CYCLOADDITION REACTIONS OF METHACRYLOYL ISOCYANATE WITH ARYLIDENEAMINES

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Abstract - Arylideneamines (**1**) added to the acyl isocyanato moiety of methacryloyl isocyanate (**MAI**) to produce the corresponding [4 + 2] cycloadducts, 2*H*-1,3,5-oxadiazin-4(3*H*)-ones (**2**). It has been clarified that even at low temperature the cycloadducts (**2**) partially dissociate to two original substrates, **MAI** and **1**, in solution on the basis of VT-nmr spectroscopy.

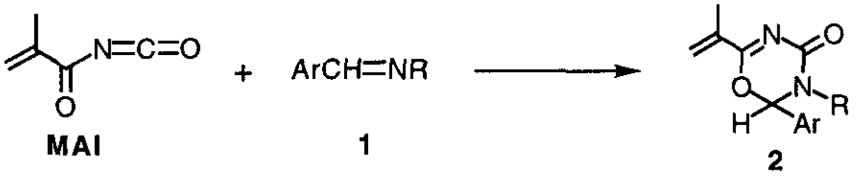
Methacryloyl isocyanate (**MAI**) is a versatile polyfunctional reagent bearing an enone moiety as well as a highly reactive acyl isocyanato group.[1] Recently, it has been found that enamines added not only to the acyl isocyanato moiety, but also to the enone moiety in **MAI**: At a higher reaction temperature initial [4 + 2] cycloadducts to the acyl isocyanato moiety dissociate to two original substrates and then the regenerated enamine addes to enone moiety in **MAI**.[1a] This offers not only the first example for thermal dissociation of [4 + 2] cycloadduct of acyl isocyanate system to C=C bonds, but also shows that **MAI** is a novel ambident heterodiene in the cycloaddition reaction.

It is well known that acyl isocyanates add to C=N bonds to give [4 + 2] and/or [2+ 2] cycloadducts whose relative yields depend on the reaction conditions as well as on the nature of substrates.[2]

Taking into account the novel reaction of **MAI** with enamines, it seemed to be of interest to study the cycloaddition reaction of **MAI** with C=N bond. We report here the cycloaddition reaction of **MAI** with arylideneamines (**1**).

Although isolation of the cycloadduct of **MAI** to benzylideneaniline (**1a**) was unsuccessful, its formation was confirmed on the basis of nmr spectroscopy of the reaction mixture as described below. In the reactions of arylidenealkylamines (**1b**-**1n**), however, the corresponding cycloadducts to **MAI** were isolated in most cases. The reactions of **MAI** with imines (**1b**-**1e**) were investigated under various conditions, and the selected results together with those of reactions of **MAI** with imines (**1g**-**1n**) are shown in Table 1. A typical procedure is as follows: To a solution of 1.95 g (10 mmol) of imine (**1b**) in ether (4 ml) was added 1.10 g (10 mmol) of **MAI** at 0 °C under dry nitrogen; white crystals immediately separated out. After the reaction mixture was stirred for 10 min at -10 °C, a rapid filtration gave the corresponding cycloadduct (**2b**) in 82% yield. In general, a similar reaction in benzene resulted in a lower

Table 1. Reactions of **MAI** with Imines (**1**)



a : Ar = R = Ph; **b** : Ar = Ph , R = $PhCH_2$; **c** : R = p-MeC_6H_4 , R = $PhCH_2$;
d : Ar = p-$MeOC_6H_4$, R = $PhCH_2$; **e** : Ar = p-ClC_6H_4 , R = $PhCH_2$;
f : Ar = p-$NO_2C_6H_4$, R = $PhCH_2$; **g** : Ar = Ph , R = c-Hex; **h** : Ar = p-MeC_6H_4 , R = c-Hex;
i : Ar = p-$MeOC_6H_4$, R = c-Hex; **j** : Ar = p-ClC_6H_4 , R = c-Hex; **k** : Ar = p-$NO_2C_6H_4$, R = c-Hex;
l : Ar = Ph , R = n-Bu; **m** : Ar = 4-Py , R = c-Hex; **n** : Ar = 2-Py , R = c-Hex

