Cationic Oligomerization of 1-Hexene Catalyzed by EtAlCl₂–Chloroacetic Acid Complexes

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Synopsis

Lower oligomers (dimer to tetramer) of 1-hexene were obtained in high yield (65 wt %) with a new cationic complex catalyst, $EtAlCl_2$—CCl_3CO_2H, in n-hexane at 70°C, trimer being the major product. A strong oxo acid, CF_3SO_3H, yielded very similar products under the same conditions. Characteristics of the 1-hexene oligomerization by these two catalysts were the high selectivity for dimers to tetramers and the absence of cracking of the product. In contrast, $EtAlCl_2$ or $AlCl_3$ alone led to oligomers with a higher molecular weight ($\sim 10^3$) and a broad molecular weight distribution, the structure of which was very complicated because of extensive cracking of products. A series of $EtAlCl_2$—chloroacetic acid ($CCl_nH_{3-n}CO_2H$, $n = 0$–3) complexes were also examined as catalysts. The yield of dimer to tetramer increased with increasing acidity of the chloroacetic acids. The mechanism of the 1-hexene oligomerization with these complex catalysts was discussed on the basis of the structure of product oligomers.

INTRODUCTION

Cationic oligomerization of α-olefins has drawn great interest in industry because of the versatile use of α-olefin oligomers and the ready availability of the starting materials. Current requirement for the α-olefin oligomerization is control of the structure, molecular weight, and molecular weight distribution (MWD) of the products. Such control cannot be achieved with conventional catalysts (usually $AlCl_3$ and alkyl aluminum chlorides) which, though very active towards α-olefins, induce extensive cracking and isomerization of the products and thus result in ill-defined oligomers with complex structures and broad MWD.[1,2]

In our recent studies on cationic oligomerization of aromatic olefins (e.g., styrenes),[3,4] we have found that oxygen-containing protonic acids are quite selective catalysts for the synthesis of linear unsaturated dimers. These so-called oxo-acid catalysts include CF_3SO_3H, p-$CH_3C_6H_4SO_3H$, and $AcClO_4$, and the nucleophilic, oxygen-containing counterions derived from them play a critical role in the selective linear dimerization. Metal halides such as BF_3OEt_2 and $EtAlCl_2$, in contrast, yield higher oligomers ($\overline{M}_n \sim 10^3$) with saturated (cyclic) end groups. These results suggest that careful selection of catalysts (namely counterions) may enable one to control the structure and MWD of oligomerization products not only for aromatic olefins but for α-olefins as well.

This study thus aims at developing selective catalysts for the cationic oligomerization of 1-hexene, a typical α-olefin, to its lower oligomers (dimer to pentamer), having well-defined structures. Extensive search for such catalysts showed that $EtAlCl_2$–chloroacetic acid ($CCl_nH_{3-n}CO_2H$, $n = 1$–3) complexes

are effective for the synthesis of linear 1-hexene oligomers. Importantly, these complex catalysts, as well as CF_3SO_3H and $AcClO_4$, oligomerized 1-hexene without its cracking. A few patients[5] claim that mixtures of $AlCl_3$ and an oxygen-containing compound (ketones, esters, etc.) are superior to $AlCl_3$ alone for preparation of low-molecular-weight α-olefin oligomers; however, no further details of the reactions have been disclosed.

We thus investigated in detail the characteristics of $EtAlCl_2$— chloroacetic acid complexes as oligomerization catalysts with emphasis on comparison with oxo-acid catalysts or $EtAlCl_2$ itself.

EXPERIMENTAL

Materials

Commercial 1-hexene (Wako Chemicals Co.) was purified by distillation over CaH_2. The purity of this monomer was better than 99% (by gas chromatography). Solvents (n-hexane and 1,2-dichloroethane) were washed with aqueous acid and/or alkali solutions and distilled twice over CaH_2 before use. CF_3SO_3H (Sumitomo 3M Co., purity $\geq 98\%$) and $EtAlCl_2$ (Nippon Aluminum Alkyls) were commercially obtained and used without further purification. BF_3OEt_2, $SnCl_4$, and CH_3SO_3H were used after distillation under reduced or atmospheric pressure. $AlCl_3$ was purified by sublimation at 130°C. p-$CH_3C_6H_4SO_3H$, CCl_3CO_2H, CCl_2HCO_2H, $CClH_2CO_2H$, and CH_3CO_2H were dried over P_2O_5 under vacuum at room temperature.

