June, 1978] BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 51 (6), 1821—1825 (1978)

The Reactions of Olefins with Chloromethoxymethane or Dimethoxymethane in Nitriles

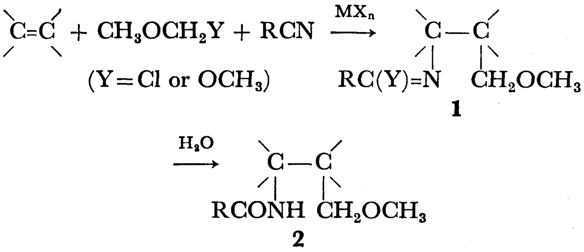
Yasuo WADA,* Takeshi YAMAZAKI,* Kazuo NISHIURA,* Shigeo TANIMOTO, and Masaya OKANO**

Institute for Chemical Research, Kyoto University, Uji, Kyoto 611

(Received November 7, 1977)

The Lewis acid-catalyzed reactions of olefins with chloromethoxymethane (CM) or dimethoxymethane (DM) and aliphatic or aromatic nitriles afforded the 1: 1: 1 adducts and/or their hydrolysis products in various yields, together with the 1: 1 olefin–CM (or DM) adducts. $AlCl_3$, $FeCl_3$, $ZnCl_2$, and $SnCl_4$ were effective catalysts for the reaction with CM, whereas BF_3 and $SnCl_4$ were effective for that with DM. In the case of cyclohexene, the addition proceeded in the *trans*-manner; *i.e.*, the methoxymethyl group and the nitrile molecule were added to the olefin from opposite sides.

Several modifications of the Ritter reaction with various positive halogen compounds (*e.g.*, Cl_2,[1)] Br_2,[1)] ClOH,[1)] BrN_3,[2)] $ClNHCONH_2$,[3)] $Cl_2NCOOEt$,[4)] and Cl_2NSO_2Ph[5)]), a nitronium salt,[6)] and a carbenium salt[7)] have been reported. However, in the last case the reaction of styrene with a methoxycarbenium salt and acetonitrile to produce *N*-(2-methoxy-1-phenylpropyl)acetamide is the sole example thus far examined, and only a brief description on it has been given. In order to know the nature of such a reaction involving the attack of a carbenium ion and to save the trouble of prepreparing a carbenium salt, we examined three-component reactions of olefins with readily available sources of a methoxymethyl cation, such as chloromethoxymethane (CM), dimethoxymethane (DM), or trimethoxymethane (TM), and nitriles in the presence of Lewis acid catalysts. Except for the case of TM, the reactions proceeded smoothly and afforded the desired adducts (**1**) and/or their hydrolysis products (**2**) in various yields (Eq. 1), together with other products, including the 1: 1 olefin–CM(or DM) adducts. The present paper will be concerned with these results.



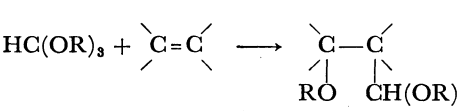
$$>C=C< + CH_3OCH_2Y + RCN \xrightarrow{MX_n} \underset{RC(Y)=N\quad CH_2OCH_3}{>C-C<} \quad (Y=Cl\ \text{or}\ OCH_3)$$

1

$$\xrightarrow{H_2O} \underset{RCONH\quad CH_2OCH_3}{>C-C<} \qquad (1)$$

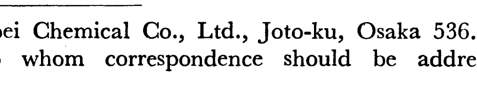
2

In this connection, the Lewis acid-catalyzed reactions of α-halo ethers,[8)] 1,1-dialkoxymethanes,[9)] or trialkoxymethanes[10)] with olefins to yield the corresponding 1: 1 adducts were known in the 1950's (Eqs. 2 and 3).



$$ROCH_2Y + >C=C< \longrightarrow \underset{Y\quad CH_2OR}{>C-C<} \qquad (2)$$

$$(Y=Br,\ Cl,\ \text{or}\ OR)$$



$$HC(OR)_3 + >C=C< \longrightarrow \underset{RO\quad CH(OR)_2}{>C-C<} \qquad (3)$$

