% yield by heating α-acetoxyphenylacetic acid **11a** and 4 equiv of DMAD in acetic anhydride at 140 °C for 4 days and proposed a mechanism for formation of **35a**: formation of an intermediate 1,3-dioxolium-4-olate **5** by intramolecular cyclization of acetic α-acetoxyphenylacetic anhydride followed by 1,3-dipolar cycloaddition and subsequent decarboxylation of the adduct.[17] Our method for generation of 1,3-dioxolium-4-olate by dehydrochlorination of α-acyloxyacetyl chlorides is much better than their method because our method can be achieved under very mild condition and gives products in better yields. To compare with the method using acid chloride, we carried out $Rh_2(OAc)_4$-catalyzed decomposition of aryldiazoacetic anhydrides **6** in the presence of DMAD, giving furandicarboxylates **35** in high yield as shown in Table 3.

Reaction of acyloxyketenes or 1,3-dioxolium-4-olates with azodicarboxylates, nitrosobenzenes, singlet oxygen, and DMAD is rationalyzed by 1,3-dipolar cycloaddition of common intermediates 1,3-dioxolium-4-olates **5**. The method that uses *p*-nitrophenyldiazoacetic anhydrides **6**, directly giving common intermediates 1,3-dioxolium-4-olates and inert nitrogen, is superior to the method that uses α-acetoxyarylacetyl chloride as shown in Tables 1−3.

Conclusion

According to PM3 calculation, 1,3-dioxolium-4-olates **5** are ca. 9 kcal/mol more unstable than their ring-opening form, α-acyloxyarylketenes **7**. Therefore, generation of 1,3-dioxolium-4-olates in the presence of ketenophiles gave [2+2]-ketene adducts in high yields. The products described here are nevertheless derived from energetic 1,3-dioxolium-4-olates on dehydrochlorination of α-acyloxyacetyl chlorides **11** in the presence of very reactive dipolarophiles such as azodicarboxylates **12**, nitrosobenzenes **20**, and DMAD, indicating that the generated α-acyloxyketenes **7** undergo ring closure to unstable 1,3-dioxolium-4-olates **5** followed by fast 1,3-dipolar cycloaddition between strongly reactive dipolarophiles and **5** in a very low concentration to give final products such as triacylbenzamidines **13**, *N*-arylimides **21**, and furandicarboxylates **35** in high or moderate yields.

Experimental Section

Melting points were not corrected. ^{1}H NMR (270.05 MHz) and ^{13}C NMR (60.40 MHz) spectra were recorded in a $CDCl_3$ solution with TMS as an internal standard. α-Acyloxyarylacetyl chlorides were prepared by refluxing the corresponding α-acyloxyarylacetic acids in thionyl chloride. Aryldiazoacetic acid anhydrides **6a**−**c** were prepared in our procedure described before.[11a]

General Procedure of α-Acyloxyketenes 7a and 7b with Azodicarboxylates 12a and 12b. A benzene solution (3 mL) of diisopropylethylamine (0.55 mmol) was added a benzene solution (5 mL) of α-acyloxyarylacetyl chlorides **11a** or **11b** (0.5 mmol) and azodicarboxylates **12a** or **12b** at room temperature and the resulting solution was stirred for 2 h. The reaction mixture was washed with water, dilute hydrochloric acid, and water and then dried over magnesium sulfate. The resulting solution was chromatographed over silica gel with toluene as an eluent, giving white solids. The solids were recrystallized from CH_2Cl_2/ether/pentane.

***N*-Acetyl-*N*,*N*′-bis(ethoxycarbonyl)benzamidine (13a) (80%):** white plates; mp 112−113 °C; ^{1}H NMR ($CDCl_3$) δ 7.84−7.81 (m, 2 H), 7.58−7.52 (m, 1 H), 7.14−7.41 (m, 2 H), 4.29 (q, 2 H, J = 7.1 Hz), 4.21 (q, 2 H, J = 7.1 Hz), 2.60 (s, 3 H), 1.32 (t, 3 H, J = 7.1 Hz), 1.16 (t, 3 H, J = 7.1 Hz); ^{13}C NMR ($CDCl_3$) δ 170.84, 159.56, 153.73, 151.25, 132.80, 132.48, 128.69, 128.36, 63.75, 62.96, 25.22, 14.31, 13.89; IR (KBr) 2987, 1759, 1716, 1650, 1450, 1369, 1270, 1228 cm^{-1}. Anal. Calcd for $C_{15}H_{18}N_2O_5$: C, 58.82; H, 5.92; N, 9.15. Found: C, 58.58; H, 5.86; N, 9.07.

