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Cyclotrimerization and Polymerization of 1-Hexyne Catalyzed by Group 5, 6 Transition Metal Chlorides[1)]

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1-Hexyne could be cyclotrimerized selectively and quantitatively by $NbCl_5$ and $TaCl_5$. The cyclotrimer formed consisted of 1,2,4- and 1,3,5-isomers. The 1,2,4/1,3,5 isomer ratio of the product was about 70/30—80/20 with $NbCl_5$, and about 55/45—70/30 with $TaCl_5$. The polymerization of 1-hexyne by $MoCl_5$- and WCl_6-based catalysts afforded a methanol-insoluble polymer and methanol-soluble products in comparable amounts. The polymer (mol wt 3000—5000) was an orange-yellow viscous material with structure $\{CH=C(n\text{-Bu})\}_n$. For comparison, the cyclotrimerization and polymerization using Ziegler catalysts were also examined.

1-Hexyne can be cyclotrimerized by transition metal catalysts [$TiCl_4$–Et_3Al,[3)] $(Ph_3P)_2Ni(CO)_2$,[4)] and $(\eta^5\text{-}C_5H_5)_2V$[5)]]. The polymer and linear oligomer of 1-hexyne, however, are often formed as by-products in the cyclotrimerization. Further, the cyclotrimer formed (tributylbenzene) is usually a mixture of 1,2,4- and 1,3,5-isomers. The selectivity of the cyclotrimerization and the 1,2,4/1,3,5 isomer ratio of cyclotrimer have hardly been clarified.

1-Hexyne can be polymerized by transition metal catalysts [$TiCl_3$–Et_3Al,[6,7)] Fe(III) naphthenate-$(i\text{-Bu})_3Al$,[8)] and $PhCH_3\cdot Mo(CO)_3$[9)]]. High molecular weight poly(1-hexyne) ($[\eta]=2$—6 dl/g) is obtained with a Ziegler catalysts, Fe(III) naphthenate-$(i\text{-Bu})_3Al$. The yield of cyclotrimer as by-product and the geometric structure of the polymer, however, have not been studied.

Acetylene[10)] and phenylacetylene[11)] are cyclotrimerized by $NbCl_5$ and $TaCl_5$. Various acetylenes are polymerized by $MoCl_5$- and WCl_6-based catalysts.[12)] Therefore, it is interesting to examine the selectivity and product structure in the cyclotrimerization of 1-hexyne by $NbCl_5$ and $TaCl_5$, and in the polymerization of the monomer by $MoCl_5$ and WCl_6.

This paper deals with the cyclotrimerization and polymerization of 1-hexyne. It has been found that the cyclotrimerization by $NbCl_5$ and $TaCl_5$ selectively yields cyclotrimer, while not only polymer but also cyclotrimer is formed in the polymerization by $MoCl_5$ and WCl_6. For comparison, the cyclotrimerization and polymerization by Ziegler catalysts were also carried out.

Experimental

1-Hexyne was purchased from Farchan Labs, USA, and distilled twice from calcium hydride under nitrogen before use. Commercially available transition metal and organometallic compounds were used without further purification. Polymerization solvents were washed with acid and/or alkaline solutions and distilled from appropriate drying agents; care was exercised to dry and deaerate them sufficiently.

Two-component catalysts were aged in solution at 30 °C for 15 min before use. Reactions of 1-hexyne were carried out under nitrogen and terminated by adding ammoniacal methanol. Monomer consumptions (conversions) were determined by ges chromatography.

Cyclotrimerization was worked up by washing reaction mixtures with dilute hydrochloric acid and water and then evaporating the solvent. The ratio of cyclotrimer to linear oligomer was determined by liquid chromatography (JASCO Triroter II chromatograph; Shodex A802, A804 polystyrene gel columns). Two isomers of cyclotrimer (1,2,4- and 1,3,5-tributylbenzenes) could be separated by gas chromatography (Shimadzu GC3B chromatograph; Silicone DC550 supported on Chromosorb W (10%) 5 m, 195 °C). The isomer with a shorter retention time was identified as 1,3,5-tributylbenzene because it showed a singlet ($\delta=6.80$) in the aromatic region in ^1H NMR (a multiplet was observed for the other isomer). Therefore the ratio of the two isomers was determined by gas chromatography.

