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The Reaction of Olefins with Chloroalkoxyalkanes and Formic Acid in Ether

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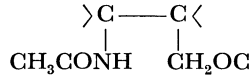
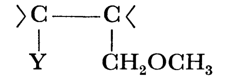
The reaction of olefins with chloromethoxymethane (CMM) and excess formic acid in ether, in the presence of $ZnCl_2$ or $HgCl_2$, afforded mainly four products, 1-chloro- and 1-formyloxy-2-(formyloxymethyl)alkanes, and 3,5-dialkyl-4-chloro- and 3,5-dialkyl-4-(formyloxy)tetrahydropyrans, in various yields. In the case of styrene, the chief products were limited to the former two. Similar products were obtained from 1-chloro-1-ethoxyethane (CEE), but their yields were quite low.

In a previous paper,[1] we reported that the Lewis acid-catalyzed reaction of olefins with chloromethoxymethane(CMM) in acetonitrile gave *N*-[2-(methoxymethyl)alkyl]acetamides (**1**) after hydrolysis. When this reaction was carried out in a mixture of formic acid (a protic and good ionizing solvent) and ether, the expected product, **2** (Y=OCOH), was not formed; instead, two formyloxymethylated products, **3** (or **4**) (Y=Cl and OCOH), were obtained, together with substituted tetrahydropyrans, **5** (Y=Cl and OCOH). This paper will deal with these results.



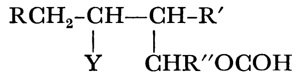
$$\begin{array}{cc} \rangle \mathrm{C} & \!\!-\!\!-\mathrm{C}\langle \\ | & | \\ \mathrm{CH_3CONH} & \mathrm{CH_2OCH_3} \end{array}$$

1



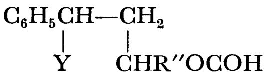
$$\begin{array}{cc} \rangle \mathrm{C} & \!\!-\!\!-\mathrm{C}\langle \\ | & | \\ \mathrm{Y} & \mathrm{CH_2OCH_3} \end{array}$$

2



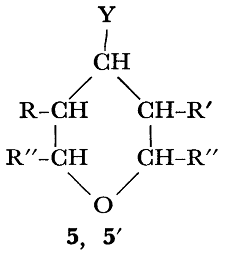
$$\begin{array}{cc} \mathrm{RCH_2\text{-}CH} & \!\!-\mathrm{CH\text{-}R'} \\ | & | \\ \mathrm{Y} & \mathrm{CHR''OCOH} \end{array}$$

3, 3′



$$\begin{array}{cc} \mathrm{C_6H_5CH} & \!\!-\mathrm{CH_2} \\ | & | \\ \mathrm{Y} & \mathrm{CHR''OCOH} \end{array}$$

4, 4′



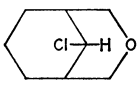
5, 5′

2, **3**—**5** (R″=H), **3′**—**5′** (R″=CH_3): Y=Cl or OCOH
3—**5**, **3′**—**5′** **a**: R, R′=$(CH_2)_3$, **b**: R=C_2H_5, R′=H,
c: R=*n*-C_3H_7, R′=H

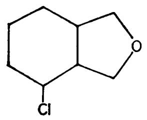
In this connection, it has been reported that the sulfuric acid-catalyzed reaction of olefins with formaldehyde in water or acetic acid (the Prins reaction) affords 1,3-dioxanes and 1,3-diols or their acetates (the homolog of **3** (Y=OCOH)) as the principal products,[2] whereas the reaction of terminal olefins with paraformaldehyde and hydrogen halides in anhydrous media yields mainly 3-alkyl-4-halotetrahydropyrans (correspond to **5** (Y=halogen)).[3]