Procedures

Oligomerization was carried out under dry nitrogen in a baked Erlenmeyer flask equipped with a three-way stopcock (moisture level <0.4 mM). Reactions, except for those with $AlCl_3$ catalyst, were initiated by the addition of a catalyst solution to a monomer solution. In the case of $AlCl_3$ catalyst, which is insoluble in either n-hexane or 1,2-dichloroethane, a weighed amount of the catalyst was kept in contact with the solvent for 1 h at the reaction temperature, and to this heterogeneous mixture a monomer solution was added. When oxygen-containing compounds were used as second catalyst components for $AlCl_3$ or $EtAlCl_2$ (see Table II), they were added to a monomer solution before addition of the aluminum compounds. The reaction was stopped by addition of isopropanol containing a small amount of aqueous ammonia. The consumption and isomerization of 1-hexene were followed by gas chromatography with cyclohexane as internal standard.

The reaction solution after quenching was washed with aqueous dilute sulfuric acid to remove the catalyst residue, and the products were recovered by evaporating the organic layer under reduced pressure.

The MWD was measured by high-performance liquid chromatography (HLC; JASCO-FLC-A700; JSP-101 polystyrene gel column, 7.2 mm i.d. × 500 mm for analysis, 21.5 mm i.d. × 500 mm for separation; $CHCl_3$ solution, refractive index detector). The structure of the products was determined by ^{13}C nuclear magnetic resonance (NMR) (JEOL NMR FX-90Q, in $CDCl_3$), infrared (Shimadzu IR 27G), and GC-mass (JEOL JMS-D300) spectroscopy.

TABLE I
Oligomerization of 1-Hexene by Acid Catalysts at 70°C for 24 h ($[M]_0 = 0.10M$, $[C]_0 = 10$ mM)

Catalyst	Oligomer yield (%)		Note
	n-hexane	$(CH_2Cl)_2$	
CF_3SO_3H	0	58	Monomer isomerization
CF_3CO_2H	0	0	
p-$CH_3C_6H_4SO_3H$.	0	0	Addition product in n-hexane
CH_3SO_3H	0	0	Addition product in n-hexane
$SnCl_4/H_2O^a$	0	0	
BF_3OEt_2/H_2O^a	0	0	Monomer isomerization
$EtAlCl_2$	41	100	
$AlCl_3$	100	100	

^{a} Catalyst/H_2O = 1/0.5.

RESULTS AND DISCUSSION

Search for Selective Catalysts for 1-Hexene Oligomerization

Oligomerization by Metal Halides or Protonic Acids

1-Hexene was treated with various acid catalysts in n-hexane and 1,2-di-chloroethane at 70°C. Table I shows yields of oligomers obtained after 24 h. With CF_3SO_3H catalyst, the strongest among the oxo acids examined, oligomers were obtained in 1,2-dichloroethane (a polar solvent) with concurrent isomerization of 1-hexene to 2-hexene; only the monomer isomerization took place in n-hexane (a nonpolar solvent). Neither oligomerization nor monomer isomerization occurred with weaker oxo acids (CF_3CO_2H, p-$CH_3C_6H_4SO_3H$, and CH_3SO_3H), but the two sulfonic acids formed adducts with 1-hexene (identified by ^1H NMR) in n-hexane. In contrast, $EtAlCl_2$ and $AlCl_3$ gave oligomers in high yields in both polar and nonpolar solvents; no monomer isomerization took place with these catalysts. $SnCl_4$ and BF_3OEt_2, weaker metal-halide catalysts, could not oligomerize 1-hexene. These trends in catalyst activity are in agreement with those for cationic polymerization of vinyl monomers.

HLC traces for the 1-hexene oligomers produced by CF_3SO_3H, $EtAlCl_2$, and $AlCl_3$ are shown in the top row in Figure 1. The HLC analysis using a refractive
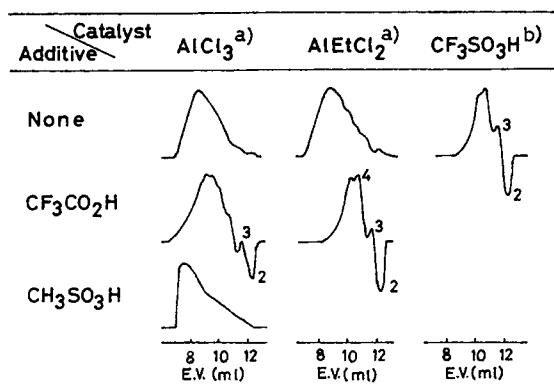

Fig. 1. HLC curves for 1-hexene oligomers obtained by acid catalysts at 70°C. $[M]_0 = 0.10M$, $[C]_0 = [\text{additive}]_0 = 10$ mM, conv 56–100%; solvent: (a) n-hexane; (b) $(CH_2Cl)_2$. Numbers on the peaks indicate the degree of polymerization.

index detector can give accurate yields of oligo(1-hexenes) higher than pentamer. However, quantities of lower oligomers (dimer to tetramer) cannot be determined by HLC because of the strong dependence of their refractive indices on the degree of polymerization. This difficulty is typically indicated by the negative HLC peaks in Figure 1. These lower oligomers were, therefore, determined separately by gas chromatography (*vide infra*).