Imine	Reaction conditions			Adduct				
	Solvent	Temp/°C[a)]	Time/h		Yield/%	mp/°C	$\nu_{C=O}$[b)]	$\nu_{C=N}$[b)]
1a	Et_2O	0	1	**2a**	not isolated (see Table 2)			
1b	C_6H_6	rt → 5	2 → 1	**2b**	72	74 - 75	1669	1634
1b	Et_2O	0 → -10	10 min	**2b**	82			
1c	C_6H_6	rt → 5	2 → 1	**2c**	78	65 - 66	1671	1636
1c	Et_2O	0 → -10	10 min	**2c**	93			
1d	C_6H_6	rt → 5	2 → 1	**2d**	68	63 - 64	1673	1640
1d	Et_2O	0 → -10	10 min	**2d**	81			
1e	C_6H_6	rt → 5	2 → 1	**2e**	97	67 - 68	1673	1634
1e	Et_2O	0 → -10	15 min	**2e**	93			
1f	Et_2O	0 → -10	10 min	**2f**	85	64 - 65	1669	1636
1g	C_6H_6	rt → 5	2 → 1	**2g**	66	75 - 76	1673	1647
1g	Et_2O	0 → -10	10 min	**2g**	82			
1h	Et_2O	-10	1	**2h**		very hygroscopic		
1i	Et_2O	rt → -10	0.5 → 0.5	**2i**	83	59 - 60	1671	1634
1j	Et_2O	rt → -10	15 min	**2j**	94	51 - 53	1669	1634
1k	Et_2O	rt → -10	0.5 → 0.5	**2k**	89	74 - 75	1673	1636
1l	C_6H_6	rt → 5	2 → 1	**2l**	60	68 - 69	1669	1634
1m	Et_2O	rt → 0	10 min	**2m**	99	70 - 71	1671	1634
1n	Et_2O	rt → 0	10 min	**2n**	86	34 - 35	1671	1636

a) r t : Room temperature.
b) Measured in KBr pellets.

yield of **2**. As all the cycloadducts (**2**), particularly, **2g**-**2k**, are very sensitive to moisture, their isolation should be carried out meticulously. Purification of **2** by recrystallization was unsuccessful because of dissociation in solution as described below.

On the basis of ir spectral data[3] and of chemical conversion, however, cycloadducts (**2**) were deduced to be 2*H*-1,3,5-oxadiazin-4(3*H*)-ones, [4 + 2] cycloadducts to the acyl isocyanato moiety in **MAI** (Table 1).

Hydrolysis of **2b** or **2g** gave readily the corresponding urea (**3**) or (**4**), which was identical with an authentic sample prepared from **MAI** and benzylamine or cyclohexylamine, respectively.[4]

Nmr spectroscopic study showed that an equilibrium is set up between the cycloadduct (**2**) and two original substrate, **MAI** and imine (**1**) in solution. Thus, the dissociation phenomena of cycloadducts (**2**) were followed by VT-nmr spectra of a mixture of equimolar amounts of **MAI** and imines (**1a**-**1i**) in $CDCl_3$, and those of **MAI-1g-2g** system as a representative example are shown in Figure 1. The ratios of **MAI/1/2** at each temperature determined by the VT-nmr spectra are listed in Table 2.

