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Generation of Acyloxyketenes from Unstable Mesoionic 1,3-Dioxolium-4-olates and Their Reaction with Ketenophiles To Give [2 + 2] Cycloadducts

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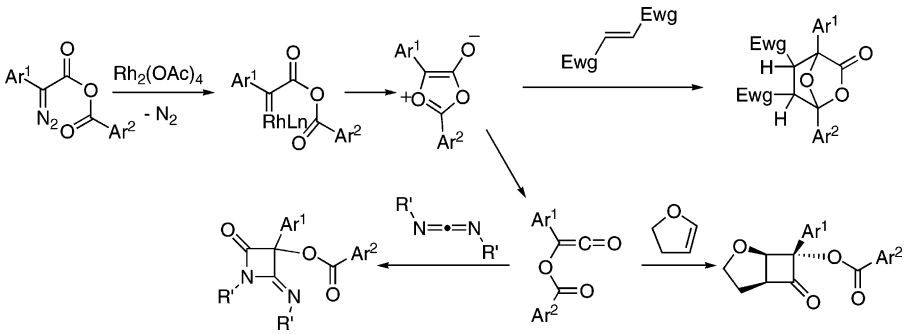
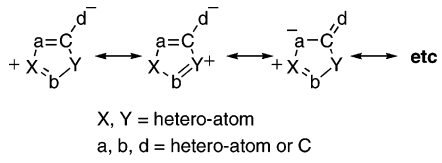
Received January 12, 2006



Fast ring opening of mesoionic 1,3-dioxolium-4-olates, generated by $Rh_2(OAc)_4$-catalyzed decomposition of phenyldiazoacetic anhydride derivatives, to acyloxyphenylketenes was demonstrated by trapping the ketenes with several ketenophiles. Reactions of phenyldiazoacetic anhydride derivatives with several ketenophiles such as dihydrofuran, carbodiimides, and imines were carried out. No 1,3-dipolar cycloadducts of the latter with 1,3-dioxolium-4-olates were observed. Instead, only their [2 + 2]-cycloadducts with the acyloxyketenes generated by ring-opening of the initially formed 1,3-dioxolium-4-olates were isolated. In the reaction with cyclopentadiene, 1,3-dipolar cycloadducts with 1,3-dioxolium-4-olates were formed as main products along with the [2 + 2]-ketene adduct. PM3 calculation of heats of formation of 2,5-diphenyl-1,3-dioxolium-4-olate and the corresponding benzoyloxyphenylketene indicates that the ring-opened acyloxyketenes are ca. 9 kcal/mol more stable than the corresponding 1,3-dioxolium-4-olates.

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



1

Typical mesoionic compounds 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, as the energy level of p-orbitals of an oxygen atom is lower than that of a nitrogen and a carbon atom, resonance stability of mesoionic systems containing an oxygen atom should be smaller than those containing nitrogen atoms.

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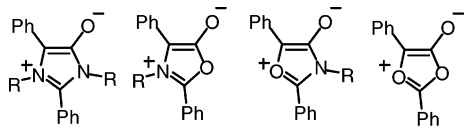
10.1021/jo060074e CCC: $33.50
Published on Web 06/16/2006

SCHEME 1



2 **3** **4** **5**

TABLE 1. Heats of Formation and Heats of Hydrogenation (kcal/mol) of Mesoionic Compounds Calculated by PM3

	2	3	4	5
ΔH_f (R = H)	38.0	4.9	17.9	−16.4
ΔH_f of hydrogenated compounds	19.2	−22.0	−18.6	−60.5
heats of hydrogenation	18.8	26.9	36.5	44.5

According to our PM3 calculation, the heats of hydrogenation for 2,5-diphenyl-substituted mesoionic 1,3-imidazolium-4-olate **2**,[4] münchnone **3**,[5] isomünchnone **4**,[3d,6,7] and 1,3-dioxolium-4-olate **5**[8,9] increase in the order of **2**, **3**, **4**, and **5** as shown in Table 1. The largest heat of hydrogenation for the 1,3-dioxolium-4-olate **5** indicates the smallest resonance stability of the system. In fact, diphenyl-substituted mesoionic 1,3-imidazolium-4-olate **2**, münchnone **3**, and isomünchnone **4** can be isolated as stable crystals, but 1,3-dioxolium-4-olates **5** cannot be isolated as stable compounds. Unstable 1,3-dioxolium-4-olate has a carbonyl ylide resonance structure. To produce the 1,3-dioxolium-4-olate, we used intramolecular carbenoid/carbonyl reaction method, which has very often been reported as a traditional method for generation of carbonyl ylides.[10] So, we prepared phenyldiazoacetic anhydride derivatives **6** as precursors of 1,3-dioxolium-4-olates. We previously carried out π-allyl palladium complex-catalyzed decomposition of **6** in the presence of very reactive olefinic and acetylenic dipolarophiles and succeeded in trapping the 1,3-dioxolium-4-olates **5**, giving 1,3-cycloadducts **7** and furan derivatives **8**, respectively, as shown in Scheme 2.[8,9] Moreover, the reaction with electron-deficient azo compounds gave triacylamidine derivatives **10** in good yields through several steps from 1,3-dipolar cycloadducts **9**.[11] The formation of **7**, **8**, and **10** indicates that generation of **5** resulted from the intramolecular carbenoid/carbonyl reaction of phenyldiazoacetic anhydride derivatives **6**. And also we observed that as soon as phenyldiazoacetic anhydride derivatives **6** were added to a benzene solution of $Rh_2(OAc)_4$ without any dipolarophiles, the solution turned to red color, which faded instantly. The very short lifetime of the red color suggests that the reddish 1,3-dioxolium-4-olates **5** generated are unstable and rapidly convert to other chemical species.

To investigate the behavior of 1,3-dioxolium-4-olates **5**, we attempted to trap the chemical species derived from **5**.

Results and Discussion

Preparation of Phenyldiazoacetic Anhydride Derivatives 6a−d. We prepared phenyldiazoacetic anhydride derivatives **6a−d** from the reaction between triethylamine salt of phenyldiazoacetic acids **14** and acyl chlorides in CH_2Cl_2 at room temperature as shown in Scheme 3. *p*-Nitro- and *p*-chlorophenyldiazoacetic acids **14a**,**b** were prepared by diazo transfer of the corresponding 2-methylthioethyl phenylacetates **11a**,**b** using $KF-Al_2O_3$[12] as base followed by isolation of sulfonium salts **13a**,**b** after quaternarization by methyl iodide, saponification, and then acidification. The procedure described in Scheme 3 can be applied to the synthesis of phenyl- and *p*-tolyldiazoacetic acids, in which the *p*-toluenesulfonylhydrazones of the corresponding 2-methylthioethyl benzoylformates were used for preparation of 2-methylthioethyl phenyldiazoacetates **12**.[13] *p*-Nitrophenyldiazoacetic acid **14a** was also prepared using pyranyl *p*-nitrophenylacetate as starting compounds according to the procedure described in the literature.[14]

$Rh_2(OAc)_4$-Catalyzed Decomposition of 6a−d in the Presence of Dihydrofuran. A benzene solution of *p*-nitrophenyldiazoacetic *p*-chlorobenzoic anhydride **6a**, a catalytic amount of $Rh_2(OAc)_4$, and 20 molar equiv of dihydrofuran **16** was stirred at 30 °C for 5 h (Scheme 4). The NMR spectrum of the reaction mixture showed almost quantitative formation of a single product.

As dihydrofuran is known to be a dipolarophile, we expected that the product might be the 1,3-dipolar cycloadduct **17a**. However, the IR spectrum exhibited two strong carbonyl absorptions at 1789 and 1716 cm^{-1}, which suggests a cyclobutanone derivative, namely, the [2 + 2] ketene adduct **18a** bearing a four-membered cyclic ketone and an ester group. Configuration of the cyclobutanone **18a** was determined on the basis of the NMR spectrum.

In the NMR spectrum of **18a**, the Ha proton (δ 3.17, ddd) of OCH_2 appeared at 0.7 ppm higher field than Hb (δ 3.89, ddd) due to the shielding effect of the *endo*-*p*-nitrophenyl group.[15] The bridgehead proton corresponding to the Hc proton of bicyclic cyclobutanone bearing an *endo*-phenyl group was reported to appear around 4.35 ppm.[15,17a] $Rh_2(OAc)_4$-catalyzed decomposition of phenyldiazoacetic anhydride **6b** and **6d** in the