Results and Discussion

The treatment of cyclohexene with CM in acetonitrile in the presence of a Lewis acid catalyst at room temperature for 24 h, followed by a work-up procedure with aqueous Na_2CO_3, gave the following three compounds as the main products: a *N*-[2-(methoxymethyl)-cyclohexyl]acetamide (**2a**, $R=CH_3$), a 1-chloro-2-(methoxymethyl)cyclohexane (**3a**, $Y=Cl$), and probably 3-methoxymethyl-1-cyclohexene (**4'a**) (see Eq. 6). The first compound corresponds to the hydrolysis product of the 1: 1: 1 olefin–CM–nitrile adduct and the second one, to the 1: 1 olefin–CM adduct, while the last one may come from the intermediate cation **5a** in the addition and/or from the 1: 1 adduct, **3a**. However, a blank experiment revealed that the latter possibility (the dehydrochlorination of **3a**) can be excluded, at least during the work-up procedure. Further, it was confirmed by a separate experiment that **3a** ($Y=Cl$) does not react with acetonitrile to afford **2a** and either **4a** or **4'a**, even in the presence of equimolar amounts of $AlCl_3$ or $FeCl_3$, under the given reaction conditions. When propionitrile and some aromatic nitriles were used as solvents in place of acetonitrile, the corresponding 1: 1: 1 adducts were obtained similarly. Generally, the reactions were accompanied by a considerable formation of tarry materials (which were probably formed by further acid-catalyzed reactions of the products, **3a**, **4a** and/or **4'a**). Several results of the reaction of cyclohexene with CM are summarized in Table 1.

As can be seen from the table, $AlCl_3$, $FeCl_3$, $ZnCl_2$, and $SnCl_4$ were superior to $HgCl_2$ and BF_3 as catalysts. When equimolar amounts of these effective catalysts were used in acetonitrile, the combined yields of **2a**, **3a**, and **4'a** were nearly 55—60% (based on the consumed cyclohexene), and the proportions of **2a** ($R=CH_3$) changed appreciably with the nature of the catalysts. The best yield (41%) of **2a** was obtained by the use of one equivalent of $AlCl_3$. Though it is known that the basicity of benzonitrile is lower than that of acetonitrile, the former nitrile afforded the corresponding amide (**2a**, $R=C_6H_5$) in considerable yields with selectivities comparable to those of the case of acetonitrile (*e.g.*, $AlCl_3$-catalyzed, the **2a**/**2a**+**3a**+**4'a** ratio was 0.69/1 for CH_3CN and 0.71/1 for C_6H_5CN). Such a result may reflect a considerable stabilization through conjuga-

---

* Koei Chemical Co., Ltd., Joto-ku, Osaka 536.

** To whom correspondence should be addressed.

TABLE 1. REACTION OF CYCLOHEXENE WITH CM IN NITRILES

Ether (CM), 100 mmol; Cyclohexene, 100 mmol; Nitrile, 1000 mmol. Reaction conditions: 20—25 °C, 24 h.

Nitrile	MX_n (equiv)	Method[a]	Product and yield (%)[b,c] **2a**	**3a** (Y=Cl)	**4'a**	Recovered olefin (mmol)[c]
CH_3CN	$ZnCl_2$(1/3)	A	22	10	17	11
CH_3CN	$ZnCl_2$(1)	B	31	9	16	5
CH_3CN	$FeCl_3$(1/3)	A	24	5	12	24
CH_3CN	$FeCl_3$(1)	A	34	13	8	0
CH_3CN	$FeCl_3$(1)	B	34	13	10	1
CH_3CN	$AlCl_3$(1/3)	A	21	3	15	17
CH_3CN	$AlCl_3$(1)	A	41	6	11	2
CH_3CN	$AlCl_3$(1)	B	41	10	8	4
CH_3CN	$SnCl_4$(1/3)	A	24	7	10	5
CH_3CN	$SnCl_4$(1)	B	33	13	9	0
CH_3CN	$HgCl_2$(1/3)	A	15	13	16	24
CH_3CN	$BF_3\cdot Et_2O$(1/3)	A	9	19	7	41
C_2H_5CN[e]	$AlCl_3$(1)	B	34	7	15	6
C_6H_5CN[e]	$ZnCl_2$(1/3)	A	17[d]	18	7	13
C_6H_5CN[e]	$AlCl_3$(1)	B	44[d]	8	10	0
p-$CH_3C_6H_4CN$[e]	$AlCl_3$(1)	B	20[d]	6	6	1
p-ClC_6H_4CN[e,f]	$ZnCl_2$(1/3)	A	11[d]	12	7	31

a) Method A: The ether was added to a mixture of olefin, nitrile, and the catalyst. Method B: The catalyst was added to a mixture of olefin, the ether, and nitrile. b) Based on the olefin consumed. c) Determined by GLC, unless otherwise noted. d) Isolated yield after chromatography. e) Experiment on the scale of 1/2. f) The amount of nitrile was 250 mmol, and CCl_4 (60 ml) was added as the solvent.

TABLE 2. REACTION OF OLEFINS WITH CM IN ACETONITRILE

Ether (CM), 100 mmol; Olefin, 100 mmol; Nitrile, 1000 mmol. Reaction conditions: 20—25 °C, 24 h.

