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Fast ring opening of unstable mesoionic 1,3-dioxolylium-4-olates to acyloxyketenes: formation of [2+2] cycloadducts of acyloxyketene with several ketenophiles

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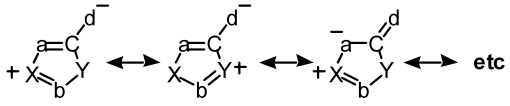
Abstract—Fast ring opening of mesoionic 1,3-dioxolylium-4-olate **5**, generated by $Rh_2(OAc)_4$-catalyzed decomposition of a phenyldiazoacetic anhydride **6**, to an acyloxyketene **10** was demonstrated by trapping the ketene **10**. $Rh_2(OAc)_4$-catalyzed decomposition of *p*-nitrophenyldiazoacetic *p*-chlorobenzoic anhydride **6a** in the presence of ketenophiles such as dihydrofuran, carbodiimides, and imines did not give 1,3-dipolar cycloadducts with the 1,3-dioxolylium-4-olates **5a**, but their [2+2]-cycloadducts with the acyloxyketene **10a**. PM3 calculation of heats of formation of a 1,3-dioxolylium-4-olate **5** and an acyloxyketene **10** indicates that the acyloxyketene **10** is 9 kcal/mol more stable than the 1,3-dioxolylium-4-olates **5**.

Since the introduction of the concept of mesoionic molecules by Baker and Ollis,[1] preparation and synthetic application of many mesoionic compounds have been reported.[2] Mesoionic compounds **1** can not be represented satisfactorily by normal covalent structures but by many resonance forms bearing positively and negatively charged atoms.

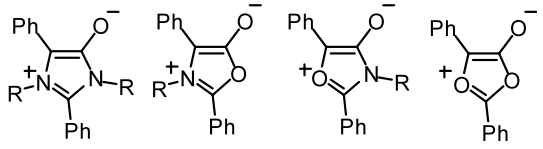


X, Y = hetero-atom
a, b, d = hetero-atom or C

1

Typical mesoionic compounds composing of nitrogen and oxygen atoms as ring hetero-atoms are shown in Scheme 1. Mesoionic compounds contain six ring electrons delocalizing over *p*-orbitals of carbon atoms and hetero-atoms, which suggests a kind of aromatic compounds. Because the energy level of *p*-orbitals of an oxygen is lower than those of a nitrogen and a carbon atom, resonance stability of mesoionic systems containing an oxygen atom should be smaller than those containing nitrogen atoms.

We calculated using PM3 method heats of hydrogenation for 2,5-diphenyl-substituted mesoionic 1,3-imidazolium-4-olate **2**,[3] münchnone **3**[4] isomünchnone **4**,[5] and 1,3-dioxolylium-4-olate **5**[6,7] as shown in Table 1. The largest heat of hydrogenation for the 1,3-dioxolylium-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**



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

Scheme 1.

