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NEW TYPE OF MESOIONIC SYSTEM. 1,3-DIPOLAR CYCLOADDITION OF ISOMÜNCHNON WITH ETHYLENIC COMPOUNDS

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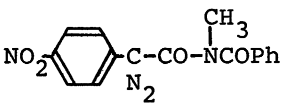
Treatment of anhydro-4-hydroxy-1,3-oxazolium hydroxide (2; named isomünchnon) with ethylenic dipolarophiles gave 1,3-dipolar cycloadducts in high yields. Stereochemistry of these cycloadducts was confirmed by the investigation of nmr coupling constants.

In a previous communication of this series, we have reported the formation of an isomünchnon (2) as the first example of a mesoionic compound which has resonance contribution of carbonyl ylide by intramolecular carbene-carbonyl reaction in the copper chelate-catalyzed decomposition of diazoimide (1).[1] We also reported that 2 readily reacted with electron-deficient acetylenic compounds to give 1,3-dipolar cycloadducts along with their retro-Diels-Alder reaction products, furans.[2] Sydnones,[3] azlactones[4] and münchnons[5] have been described to react with olefins affording pyrazolines and pyrrolines via 1,3-dipolar cycloaddition followed by elimination of carbon dioxide and hydrogen shift. Isolation of a cycloadduct of 2 with dimethyl fumarate,[1] and the difficulty of extrusion of methyl isocyanate from the cycloadducts with acetylenes[2] suggest that the cycloadducts of 2 with other olefins could be isolable without further decomposition. Therefore, it may be possible to investigate the stereochemistry of this cycloaddition in contrast to the case of sydnones and münchnons.



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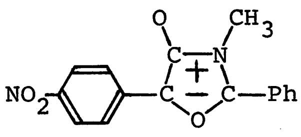

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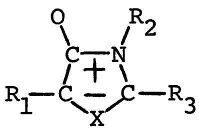
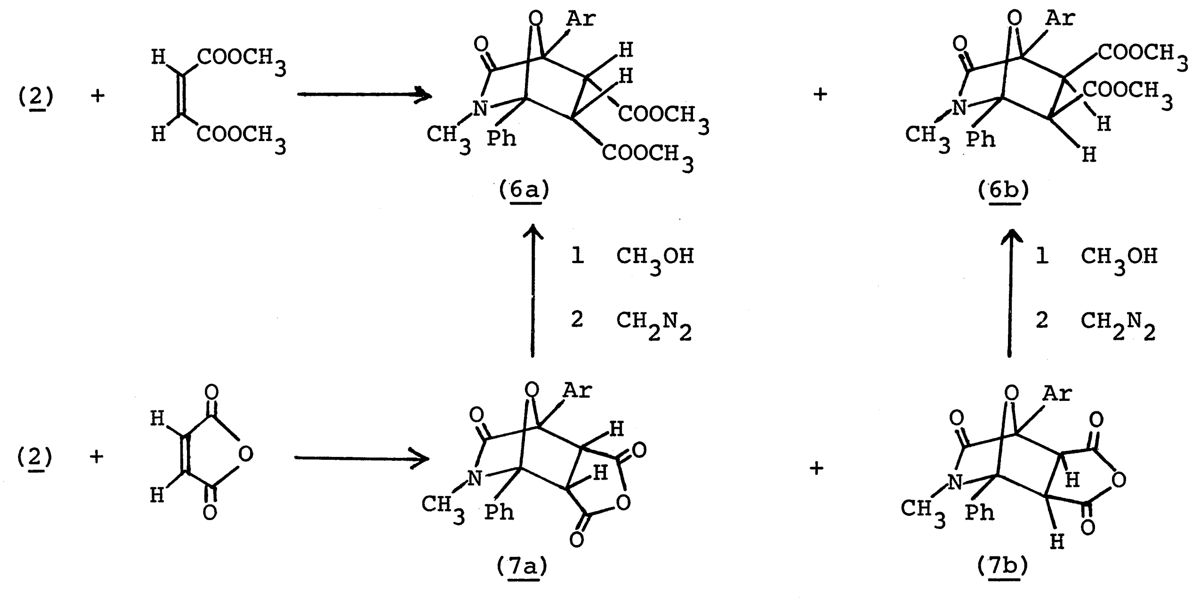


