

Selective Dimerization of Diisobutylene by Oxo Acids: Synthesis of Isobutylene Tetramer

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Synopsis

Isobutylene tetramers (IB₄) were obtained in high yield by the cationic dimerization of commercial diisobutylene (DIB) (2,4,4-trimethyl-1-pentene with isomeric impurities) with CF₃SO₃H or CH₃COClO₄ as catalyst. The best IB₄ yields (80–90%) were achieved at 0–30°C in nonpolar solvents (*n*-hexane and CCl₄). The major components in the IB₄ produced under these conditions were 2,2,6,6,8,8-hexamethyl-4-methylenonane (8) and 2,2,4,6,6,8,8-heptamethyl-4-nonene (9) that arose via simple linear dimerization of DIB. The yield of IB₄ was almost independent of the monomer concentration ranging from 10 to 50 vol % at 0°C, but decreased at higher temperatures (≥50°C) or in a polar solvent [(CH₂Cl)₂] because of the formation of higher oligomers and side reactions such as cracking. A Lewis acid catalyst (AlEtCl₂) resulted in a very complex mixture of C₁₂–C₂₀ hydrocarbons at 0°C in CCl₄; the yield of IB₄ was less than 40%. The catalytic difference between oxo acids and metal halides is discussed.

INTRODUCTION

The selective synthesis of trimers (IB₃) or tetramers (IB₄) of isobutylene is industrially interesting because these oligomers are useful as solvents or additives. Although mixtures of IB₃ and IB₄ can be obtained by the cationic oligomerization of isobutylene by sulfuric acid¹ and ion exchange resin,² it has been difficult to prepare IB₃ or IB₄ selectively in high yield.

Another approach to the synthesis of IB₄ may be dimerization of diisobutylene (DIB), which can propagate no further than the dimer stage because of steric hindrance. In the presence of a Lewis acid (AlCl₃, etc.), however, DIB undergoes not only dimerization but side reactions such as cracking and isomerization.³ These side reactions have rendered cationic DIB dimerization complicated and nonselective.³ On the other hand, using pure DIB in conjunction with weaker Lewis acids (AlR₂Cl or AlR₃, R = CH₃, C₂H₅), Kennedy and Rengachary have obtained DIB dimers (isomeric mixtures of IB₄) in high yield at low temperatures below –30°C.³ Kennedy's work is mostly focused on model studies of the transfer and termination in isobutylene polymerization by Lewis acids.

In the course of our oligomerization studies with oxo acid catalysts (oxygen-containing protonic acids and their derivatives),⁴ we have been interested in the practical aspects of DIB dimerization. DIB is industrially supplied as a mixture of 2,4,4-trimethyl-1-pentene, and several other C₃ alkenes (see Fig. 1). The main object of this study is to prepare IB₄ selectively from such commercial DIB (containing isomeric impurities) with oxo-acid catalysts (e.g., CF₃SO₃H). These catalysts are known to be particularly effective for selective linear dimerization as demonstrated with styrene and related monomers.⁴ The DIB dimerization was carried out at relatively high temperature (0–70°C) to achieve industrially attractive processes.

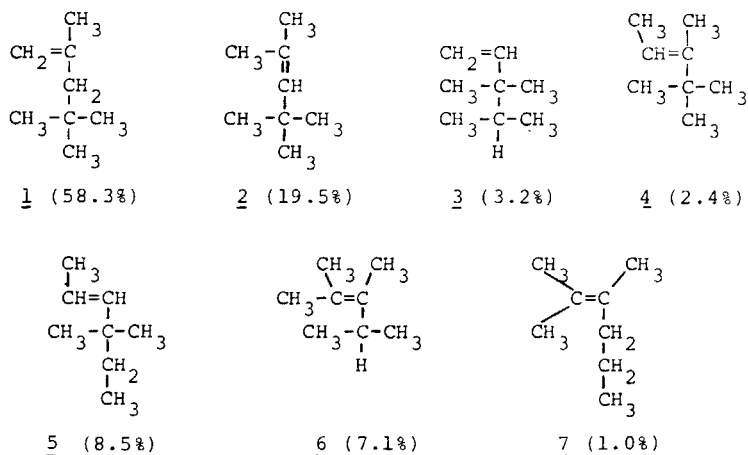


Fig. 1. Composition of the starting material used in this work.