***N*-Acetyl-*N*,*N*′-bis(methoxycarbonyl)benzamidine (13b) (71%):** white needles; mp 63−64 °C; ^{1}H NMR ($CDCl_3$) δ 7.85−7.81 (m, 2 H), 7.60−7.53 (m, 1 H), 7.49−7.42 (m, 2 H), 3.85 (s, 3 H), 3.77 (s, 3 H), 2.62 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 170.89, 160.15, 154.01, 151.87, 133.05, 132.21, 128.81, 128.47, 54.28, 53.92, 25.21; IR (KBr) 3019, 2953, 1766, 1726, 1653, 1581, 1436, 1371, 1278, 1139, 1083, 1025, 986, 930, 897, 823 cm^{-1}. Anal. Calcd for $C_{13}H_{14}N_2O_5$: C, 56.11; H, 5.07; N, 10.07. Found: C, 56.20; H, 5.03; N, 10.04.

***N*-Anisoyl-*N*,*N*′-bis(ethoxycarbonyl)-*p*-nitrobenzamidine (13c) (53%):** yellowish oil; ^{1}H NMR ($CDCl_3$) δ 8.29 (d, 2 H, J = 8.6 Hz), 8.01−7.95 (m, 2 H), 7.78 (d, 2 H, J = 8.6 Hz), 6.95 (d, 2 H, J = 8.6 Hz), 4.17−4.09 (m, 4 H), 3.89 (s, 3 H), 1.15 (t, 3 H, J = 7.3 Hz), 1.03 (t, 3 H, J = 6.9 Hz); ^{13}C NMR ($CDCl_3$) δ 168.87, 163.91, 159.00, 151.91, 149.63, 139.37, 131.65, 129.25, 125.10, 123.75, 113.88, 64.16, 63.34, 55.55, 13.96, 13.75; IR (KBr) 2984, 1734, 1604, 1527, 1247, 1171, 1027, 851 cm^{-1}. HRMS (EI+) calcd for $C_{21}H_{21}N_3O_8$ M^+ 443.1329, found M^+ 443.1331.

***N*-Anisoyl-*N*,*N*′-bis(methoxycarbonyl)-*p*-nitrobenzamidine (13d) (60%):** white crystals; mp 116−117 °C; ^{1}H NMR ($CDCl_3$) δ 8.29 (d, 2 H, J = 8.9 Hz), 8.00−7.94 (m, 2 H), 7.78 (d, 2 H, J = 8.9 Hz), 6.96 (d, 2 H, J = 8.9 Hz), 3.89 (s, 3 H), 3.71 (br s, 3 H), 3.69 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 168.71, 164.06, 159.56, 152.48, 149.74, 139.05, 131.74, 129.28, 124.83, 123.87, 114.02, 55.60, 54.57, 54.02; IR (KBr) 2360, 1742, 1699, 1649, 1603, 1527, 1354, 1254, 1173 cm^{-1}. Anal. Calcd for $C_{19}H_{17}N_3O_8$: C, 54.94; H, 4.13; N, 10.12. Found: C, 54.78; H, 4.18; N, 10.12.

General Procedure for $Rh_2(OAc)_4$-Catalyzed Reaction of Aryldiazoacetic Anhydrides 6a−c in the Presence of Azodicarboxylates. A benzene solution (5 mL) of diazo acid anhydride **6** (0.5 mmol), azodicarboxylates **11** (0.55 mmol), and a catalytic amount of $Rh_2(OAc)_4$ was stirred at 50 °C for 2 h. The reaction mixture was chromatographed over silica gel with toluene as an eluent, giving white solids. The solids were recrystallized from CH_2Cl_2/ether/pentane.