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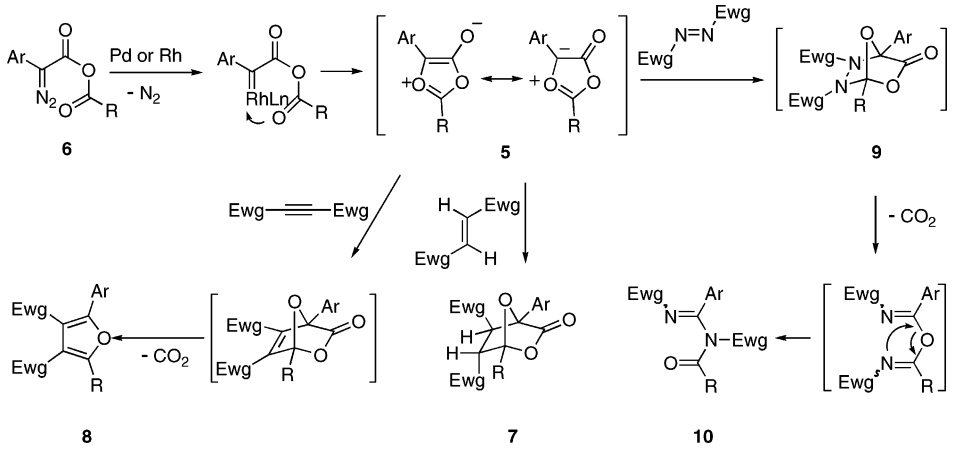
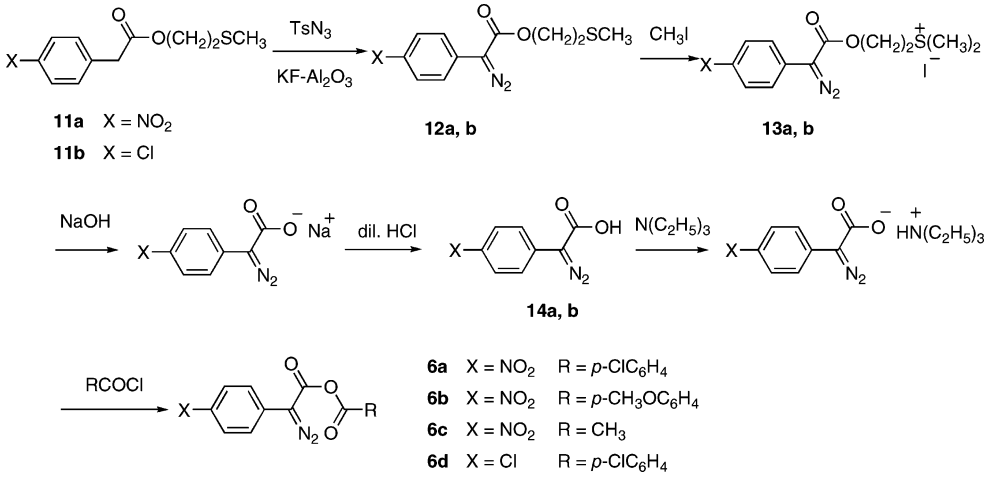
SCHEME 2



SCHEME 3



presence of dihydrofuran also gave single [2 + 2] ketene adducts **18b** and **18d** in good yields (Table 2). Reaction of acetic *p*-nitrophenyldiazoacetic anhydride **6c** with dihydrofuran also gave a single product, the bicyclic cyclobutanone **18c**. The structure of **18c** was confirmed by X-ray analysis.[16] The IR and NMR spectra of **18c** showed very pattern similar to those of **18a**,**b**,**d** as shown in Table 2. In particular, similarities of signals of furan ring protons of **18a**−**d** strongly support *endo*-phenyl groups in **18a**−**d**. The predominant formation of cyclobutanones **18a**−**d** indicates that 1,3-dioxolium-4-olates **5a**−**d** initially formed by intramolecular carbenoid/carbonyl reaction undergo ring-opening to acyloxyketenes **15a**−**d** faster than 1,3-dipolar cycloaddition with dihydrofuran, and the resultant acyloxyketenes **15a**−**d** undergo [2 + 2] cycloaddition with dihydrofuran. The bicyclic cyclobutanones **18a**−**d** bearing the *endo*-*p*-nitrophenyl group should be sterically more crowded than the other isomer bearing the *exo*-*p*-nitrophenyl group. The formation of sterically crowded cyclobutanones in the [2 + 2] cycloaddition of unsymmetrical ketenes with the ketenophiles has been reported.[17] The predominant formation of sterically crowded cyclobutanones in the [2 + 2] cycloaddition of ketenes has been explained by kinetic control, that is, initial crosswise approach of both components with minimum steric repulsion of a bulky substituent of ketene with a ketenophile ([π2s + π2a]) followed by bond formation in a way of smooth increase in overlap as

TABLE 2. Yields and Chemical Shifts of Ha, Hb, Hc, and Hd Protons of Cyclobutanones 18 from Acyloxyketenes 15 and Dihydrofuran

		chemical shift/δ			
	isolated yields/%	Ha	Hb	Hc	Hd
18a	86	3.17	3.89	4.49	5.36
18b	90	3.16	4.88	4.49	5.35
18c	74	3.10	4.84	4.37	5.22
18d	84	3.13	4.86	4.41	5.33

(15) Naidorf-Meir, S. Hassner, A. *J. Org. Chem*. **1992**, *57*, 5102. NMR spectrum of the adduct between dihydrofuran and phenylchloroketene showed very similar pattern. Chemical shifts of the furan ring protons of the adduct: δ 5.08 (d, J = 6 Hz, H−l), 4.35 (dddt, J = 9.5, 6, 1.5, 0.5 Hz, H-5), 3.95 (ddd, J = 10, 8, 2 Hz, H-3 eq), 3.40 (dddt, J = 11, 9.6, 0.5 Hz, H-3 ax), 2.27 (ddddd, J = 13, 7, 4.5, 2, 0.5 Hz, H-4 eq), 2.04 (dddd, J = 13, 10.5, 9, 8 Hz, H-4 ax).

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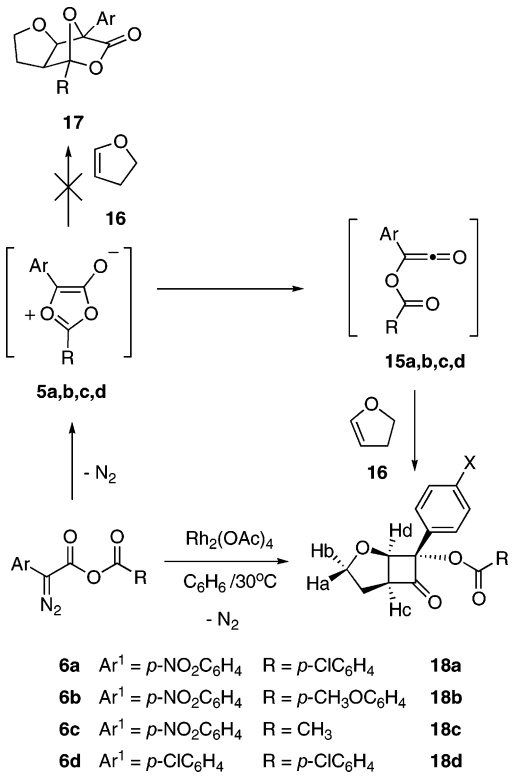
SCHEME 4



the new σ-bonds leads to the prediction that the larger substituent of the ketene will be *endo* in the cycloadduct.[17d,e]

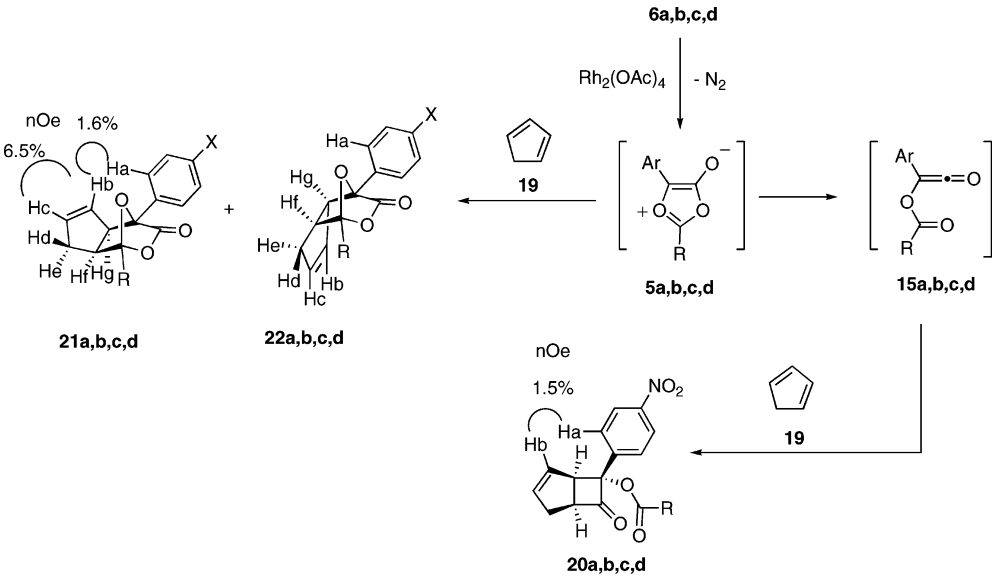
$Rh_2(OAc)_4$-Catalyzed Decomposition of 6a−d in the Presence of Cyclopentadiene. Cylopentadiene **19** is one of the most well-known ketenophiles, which has very often been used in the reaction with ketenes. However, on decomposition of diazoacetic anhydride **6a** in the presence of 5 molar equiv of cyclopentadiene **19**, only [2 + 2] ketene adducts **20a** was isolated in a low yield by column chromatography on *silica gel*. However, NMR spectrum of the reaction mixture showed formation of 1,3-dipolar cycloadducts **21a** and **22a** between 1,3-dioxolium-4-olate **5a** and **19** in a ratio of ca. 2:1 as main products along with **20a** as a minor product (Scheme 5, Table 3). The structure of **20a** was determined on the basis of IR spectrum showing two carbonyl absorptions at 1787 and 1717 cm^{-1} and NOE difference analysis. NOE (1.5%) of the olefinic proton Hb at higher field was observed on irradiation of the nitrophenyl proton Ha, indicating *endo-p*-nitrophenyl group. 1,3-Cycloadducts **21a** and **22a** were decomposable over *silica gel* in chromatography. We succeeded in crystallization of major component **21a** by treatment of the reaction mixtures with ether. IR spectrum of the major adduct **21a** exhibited a single carbonyl absorption at 1793 cm^{-1}, which is characteristic of a strained bicyclic lactone, namely, a 1,3-dipolar cycloadduct between 1,3-dioxolium-4-olate **5a** and cyclopentadiene **19**. The configuration of **21a** was determined by NOE difference analysis. NOE of the signals of Ha (1.6%), Hc (6.5%), and Hg (4.9%) was observed on the irradiation of the signal of the olefinic proton Hb. Small coupling constant between Hg and Hf also supports the *exo*-adduct **21a**. Although [2 + 2] ketene adducts **20b**,**c**,**d** in the reaction of **6b**−**d** with **19** were isolated without decomposition by column chromatography, major products **21b**,**c**,**d** decomposable in column chromatography were isolated by treatment of the reaction mixture with ether. In the reaction of **6c**, isomeric 1,3-cycloadducts **21c** and **22c** were isolated in a pure state by fractional recrystallization. Although the other adducts **22a**,**b**,**d** could not be isolated, their NMR spectra were analyzed from the NMR spectra of the filtrate containing **20a**,**b**,**d**, **21a**,**b**,**d**, and **22a**,**b**,**d** after isolation of **21a**,**b**,**d**. ^{1}HNMR and difference NOE analysis of pure **21c** and **22c** were inspected in detail, leading to the structural determination as shown in Scheme 6. Chemical shifts and coupling patterns of **21a**,**b**,**d** and **22a**,**b**,**d** closely resemble **21c** and **22c**, respectively, as shown in Tables 4 and 5. Formation of **21** and **22** can be rationalized by the fact that cyclopentadiene **19** is a reactive