The polymeric product in polymerization was recovered by precipitation in a large amount of methanol, and its yield was determined by gravimetry. The oligomeric product was dealt with similarly to the cyclotrimerization product. Number-average molecular weights, $\overline{M}_n$, of polymers were obtained by vapor pressure osmometry (Hitachi 117 molecular weight apparatus). Differential thermal analysis (DTA) was performed under nitrogen with a Shimadzu 20B analyzer.

Results and Discussion

Cyclotrimerization. The cyclotrimerization of 1-hexyne by $NbCl_5$ and $TaCl_5$ proceeded quantitatively under the conditions shown in Table 1. Hydrocarbons and halogenated hydrocarbons were useful solvents, whereas ethers, esters and ketones were not. The products consisted exclusively of cyclotrimer, which was a mixture of two isomers, that is, 1,2,4- and 1,3,5-tributylbenzenes. The 1,2,4/1,3,5 isomer ratio of the product was about 70/30—80/20 with $NbCl_5$, and about 55/45—70/30 with $TaCl_5$; the former catalyst generally yielded more 1,2,4-isomer. The ratio was affected only slightly by the solvents used.

The effect of temperature on the cyclotrimerization was examined between 0 and 60 °C (Table 2). The reaction rate greatly reduced with decreasing temperature. The 1,2,4/1,3,5 isomer ratio of product somewhat decreased with both $NbCl_5$ and $TaCl_5$, as the reaction temperature was lowered.

Thus $NbCl_5$ and $TaCl_5$ effected highly selective cyclotrimerization of 1-hexyne similarly to the case of phenylacetylene.[11)] The 1,2,4/1,3,5 isomer ratio varied only in a range of 54/46—78/22 with reaction con-

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Table 1. 1,2,4/1,3,5 Isomer ratios of products in the cyclotrimerization of 1-hexyne by NbCl5 and TaCl5[a]

Cat	Benzene	Toluene	Hexane	Cyclohexane	CCl_4	$CHCl_3$	$(CH_2Cl)_2$
$NbCl_5$	78/22	78/22	75/25	76/24	78/22	74/26	72/28
$TaCl_5$	72/28	68/32	54/46	56/44	72/28	57/43	62/38

a) $[1\text{-Hexyne}]_0=1.0$ mol dm^{-3}, $[cat]=10$ mmol dm^{-3}, 60 °C (50 °C for $CHCl_3$), 2 h: cyclotrimer (1,2,4- and 1,3,5-isomers) was selectively and quantitatively obtained.

Table 2. Temperature dependence of the cyclotrimerization of 1-hexyne by $NbCl_5$ and $TaCl_5$[a]

Cat	1,2,4/1,3,5 ratio		
	60 °C	30 °C	0 °C
$NbCl_5$	78/22	76/24	73/27
$TaCl_5$	68/32	60/40	55/45

a) $[1\text{-Hexyne}]_0=1.0$ mol dm^{-3}. $[cat]=10$ (60 °C) or 30 (30°, 0 °C) mmol dm^{-3}, in toluene, 2 (60 °C), 24 (30 °C) or 120 (0 °C) h: cyclotrimer (1,2,4- and 1,3,5-isomers) was selectively and quanitatively obtained.

Table 3. Cyclotrimerization of 1-hexyne by Ziegler catalysts[a]

Cat	Cocat	Conversion %	Yield/%		
			Cyclotrimer		Linear oligomer
			1,2,4	1,3,5	
$TiCl_4$	Et_2AlCl	100	53	47	0
$TiCl_4$	Et_3Al	85	33	37	15
VCl_4	Et_2AlCl	96	21	50	25
VCl_4	Et_3Al	95	26	26	43
$VOCl_3$	Et_2AlCl	90	52	38	0
$VOCl_3$	Et_3Al	95	13	11	71

a) $[1\text{-Hexyne}]_0=1.0$ mol dm^{-3}, $[cat]=30$ mmol dm^{-3}, $[cocat]=45$ mmol dm^{-3}, in toluene, 30 °C, 24 h; catalyst aging 30 °C, 15 min.

ditions (catalyst, solvent and temperature). This contrast with a larger variance of the ratio (17/83—94/6) in the cyclotrimerization of phenylacetylene with similar changes in reaction conditions. Metallacyclopentadienes should be involved as intermediates in the cyclotrimerizaton of acetylenes with transition metal catalysts.[13] Since the phenyl group is bulkier than the butyl group, it is reasonable that the orientation of two acetylene molecules during the formation of a metallacyclopentadiene is more dependent on reaction conditions in phenylacetylene than in 1-hexyne.