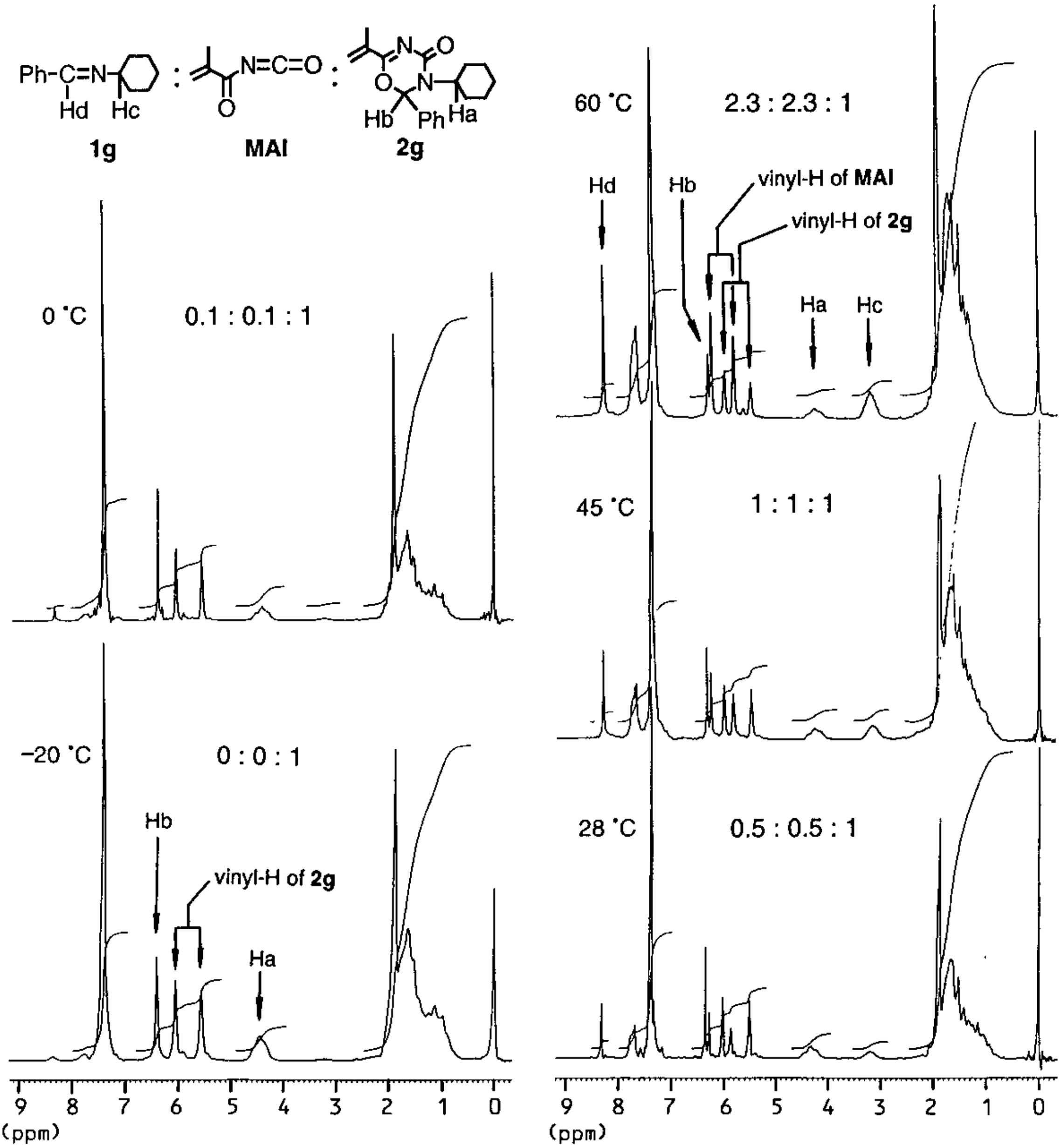
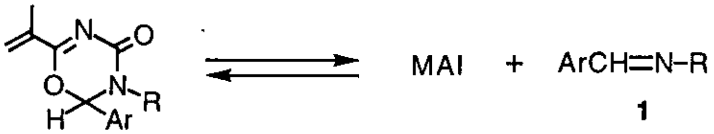


Figure 1. VT-nmr spectra of MAI-1g-2g system in $CDCl_3$

Table 2. Dissociation of cycloadduct (**2**) to **MAI** and Imine (**1**)



