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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

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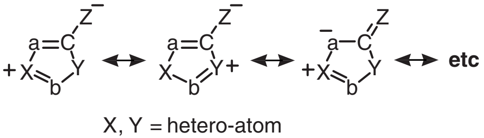
Abstract—Reaction of azodicarboxylates with acyloxyketenes arising from dehydrochlorination of acyloxyphenylacetyl chlorides was carried out to give triacylamidine derivatives in good yields. The same triacylamidine derivatives were also obtained in good yields from the reaction with mesoionic 1,3-dioxolium-4-olates generated by $Rh_2(OAc)_4$-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.

Since the synthesis of sydonones via cyclodehydration of *N*-nitroso α-amino acids by Earl and Mackney[1] 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]



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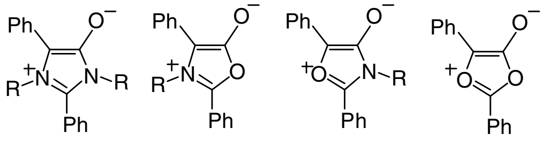
Typical mesoionic compounds **1** compose of nitrogen and oxygen atoms as ring heteroatoms as shown in Scheme 1. Mesoionic compounds contain six ring electrons delocalizing over p-orbitals of carbon atoms and heteroatoms, which suggests a kind of aromatic compounds. Therefore, the energy level of p-orbital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



2 3 4 5

Scheme 1.

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 $Rh_2(OAc)_4$ in

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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 benzylidenemalonate.[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 $Rh_2(OAc)_4$ was heated at 50 °C for 2 h. Column chromatography of the reaction mixture gave colorless needles in the yield of 86%. The 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 imidoyl imidate **14**.

A benzene solution of *i*-$PrNEt_2$ 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 shown in Table 1. Isolation of the same compounds **11c**,**d** from the different starting materials, 1,3-dioxolylium-4-olate and acyloxyketene precursors indicates the same intermediates for the formation of **11**. The intermediates seem to be 1,3-dioxolylium-4-olates **5**, which is supported by higher isolated yields of **11** on using 1,3-dioxolylium-4-olate precursors than acyloxyketene precursors.

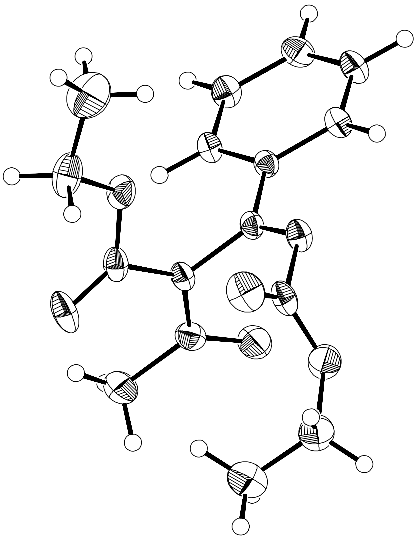
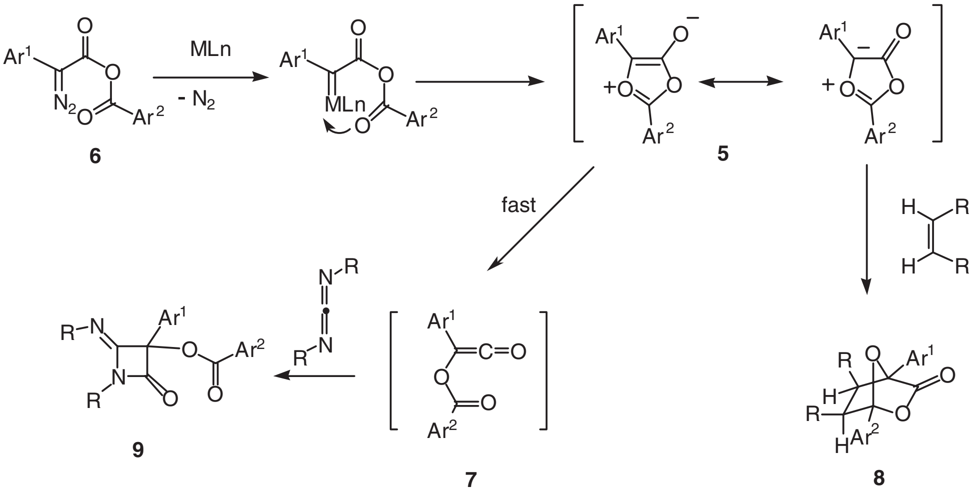


Figure 1. ORTEP drawing of **11e**.