The cyclotrimerization of 1-hexyne by Ziegler catalysts was investigated for comparison. Though various combinations of transition metal chlorides and organoaluminums were employed as catalysts, most of them yielded not only cyclotrimer but also linear oligomer. Chlorides of Ti and V were most effective among various transition metal chlorides. $EtAlCl_2$ possessed a high Lewis acidity to give linear oligomer by the cationic mechanism. The catalyst systems that showed relatively high selectivity for cyclotrimerization are given in Table 3. The 1,2,4/1,3,5 isomer ratios were usually close to unity.

Polymerization. Table 4 shows results for the polymerization of 1-hexyne by $MoCl_5$- and WCl_6-based catalysts. Both $MoCl_5$- and WCl_6-based catalysts worked effectively, the latter being somewhat more active. Methanol-insoluble polymers were about half the whole products in quantity. The polymers had relatively low molecular weights (3000—5000). Methanol-soluble oligomers consisted of linear oligomer and cyclotrimer (both 1,2,4- and 1,3,5-isomers involved). The observed cocatalyst effect shows that both or either of methanol and Ph_4Sn is useful to increase conversion and polymer yield. Nonpolar solvents such as benzene, cyclohexane and carbon tetrachloride were preferable.

Table 4. Polymerization of 1-hexyne by $MoCl_5$ and WCl_6[a]

Cat	Coat	Solvent	Conversion %	Polymer[b]	
				Yield %	$\bar{M}_n$
$MoCl_5$	None	Benzene	41	13	—
$MoCl_5$	CH_3OH	Benzene	75[c]	38	3200
$MoCl_5$	Ph_4Sn	Benzene	20	8	—
$MoCl_5$	CH_3OH	Cyclohexane	91	35	3200
$MoCl_5$	CH_3OH	CCl_4	95	47	4900
WCl_6	None	Benzene	62	9	—
WCl_6	CH_3OH	Benzene	83	51	3500
WCl_6	Ph_4Sn	Benzene	90[d]	62	4300
WCl_6	Ph_4Sn	Cyclohexane	100	58	3100
WCl_6	Ph_4Sn	CCl_4	100	63	3900

a) $[1\text{-Hexyne}]_0=1.0$ mol dm^{-3}, $[cocat]=10$ (CH_3OH) or 20 (Ph_4Sn) mmol dm^{-3}, 30 °C, 3 h. b) The methanol-insoluble product. c) Yields of methanol-soluble products: linear oligomer 19%, 1,2,4-cyclotrimer 7%, 1,3,5-cyclotrimer 11%. d) Yields of methanol-soluble products: limear oligomer 15%, 1,2,4-cyclotrimer 3%, 1,3,5-cyclotrimer 10%.

For comparison, the polymerization by Ziegler catalysts was examined. In acetylene polymerization, polymer is selectively formed only when both transition metal and organoaluminum compounds have low Lewis acidities.[14] Therefore, we chose combinations of transition metal acetylacetonates and Et_3Al as catalyst systems. A high polymer yield was achieved in the polymerization using $Fe(acac)_3$ in cyclohexane solution (Table 5). Though $VO(acac)_3$ and $Co(acac)_3$ were also effective, the polymer yields were rather low. The main products were methanol-insoluble polymers; small amounts of linear oligomer and cyclotrimer were also formed. Polymer molecular weights were 5000—13000, higher than those with $MoCl_5$- and WCl_6-based catalysts. Aliphatic and aromatic hydrocarbons were

Table 5. Polymerization of 1-hexyne by Ziegler catalysts[a]

Cat	Solvent	Conversion %	Polymer[b] Yield %	Polymer[b] $\overline{M}_n$
$Fe(acac)_3$	Cyclohexane	100[c]	85	6000
$Fe(acac)_3$	Toluene	0	0	—
$VO(acac)_3$	Cyclohexane	40	27	7900
$VO(acac)_3$	Toluene	60	39	13200
$Co(acac)_3$	Cyclohexane	44	19	5000
$Co(acac)_3$	Toluene	35	22	11300

a) $[1\text{-Hexyne}]_0$=1.0 mol dm^{-3}, [cat]=20 mmol dm^{-3}, cocatalyst: Et_3Al (60 mmol dm^{-3}), 30 °C, 3 h; catalyst aging 30 °C, 15 min. b) The methanol-insoluble product. c) Yields of methanol-soluble products: linear oligomer 9%, 1,2,4-cyclotrimer 3%, 1,3,5-cyclotrimer 3%.