EXPERIMENTAL

Materials

Commercial DIB mixture was distilled over CaH_2 . Gas-mass spectroscopic analysis showed that the DIB consisted of 2,4,4-trimethyl-1-pentene (1, 58.3%), 2,4,4-trimethyl-2-pentene (2, 19.5%), and minor C_8 alkenes (3–7) [Figs. 1 and 2(a)]; saturated hydrocarbons and other impurities were not detected. Commercial 1 and 2 (Wako Chemicals Co., purity $\geq 99\%$) were distilled over CaH_2 .

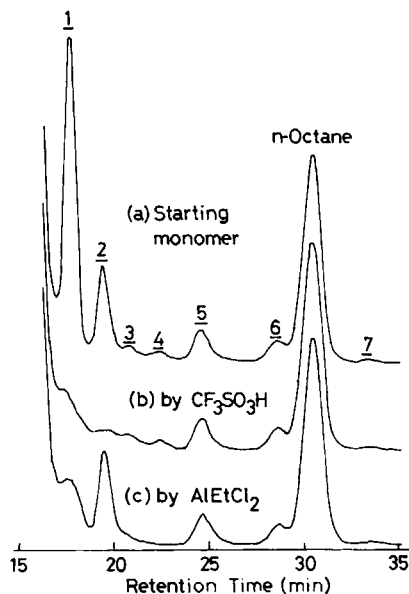


Fig. 2. Gas chromatograms for the starting material (a) and the residual monomers (b, c) recovered after 24 h in the reactions by $\text{CF}_3\text{SO}_3\text{H}$ and AlEtCl_2 in CCl_4 at 0°C ($[\text{M}]_0 = 10 \text{ vol } \%$, $[\text{C}]_0 = 10 \text{ mM}$). Numbers on the peaks indicate the monomers shown in Figure 1.

The distillate was used as monomer without further fractionation. Solvents were washed with aqueous acid and/or alkali solutions and distilled at least twice over CaH_2 before use. Commercial $\text{CF}_3\text{SO}_3\text{H}$ (Sumitomo 3M Co., purity $\geq 98\%$) and AlEtCl_2 (Wako Chemicals Co., purity $\geq 98\%$) were used without further purification. $\text{CH}_3\text{COCIO}_4$,⁵ *p*-toluenesulfonic acid,⁶ and poly(styrenesulfonic acid) (Amberlyst 15)⁶ were obtained, as described elsewhere.

Procedures

Oligomerization was carried out in an Erlenmeyer flask equipped with a three-way cock under a dry nitrogen atmosphere. The reaction was initiated by addition of a catalyst solution into a monomer solution. In this procedure the concentration of water in the reaction mixture was less than 0.3 mM (by the Karl-Fischer titration). After a certain interval the reaction was stopped by addition of methanol containing a small amount of aqueous ammonia. The extent of monomer consumption was determined by gas chromatography (GC) (column: Silicon DC 550, 5 m \times 3 mm id; oven temperature 80°C; *n*-octane as internal standard).

The molecular weight distribution (MWD) was measured by high performance liquid chromatography (HLC) for higher oligomers ($\geq \text{IB}_4$) and by GC for lower oligomers ($\leq \text{IB}_4$) under the following conditions: HLC, JASCO TRIROTAR chromatograph; JSP-101 polystyrene gel column, 500 mm \times 21.5 mm id; chloroform solution, refractive index detector; GC, Silicone SE-30 column, 2 m \times 3 mm id; oven temperature, 120°C. The MWD was determined also by fractionation using the same HLC instrument. At the outlet of the column, fractions (0.75 mL each) of eluate were collected in small vials, and after evaporation of volatiles in vacuo, the weight of oligomers in each fraction was measured. ^{13}C — and ^1H —NMR spectra were measured on a JEDL-FX90Q spectrometer in CDCl_3 solution. GC-mass spectra were obtained on a JEOL JMS-D300 spectrometer (ionization volt, 70 eV; ionization current, 300 μA ; ion multiplier, 1.10 kV; column, Silicon SE-30, 2 m \times 3 mm id). IR spectra were measured on a Shimadzu IR-117 spectrometer.