***N*-Acetyl-*N*,*N*′-bis(ethoxycarbonyl)-*p*-nitrobenzamidine (13e) (86%):** colorless needles; mp 103−104 °C; ^{1}H NMR ($CDCl_3$) δ 8.29 (d, 2 H, J = 8.9 Hz), 7.99 (d, 2 H, J = 8.9 Hz), 4.32 (q, 2 H, J = 7.1 Hz), 4.24 (q, 2 H, J = 7.1 Hz), 2.63 (s, 3 H), 1.34 (t, 3 H, J = 7.1 Hz), 1.19 (t, 3 H, J = 7.1 Hz); IR (KBr) 2989, 1759, 1734, 1659, 1607, 1530, 1354, 1276, 1245, 1225, 996, 855, 759 cm^{-1}. Anal. Calcd for $C_{15}H_{17}N_3O_7$: C, 51.28; H, 4.88; N, 11.96. Found: C, 51.33; H, 4.82; N, 11.92.

***N*-Acetyl-*N*,*N*′-bis(methoxycarbonyl)-*p*-nitrobenzamidine (13f) (95%):** colorless needles; mp 92−94 °C; ^{1}H NMR ($CDCl_3$) δ 8.30 (d, 2 H, J = 8.9 Hz), 8.00 (d, 2 H, J = 8.9 Hz), 3.88 (s, 3 H), 3.79 (s, 3 H), 2.64 (s, 3 H); IR (KBr) 1766, 1737, 1654, 1528, 1438, 1349, 1289, 1255, 1234 cm^{-1}. Anal. Calcd for $C_{13}H_{13}N_3O_7$: C, 48.30; H, 4.05; N, 13.00. Found: C, 48.23; H, 4.05; N, 12.96.

***N*-Anisoyl-*N*,*N*′-bis(ethoxycarbonyl)-*p*-nitrobenzamidine** (**13c**) was isolated in a yield of 81% in the reaction of **6b** with **12a**.

(16) (a) Boyer, R. F.; Lindstrom, C. G.; Darby, B.; Hylarides, M. *Tetrahedron Lett.* **1975**, 4111. (b) Nahavandi, F.; Razmara, F.; Stevens, N. P. *Tetrahedron Lett.* **1973**, 301. (c) Bergmann, R. D.; Blumberg, Sh.; Bracha, F.; Epstein, Sh. *Tetrahedron* **1964**, *20*, 195.

(17) Berk, H. C.; Zwikelmaier, K. E.; Franz, J. E. *Synth. Commun.* **1980**, *10*, 707.

***N*-Anisoyl-*N*,*N*′-bis(methoxycarbonyl)-*p*-nitrobenzamidine (13d)** was isolated in a yield of 92% in the reaction of **6b** with **12b**.

***N*-*p*-Chlorobenzoyl-*N*,*N*′-bis(ethoxycarbonyl)-*p*-nitrobenzamidine (13g) (70%):** white powders; mp 90.5−91.0 °C; ^{1}H NMR ($CDCl_3$) δ 8.31 (d, 2 H, J = 8.9 Hz), 8.00 (d, 2 H, J = 8.4 Hz), 7.70 (d, 2 H, J = 8.4 Hz), 7.46 (d, 2 H, J = 8.7 Hz), 4.18 (q, 2 H, J = 6.9 Hz), 4.12 (d, 2 H, J = 7.1 Hz), 1.19 (t, 3 H, J = 7.1 Hz), 1.03 (t, 3 H, J = 7.1 Hz); IR (KBr) 1744, 1593, 1523, 1348, 1252, 1091, 1011 cm^{-1}. Anal. Calcd for $C_{20}H_{18}ClN_3O_7$: C, 53.64; H, 4.05; N, 9.38. Found: C, 53.47; H, 3.88; N, 9.30.

***N*-*p*-Chlorobenzoyl-*N*,*N*′-bis(methoxycarbonyl)-*p*-nitrobenzamidine (13h) (45%):** white needles; 140.0−140.5 °C; δ 8.31 (d, 2 H, J = 9.1 Hz), 7.99 (d, 2 H, J = 8.6 Hz), 7.70 (d, 2 H, J = 8.7 Hz), 7.47 (d, 2 H, J = 8.9 Hz), 3.75 (s, 3H), 3.69 (s, 3H); IR (KBr) 1747, 1593, 1523, 1348, 1253, 1090, 1012, 853, 752 cm^{-1}. Anal. Calcd for $C_{18}H_{14}ClN_3O_7$: C, 51.50; H, 3.36; N, 10.01. Found: C, 51.60; H, 3.32; N, 9.96.

