Lewis Acid-Induced Ring-Opening of
2, 4-Dioxaspiro [5.5] undecan-7-one

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In a previous paper[1], we reported that the cyclohexanone ring-opening reaction of 2, 4-dioxaspiro [5.5] undecan-7-one[2] with lead tetraacetate carried out to know organoleptic properties of the products having 1, 3-dioxane moiety. This paper will report on 1, 3-dioxane ring-opening of the above spiro-ketone with Lewis acids (MX$_n$, n=2−4) in acetic anhydride (Ac$_2$O) ; the experiments were undertaken in order to clarify the effects of Lewis acid and reaction variables.

Result and Discussion

The 1, 3-dioxane ring-opening reactions of 2, 4-dioxaspiro [5.5] undecan-7-one (1) with various Lewis acids, such as SnCl$_4$, BF$_3$(OEt$_2$), ZnCl$_2$, FeCl$_3$, CuCl$_2$ and AlCl$_3$, were performed in Ac$_2$O under reflux to give 1-acetoxymethyl-3, 5-dioxabicyclo [4. 4. 0] decan-6-ene (2), 2-acetoxymethyl-2-hydroxymethylcyclohexanone (3), 1-acetoxy-methyl-3-oxabicyclo [3. 3. 1]-nonan-9-one (4), 2, 2-diacetoxymethylcyclohexanone (5), 2-[(acetoxymethoxy) methyl]-2-acetoxymethyl-cyclohexanone (6) and 1,5-diacetoxy-methyl-3-oxabicyclo [3. 3. 1] nonan-9-one (7). The reactions in acetic acid (AcOH) were also attempted to clear the cleavage mechanism, however, proceeded hardly at all to afford only small amounts of 2, 3 and 5. The results are summarized in the Table.
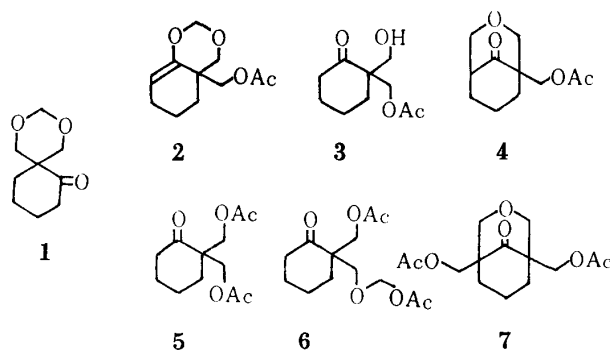
Table.   Reaction of 2, 4-Dioxaspiro [5. 5] undecan-7-one with various
Lewis acids in Ac_2O or AcOH

Spiro-ketone (1) 11.8 mmol (2.00g) ; Lewis acid 1.1 mmol; Ac_2O or AcOH 9.8 mmol,
19.6 mmol

Reaction conditions: Reflux, 3 h

Lewis acid	Reaction mixture							
	Yield (g)	Component ratio %)[a]						
		1*	2	3	4	5	6	7
in Ac_2O								
SnCl$_4$	2.51(2.98)	13(1)	7(—)	4(1)	24(46)	18(33)	9(4)	25(15)
BF$_3$[b]	2.52(2.89)	25(—)	t(—)	10(—)	6(22)	43(53)	—(—)	16(25)
ZnCl$_2$	2.02(2.31)	80(2)	—(—)	t(3)	8(44)	12(51)	—(—)	—(—)
FeCl$_3$	2.27(2.61)	72(11)	—(t)	2(5)	5(35)	21(35)	—(—)	—(14)
CuCl$_2$	2.92(2.85)	60(—)	10(3)	t(—)	9(3)	21(29)	—(56)	—(9)
AlCl$_3$	1.67(1.03)	47(15)	10(15)	t(t)	7(4)	36(6)	—(60)	—(—)
in AcOH								
SnCl$_4$	2.14(2.35)	83(64)	6(13)	8(8)	—(—)	3(15)	—(—)	—(—)
BF$_3$[b]	2.21(1.47)	83(61)	—(t)	10(14)	—(—)	7(25)	—(—)	—(—)
ZnCl$_2$	1.01(0.75)	100(100)	—(—)	—(—)	—(—)	—(—)	—(—)	—(—)
FeCl$_3$	2.16(2.03)	96(88)	—(—)	4(12)	—(—)	—(—)	—(—)	—(—)
CuCl$_2$	1.31(1.09)	90(95)	t(t)	5(2)	—(—)	5(3)	—(—)	—(—)
AlCl$_3$	2.09(2.43)	72(68)	t(t)	14(13)	—(—)	14(19)	—(—)	—(—)

a) Determined by GLC. The value in the parentheses show the ratio in the case of using
19.6 mmol Ac_2O or AcOH.   b) Etherate   * : Unreacted 1   t: Trace
☐ : Enclose the values concerned in the discussion.