RESULTS AND DISCUSSION

Time Course of DIB Oligomerization

The DIB containing several C_8 alkenes (Fig. 1) was oligomerized with an oxo acid ($\text{CF}_3\text{SO}_3\text{H}$) and a Lewis acid (AlEtCl_2) in CCl_4 solvent at 0°C. Figure 2 shows the gas chromatograms of the residual monomers recovered after 24 h. With $\text{CF}_3\text{SO}_3\text{H}$ catalyst, 1 and 2 disappeared rapidly but 3–7 remained unreacted. The rates of consumption of 1 and 2 were almost the same (ca. 90% in 1 h under the conditions shown in Fig. 2). With AlEtCl_2 , on the other hand, 1 was oligomerized whereas 2 was scarcely consumed; 3 and 4, minor components in the starting monomer mixture, also reacted. This catalytic difference between $\text{CF}_3\text{SO}_3\text{H}$ and AlEtCl_2 will be discussed later.

Molecular Weight Distribution of the Products

Effect of Catalysts

Figure 3 shows the MWDs of the products obtained by $\text{CF}_3\text{SO}_3\text{H}$ and AlEtCl_2 in CCl_4 solvent at 0°C ($[\text{M}]_0 = 10 \text{ vol } \%$). The full lines indicate the MWDs determined by HLC with a refractive index detector; the histograms in broken line show the MWDs obtained by fractionation (see Experimental). The numbers on the peaks indicate the degree of polymerization based on the isobutylene unit (e.g., $n = 4$ for IB_4). The MWDs measured by the two methods were in good agreement in the molecular weight region higher than ~ 200 ($n \geq 4$). However, the MWD in the lower molecular weight region ($\leq \text{IB}_3$) was difficult to evaluate accurately by both methods because (i) refractive indices of oligomers in this region depend strongly on the degree of polymerization as exemplified by the negative peak at elution volume 90 mL (corresponding to IB_3) and (ii) these lower oligomers were too volatile to be isolate quantitatively for gravimetric analysis in the fractionation. Therefore, the lower oligomers were analyzed by GC=MS spectroscopy (Fig. 4).

In the oligomerization with $\text{CF}_3\text{SO}_3\text{H}$, IB_4 was produced in high yield ($\geq 85\%$) with a small amount of higher oligomers, as shown in Figure 3(a). A trace amount of C_{12} and C_{13} hydrocarbons (less than 4%) was also detected by GC=MS analysis [Fig. 4(a)]. Figure 4(a) further shows that the IB_4 (C_{16}) consists of six isomers.

AlEtCl_2 catalyst gave a product with a broad MWD [Fig. 3(b)]. The yield of IB_4 ca. 40% and much smaller than that obtained by $\text{CF}_3\text{SO}_3\text{H}$. GC=MS analysis revealed the presence of hydrocarbons having all carbon numbers from 12 to 20 [Fig. 4(b)]. The formation of C_{12} and C_{20} hydrocarbons, probably IB_3 and IB_5 , respectively, may be explained in terms of the depolymerization of DIB to isobutylene. In addition, the broad MWD extending in the C_{12} – C_{20} region indicates extensive side reaction such as cracking of DIB or its oligomers.

In the oxo-acid-catalyzed oligomerization in a nonpolar solvent, the propagating carbocation should be a nondissociated tight ion pair with a nucleophilic

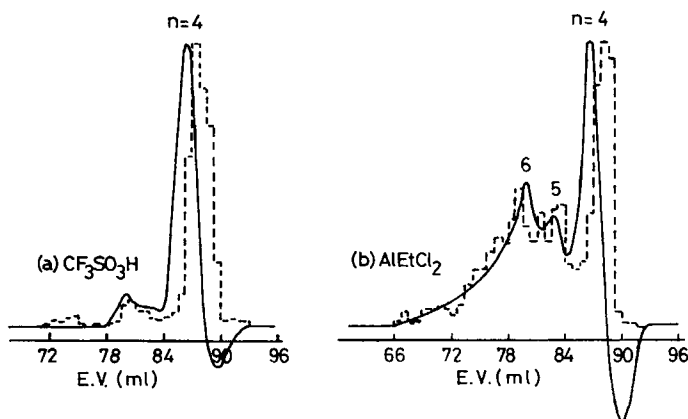


Fig. 3. MWD of DIB oligomers obtained by $\text{CF}_3\text{SO}_3\text{H}$ (a) and AlEtCl_2 (b) under the condition of Figure 2. (—) Determined by HLC with a refractive index detector; (---) by fractionation (see Experimental).