Results and Discussion

When cyclohexene was allowed to react with CMM and excess formic acid in ether at room temperature for 24 h, in either the presence or absence of a metal chloride, the main distillate from the reaction mixture was found to consist of the following products: *trans*-1-chloro-2-(formyloxymethyl)cyclohexane (**3a**, Y=Cl), *trans*-1-formyloxy-2-(formyloxymethyl)cyclohexane (**3a**, Y=OCOH), and 9-chloro-3-oxabicyclo[3.3.1]nonane (**5a**, Y=Cl), accompanied by a slight amount of probably 9-formyloxy-3-oxabicyclo[3.3.1]nonane (**5a**, Y=OCOH). Besides, small amounts of cyclohexyl chloride and cyclohexyl formate (combined yield, *ca.* 15%) were found in the low-boiling fraction, and some tarry materials remained after distillation. For each of the products purely isolated, the structure was assigned by means of ^1H NMR and elemetal analyses. The presumed 3-oxabicyclo[3.3.1]nonane structure(A) for **5a**(Y=Cl) was confirmed by ^{13}C NMR study. The decoupled spectrum had five signals, as was to be expected from its symmetrical structure (the δ values are given in Table 3). If **5a** (Y=Cl) had the isomeric 3-oxabicyclo[4.3.0]nonane structure(B), it should give rise to eight separate signals.



A



B

In the reaction without any additive, the total yield of **3a**(Y=Cl and OCOH) and **5a**(Y=Cl) was *ca.* 30%; a considerable amount of unreacted cyclohexene was also recovered. However, when $ZnCl_2$, $HgCl_2$, or $SnCl_4$ (1/4—1 eqiv.) was added to the reaction system, the total yield was improved up to around 50%, with the proportion of **3a**(Y=Cl) increasing considerably, and most of the cyclohexene was consumed. For equimolar addition, the above chlorides were nearly equal in their ability to carry Cl^-, but $ZnCl_2$ exhibited a slightly inferior tendency, and $AlCl_3$ and $BF_3 \cdot Et_2O$ were almost ineffective. When the ether solvent was replaced by dichloromethane, the yields of **3a** (Y=Cl and OCOH) decreased significantly. Further, when acetic acid (a less-ionizing solvent) was used in the place of formic acid, the reaction was quite slow and did not afford any of the products expected under the given conditions.

In cases where 1-hexene or styrene was used as an olefin component, the product distributions varied significantly. In the presence of $ZnCl_2$ or $HgCl_2$, the

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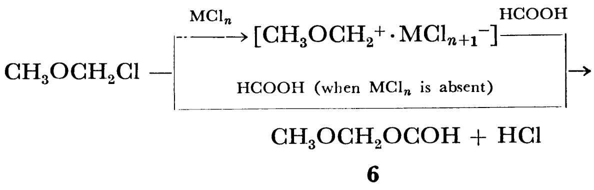
products **3c** and **5c** (Y=Cl and OCOH for both) were obtained from 1-hexene in a total yield of 55%. On the other hand, styrene, which does not contain an allylic H atom, gave mainly **4** (Y=Cl and OCOH) in a good total yield, without any accompanying tetrahydropyran derivatives, as had been expected. Here, the ring size for **5c** (Y=Cl and OCOH) was assigned mainly on the basis of the C–O–C stretching frequency (1090 cm^{-1} for both) in the IR spectrum, which corresponds fairly well to that exhibited by tetrahydropyran (1090 cm^{-1}), but not to that of tetrahydrofuran (1070 cm^{-1}).[4] Although both **5c**(Y=Cl and OCOH) were chromatographically (by GLC) homogeneous, the decoupled ^{13}C NMR spectrum of **5c** (Y=Cl) exhibited two similar sets of eight signals which can be assigned to a mixture of 4-chloro-3-propyltetrahydropyran and its isomer, probably 3-(1-chlorobutyl)tetrahydrofuran, in the ratio of *ca.* 4:1, while the ^{13}C analysis of **5c**(Y=OCOH) showed the existence of 4-formyloxy-3-propyltetrahydropyran alone (see Table 3). It should also be noted that the ratio of **3**(Y=Cl)+**3**(Y=OCOH)/**5**(Y=Cl)+**5** (Y=OCOH) varied from *ca.* 85/15 to *ca.* 35/65 as the olefin component was changed from cyclohexene to 1-hexene. The considerable difficulty in cyclization for the former olefin may be explained by the hindering effect in the ring-closure step (see Eq. 3).