In the oligomerization with CF_3SO_3H, only dimers to tetramers were obtained in 1,2-dichloroethane. On the other hand, $EtAlCl_2$ and $AlCl_3$ gave higher oligomers with a broad MWD ($\overline{M}_n \simeq 1500$) in both 1,2-dichloroethane and *n*-hexane. No difference in MWD was detected between the oligomers obtained with $EtAlCl_2$ and $AlCl_3$.

Oligomerization by Binary Complexes between $AlCl_3$ or $EtAlCl_2$ and Weak Organic Acids

The oligomerization of 1-hexene by $AlCl_3$ or $EtAlCl_2$ was carried out in the presence of oxo acids (CF_3CO_2H and CH_3SO_3H). Table II and Figure 1 show yields and MWDs, respectively, of the products obtained in *n*-hexane at 70°C after 24 h. These oxo acids alone are inactive for the oligomerization of 1-hexene under these conditions. In these experiments the organic acids were added in advance to a monomer solution in the absence of $AlCl_3$ or $EtAlCl_2$ catalyst (see Experimental). When they were premixed with $AlCl_3$ or $EtAlCl_2$ prior to initiation, yields of oligomers decreased. This decrease of the yields by premixing catalyst components was more pronounced with $EtAlCl_2$ than with $AlCl_3$.

As Figure 1 shows, the effect of additives on the MWD of the products is remarkable. The addition of CF_3CO_2H clearly increased the contents of lower oligomers (dimer to tetramer) (Figure 1), while retaining high yields (Table II), and thus decreased the number-average molecular weights ($\overline{M}_n$) of the products. For example, $\overline{M}_n = 1,500$ with $AlCl_3$ or $EtAlCl_2$; 600 with $AlCl_3$—CF_3CO_2H; and 330 with $EtAlCl_2$—CF_3CO_2H.

The products obtained with these complex catalysts, especially with $EtAlCl_2$—CF_3CO_2H, had a very similar MWD to that obtained with CF_3SO_3H alone. This fact suggests that the weak oxo acid (CF_3CO_2H) interacts with the aluminum compounds to form oxygen-containing complex counterions which are similar in nature to those derived from a strong oxo acid (e.g., CF_3SO_3H).

CH_3SO_3H, a stronger oxo acid than CF_3CO_2H, affected little the MWD of the products, but reduced yields probably by forming an inactive adduct with 1-hexene (*vide supra*). Carbonyl compounds inhibited oligomerization of 1-hexene completely.

TABLE II
Effect of Additives on Yield of 1-Hexene Oligomers Obtained by $AlCl_3$ and $EtAlCl_2$ in *n*-hexane at 70°C for 24 h ($[M]_0 = 0.10M$, $[C]_0 = [\text{additive}]_0 = 10$ mM)

Additive	Yield (%)	
	$AlCl_3$	$EtAlCl_2$
None	100	41
CF_3CO_2H	100	35
CH_3SO_3H	56	0

Oligomerization by EtAlCl$_2$—Chloroacetic Acid Complexes

The above-described results suggest that EtAlCl$_2$–weak oxo acid complex systems are effective catalysts for preparing low-molecular-weight oligomers of 1-hexene. Therefore, we then examined in detail EtAlCl$_2$–chloroacetic acid (CCl$_n$H$_{3-n}$CO$_2$H, n = 0–3) complexes as catalysts.

Effect of the Acidity of Chloroacetic Acids

Figure 2 shows the time courses of the 1-hexene oligomerization with EtAlCl$_2$ in conjunction with a series of chloroacetic acids (equimolar with EtAlCl$_2$) in n-hexane at 70°C. Separate experimetns showed that these acids alone can neither oligomerize nor add to 1-hexene under similar conditions. The rate of polymerization decreased with a decrease in the acidity of the carboxylic acids, and the monomer was not consumed at all in the presence of CH$_3$CO$_2$H.