Olefin	MX_n (equiv)	Method[a]	Product and yield (%)[b,c] **2**	**3** (Y=Cl)	**4** or **4'**
n-$C_4H_9CH=CH_2$	$AlCl_3$(1)	B	44	5	4
n-$C_4H_9CH=CH_2$	$ZnCl_2$(1/3)	A	24	20	7
$(CH_3)_2C=CH_2$	$FeCl_3$(1)	B	7	0	0
$C_6H_5CH=CH_2$	$ZnCl_2$(1)	B	9	6[d]	0

a), b), c) See footnotes in Table 1. d) The 2 : 1 styrene–CM adduct was also formed (4%).

tion in the imidoyl cation, **6**, formed by the attack of benzonitrile on the cation **5** (see Eq. 6).

When the reaction was applied to three typical terminal olefins in acetonitrile, the yields of the 1 : 1 : 1 adducts varied significantly (Table 2). From 1-hexene, the expected adduct **2b** ($R=CH_3$), following Markovnikov's rule, was obtained in a yield similar to that in the case of cyclohexene. Although the successful addition of nitriles to 2-methylpropene has been known in the Ritter reaction (in H_2SO_4–HOAc),[1] our reaction gave a poor yield of the expected adduct **2c** ($R=CH_3$) and a large amount of a tarry product. In the case of styrene, the 1 : 1 adduct **3d** (Y=Cl) became the principal product, and the yield of the desired adduct, **2d** ($R=CH_3$), was also quite poor.

Next, a similar treatment of cyclohexene with DM in place of CM in acetonitrile resulted in the formation of the following four products: a methyl *N*-[2-(methoxymethyl)cyclohexyl]ethanimidate (**1a**, $Y=OCH_3$, $R=CH_3$), the actamide **2a** ($R=CH_3$), a 1-methoxy-2-(methoxymethyl)cyclohexane (**3a**, $Y=OCH_3$), and the olefin **4'a** (see Eq. 6). The first and third compounds correspond to the 1 : 1 : 1 olefin–DM–nitrile adduct and the 1 : 1 olefin–DM adduct respectively. For this reaction, the apparent effectiveness of catalysts decreased in this order: $BF_3>SnCl_4>AlCl_3>FeCl_3\gg ZnCl_2$ and $HgCl_2$ (both almost ineffective), in contrast to the case of CM. When two-thirds equivalents of $BF_3\cdot Et_2O$ was used, the combined yield of **1a** and **2a** ($R=CH_3$ each) was found to be 39%; this value was comparable to the highest yield of **2a** ($R=CH_3$) in the reaction with CM. By a separate experiment, it was confirmed that **1a** ($Y=OCH_3$, $R=CH_3$) can be readily converted into **2a** ($R=CH_3$) by hydrolysis with 5% aqueous NaOH (under reflux, 2 h). Most of the **2a** product may arise from **1a** ($Y=OCH_3$) during the work-up procedure, but another route *via* **1a** (Y=Cl) can not be excluded when metal chlorides are used as catalysts. In addition, a controlled experiment revealed that **3a** ($Y=OCH_3$) does not react with acetonitrile in the presence of $BF_3\cdot Et_2O$ to afford **1a** or **2a** under the given reaction conditions. Some typical data of the reaction with DM are given in Table 3.

1-Hexene and styrene can be used as the olefin component for this reaction, but 2-methylpropene failed to undergo the reaction (Table 4). Here, it would be worthwhile to note that the reaction with CM is somewhat preferable to that with DM for the one-step preparation of the 1 : 1 : 1 adducts, **2**, from cyclohexene or 1-hexene, but the latter reaction is prefered for the preparation of **2** (*via* **1**) from styrene.

The following pathway, which is analogous to that of the Ritter reaction, appears to be consistent with all

TABLE 3. REACTION OF CYCLOHEXENE WITH DM IN NITRILES

Ether, (DM) 100 mmol; Cyclohexene, 100 mmol; Nitrile, 1000 mmol, Reaction conditions: 20—25 °C, 24 h.

Nitrile	MX_n (equiv)	Method[a]	Product and yield (%)[b,c]				Recovered olefin (mmol)[c]
			1a (Y=OCH_3)	**2a**	**3a** (Y=OCH_3)	**4′a**	
CH_3CN	$BF_3\cdot Et_2O$(1/2)	B	21	13	1	7	16
CH_3CN	$BF_3\cdot Et_2O$(2/3)	B	25	11	1	9	13
CH_3CN[e]	$BF_3\cdot Et_2O$(2/3)	B	24	11	1	11	12
CH_3CN	$BF_3\cdot Et_2O$(1)	B	1	5	1	7	9
CH_3CN	$SnCl_4$(1/2)	B	21	8	2	10	11
CH_3CN	$SnCl_4$(2/3)	B	16	9	1	9	8
CH_3CN	$AlCl_3$(1/2)	B	9	15	1	11	26
CH_3CN	$FeCl_3$(1/2)	B	3	15	1	6	49
C_6H_5CN[f]	$BF_3\cdot Et_2O$(2/3)	B	36	2[d]	3	14	21
C_6H_5CN[f]	$SnCl_4$(1/2)	B	28	4[d]	2	12	13

a), b), c), d) See footnotes in Table 1. e) Reaction time: 48 h. f) Experiment on the scale of 1/2.