Some typical data on the reaction of olefins with CMM and formic acid are shown in Table 1.

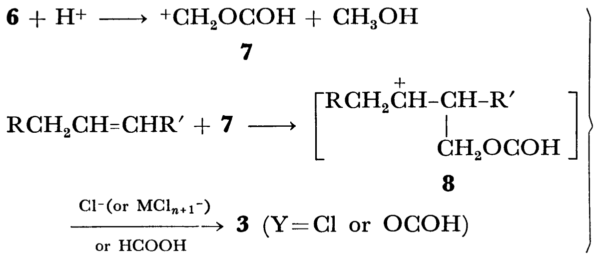
CMM is known to be accessible to the β-chloro-α-methoxymethylation of olefins in the presence of Lewis acids in aprotic solvents.[5] However, the present reaction showed quite a different pattern in which the introduction of a formyloxymethyl group, not a methoxymethyl group, occurred at an olefinic C; this might suggest that the formolysis of CMM leading to **6** is involved at an early stage of the reaction (Eq. 1).



$$CH_3OCH_2Cl \xrightarrow[\text{HCOOH (when } MCl_n \text{ is absent)}]{MCl_n} [CH_3OCH_2^+\cdot MCl_{n+1}^-] \xrightarrow{HCOOH} \underset{\mathbf{6}}{CH_3OCH_2OCOH} + HCl \qquad (1)$$

The formation of cyclohexyl chloride as a by-product and the following experimental result appear to support such a pathway *via* **6**: when an equimolar mixture of cyclohexene and **6** (prepared independently) was treated with HCl in formic acid in the presence of $ZnCl_2$, a mixture of **3a**(Y=Cl and OCOH) and **5a** (Y=Cl) was formed, analogous to the cyclohexene–CMM–formic acid reaction.

The succeeding protolysis of **6** may occur at the more basic ethereal O atom to afford the formyloxymethyl cation (**7**), and the addition of this cation and Cl$^-$ (including MCl_{n+1}^-) or formic acid to olefins results in the formation of **3**(Y=Cl or OCOH respectively) (Eq. 2).



$$\left.\begin{array}{l} \mathbf{6} + H^+ \longrightarrow \underset{\mathbf{7}}{{}^+CH_2OCOH} + CH_3OH \\ RCH_2CH{=}CHR' + \mathbf{7} \longrightarrow \underset{\mathbf{8}}{\left[\begin{array}{l} RCH_2\overset{+}{C}H\text{-}CH\text{-}R' \\ \qquad\quad |\\ \qquad\quad CH_2OCOH \end{array}\right]} \\ \xrightarrow[\text{or HCOOH}]{Cl^-(\text{or } MCl_{n+1}^-)} \mathbf{3}\ (Y{=}Cl \text{ or } OCOH) \end{array}\right\} \qquad (2)$$

Here, **3**(Y=Cl and OCOH) might be formed by another route, *via* the 1:1 olefin–CMM adduct (**2**, Y=Cl). However, such a possibility can be ruled out for the following reason: if **2**(Y=Cl) undergoes formolysis, the substitution would occur at the secondary C bearing Cl and would give rise to **2**(Y=OCOH),

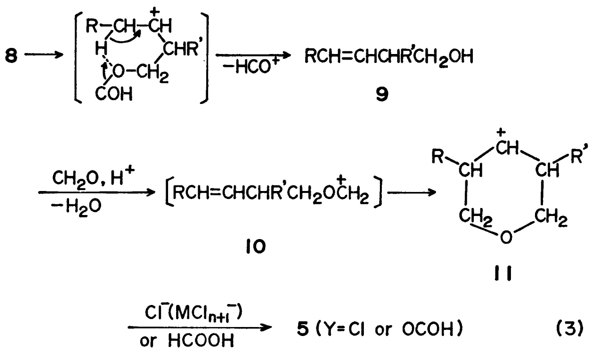
Table 1. Reaction of olefins with CMM and formic acid in ether
Olefin 0.1 mol, CMM 0.1 mol, formic acid 1 mol, ether 45 ml.
Reaction conditions: 20—25 °C, 24 h.