Added CCl$_3$CO$_2$H or CCl$_2$HCO$_2$H induced the isomerization of 1-hexene to 2-hexene (dashed lines, Fig. 2), which was absent in the reaction with EtAlCl$_2$ alone (Table I). Note that CF$_3$SO$_3$H alone also promoted the monomer isomerization (Table I).

The MWD of 1-hexene oligomers obtained as above are shown in Figure 3. Table III lists compositions of these oligomers. The contents of dimer to tetramer were determined by gas chromatography; those of higher oligomers (n ≥ 5) were obtained from HLC traces with refractive index detection (*vide supra*).

The molecular weight of the products obtained in the presence of chloroacetic acids decreased systematically with increasing acidity of the additives. For instance, the M_n of the product with EtAlCl$_2$ alone was ca. 1,500, whereas that with EtAlCl$_2$—CClH$_2$CO$_2$H catalyst was ca. 1,000 (peak molecular weight of the HLC trace). The yield of oligomers lower than tetramer in turn increased in the following order: none (~0%) ≈ CClH$_2$CO$_2$H (≲1%) ≪ CCl$_2$HCO$_2$H (44%) < CCl$_3$CO$_2$H (65%). It should also be noted that the MWD of the oligomers formed by EtAlCl$_2$—CCl$_3$CO$_2$H catalyst is strikingly similar to that with CF$_3$SO$_3$H; both catalysts yielded dimer or trimer as the main product.

In 1,2-dichloroethane, a polar solvent, added chloroacetic acids affected neither the reaction rate nor the MWD of the products.
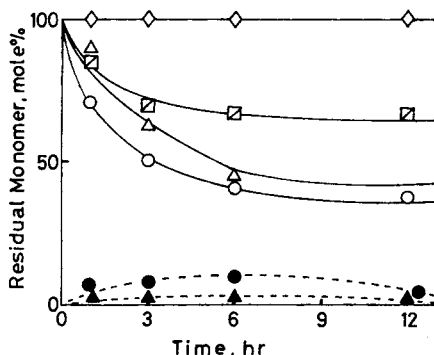
Fig. 2. Time courses of the oligomerization of 1-hexene with EtAlCl$_2$–chloroacetic acid complexes in n-hexane at 70°C. [M]$_0$ = 1.0M, [EtAlCl$_2$]$_0$ = [CCl$_n$H$_{3-n}$CO$_2$H]$_0$ = 30 mM): (——) consumption of 1-hexene; (- - -) concurrent formation of 2-hexene. Catalyst: (○, ●) EtAlCl$_2$—CCl$_3$CO$_2$H; (△, ▲) EtAlCl$_2$—CCl$_2$HCO$_2$H; (▨) EtAlCl$_2$—CClH$_2$CO$_2$H; (◇) EtAlCl$_2$—CH$_3$CO$_2$H.
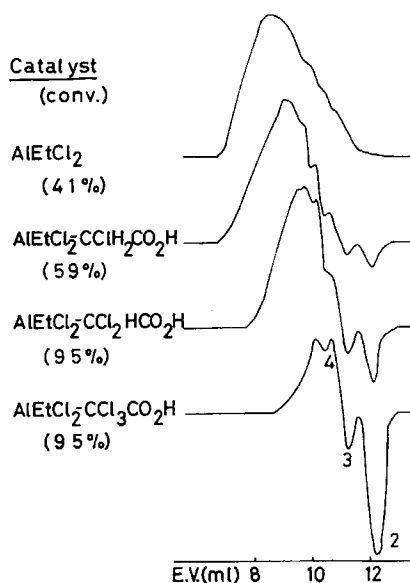
Fig. 3. HLC curves for 1-hexene oligomers obtained by EtAlCl$_2$–chloroacetic acid complexes in n-hexane at 70°C ([M]$_0$ = 1.0M, [EtAlCl$_2$]$_0$ = [CCl$_n$H$_{3-n}$CO$_2$H]$_0$ = 30 mM).

Possible interaction between EtAlCl$_2$ and chloroacetic acids was studied by infrared spectroscopy. When equimolar amounts of EtAlCl$_2$ and CCl$_3$CO$_2$H were mixed in n-hexane at room temperature, the carbonyl stretching band of CCl$_3$CO$_2$H appeared at 1630 cm^{-1}, clearly shifting from 1750 cm^{-1} in the absence of EtAlCl$_2$. This shift indicates that EtAlCl$_2$ is coordinated by the carbonyl group of the acid.[6] Infrared spectra of equimolar mixture of EtAlCl$_2$ and CCl$_2$HCO$_2$H or CClH$_2$CO$_2$H in n-hexane could not be obtained, because precipitates formed at room temperature. However, the formation of the precipitates does indicate interaction between EtAlCl$_2$ and these acids.

