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The Ionic Telomerization of Conjugated Diene Compounds. II. The Solvent Effects on the Cationic Telomerization of Butadiene with Its Hydrochloride

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The telomerizations of butadiene with its hydrochlorides (1-chlorobutene-2 and 3-chlorobutene-1) in several sorts of solvents in the presence of Lewis acids were investigated. Titanium tetrachloride in ethyl bromide has a considerable catalytic ability at low temperatures and gives telomers with higher average molecular weights than ferric chloride and aluminum chloride at almost the same conversions of reaction. On the other hand, antimony pentachloride gives only a small amount of product with lower average molecular weights. The telomerizations in methylene dichloride and chloroform give almost the same amounts of telomers with molecular weights higher somewhat in the former solvent than the latter. The telomerization in toluene gives primarily the products of Friedel-Crafts reaction, and a small amount of telomers of butadiene with crotyl chloride is obtained. The use of ethyl ether, acetonitrile and acetic anhydride as solvents at low temperatures in the presence of ferric chloride affords poor yields of the telomers in contrast to the cases of halogenated hydrocarbons. In ethyl ether, an appreciable amount of telomers is obtained only at the temperatures above 0°C. The telomers thus obtained have a lower average molecular weight and a larger degree of residual unsaturation than the telomers obtained in halogenated hydrocarbons. The use of nitromethane and nitrobenzene as solvents leads to the formation of an amount of telomers smaller a little than halogenated hydrocarbons. There are scarcely observed differences in the compositions of fractions in 1 : 1 adducts of butadiene and its hydrochloride obtained in the various solvents. The infrared spectra of the higher telomers are almost the same each other and it was concluded that the reactions proceed on the same mechanism irrespective of the variation of solvents.

The telomerizations of butadiene with its hydrochlorides in methylene dichloride in the presence of stannic chloride[1] and in ethyl bromide in the presence of ferric chloride and aluminum chloride[2] have been investigated. It was shown that the average molecular weight of the products and the yield of the 1 : 1 adducts depend primarily on the conversion of reaction and the initial ratio of chlorobutene to butadiene. It was also found that the 1, 4 and 1, 2 additions occur, and their proportion varies scarcely with the changes in the reaction conditions.

In this paper, the results of the telomerizations of butadiene with its hydrochlorides in halogenated hydrocarbons and oxygen- and nitrogen-containing solvents in the presence of Lewis acids are described, and the effects of the solvents on the yield and the properties of the resultant telomers are discussed. On the results of the analysis of the telomers by infrared spectra, gas chromatography and the measurement of the amounts of the residual unsaturation in the telomers, the usefullness of the solvents in the telomerizations will be evaluated.

The reaction is cationic, and therefore it is supposed that it is affected by the polarity of the media. Aluminum chloride and ferric chloride are often excessively active and initiate undesirable side reactions. Many of the oxygen- and nitrogen-containing solvents form complexes with Lewis acids which usually result in the decrease in the activity of the catalysts. In such solvents, the reaction of the catalysts with crotyl chloride is probably competitive with the complex formation between the solvents and the catalysts.

Experimental

Chlorobutenes. The preparation and purification of butadiene hydrochlorides, which was used as telogens, were described in the preceeding paper.[2] The product of hydrochlorination of butadiene contained two isomers, 1-chlorobutene-2 (crotyl chloride) and 3-chlorobutene-1 (γ-methyl allyl chloride), and the mixture of them which contained about 80% crotyl chloride was used. It has been confirmed that the two isomers give the same product when they are used as the telogens.[2]

Solvents. Methylene dichloride was washed several times with a dilute sodium carbonate solution and with

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[1] A. A. Petrov, Kh. V. Bal'yan, L. I. Bunina-Krivorukova and T. V. Yakovleva, *Zhur. Obshch. Khim.*, **29**, 1576 (1959).

[2] T. Asahara and H. Kise, This Bulletin, **39**, 2739 (1966).

water, dried on calcium chloride, and distilled. Chloroform was washed several times with a concentrated sulfuric acid, with a 5% sodium hydroxide solution, and with water, dried on calcium chloride, and distilled. Toluene was washed several times with a concentrated sulfuric acid, with a 5% sodium hydroxide solution, and with water, dried on calcium chloride and metallic sodium, then distilled. Ethyl ether was washed several times with a 10% sodium chloride solution, dried on calcium chloride and metallic sodium, then distilled. Acetic anhydride was stood overnight with metallic sodium and distilled. Nitromethane and nitrobenzene of special grade were used without further purification.