General Procedure for Dehydrochlorination of α-Acyloxyarylacetyl Chloride in the Presence of Nitrosobenzenes. A benzene solution (5 mL) of diisopropylethylamine (0.55 mmol) was added to a benzene solution (5 mL) of α-acyloxyarylacetyl chlorides **11a** or **11b** (0.5 mmol) and nitrosobenzene **20a** or *p*-nitrosobenzene **20b** at room temperature and the resultant solution was stirred overnight. The reaction mixture was washed with water, dilute hydrochloric acid, and water and then dried over magnesium sulfate. The resultant solution was chromatographed over silica gel with toluene as an eluent, giving white solids. The solids were recrystallized from CH_2Cl_2/ether/pentane.

***N*-Acetyl-*N*-phenylbenzamide (21a) (84%):** white needles; mp 64−65 °C; ^{1}H NMR ($CDCl_3$) δ 7.63−7.59 (m, 2 H), 7.41−7.25 (m, 6 H), 7.17−7.14 (m, 2 H), 2.44 (s, 3 H); IR (KBr) 3060, 3013, 1694, 1598, 1489, 1371, 1263, 1210, 1127, 1079, 1015, 923, 894, 793, 758 cm^{-1}. Anal. Calcd for $C_{15}H_{13}NO_2$: C, 75.30; H, 5.48; N, 5.85. Found: C, 75.16; H, 5.59; N, 5.85.

***N*-Acetyl-*N*-*p*-cyanophenylbenzamide (21b) (67%):** white powder; mp 118−119 °C; ^{1}H NMR ($CDCl_3$) δ 7.61 (d, 2 H, J = 8.9 Hz), 7.58−7.55 (m, 2 H), 7.48−7.42 (m, 1 H), 7.36−7.30 (m, 2 H), 7.24 (d, 2 H, J = 8.9 Hz), 2.51 (s, 3 H); IR (KBr) 2233, 1693, 1603, 1367, 1282, 1259, 1204, 832 cm^{-1}. Anal. Calcd for $C_{16}H_{12}N_2O_2$: C, 72.72; H, 4.58; N, 10.60. Found: C, 72.68; H, 4.67; N, 10.55.

***N*-*p*-Anisoyl-*N*-phenyl-*p*-nitrobenzamide (21c) (61%):** mp 132−133 °C; ^{1}H NMR ($CDCl_3$) δ 8.19 (d, 2 H, J = 8.9 Hz), 7.85 (d, 2 H, J = 8.9 Hz), 7.72 (d, 2 H, J = 8.9 Hz), 7.40−7.16 (m, 5 H), 6.82 (d, 2 H, J = 8.9 Hz), 3.80 (s, 3 H); IR (KBr) 1697, 1682, 1602, 1523, 1349, 1287, 1259, 1166, 1025, 849 cm^{-1}. Anal. Calcd for $C_{21}H_{16}N_2O_5$: C, 67.02; H, 4.28; N, 7.44. Found: C, 67.35; H, 4.53; N, 7.39.

***N*-*p*-Anisoyl-*N*-*p*-cyanophenyl-*p*-nitrobenzamide (21d) (52%):** mp 256−258 °C; ^{1}H NMR ($CDCl_3$) δ 8.24 (d, 2 H, J = 8.9 Hz), 7.85 (d, 2 H, J = 8.9 Hz), 7.69 (d, 2 H, J = 8.9 Hz), 7.68 (d, 2H, J = 8.9 Hz), 7.30 (d, 2 H, J = 8.9 Hz), 6.85 (d, 2 H, J = 8.9 Hz), 3.84 (s, 3 H); IR (KBr) 2231, 1683, 1603, 1525, 1349, 1256, 1169, 1110, 1025, 846 cm^{-1}; HRMS (EI+) calcd for $C_{22}H_{15}N_3O_5$ M^+ 401.1012, found M^+ 401.1006.

General Procedure for $Rh_2(OAc)_4$-Catalyzed Reaction of Aryldiazoacetic Anhydrides 6a−c in the Presence of Nitrosobenzenes 20. A benzene solution (5 mL) of arydiazoacetic anhydrides 6 (0.5 mmol), nitrosobenzenes 17 (0.55 mmol), and a catalytic amount of $Rh_2(OAc)_4$ was stirred at 50 °C for 2 h. The reaction mixture was chromatographed over silica gel with toluene as an eluent, giving white solids. The solids were recrystallized from CH_2Cl_2/ether/pentane.