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 imidoyl imidate derivatives **14**. The imidoyl imidate 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-dioxolylium-



Scheme 2.

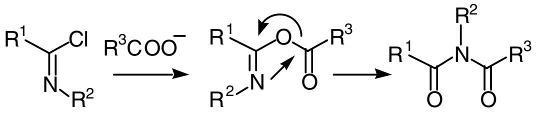
Table 1. Yields of triacylamidines **11**

11	Substrate	Ar	R	R′	Yield (%)
11a	**6a**	*p*-$NO_2C_6H_4$	CH_3	C_2H_5	86
11b	**6a**	*p*-$NO_2C_6H_4$	CH_3	CH_3	95
11c	**6c**	*p*-$NO_2C_6H_4$	*p*-$CH_3OC_6H_4$	C_2H_5	81
11d	**6c**	*p*-$NO_2C_6H_4$	*p*-$CH_3OC_6H_4$	CH_3	92
11e	**15b**	C_6H_5	CH_3	C_2H_5	80
11f	**15b**	C_6H_5	CH_3	CH_3	71
11c	**15c**	*p*-$NO_2C_6H_4$	*p*-$CH_3OC_6H_4$	C_2H_5	53
11d	**15c**	*p*-$NO_2C_6H_4$	*p*-$CH_3OC_6H_4$	CH_3	60

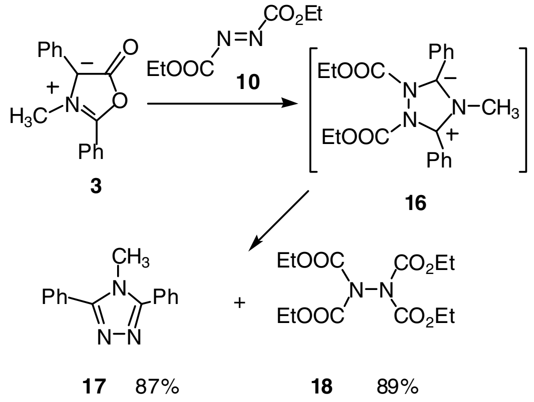
4-olate **5** and the corresponding acyloxyketene **7** indicates that the 1,3-dioxolium-4-olates 5 is 9 kcal/mol less stable than the acyloxyketene **7**.[9] These facts suggest that very low concentration of 1,3-dioxolium-4-olates **5** in equilibrium state between **5** and **7** could be captured only by very reactive dipolarophiles such as azodicarboxylate.

However, the related mesoionic compound münchnone **3** bearing a lactone moiety reacted with DEAD to afford quite different products **17** and **18** in good yields (Scheme 5).[14]

In conclusion, we have shown that using the different starting materials, 1,3-dioxolium-4-olate precursor **5** and acyloxyketene precursors **15**, the same products triacylamidine derivatives **11** were obtained in the reaction with DEAD and **10b** in good yields and that very reactive dipolarophiles electron deficient N=N bonds can react with very low concentration of unstable **5** in the equilibrium state between 1,3-dioxolylium-4-olates **5** and acyloxyketenes **7**.



Scheme 4.



Scheme 5.