TABLE 3. Ratios of 20, 21, and 22 in the Reaction with Cyclopentadiene 19[a]

	X	R	**20**/%	**21**/%	**22**/%
a	NO_2	p-ClC_6H_4	21	55	24
b	NO_2	*p*-$CH_3OC_6H_4$	31	50	19
c	NO_2	CH_3	17	55	28
d	Cl	*p*-ClC_6H_4	13	60	27

[a] Determined by ^{1}H NMR.

SCHEME 5



SCHEME 6

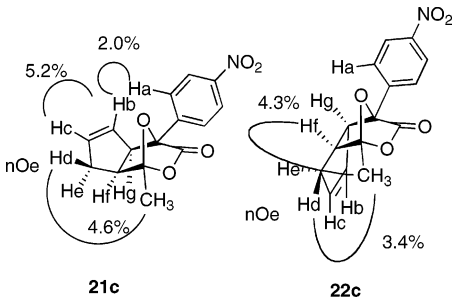


TABLE 4. Chemical Shifts of Ha, Hb, Hc, Hd, He, Hf, and Hg Protons of 1,3-Adducts 21 between 5 and Cyclopentadiene 19

	chemical shift/δ						
21	Ha	Hb	Hc	Hd	He	Hf	Hg
21a	7.83	5.01	5.78	2.07	2.51	3.59	3.81
21b	7.84	5.00	5.77	2.14	2.53	3.62	3.79
21c	7.73	4.96	5.82	2.41	2.66	3.17	3.67
21d	7.57	5.09	5.73	2.04	2.47	3.55	3.74

TABLE 5. Chemical Shifts of Ha, Hb, Hc, Hd, He, Hf, and Hg Protons of 1,3-Adducts 22 between 5 and Cyclopentadiene 19

	chemical shift/δ					
22	Ha	Hb	Hc	Hd−He	Hf	Hg
22a	7.86	5.82	6.06	2.50−2.70	3.60	3.80
22b	7.87	5.81	6.05	2.61−2.65	3.67	3.77
22c	7.80	5.74	6.00	2.47−2.52	3.18	3.63
22d	*a*	5.78	5.00	2.47−2.59	3.54	3.81

[a] Aromatic protons of **22d** were obscured by **20d** and **21d**.

dipolarophile due to the strained conjugated double bonds as well as a reactive ketenophile.

Therefore, large parts of 1,3-dioxolium-4-olate **5** generated could undergo rapid 1,3-dipolar cycloaddition with **19** to give isomeric 1,3-adducts **21** and **22** before the ring opening to acyloxyketenes **15**. The acyloxyketenes **15** generated from the remaining 1,3-dioxolium-4-olate **5** would react with **19** to give a single isomer of [2 + 2] ketene adducts **20** bearing *endo*-aryl groups in low yields. Product distribution in the reaction of **6a**−**d** with cyclopentadiene was shown in Table 3.

$Rh_2(OAc)_4$-Catalyzed Decomposition of 6a−d in the Presence of Carbodiimides 23a,b. We attempted to trap the acyloxyketene using more reactive ketenophiles (Scheme 7). Generation of **5a** in the presence of diisopropylcarbodiimide **23a** or dicyclohexylcarbodiimide **23b** (DCC) resulted in quantitative formation of [2 + 2] cycloadducts **24a** and **24b**, respectively. Other aryldiazoacetic anhydrides **6b**−**d** with **23a**,**b** also gave 3-acyloxy-2-imino-4-oxoazetidine derivatives **24c**−**h** in high isolated yields as shown in Table 6. IR spectra of **24a**−**h** exhibited characteristic absorptions of 3-acyloxy-2-imino-4-oxoazetidines at ca. 1820 (β-lactam C═O), 1720 (ester C═O), and 1700 cm^{-1} (imino R′−N═C).

$Rh_2(OAc)_4$-Catalyzed Decomposition of 6a in the Presence of the Imine 25. A benzene solution of **6a**, a catalytic amount of $Rh_2(OAc)_4$, and 5 equiv of *N*-*p*-chlorobenzylidene-*p*-toluidine **25** was stirred at 50 °C for 2 h. The reaction mixture was chromatographed over silica gel to give the β-lactams **26** and **27** in a ratio of 7:3 (54% isolated yield) (Scheme 8). Structures of **26** and **27** were determined on the basis of their NMR spectra. *p*-Nitrophenyl and *p*-chlorophenyl protons of **26** appeared at higher field than the corresponding protons of **27**.

SCHEME 7

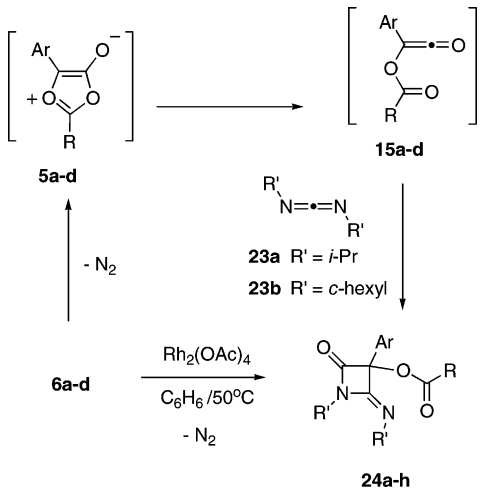
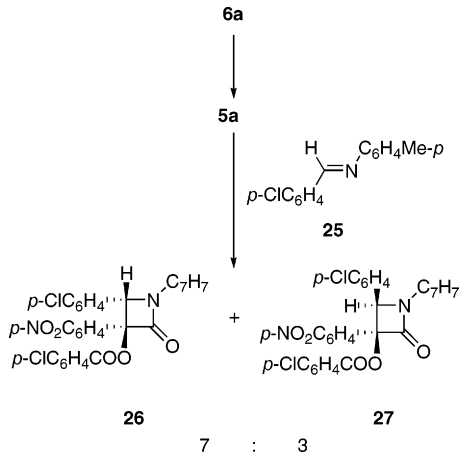


TABLE 6. Isolated Yields of Cycloadducts 24 in the Reaction of 6a−d with carbodiimides 23a and 23b

24	Ar	R	R′	isolated yields/%
24a	*p*-$NO_2C_6H_4$	*p*-ClC_6H_4	^{i}Pr	96
24b	*p*-$NO_2C_6H_4$	*p*-ClC_6H_4	c-C_6H_{11}	96
24c	*p*-$NO_2C_6H_4$	*p*-$CH_3OC_6H_4$	^{i}Pr	90
24d	*p*-$NO_2C_6H_4$	*p*-$CH_3OC_6H_4$	c-C_6H_{11}	96
24e	*p*-$NO_2C_6H_4$	CH_3	^{i}Pr	92
24f	*p*-$NO_2C_6H_4$	CH_3	c-C_6H_{11}	90
24g	*p*-ClC_6H_4	*p*-ClC_6H_4	^{i}Pr	95
24h	*p*-ClC_6H_4	*p*-ClC_6H_4	c-C_6H_{11}	92

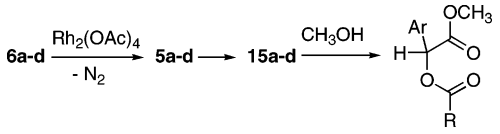
SCHEME 8



$Rh_2(OAc)_4$-Catalyzed Decomposition of 6a−d in the Presence of Methanol. Generation of **5a** from $Rh_2(OAc)_4$-catalyzed decomposition of diazoacetic anhydride **6a** in the presence of 5-fold molar excesses of methanol resulted in almost quantitative formation of methyl α-*p*-chlorobenzoyloxy-*p*-nitrophenylacetate **28a** (isolated yield 92%). Phenyldiazoacetic anhydride derivatives **6b**−**d** also gave the same results (Scheme 9).

