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Why Do Catalytic Quantities of Lewis Acid Generally Yield More Product than 1.1 Equivalent in the Intramolecular Diels-Alder Reaction with a Furan Diene? Competitive Complexation NMR Studies Provide an Answer

Ian R. Hunt, Christine Rogers, Simon Woo, Arvi Rauk, and Brian A. Keay
pp 1049 – 1056.

Abstract:

Abstract: The results presented here provide experimental support for a hypothesis made by us to rationalize literature observations on intramolecular Diels–Alder reactions (IMDA) and our own observations on IMDA with a furan diene (IMDAF) regarding the quantity (catalytic or stoichiometric) of Lewis acid required to facilitate reaction. Evidence suggests that the reactions can be divided into two classes: those that proceed with catalytic quantities of Lewis acid (herein defined as type A) and those that require a stoichiometric quantity of Lewis acid (type B). We believe that the relative basicity of the controlling functional groups in addend and adduct can be critical in determining the quantity of Lewis acid required. The relative Lewis basicity has been studied using competitive complexation studies using low-temperature NMR experiments to study the coordination of methylaluminum dichloride (MAC) and $\text{BF}_3 \cdot \text{Et}_2\text{O}$ with model oxygen Lewis bases and IMDAF addends and adducts.

Figures:

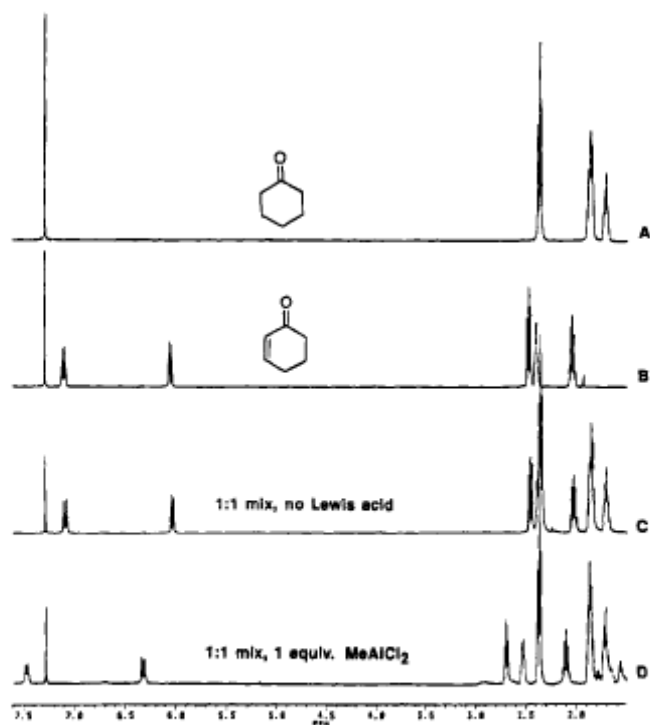


Figure 1. ^1H NMR spectra (-60°C in CDCl_3) of competitive complexation experiment 1, Table 3, between cyclohexenone (7) and cyclohexanone (8). A = 7; B = 8; C = 1:1 mixture of 7:8; D = 1:1:1 mixture of 7:8:MAC.