Catalysts. Titanium tetrachloride, antimony pentachloride and ferric chloride of the first grade were used without further purification.

Telomerization. The apparatus and the method of the telomerization are described in the previous paper.²⁾ The reactions were stopped by the addition of a small amount of pyridine and then the precipitates of pyridine/catalyst complexes were separated. In acetonitrile, acetic anhydride and nitromethane, the complexes do not precipitate, then the complexes were extracted with water after ether was added to the reaction mixture.

The Analysis of the Telomers. The molecular weight of the products was measured with a Mechrolab vapor pressure osmometer model 301 A. The degree of unsaturation of the telomers was determined by the Wijs method. The infrared spectra of the products were taken with a Hitachi-Perkin-Elmer double-beam grating spectrophotometer model 125. The 1 : 1 adducts of butadiene and crotyl chloride were analyzed by a Hitachi-Perkin-Elmer F-6 gas chromatography with the separation column packed with Diasolid L (Nihon Chromato Kogyo Ltd.), and the liquid phase was carbowax 20 M.

Results and Discussion

Halogenated Hydrocarbons. Titanium tetrachloride and antimony pentachloride in halogenated hydrocarbons were used as the catalyst for the telomerizations of butadiene with crotyl chloride at low temperatures. Titanium tetrachloride has a considerable catalytic ability and gives a fairly good yield of telomer, whereas antimony pentachloride gives only a small amount of telomer (Table 1). The order of the catalytic abilities of the Lewis acids used in the present and the previous studies²⁾ in the halogenated hydrocarbons with nearly the same polarities is shown as follows:

$$FeCl_3 \simeq AlCl_3 > TiCl_4 \gg SbCl_5 > SnCl_4 \simeq BF_3 \cdot OEt_2.$$

It is known that the differences in the catalytic activities of Lewis acids do not always reflect fairly the differences in their acid strength, and the order of catalytic activities differs according to the reactions. The reactions which are catalyzed by Lewis acids and proceeded by way of carbonium ions have been investigated by many workers. Some differences in the activities of Lewis acids are found between the present telomerization and some other reactions. For example, in the racemization of α-phenyl ethylchloride³⁾ and the acylation of toluene⁴⁾ by Lewis acids, ferric chloride and aluminum chloride have the largest catalytic abilities and stannic chloride is more active than titanium tetrachloride. In the isomerization of pinen hydrochloride to bornylchloride,⁵⁾ the catalytic ability of Lewis acids decreases in the order, $SbCl_5 > SnCl_4 > FeCl_3$. It should be noted that these activities of catalysts were evaluated based on the yields of the reaction products. In the telomerization of butadiene with crotyl chloride, the rate of propagation may be affected by the catalyst anions used, and the structure of the chlorides may also bring about some changes in the activities of the catalysts.

Titanium tetrachloride gives the telomers of higher average molecular weights and of lower degrees of unsaturation than ferric chloride at nearly the same conversions of reaction. It is obvious that the catalyst is one of the factors to decide the molecular weight of the telomers. However, the composition of the isomers in the 1 : 1 adducts of butadiene and crotyl chloride are nearly the same from the analysis of gas chromatography, despite of the variation of catalysts, and the higher telomers give also nearly the same infrared spectra.

The telomerizations in three different halogenated hydrocarbons listed in Table 1 afford the telomers which have structures different little from each other. It is concluded from these results that the amounts of 1, 4 and 1, 2 linkages in the telomers are not affected by the variation of catalysts and solvents.

Toluene. The reaction of butadiene with crotyl chloride in toluene in the presence of titanium tetrachloride affords the products which contain benzene nucleus. They were fractionally distilled to three fractions, the amounts and the average molecular weight of which are shown as follows:

Fraction 1: bp 62.2—63.7°C/6.5 mmHg; 35.1%; mol wt, 145.
Fraction 2: bp 98.0—112.4°C/0.5 mmHg; 22.4%; mol wt, 215.
Residual: 42.5%; mol wt, 360.