Table 6. Relationship between monomer structure and product in the polymerization of monosubstituted acetylenes by $MoCl_5$ and WCl_6

Monomer: Steric effect[a]	Monomer: Example	Ref	Product: Mol wt of polymer	Product: Cyclotrimer[b]
	HC≡C(*n*-Bu)	This work		
Small	HC≡C(*n*-C_6H_{11})	15	10^3—10^4	Comparable
	HC≡C(*i*-Bu)	15		
	HC≡C(*s*-Bu)	15		
Medium	HC≡C(*c*-C_6H_{11})	15	10^4—10^5	<1/10
	HC≡CPh	16		
Large	HC≡C(*t*-Bu)	17	10^5—10^6	0

a) Steric effect of the substituent in monomer. b) Relative yields of cyclotrimer to polymer.

useful polymerization solvents. It is not clear why the polymerization using the $Fe(acac)_3$ system did not occur in toluene.

Table 6 summarizes polymer molecular weights and cyclotrimer(by-product) yields in the $MoCl_5$- and WCl_6-catalyzed polymerization of monosubstituted acetylenes. As the substituent in the monomer becomes bulkier and shows a greater steric effect, polymer molecular weight clearly increases and cyclotrimer yield approaches zero. As an extreme case, *t*-butylacetylene affords a very high polymer and does not form cyclotrimer; on the contrary, Ziegler catalysts cannot polymerize this monomer.[17] It does not appear an important factor whether the substituent is an alkyl or an aryl group. Table 6 leads to the conclusion that $MoCl_5$- and WCl_6-based catalysts are particularly effective towards sterically hindered acetylenes [*e.g.*, HC≡C(*t*-Bu)], while not so effective to sterically unhindered acetylenes [*e.g.*, HC≡C(*n*-Bu)]. It has been inferred that two acetylene molecules coordinate to a transition metal to form the intermediate in cyclotrimerization,[13] while one acetylene molecule in polymerization.[12]

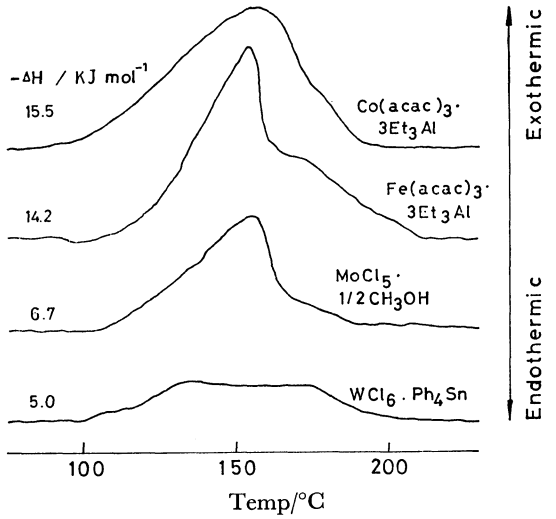

Fig. 1. DTA thermograms of poly(1-hexyne)s.

Therefore, polymerization will not suffer the steric effect so greatly as cyclotrimerization, which seems responsible for the selective polymerization of *t*-butylacetylene.

Spectral data of the poly(1-hexyne) obtained with $WCl_6 \cdot Ph_4Sn$ in toluene are as follows: IR 1650—1600 cm^{-1} (w; conjugated C=C). ^1H NMR ($CDCl_3$) δ 5.87 (s, 1, –CH=), 2.21 (s, 2, $=CCH_2-$), 1.30 (s, 4, $-CH_2CH_2Me$), 0.90 (s, 3, CH_3). ^{13}C NMR ($CDCl_3$) δ 140.0 (C_2), 126.1 (C_1), 31.0 (C_3), 23.0, 22.6 (C_4, C_5), 14.0 (C_6). UV (hexane) λ_{max} 285 nm (ε 1600); the absorption continued as far as 450 nm. All the poly(1-hexyne)s obtained in the present study showed practically the same spectra. These data lead to the conclusion that the polymer has the conjugated polyene structure –[–CH=C(*n*-Bu)–]–.