***N*-Acetyl-*N*-phenyl-*p*-nitrobenzamide (21e) (84%):** white needles; mp 143−145 °C; ^{1}H NMR ($CDCl_3$) δ 8.18 (d, 2 H, J = 8.9 Hz), 7.71 (d, 4 H, J = 8.9 Hz), 7.44−7.36 (m, 3 H), 7.20−7.16 (m, 2 H), 2.39 (s, 3 H); IR (KBr) 3112, 1716, 1696, 1602, 1518, 1368, 1351, 1304, 1245, 1093, 1035, 860, 838 cm^{-1}. Anal. Calcd for $C_{15}H_{12}N_2O_4$: C, 63.38; H, 4.25; N, 9.85. Found: C, 63.41; H, 4.34; N, 9.90.

***N*-Acetyl-*N*-*p*-cyanophenyl-*p*-nitrobenzamide (21f) (95%):** pale green cube; mp 150−152 °C; ^{1}H NMR ($CDCl_3$) δ 8.20 (d, 2 H, J = 8.6 Hz), 7.70 (d, 4 H, J = 8.6 Hz), 7.30 (d, 2 H, J = 8.6 Hz), 2.45 (s, 3 H); IR (KBr) 2229, 1691, 1604, 1520, 1349, 1309, 1245 cm^{-1}. Anal. Calcd for $C_{16}H_{11}N_3O_4$: C, 62.14; H, 3.58; N, 13.59. Found: C, 62.27; H, 3.70; N, 13.61.

***N*-*p*-Anisoyl-*N*-phenyl-*p*-nitrobenzamide (21c)** was isolated in a yield of 84% in the reaction of **6b** with **17a**.

***N*-*p*-Anisoyl-*N*-*p*-cyanophenyl-*p*-nitrobenzamide (21d)** was isolated in a yield of 95% in the reaction of **6b** with **17b**.

***N*-*p*-Chlorobenzoyl-*N*-phenyl-*p*-nitrobenzamide (21g) (81%):** white cubes; mp 163−164 °C; ^{1}H NMR ($CDCl_3$) δ 8.23 (d, 2 H, J = 8.9 Hz), 7.86 (d, 4 H, J = 8.9 Hz), 7.67 (d, 2 H, J = 8.6 Hz), 7.42−7.36 (m, 3 H), 7.34 (d, 2 H, J = 8.6 Hz), 7.17−7.14 (m, 2 H); IR (KBr) 1715, 1667, 1591, 1525, 1352, 1267, 849 cm^{-1}. Anal. Calcd for $C_{20}H_{13}ClN_2O_4$: C, 63.08; H, 3.44; N, 7.36. Found: C, 63.00; H, 3.54; N, 7.48.

***N*-*p*-Chlorobenzoyl-*N*-*p*-cyanophenyl-*p*-nitrobenzamide (21h) (60%):** white crystals; mp 113−114 °C; ^{1}H NMR ($CDCl_3$) δ 8.25 (d, 2 H, J = 9.1 Hz), 7.85 (d, 4 H, J = 8.9 Hz), 7.69 (d, 2 H, J = 8.7 Hz), 7.64 (d, 2 H, J = 8.7 Hz), 7.37 (d, 2 H, J = 8.7 Hz), 7.27 (d, 2 H, J = 9.1 Hz); IR (KBr) 2232, 1692, 1525, 1603, 1505, 1401, 1291, 1261, 1230, 848 cm^{-1}; HRMS (EI+) calcd for $C_{21}H_{12}ClN_3O_4$ M^+ 405.0516, found M^+ 405.0511.