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

Keywords: mesoionic compounds; 1,3-dioxolylium-4-olates; ring opening; ketenes; [2+2]-cycloaddition.
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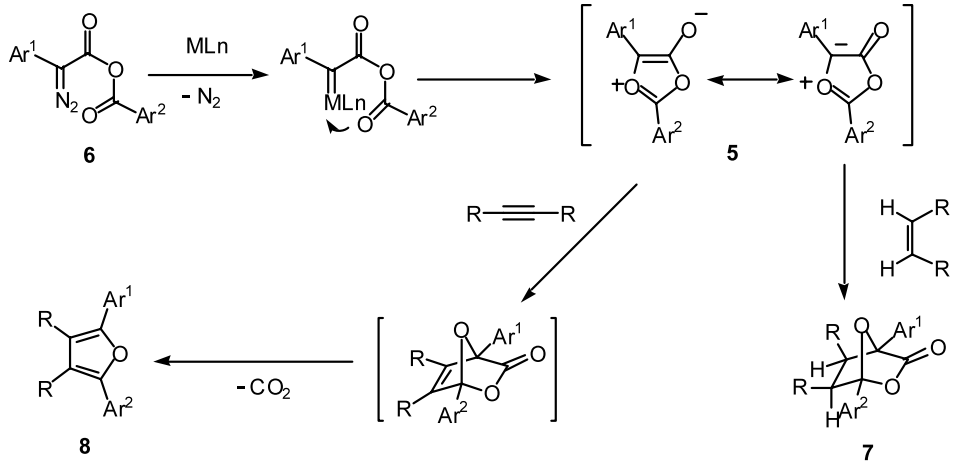
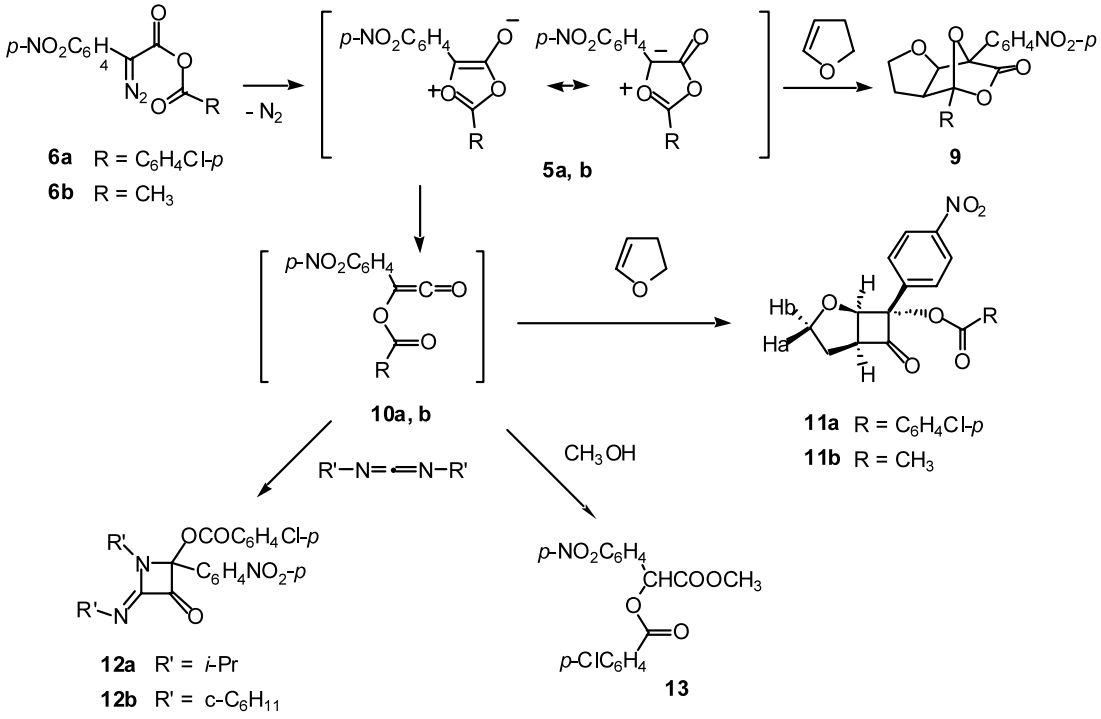
can be isolated as stable crystals, but 1,3-dioxolylium-4-olates **5** cannot be isolated as stable compounds. We observed that as soon as diazoacetic anhydride derivatives **6** were added to a benzene solution of $Rh_2(OAc)_4$, the solution turned a red color, indicating generation of **5**, which faded instantly. Very short life time of the red color suggests that 1,3-dioxolylium-4-olates **5** formed are unstable and convert to other chemical species momentarily. Formation of **5** from $Rh_2(OAc)_4$-catalyzed decomposition of **6** resulted from the intramolecular carbenoid/carbonyl reaction as shown in Scheme 2. However, 1,3-dioxolylium-4-olates having carbonyl ylide resonance structures, we succeeded in trapping the 1,3-dioxolylium-4-olates **5** by olefinic and acetylenic dipolarophiles, giving 1,3-dipolar cycloadducts **7** and furan derivatives **8**, respectively (Scheme 2).[6,7] In order to investigate the fatal behavior of 1,3-dioxolylium-4-olates **5**, we attempted to trap the chemical species derived from **5**.