Olefin	Additive (equiv.)	Product and yield (%)[a)			
		3 or **4** (Y=Cl)	**3** or **4** (Y=OCOH)	**5** (Y=Cl)	**5** (Y=OCOH)
Cyclohexene	None	8.9	22.3	2.4	
	$ZnCl_2$(1)	27.2	15.6	8.1	
	$ZnCl_2$(1/2)	26.2	18.7	7.2	
	$ZnCl_2$(1/4)	24.3	19.9	5.5	
	$ZnCl_2$(1/2)[b)	16.7	10.5	7.1	
	$HgCl_2$(1)[c)	27.9	15.4	6.3	
	$SnCl_4$(1/2)	27.8	17.3	8.1	
	$FeCl_3$(1)	21.9	14.7	7.5	
	$AlCl_3$(1/2)	11.7	18.4	2.7	
	$BF_3\cdot Et_2O$(1)	7.4	20.3	3.3	
1-Hexene	$ZnCl_2$(1)	10.5	9.0	21.0[d)	14.7
	$HgCl_2$(1)[c)	11.0	10.0	18.9[d)	13.6
Styrene	$ZnCl_2$(1)	38.2	33.6	0	0

a) Based on olefin (determined by GLC). b) CH_2Cl_2(60 ml) was used as the solvent. c) Experiment on the scale of 1/2. d) A mixture of **5c** (Y=Cl) and its isomer (see Footnote d in Table 3).

not **3**(Y=Cl and OCOH). Moreover, it was proved by a blank experiment that the 1:1 cyclohexene–CMM adduct does not react with formic acid, at least under the given conditions.

A reasonable pathway to tetrahydropyrans **5**(Y=Cl and OCOH) is given below (Eq. 3), in which the route from **9** is essentially the same as that proposed by Stapp:[3)]



(3)

As to the transformation from **8** to **9**, another path involving the deprotonation of **8**, followed by hydrolysis, is possible. However, a separate experiment revealed that, in the cyclohexene–CMM reaction, the use of *dried* formic acid[6)] did not cause any appreciable changes in the yields of all the products; this fact may suggest the participation of a process other than hydrolysis. For the same reason, the formaldehyde, which is required for the conversion of **9** to **10**, may be supposed to be formed by another reaction, such as the acid-catalyzed intramolecular methanolysis of **6** or the splitting of **7** itself, rather than by the acid hydrolysis of CMM or **6**. In view of the moisture-sensitive nature of **6**,[7)] however, it seems to be difficult to rule out completely the possibility of its hydrolysis by external moisture.

The ring closure of the **10** cation may proceed in two ways to afford tetrahydropyran derivatives (*via* **11**) and/or tetrahydrofuran ones. In practice, the former type of product was formed either predominantly or exclusively, as has been described above. A quite similar trend has been observed in some related reactions. For example, the modification of the Prins reaction yields the above type of cyclic ethers as the main or side products, in which tetrahydropyran derivatives are either exclusive or predominant.[3,8)] Further, in the intramolecular acylation of ω-arylalkanoic acids to give cyclic ketones, the fact that six-membered rings are formed in preference to five-membered ones has been demonstrated by several examples.[9)]

Next, the reaction of olefins with 1-chloro-1-ethoxyethane(CEE) was examined under the same conditions as with CMM, but it was rather slow and the yields of products were generally very low (Table 2). Moreover, the ratios of the two formyloxyalkylated products differed from those in the case of CMM. Thus, in the reactions of 1-hexene with CMM and CEE (additive: $ZnCl_2$, 1 equiv.), the **3**(Y=Cl)/**3**(Y=OCOH) and **3'**(Y=Cl)/**3'**(Y=OCOH) ratios were 1.2 and 2.0 respectively, while in those of cyclohexene these ratios were 1.7 and 8.9 respectively. The large difference in the latter system may arise from a severe steric interference between the neighboring 1-(formyloxy)ethyl group of the cation corresponding to **8** and the attacking formic acid molecule (present as a cyclic dimer[11)]).