Effect of Reagent Concentrations

The results described in preceding section show that EtAlCl$_2$—CCl$_3$CO$_2$H complex is the best catalyst for the synthesis of low-molecular-weight oligomers of 1-hexene. With this catalyst, therefore, effects of reaction conditions on 1-hexene oligomerization were investigated in detail. Table IV shows the effects of the catalyst composition ([CCl$_3$CO$_2$H]/[EtAlCl$_2$] ratio) and the initial monomer concentration ([M]$_0$) on the MWD of product oligomers.

TABLE III
Composition of 1-Hexene Oligomers Obtained by EtAlCl$_2$–Chloroacetic Acid Complexes[a]

Catalyst	Oligomer (wt %)[b]			
	$n = 2$	3	4	≥5
EtAlCl$_2$	<1	<1	<1	>99
EtAlCl$_2$—CClH$_2$CO$_2$H	<1	<1	<1	99
EtAlCl$_2$—CCl$_2$HCO$_2$H	3	17	24	56
EtAlCl$_2$—CCl$_3$CO$_2$H	18	37	10	35

[a] Reaction conditions are shown in Figure 3.

[b] Determined by gas chromatography.

TABLE IV
Effect of Reagent Concentrations on Composition of 1-Hexene Oligomers Obtained by EtAlCl$_2$—
CCl$_3$CO$_2$H Catalyst in n-Hexane at 70°C

No.	[M]$_0$ (M)	[EtAlCl$_2$]/[CCl$_3$CO$_2$H] (mM/mM)	Conv (%)	Oligomer (wt %)[a]			
				$n = 2$	3	4	≥ 5
1	1.0	30/3	99	3	10	15	72
2	0.1	30/30	79	40	13	10	37
3	1.0	30/30	95	18	37	10	35
4	3.0	30/30	92	8	24	26	42

[a] Determined by gas chromatography.

When EtAlCl$_2$ was in excess of CCl$_3$CO$_2$H ([CCl$_3$CO$_2$H]/[EtAlCl$_2$] = 0.1; no. 1), the combined yield of dimer to tetramer was only 28%, but the yield increased to 65% with an equimolar mixture of EtAlCl$_2$ and CCl$_3$CO$_2$H (no. 3), the main product being trimers. The product composition no longer changed at higher [CCl$_3$CO$_2$H]/[EtAlCl$_2$] ratios. Thus, at least an equimolar amount of CCl$_3$CO$_2$H with EtAlCl$_2$ is necessary to modify the nature of EtAlCl$_2$ catalyst.

The effect of the monomer concentration is remarkable, as Table IV shows (nos. 2–4). Although the combined yield of dimer to tetramer remained almost unchanged (58–63%) with varying [M]$_0$, the relative amounts of these lower oligomers depended on [M]$_0$. The dimer content was highest (40%) at the lowest [M]$_0$ (0.10M) and trimers and tetramers increased with increasing [M]$_0$.

Effect of Reaction Temperature

Figure 4 and Table V show, respectively, the HLC traces and the composition of the oligomers obtained at 30–70°C with EtAlCl$_2$—CCl$_3$CO$_2$H complex in n-hexane. The products obtained at 50°C and 70°C consisted of 42–65% lower oligomers (dimer to tetramer), but these oligomers were scarcely produced at
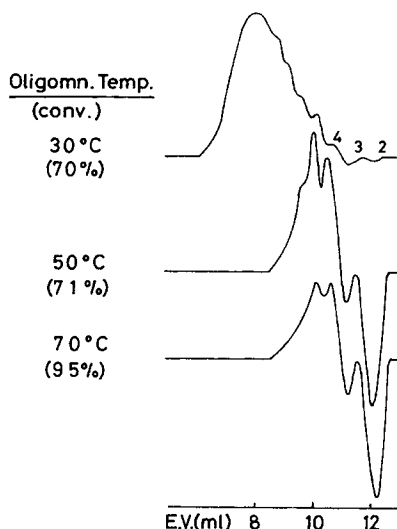

Fig. 4. Effect of temperature on the MWD of 1-hexene oligomers obtained by EtAlCl$_2$—CCl$_3$CO$_2$H catalyst in n-hexane ([M]$_0$ = 1.0M, [EtAlCl$_2$]$_0$ = [CCl$_3$CO$_2$H]$_0$ = 30 mM).