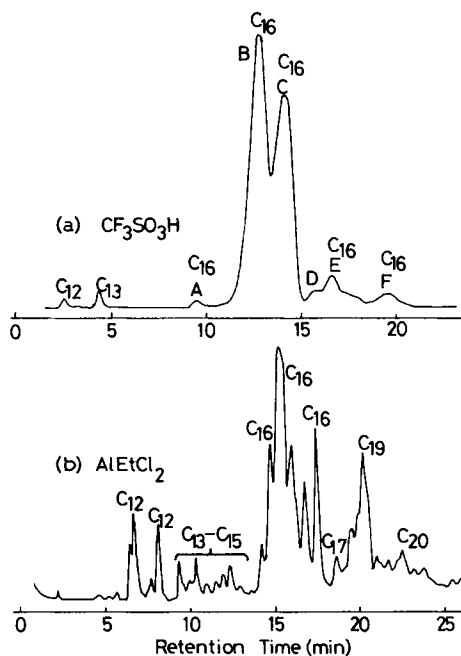


Fig. 4. GC=MS analysis of lower oligomers of DIB obtained by $\text{CF}_3\text{SO}_3\text{H}$ (a) and AlEtCl_2 (b). As to the reaction conditions, see Figure 2.

oxo-acid counteranion.⁴ Therefore, addition of monomer to the carbocation (propagation) is suppressed and β -proton elimination (chain transfer) is in turn promoted to form DIB dimer (IB_4) in high yield.

Oligomerizations of DIB catalyzed by oxo acids other than $\text{CF}_3\text{SO}_3\text{H}$ were also investigated in CCl_4 at 0°C . The yields of IB_4 with three catalysts were as follows: $\text{CH}_3\text{COCIO}_4$, $\sim 70\%$; poly(styrenesulfonic acid) (Amberlyst 15), $\sim 50\%$; *p*-toluenesulfonic acid, none (no reaction). The solid polymeric oxo acid (Amberlyst 15) yielded IB_4 and higher oligomers only; IB_3 was not produced. Thus $\text{CF}_3\text{SO}_3\text{H}$, giving $>85\%$ yield of IB_4 under the same conditions, is the most effective oxo acid for the synthesis of IB_4 .

Effect of Reaction Conditions in the Dimerization by $\text{CF}_3\text{SO}_3\text{H}$

The MWDs of the products obtained with $\text{CF}_3\text{SO}_3\text{H}$ under various conditions are shown in Figure 5 (measured by HLC with a refractive index detector). Table I lists the IB_3/IB_4 ratios determined by GC.

In nonpolar solvents such as *n*-hexane and CCl_4 , IB_4 was obtained predominantly ($\geq 85\%$) and IB_3 was scarcely formed (Table I). Higher oligomers and IB_3 increased in the products obtained in a polar solvent $[(\text{CH}_2\text{Cl})_2]$. The yield of IB_4 was almost independent of the initial monomer concentrations ($[\text{M}]_0$) in the range of 10–50 vol % in CCl_4 at 0°C . On the other hand, reaction temperature greatly affected the composition of the products, especially the IB_3/IB_4 ratios. The contents of IB_3 and higher oligomers increased at higher temperatures.