Experimental

Except for the case of CEE, commercial organic materials were used after distillation. The CEE was prepared from paraaldehyde, ethanol, and HCl,[12)] and was used after distillation. Commercial inorganic materials were used without further purification. The ^1H NMR spectra (in $CDCl_3$) were recorded with a Varian A-60 apparatus and a JEOL MH-100 apparatus. The ^{13}C NMR spectra were recorded on a JEOL FX-100 spectrometer in the pulse Fourier transform mode at 25.15 MHz in $CDCl_3$. The IR spectra were determined with a Hitachi EPI-S2 spectrometer. The GLC analyses were carried out on a Shimadzu 5APTF apparatus, using EGSS-X (30%)-Chromosorb-W(1m) (with N_2 as the carrier gas).

Reactions of Olefins with CMM or CEE and Formic Acid. A typical example is given below. To a stirred mixture of cyclohexene (8.2 g, 0.1 mol), formic acid (46 g, 1 mol), and $ZnCl_2$ (13.6 g, 0.1 mol) in ether (45 ml), CMM (8.0 g, 0.1 mol) was added, drop by drop, at 0—5 °C. The mixture was stirred for 24 h at room temperature, and then it was slowly added to a suspension of $CaCO_3$ (50 g) in water. After this mixture had been stirred for 1 h, ether was added and inorganic precipitate was filtered off. The organic layer separated from the aqueous one was washed with aqueous NaCl and dried over $MgSO_4$,

Table 2. Reaction of olefins with CEE and formic acid in ether
Olefin 0.1 mol, CEE 0.1 mol, formic acid 1 mol, ether 45 ml.
Reaction conditions: 20—25 °C, 24 h.

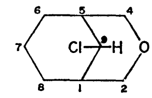
Olefin	Additive (equiv.)	Product and yield (%)[a)]			
		3' or **4'** (Y=Cl)	**3'** or **4'** (Y=OCOH)	**5'** (Y=Cl)	**5'** (Y=OCOH)
Cyclohexene	$ZnCl_2$(1)	8.9	1.0	2.5	
	$SnCl_4$(1/2)	7.0	0.8	1.4	
1-Pentene	$ZnCl_2$(1)	5.8	3.1	6.1	2.5
1-Hexene	$ZnCl_2$(1)	8.0	4.0	5.5	—[b)]
Styrene	$ZnCl_2$(1)	11.5	5.4	0	0[c)]

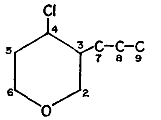
a) Based on olefin (determined by GLC). b) Not determined. c) Other product, $C_6H_5CH_2CH_2CH(CH_3)OCOH$ (29%).[10)]

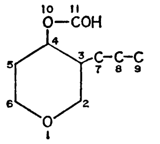
TABLE 3. PHYSICAL PROPERTIES AND ANALYTICAL DATA OF SOME REPRESENTATIVE PRODUCTS