TABLE V
Effect of Temperature on Composition of 1-Hexene Oligomers Obtained by EtAlCl$_2$—CCl$_3$CO$_2$H Catalyst[a]

	Oligomer (wt %)[b]			
Temp	$n = 2$	3	4	≥ 5
30°C	<1	<1	<1	>98
50°C	3	16	23	58
70°C	18	37	10	35

[a] Reaction conditions are shown in Figure 4.

[b] Determined by gas chromatography.

30°C. The product at this temperature had a high molecular weight ($\overline{M}_n = 1,500$) and a broad MWD similar to that of the product obtained with EtAlCl$_2$ alone at 70°C (cf. Fig. 1). EtAlCl$_2$—CCl$_3$CO$_2$H catalyst aged at 70°C for 5 h in n-hexane and one aged at room temperature otherwise under the same conditions gave products having nearly the same MWD. The position of the carbonyl band (1650 cm^{-1}) of an equimolar EtAlCl$_2$/CCl$_3$CO$_2$H mixture remained unchanged before and after aging at 70°C in n-hexane for 5 h. These facts indicate that the interaction between EtAlCl$_2$ and CCl$_3$CO$_2$H does not depend on the temperature and length of aging.

Structure of the Oligomers

Figure 5 shows GC–MS analysis of the 1-hexene oligomers obtained with CF$_3$SO$_3$H, EtAlCl$_2$, and EtAlCl$_2$—CCl$_3$CO$_2$H complex. The numbers on the peaks in Figure 5 indicate the carbon number of each fraction. The CF$_3$SO$_3$H and EtAlCl$_2$—CCl$_3$CO$_2$H complex produced selectively lower oligomers [C$_{12}$ (dimer), C$_{18}$ (trimer), and C$_{24}$ (tetramer) hydrocarbons] without any byproducts having similar carbon numbers. This result agrees with the composition data (by GC) given in Table III, and confirms the absence of cracking in the oligomerization by the two catalysts. On the other hand, the oligomers obtained with

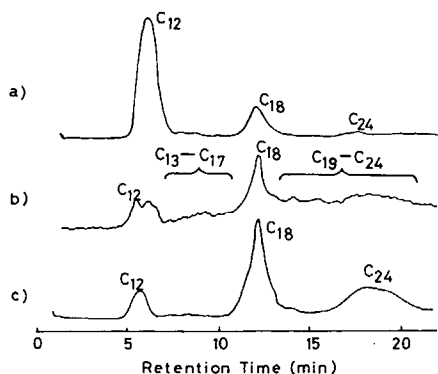Fig. 5. GC–MS analysis of lower oligomers of 1-hexene obtained at 70°C ([M]$_0$ = 1.0M). (a) [CF$_3$SO$_3$H]$_0$ = 30 mM in (CH$_2$Cl)$_2$; (b) [EtAlCl$_2$]$_0$ = 30 mM in n-hexane; (c) [EtAlCl$_2$]$_0$ = [CCl$_3$CO$_2$H]$_0$ = 30 mM in n-hexane.

EtAlCl$_2$ consisted of hydrocarbons having all carbon numbers from 12 to 24, indicating the presence of extensive side reactions such as cracking and rearrangement.[7]

The dimer obtained with CF$_3$SO$_3$H was separated by HLC and analyzed by ^{13}C–NMR spectroscopy (Fig. 6). The observed ^{13}C chemical shifts of the methyl groups (10–20 ppm) were compared with the calculated ones by the method of Lindeman and Adams.[8] Corno et al. have recently investigated the structure of cationically obtained olefin oligomers in the same way.[9] The two signals between 10 and 12 ppm are attributable to the methyl carbons of terminal ethyl (CH$_3$CH$_2$—) groups (calcd: 11.36 ppm). The presence of the ethyl groups means involvement of 2-hexene in the oligomerization (*vide infra*). The peaks between 19 and 20 ppm are assigned to the methyl carbons of CH$_3$CH< groups (calcd: 19.63 ppm). The most intense signals of the spectrum appeared at 14.0 and 14.3 ppm, and can be assigned to the methyl carbons of *n*-butyl (calcd: 13.86 ppm) and *n*-propyl (calcd: 14.35 ppm) groups, respectively. Thus, the calculated chemical shifts for methyl carbons agreed well with the observed values. The presence of *n*-butyl and *n*-propyl units was also confirmed by mass spectroscopy (*M/e* = 41, 55, and 126).

The infrared spectrum of the dimer showed an absorption at 970 cm^{-1}, attributable to the *trans* double bond; absorptions due to a trisubstituted double bond (840–790 cm^{-1}) were absent.

From these results it was concluded that the dimer fraction obtained with CF$_3$SO$_3$H is a mixture of isomers (IV, V, IX, X) produced through the two paths shown in Scheme A on the following page.