In previous papers describing isolation of 1,3-dipolar cycloadducts **7** and furans **8** in the reaction of **6** with olefinic and acetylenic dipolarophiles, we used a π-allyl palladium complex as a catalyst.[8,9] To investigate the effects of catalysts on formation of 1,3-dioxolium-4-olates **5** or the acyloxyketenes, $Rh_2(OAc)_4$-catalyzed decomposition of **6** in the presence of reactive olefinic and acetylenic dipolarophiles was carried out, giving the same results as the case of the Pd catalyst, which indicates that the rhodium carbenoid also attacks the intramo-

SCHEME 9



28a-d

			isolated yield
28a	Ar = *p*-$NO_2C_6H_4$	R = *p*-ClC_6H_4	92%
28b	Ar = *p*-$NO_2C_6H_4$	R = *p*-$CH_3OC_6H_4$	98%
28c	Ar = *p*-$NO_2C_6H_4$	R = CH_3	95%
28d	Ar = *p*-ClC_6H_4	R = *p*-ClC_6H_4	99%

TABLE 7. Heats of Formation of 1,3-Dioxolium-4-olates 5 and the Corresponding Acyloxyketenes 15

			ΔH_f[a]/kcal mol^{-1}		
entry	Ar	R	**5**	**15**	$\Delta\Delta H_f$/kcal mol^{-1}
1	Ph	Ph	−16.4	−25.4	9.0
2	Ph	CH_3	−50.5	−60.0	9.5
3	CH_3	Ph	−48.8	−58.3	9.5

[a] Calculated by PM3.

lecular carbonyl oxygen atom to initially produce the 1,3-dioxolium-4-olate **5**.

Transient appearance and rapid disappearance of the red color of the 1,3-dioxolium-4-olate **5a** and the formation of the acyloxyketene adducts **18a**−**d**, **20a**, **24a**−**h**, **26**, and **27** in the presence of ketenophiles such as dihydrofuran, cyclopentadiene, carbodiimides **23**, and the imine **25** indicates that the initially formed 1,3-dioxolium-4-olates **5** are too unstable to survive and undergo rapid ring-opening to the acyloxyketenes **15**, which react with ketenophiles to give [2 + 2] cycloadducts.

PM3 calculation of heats of formation of the 2,5-diphenyl-1,3-dioxolium-4-olate **5** and the corresponding acyloxyketene **15** indicates that the acyloxyketene **15** is 9−9.5 kcal/mol more stable than the 1,3-dioxolium-4-olate **5** as shown in Table 7, strongly supporting that 1,3-dioxolium-4-olates **5** undergo fast ring opening to the acyloxyketenes **15** followed by [2 + 2] cycloaddition with the ketenophiles.

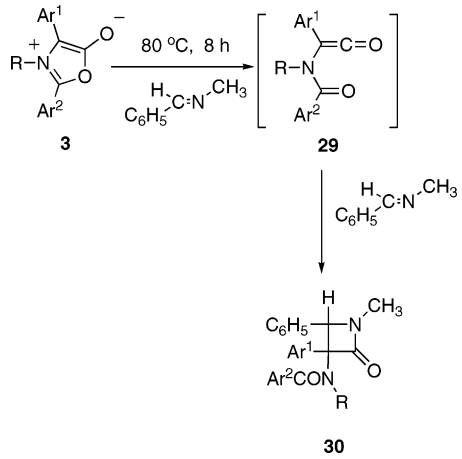
Although ring-opening of an isolable mesoionic compound to a ketene was observed in münchnones **3**, the ring-opening of **3** to acylaminoketenes **29** requires long heating of **3** in the presence of ketenophiles such as imines, carbodiimides, and enamines, resulting in formation of [2 + 2] ketene adducts **30** (Scheme 10).[18] According to our PM3 calculation, the ring-opened acylaminoketene **29** is 2.2 kcal/mol less stable than the ring-closed münchnone **3**, indicating that long heating of münchnone was required in order to react as acylaminoketene with ketenophiles.

Conclusion

We have showed that the 1,3-dioxolium-4-olates **5** generated from aryldiazoacetic anhydride derivatives **6** are the most unstable mesoionic system among the related mesoionic compounds, so that they cannot exist as stable compounds and undergo rapid ring-opening to acyloxyketenes **15**, which are

(18) (a) Huisgen, R.; Funke, E.; Schaefer, F. C.; Knorr, R. *Angew. Chem., Int. Ed. Engl.* **1967**, *6*, 367. (b) Bayer, H. O.; Huisgen, R.; Knorr, R.; Schaefer, F. C. *Chem. Ber.* **1971**, *104*, 3222.

SCHEME 10



captured by various ketenophiles to give [2 + 2] cycloadducts such as cyclobutanones **18**, **20**, 4-iminoazetidine-2-ones **24**, and *β*-lactams **26**, **27**. However, in the reaction with cyclopentadiene **19**, large parts of 1,3-dioxolium-4-olates **5** were trapped before the ring-opening to acyloxyketenes **15** by **19** as reactive dipolarophile to give 1,3-adducts **21**, **22** as main products and [2 + 2] ketene adduct **20** as minor product.

Experimental Section

General Methods. 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 using TMS as an internal standard.

Preparation of Aryldiazoacetic Acid (14). Method A: According to the procedure described in the literature, *p*-nitrophenyldiazoacetic acid was prepared by diazo transfer of 1-pyranyl *p*-nitrophenylacetate followed by hydrolysis.[14] Method B: KF−Al_2O_3 (41 g) was added to an acetonitrile solution (400 mL) of toluenesulfonyl azide (0.1 mol) and 2-methylthioethyl aryl acetate **11** (0.1 mol), prepared from the corresponding acid chloride and 2-methylthioethanol in CH_2Cl_2, and the resultant solution was stirred for 120 h at room temperature. After filtration of the reaction mixture, acetonitrile was removed under the reduced pressure and the residue was recrystallized from ether/pentane.

2-Methylthioethyl *p*-nitrophenylacetate (11a): 80%; mp 42−43 °C; ^{1}H NMR ($CDCl_3$) δ 8.19 (d, 2 H, J = 8.7 Hz), 7.47 (d, 2 H, J = 8.9 Hz), 4.30 (t, 2 H, J = 6.7 Hz), 3.76 (s, 2H), 2.72 (t, 2 H, J = 6.9 Hz), 2.12 (s, 3 H); IR (KBr) 2924, 2104, 1704, 1593, 1514, 1330, 1228, 1161, 1025, 851 cm^{-1}. Anal. Calcd for $C_{11}H_{13}O_4NS$: C, 51.7; H, 5.13; N, 5.49. Found: C, 51.50; H, 5.01; N, 5.49.

2-Methylthioethyl *p*-nitrophenyldiazoacetate (12a): yellow needles; mp 51−52 °C; ^{1}H NMR ($CDCl_3$) δ 8.23 (d, 2 H, J = 8.6 Hz), 7.66 (d, 2 H, J = 8.7 Hz), 4.48 (t, 2 H, J = 6.7 Hz), 2.82 (t, 2 H, J = 6.7 Hz), 2.18 (s, 3 H); IR (KBr) 2926, 1731, 1605, 1519, 1348, 1164, 717 cm^{-1}. Anal. Calcd for $C_{11}H_{11}O_4N_3S$: C, 46.98; H, 3.94; N, 14.98. Found: C, 47.07; H, 3.92; N, 14.61.

2-*p*-Nitrophenyldiazoacetoxyethyl dimethylsulfonium iodide (13a): mp 123 °C; ^{1}H NMR (DMSO-d_6) δ 8.27 (d, 2 H, J = 8.7 Hz), 7.81 (d, 2 H, J = 8.7 Hz), 4.73−4.68 (m, 2 H), 3.78−3.70 (m, 2 H), 2.92 (s, 6 H); IR (KBr) 2975, 2099, 1689, 1595, 1498, 1385, 1339, 1232, 1163 cm^{-1}. Anal. Calcd for $C_{12}H_{14}O_4N_3SI$: C, 34.05; H, 3.33; N, 9.93. Found: C, 34.21; H, 3.28; N, 9.96.

***p*-Nitrophenyldiazoacetic acid (14a)**: 82%; mp 133−136 °C (lit.[14] mp 125 °C).

2-Methylthioethyl *p*-chlorophenylacetate (11b): colorless oil; bp 145 °C/1 mmHg; ^{1}H NMR ($CDCl_3$) δ 7.30 (d, 2 H, J = 8.6 Hz), 7.21 (d, 2 H, J = 8.6 Hz), 4.27 (t, 2H, J = 6.9 Hz), 3.61 (s, 2H), 2.71 (t, 2 H, J = 6.9 Hz), 2.11 (s, 3 H); IR (KBr) 2919, 1738,

1493, 1410, 1252, 1155, 1091, 1016, 808 cm^{-1}; HRMS calcd for $C_{11}H_{13}ClO_2S$ 244.0325, found 244.0331.

2-Methylthioethyl *p*-chlorophenyldiazoacetate (12b): mp 30 °C; ^1H NMR ($CDCl_3$) δ 7.42 (d, 2 H, J = 8.9 Hz), 7.35 (d, 2 H, J = 8.9 Hz), 4.44 (t, 2 H, J = 6.9 Hz), 2.80 (t, 2 H, J = 6.9 Hz), 2.17 (s, 3 H); IR (KBr) 2089, 1702, 1495, 1340, 1244, 1155 cm^{-1}. Anal. Calcd for $C_{11}H_{11}O_2SN_2Cl$: C, 48.80; H, 4.10; N, 10.35. Found: C, 48.94; H, 4.07; N, 10.31. An etherial solution (20 mL) of 2-methylthioethyl 4-chlorophenyldiazoacetate (**12b**) (5.4 g, 20 mmol) and methyl iodide (15 g, 106 mmol) was allowed to stand for 7 days. Precipitated crystal was filtered and washed with ether (yield 85%).

2-*p*-Chlorophenyldiazoacetoxyethyl dimethylsulfonium iodide (13b): mp 119−120 °C; ^1H NMR (DMSO-d_6) δ 7.56 (d, 2 H, J = 8.9 Hz), 7.50 (d, 2 H, J = 8.7 Hz), 4.69−4.64 (m, 2 H), 3.73−3.68 (m, 2 H), 2.94 (s, 6 H); IR (KBr) 2974, 2900, 2094, 1695, 1497, 1381, 1342, 1236, 1162, 1052, 808 cm^{-1}. Anal. Calcd for $C_{12}H_{14}O_2SN_2ClI$: C, 34.93; H, 3.42; N, 6.79. Found. C, 34.96; H, 3.39; N, 6.72.