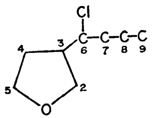
Product	Bp (°C/Torr)	^{1}H- and ^{13}C-NMR, δ (ppm from TMS, in CDCl$_3$)		Found(Calcd) (%)	
				C	H
3a (Y=Cl)[a]	118—120/20	^{1}H	8.05(s, 1H), 4.28(d, 2H), 3.77(d of t, 1H), 2.4—1.0(m, 9H)	54.86 (54.40)	7.67 (7.42)
3a (Y=OCOH)[a]	131—133/20	^{1}H	8.05(s, 2H), 4.80(d of t, 1H), 4.15(d, 2H), 2.3—0.9(m, 9H)	58.46 (58.05)	7.88 (7.58)
5a (Y=Cl)	132/70[b]	^{1}H	4.42(s, 1H), 4.04(d, 2H), 3.72(d, 2H), 2.3—1.4(m, 8H)	59.34 (59.81)	8.18 (8.15)
		^{13}C[c]	73.8(t, C-2,4), 63.8(d, C-9), 37.5(d, C-1,5), 24.2(t, C-6,8), 21.0(t, C-7)		
3c (Y=Cl)	98—100/13.5	^{1}H	8.00(s, 1H), 4.32(t, 2H), 3.98(m, 1H), 2.2—0.7(m, 11H)	54.44 (53.78)	8.98 (8.46)
3c (Y=OCOH)	84—86/2	^{1}H	8.05(s, 2H), 5.05(m, 1H), 4.20(t, 2H), 2.1—0.7(m, 11H)	57.77 (57.43)	8.88 (8.57)
5c (Y=Cl)[d]	199—201[e]	^{1}H	4.12—3.60(m, 3H), 3.6—3.0(m, 2H), 2.2—0.8(m, 10H)	60.10 (59.07)	9.89 (9.29)
		^{13}C[c]	71.0(t, C-2), 66.9(t, C-6), 61.9(d, C-4), 44.8(d, C-3), 36.6(t, C-5), 31.8(t, C-7), 19.8(t, C-8), 14.2(q, C-9)		
5c (Y=OCOH)[a]	108—109/18	^{1}H	8.06(s, 1H), 4.80(d of t, 1H), 4.1—3.8(m, 2H), 3.6—3.0(m, 2H), 2.2—0.8(m, 10H)	63.39 (62.76)	8.72 (9.37)
		^{13}C[c]	160.5(d, C-11), 73.6(d, C-4), 70.0(t, C-2), 65.7(t, C-6), 40.6(d, C-3), 31.3(t, C-5), 30.7(t, C-7), 19.9(t, C-8), 14.2(q, C-9)		
4 (Y=Cl)	122—124/9	^{1}H	8.05(s, 1H), 7.7—7.0(m, 5H), 5.05(t, 1H), 4.30(t, 2H), 2.40(q, 2H)	60.08 (60.46)	5.58 (5.58)
4 (Y=OCOH)	137/7	^{1}H	8.00(s, 2H), 7.4—7.1(m, 5H), 5.95(t, 1H), 4.15(t, 2H), 2.25(q, 2H)	63.66 (63.45)	6.02 (5.81)
3′a (Y=Cl)	—[f]	^{1}H	8.05(s, 1H), 5.50(q, 1H), 4.0—3.5(m, 1H), 2.4—1.4(m, 9H), 1.4—1.1(m, 3H)	58.08 (56.69)	8.25 (7.93)
3′a (Y=OCOH)	—[f]	^{1}H	8.05(s, 2H), 5.6—4.6(m, 2H), 2.4—0.7(m, 12H)	60.60 (59.99)	8.63 (8.04)
5′a (Y=Cl)	—[f]	^{1}H	4.38(s, 1H), 4.05—3.60(m, 2H), 2.3—1.4 (m, 8H), 1.22(d, 6H)	64.07 (63.65)	9.20 (9.08)
4′ (Y=Cl)	—[f]	^{1}H	7.95(s, 1H), 7.4—7.1(m, 5H), 5.5—4.6 (m, 2H), 2.6—1.9(m, 2H), 1.32(d, 3H)	62.63 (62.11)	6.23 (6.16)
4′ (Y=OCOH)	—[f]	^{1}H	8.02(s, 2H), 7.6—7.2(m, 5H), 5.92(t, 1H), 5.4—4.8(m, 1H), 2.6—1.8(m, 2H), 1.25(d, 3H)	65.72 (64.85)	6.61 (6.35)