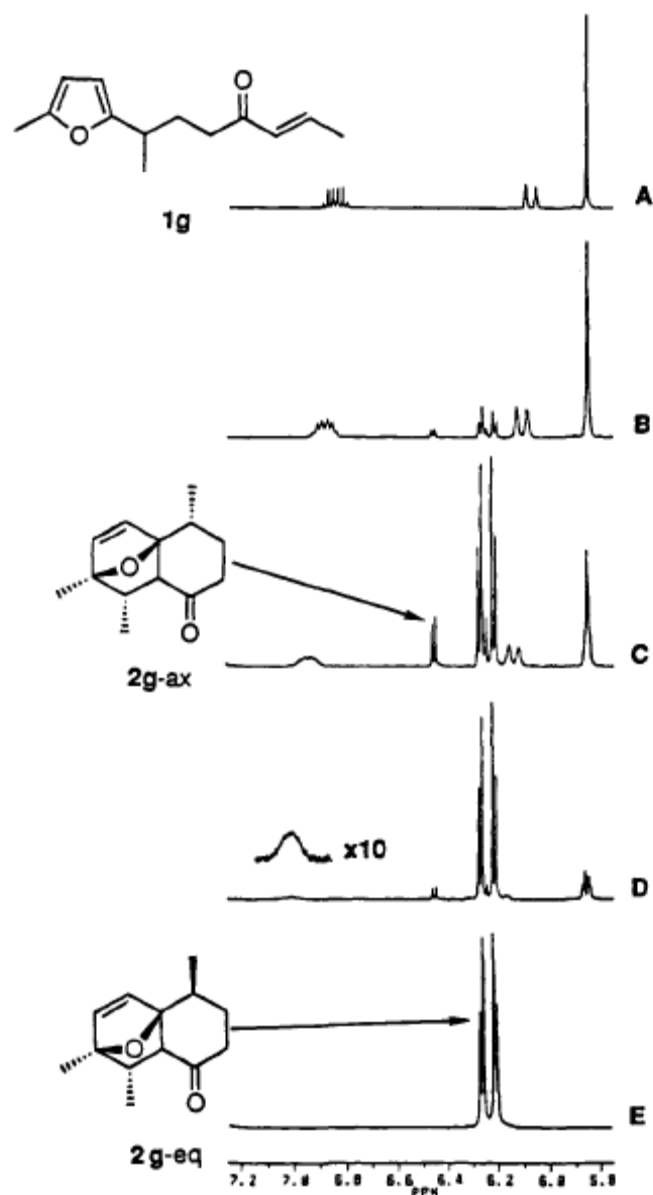


Figure 2. ^1H NMR spectra (-60°C in CDCl_3) obtained for the IMDAF reaction of **1g** to **2g** in the presence of 0.1 equiv of MAC. A = **1g**; B = **1g** + 0.1 MAC, 5 min; C = **1g** + 0.1 MAC, 15 min; D = **1g** + 0.1 MAC, 3 h; E = **2g**.

Tables:

Table 1. Isolated SM:P Ratios for the Example Reactions of Schemes 1 and 2

SM	0.1 equiv of MAC ^a	1.1 equiv of MAC ^a
1a	0:100	0:100
1b	31:69	78:22
1c	95:5	100:0
1d	24:76	82:18
1e	27:73	73:27
1f	100:0	100:0
1g	17:83 ^b	79:21 ^b
3a		0:100 ^c
3h	99:1	13:87 ^c

^a Conditions are 1.1 equiv of MAC, CH₂Cl₂, 8 h, -78 °C and 0.1 equiv of MAC, CH₂Cl₂, 2 h, -65 °C,^{9b,10} unless indicated otherwise. Isolated yields are generally good, and no decomposition products are detected. ^b In this example two products are formed in the ratios 79:4 (0.1 equiv of MAC) and 16:5 (1.1 equiv of MAC). ^c 1.1 or 0.1 equiv of DMAC, -50 °C, 2.5 h. Note that DMAC was used to reduce aromatization of adducts that was seen with MAC.

Table 2. Change in the Chemical Shift, $\Delta\delta$, for Nucleus *i* of Each of the Model Compounds Complexed in the Presence of 1 Equiv of MAC, Relative to the Uncomplexed Base, in CDCl₃ at - 60 °C^a

base	<i>i</i>	$\Delta\delta/\text{ppm}^b$					
		1	2	3	4	5	6
cyclohexenone	¹ H		0.60	0.76	0.27	0.14	0.45
	¹³ C	13.5	-0.9	19.3	-0.9	-1.2	0.9
cyclohexanone	¹ H		0.52	0.25	0.13		
	¹³ C	2.7	1.3	0.9	-1.2		
methyl propionate	¹ H		0.41	0.32	0.22		
	¹³ C	8.3	0.7	5.4	-0.5		
methyl acrylate	¹ H		0.39	0.43	0.29		
	¹³ C	7.4	-3.1	10.2	5.7		
THF	¹ H	0.63	0.36				
	¹³ C	5.5	-0.1				

^a 2-Methylfuran polymerized under the experimental conditions and has been omitted from the table. ^b Column headings refer to the positions defined in the structural diagrams.

Table 3. Change in the Proton Chemical Shift, $\Delta\delta$, and Percent Complex for Each of the Model Compounds Complexed in the Presence of 1 equiv of $\text{BF}_3\cdot\text{Et}_2\text{O}$ in CDCl_3 at -60°C^a

base	% complex	$\Delta\delta_{\text{H}}/\text{ppm}^b$					
		1	2	3	4	5	6
cyclohexenone	72		brd ^c	0.94	0.34	0.14	0.58
cyclohexanone	26		0.55	0.25	nd ^d		
methyl propionate	9		0.64	nd ^e	0.51		
methyl acrylate	0 ^f						
THF	79	0.61	0.37				

^a 2-Methylfuran was not included in this study. ^b Column headings refer to the positions defined in the structural diagrams. ^c The H2 peak for the complex is broad due to exchange between *syn* and *anti* forms at -60°C . At -90°C , both the H2 and H3 peaks are resolved into two signals of approximately equal intensity, with $\Delta\delta_{\text{H2}} = 0.84, 0.47$ ppm and $\Delta\delta_{\text{H3}} = 0.97, 0.88$ ppm for the *syn* and *anti* forms. ^d The shift of this peak could not be accurately determined due to overlap with H2 of the free base. ^e The shift of this peak could not be accurately determined due to overlap with peaks from Et_2O . ^f No evidence of complexation (even in the presence of 5 equiv of $\text{BF}_3\cdot\text{Et}_2\text{O}$).