The infrared spectra of these fractions exhibit characteristic bands of benzene ring (745 and 803 cm^{-1}) and internal C=C double bond (965 cm^{-1}). The band of benzene ring decreases in intensity with the raise of the boiling point of fractions. Fraction 1 was found by elementary analysis and the determination of the molecular weight to be mainly the mixture of butenyl substituted toluenes.

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3) R. Adams, "Organic Reactions," John Wiley & Sons, Inc., New York (1963), p. 854.

4) O. C. Dermer, D. M. Wilson, F. N. Johnson and V. H. Dermer, *J. Am. Chem. Soc.*, **63**, 2881 (1941).

5) H. Meerwein and K. van Emster, *Ber.*, **53**, 1815 (1920).

TABLE 1. THE TELOMERIZATIONS IN HALOGENATED HYDROCARBONS

RCl/BD[a)	S.	S/BD[b)	C.	C/BD[c) $\times 10^2$	Yield %	1 : 1 Adduct, %	Av. mol wt[d)	Unsaturation, %
1.37	EtBr	1.00	$TiCl_4$	0.747	48.0	12.7	654	49.1
1.00	CH_2Cl_2	1.50	$TiCl_4$	1.00	60.9	11.1	782	46.4
1.00	$CHCl_3$	1.50	$TiCl_4$	1.00	57.9	15.7	702	51.1
1.00	Ph-CH_3	1.50	$TiCl_4$	1.00	49.9	—	—	—
1.00	CH_2Cl_2	1.41	$SbCl_5$	1.51	3.8	—	264	50.8

Reaction temperature, −35—−54°C. Reaction time, 4 hr.
a) Molar ratio.
b) Volume ratio.
c) Molar ratio.
d) The average molecular weight of the telomers other than the 1 : 1 adduct.

TABLE 2. THE TELOMERIZATIONS IN THE OXYGEN- AND NITROGEN-CONTAINING SOLVENTS

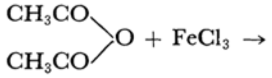
S.	S/BD[a)	C/BD[b) $\times 10^2$	Temp. °C	Time min	Yield %	1 : 1 Adduct, %	Av. mol wt[c)	Unsaturation, %
Et_2O	1.85	2.89	−52	240	0.4	—	—	—
Et_2O	0.781	3.47	12	300	40.6	34.2	279	71.2
Et_2O	0.800	5.00	12	300	65.1	23.3	307	65.8
Et_2O[d)	0.800	5.00	12	300	56.4	30.9	307	61.3
CH_3CN	1.60	1.50	−42	250	~0	—	—	—
CH_3CN	1.23	5.50	14	280	0.6	23.2	254	63.9
Ac_2O	1.39	5.49	−47	240	~0	—	—	—
CH_3NO_2	1.75	3.00	−25	240	29.9	7.5	213	78.8
Ph-NO_2	0.848	0.444	8	240	48.1	36.1	354	62.7
Et_2O+ CH_2Cl_2[e)	1.40	4.00	14	360	5.0	58.3	251	79.1

Catalyst, $FeCl_3$. RCl/BD=1.00 (molar ratio).
a) Volume ratio.
b) Molar ratio.
c) The average molecular weight of the telomers other than the 1 : 1 adduct.
d) RCl/BD=1.50 (molar ratio).
e) Catalyst, $TiCl_4$. The mixed solvent of ethyl ether and dichloromethane in 1 : 1 volume ratio was used.

Only a small amount of the adduct of butadiene with crotyl chloride is contained in the fraction 1. These results indicate that the Friedel-Crafts reaction of toluene with crotyl chloride (and possibly with butadiene) occurs in preference to the telomerization in this reaction condition. The substruction of chlorine from crotyl chloride by the catalyst is supposed to be followed by the addition of the resultant carbonium ion to the benzene ring of toluene rather than to the double bond of butadiene. Namely, the π-basicity of toluene is probably stronger than that of butadiene.

Acetic Anhydride and Acetonitrile. The telomerization in acetic anhydride and in acetonitrile at low temperatures in the presence of ferric chloride gives only small amounts of telomers as shown in Table 2. Raising temperatures has a small effect on the yield of the products.