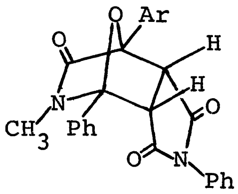
(3)

a $X = N\text{-}R_4$
b $X = S$

This communication deals with the 1,3-dipolar cycloaddition of ethylenic dipolarophiles with isomünchnon (2) in comparison with the reaction of imidazolium-4-oxide (3a)[6] and thiazolium-4-oxide (3b)[7] which have resonance contribution of azomethine ylide and thiocarbonyl ylide, respectively. The diazocompound (1) was decomposed at 80°C in benzene in the presence of 2.0 molar amount of trans-1,2-dibenzoylethylene and a catalytic amount of Cu(acac)$_2$. Column chromatography (silica gel-benzene) gave two crystalline products (4a, mp 207-208°C, 23%; 4b, mp 195-196°C, 77%) which were identified as 1,3-dipolar cycloadducts on the basis of the following spectroscopic data and the results of elemental analysis.[8] Ir of 4a (KBr): 1715 (cyclic amide), 1680 (C=O), 1520 and 1350 cm^{-1} (NO$_2$) ; nmr of 4a (in CDCl$_3$): 7.10 (s, 3H, NCH$_3$), 5.47 (d, 1H, J=5.6 Hz), 4.50 (d, 1H, J=5.6 Hz) and 2.0-3.0 τ (m, 19H, aromatic). Ir of 4b (KBr): 1715 (cyclic amide), 1672 (C=O), 1517 and 1350 cm^{-1} (NO$_2$) ; nmr of 4b: 7.17 (s, 3H, NCH$_3$), 5.40 (d, 1H, J=4.8 Hz), 4.60 (d, 1H, J=4.8 Hz) and 1.8-3.0 τ (m, 19H, aromatic). The small coupling constants of methine protons of 4a and 4b may indicate that the two benzoyl groups locate in trans configuration each other. In the case of dimethyl fumarate, only one cycloadduct with trans configuration was obtained.[1] On the other hand, reaction with dimethyl maleate gave two adducts (6a, mp 157-158°C, 34% and 6b, mp 217-219°C, 61%). Nmr of 6a: 7.10 (s, 3H, NCH$_3$), 6.28 (d, 1H, J=10.6 Hz) 6.23 (s, 6H, OCH$_3$), 5.78 (d, 1H, J=10.6 Hz) and 1.5-2.6 τ (m, 9H, aromatic). Nmr of 6b: 7.37 (s, 3H, NCH$_3$), 6.55 and 6.63 (s, 3H, OCH$_3$), 6.20 (d, 1H, J=9.4 Hz), 5.97 (d, 1H, J=9.4 Hz) and 1.5-2.6 τ (m, 9H, aromatic). Large values of methine coupling constants indicate cis configuration of the two methoxycarbonyls in 6a and 6b. On the basis of the facts that methyl chemical shift of the two methoxycarbonyls of 6b are at higher field than those of 6a, 6b is assigned to exo-adduct and 6a to endo-adduct. In spite of careful experiments on column chromatography, no adduct with trans configuration was obtained.



Reaction with maleic anhydride also gave a mixture of two adducts (7a and 7b) in total yield of 84% which yielded 6a and 6b in the ratio of 2:7 on treatment with methanol followed by esterification by diazomethane.



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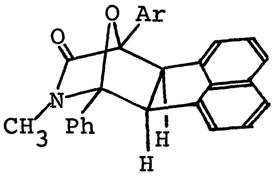

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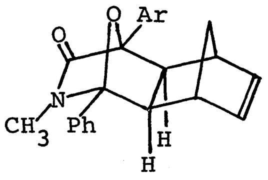


(11)