Table 4. Shifts Observed for Each of the Bases in the Competitive Complexation Experiments with 1 equiv of MAC, in CDCl_3 at -60°C

expt	base X	H	$\Delta\delta/\text{ppm}^a$	base Y	H	$\Delta\delta/\text{ppm}^a$
1	cyclohexenone	3	0.36	cyclohexanone	2	0.00
2	methyl propionate	2	0.38	methyl acrylate	3	0.04
3	cyclohexenone	3	0.66	2-methylfuran		^b
4	cyclohexenone	3	0.01	THF	1	0.16
5	cyclohexanone	2	0.01	THF	1	0.36

^a Values are for the shift of the ^1H peak that exhibited the largest shift on complexation in the model studies. ^b No figure is available for 2-methylfuran because of the polymerization observed during the model studies.

Table 5. Percentage of Each Base Complexed in the Competitive Complexation Experiments with 1 equiv of $\text{BF}_3\cdot\text{Et}_2\text{O}$, in CDCl_3 at -60°C

expt	base X	% complex ^a	base Y	% complex
6	cyclohexenone	65	cyclohexanone	5
7	methyl propionate	9	methyl acrylate	0
8	cyclohexenone	70	2-methylfuran	0
9	cyclohexenone	6	THF	83
10	cyclohexanone	1	THF	87

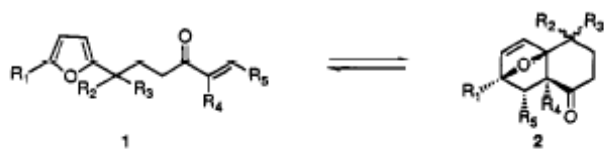
^a Values are based on peak integrals of free and complexed species.

Table 6. Isolated SM:P Ratios for $1\text{d} \rightarrow 2\text{d}$ with 0.1 and 1.0 equiv of Various Lewis Acids, 2 h, -78°C , CH_2Cl_2

Lewis acid	0.1 equiv of LA	1.1 equiv of LA
AlCl_3	8:92	68:32
MeAlCl_2	24:76	82:28
Me_3Al	100:0	
$\text{BF}_3\cdot\text{Et}_2\text{O}$	96:4	63:37
TiCl_4	27:73	89:11
$\text{Ti}(\text{O}-i\text{-Pr})_4$	100:0	100:0

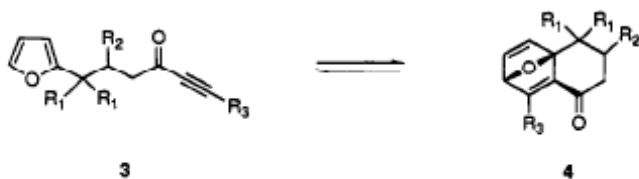
Schemes:

Scheme 1



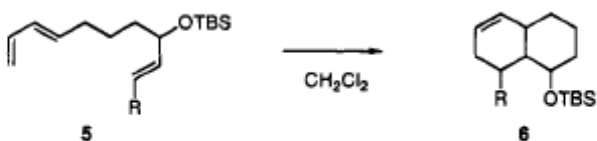
	R ₁	R ₂	R ₃	R ₄	R ₅
a	H	H	H	H	H
b	H	H	H	H	Me
c	H	H	H	Me	Me
d	Me	H	H	H	Me
e	H	Me	Me	H	Me
f	H	Me	Me	Me	Me
g	Me	Me	H	H	Me

Scheme 2



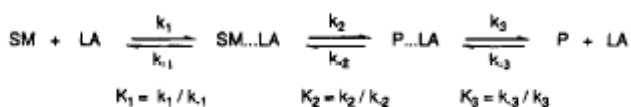
- a R₁ = R₃ = Me, R₂ = H
 b R₁ = H, R₂ = Me, R₃ = TMS

Scheme 3



- a. R = CHO, 0.2 EtAlCl₂, -78°C, 62%
 b. R = CO₂iPr, 1.0 EtAlCl₂, 8°C, 60%

Scheme 4



$$K_{\text{eq}} = [\text{P}] / [\text{SM}] = K_1 K_2 / K_3$$

$$K_{\text{obs}} = \frac{[\text{P}] + [\text{P} \cdots \text{LA}]}{[\text{SM}] + [\text{SM} \cdots \text{LA}]}$$