The product of the telomerization in acetic anhydride gives the infrared spectrum which has the bands of carbonyl group (1745 cm^{-1}) and ether group (1240 cm^{-1}) together with the band of internal C=C double bond (965 cm^{-1}). It is clear that acetic anhydride enters in the reaction with butadiene by the aid of ferric chloride. In order to take an insight of the reaction of butadiene with acetic anhydride and the product thereof, the polymerization of butadiene in acetic anhydride in the presence of ferric chloride was investigated. The oligomer of average molecular weight 212 was obtained ($[Ac_2O]/[BD]=1.00$ molar ratio; $[FeCl_3]/[BD]=0.055$ molar ratio; reaction temperature, −25°C; reaction time, 5 hr; yield based on butadiene, 29.2%). The infrared spectrum of the oligomer has the strong bands of carbonyl and ether groups together with a rather weak band of internal C=C double bond. The band characteristic of hydroxyl group is not observed. The reaction mechanism can be illustrated for the formation of the oligomer as shown below.



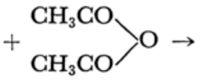
$$(CH_3CO)_2O + FeCl_3 \rightarrow$$

$$CH_3CO^+ + [CH_3COO\cdot FeCl_3]^-$$

$$CH_3CO^+ + CH_2{=}CHCH{=}CH_2 \rightarrow CH_3COCH_2CH{=}CHCH_2^+$$

$$CH_3COCH_2CH{=}CHCH_2^+ + (n-1)CH_2{=}CHCH{=}CH_2 \rightarrow CH_3CO(CH_2CH{=}CHCH_2)_{n-1}CH_2CH{=}CHCH_2^+$$

$$CH_3CO(CH_2CH{=}CHCH_2)_{n-1}CH_2CH{=}CHCH_2^+$$



$$+ (CH_3CO)_2O \rightarrow CH_3CO(CH_2CH{=}CHCH_2)_nOCOCH_3 + CH_3CO^+$$

The mean value of $n=2.03$ was calculated from the average molecular weight of the product.

Found: C, 67.3; H, 8.1%. Calcd for $CH_3CO(CH_2CH{=}CHCH_2)_{2.03}OCOCH_3$: C, 68.7; H, 8.7%.

The iodine value of the products was 230, which corresponds to 94.6% of the theoretical value.

These results indicate that in acetonitrile and acetic anhydride, the catalyst is consumed by the interaction with the solvents to produce the complexes which results in the decrease in the activity for the telomerization.

Ethyl Ether. The telomerization in ethyl ether at a low temperature in the presence of ferric chloride leads to the formation of only a small amount of the product compared with those in halogenated hydrocarbons. However, appreciable amounts of the telomer are obtained at the temperaturs above 0°C (Table 2).

It is known that ethyl ether, likewise ethyl bromide, associates with Lewis acids at shown below.

$$EtBr + FeCl_3 \rightleftarrows EtBr\cdot FeCl_3 \quad (1)$$

$$Et_2O + FeCl_3 \rightleftarrows Et_2O\cdot FeCl_3 \quad (2)$$

Namely, these solvents act as Lewis bases to the catalysts. Crotyl chloride used as a telogen is also a Lewis base, and forms a complex with the catalyst.

$$RCl + FeCl_3 \rightleftarrows RCl\cdot FeCl_3 \quad (3)$$

$$R:\ CH_3CH{=}CHCH_2$$

Therefore, in the telomerization of butadiene with crotyl chloride in ethyl ether in the presence of ferric chloride, the complexes are formed according to Eq. (2) or (3), depending on the difference in basicities between the solvent and crotyl chloride. If the solvent is a weaker base than crotyl chloride, the telomerization may proceed as follows:

$$Et_2O\cdot FeCl_3 + RCl \rightarrow RCl\cdot FeCl_3 + Et_2O \quad (4)$$

$$RCl\cdot FeCl_3 \rightarrow R^+ + FeCl_4^- \quad (5)$$

It is now apparent that the decrease in the activity of the catalyst for the telomerization in most of the oxygen- and nitrogen-containing solvents is attributed to the tendency of the solvents to form complexes with the catalyst.

There are informations about the quantitative measurements of the basicity of Lewis bases by chemical and physical methods. It has been shown that the heats of mixing of organic solvents with Lewis acids reflect the energy of the co-ordinate links formed between them.[6)]

$$\tfrac{1}{2}Al_2Cl_6(\text{solid}) + nX(\text{liquid}) \rightarrow X_n\cdot AlCl_3(\text{solid or solution}) + Q \quad (6)$$

where X is the solvent and Q is the measured heat of mixing, and the analyses gave $n=1$ for oxygen compounds generally. The small values of $Q=8.2$ and 4.1 kcal/mol for anisol and diphenyl ether respectively suggest that the donor strength of ether compounds is lower than most of other oxygen- and nitrogen-containing compounds.