Path (1) is simple dimerization of 1-hexene (I) via the protonated 1-hexene cation (II) to give dimers IV and V. Path (2) involves 2-hexene (VI) formed by proton elimination from cation II. The protonated 2-hexene cation (VII), which may form from either II (by hydride transfer) or VI (by protonation), then reacts with 1-hexene to yield dimers IX and X. The reason why cations II and VII do not attack 2-hexene (VI) is the steric hindrance in VI. The ^{13}C–NMR peak intensity ratio of the two methyl signals at 10–12 ppm (CH$_3$CH$_2$—; IX and X) ansd 19–20 ppm (CH$_3$CH<; IV and V) indicates that the dimerization via path (1) is more frequent than that via path (2). The trimer and tetramer fractions produced
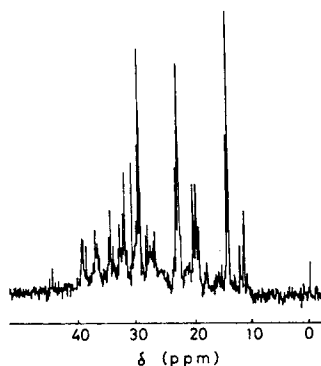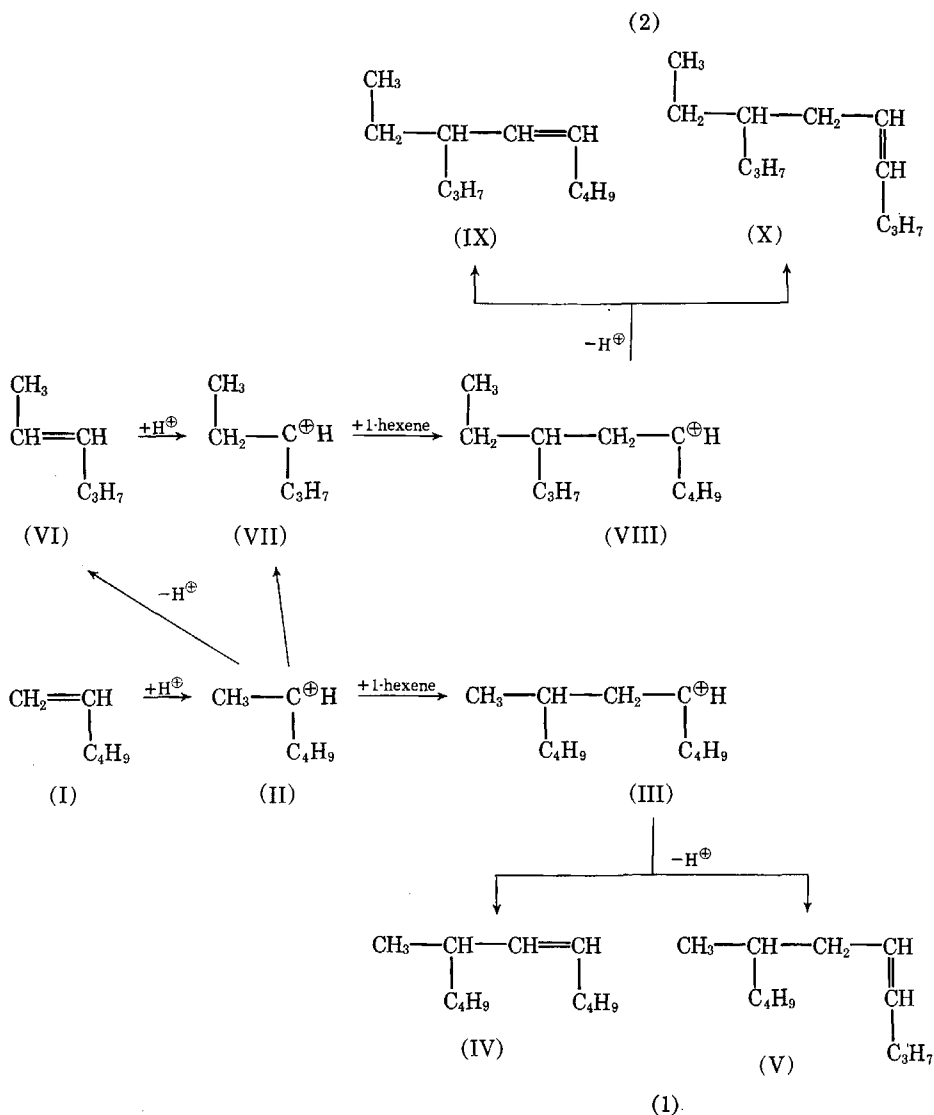

Fig. 6. ^{13}C–NMR spectrum of a dimer fraction obtained by CF$_3$SO$_3$H in (CH$_2$Cl)$_2$ at 70°C.

