

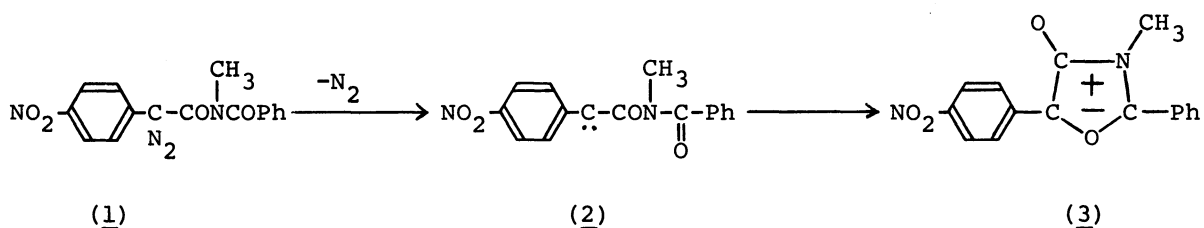
NEW TYPE OF MESOIONIC SYSTEM. 1,3-DIPOLAR CYCLOADDITION OF ANHYDRO-4-HYDROXY-1,3-OXAZOLIUM HYDROXIDE WITH ACETYLENIC COMPOUNDS

Toshikazu IBATA,* Masashi HAMAGUCHI, and Hideo KIYOHARA
 Department of Chemistry, College of General Education,
 Osaka University, Toyonaka, Osaka 560

The reaction of anhydro-4-hydroxy-1,3-oxazolium hydroxide (3) with acetylenic dipolarophiles gave 1,3-dipolar cycloadducts (4) along with furans (5). On heating above 80°C, most cycloadducts decomposed to the corresponding furans under release of methyl isocyanate.

We have reported the formation of anhydro-4-hydroxy-3-methyl-5-(p-nitrophenyl)-2-phenyl-1,3-oxazolium hydroxide (3) as the first example of the formation of mesoionic compound by intramolecular carbene-carbonyl reaction in the copper chelate catalyzed decomposition of N-methyl-N-(diazo-p-nitrophenylacetyl)benzamide (1).¹

This communication deals with the 1,3-dipolar cycloaddition of the mesoionic 1,3-oxazol-4-one (3) with various acetylenic dipolarophiles.



The diazo compound (1) was decomposed at 80°C in the presence of 1.2 molar amount of dimethyl acetylenedicarboxylate and a catalytic amount of copper(II) acetylacetonate in benzene solution (Method A). The reaction mixture was separated by column chromatography (silica gel-benzene) and yellow needles (5a), mp 162-163°C, and colorless plates (4a), mp 98-99°C, were obtained in yields of 54 and 42%, respectively. The yellow needles were identified as dimethyl 2-(p-nitrophenyl)-5-phenyl-

furan-3,4-dicarboxylate (5a) on the basis of the following spectroscopic data and the result of elemental analysis²; ir of 5a (KBr): 1724 (ester C=O), 1515 and 1343 (NO₂) and 852 cm⁻¹ (furan); nmr of 5a (CDCl₃): 6.10 (s, 3H, OCH₃), 6.08 (s, 3H, OCH₃) and 1.6-2.6 τ (m, 9H, aromatic protons). The ir and nmr spectra show that the colorless product is the cycloadduct (4a) of the mesoionic oxazolone (3) with dimethyl acetylenedicarboxylate; ir of 4a (KBr): 1730 (broad, ester C=O and cyclic amide), 1525