In general, poly(1-hexyne) was an orange-yellow viscous material soluble in hydrocarbons and halogenated hydrocarbons. This polymer was gradually oxidized by air at room temperature, as confirmed by a carbonyl band at 1710 cm^{-1} in the IR spectrum. This contrasts with the fact that poly(*t*-butylacetylene), which cannot take a planar conformation, is very stable.[17]

Poly(1-hexyne)s obtained with several catalysts showed exothermic peaks of different magnitudes in the same temperature range in the DTA thermograms (Fig. 1). It is known that polyacetylene[18] and poly(phenylacetylene)[19] show exothermic peaks in DTA due to their isomerization from cis to more stable trans form. The cis content of poly(phenylacetylene) has been qualitatively estimated by the isomerization exotherm. Based on a similar discussion, one can conclude from Fig. 1 that the cis content of poly(1-hexyne) decreases in the following order of catalyst: $Co(acac)_3 \cdot 3Et_3Al$ > $Fe(acac)_3 \cdot 3Et_3Al$ > $MoCl_5 \cdot (1/2)CH_3OH$ > $WCl_6 \cdot Ph_4Sn$. A similar order has been observed with poly(phenylacetylene): $Fe(acac)_3 \cdot 3Et_3Al > MoCl_5 \cdot (1/2)CH_3OH > WCl_6 \cdot Ph_4Sn$.[19b] Thus $MoCl_5$- and WCl_6-based catalysts tend to give polymers with higher trans contents than do Ziegler catalysts.

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References

1) Part VI of "Polymerization of Aliphatic Acetylenes," For part V, see Ref. 2.
2) Y. Okano, T. Masuda, and T. Higashimura, *Polym. J.*, **14**, 477 (1982).
3) E. F. Lutz, *J. Am. Chem. Soc.*, **83,** 2551 (1961).
4) L. S. Meriwether, E. C. Colthup, G. W. Kennerly, and R. N. Reusch, *J. Org. Chem.*, **26,** 5155 (1961).
5) R. Tsumura and N. Hagihara, *Bull. Chem. Soc. Jpn.*, **37,** 1889 (1964).
6) Natta, G. Mazzanti, and P. Pino, *Angew. Chem.*, **69**, 685 (1957).
7) A. A. Berlin, E. F. Vainshtein, M. I. Cherkashin, and Yu. Sh. Moshkovskii, *Vysokomol. Soedin.*, **5**, 1354 (1963).
8) W. J. Trepka and R. J. Sonnenfeld, *J. Polym. Sci., Part A-1*, **8**, 2721 (1970).
9) P. S. Woon and M. F. Farona, *J. Polym. Sci., Polym. Chem. Ed.*, **12,** 1749 (1974).
10) G. Dändliker, *Helv. Chim. Acta*, **52,** 1482 (1969).
11) T. Masuda, T. Mouri, and T. Higashimura, *Bull. Chem. Soc. Jpn.*, **53,** 1152 (1980).
12) For a review, T. Masuda, *Kagaku*, **37,** 570 (1982).
13) D. R. McAlister, J. E. Bercaw, and R. G. Bergman, *J. Am. Chem. Soc.*, **99,** 1666 (1977); H. Yamazaki and Y. Wakatsuki, *J. Organomet. Chem.*, **139,** 157 (1977); Y. Wakatsuki and H. Yamazaki, *ibid.*, **139,** 169 (1977).
14) T. Ito, H. Shirakawa, and S. Ikeda, *J. Polym. Sci., Polym. Chem. Ed.*, **12,** 11 (1974); H. Shirakawa and S. Ikeda, *J. Polym. Sci., Polym. Chem. Ed.*, **12,** 929 (1974).
15) T. Masuda, M. Kawasaki, T. Takahashi, Y. Okano, and T. Higashimura, *Polym. Preprints, Jpn.*, **31**, 1197 (1982); T. Masuda, M. Kawasaki, Y. Okano, and T. Higashimura, *Polym. J.*, **14,** 371 (1982).
16) T. Masuda, T. Takahashi, K. Yamamoto, and T. Higashimura, *J. Polym. Sci., Polym. Chem. Ed.*, **20,** 2603 (1982).
17) T. Masuda, Y. Okano, Y. Kuwane, and T. Higashimura, *Polym. J.*, **12,** 907 (1980).
18) T. Ito, H. Shirakawa, and S. Ikeda, *J. Polym. Sci., Polym. Chem. Ed.*, **13,** 1943 (1975).
19) C. I. Simionescu, S. Dumitrescu, and V. Percec, *J. Polym. Sci., Polym. Symp.*, **64,** 209 (1978); T. Masuda, T. Ohtori, and T. Higashimura, *Polym. Preprints*, **20**, 731 (1979).