Reaction of 1,3-Dioxolium-4-olate 5b with Singlet Oxygen. A benzene solution (5 mL) of **6b** (0.5 mmol) was added dropwise over 1 h to a benzene solution (10 mL) of $Rh_2(OAc)_4$ (0.5 mg) and 9,10-diphenylanthracene (2 mg) at 30 °C under irradiation of tungsten lamp while oxygen was bubbling through the mixture and stirred until the light red solution turned clear. After the solvent was distilled off, the NMR spectrum of the reaction mixture showed the presence of *p*-anisic *p*-nitrobenzoylformic anhydride **28b** and *p*-anisic *p*-nitrobenzoic anhydride **27b** in a ratio of ca. 5:4. The mixture was dissolved in absolute methanol and left at room temperature overnight. After methanol was removed, the residue was dissolved in ether and the ether solution was washed with an aqueous sodium bicarbonate solution. The NMR spectrum of the ethereal extract showed methyl *p*-nitrobenzoylformate **29** (41%) and methyl *p*-nitrobenzoate **30** (35%) in a ratio of ca. 1:0.85. *p*-Anisic acid **31** (89%) was obtained by acidification of aqueous solution. Methyl *p*-nitrobenzoylformate **29** and methyl *p*-nitrobenzoate **30** proved identical with independently synthesized authentic samples.

28b: ^{1}H NMR ($CDCl_3$) δ 8.39 (d, 2 H, J = 8.9 Hz), 8.26 (d, 2 H, J = 9.0 Hz), 8.06 (d, 2 H, J = 9.0 Hz), 7.00 (d, 2 H, J = 8.9 Hz), 3.91 (s, 3H).

Preparation of *p*-Anisic *p*-Nitrobenzoic Anhydride 27b. A CH_2Cl_2 solution (3 mL) of anisoyl chloride (0.43 g) was added dropwise to a CH_2Cl_2 solution (6 mL) of *p*-nitrobenzoic acid (0.42 g) and triethylamine (0.25 g) at 0 °C with stirring. After the solution had been stirred for 1 h, *p*-anisic *p*-nitrobenzoic anhydride **27b** (0.054 g) deposited as white solids. The CH_2Cl_2 solution was washed with dilute hydrochloric acid, aqueous sodium bicarbonate, and water and then dried over anhydrous $MagSO_4$. After evaporation of the solvent, the residue and the white solids were conbined and recrystallized with CH_2Cl_2/ether to give **27b** as light yellowish plates (0.61 g, 81%). ***p*-Anisic *p*-nitrobenzoic anhydride 27b:** mp 157−158 °C; ^{1}H NMR ($CDCl_3$) δ 8.38 (d, 2 H, J = 9.2 Hz), 8.33 (d, 2 H, J = 9.2 Hz), 8.09 (d, 2 H, J = 8.9 Hz), 7.01 (d, 2 H, J = 8.9 Hz), 3.92 (s, 3H); IR (KBr) 1785, 1720, 1605, 1521, 1346, 1234, 1166, 1080 cm^{-1}. Anal. Calcd for $C_{15}H_{11}NO_6$: C, 59.80; H, 3.68; N, 4.65. Found: C, 59.60; H, 3.68; N, 4.70.

General Procedure of Dehydrochlorination of α-Acyloxyarylacetyl Chloride in the Presence of Dimethyl Acetylenedicarboxylate (DMAD). A benzene solution of 1.1 equiv of *i*-Pr_2NEt was added dropwise to a benzene solution of α-acyloxyphenylacetyl chloride **11** and 2 equiv of DMAD and stirred for 2 h at room

temperature. The reaction mixture was washed with water, dilute hydrochloric acid, and water and then dried over magnesium sulfate. The resultant solution was chromatographed over silica gel with toluene as an eluent, giving white solids. The solids were recrystallized from CH_2Cl_2/ether/pentane.

Dimethyl 2-methyl-5-phenylfuran-3,4-dicarboxylate (35a) (64%): white needles; mp 60−60.5 °C; ^{1}H NMR ($CDCl_3$) δ 7.69−7.65 (m, 2 H), 7.43−7.37 (m, 3 H), 3.89 (s, 3 H), 3.84 (s, 3 H), 2.61 (s, 3 H); IR (KBr) 2964, 1724, 1567, 1441, 1396, 1220, 1098 cm^{-1}. Anal. Calcd for $C_{15}H_{14}O_5$: C, 65.69; H, 5.14. Found: C, 65.63; H, 5.23.

Dimethyl 2-*p*-methoxyphenyl-5-*p*-nitrophenylfuran-3,4-dicarboxylate (35c) (40%): yellow needles; mp 150−151 °C (lit.[18] mp 149−150 °C).