The telomerization in the mixed solvent of ethyl ether and dichloromethane (1 : 1) in the presence of titanium tetrachloride gives a very small amount of the telomer. The result suggests the formation of a stable complex between ethyl ether and titanium tetrachloride.

It has been confirmed that the molecular weights of the telomers and the ratio of the amount of the 1 : 1 adduct of butadiene and crotyl chloride to the total product are affected primarily by the conversion of reaction and the initial ratio of crotyl chloride to butadiene. When ethyl ether is used as a solvent, the telomer obtained has a lower average molecular weight and a higher ratio of 1 : 1 adduct to the total product than the telomers obtained in halogenated hydrocarbons. Moreover, the degree of unsaturation in the telomer formed in ethyl ether is 10—20% larger than those formed in halogenated hydrocarbons.[2)] This indicates that, in ethyl ether, side reactions, for example, grafting (branching) and cyclization which cause the loss of unsaturation in the telomers are suppressed, and the formation of the telomers of lower molecular weights is feasible.

Nitromethane and Nitrobenzene. The telomerization in nitromethane in the presence of ferric chloride gives an appreciable amount of telomer even at the temperatures below −20°C. The reaction products in nitromethane and nitrobenzene have also relatively low molecular weights and large amounts of unsaturation.

Nitro-compounds form monomolecular addition complexes with Lewis acids. Aluminum chloride,

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6) M. H. Dilke, D. D. Eley and M. G. Sheppard *Trans. Faraday Soc.*, **46**, 261 (1950).

for example, dissolves in nitrobenzene, and the heat of formation of the complex is small compared to the complexes of amines and ketones, suggesting the small basicity of the nitrobenzene.[7] This may illustrates the catalytic activity of ferric chloride in nitromethane and nitrobenzene for the telomerization. The use of nitro-compounds as the solvents for alkylation reactions is advantageous because of their high solvent power for aluminum chloride and ferric chloride and because of the suppression of some side reactions, *e. g.*, the isomerization and reduction. It was suggested that the active component in the nitroparaffins solution of aluminum chloride is not aluminum chloride but rather the addition compound, $AlCl_3 \cdot R'NO_2$.[8] However, there is no any direct evidence for the catalytic activity of the complex. As will be shown in the subsequent paper,[9] the addition of nitroethane to the reaction mixture of butadiene with crotyl chloride in ethyl bromide in the presence of aluminum chloride accelerates the reaction. If , in this case, the complex of aluminum chloride with nitroethane is the actual active component, the rate of reaction should decrease. Thus, in the telomerization in the nitro-compounds, the complex once formed is supposed to react with crotyl chloride to form the complex of ferric chloride with crotyl chloride.

$$R'NO_2 \cdot FeCl_3 + RCl \rightarrow RCl \cdot FeCl_3 + R'NO_2 \tag{7}$$

$$RCl \cdot FeCl_3 \rightarrow R^+ + FeCl_4^- \tag{8}$$

The low average molecular weight of the telomers obtained in the nitro-compounds solutions may be attributed to the small occuration of grafting and cyclization which cause the loss of unsaturation. The relatively high value of the theoretical unsaturation in the telomers may indicates the suppression of such side reactions.

The infrared spectra of the telomers obtained in ethyl ether, nitromethane and nitrobenzene are nearly the same as those of the telomers obtained in halogenated hydrocarbons, and it is clear that the amounts of 1, 4 and 1, 2 linkages in the telomers are not much affected by the variation of the solvents. The reaction is considered to proceed on the same mechanism[2] in all the solvents used, except when the solvents themselves enter into the reaction with the catalysts.

The authors wish to express their gratitude to Mr. Kikuo Fusano and Mr. Toshiharu Kawano for their kind help in the experiments.

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[7] H. C. Brown and R. R. Holmes, *J. Am. Chem. Soc.*, **78**, 2173 (1956).

[8] L. Schmerling, *Ind.* & *Eng. Chem.*, **40**, 2072 (1948).

[9] T. Asahara and H. Kise, to be published.