Preparation of *p*-Chlorophenyldiazoacetic Acid (14b). 2-*p*-Chlorophenyldiazoacetoxyethyl dimethylsulfonium iodide (**13b**) (4.13 g, 10 mmol) and a small amount of phenolphthalein as indicator were dissolved in 500 mL of water at 50 °C. A diluted aqueous sodium hydroxide (1%) solution was added dropwise to the resultant solution under stirring in ice/water bath until the solution turned red. After filtration of the aqueous reaction mixture, the solution was acidified with diluted hydrochloric acid, giving white crystals. The crystal was extracted with ether and dried over magnesium sulfate. After evaporation of ether, *p*-chlorophenyldiazoacetic acid was crystallized as yellow powder (82%).

14b: 82%; mp 109−110 °C dec; ^1H NMR ($CDCl_3$) δ 7.48 (d, 2 H, J = 8.6 Hz), 7.36 (d, 2 H, J = 8.6 Hz); IR (KBr) 3285, 2100, 1742, 1672, 1493, 1407, 1235, 1192, 1093, 1014, 834 cm^{-1}. Anal. Calcd for $C_8H_5O_2N_2Cl$: C, 48.87; H, 2.56; N, 14.25. Found: C, 48.95; H, 2.59; N, 14.23.

Preparation of Aryldiazoacetic Acid Anhydrides 6. Acyl chloride (10 mmol) in CH_2Cl_2 (10 mL) was dropwise added to a dichloromethane solution (20 mL) of aryldiazoacetic acid (10 mmol) and triethylamine (10 mmol) at 0 °C. After the resultant solution was stirred for 3 h, the reaction mixture was washed with water, aqueous $NaHCO_3$, diluted hydrochloric acid, and water and dried over anhydrous $MgSO_4$. After evaporation of CH_2Cl_2, treatment of the residue with CH_2Cl_2/ether gave yellow crystals of diazoacetic acid anhydrides.

***p*-Chlorobenzoic *p*-nitrophenyldiazoacetic anhydride (6a):** 55%; yellow powder; mp 148−149 °C; ^1H NMR ($CDCl_3$) δ 8.30 (d, 2 H, J = 9.2 Hz), 8.01 (d, 2 H, J = 8.9 Hz), 7.73 (d, 2 H, J = 9.2 Hz), 7.51 (d, 2 H, J = 8.9 Hz); IR (KBr) 2113, 1770, 1704, 1592, 1508, 1337, 1260, 1224, 1115, 1036, 1008, 853 cm^{-1}. Anal. Calcd for $C_{15}H_8ClN_3O_5$: C, 52.12; H, 2.33; N, 12.16. Found: C, 52.00; H, 2.47; N, 12.23.

***p*-Methoxybenzoic *p*-nitrophenyldiazoacetic anhydride (6b):** 63%; yellow powder; mp 138−139 °C; ^1H NMR ($CDCl_3$) δ 8.29 (d, 2 H, J = 9.2 Hz), 8.02 (d, 2 H, J = 8.9 Hz), 7.74 (d, 2 H, J = 9.2 Hz), 6.99 (d, 2 H, J = 8.9 Hz), 3.91 (s, 3 H); IR (KBr) 2115, 1773, 1601, 1514, 1335, 1260, 1220, 1118, 1020, 996 cm^{-1}. Anal. Calcd for $C_{16}H_{11}N_3O_6$: C, 56.31; H, 3.25; N, 12.31. Found: C, 56.20; H, 3.36; N, 12.37.

Acetic *p*-nitrophenyldiazoacetic anhydride (6c): 60%; yellow powder; mp 96−97 °C; ^1H NMR ($CDCl_3$) δ 8.28 (d, 2 H, J = 9.2 Hz), 7.69 (d, 2 H, J = 9.2 Hz), 2.33 (s, 3 H); IR (KBr) 2111, 1801, 1709, 1592, 1509, 1337, 1159, 1092, 1002, 951, 854 cm^{-1}. Anal. Calcd for $C_{10}H_7N_3O_5$: C, 48.20; H, 2.83; N, 16.86. Found: C, 48.29; H, 2.91; N, 16.51.

***p*-Chlorobenzoic *p*-chlorophenyldiazoacetic anhydride (6d):** yellow plates; mp 144−145 °C; ^1H NMR ($CDCl_3$) δ 7.99 (d, 2 H, J = 8.6 Hz), 7.51−7.39 (m, 6 H); IR (KBr) 2117, 1775, 1700, 1593, 1493, 1280, 1257, 1216, 1092, 1039, 1007, 929, 826 cm^{-1}. Anal. Calcd for $C_{15}H_8O_3N_2Cl_2$: C, 53.76; H, 2.41; N, 8.36. Found: C, 53.71; H, 2.51; N, 8.46.

Reaction of Aryldiazoacetic Anhydride 6a−d with 2,3-Dihydrofuran. A benzene solution (10 mL) of diazo acid anhydride 6 (0.5 mmol), dihydrofuran (10 mmol), and a catalytic amount of $Rh_2(OAc)_4$ was stirred at 30 °C for 5 h. The NMR spectrum of the reaction mixture indicated the quantitative formation of single adducts **18**. The reaction mixture was chromatographed over silica gel using benzene as an eluent. The adducts **18** were recrystallized from ether/pentane.

7-(*p*-Nitrophenyl)-6-oxo-2-oxabicyclo[3.2.0]hept-7-yl *p*-chlorobenzoate (18a): 86%; white crystal; mp 117−118 °C; ^1H NMR ($CDCl_3$) δ 8.29 (d, 2 H, J = 8.9 Hz), 7.86 (d, 2 H, J = 8.9 Hz), 7.83 (d, 2 H, J = 8.9 Hz), 7.40 (d, 2 H, J = 8.9 Hz), 5.36 (d, 1 H, J = 6.9 Hz), 4.49 (ddd, 1 H, J = 10.6, 7.3, 3.3 Hz), 3.89 (ddd, 1 H, J = 9.2, 7.9, 4.0 Hz), 3.17 (td, 1 H, J = 9.2, 6.9 Hz), 2.21−2.04 (m, 2 H); IR (KBr) 1789, 1716, 1594, 1521, 1347, 1294, 1097, 1015, 854 cm^{-1}. Anal. Calcd for $C_{19}H_{14}ClNO_6$: C, 58.85; H, 3.64; N, 3.61. Found: C, 58.65; H, 3.66; N, 3.64.

7-(*p*-Nitrophenyl)-6-oxo-2-oxabicyclo[3.2.0]hept-7-yl *p*-methoxybenzoate (18b): 90%; white cubes; mp 112−113 °C; ^1H NMR ($CDCl_3$) δ 8.28 (d, 2H, J = 8.9 Hz), 7.87 (d, 2H, J = 8.9 Hz), 7.83 (d, 2H, J = 8.9 Hz), 6.80 (d, 2H, J = 8.9 Hz), 5.35 (d, 1H, J = 6.9 Hz), 4.49 (ddd, 1H, J = 10.6, 6.9, 3.3 Hz), 3.91−3.84 (m, 1H), 3.85 (s, 3H), 3.16 (td, 1H, J = 9.2, 7.3 Hz), 2.20−2.04 (m, 2H); IR (KBr) 1784, 1703, 1606, 1522, 1347, 1289, 1261, 1174, 1090, 854 cm^{-1}. Anal. Calcd for $C_{20}H_{17}NO_7$: C, 62.66; H, 4.47; N, 3.65. Found: C, 62.79; H, 4.58; N, 3.68.

7-(4-Nitrophenyl)-6-oxo-2-oxabicyclo[3.2.0]hept-7-yl acetate (18c): 74%; colorless cubes; mp 118−119 °C; ^1H NMR ($CDCl_3$) δ 8.24 (d, 2 H, J = 8.9 Hz), 7.74 (d, 2 H, J = 8.9 Hz), 5.22 (d, 1 H, J = 6.9 Hz), 4.37 (ddd, 1 H, J = 10.2, 6.9, 3.6 Hz), 3.84 (ddd, 1 H, J = 9.2, 7.6, 4.0 Hz), 3.10 (td, 1 H, J = 9.2, 7.3 Hz), 2.18−1.95 (m, 2 H), 2.11 (s, 3 H); IR (KBr) 1790, 1727, 1606, 1533, 1349, 1231, 1074, 1011, 849 cm^{-1}. Anal. Calcd for $C_{14}H_{13}NO_6$: C, 57.73; H, 4.50; N, 4.81. Found: C, 57.52; H, 4.47; N, 4.82.

7-(*p*-Chlorophenyl)-6-oxo-2-oxabicyclo[3.2.0]hept-7-yl *p*-chlorobenzoate (18d): 84%; colorless cubes; mp 119−120 °C; ^1H NMR ($CDCl_3$) δ 7.85 (d, J = 8.9 Hz), 7.56 (d, 2 H, J = 8.9 Hz), 7.41 (d, 2 H, J = 8.9 Hz), 7.38 (d, 2 H, J = 8.9 Hz), 5.33 (d, 1 H, J = 6.9 Hz), 4.41 (ddd, 1 H, J = 10.6, 7.3, 3.6 Hz), 3.86 (ddd, 1 H, J = 9.2, 7.9, 3.6 Hz), 3.13 (td, 1 H, J = 9.6, 3.3 Hz), 2.17−1.99 (m, 2 H); IR (KBr) 2877, 1781, 1719, 1595, 1492, 1402, 1296, 1235, 1091, 1014, 826, 756 cm^{-1}. Anal. Calcd for $C_{19}H_{14}Cl_2O_4$: C, 60.50: H, 3.74. Found: C, 60.43; H, 3.83.