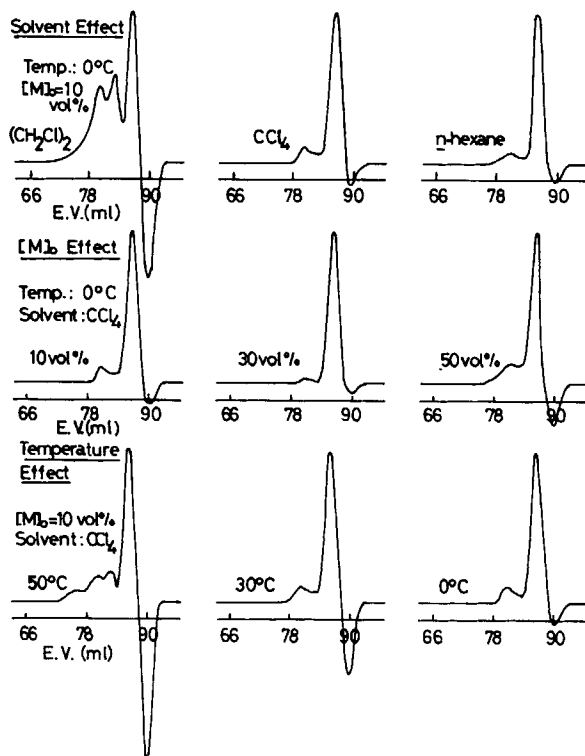


Fig. 5. Effect of reaction conditions on the MWD of products obtained by $\text{CF}_3\text{SO}_3\text{H}$. The MWD was determined by HLC with refractive index detection.

These results show that IB_4 can be conveniently prepared in high yield with $\text{CF}_3\text{SO}_3\text{H}$ catalyst in nonpolar solvents at temperatures between 0°C to 30°C .

TABLE I
 IB_3/IB_4 Ratios for DIB Oligomers Produced by $\text{CF}_3\text{SO}_3\text{H}$ under Various Reaction Conditions
 ($[\text{CF}_3\text{SO}_3\text{H}]_0 = 10 \text{ mM}$)

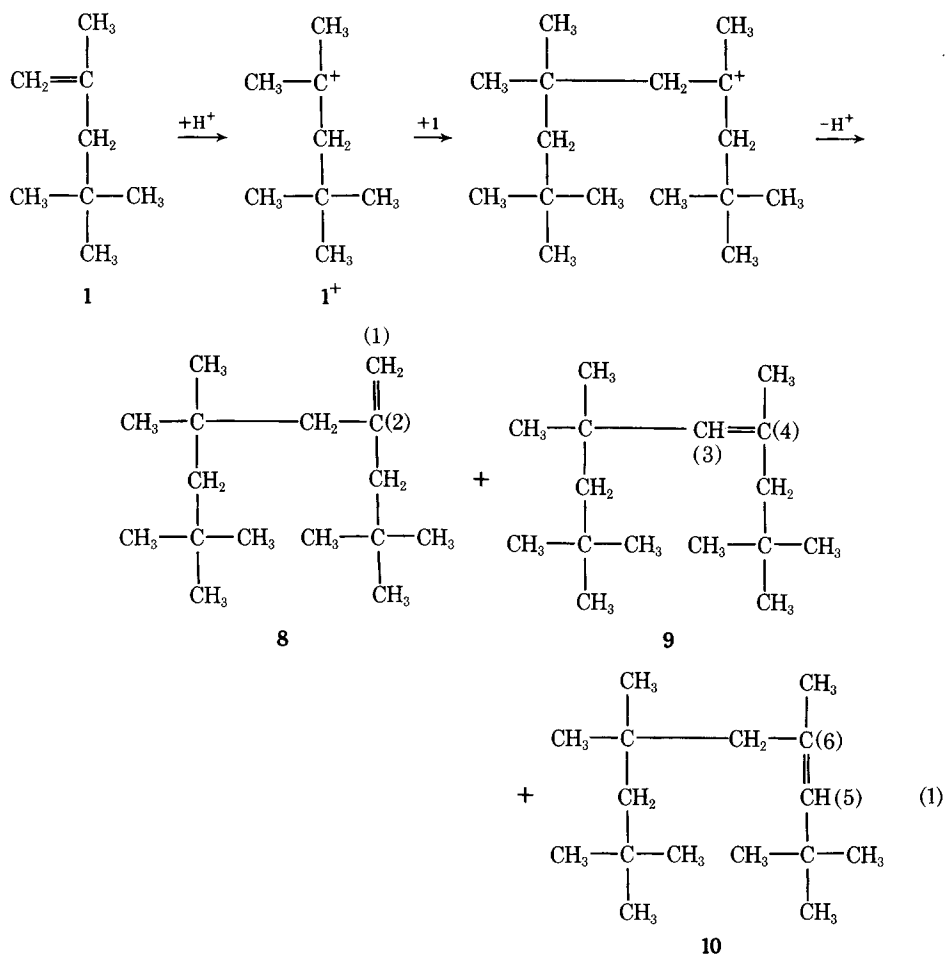
	Solvent	Temperature ($^\circ\text{C}$)	$[\text{M}]_0$ (vol %)	$\text{IB}_3/\text{IB}_4^a$
Solvent effect	CCl_4	0	10	0.042
	<i>n</i> -hexane	0	10	0.007
	$(\text{CH}_2\text{Cl})_2$	0	10	0.880
$[\text{M}]_0$ effect	CCl_4	0	10	0.042
	CCl_4	0	30	$\sim 0^b$
	CCl_4	0	50	0.069
Temperature effect	CCl_4	-20	10	0
	CCl_4	0	10	0.042
	CCl_4	30	10	0.048
	CCl_4	50	10	0.419
	CCl_4	70	10	0.760