a) *trans*-Isomer. b) Lit, 147 °C/110 Torr. [N. P. Volynskii, G. D. Galpern, and A. B. Urin, *Zh. Org. Khim.*, **2**, 1043 (1966); *Chem. Abstr.*, **65**, 15306 (1966)]. c) The numbering of C atoms is shown below. d) A mixture of **5c** (Y=Cl) and its isomer, probably 3-(1-chlorobutyl)tetrahydrofuran, in an approximate ratio of 4:1. The δ values (in ^{13}C NMR) of the isomer[c]: 67.1(t, C-2), 62.5(t, C-5), 60.8(d, C-6), 40.8(d, C-3), 30.8(t, C-4), 34.7(t, C-7), 19.3(t, C-8), 14.1(q, C-9). e) Lit,[3] 91—95 °C/15 Torr. f) Because of its small quantity, the bp could not be determined.









and most of the solvent was evaporated. Subsequent GLC analysis of the residue, using diphenylmethane as the internal standard, showed the presence of **5a** (Y=Cl) (1.3 g, 8.1 mmol) **3a** (Y=Cl) (4.8 g, 27.2 mmol), probably **5a** (Y=OCOH) (*ca.* 0.3 g), and **3a** (Y=OCOH) (2.9 g, 15.6 mmol). Each compound, except for **5a** (Y=OCOH), was isolated in an analytically pure state by duplicate distillation. The configuration and conformation of **3a** (Y=Cl and OCOH) were deduced from the splittings of the C$\underline{\underline{\mathrm{H}}}$Cl and C$\underline{\underline{\mathrm{H}}}$(OCOH) protons respectively in the ^{1}H NMR (100 MHz) spectrum, which indicate these protons are in an axial position, coupled strongly to two adjacent axial protons (δ=3.77, d of t, for C$\underline{\underline{\mathrm{H}}}$Cl; 4.80, d of t, for C$\underline{\underline{\mathrm{H}}}$OCOH; and J=4 and 10 Hz for both).

In cases where the complete separation of the products by distillation was difficult, the analytically pure compounds were isolated from the corresponding raw distillates by column chromatography [Wakolgel, hexane–ether (5—10:1), petroleum ether–ether (10—20:1), or hexane–dichloromethane (20:1)].

The NMR spectra and analytical data of pure products satisfied all the given structures. Some representative data are given in Table 3.

*Reaction of Cyclohexene with Methoxymethyl Formate (**6**) and Formic Acid in the Presence of ZnCl$_2$ and HCl.* The formate, **6**, was prepared from CMM and (HCOO)$_2$Pb.[13] Into a stirred mixture of cyclohexene (4.1 g, 50 mmol), formic acid (23 g, 0.5 mol), **6** (4.5 g, 50 mmol), and $ZnCl_2$ (6.8 g, 50 mmol) in ether (23 ml), dry HCl (*ca.* 2 g, 50 mmol) was introduced at -10—-20 °C. The mixture was then kept for 24 h at room temperature under stirring. The work-up procedure was the same as above. Subsequent GLC analysis revealed the formation of **3a** (Y=Cl and OCOH) and **5a** (Y=Cl) (an approximate molar ratio, 11:4:5; total yield, *ca.* 35%).

Attempted Formolysis of 1-Chloro-2-(methoxymethyl)cyclohexane (1:1 Cyclohexene–CMM Adduct). The adduct was prepared by the reported method (in CS_2; cat., $ZnCl_2$).[14] To a stirred suspension of $ZnCl_2$ (6.8 g, 50 mmol) and formic acid (23 g, 0.5 mol) in ether (23 ml), the above adduct (8.1 g, 50 mmol) was added slowly, and then the mixture was stirred for 24 h at room temperature. GLC analysis after the usual work-up procedure showed that only the unreacted adduct was present.

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