Dimethyl 2-*p*-nitrophenyl-5-*p*-tolylfuran-3,4-dicarboxylate (35d) (44%): yellowish crystals; mp 154−155 °C; ^{1}H NMR ($CDCl_3$) δ 8.25 (d, 2 H, J = 8.6 Hz), 7.74 (d, 2 H, J = 8.6 Hz), 7.36 (d, 2 H, J = 8.6 Hz), 7.12 (d, 2 H, J = 8.6 Hz), 3.90 (s, 3 H), 3.85 (s, 3 H), 2.35 (s, 3 H); IR (KBr) 1724, 1530, 1443, 1392, 1234, 1120, 985, 755 cm^{-1}. Anal. Calcd for $C_{21}H_{17}O_7N$: C, 63.79; H, 4.33; N, 3.54. Found: C, 63.70; H, 4.47; N, 3.54.

Dimethyl 2-methyl-5-*p*-tolylfuran-3,4-dicarboxylate (35e) (48%): white needles; mp 94 °C; ^{1}H NMR ($CDCl_3$) δ 7.36 (d, 2 H, J = 8.9), 7.12 (d, 2 H, J = 8.9 Hz), 3.89 (s, 3 H), 3.85 (s, 3 H), 3.59 (s, 3 H), 2.35 (s, 3H); IR (KBr) 1726, 1575, 1440, 1396, 1220, 995 cm^{-1}. Anal. Calcd for $C_{16}H_{16}O_5$: C, 66.66; H, 5.59. Found: C, 66.70; H, 5.63.

(18) Clawson, P.; Whiting, D. A. *J. Chem. Soc., Perkin Trans. 1* **1990**, 1193.

Dimethyl 2,5-diphenylfuran-3,4-dicarboxylate (35f) (29%): white needles; mp 78−79 °C; ^{1}H NMR ($CDCl_3$) δ 7.87−7.83 (m, 4 H), 7.46−7.32 (m, 6 H), 3.88 (s, 6 H); IR (KBr) 1952, 1725, 1493, 1441, 1386, 1234, 1112, 993, 762 cm^{-1}. Anal. Calcd for $C_{20}H_{16}O_5$: C, 71.42; H, 4.79. Found: C, 71.26; H, 4.88.

General Procedure for the $Rh_2(OAc)_4$-Catalyzed Reaction of Aryldiazoacetic Anhydrides 6a−c in the Presence of DMAD. A benzene solution (5 mL) of diazo acid anhydrides **6a−c** (0.5 mmol), DMAD (2.0 mmol), and a catalytic amount of $Rh_2(OAc)_4$ was stirred at 50 °C for 2 h. The reaction mixture was chromatographed over silica gel with toluene as an eluent, giving yellowish solids. The solids were recrystallized from CH_2Cl_2/ether/pentane.

Dimethyl 2-methyl-5-*p*-nitrophenylfuran-3,4-dicarboxylate (35g) (80%): yellow needles; mp 144−145 °C; ^{1}H NMR ($CDCl_3$) δ 8.26 (d, 2H, J = 9.2 Hz), 7.85 (d, 2H, J = 9.2 Hz), 3.93 (s, 3H), 3.87 (s, 3H), 2.66 (s, 3 H); IR (KBr) 1736, 1719, 1519, 1451, 1347, 1222, 1094 cm^{-1}. Anal. Calcd for $C_{15}H_{13}NO_7$: C, 56.43; H, 4.10; N, 4.39. Found: C, 56.32; H, 4.05; N, 4.36.

Dimethyl 2-anisyl-5-*p*-nitrophenylfuran-3,4-dicarboxylate (**35c**) was isolated in a yield of 88% in the reaction of **6b** with DMAD.

Dimethyl 2-*p*-chlorophenyl-5-*p*-nitrophenylfuran-3,4-dicarboxylate (35h) (95%): yellow needles; mp 192−193 °C; ^{1}H NMR ($CDCl_3$) δ 8.31 (d, 2H, J = 9.2 Hz), 8.04 (d, 2H, J = 9.2 Hz), 7.83 (d, 2H, J = 8.9 Hz), 7.46 (d, 2H, J = 8.9 Hz), 3.93 (s, 3H), 3.89 (s, 3H); IR (KBr) 1721, 1517, 1489, 1344, 1236, 1093, 991, 855 cm^{-1}. Anal. Calcd for $C_{20}H_{14}ClNO_7$: C, 57.77; H, 3.39; N, 3.37. Found: C, 57.71; H, 3.46; N, 3.41.

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