2 **1**

Temp. °C	60	45	28	0	−20	−30
MAI / **1a** / **2a**	1 / 1 / 0	1 / 1 / 0	1 / 1 / 0	12 / 12 / 1	5 / 5 / 1	5 / 5 / 1
MAI / **1b** / **2b**	0.5 / 0.5 / 1	0.2 / 0.2 / 1	0.1 / 0.1 / 1	**2b** only	—	—
MAI / **1c** / **2c**	0.5 / 0.5 / 1	0.3 / 0.3 / 1	0.2 / 0.2 / 1	0.1 / 0.1 / 1	**2c** only	—
MAI / **1d** / **2d**	0.6 / 0.6 / 1	0.4 / 0.4 / 1	0.1 / 0.1 / 1	**2d** only	—	—
MAI / **1e** / **2e**	0.7 / 0.7 / 1	0.3 / 0.3 / 1	0.2 / 0.2 / 1	**2e** only	—	—
MAI / **1f** / **2f**	0.6 / 0.6 / 1	0.3 / 0.3 / 1	0.1 / 0.1 / 1	**2f** only	—	—
MAI / **1g** / **2g**	2.3 / 2.3 / 1	1 / 1 / 1	0.5 / 0.5 / 1	0.1 / 0.1 / 1	**2g** only	—
MAI / **1h** / **2h**	3 / 3 / 1	1 / 1 / 1	0.5 / 0.5 / 1	0.1 / 0.1 / 1	**2h** only	—
MAI / **1i** / **2i**	3.1 / 3.1 / 1	1.3 / 1.3 / 1	0.8 / 0.8 / 1	0.3 / 0.3 / 1	**2i** only	—
MAI / **1j** / **2j**	3 / 3 / 1	1.7 / 1.7 / 1	0.8 / 0.8 / 1	0.2 / 0.2 / 1	**2j** only	—
MAI / **1k** / **2k**	6 / 6 / 1	3.5 / 3.5 / 1	1.6 / 1.6 / 1	0.4 / 0.4 / 1	0.2 / 0.2 / 1	0.1 / 0.1 / 1

As shown in Table 2, **MAI/1/2** ratios depended on temperature; the lower temperature, the lower the dissociation of cycloadduct (**2**) becomes. Surprisingly, cycloadduct (**2a**) highly dissociates to **MAI** and **1a** even at -30 °C; thus **2a** can not be isolated in a routine manner.

The above fact offers the first example for the thermal dissociation of [4 + 2] cycloadduct of acyl isocyanate system to C=N bond.

REFERENCES AND NOTES

1. a) O. Tsuge, T. Hatta, R. Mizuguchi, and H.Kato, Chem. Lett., **1993**, 631; b) O. Tsuge, T. Hatta, and R. Mizuguchi, Heterocycles, 1994, **38**, 235; c) S. Urano, K. Aoki, N. Tsuboniwa, R. Mizuguchi, and O. Tsuge, Prog. Org. Coat., 1992, **20**, 471.
2. O. Tsuge, 'Acyl and Thioacyl Derivatives,' in The Chemistry of Cyanates and Their Derivatives, Part 1, ed.by S. Patai, John Wiley & Sons, New York, 1977, pp. 104-165.
3. It has been reported that the ir spectra of 2*H*-1,3,5-oxadiazin-4(3*H*)-ones prepared from benzoyl isocyanates and imine (**1b**) showed the characteristic bands due to $\nu_{C=O}$ and $\nu_{C=N}$ at around 1670 and 1640 cm^{-1}, respectively (O. Tsuge and S. Kanemasa, Bull. Chem. Soc. Jpn., 1972, **45**, 2877).
4. Hydrolysis of **2b** or **2g** with 10% hydrochloric acid in ethanol at room temperature afforded 1-benzyl- (**3**), mp 90 °C, or 1-cyclohexyl-3-methacryloylurea (**4**), mp 74 °C, in 73 or 75% yield, respectively.

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