

Reaction of electron deficient N=N bonds with acyloxyketenes and mesoionic 1,3-dioxolium-4-olates: fast equilibrium between acyloxyketenes and mesoionic 1,3-dioxolium-4-olates

Masashi Hamaguchi,* Naoki Tomida, Eiko Mochizuki and Takumi Oshima

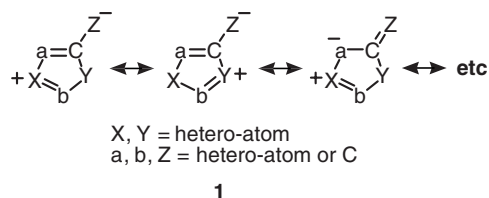
Department of Materials Chemistry, Graduate School of Engineering, Osaka University, Suita 565-0871, Japan

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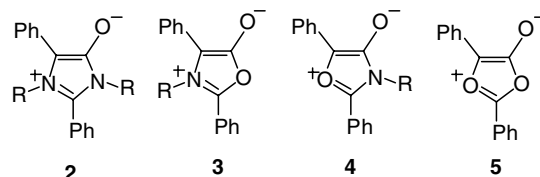
Abstract—Reaction of azodicarboxylates with acyloxyketenes arising from dehydrochlorination of acyloxyphenylacetyl chlorides was carried out to give triacylamidine derivatives in good yields. The same triacylamidine derivatives were also obtained in good yields from the reaction with mesoionic 1,3-dioxolium-4-olates generated by $\text{Rh}_2(\text{OAc})_4$ -catalyzed decomposition of phenyldiazoacetic anhydride derivatives. Formation of the same compounds from different starting materials is explained by 1,3-dipolar addition between electron deficient N=N bonds and mesoionic 1,3-dioxolium-4-olates, indicating fast equilibrium between acyloxyketenes and mesoionic 1,3-dioxolium-4-olates.

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Since the synthesis of sydonones via cyclodehydration of *N*-nitroso α -amino acids by Earl and Mackney¹ and the introduction of the concept of mesoionic molecules by Baker et al.,² preparation and synthetic application of many mesoionic compounds have been reported.³



Typical mesoionic compounds **1** compose of nitrogen and oxygen atoms as ring heteroatoms as shown in Scheme 1. Mesoionic compounds contain six ring electrons delocalizing over p-orbitals of carbon atoms and heteroatoms, which suggests a kind of aromatic compounds. Therefore, the energy level of p-orbital of an oxygen atom is so lower than those of a nitrogen and a carbon atom, resonance stability of mesoionic systems



Scheme 1.

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

According to PM3 calculation, heats of hydrogenation for some mesoionic compounds increase in order of 1,3-imidazolium-4-olate **2**,⁴ münchnone **3**,^{5,3d} isomünchnone **4**,⁶ and 1,3-dioxolium-4-olate **5**^{7–9} 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 nitrogens.⁹ 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. We have been studying on chemical behaviors of this unstable mesoionic compound.

We observed that on addition of diazoacetic anhydride derivatives **6** to a benzene solution of $\text{Rh}_2(\text{OAc})_4$ in

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* Corresponding author. Tel.: +81 6 6879 4593; fax: +81 6 6879 4593; e-mail: hamaro@ch.wani.osaka-u.ac.jp

the presence of strongly reactive dipolarophiles such as *N*-phenylmaleimide or DMAD, adducts **7** of 1,3-dioxolium-4-olate **5** with dipolarophiles or furandicarboxylates were isolated. However, **5** does not react with not very reactive dipolarophiles such as dimethyl benzylidene-malonate.¹⁰ As soon as **5** was formed, the solution red color, which faded instantly. These phenomena suggest that **5** is so unstable to undergo ring opening to acyloxyketenes **7**. We confirmed the fast ring opening to **7** by isolation of [2+2]-cycloadducts **9** of acyloxyketenes with ketenophiles such as carbodiimides or dihydrofuran in good yields (Scheme 2).

We would like to report a novel finding on the generation of 1,3-dioxolium-4-olates **5** from diazoacetic anhydride derivatives **6** or acyloxyketenes **7** from dehydrochlorination of acyloxyacetyl chloride **14** in the presence of electron deficient azo compounds.

A benzene solution of *p*-nitrophenyldiazoacetic acetic anhydride **6a** and 1.1 equiv of diethyl azodicarboxylate **10a** (DEAD) and a catalytic amount of Rh₂(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 NMR and IR spectra showed the presence of non-equivalent ethyl esters. IR spectrum exhibited two ester groups at 1759 and 1734 cm⁻¹, which exclude imidoil imide **14**.