Reaction of Aryldiazoacetic Anhydride 6a−d with Cyclopentadiene 19. A benzene solution (10 mL) of diazo acid anhydride **6** (0.5 mmol), cyclopentadiene **19** (2.5 mmol), and a catalytic amount of $Rh_2(OAc)_4$ was stirred at 30 °C for 5 h. The NMR spectrum of the reaction mixture indicated mixtures of 1,3-dipolar adducts **21** and **22** between 1,3-dioxolium-4-olates **5** and **19** and [2 + 2] ketene adducts **20**. After benzene was removed under reduced pressure, on treatment of the reaction mixtures with ether, main products 1,3-dipolar adducts **21** crystallized as white solids. Ether-soluble part was chromatographed over silica gel using toluene as an eluent to give acyloxyketene adducts **20**. In the reaction of **6c** with cyclopentadiene, **21c** and **22c** were separated in a pure state by fractional recrystallization from the reaction mixture.

7-(*p*-Nitrophenyl)-6-oxo-2-bicyclo[3.2.0]hept-7-yl *p*-chlorobenzoate (20a): 21%; white powder; mp 126−127 °C; ^1H NMR ($CDCl_3$) δ 8.22 (d, 2 H, J = 9.0 Hz), 7.95 (d, 2 H, J = 8.4 Hz), 7.59 (d, 2 H, J = 9.0 Hz), 7.44 (d, 2 H, J = 8.6 Hz), 5.82 (dq, 1 H, J = 5.6, 1.8 Hz), 5.29 (dq, 1 H, J = 5.6, 2.5 Hz), 4.52 (ddd, 1 H, J = 9.8, 8.4, 2.1 Hz), 4.18 (br d, 1 H, J = 8.5 Hz), 2.80 (d quintet, 1 H, J = 17.8, 2.5 Hz), 2.61 (ddq, 2 H, J = 17.8, 9.7, 2.5 Hz); ^{13}C NMR ($CDCl_3$) δ 205.15, 163.87, 147.68, 141.18, 140.39, 136.04, 131.22, 128.95, 128.20, 127.81, 127.71, 123.43, 97.45, 60.22, 53.00, 34.78; IR (KBr) 1787, 1717, 1593, 1349 cm^{-1}. Anal.

Calcd for $C_{20}H_{14}O_5NCl$; C, 62.57; H, 3.68; N, 3.65. Found: C, 62.72; H, 3.80; N, 3.65.

***exo*-Adduct (21a):** white powder; mp 161−162 °C; ^{1}H NMR ($CDCl_3$) δ 8.32 (d, 2 H, J = 8.9 Hz), 7.83 (d, 2 H, J = 8.9 Hz), 7.60 (d, 2 H, J = 8.6 Hz), 7.49 (d, 2 H, J = 8.7 Hz), 5.78 (dq, 1 H, J = 5.8, 1.8 Hz), 5.01 (dq, 1 H, J = 5.8, 2.3 Hz), 3.77−3.84 (m, 1 H), 3.59 (ddd, 1 H, J = 9.7, 7.1, 3.3 Hz), 2.51 (ddq, 1 H, J = 17.8, 9.7, 1.5 Hz), 2.07 (dquint, 1 H, J = 18.0, 3.1 Hz); ^{13}C NMR ($CDCl_3$) δ 170.35, 147.94, 137.54, 136.46, 135.80, 129.47, 128.95, 127.96, 126.86, 124.20, 123.51, 113.79, 87.61, 56.32, 50.69, 36.31; IR (KBr) 1793, 1605, 1522, 1367, 1351, 1090, 828 cm^{-1}. Anal. Calcd for $C_{20}H_{14}O_5NCl$; C, 62.57; H, 3.68; N, 3.65. Found: C, 62.38; H, 3.60; N, 3.66.

***endo*-Adduct (22a):** ^{1}H NMR ($CDCl_3$) δ 8.32 (d, 2 H, J = 8.9 Hz), 7.86 (d, 2 H, J = 8.9 Hz), 7.63 (d, 2 H, J = 8.8 Hz), 7.49 (d, 2 H, J = 8.6 Hz), 6.06 (dq, 1 H, J = 5.7, 2.0 Hz), 5.82 (dq, 1 H, J = 5.7, 2.2 Hz), 3.77−3.84 (m, 1 H), 3.60 (dt, 1 H, J = 9.3, 3.5 Hz), 2.61−2.65 (m, 2 H).

7-(*p*-Nitrophenyl)-6-oxo-2-bicyclo[3.2.0]hept-7-yl *p*-methoxybenzoate (20b): 24%; white powder; mp 142−143 °C; ^{1}H NMR ($CDCl_3$) δ 8.21 (d, 2 H, J = 9.0 Hz), 7.98 (d, 2 H, J = 8.9 Hz), 7.59 (d, 2 H, J = 9.0 Hz), 6.94 (d, 2 H, J = 9.0 Hz), 5.81 (dq, 1 H, J = 5.5, 2.2 Hz), 5.28 (dq, 1 H, J = 5.5, 2.4 Hz), 4.53 (ddd, 1 H, J = 10.1, 8.6, 2.2 Hz), 4.18 (br d, 1 H, J = 8.4 Hz), 3.87 (s, 3 H), 2.79 (d quintet, 1 H, J = 17.8, 2.2 Hz), 2.60 (ddq, 1 H, J = 17.8, 10.1, 2.2 Hz); ^{13}C NMR ($CDCl_3$) δ 205.61, 164.42, 163.94, 147.59, 141.65, 135.87, 132.03, 128.16, 127.99, 123.31, 120.74, 113.85, 97.12, 60.11, 55.55, 53.17, 34.67; IR (KBr) 1778, 1711, 1605, 1517, 1345, 1257, 1169 cm^{-1}. Anal. Calcd for $C_{20}H_{17}O_6N$; C, 66.49; H, 4.52; N, 3.69. Found: C, 66.46; H, 4.52; N, 3.69.

***exo*-Adduct (21b):** white powder; mp 159.5−160.0 °C; ^{1}H NMR ($CDCl_3$) δ 8.31 (d, 2 H, J = 8.9 Hz), 7.84 (d, 2 H, J = 9.1 Hz), 7.58 (d, 2 H, J = 8.9 Hz), 7.01 (d, 2 H, J = 8.9 Hz), 5.77 (dq, 1 H, J = 5.8, 1.8 Hz), 5.00 (dq, 1 H, J = 5.8, 2.3 Hz), 3.87 (s, 3 H), 3.79 (br d, 1 H, J = 6.9 Hz), 3.62 (ddd, 1 H, J = 9.7, 7.1, 3.3 Hz), 2.53 (ddq, 1 H, 18.0, 9.7, 1.5 Hz), 2.14 (dquint, 1 H, J = 18.0, 3.0 Hz); IR (KBr) 1791, 1608, 1523, 1349, 1251, 1173 cm^{-1}. Anal. Calcd for $C_{20}H_{17}O_6N$; C, 66.49; H, 4.52; N, 3.69. Found: C, 66.21; H, 4.54; N, 3.69.

***endo*-Adduct (22b):** ^{1}H NMR ($CDCl_3$) δ 8.32 (d, 2 H, J = 8.9 Hz), 7.87 (d, 2 H, J = 9.1 Hz), 7.62 (d, 2 H, J = 8.9 Hz), 7.01 (d, 2 H, J = 8.8 Hz), 6.05 (dq, 1 H, J = 5.8, 2.0 Hz), 5.81 (dq, 1 H, J = 5.6, 2.2 Hz), 3.87 (s, 3 H), 3.77 (dquint, 1 H, 9.3, 1.8 Hz), 3.67 (dt, 1 H, 9.4, 3.5 Hz), 2.50−2.7 (m, 2 H).

7-(*p*-Nitrophenyl)-6-oxo-2-bicyclo[3.2.0]hept-7-yl acetate (20c): 14%; white powder; mp 109.5−110.0 °C; ^{1}H NMR ($CDCl_3$) δ 8.18 (d, 2 H, J = 9.1 Hz), 7.50 (d, 2 H, J = 9.1 Hz), 5.77 (dq, 1 H, J = 5.6, 2.1 Hz), 5.23 (dq, 1 H, J = 5.6, 2.3 Hz), 4.42 (ddd, 1 H, J = 10.1, 8.4, 2.3 Hz), 4.02 (br d, 1 H, J = 7.9 Hz), 2.74 (d quint, 1 H, J = 17.8, 2.3 Hz), 2.56 (ddq, 1 H, J = 17.8, 10.1, 2.0 Hz), 2.15 (s, 3 H); IR(KBr) 1780, 1733, 1606, 1524, 1347, 1253, 1236 cm^{-1}. Anal. Calcd for $C_{15}H_{13}O_5N$; C, 62.72; H, 4.56; N, 4.88. Found: C, 62.58; H, 4.53; N, 4.82.

***exo*-Adduct (21c):** white powder; mp 157−158 °C; ^{1}H NMR ($CDCl_3$) δ 8.28 (d, 2 H, J = 8.8 Hz), 7.73 (d, 2 H, J = 8.8 Hz), 5.82 (dq, 1 H, J = 5.7, 2.0 Hz), 4.96 (dq, 1 H, J = 5.6, 2.3 Hz), 3.67 (br d, 1 H, J = 7.2 Hz), 3.17 (ddd, 1 H, J = 9.8, 7.2, 3.3 Hz), 2.66 (ddq, 1 H, J = 17.9, 9.8, 1.6 Hz), 2.41 (dquint, 1 H, J = 17.9, 2.8 Hz), 1.88 (s, 3 H); IR (KBr) 1790, 1605, 1525, 1401, 1353 cm^{-1}. Anal. Calcd for $C_{15}H_{13}O_5N$; C, 62.72; H, 4.56; N, 4.88. Found: C, 62.47; H, 4.49; N, 4.79.