TABLE 4. REACTION OF OLEFINS WITH DM IN ACETONITRILE

Ether (DM), 100 mmol; Olefin, 100 mmol; Nitrile, 1000 mmol. Reaction conditions: 20—25 °C, 24 h.

Olefin	MX_n (equiv)	Method[a]	Product and Yield (%)[b,c]			
			1 (Y=OCH_3)	**2**	**3** (Y=OCH_3)	**4** or **4′**
n-$C_4H_9CH=CH_2$	$BF_3\cdot Et_2O$(2/3)	B	19	8	3	22
n-$C_4H_9CH=CH_2$	$SnCl_4$(1/2)	B	19	8	2[d]	12
$C_6H_5CH=CH_2$	$BF_3\cdot Et_2O$(2/3)	B	28	4	19	0
$C_6H_5CH=CH_2$	$SnCl_4$(1/2)	B	18	6	19[d]	0

a), b), c) See footnotes in Table 1. d) No **3** (Y=Cl) was detected.

TABLE 5. PHYSICAL PROPERTIES AND ANALYTICAL DATA OF THE **1** AND **2** PRODUCTS

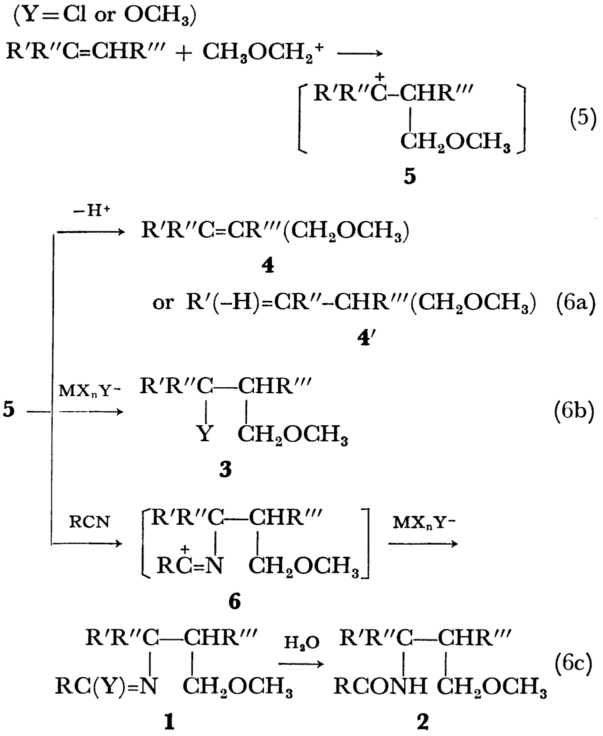
Product; Bp(°C/Torr)[Mp(°C)]	H NMR (δ) (in $CDCl_3$)	Found (Calcd) (%)		
		C	H	N
1a (Y=OCH_3, R=CH_3)[a]; 105—106/15	3.50 (s, 3H), 3.20 (s, 3H), 3.6—2.7 (m, 3H), 1.80 (s, 3H), 2.0—1.0 (m, 9H)	66.43 (66.29	10.16 10.62	6.82 7.03)
1a (Y=OCH_3, R=C_6H_5); 108—110/2—3	7.5—7.2 (m, 5H), 3.75 (s, 3H), 3.20 (s, 3H), 3.5—2.8 (m, 3H), 2.1—0.8 (m, 9H)	73.64 (73.53	8.87 8.87	5.10 5.36)
1b (Y=OCH_3, R=CH_3); 105—107/28	3.58 (s, 3H), 3.4—3.1 (m, 3H), 3.30 (s, 3H), 1.84 (s, 3H), 1.8—1.0 (m, 8H), 0.9 (t, 3H)	65.93 (65.63	11.74 11.52	6.67 6.96)
1d (Y=OCH_3, R=CH_3); 101—103/2—3	7.4—7.1 (m, 5H), 4.65—4.25 (m, 1H), 3.65 (s, 3H), 3.30 (s, 3H), 3.5—3.15 (m, 2H), 1.82 (s, 3H), 2.2—1.7 (m, 2H)	70.87 (70.56	8.97 8.65	6.26 6.33)
2a (R=CH_3)[a]; 120—122/2—3, [110]	5.8 (b, 1H), 3.25 (s, 3H), 3.7—2.9 (m, 3H), 1.90 (s, 3H), 2.2—0.7 (m, 9H)	64.40 (64.83	10.21 10.34	7.47 7.56)
2a (R=C_2H_5); [90—90.5]	6.4 (b, 1H), 3.23 (s, 3H), 3.7—2.9 (m, 3H), 2.10 (q, 2H), 1.10 (t, 3H), 2.2—0.7 (m, 9H)	66.06 (66.29	10.75 10.62	6.94 7.03)
2a (R=C_6H_5); [120—121]	7.8—7.2 (m, 5H), 7.0 (b, 1H), 3.20 (s, 3H), 3.8—3.1 (m, 3H), 2.2—0.8 (m, 9H)	72.56 (72.84	8.76 8.56	5.55 5.56)
2a (R=p-$CH_3C_6H_4$); [129—129.5]	7.8—7.1 (m, 4H), 6.7 (b, 1H), 3.25 (s, 3H), 3.8—3.1 (m, 3H), 2.40 (s, 3H), 2.2—0.8 (m, 9H)	73.52 (73.53	9.06 8.87	5.48 5.36)
2a (R=p-ClC_6H_4); [160—162]	7.8—7.3 (m, 4H), 6.8 (b, 1H), 3.25 (s, 3H), 3.8—3.1 (m, 3H), 2.2—0. 8 (m, 9H)	63.82 (63.94	7.29 7.15	5.12 4.97)
2b (R=CH_3); 128—130/3, [115—116]	7.5 (b, 1H), 4.1—3.6 (m, 1H), 3.35 (t, 2H), 3.25 (s, 3H), 1.90 (s, 3H), 1.9—1.1 (m, 8H), 0.9 (t, 3H)	63.97 (64.13	11.07 11.30	7.61 7.48)
2c (R=CH_3); 109—110/4	7.1 (b, 1H), 3.40 (t, 2H), 3.30 (s, 3H), 1.86 (s, 3H), 1.86 (t, 3H), 1.33 (s, 6H)	60.14 (60.34	10.66 10.76	8.82 8.80)
2d (R=CH_3); 138—140/3	8.2 (b, 1H), 7.4—7.0 (m, 5H), 5.3—4.9 (m, 1H), 3.25 (s, 3H), 3.5-3.1 (m, 2H), 1.90 (s, 3H), 2.2—1.7 (m, 2H)	70.12 (69.53	8.02 8.27	6.16 6.76)