(2)

$$
\begin{array}{cc}
\begin{array}{c}
CH_3 \\
| \\
CH_2-CH-CH=CH \\
\quad\quad | \quad\quad\quad | \\
\quad\quad C_3H_7 \quad\quad C_4H_9 \\
\text{(IX)}
\end{array}
&
\begin{array}{c}
CH_3 \\
| \\
CH_2-CH-CH_2-CH \\
\quad\quad | \quad\quad\quad\quad \| \\
\quad\quad C_3H_7 \quad\quad\quad CH \\
\quad\quad\quad\quad\quad\quad\quad | \\
\quad\quad\quad\quad\quad\quad\quad C_3H_7 \\
\text{(X)}
\end{array}
\end{array}
$$

$-H^{\oplus}$

$$
\begin{array}{ccc}
\begin{array}{c}
CH_3 \\
| \\
CH=CH \\
\quad | \\
\quad C_3H_7 \\
\text{(VI)}
\end{array}
& \xrightarrow{+H^{\oplus}} &
\begin{array}{c}
CH_3 \\
| \\
CH_2-C^{\oplus}H \\
\quad\quad | \\
\quad\quad C_3H_7 \\
\text{(VII)}
\end{array}
\xrightarrow{+1\text{-hexene}}
\begin{array}{c}
CH_3 \\
| \\
CH_2-CH-CH_2-C^{\oplus}H \\
\quad\quad | \quad\quad\quad\quad | \\
\quad\quad C_3H_7 \quad\quad\quad C_4H_9 \\
\text{(VIII)}
\end{array}
\end{array}
$$

$-H^{\oplus}$

$$
\begin{array}{ccc}
\begin{array}{c}
CH_2=CH \\
\quad\quad | \\
\quad\quad C_4H_9 \\
\text{(I)}
\end{array}
& \xrightarrow{+H^{\oplus}} &
\begin{array}{c}
CH_3-C^{\oplus}H \\
\quad\quad | \\
\quad\quad C_4H_9 \\
\text{(II)}
\end{array}
\xrightarrow{+1\text{-hexene}}
\begin{array}{c}
CH_3-CH-CH_2-C^{\oplus}H \\
\quad\quad | \quad\quad\quad\quad | \\
\quad\quad C_4H_9 \quad\quad\quad C_4H_9 \\
\text{(III)}
\end{array}
\end{array}
$$

$-H^{\oplus}$

$$
\begin{array}{cc}
\begin{array}{c}
CH_3-CH-CH=CH \\
\quad\quad | \quad\quad\quad\quad | \\
\quad\quad C_4H_9 \quad\quad\quad C_4H_9 \\
\text{(IV)}
\end{array}
&
\begin{array}{c}
CH_3-CH-CH_2-CH \\
\quad\quad | \quad\quad\quad\quad \| \\
\quad\quad C_4H_9 \quad\quad\quad CH \\
\quad\quad\quad\quad\quad\quad\quad | \\
\quad\quad\quad\quad\quad\quad\quad C_3H_7 \\
\text{(V)}
\end{array}
\end{array}
$$

(1)

Scheme A.

by CF_3SO_3H were also separated and found by ^{13}C–NMR analysis to have the same end group as dimers IV and V or IX and X.

IR, ^{13}C–NMR, and GC–MS analyses showed that the products obtained with $EtAlCl_2$—CCl_3CO_2H complex have the same structure as those with CF_3SO_3H. This supports that $EtAlCl_2$—CCl_3CO_2H complex is quite similar in nature to strong oxo acids, although trimers were produced more than dimers by the complex catalyst.

The structure of the products obtained with $EtAlCl_2$ alone were too complicated to be determined.

In conclusion, $EtAlCl_2$—CCl_3CO_2H complex was found to be a convenient catalyst for α-olefin oligomerization and acts similarly to CF_3SO_3H or $AcClO_4$. One of the practical advantages of this complex catalyst is that it does not contain

perfluorinated alkyl and perchlorate groups that require expensive and cumbersome post-treatment of catalyst residues.   Moreover, with a series of Et-AlCl$_2$—chloroacetic acid complexes, the MWD of the products can be controlled by changing the acidity of the added carboxylic acids.   These results indicate that the nucleophilicity of a counterion produced from a catalyst greatly affects the cationic oligomerization of α-olefins.

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