1,3-Dipolar Cycloaddition of Anhydro-4-hydroxy-1,3-oxazolium Hydroxides with Carbonyl Compounds

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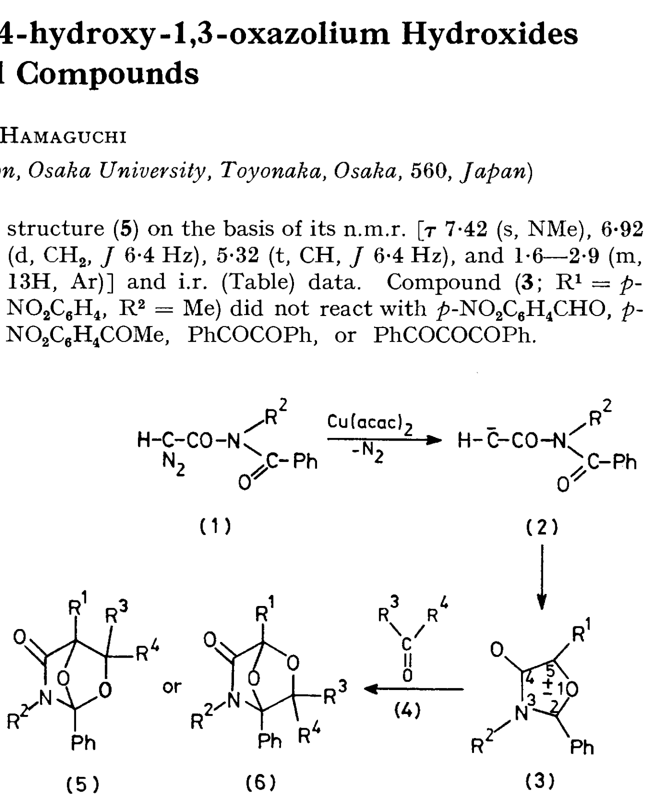
Summary Cycloadducts of mesoionic compounds with carbonyl compounds were isolated for the first time in the reaction of isomunchnones (anhydro-4-hydroxy-1,3-oxazolium hydroxides) with benzoylacetaldehyde, *p*-chloro- and *p*-nitro-benzaldehyde, *p*-nitroacetophenone, and benzil.

THERE has been only one report on the reaction of mesoionic compounds with carbonyl compounds, by Huisgen and his co-workers, who failed to isolate a 1,3-dipolar cycloadduct in the reaction between münchnones (anhydro-5-hydroxy-1,3-oxazolium hydroxides) and carbonyl compounds, but obtained decomposition products instead.

We recently reported the stability of cycloadducts of anhydro-4-hydroxy-1,3-oxazolium hydroxides (isomünchnones)[2] with acetylenic and olefinic compounds, owing to the low tendency towards elimination of isocyanate from the adducts and the high reactivity of the isomünchnones.[3] The isolation of 1,3-dipolar cycloadducts of isomünchnones with carbonyl compounds would thus be expected. Treatment of compound (**3**; $R^1 = p\text{-}NO_2C_6H_4$, R^2 = Me) with benzoylacetaldehyde (**4**; $R^3 = p\text{-}ClC_6H_4$, $R^4 = CH_2CHO$) at 80 °C gave an adduct (57% yield) which was assigned structure (**5**) on the basis of its n.m.r. [τ 7·42 (s, NMe), 6·92 (d, CH_2, *J* 6·4 Hz), 5·32 (t, CH, *J* 6·4 Hz), and 1·6—2·9 (m, 13H, Ar)] and i.r. (Table) data. Compound (**3**; $R^1 = p\text{-}NO_2C_6H_4$, R^2 = Me) did not react with $p\text{-}NO_2C_6H_4CHO$, $p\text{-}NO_2C_6H_4COMe$, PhCOCOPh, or PhCOCOCOPh.



acac = $MeCOCH_2COMe$

TABLE. Yields, m.p.s, and spectral properties of the adducts (**5**) and (**6**)

Isomünchnone (**3**)		Dipolarophile (**4**)					
R^1	R^2	R^3	R^4	Adduct (% yield)	M.p./°C	ν_{max}/cm^{-1}	τ (bridgehead) (R^1 = H)
$p\text{-}NO_2C_6H_4$	Me	$p\text{-}ClC_6H_4$	CH_2CHO	(**5**) (57)	190—192	1730, 1680	—
H	Ph	$p\text{-}NO_2C_6H_4$	H	(**5**) (59)	172—174	1740	4·95
,,	,,	$p\text{-}ClC_6H_4$	,,	(**5**) (65)	149—150	1750	5·00
,,	,,	$p\text{-}NO_2C_6H_4$	Me	(**5**) (31)	164—166	1740	4·93
,,	,,	PhCO	Ph	(**6**) (67)	131—132	1750, 1680	3·87
H	$p\text{-}ClC_6H_4$	$p\text{-}NO_2C_6H_4$	H	(**5**) (55)	175—177	1740	4·93
,,	,,	$p\text{-}ClC_6H_4$	,,	(**5**) (34)	163—164	1738	5·00
,,	,,	$p\text{-}NO_2C_6H_4$	Me	(**5**) (57)	146—148	1750	4·90
,,	,,	PhCO	Ph	(**6**) (79)	138—140	1760, 1670	3·83

Isomünchnones having no substituent on C-5 are much more reactive in cycloadditions with olefins,[4] and so we studied the reaction of *p*-nitrobenzaldehyde with 2,3-diphenylisomünchnone (**3**; $R^1 = H$, $R^2 = Ph$) which was generated by the $Cu(acac)_2$ catalysed decomposition of the corresponding diazo-compound (**1**) *via* intramolecular carbene–carbonyl reaction of the intermediate carbene (**2**). An adduct was obtained in 59% yield, which was assigned structure (**5**) on the basis of comparison of the chemical shifts for the two singlet signals (τ 4·75 and 4·95) in its n.m.r. spectrum with the bridgehead methine proton signals of the cycloadducts of (**3**; $R^1 = H$, $R^2 = Ph$) with olefinic dipolarophiles (in the range τ 4·6—5·3). The coupling constant of the methine proton (J 0 Hz) indicates that the *p*-nitrophenyl group is *exo*. *p*-Chlorobenzaldehyde and *p*-nitroacetophenone also afforded similar cycloadducts.

However, the adduct of benzil with (**3**; $R^1 = H$, $R^2 = Ph$) has a bridgehead methine proton signal at lower field (τ 3·87) than for the above adducts, which indicates the reverse direction of cycloaddition to give another type of the adduct (**6**). 3-*p*-Chlorophenyl-2-phenylisomünchnone (**3**; $R^1 = H$, $R^2 = p\text{-}ClC_6H_4$) which was generated *in situ* by the decomposition of the corresponding diazo-compound (**1**) also gave similar results (see Table).

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[2] M. Hamaguchi and T. Ibata, *Tetrahedron Letters*, 1974, 4475.

[3] T. Ibata, M. Hamaguchi, and H. Kiyohara, *Chem. Letters*, 1975, 21; M. Hamaguchi, and T. Ibata, *ibid.*, 9. 499.

[4] M. Hamaguchi, unpublished results.