A benzene solution of *p*-nitrophenyldiazoacetic *p*-chlorobenzoic anhydride **6a**, a catalytic amount of $Rh_2(OAc)_4$, and 20 molar equiv. of dihydrofuran was stirred at 30°C for 5 h. The NMR spectrum of the reaction mixture showed almost quantitative formation of a single product. As dihydrofuran is known to be a dipolarophile and a ketenophile, the product may be the 1,3-dipolar cycloadduct **9a** or the ketene [2+2]-adduct **11a**. The IR spectrum exhibited two strong carbonyl absorptions at 1789 and 1716 cm^{-1}, which suggests a cyclobutanone derivative bearing a four-membered cyclic ketone and an ester group. Configura-



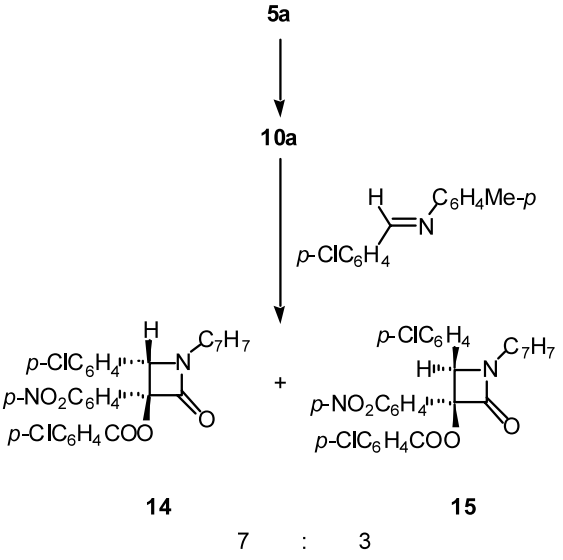
Scheme 2.



Scheme 3.

tion of the cyclobutanone **11a** was determined on the basis of the NMR spectrum.[8] Ha proton of OCH_2 (3.89, ddd) appeared in 0.6 ppm higher field than Hb (δ 4.49, ddd) due to the shielding effect of *endo*-*p*-nitrophenyl group. Reaction of *p*-nitrophenyldiazoacetic acetic anhydride **6b** with dihydrofuran also gave a single product, the cyclobutanone **11b** (Scheme 3). IR and NMR spectrum of **11b** showed a very similar pattern to those of **11a**. Especially, similarity of signals of furan ring proton of **11b** and **11a** supports the presence of *endo*-*p*-nitrophenyl group. The structure of **11b** was also confirmed by X-ray analysis as shown in Figure 1.[9] The cyclobutanone **11a**,**b** bearing *endo*-*p*-nitrophenyl group should be sterically more crowded than the other isomer bearing *exo*-*p*-nitrophenyl group. The predominant formation of sterically crowded cyclobutanones in the [2+2]-cycloaddition of ketenes with the ketenophiles have been reported.[10] The predominant formation of sterically crowded cyclobutanones in the [2+2]-cycloaddition of ketenes have been explained as 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 the new σ-bonds leads to the prediction that the larger substituent of the ketene will be *endo* in the cycloadduct.[10c]