***endo*-Adduct (22c):** white powder; mp 154−155 °C; ^{1}H NMR ($CDCl_3$) δ 8.30 (d, 2 H, J = 8.8 Hz), 7.80 (d, 2 H, J = 8.9 Hz), 6.00 (dq, 1 H, J = 5.7, 1.9 Hz), 5.74 (dq, 1 H, J = 5.7, 1.9 Hz), 3.63 (dquint, 1 H, J = 9.0, 1.9 Hz), 3.18 (ddd, 1 H, J = 9.2, 8.2, 4.8 Hz), 2.47−2.52 (m, 2 H), 1.88 (s, 3 H); IR (KBr) 1792, 1605, 1524, 1402, 1348 cm^{-1}; HRMS(CI+) calcd for $C_{15}H_{14}NO_5$ MH^+ = 288.0872, found MH^+= 288.0876.

7-(*p*-Chlorophenyl)-6-oxo-2-bicyclo[3.2.0]hept-7-yl *p*-chlorobenzoate (20d): 11%; oil; ^{1}H NMR ($CDCl_3$) δ 7.94 (d, 2 H, J = 8.6 Hz), 7.41 (d, 2 H, J = 8.6 Hz), 7.34 (d, 4 H, J = 2.1 Hz), 5.76 (dq, 1 H, J = 5.6, 1.8 Hz), 5.35 (dq, 1 H, J = 5.6, 2.3 Hz), 4.46 (ddd, 1 H, J = 9.9, 8.7, 2.5 Hz), 4.14 (br d, 1 H, J = 8.6 Hz), 2.74 (dquint, 1 H, J = 17.6, 2.5 Hz), 2.74 (dquint, 1 H, J = 17.6, 2.5 Hz), 2.56 (ddq, 3 H, J = 17.6, 9.9, 2.5 Hz); IR (KBr) 1788, 1722, 1592, 1247, 1228, 1009 cm^{-1}; HRMS(CI+) calcd for $C_{20}H_{15}Cl_2O_3$ MH^+ = 373.0398, found MH^+ = 373.0401.

***exo*-Adduct (21d):** white powder; mp 167.5−168 °C; ^{1}H NMR ($CDCl_3$) δ 7.59 (d, 2 H, J = 8.7 Hz), 7.57 (d, 2 H, J = 8.9 Hz), 7.47 (d, 2 H, J = 8.7 Hz), 7.43 (d, 2 H, J = 8.7 Hz), 5.73 (dq, 1 H, J = 5.8, 2.1 Hz), 5.09 (dq, 1 H, J = 5.8, 2.3 Hz), 3.74 (br d, 1 H, J = 7.6 Hz), 3.55 (ddd, 1 H, J = 9.7, 7.3, 3.5 Hz), 2.47 (ddq, 1 H, J = 17.8, 9.7, 1.3 Hz), 2.04 (dquint, 1 H, J = 18.0, 2.3 Hz); IR (KBr) 1793, 1605, 1494, 1372, 1092, 813 cm^{-1}. Anal. Calcd for $C_{20}H_{12}Cl_2O_3$; C, 64.36; H, 3.78. Found: C, 64.07; H, 3.82.

***endo*-Adduct (22d):** ^{1}H NMR ($CDCl_3$) δ 6.00 (dq, 1 H, J = 5.9, 1.8 Hz), 5.78 (dq, 1 H, J = 5.8, 2.1 Hz), 3.81 (dquint, 1 H, J = 9.7, 1.8 Hz), 3.51−3.57 (m, 1 H,), 2.47−2.59 (m, 2 H) (aromatic protons of **22d** were obscured by **20d** and **21d**).

General Procedure of the Reaction of Aryldiazoacetic Anhydride 6a−d with Diisopropylcarbodiimides 23a and Dicyclohexylcarbodiimides 23b. A benzene solution (5 mL) of aryldiazoacetic acid anhydride 6 (0.5 mmol), carbodiimide (0.55 mmol), and a catalytic amount of $Rh_2(OAc)_4$ was stirred at 50 °C for 1 h. After evaporation of benzene, treatment of the residue with CH_2Cl_2/pentane gave white crystals.

1-Isopropyl-2-isopropylimino-3-(*p*-nitrophenyl)-4-oxoazetidin-3-yl *p*-chlorobenzoate (24a): 96%; white cubes; mp 209−210 °C; ^{1}H NMR ($CDCl_3$) δ 8.36 (d, 2 H, J = 8.9 Hz), 8.03 (d, 2 H, J = 8.6 Hz), 7.76 (d, 2 H, J = 8.9 Hz), 7.50 (d, 2 H, J = 8.6 Hz), 4.15 (septet, 1 H, J = 6.9 Hz), 3.47 (septet, 1 H, J = 8.3 Hz), 1.56 (d, 3 H, J = 6.9 Hz), 1.53 (d, 3 H, J = 6.9 Hz), 1.00 (d, 3 H, J = 6.3 Hz), 0.91 (d, 3 H, J = 6.3 Hz); IR (KBr) 2970, 1820, 1736, 1704, 1524, 1348, 1274, 1089, 1011, 856, 753 cm^{-1}. Anal. Calcd for $C_{22}H_{22}O_5N_3Cl$: C, 59.53; H, 5.00; N, 9.47. Found: C, 59.47; H, 5.00; N, 9.43.

1-Cyclohexyl-2-cyclohexylimino-3-(*p*-nitrophenyl)-4-oxoazetidin-3-yl *p*-chlorobenzoate (24b): 96%; colorless powder; mp 245−246 °C; ^{1}H NMR ($CDCl_3$) δ 8.35 (d, 2 H, J = 8.9 Hz), 8.01 (d, 2 H, J = 8.9 Hz), 7.76 (d, 2 H, J = 8.9 Hz), 7.49 (d, 2 H, J = 8.9 Hz), 3.83−3.74 (m, 1 H), 3.65−3.08 (m, 1 H), 2.18−0.97 (m, 20 H); IR (KBr) 2927, 2853, 1833, 1738, 1714, 1594, 1519, 1348, 1273, 1167, 1167, 1091 cm^{-1}. Anal. Calcd for $C_{28}H_{30}O_5N_3Cl$: C, 64.18; H, 5.77; N, 8.02. Found: C, 63.92; H, 5.80; N, 7.92.

1-Isopropyl-2-isopropylimino-3-(*p*-nitrophenyl)-4-oxo-azetidin-3-yl *p*-methoxybenzoate (24c): 90%; white cubes; mp 179−180 °C; ^{1}H NMR ($CDCl_3$) δ 8.35 (d, 2 H, J = 9.2 Hz), 8.04 (d, 2 H, J = 9.2 Hz), 7.77 (d, 2 H, J = 9.2 Hz), 6.96 (d, 2 H, J = 9.2 Hz), 4.15 (septet, 1 H, J = 6.6 Hz), 3.48 (septet, 1 H, J = 6.3 Hz), 1.56 (d, 3 H, J = 6.6 Hz), 1.53 (d, 3 H, J = 6.6 Hz), 0.98 (d, 3 H, J = 6.3 Hz), 0.92 (d, 3 H, J = 6.3 Hz); IR (KBr) 2971, 1821, 1721, 1700, 1604, 1531, 1512, 1459, 1347, 1264, 1167, 1078 cm^{-1}. Anal. Calcd for $C_{23}H_{25}N_3O_6$: C, 62.86; H, 5.73; N, 9.56. Found: C, 62.62; H, 5.82; N, 9.44.

1-Cyclohexyl-2-cyclohexylimino-3-(*p*-nitrophenyl)-4-oxoazetidin-3-yl 4-methoxybenzoate (24d): 96%; white cubes; mp 205−206 °C; ^{1}H NMR ($CDCl_3$) δ 8.33 (d, 2 H, J = 8.9 Hz), 8.03 (d, 2 H, J = 8.9 Hz), 7.77 (d, 2 H, J = 8.9 Hz), 6.97 (d, 2 H, J = 8.9 Hz), 3.89−3.74 (m, 1 H), 3.89 (s, 3 H), 3.15−3.10 (m, 1 H), 2.17−1.05 (m, 20 H); IR (KBr) 2932, 2856, 1822, 1700, 1604, 1522, 1347, 1263, 1166, 1082 cm^{-1}. Anal. Calcd for $C_{29}H_{33}N_3O_6$: C, 67.04; H, 6.40; N, 8.09. Found: C, 67.05; H, 6.42; N, 8.11.

1-Isopropyl-2-isopropylimino-3-(*p*-nitrophenyl)-4-oxoazetidin-3-yl acetate (24e): 92%; colorless cubes; mp 116−117 °C; ^{1}H NMR ($CDCl_3$) δ 8.30 (d, 2 H, J = 9.2 Hz), 7.66 (d, 2 H, J = 9.2 Hz), 4.09 (septet, 1 H, J = 6.6 Hz), 3.42 (septet, 1 H, J = 6.3 Hz), 1.50 (d, 3 H, J = 6.6 Hz), 1.48 (d, 3 H, J = 6.6 Hz), 1.06 (d, 3 H,

J = 6.3 Hz), 0.97 (d, 3 H, J = 6.3 Hz); IR (KBr) 2965, 1825, 1756, 1700, 1527, 1348, 1218, 1049, 1009 cm^{-1}. Anal. Calcd for $C_{22}H_{22}Cl_2N_2O_3$: C, 58.78; H, 6.09; N, 12.10. Found: C, 58.78; H, 6.09; N, 12.10.