a) *trans*-Isomer.

of the results:

$$CH_3OCH_2Y + MX_n \rightleftarrows CH_3OCH_2^+ + MX_nY^- \quad (4)$$

$(Y{=}Cl \text{ or } OCH_3)$



$$R'R''C{=}CHR''' + CH_3OCH_2^+ \longrightarrow \left[\begin{array}{l} R'R''\overset{+}{C}\text{-}CHR''' \\ \qquad\quad | \\ \qquad\quad CH_2OCH_3 \end{array}\right] \quad (5)$$

5

$$5 \xrightarrow{-H^+} R'R''C{=}CR'''(CH_2OCH_3) \ \mathbf{4} \quad \text{or } R'(-H){=}CR''\text{-}CHR'''(CH_2OCH_3) \ \mathbf{4'} \quad (6a)$$

$$5 \xrightarrow{MX_nY^-} \begin{array}{l} R'R''C\text{—}CHR''' \\ \ \ |\qquad | \\ \ \ Y \quad CH_2OCH_3 \end{array} \ \mathbf{3} \quad (6b)$$

$$5 \xrightarrow{RCN} \left[\begin{array}{l} R'R''C\text{—}CHR''' \\ \quad \overset{+}{|}\qquad | \\ RC{=}N \quad CH_2OCH_3 \end{array}\right] \mathbf{6} \xrightarrow{MX_nY^-} \begin{array}{l} R'R''C\text{—}CHR''' \\ \qquad |\qquad | \\ RC(Y){=}N \quad CH_2OCH_3 \end{array} \mathbf{1} \xrightarrow{H_2O} \begin{array}{l} R'R''C\text{—}CHR''' \\ \qquad |\qquad | \\ RCONH \ CH_2OCH_3 \end{array} \mathbf{2} \quad (6c)$$

a: $R', R''' = (CH_2)_4, R'' = H$
b: $R' = n\text{-}C_4H_9, R'' = R''' = H$
c: $R' = R''' = CH_3, R'' = H$
d: $R' = C_6H_5, R'' = R''' = H$

The attemped reaction using TM as the source of the methoxymethyl moiety under similar reaction conditions was unsuccesful. For example, when an equimolar mixture of cyclohexene and TM was treated with excess acetonitrile in the presence of $BF_3 \cdot Et_2O$ (2/3 equiv.) at room temperature for 48 h, only a small amount of a tarry product was formed, and most of the olefin was recovered.