We attempted to trap the acyloxyketene using more reactive ketenophiles. Generation of **5a** in the presence of DCC or diisopropylcarbodiimide resulted in quantitative formation of [2+2]-cycloadducts **12a** and **12b**, respectively (Scheme 3). A benzene solution of **6a**, a catalytic amount of $Rh_2(OAc)_4$, and 5 equiv. of *N*-*p*-chlorobenzylidene-*p*-toluidine **8** was stirred at 50°C for 2 h. The reaction mixture was chromatographed over silica gel to give the β-lactams **14** and **15** in a ratio of 7:3 (54% yield). Structures of **14** and **15** were determined on the basis of their NMR spectra. *p*-Nitrophenyl and *p*-chlorophenyl protons of **14** appeared at higher field than the corresponding protons of **15**.[11] Generation of **5a** from the diazoacetic anhydride **6a** in the presence of 5 molar equiv. amount of methanol gave methyl *N*-*p*-chlorobenzoyloxy-*p*-nitrophenylacetate **13** (isolated yield 92%). In previous papers describing isolation of 1,3-dipolar cycloadducts **7** in the reaction of **6** with dipolarophiles, we used a π-allyl palladium complex as a catalyst.[6,7] In order to investigate the effects of catalysts on formation of **5** or the acyloxyketenes, $Rh_2(OAc)_4$-catalyzed decomposition of **6** in the presence of reactive dipolarophiles was carried out, giving the same results as the case of the Pd-catalyst, which indicates that the rhodium carbenoid also attacks the intramolecular carbonyl oxygen atom initially to produce the 1,3-dioxolylium-4-olate **5**.



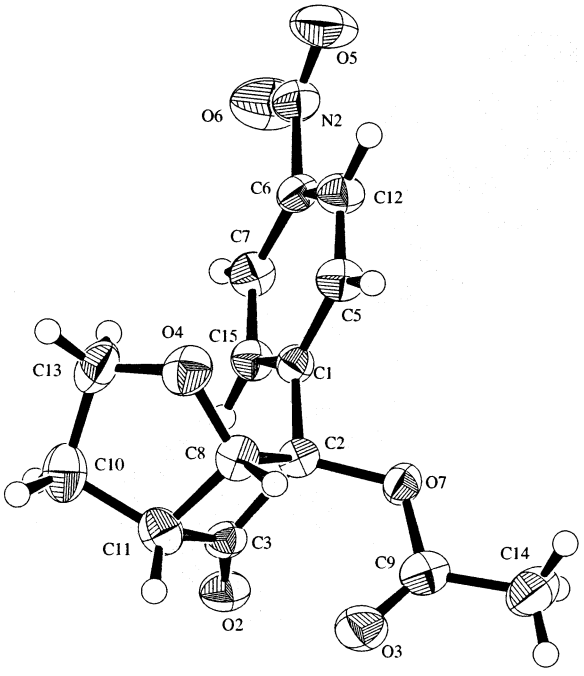


Figure 1. ORTEP drawing of **11b**.

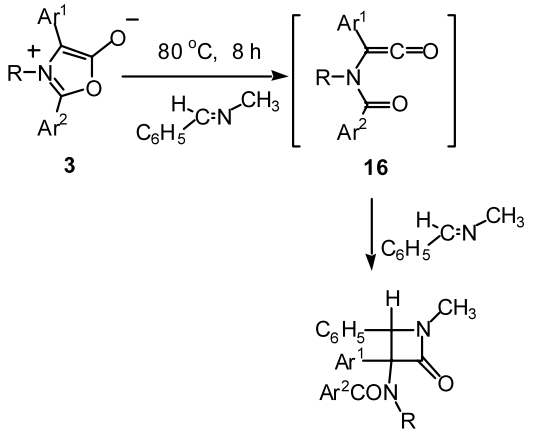
Transient appearance and rapid disappearance of the red color of the 1,3-dioxolylium-4-olate **5a** and the formation of the acyloxyketene adducts **11**, **12**, **13**, **14**, and **15** in the reaction with ketenophiles such as dihydrofuran, carbodiimides, and the imine indicate that the initially formed 1,3-dioxolylium-4-olate **5** is too unstable to be isolated and, in the absence of reactive dipolarophiles, undergoes rapid ring opening to the acyloxyketene **10**.

PM3 calculation of heats of formation of the 2,5-diphenyl-1,3-dioxolylium-4-olate **5** and the corresponding acyloxyketene **10** indicates that the acyloxyketene **10** is 9 kcal/mol more stable than the 1,3-dioxolylium-4-olates **5**, strongly supporting fast ring opening of **5** to the ketene **10** followed by [2+2]-cycloaddition with the ketenophile.

