

## 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.

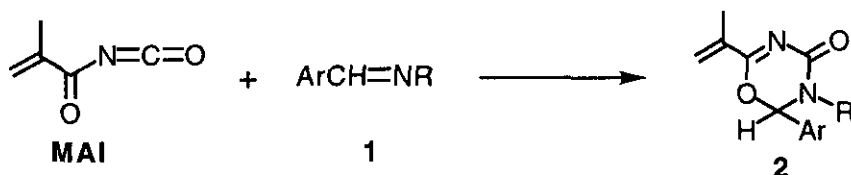
Methacryloyl isocyanate (**MAI**) is a versatile polyfunctional reagent bearing an enone moiety as well as a highly reactive acyl isocyanato group.<sup>1</sup> Recently, it has been found that enamines added not only to the acyl isocyanato moiety, but also to the enone moiety in **MAI**: At a higher reaction temperature initial [4 + 2] cycloadducts to the acyl isocyanato moiety dissociate to two original substrates and then the regenerated enamine adds to enone moiety in **MAI**.<sup>1a</sup> 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.<sup>2</sup>

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<sub>2</sub>; **c** : R = p-MeC<sub>6</sub>H<sub>4</sub>, R = PhCH<sub>2</sub>;  
**d** : Ar = p-MeOC<sub>6</sub>H<sub>4</sub>, R = PhCH<sub>2</sub>; **e** : Ar = p-ClC<sub>6</sub>H<sub>4</sub>, R = PhCH<sub>2</sub>;  
**f** : Ar = p-NO<sub>2</sub>C<sub>6</sub>H<sub>4</sub>, R = PhCH<sub>2</sub>; **g** : Ar = Ph, R = c-Hex; **h** : Ar = p-MeC<sub>6</sub>H<sub>4</sub>, R = c-Hex;  
**i** : Ar = p-MeOC<sub>6</sub>H<sub>4</sub>, R = c-Hex; **j** : Ar = p-ClC<sub>6</sub>H<sub>4</sub>, R = c-Hex; **k** : Ar = p-NO<sub>2</sub>C<sub>6</sub>H<sub>4</sub>, 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 <sup>a)</sup>	Time/h	Yield/%	mp/°C	V <sub>C=O</sub> <sup>b)</sup>	V <sub>C=N</sub> <sup>b)</sup>
<b>1a</b>	Et <sub>2</sub> O	0	1	<b>2a</b>	not isolated ( see Table 2 )		
<b>1b</b>	C <sub>6</sub> H <sub>6</sub>	rt → 5	2 → 1	<b>2b</b>	72	74 - 75	1669
<b>1b</b>	Et <sub>2</sub> O	0 → -10	10 min	<b>2b</b>	82		1634
<b>1c</b>	C <sub>6</sub> H <sub>6</sub>	rt → 5	2 → 1	<b>2c</b>	78	65 - 66	1671
<b>1c</b>	Et <sub>2</sub> O	0 → -10	10 min	<b>2c</b>	93		1636
<b>1d</b>	C <sub>6</sub> H <sub>6</sub>	rt → 5	2 → 1	<b>2d</b>	68	63 - 64	1673
<b>1d</b>	Et <sub>2</sub> O	0 → -10	10 min	<b>2d</b>	81		1640
<b>1e</b>	C <sub>6</sub> H <sub>6</sub>	rt → 5	2 → 1	<b>2e</b>	97	67 - 68	1673
<b>1e</b>	Et <sub>2</sub> O	0 → -10	15 min	<b>2e</b>	93		1634
<b>1f</b>	Et <sub>2</sub> O	0 → -10	10 min	<b>2f</b>	85	64 - 65	1669
<b>1g</b>	C <sub>6</sub> H <sub>6</sub>	rt → 5	2 → 1	<b>2g</b>	66	75 - 76	1673
<b>1g</b>	Et <sub>2</sub> O	0 → -10	10 min	<b>2g</b>	82		1647
<b>1h</b>	Et <sub>2</sub> O	-10	1	<b>2h</b>	very hygroscopic		
<b>1i</b>	Et <sub>2</sub> O	rt → -10	0.5 → 0.5	<b>2i</b>	83	59 - 60	1671
<b>1j</b>	Et <sub>2</sub> O	rt → -10	15 min	<b>2j</b>	94	51 - 53	1669
<b>1k</b>	Et <sub>2</sub> O	rt → -10	0.5 → 0.5	<b>2k</b>	89	74 - 75	1673
<b>1l</b>	C <sub>6</sub> H <sub>6</sub>	rt → 5	2 → 1	<b>2l</b>	60	68 - 69	1669
<b>1m</b>	Et <sub>2</sub> O	rt → 0	10 min	<b>2m</b>	99	70 - 71	1671
<b>1n</b>	Et <sub>2</sub> O	rt → 0	10 min	<b>2n</b>	86	34 - 35	1671
							1636

a) rt : 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<sup>3</sup> and of chemical conversion, however, cycloadducts (**2**) were deduced to be 2H-1,3,5-oxadiazin-4(3H)-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.<sup>4</sup>

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<sub>3</sub>, 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.