It has generally been called[3] that the order of Lewis acids catalyst activities
in Friedel-Crafts reactions is $AlCl_3 > FeCl_3 > BF_3 > ZnCl_2 > SnCl_4 > CuCl_2$. While in
the reaction with 1 having both ethereal and carbonyl oxygens, the order of their
reactivities in 9.8 mmol Ac_2O revealed $SnCl_4 > BF_3 > AlCl_3 > CuCl_2 > FeCl_3 > ZnCl_2$ on
the basis of the unreacted 1. By use of double the molar quantity of Ac_2O, each
reactivity so remarkably increased that the order cannot be compared.

When the results of the reactions using 19.6 mmol Ac_2O were aligned as is
shown in Table, we found that the Lewis acids are classified into two groups ac-
cording to tendency for formation of the products, that is, $AlCl_3$ and $CuCl_2$ belong
to the Ist group, and $SnCl_4$, BF_3, $ZnCl_2$ and $FeCl_3$ are included in the IInd group.
The reactions of both the groups gave 5 as a common product. In addition, the
former group afforded the acetoxymethoxymethyl compound (6) as the character-
istic product with a small amounts of 2. On the other hand, in the presence of
the latter group, the reactions gave the oxabicyclo compound (4) in substantial

quantity together with **7** analogous to **4**.

It seems that these reactions are at first induced by either the acylium ion

$(CH_3\overset{+}{C} = O \cdot \overline{MX}_{n+1}: CH_3CO_2MX_{n-1})$ or the oxonium compound $(CH_3\overset{\delta+}{C} = O \cdot \overset{\delta-}{MX}_n)$

$$\begin{array}{c} \diagdown O \\ \diagup \\ CH_3\overset{|}{C} = O \end{array}$$
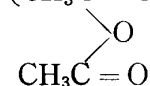
which may be formed by the reaction of Lewis acid with Ac$_2$O. In the 1, 3-dioxane

ring-opening, both the acylium ion and the oxonium compound ought to provide an

intermediate having carbonium ion respectively. On the basis

of such a concept, the reaction mechanism can be explained

as follows.
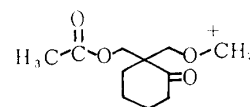
i) : It is obvious that the common product **5** was formed by the following deformy-

lation and acetoxylation from the carbonium ion. ii) : In the reaction of the acylium

ion bearing a strong reactivity, the carbonium ion was directly acetoxylated into **6**

in preference to the deformylation. Since **6** gradually changed to **2** on standing at

room temperature, it is assumed that **2** was produced through a kind of intramole-

cular acetalation with the elimination of acetyl group from **6**. iii) : In the case of

the oxonium compound less polarized than the acylium ion, the same carbonium

ion mildly cyclized with the activated methylene adjacent to the carbonyl group

to give **4**. The similar cyclization was caused in concert to afford **7** with **5** *via*

bimolecular condensation of the carbonium ion intermediates, followed by cleavage

of ether linkage. iv) : The formation of the hydroxy compound (**3**) is due to AcOH

produced as by-product in these reactions.

These results suggest that the Lewis acids of Ist and IInd groups, respectively,

participated in the reaction as the acylium ion and the oxonium compound.

Experimental

The melting point is uncorrected. IR spectra were measured with a JASCO

model IRA-I spectrometer. ^{1}H-NMR and ^{13}C-NMR spectra were recorded with

JEOL JNM-MH-60-II and JNM-FX 100 spectrometers using tetramethylsilane as an

internal standard, respectively. Mass spectra were determined on a JEOL JMS-D

300 spectrometer. GLC were performed using Yanaco model G-180 gas chromato-

graphs equipped with a 3mm×75cm Silicone OV-1 (*3%*) column.

Preparation of 2, 4-dioxaspiro [5. 5] undecan-7-one (**1**)

2, 4-dioxaspiro [5. 5] undecan-7-one was prepared according to the procedure

described in a previous paper[1].