Lastly, we wish to add a short comment on the stereochemical results of the reactions of cyclohexene in acetonitrile. When crude **2a** ($R{=}CH_3$) (obtained by the reaction with CM) was hydrolyzed by refluxing in aqueous HCl, *trans*-2- and probably *cis*-3-(methoxymethyl)cyclohexylamines (*trans*-**7** and *cis*-**8** respectively) were formed in a ratio of 9: 1, and no other products, including the *cis*-isomer of **7**, were found.[11] The configuration and conformation of **7** were deduced from the splitting of the $\underline{C}\underline{H}(NH_2)$ proton in its NMR (100 MHz) spectrum, which indicates that this proton is in an *axial* position, coupled strongly to two adjacent *axial* protons and weakly to one adjacent *equatorial* proton ($\delta{=}2.42$, d of t, $J{=}4$ and 10 Hz). In addition, the $C\underline{H}Cl$ proton of **3a** ($Y{=}Cl$) showed a quite similar splitting pattern at $\delta{=}3.74$, indicating that its structure is also *trans* (diequatorial). An almost exclusive formation of *trans*-**7** was also observed when crude **1a** ($Y{=}OCH_3$) and crude **2a** ($R{=}CH_3$) (both obtained by the reaction with DM) were each subjected to hydrolysis in 10% aqueous HCl.[13] These results imply that the methoxymethyl cation and the nitrile molecule or Cl^- are added to cyclohexene from opposite sides. Since the absence of γ-methoxyl group participation in solvolytic reactions has been established by Winstein *et al.*,[14] the *trans*-addition *via* a four-membered cyclic oxonium ion intermediate is unlikely. The high stereoselectivity might be explained by assuming that, on the attack by the nucleophile upon the **5a** cation, the course leading to a thermodynamically more stable isomer becomes quite favorable for some reason.

Experimental

All the organic and inorganic materials were commercial products. The NMR spectra (in $CDCl_3$) were recorded with a Varian A-60 apparatus and a JEOL MH-100 apparatus. The GLC analyses were carried out on a Shimadzu 5APTF apparatus, using EGSS-X (30%)-Chromosorb-W(1 m) and PEG 6000 (3 m) columns (with N_2 as the carrier gas).

Reactions of Cyclohexene with CM or DM in Nitriles. Some typical examples are given below.

Method A: To a stirred mixture of cyclohexene (8.2 g, 100 mmol) and $FeCl_3$ (16.2 g, 100 mmol) in acetonitrile (41 g, 1000 mmol), CM (8.0 g, 100 mmol) was added, drop by drop, the temperature being maintained at near 5 °C by cooling with ice water. The mixture was stirred for 24 h at room temperature (20—25 °C) and then poured into a cooled solution of aqueous Na_2CO_3. After the basic mixture had then been stirred for 2 h at room temperature, the precipitated inorganic substance was filtered off and the filtrate was extracted with ether. Then the organic layer separated from the aqueous one was washed with aqueous NaCl and dried over anhydrous $MgSO_4$, and most of the solvent was evaporated. GLC analysis of the residue indicated the presence of **4'a** (probably) (1.0 g, 8 mmol), **3a** ($Y{=}Cl$) (2.1 g, 13 mmol), and **2a** ($R{=}CH_3$) (6.3 g, 34 mmol). Distillation afforded the following fractions: bp 65—95 °C/25 Torr [a mixture of **4'a** and **3a** ($Y{=}Cl$), 3 g], bp 119—123 °C/2—3 Torr [crude **2a** ($R{=}CH_3$), 6.5 g], and a brown, tarry residue (3.6 g).

Method B: To a stirred solution of cyclohexene (8.2 g, 100 mmol) and DM (7.6 g, 100 mmol) in acetonitrile (41 g, 1000 mmol), $BF_3 \cdot Et_2O$ (9.5 g, 67 mmol) was added slowly at near 5 °C; the resulting mixture was stirred for 24 h at room temperature. The work-up procedure was the same as above. GLC analysis showed the presence of unreacted cyclohexene (1.1 g, 13 mmol), **4'a** (1.0 g, 8 mmol), **3a** ($Y{=}OCH_3$) (0.1 g, 1 mmol), **1a** ($Y{=}OCH_3$, $R{=}CH_3$) (4.4 g, 22 mmol), and **2a** ($R{=}CH_3$) (1.8 g, 10 mmol). Distillation gave the following fractions: bp 65—95 °C/25 Torr [a mixture of **4'a** and **3a** ($Y{=}OCH_3$), 1.0 g], bp 103—108 °C/15 Torr [crude **1a** ($Y{=}OCH_3$, $R{=}CH_3$), 4.0 g], bp 119—123 °C/2—3 Torr [crude **2a** ($R{=}CH_3$), 1.6 g], and a tarry resudue (2.8 g).