^a Measured by GC.

^b A trace amount of IB_3 was detected.

Structure of IB₄

IB₄ was isolated from the products by preparative HLC for structural analysis by ¹H= and ¹³C-NMR, IR, and GC=MS spectroscopy. If DIB (1) dimerizes without any side reactions, three unsaturated IB₄, 8-10, will be formed by proton elimination from the IB₄ cation as shown in eq. (1) (geometric isomers were omitted for simplicity):



Although the starting materials contained the seven hydrocarbons (Fig. 1), only the dimerization of 1 [eq. (1)] was considered in our structural analysis for the following reasons: (i) The major component 1 reacted almost quantitatively under our reaction conditions; (ii) 2 was found, as described later, to isomerize to 1 prior to propagation in the presence of CF₃SO₃H; (iii) the minor components, 3-7, did not oligomerize with CF₃SO₃H; and (iv) even in the reaction catalyzed by AlEtCl₂, in which 3 and 4 were consumed, their oligomers should be of very minor importance in the total product.

Structure of IB₄ Obtained by CF₃SO₃H

As shown in Figure 4, the IB₄ fraction produced by CF₃SO₃H in CCl₄ at 0°C was composed of several isomers, two of which, B and C, comprised more than 90%.

Figure 6 shows the ¹³C=NMR spectrum of this IB₄ fraction. Four olefinic resonances were observed between δ 116 and 145 ppm. In the off-resonance experiments, the signal at 116 ppm split into triplet and the one at 139 ppm into doublet; the other two, at 130 and 145 ppm remained singlet. These results indicate that the IB₄ fraction contains two olefinic groups, CH₂=C< and —CH=C<. The IR spectra showed an absorption at 890 cm⁻¹ due to a vinylidene group and the ¹H=NMR spectra also showed signals at δ 4.85 (CH₂=C<) and 5.2 ppm (—CH=C<). The ¹H=NMR and IR data agreed with those observed by Kennedy and Rengachary³ for IB₄ obtained with R₂AlCl catalyst at low temperature.

The ¹³C chemical shifts of the olefinic carbons in 8–10 calculated by the method of Roberts⁷ were compared with the observed values in Table II. The signals at δ=115 and 145 ppm were assigned to carbons 1 and 2 of 8 on the basis of the good agreement between the calculated and observed values. The calculated chemical shifts for C-3 and C-4 of 9 seem to be close to the observed values, but the assignment is not conclusive because similar calculated values were obtained for isomer 10.

The compounds B and C in Figure 4(a) were further analyzed by GC=MS spectroscopy. Table III summarizes the *M/e* values of some characteristic fragments. B and C gave completely different fragment patterns. Table III also shows fragments expected for 8–10 when fragmentation occurs at the allylic position of each olefinic double bond⁸ (see Footnote b, Table III). Comparison of the observed fragments with the hypothetical ones indicates that B can be assigned to 9 and C to 8.