A typical procedure

A mixture of **1** (11.8 mmol, 2.00g), $SnCl_4$ (1.1 mmol) and Ac_2O (9.8 mmol) was refluxed with stirring at 110°C for 3 h. The cooled mixture was extracted with chloroform, and the solution was washed with brine, sodium carbonate solution and water, dried over sodium sulfate, and concentrated *in vacuo* to viscous oil, whose GLC (Silicone OV-1, 150°C, N_2 0.4 kg/cm^2 and H_2 0.6 kg/cm^2 of carrier gas) shows seven major peaks with Rt 1.3, 2.7, 3.1, 3.8, 5.6, 11.3 and 22.5 min in a relative intensity of 13 : 7 : 4 : 24 : 18 : 9 : 25 for unreacted **1**, 1-acetoxymethyl-3, 5-dioxabicyclo [4. 4. 0] decan-6-ene (**2**), 2-acetoxymethyl-2-hydroxymethylcyclohexanone (**3**), 1-acetoxymethyl-3-oxabicyclo [3. 3. 1] nonan-9-one (**4**), 2, 2-diacetoxymethylcyclohexanone (**5**), 2-[(acetoxymethoxy) methyl]-2-acetoxymethylcyclohexanone (**6**) and 1, 5-diacetoxymethyl-3-oxabicyclo [3. 3. 1] nonan-9-one (**7**). The viscous oil was chromatographed on silica gel, using hexane-acetone-ether (40 : 2 : 1 in volume,), hexane-acetone-ethyl acetate (45 : 4 : 3), hexane-acetone-ethyl acetate (30 : 1 : 1), hexane-ether-chloroform (10 : 8 : 1), hexane-ether (1 : 1) and hexane-acetone (7 : 1) as the eluent, to afford **1, 2, 3, 4, 5, 6** and **7,** respectively. The structures of the products were confirmed on the basis of the IR, ^{1}H-NMR, ^{13}C-NMR and Mass spectra.

In a similar manner, the reactions of **1** with various Lewis acids were examined. Spectral data of the products are given below.

2: Colorless oil; n_D^{25} : 1.4903; IR(neat) : 2920, 2850, 2760, 1755, 1670, 1450, 1365, 1195, 1160, 1130, 1090, 1050, 1030 cm^{-1}; ^{1}H-NMR(CDCl$_3$) : δ 1.45–2.19 (m, 6H, CH$_2$×3), 2.16 (s, 3H, OCOCH$_3$), 3.75 (s, 4H, CH$_2$O+CH$_2$OCO), 4.77 (AB-q, J=6Hz, 2H, OCH$_2$O), 5.48 (t, J=4Hz, 1H, =CH); ^{13}C-NMR (CDCl$_3$) : δ 169.3 (s, OC=O), 146.6 (s, OC=), 119.8 (d, =CH), 93.6 (t, OCH$_2$O), 72.4 (t, CH$_2$O×2), 38.4 (s, C), 29.8 (t, CH$_2$), 24.1 (t, CH$_2$), 20.9 (q, CH$_3$), 18.1 (t, CH$_2$); EIMS (70eV) : m/e 170 (17%), 152(21), 140(12), 122(25), 110(100), 95(24), 79(25), 67(29), 55(17), 44(76); CIMS (200eV) : m/e Isobutane 213 (M+H)$^+$, Ammonia 230 [(M+NH$_4$)$^+$, 100%]

3: Colorless oil; n_D^{25} : 1.4842; IR (neat) : 3450, 2910, 2840, 1730, 1700, 1440, 1370, 1220, 1030 cm^{-1}; ^{1}H-NMR (CDCl$_3$) : δ 1.28–2.08 (m, 7H, CH$_2$×3+OH), 2.04 (s, 3H, OCOCH$_3$), 2.24–2.52 (m, 2H, CH$_2$C=O), 3.54–4.04 (m, 2H, CH$_2$OH), 4.26 AB-q, J=12Hz, 2H, CH$_2$OCO); ^{13}C-NMR(CDCl$_3$) : δ 212.4 (s, C=O), 170.7 (s, OC=O), 64.7 (t, CH$_2$OCO), 63.7 (t, CH$_2$OH), 53.8 (s, C), 39.6 (t, CH$_2$), 31.5 (t, CH$_2$), 27.0 (t, CH$_2$), 20.8 (t, CH$_2$), 20.7 (q, COCH$_3$); EIMS (22eV) : m/e 200 (M$^+$, 3%), 158(34), 140(59), 123(51),95(100), 94(34), 43(86); CIMS (200eV) : m/e Isobutane 201 [(M+H)$^+$, 100%]