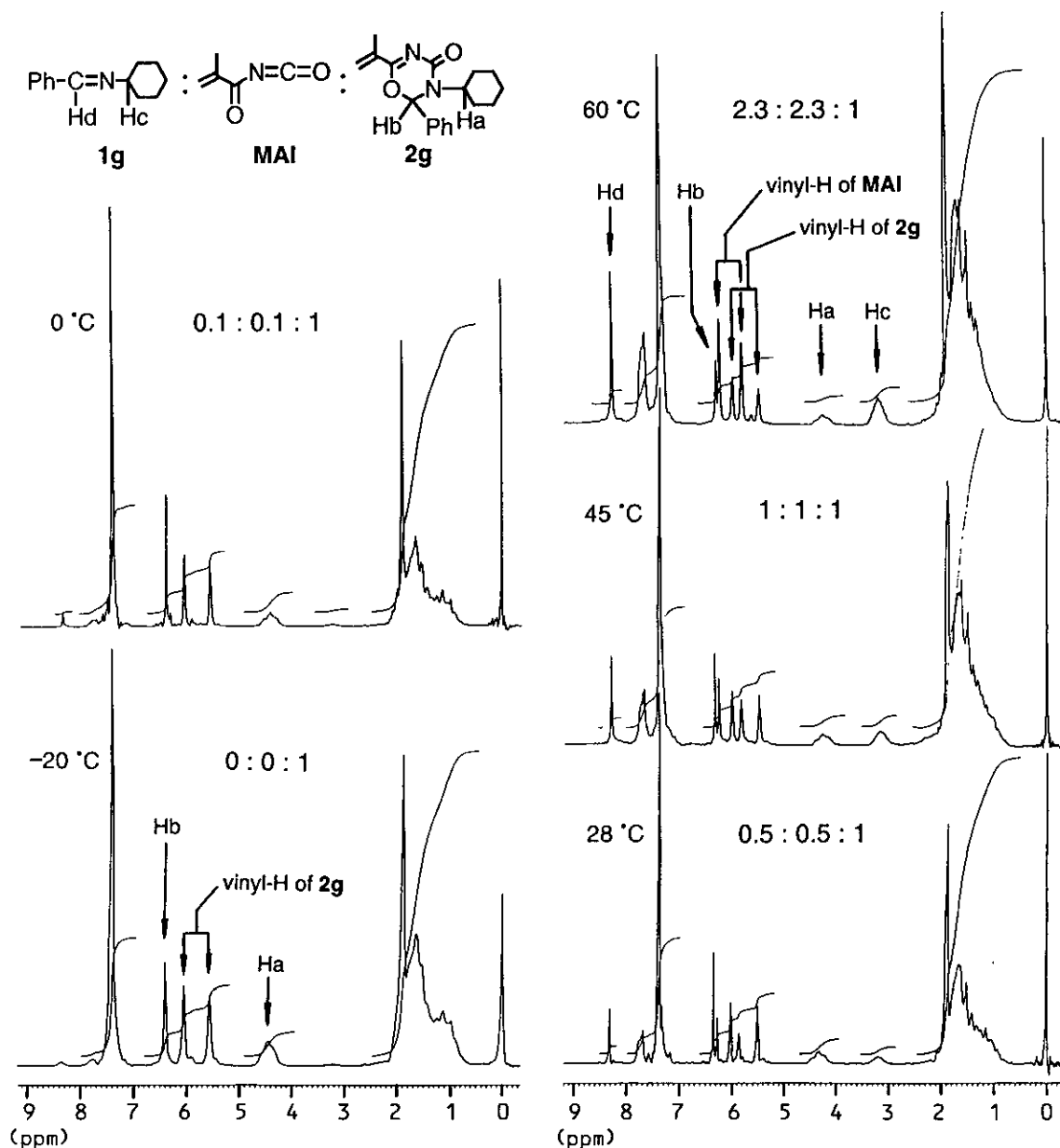
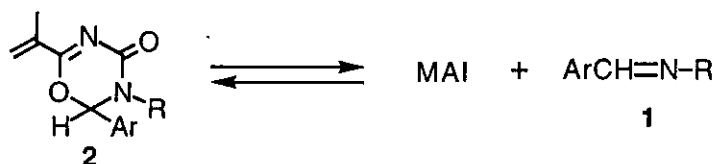


Figure 1. VT-nmr spectra of MAI-**1g-2g** system in CDCl<sub>3</sub>

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

Temp. °C	60	45	28	0	-20	-30
MAI/ <b>1a</b> / <b>2a</b>	1/1/0	1/1/0	1/1/0	12/12/1	5/5/1	5/5/1
MAI/ <b>1b</b> / <b>2b</b>	0.5/0.5/1	0.2/0.2/1	0.1/0.1/1	<b>2b</b> only	—	—
MAI/ <b>1c</b> / <b>2c</b>	0.5/0.5/1	0.3/0.3/1	0.2/0.2/1	0.1/0.1/1	<b>2c</b> only	—
MAI/ <b>1d</b> / <b>2d</b>	0.6/0.6/1	0.4/0.4/1	0.1/0.1/1	<b>2d</b> only	—	—
MAI/ <b>1e</b> / <b>2e</b>	0.7/0.7/1	0.3/0.3/1	0.2/0.2/1	<b>2e</b> only	—	—
MAI/ <b>1f</b> / <b>2f</b>	0.6/0.6/1	0.3/0.3/1	0.1/0.1/1	<b>2f</b> only	—	—
MAI/ <b>1g</b> / <b>2g</b>	2.3/2.3/1	1/1/1	0.5/0.5/1	0.1/0.1/1	<b>2g</b> only	—
MAI/ <b>1h</b> / <b>2h</b>	3/3/1	1/1/1	0.5/0.5/1	0.1/0.1/1	<b>2h</b> only	—
MAI/ <b>1i</b> / <b>2i</b>	3.1/3.1/1	1.3/1.3/1	0.8/0.8/1	0.3/0.3/1	<b>2i</b> only	—
MAI/ <b>1j</b> / <b>2j</b>	3/3/1	1.7/1.7/1	0.8/0.8/1	0.2/0.2/1	<b>2j</b> only	—
MAI/ <b>1k</b> / <b>2k</b>	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  $\nu_{\text{C=O}}$  and  $\nu_{\text{C=N}}$  at around 1670 and 1640  $\text{cm}^{-1}$ , 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.