1-Cyclohexyl-2-cyclohexylimino-3-(*p*-nitrophenyl)-4-oxoazetidin-3-yl acetate (24f): 90%; colorless cubes; mp 123−124 °C; ^{1}H NMR ($CDCl_3$) δ 8.29 (d, 2H, J = 8.9 Hz), 7.67 (d, 2H, J = 8.9 Hz), 3.73 (m, 1H), 3.07 (m, 1H), 2.25 (s, 3H), 2.09−1.00 (m, 20H); IR (KBr) 2931, 1820, 1762, 1705, 1522, 1345, 1224, 1028 cm^{-1}. Anal. Calcd for $C_{23}H_{29}N_3O_5$: C, 64.62; H, 6.84; N, 9.83. Found: C, 64.32; H, 6.91; N, 9.73.

1-Isopropyl-2-isopropylimino-3-(4-chlorophenyl)-4-oxoazetidin-3-yl 4-chlorobenzoate (24): 95%; colorless cubes; mp 176−177 °C; ^{1}H NMR ($CDCl_3$) δ 8.01 (d, 2 H, J = 8.6 Hz), 7.52−7.44 (m, 6 H), 4.11 (septet, 1 H, J = 6.6 Hz), 3.53 (septet, 1 H, J = 6.3 Hz), 1.54 (d, 3 H, J = 6.6 Hz), 1.50 (d, 3 H, J = 6.6 Hz), 1.02 (d, 3 H, J = 6.3 Hz), 0.90 (d, 3 H, J = 6.3 Hz); IR (KBr) 2969, 1820, 1732, 1699, 1594, 1491, 1400, 1273, 1092, 1050, 1011 cm^{-1}. Anal. Calcd for $C_{22}H_{22}Cl_2N_2O_3$: C, 60.98; H, 5.12; N, 6.46. Found: C, 60.82; H, 5.14; N, 6.44.

1-Cyclohexyl-2-cyclohexylimino-3-(*p*-chlorophenyl)-4-oxoazetidin-3-yl *p*-chlorobenzoate (24h): 92%; white cubes; mp 221−222 °C; ^{1}H NMR ($CDCl_3$) δ 7.99 (d, 2 H, J = 8.6 Hz), 7.53−7.43 (m, 6 H), 3.81−3.69 (m, 1 H), 3.23−3.12 (m, 1 H), 2.17−0.92 (m, 20H); IR (KBr) 2935, 2856, 1828, 1731, 1705, 1592, 1491, 1401, 1271, 1173, 1092, 1011 cm^{-1}. Anal. Calcd for $C_{28}H_{30}Cl_2N_2O_3$: C, 65.50; H, 5.89; N, 5.46. Found: C, 65.24; H, 5.89; N, 5.45.

Reaction of *p*-Nitrophenyldiazoacetic *p*-Chlorobenzoic Anhydride 6a with *N*-*p*-Chlorobenzylidene-*p*-toluidine 25. A benzene solution (5 mL) of **6a** (173 mg, 0.5 mmol), *N*-*p*-chlorobenzylidene-*p*-toluidine **25** (122 mg, 0.53 mmol), and a catalytic amount of $Rh_2(OAc)_4$ was stirred at 50 °C for 2.5 h. The reaction mixture was chromatographed over silica gel using benzene as an eluent, giving two crystalline products. They were recrystallized from CH_2Cl_2/pentane.

***dl*-(2*R*,3*R*)-2-(*p*-Chlorophenyl)-3-(*p*-nitrophenyl)-4-oxo-1-*p*-tolylazetidin-3-yl *p*-chlorobenzoate (26):** 39%; a white crystalline solid; mp 187−188 °C; ^{1}H NMR ($CDCl_3$) δ 8.06 (d, 2 H, J = 8.6 Hz), 7.99 (d, 2 H, J = 8.6 Hz), 7.59 (d, 2 H, J = 8.6 Hz), 7.44 (d, 2 H, J = 8.6 Hz), 7.25 (d, 2 H, J = 8.6 Hz), 7.17 (d, 2 H, J = 8.6 Hz), 7.11 (d, 2 H, J = 8.6 Hz), 7.08 (d, 2 H, J = 8.6 Hz), 5.82 (s, 1H), 2.30 (s, 3 H); IR (KBr) 2923, 1767, 1732, 1594, 1517, 1492, 1348, 1296, 1174, 1092, 1014, 854, 756 cm^{-1}. Anal. Calcd for $C_{29}H_{20}O_5N_2Cl_2$: C, 63.63; H, 3.68; N, 5.12. Found: C, 63.69; H, 3.68; N, 5.11.

***dl*-(2*R*,3*S*)-2-(*p*-Chloroprene)-3-(*p*-nitrophenyl)-4-oxo-1-*p*-tolylazetidin-3-yl *p*-chlorobenzoate (27):** 15%; a white crystalline solid; mp 120−121 °C; ^{1}H NMR ($CDCl_3$) δ 8.30 (d, 2 H, J = 8.9 Hz), 7.87 (d, 2 H, J = 8.9 Hz), 7.57 (d, 2 H, J = 8.9 Hz), 7.40 (d, 2 H, J = 8.6 Hz), 7.31 (d, 2 H, J = 8.9 Hz), 7.30 (d, 2 H, J = 8.6 Hz), 7.24 (d, 2 H, J = 8.3 Hz), 7.11 (d, 2 H, J = 8.3 Hz), 5.70 (s, 1 H), 2.30 (s, 3 H); IR (KBr) 1767, 1732, 1595, 1520, 1388, 1349, 1266, 1092, 1014, 844, 756 cm^{-1}. Anal. Calcd for $C_{29}H_{20}O_5N_2Cl_2$: C, 63.63; H, 3.68; N, 5.12. Found: C, 63.78; H, 3.75; N, 5.23.

$Rh_2(OAc)_4$-Catalyzed Decomposition of 6a in the Presence of Methanol. A benzene solution (10 mL) of diazoacetic anhydride **6a** (211 mg, 0.6 mmol), methanol (86 mg), and a catalytic amount of $Rh_2(OAc)_4$ was stirred at 40 °C for 1 h. After evaporation of benzene, methyl 2-*p*-chlorobenzoyloxy-*p*-nitrophenylacetate was recrystallized from CH_2Cl_2/ether.

Methyl 2-*p*-chlorobenzoyloxy-*p*-nitrophenylacetate (28a): 92%; white needles; mp 133−135 °C; ^{1}H NMR ($CDCl_3$) δ 8.29 (d, 2 H, J = 8.6 Hz), 8.06 (d, 2 H, J = 8.6 Hz), 7.77 (d, 2 H, J = 8.6 Hz), 7.46 (d, 2 H, J = 8.6 Hz), 6.28 (s, 1 H), 3.78 (s, 3H); IR (KBr) 2959, 1759, 1724, 1591, 1515, 1435, 1401, 1346, 1260, 1218, 1166, 1103, 1040, 1012, 968, 856 cm^{-1}. Anal. Calcd for $C_{16}H_{12}O_6NCl$: C, 54.95; H, 3.46; N, 4.01. Found: C, 55.04; H, 3.50; N, 4.02.

Methyl 2-*p*-anisoyloxy-*p*-nitrophenylacetate (28b): 98%; white needles; mp 133.5−134.5 °C; ^{1}H NMR ($CDCl_3$) δ 8.29 (d, 2 H, J = 8.9 Hz), 8.08 (d, 2 H, J = 9.0 Hz), 7.78 (d, 2 H, J = 8.6 Hz), 6.96 (d, 2 H, J = 8.9 Hz), 6.26 (s, 1 H), 3.88 (s, 3 H), 3.77 (s, 3 H); IR (KBr) 2951, 1747, 1709, 1602, 1517, 1425, 1350, 1260, 1170, 1101, 1010, 970 cm^{-1}. Anal. Calcd for $C_{17}H_{15}O_7N$: C, 59.13; H, 4.38; N, 4.06. Found: C, 59.05; H, 4.32; N, 4.08.

Methyl 2-methoxy-*p*-nitrophenylacetate (28c): 95%; white needles; mp 90.5−91.0 °C; ^{1}H NMR ($CDCl_3$) δ 8.25 (d, 2 H, J = 8.9 Hz), 7.68 (d, 2 H, J = 8.9 Hz), 6.05 (s, 1 H), 3.75 (s, 3 H), 2.24 (s, 3 H); IR (KBr) 2960, 1766, 1724, 1607, 1524, 1443, 1402, 1348, 1212, 1074, 1011, 983, 880 cm^{-1}. Anal. Calcd for $C_{11}H_{11}O_6N$: C, 52.18; H, 4.38; N, 5.53. Found: C, 52.14; H, 4.32; N, 5.47.

Methyl 2-*p*-chlorobenzoyloxy-*p*-chlorophenylacetate (28d): 99%; white needles; mp 81−2 °C; ^{1}H NMR ($CDCl_3$) δ 8.04 (d, 2 H, J = 8.6 Hz), 7.50 (d, 2 H, J = 8.4 Hz), 7.43 (d, 2 H, J = 8.9 Hz), 7.40 (d, 2 H, J = 8.5 Hz), 6.12 (s, 1 H), 3.75 (s, 3 H); IR (KBr) 2958, 1744, 1720, 1593, 1492, 1439, 1405, 1291, 1176, 1119, 1093, 1013, 850 cm^{-1}. Anal. Calcd for $C_{16}H_{12}Cl_2O_4$: C, 56.66; H, 3.57. Found: C, 56.53; H, 3.56.

JO060074E