A benzene solution of *i*-PrNEt₂ was added dropwise to a benzene solution of α -acetoxyphenylacetyl chloride **14b** and DEAD and stirred for 2 h at room temperature. Work up of the reaction mixture gave *N*-acetyl-*N,N'*-bis(ethoxycarbonyl)benzamidine derivative **11e** (80%), which structure was determined by X-ray analysis as shown in Figure 1.¹¹ The product from **6a** showed quite similar IR and NMR spectra to the triacylamidine **11e**, indicating the same amidine structure **11a**.¹² Using diazoacetic anhydride **6c** or α -anisoyloxy-*p*-nitrophenylacetyl chloride **14c** and DEAD **10a** or dimethyl azodicarboxylate **10b**, triacylamidine derivatives **11c** and **11d** were isolated in good yields, respectively, as

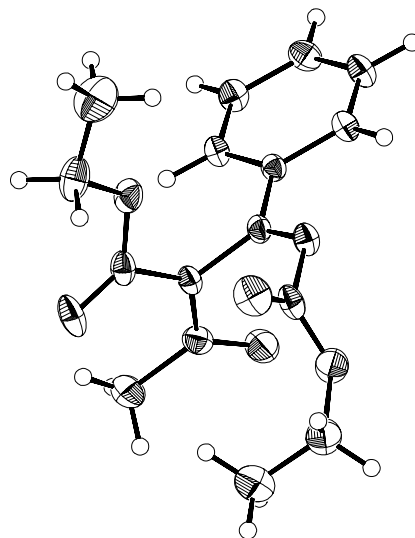
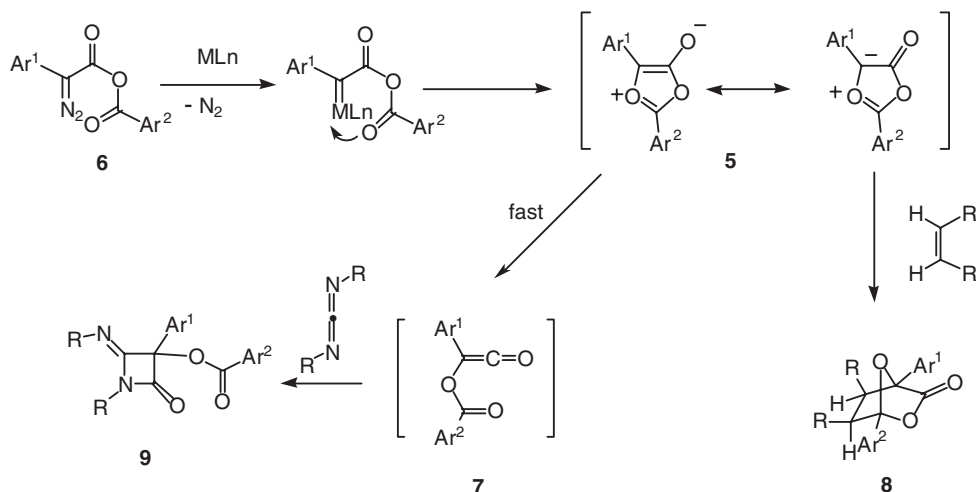


Figure 1. ORTEP drawing of **11e**.

shown in Table 1. Isolation of the same compounds **11c,d** from the different starting materials, 1,3-dioxolium-4-olate and acyloxyketene precursors indicates the same intermediates for the formation of **11**. The intermediates seem to be 1,3-dioxolium-4-olates **5**, which is supported by higher isolated yields of **11** on using 1,3-dioxolium-4-olate precursors than acyloxyketene precursors.

The formation of triacylamidines **11** can be explained by ring closure of acyloxyketenes **7** to 1,3-dioxolium-4-olates **5** followed by 1,3-dipolar cycloaddition with azodicarboxylates **10** to give adducts **12** followed by decarboxylation to afford carbonyl ylides **13** (Scheme 3). Ring opening of the carbonyl ylides **13** leads to imidoil imide derivatives **14**. The imidoil imide derivatives rearrange to **11** in a similar fashion of the rearrangement of acyl imidates to imides well known as Mumm rearrangement (Scheme 4).¹³ However, PM3 calculation of heats of formation of the 2,5-diphenyl-1,3-dioxolium-



Scheme 2.

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