In the reaction with CM or DM in benzonitrile, the **1a** adduct ($Y{=}OCH_3$, $R{=}C_6H_5$) could be separated by distillation, whereas the **2a** adduct ($R{=}C_6H_5$) was purely isolated from the residual solid by column chromatography [Wakogel, hexane–ether (1:2)].

In GLC analysis, ethyl acetate, *p*-chlorotoluene, *p*-nitrotoluene, and benzophenone were used as internal standards for the estimation of cyclohexene, **4'a** and **3a** ($Y{=}Cl$), **3a** ($Y{=}OCH_3$) and **1a** ($Y{=}OCH_3$, $R{=}CH_3$), and **1a** ($Y{=}OCH_3$, $R{=}C_6H_5$) and **2a** ($R{=}CH_3$) respectively.

The physical properties of the products collected by means of the GLC technique, careful distillation, or recrystallization are as follows: **4'a**[15]: bp 77—78 °C/50 Torr (lit,[9b] bp 158 °C); NMR, $\delta{=}5.9{-}5.4$ (m, 2H), 3.20 (s, 3H), 3.10

(d, 2H), 2.5—1.0 (m, 7H). *trans*-**3a** (Y=Cl): bp 95—97 °C/25 Torr (lit,[17,18] bp 109—113 °C/49 Torr); NMR (100 MHz), $\delta=3.74$ (d of t, $J=4$ and 10 Hz, 1H), 3.50 (d, $J=4$ Hz, 2H), 3.30 (s, 3H), 2.3—1.0 (m, 9H). **3a** (Y=OCH_3): bp 106—108 °C/50 Torr (lit,[9b,18] bp 192—192.5 °C); NMR (100 MHz), $\delta=3.6$—3.0 (m, 3H), 3.30 (s, 6H), 2.2—0.8 (m, 9H). The data on *trans*-**1a** (Y=OCH_3, R=CH_3), **1a** (Y=OCH_3, R=C_6H_5), *trans*-**2a** (R=CH_3), **2a** (R=C_2H_5), **2a** (R=C_6H_5), **2a** (R=*p*-$CH_3C_6H_4$), and **2a** (R=*p*-ClC_6H_4) are given in Table 5.

Hydrolysis of 1a and 2a. When **1a** (Y=OCH_3, R=CH_3) (*ca.* 10 mmol) was heated in 5% NaOH under reflux for 2 h, **2a** (R=CH_3) was obtained in a *ca.* 95% yield. On the other hand, the hydrolysis of **1a** (*ca.* 10 mmol) with 10% HCl under reflux for 6 h afforded almost pure *trans*-**7** in a *ca.* 90% yield. When crude **2a** (R=CH_3) (prepared by the reaction with CM) (*ca.* 10 mmol) was hydrolyzed with 10% HCl under reflux for 6 h, a mixture of *trans*-**7** and *cis*-**8** (9: 1) was obtained in a high yield, whereas the acid-catalyzed hydrolysis of crude **2a** (R=CH_3) (obtained by the reaction with DM) afforded *trans*-7 almost exclusively. *trans*-**7**: bp 87—88 °C/19 Torr; Found (Calcd): C, 66.87 (67.09), H, 11.66 (11.96), N. 9.60 (9.78)%; NMR (100 MHz), $\delta=3.30$ (d, $J=4.5$ Hz, 1H), 3.28 (d, $J=4.5$ Hz, 1H), 3.20 (s, 2H), 2.42 (d of t, $J=4$ and 10 Hz, 1H), 1.36 (s, 2H), 2.0—0.8 (m, 9H). *cis*-**8**: NMR (100 MHz), $\delta=3.25$ (s, 3H), 3.15 (d, $J=4.5$ Hz, 1H), 3.31 (d, $J=4.5$ Hz, 1H), 2.60 (t of t, $J=4$ and 10 Hz, 1H), 1.25 (s, 2H), 2.1—0.7 (m,9H).