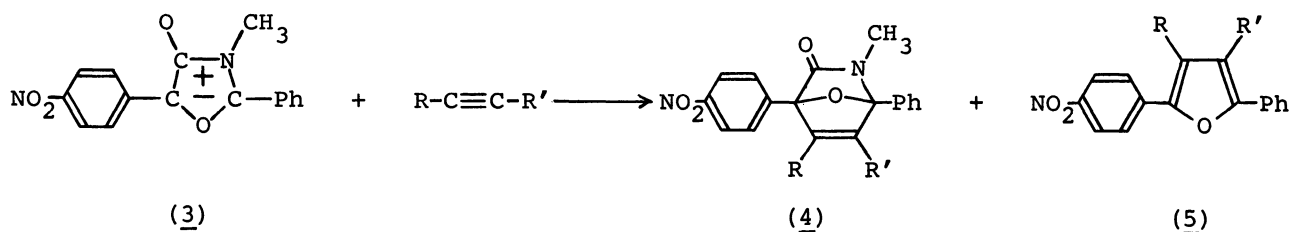


Table. Reaction of 3 with Acetylenic Dipolarophiles

Acetylenes	Reaction Conditions			yields and mp (%) (°C)		yields and mp (%) (°C)	
	Temp (°C)	Time (hr)		of <u>4</u>		of <u>5</u>	
a CH ₃ OOC-C≡C-COOCH ₃	30	2	B	92	98-99	5	162-163
	80	1	A	42		54	
	120	1	A	-		83	
b PhCO-C≡C-COPh	30	1	B	69	137	-	
	120	1	A	-		88	160-162
c H-C≡C-COOCH ₃	30	2	B	82	162-164	1	164-166
	80	1	A	35		44	
d CH ₃ -C≡C-COOCH ₃	80	2	A	-		81	137-138
e Ph-C≡C-COOCH ₃	80	2	A	-		91	135-137
f Ph-C≡C-Ph	120	3	A	-		27	186-187
g H-C≡C-Ph	80	5	A	-		82	139-141
						3	184-186
h H-C≡C-C ₄ H ₉ ⁿ	100	2	A	-		75	100-102

A; The diazoimide (1) was catalytically decomposed in the presence of acetylenic dipolarophiles.

B; The isolated mesoionic oxazolone (3) was treated with acetylenic compounds.

and 1340 cm^{-1} (nitrophenyl); nmr of 4a (CDCl_3): 7.02 (s, 3H, NCH_3), 6.33 (s, 3H, OCH_3), 6.15 (s, 3H, OCH_3) and 1.6-2.4 τ (m, 9H, aromatic protons).

When the reaction was carried out in xylene at 120°C , the cycloadduct (4a) disappeared and furan (5a) was isolated as the sole product (83%). Gaseous product was swept into a solution of aniline in cyclohexane by bubbling nitrogen gas through the reaction mixture and methyl isocyanate was trapped as N-methyl-N'-phenylurea.

When the mesoionic oxazolone (3) was treated with dimethyl acetylenedicarboxylate at 30°C in benzene (Method B), the yield of furan derivative (5a) was decreased to 5% with an accompanying increase in the yield of the cycloadduct (4a) to 92%. Therefore, it is suggested that the thermal instability of the cycloadduct (4a) allows the conversion of 4a into the furan (5a) and methyl isocyanate by the thermal retro-Diels-Alder reaction. This process was confirmed by the observation that the corresponding furan (5a) was obtained quantitatively by the thermal decomposition of 4a at 110°C in xylene.

Dibenzoylacetylene also gave similar results as is shown in the Table (run b) affording cycloadduct (4b) at low temperature and furan (5b) at high temperature.

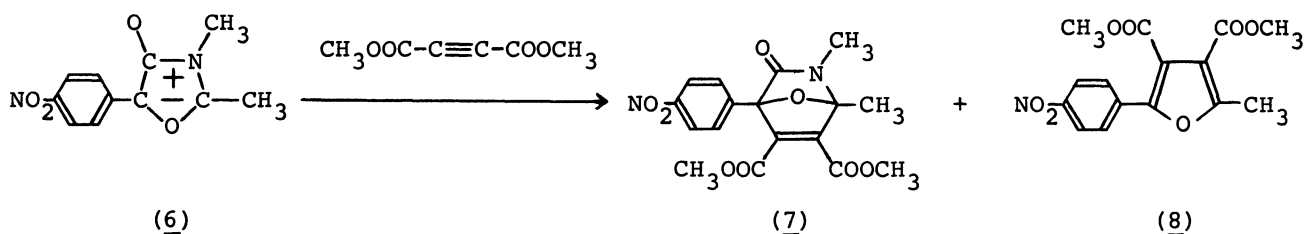
Although there are two possible directions of the cycloaddition in the reaction of asymmetric acetylenes, methyl propiolate gave only one cycloadduct (4c) in 82% yield at 30°C , and also gave single 4c and furan (5c) in yields of 35 and 44% respectively at 80°C . The direction of the cycloaddition has not been determined yet. Similar furans were obtained in the reaction with methyl tetrolate (run d), methyl phenylpropiolate (run e) and 1-hexyne (run h). However, the corresponding cycloadducts (4) were not obtained in these cases.