Ar = p-$NO_2C_6H_4$

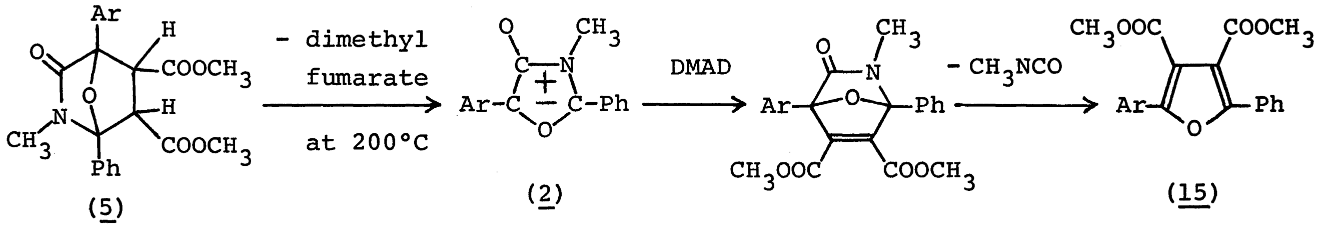
N-Phenylmaleimide gave only one adduct (8), mp 209-210°C, in yield of 87%. Nmr signal of methine protons of 8 shows AB system (at 5.65 and 6.18 τ, J=8.8 Hz). Cycloadduct of acenaphthylene was obtained in quantitative yield (9, mp 270-273°C,). Nmr signal of methine protons of 9 showed AB pattern (at 5.77 and 5.20 τ, J=6.0 Hz) of which smaller coupling constant than those of usual cis protons of 7 and 8 exhibits that 9 is exo-adduct.[8]

Table. Yields, Melting Points and Nmr Data of Cycloadducts

dipolarophile	adduct	yield(%)	mp (°C)	nmr (τ)			
				NCH_3	methine		J(Hz)
trans-1,2-dibenzoylethylene	4a	23	207-208	7.10	5.47	4.50	5.6
	4b	77	195-196	7.17	5.40	4.60	4.8
dimethyl fumarate	5	100	162-164	7.34	6.34	5.99	4.0
dimethyl maleate	6a	34	157-158	7.10	6.28	5.78	10.6
	6b	61	217-219	7.37	6.20	5.97	9.4
N-phenylmaleimide	8	87	209-210	7.47	6.18	5.65	8.8
acenaphthylene	9	100	270-273	7.10	5.57	5.20	6.0
norbornadiene	11	55	185-186	7.43	m	m	-
tetramethyl ethylenetetracarboxylate	12	31	164-167	7.07	-	-	-
trans-stilbene	13a	29	oil	7.17	6.22	5.90	4.8
	13b	17	oil	7.37	6.50	5.92	4.8
cis-stilbene	14	59	255-256	7.36	5.72	5.57	8.8

Isomünchnon (2) reacts with strained olefins such as norbornadiene. Copper chelate-catalyzed decomposition of 1 in the presence of norbornadiene at 80°C gave two products. Minor component (10; mp 163-166°C, 21%) was assigned 1,3-dipolar cycloadduct of diazoimide (1) with norbornadiene,[9] and major component (11; mp 185-186°C, 55%) was identified as cycloadduct of isomünchnon (2) with norbornadiene. Isomünchnon (2) undergoes 1,3-dipolar cycloaddition with dipolarophiles of poor reactivity such as tetramethyl ethylenetetracarboxylate and trans- and cis-stilbene in slightly low yields (31%, 46%, and 59%, respectively). Nmr of cycloadduct (12) with tetramethyl ethylenetetracarboxylate showed singlet signals of ester methyl at 6.80, 6.53, 6.20 and 6.13 τ. Of these, two signals at higher field (6.80 and 6.53 τ) was assigned to exo-ester methyls and lower field protons to endo-ester methyls. Trans-stilbene gave a mixture of two isomers (13a, 29% and 13b, 17%) having trans configuration, and cis-stilbene gave an adduct (14, 59%) of cis configuration.

These results exhibit that 2 adds to olefins stereospecifically to give 1,3-dipolar cycloadducts without further decomposition different from the results of sydnones, azlactones and münchnons. Isomünchnon (2) was found to have higher reactivity than imidazolium-4-oxide (3a), which gave no normal cycloadduct with ethylenic dipolarophiles,[6] and thiazolium-4-oxide (3b).[7]



When the adduct (5) was treated with five fold excess of dimethyl acetylenedicarboxylate (DMAD) in o-dichlorobenzene at 200°C for two hours, dimethyl 2-(p-nitrophenyl)-5-phenyl-3,4-furandicarboxylate (15)[2] was obtained in quantitative yield along with considerable amount of dimethyl fumarate. This may indicate that elimination of methyl isocyanate from the adduct (5) does not occur even at high temperature of 200°C. Formation of furan derivative (15) may reasonably be explained by the above scheme; elimination of dimethyl fumarate by retro-1,3-dipolar cycloaddition of 5 gives isomünchnon (2), which is trapped by dimethyl acetylenedicarboxylate followed by extrusion of methyl isocyanate to give furan derivative (15).

References and Note

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