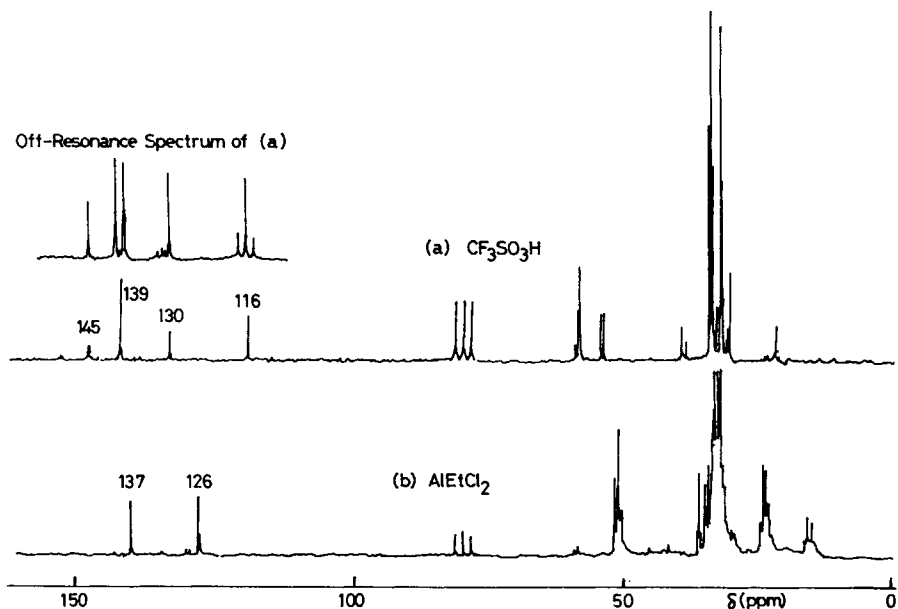


Fig. 6. ¹³C=NMR spectra of IB₄ produced by CF₃SO₃H (a) and AlEtCl₂ (b). As to the reaction conditions, see Figure 2.

TABLE II
¹³C Chemical Shifts of Olefinic Carbons for IB₄ Isomers

Compound ^a	Carbon ^a	Chemical shift (δ , ppm)		Peak multiplicity (off-resonance coupled)
		Calcd	Obd.	
8	{ 1	115.4	116.0	triplet
	{ 2	145.1	145.0	singlet
9	{ 3	142.3	139.1	doublet
	{ 4	129.8	130.3	singlet
10	{ 5	143.8	— ^b	— ^b
	{ 6	128.0	— ^b	— ^b

^a See eq. (1).

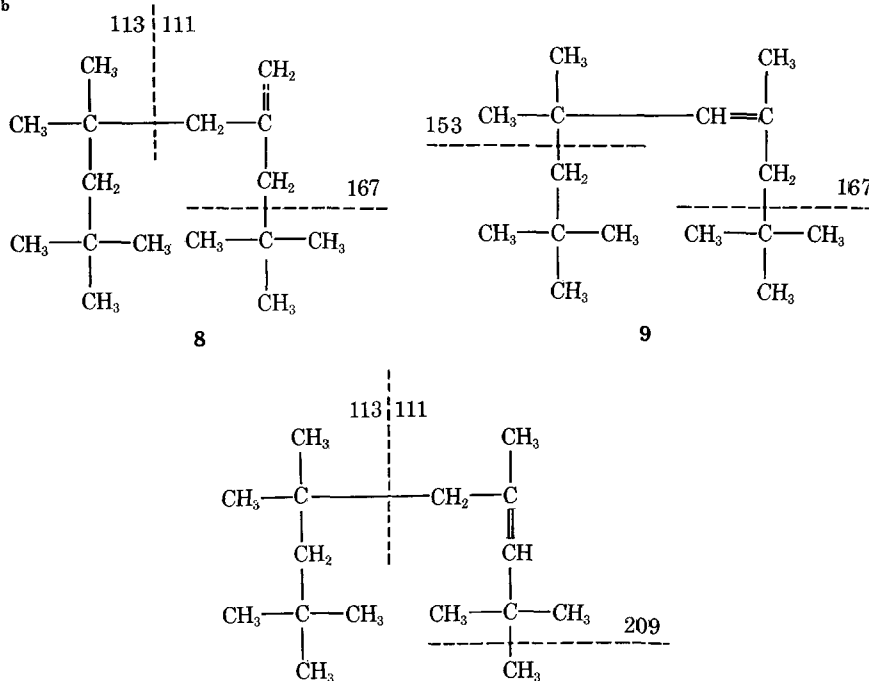
^b Not observed.

From the results mentioned above, it was concluded that the IB₄ produced by CF₃SO₃H consists mainly of 8 and 9. The ratio of 8/9 was 9/11 according to the GC trace given in Figure 4.