On the other hand, phenylacetylene gave two furans, one was yellow needles melted at $139\text{-}141^\circ\text{C}$ (82%) and the other was red needles melted at $184\text{-}186^\circ\text{C}$ (3%). The product ratio seems to depend on the reaction temperature. Similar ir spectra³ of these products indicate that they are the isomers of furan (5g) only different in the direction of the cycloaddition. Experiments to determine these structures are now in progress.

Because of its low reactivity, diphenylacetylene^{4,5} did not react at 80°C but reacted at higher temperature of 120°C in xylene affording a furan (5f) and some decomposition products⁶ of mesoionic oxazolone (3).

The reaction of anhydro-2,3-dimethyl-4-hydroxy-5-(p-nitrophenyl)-1,3-oxazolium hydroxide (6) with dimethyl acetylenedicarboxylate gave furan (5a) in 94% yield

(Method B). Mesoionic oxazolone (6) also reacted with dimethyl acetylenedicarboxylate (Method A) to give cycloadduct (7) and furan (8) in 81 and 16% yields, respectively.² 7; mp 122-123°C, ir(KBr): 1738 and 1710 (C=O) 1523 and 1334 cm^{-1} (NO_2), nmr(CDCl_3): 8.03 (s, 3H, CH_3), 7.13 (s, 3H, NCH_3), 6.36 (s, 3H, OCH_3), 6.31 (s, 3H, OCH_3), and 1.6-2.5 τ (m, 4H, aromatic-H). 8; mp 144-145°C, ir(KBr): 1724 (C=O), 1517 and 1325 cm^{-1} (NO_2), nmr(CDCl_3): 7.36 (s, 3H, CH_3), 6.16 (s, 3H, OCH_3), 6.07 (s, 3H, OCH_3) and 1.7-2.3 τ (m, 4H, aromatic-H).



Sydnones⁷ and münchnons⁵ readily undergo cycloaddition with acetylenic dipolarophiles to give pyrazoles and pyrroles under the spontaneous extrusion of carbon dioxide without isolation of cycloadducts. These results may be explained by the fact that methyl isocyanate is not so good leaving group as carbon dioxide in the retro-Diels-Alder reaction of the cycloadducts. Similar results have been observed in the cycloaddition of benzyne with 1,3-thiazol-4-one⁸ and 1,3-oxazol-4-one.⁹

References

- 1) M.Hamaguchi and T.Ibata, *Tetrahedron Lett.*, in press.
- 2) Satisfactory elemental analyses were obtained for all new compounds reported here.
- 3) Ir of yellow crystals (KBr): 1594, 1508, 1485, 1447, 1330, 1102, 950, 930, 850, 760, 700 cm^{-1} .
Ir of red crystals (KBr): 1594, 1508, 1443, 1330, 1102, 940, 850, 790, 750, 695 cm^{-1} .
- 4) R.Huisgen and H.Gotthardt, *Chem.Ber.*, 101, 1059 (1968).
- 5) R.Huisgen, H.Gotthardt, H.O.Bayer, and F.C.Schaefer, *Chem.Ber.*, 103, 2611 (1970).
- 6) These results will be published elsewhere.
- 7) R.Huisgen, H.Gotthardt, and R.Grashey, *Chem.Ber.*, 101, 536 (1968).
- 8) S.Nakazawa, T.Kiyosawa, K.Hirakawa, and H.Kato, *Chem.Commun.*, 621 (1974).
- 9) T.Ibata and M.Hamaguchi, unpublished results.

(Received November 5, 1974)