Although ring opening of a stable mesoionic compound to a ketene was observed in münchnones **3**, the ring opening of **3** to acylaminoketenes **16** requires long heating **3** in the presence of ketenophiles such as imines,

carbodiimides, and enamines, resulting in formation of [2+2]-ketene adducts.[12] According to PM3 calculation, ring-closure derivatives **3** is 2.2 kcal/mol more stable than ring-opened derivatives **16**.

In conclusion, we have showed that the 1,3-dioxolylium-4-olates **5** generated from diazoacetic anhydrides **6** are the most unstable mesoionic system among the related mesoionic compounds, so that they can not exist as stable compounds and that they undergo rapid ring opening to acyloxyketenes **6**, which are captured by ketenophiles to give cyclobutanone derivatives.



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8. ^{1}H NMR spectrum of **11a** ($CDCl_3$): δ 8.29 (d, 2H, $J=8.9$ Hz), 7.86 (d, 2H, $J=8.9$ Hz), 7.83 (d, 2H, $J=8.9$ Hz), 7.40 (d, 2H, $J=8.9$ Hz), 5.36 (d, 1H, $J=6.9$ Hz), 4.49 (ddd, 1H, $J=10.6$, 7.3, 3.3 Hz), 3.89 (ddd, 1H, $J=9.2$, 7.9, 4.0 Hz), 3.17 (td, 1H, $J=9.2$, 6.9 Hz), 2.21–2.04 (m, 2H). ^{1}H NMR spectrum of **11b** ($CDCl_3$): δ 8.24 (d, 2H, $J=8.9$ Hz), 7.74 (d, 2H, $J=8.9$ Hz), 5.22 (d, 1H, $J=6.9$ Hz), 4.37 (ddd, 1H, $J=10.2$, 6.9, 3.6 Hz), 3.84 (ddd, 1H, $J=9.2$, 7.6, 4.0 Hz), 3.10 (td, 1H, $J=9.2$, 7.3 Hz), 2.18–1.95 (m, 2H), 2.11 (s, 3H).
9. Crystallographic data for compound **11b** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC 218209. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44(0)-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk).
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11. ^{1}H NMR spectrum of **14** ($CDCl_3$): δ 8.06 (d, 2H, $J=8.6$ Hz, $NO_2C_6H_4$), 7.99 (d, 2H, $J=8.6$ Hz, ClC_6H_4), 7.59 (d, 2H, $J=8.6$ Hz, $NO_2C_6H_4$), 7.44 (d, 2H, $J=8.6$ Hz, ClC_6H_4), 7.25 (d, 2H, $J=8.6$ Hz, $CH_3C_6H_4$), 7.17 (d, 2H, $J=8.6$ Hz, ClC_6H_4), 7.11 (d, 2H, $J=8.6$ Hz, $CH_3C_6H_4$), 7.08 (d, 2H, $J=8.6$ Hz, ClC_6H_4), 5.82 (s, 1H), 2.30 (s, 3H). ^{1}H NMR spectrum of **15** ($CDCl_3$): δ 8.30 (d, 2H, $J=8.9$ Hz, $NO_2C_6H_4$), 7.87 (d, 2H, $J=8.9$ Hz, $NO_2C_6H_4$), 7.57 (d, 2H, $J=8.9$ Hz, ClC_6H_4), 7.40 (d, 2H, $J=8.6$ Hz, ClC_6H_4), 7.31 (d, 2H, $J=8.9$ Hz, ClC_6H_4), 7.30 (d, 2H, $J=8.6$ Hz, ClC_6H_4), 7.24 (d, 2H, $J=8.3$ Hz, $CH_3C_6H_4$), 7.11 (d, 2H, $J=8.3$ Hz, $CH_3C_6H_4$), 5.70 (s, 1H), 2.30 (s, 3H).
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