 TABLE III
 Mass Spectra of the IB₄ Produced by CF₃SO₃H

Product	<i>M/e</i> (fragment)			
Observed ^a	{ B	224(M ⁺)	168(M ⁺ - C ₄ H ₉ + 1)	153(M ⁺ - C ₅ H ₁₁)
	{ C	224(M ⁺)	168(M ⁺ - C ₄ H ₉ + 1)	111(M ⁺ - C ₈ H ₁₇)
Expected ^b	{ 8	224(M ⁺)	168	113, 111
	{ 9	224(M ⁺)	168	153
	{ 10	224(M ⁺)	209	111

^a Fractions B and C in Figure 4.

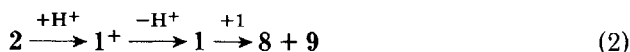
^b


10

Monomer Isomerization of 2 to 1 Catalyzed by CF₃SO₃H

Alkene **2** in the DIB mixture was consumed in the reaction catalyzed by CF₃SO₃H, whereas it remained intact in the presence of AlEtCl₂. To clarify this difference, oligomerizations of pure **1** and **2** by these two catalysts were carried out in CCl₄ at 0°C. Pure **1** gave its oligomers with both CF₃SO₃H and AlEtCl₂ catalysts.

With CF₃SO₃H, pure **2** was rapidly consumed in a few minutes (the full line in Fig. 7). However, GC analysis of the reaction mixture revealed concurrent quantitative formation of isomer **1**; i.e., the rapid consumption of **2** is due to its isomerization to **1** promoted by CF₃SO₃H. The isomerized monomer **1** was then converted into an oligomeric product (the dashed line in Fig. 7). The ¹³C=NMR spectrum of this product agreed with that of the oligomers produced from pure **1**. It is well known that **1**⁺ formed by dehydration of 2,4,4-trimethylpentan-2-ol yields **1** in high yield.⁹ Further, the oligomerization of unstable olefins by an oxo acid often involves isomerization of the monomer to a more stable olefin prior to propagation.¹⁰ Therefore, we concluded that **2** undergoes "monomer-isomerization" oligomerization¹⁰ [eq. (2)] in the presence of CF₃SO₃H:



AlEtCl₂ did not oligomerize and isomerize pure **2**. This result is good agreement with our observation that AlEtCl₂ is incapable of inducing monomer isomerization of unstable olefins.¹⁰

Structure of IB₄ Produced by AlEtCl₂

Figure 4(b) shows the formation of at least seven C₁₆ hydrocarbons with AlEtCl₂ catalyst. The ¹³C=NMR spectrum of the C₁₆ (IB₄) fraction exhibited two olefinic resonances [Fig. 6(b)] whose chemical shifts (δ 126 and 137 ppm) were completely different from those for the IB₄ produced by CF₃SO₃H. The two signals remained singlet on off-resonance coupling. This suggests that the IB₄ produced by AlEtCl₂ is a mixture of tetra-substituted olefins. The GC=MS spectra gave a very complex fragment pattern, indicating that the product is a complicated mixture. Further studies are required to clarify the reaction pathway with AlEtCl₂ catalyst.

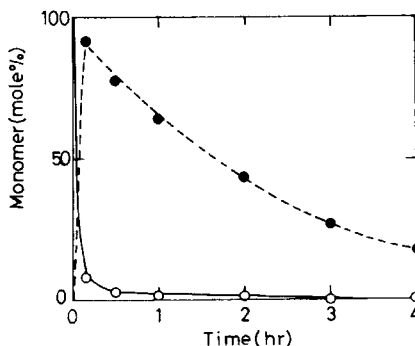


Fig. 7. Time course of the oligomerization of **2** (2,4,4-trimethyl-2-pentene) catalyzed by CF₃SO₃H in CCl₄ at 0°C ([M]₀ = 10 vol %, [C]₀ = 10 mM). (—○—) Consumption of **2**; (---●---) concurrent formation of **1**.

CONCLUSIONS

This work has shown that commercial DIB containing isomeric impurities can be dimerized with $\text{CF}_3\text{SO}_3\text{H}$ and other oxo-acid catalysts near room temperature to give isobutylene tetramers in high yield. The major products are unsaturated C_{16} hydrocarbons (two kinds) formed via simple linear dimerization of DIB.

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