4: Colorless oil; $n_D{}^{25}$: 1.4371; IR (neat): 2910, 2835, 1735, 1720, 1450, 1360, 1225, 1130, 1035 cm^{-1}; ^{1}H-NMR (CDCl$_3$): δ 0.97–2.04 (m, 6H, CH$_2$×3), 2.05 (s, 3H, OCOCH$_3$), 2.32–2.51 (m, 1H, CHC=O), 3.95 (AB-q, J=12Hz, 2H, CH$_2$O), 4.06 (s, 2H, CH$_2$OCO), 4.07 (AB-q, J=11Hz, 2H, CH$_2$O); ^{13}C-NMR (CDCl$_3$): δ 212.7 (s, C=O), 170.1 (s, OC =O), 76.4 (t, CH$_2$O), 74.8 (t, CH$_2$O), 64.9 (t, CH$_2$OCO), 51.4 (s, C), 49.2 (d, CH), 37.0 (t, CH$_2$), 34.1 (t, CH$_2$), 20.6 (t, CH$_2$), 20.6 (q, CH$_3$); EIMS (22eV): m/e 212 (M$^+$, 6%), 170(7), 152(100), 140(11), 122(25), 110(15), 94(20), 79(23)

5: Colorless oil; $n_D{}^{25}$: 1.4650; IR (neat): 2925, 2850, 1730, 1700, 1365, 1220 cm^{-1}; ^{1}H-NMR (CDCl$_3$): δ 1.57–1.94 (m, 6H, CH$_2$×3), 1.98 (s, 6H, OCOCH$_3$×2), 2.19–2.60 (m, 2H, CH$_2$C=O), 4.13 (AB-q, J=12Hz, 4H, CH$_2$OCO×2); ^{13}C-NMR (CDCl$_3$): δ 209.4 (s, C=O), 170.3 (s, OC=O×2), 64.4 (t, CH$_2$O×2), 51.7 (s, C), 39.1 (t, CH$_2$), 32.2 (t, CH$_2$), 26.8 (t, CH$_2$), 20.8 (t, CH$_2$), 20.8 (q, COCH$_3$×2); EIMS (22eV): m/e 242(M$^+$, 2%), 182(7), 140 (100), 122 (59), 111(20), 95(17), 79(9)

6: Colorless oil; $n_D{}^{25}$: 1.4659; IR (neat): 2920, 1740, 1725, 1700, 1440, 1358, 1225, 1150 cm^{-1}; ^{1}H-NMR (CDCl$_3$): δ 1.19–1.93 (m, 6H, CH$_2$×3), 2.02 (s, 3H, OCOCH$_3$), 2.08 (s, 3H, OCOCH$_3$), 2.16–2.67 (m, 2H, CH$_2$C=O), 3.83 (AB-q, J=10Hz, 2H, CH$_2$OCO), 4.30 (AB-q, J=12Hz, 2H, CH$_2$OCH$_2$), 5.22 (s, 2H, OCH$_2$O); ^{13}C-NMR (CDCl$_3$): δ 210.4 (s, C=O), 170.4 (s, OC=O), 170.1 (s, OC=O), 89.1 (t, OCH$_2$O), 70.9 (t, CH$_2$O), 64.6 (t, CH$_2$O), 52.6 (s, C), 39.3 (t, CH$_2$), 32.3 (t, CH$_2$), 27.0 (t, CH$_2$), 20.9 (q,COCH$_3$), 20.7 (t, CH$_2$), 20.7 (q, COCH$_3$); EIMS (22eV): m/e 182(15%), 170 (10), 152(68) ,140(61), 122(100), 110(61), 94 (36); CIMS (200eV): m/e Ammonia 290 [(M+NH$_4$)$^+$, 100%], 213 [(M+H−AcOH)$^+$, 75]

7: White crystals; mp: 93.5–95.0°C (from ether); IR (KBr): 2900, 2815, 1720, 1715, 1685, 1425, 1350, 1225, 1155, 1025 cm^{-1}; ^{1}H-NMR (CDCl$_3$): δ 1.41–2.46 (m, 6H, CH$_2$×3), 2.04 (s, 6H, OCOCH$_3$×2), 3.96 (AB-q, J=12 Hz, 4H, CH$_2$O×2), 4.09 (s, 4H, CH$_2$OCO×2); ^{13}C-NMR (CDCl$_3$): δ 211.2 (s, C=O), 170.3 (s, OC=O), 76.6 (t, CH$_2$O×2), 64.7 (t, CH$_2$OCO×2), 51.0 (s, C×2), 37.1 (t, CH$_2$×2), 20.8 (q, CH$_2$×2), 20.0 (t, CH$_2$); EIMS (22eV): m/e 284 (M$^+$, 2%), 224(49), 195(23), 182(26), 164(86), 151(40), 136(100), 134(91), 122(26), 108(27)

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