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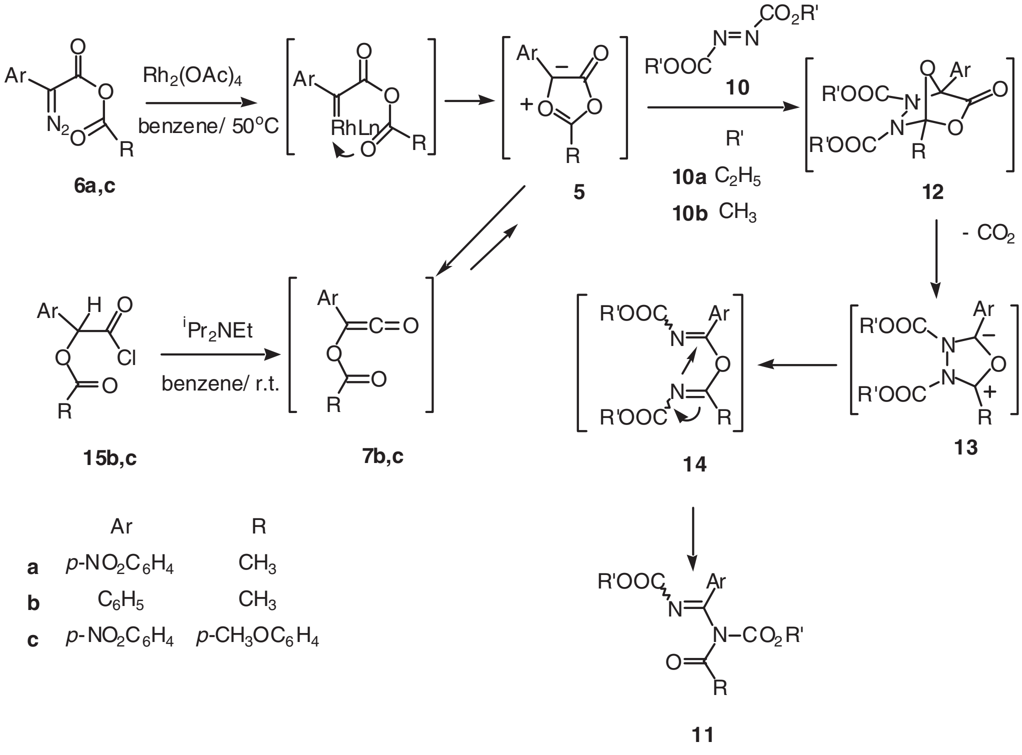

Scheme 3.

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11. Crystallographic data for compound **11e** 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)-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk).
12. Compound **11a**: colorless cubes, mp 103–104 °C. ^{1}H NMR ($CDCl_3$): δ 8.29 (d, 2H, $J = 8.9$ Hz), 7.99 (d, 2H, $J = 8.9$ Hz), 4.32 (q, 2H, $J = 7.1$ Hz), 4.24 (q, 2H, $J = 7.1$ Hz), 2.63 (s, 3H), 1.34 (t, 3H, $J = 7.1$ Hz), 1.19 (t, 3H, $J = 7.1$ Hz); 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. Compound **11c**: yellow oil. ^{1}H NMR ($CDCl_3$): δ 8.29 (d, 2H, $J = 8.6$ Hz), 8.01–7.95 (m, 2H), 7.78 (d, 2H, $J = 8.6$ Hz), 6.95 (d, 2H, $J = 8.6$ Hz), 4.17–4.09 (m, 4H), 3.89 (s, 3H), 1.15 (t, 3H, $J = 7.3$ Hz), 1.03 (t, 3H, $J = 6.9$ Hz); HRMS. Calcd for $C_{21}H_{21}N_3O_8$: 443.1329; Found: 443.1331. Compound **11e** ($CDCl_3$): colorless cubes, mp 112–113 °C. ^{1}H NMR ($CDCl_3$): δ 7.84–7.81 (m, 2H), 7.58–7.52 (m, 1H), 7.14–7.41 (m, 2H), 4.29 (q, 2H, $J = 7.1$ Hz), 4.21 (q, 2H, $J = 7.1$ Hz), 2.60 (s, 3H), 1.32 (t, 3H, $J = 7.1$ Hz), 1.16 (t, 3H, $J = 7.1$ Hz). 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, 9.15.
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