Reactions of Other Olefins with CM or DM in Nitriles The reactions were performed analogously to the cyclohexene experiment. The physical properties of the products (other than **1** and **2**, shown in Table 5) from other olefins are given below. *trans*-**4′b** (probably *trans*-1-methoxy-3-heptene): bp 78—79 °C/100 Torr (lit,[18,19] bp 58—59 °C/30 Totr); IR, 965 cm^{-1} (*trans*-CH=CH); NMR, 5.7—5.3 (m, 2H), 3.35 (t, $J=6$ Hz, 2H), 3.30 (s, 3H), 2.5—1.8 (m, 4H), 1.6—1.2 (m, 2H), 0.9 (t, 3H). **3b** (Y=Cl): bp 90—92 °C/23—25 Torr; Found (Calcd): C, 58.99 (58.35), H, 10.95 (10.40)%; NMR, $\delta=4.1-3.8$ (m, 1H), 3.30 (t, $J=5.5$ Hz, 2H), 3.20 (s, 3H), 1.8—1.1 (m, 8H), 0.9 (t, 3H). **3b** (Y=OCH_3): bp 104—105 °C/100 Torr; Found (Calcd): C, 67.12 (67.45), H, 12.77 (12.58)%; NMR, $\delta=3.6$—3.1 (m, 3H), 3.30 (s, 6H), 1.9—1.1 (m, 8H), 0.9 (t, 3H). **3d** (Y=Cl): bp 83—84 °C/3 Torr (lit,[20] bp 100—101.5 °C/6 Torr); NMR, $\delta=7.4$—7.1 (m, 5H), 5.2—4.8 (m, 1H), 3.25 (s, 3H), 3.7—3.2 (m, 2H), 2.4—2.0 (m, 2H). **3d** (Y=OCH_3): bp 105 °C/11 Torr (lit,[90] bp 151 °C/74 Torr); NMR, $\delta=7.4$—7.2 (m, 5H), 4.4—4.1 (m, 1H), 3.30 (s, 3H), 3.20 (s, 3H), 3.6—3.2 (m, 2H), 2.2—1.75 (m, 2H).

We wish to thank Dr. Sakae Uemura, Institute for Chemical Research, Kyoto University, for his helpful discussions of the NMR data.

References

1) L. I. Krimen and D. J. Cota, *Org. React.*, **17**, 246 (1969).

2) F. Boerwinkle and A. Hassner, *Tetrahedron Lett.*, **1968**, 3921.

3) Y. Wada and R. Oda, *Bull. Chem. Soc. Jpn.*, **43**, 2167 (1970).

4) B. Crookes, T. P. Seden, and R. W. Turner, *J. Chem. Soc. Chem. Commun.*, **1968**, 342.

5) W. Theilacker, *Angew. Chem. Int. Ed. Engl.*, **6**, 94 (1967).

6) M. L. Scheinbaum and M. Dines, *J. Org. Chem.*, **36**, 3641 (1971).

7) W. A. Smit, A. V. Semenovsky, V. F. Kucherov, T. N. Chernova, M. Z. Krimer, and O. V. Lubinskaya, *Tetrahedron Lett.*, **1971**, 3101.

8) H. Gross and E. Höft, *Angew. Chem. Int. Ed. Engl.*, **6**, 342 (1967).

9) (a) R. Paul and S. Tchelitcheff, *Bull. Soc. Chim. Fr.*, **1951**, 125; (b) D. C. Dermer and J. J. Hawknis, *J. Am. Chem. Soc.*, **74**, 4595 (1952).

10) J. W. Copenhaver, U. S. Patent, 2677708 (1954) [*Chem. Abster.*, **49**, 1812 (1955)].

11) The minor product, *cis*-**8**, which is believed to be thermodynamically more stable than the *trans*-isomer,[12] may come from the attack of the nitrile on the 3-(methoxymethyl)-cyclohexyl cation formed from isomeric **5a** by a 1,2-hydride shift.

12) *Cf.* E. L. Eliel, N. L. Allinger, S. J. Angyal, and G. A. Morrison, "Conformational Analysis," Interscience Publishers, New York (1965), p. 53.

13) An attempt to elucidate the configuration and conformation of **3a** (Y=OCH_3) by NMR (100 MHz) failed because of an overlapping of the absorptions of the $C\underline{H}(OCH_3)$ and $C\underline{H}_2OCH_3$ protons.

14) S. Winstein, E. Allred, R. Heck, and R. Glick, *Tetrahedron*, **3**, 1 (1958).

15) The structure of the 1: 1 adduct was tentatively assigned as 1-methoxymethyl-1-cyclohexene by Dermer *et al.*,[9b] but our reinvestigation revealed that its structure should be 3- or 4-methoxymethyl-1-cyclohexene, not that of the 1-methoxymethyl isomer (based on its NMR spectral data). Though no decisive data are available at present, the 3-methoxymethyl structure seems more likely, judging from its boiling point (*cf.* the bp of the 4-methoxymethyl isomer,[16] 86—88 °C/100 Torr).

16) L. N. Owen and P. A. Robins, *J. Chem. Soc.*, **1949**, 331

17) S. D. Mekhtiev, B. F. Pishnamazzade, Sh. D. Gasanova, and R. M. Mamedova, *Dokl. Akad. Nauk Az. SSR*, **15**, 1115 (1959) [*Chem. Abstr.*, **54**, 24450 (1960)].

18) No stereochemical assignment was given in the literature cited.

19) A. N. Pudovik and V. I. Nikitina, *Zh. Obshch. Khim.*, **22**, 1553 (1952) [*Chem. Abstr.*, **47**, 8632 (1952)].

20) S. Mamedov and D. N. Khydyrov, *Zh. Obshch. Khim.*, **31**, 3905 (1961) [*Chem. Abstr.*, **57**, 11073 (1962)].