[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

Intermolecular–Intramolecular Polymerization of α-Diolefins by Metal Alkyl Coördination Catalysts[1]

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RECEIVED OCTOBER 28, 1957

The α-diolefins 1,6-heptadiene, 1,5-hexadiene and 2,5-dimethyl-1,5-hexadiene have been polymerized by metal alkyl coördination catalysts to yield soluble polymers which are believed to contain carbocyclic rings in the polymer chain. Poly-1,6-heptadiene has been dehydrogenated to yield a polymer which shows aromatic and *meta* substitution absorption in the infrared region and absorption for a benzene nucleus in the ultraviolet region. A new synthesis for 1,6-heptadiene is described.

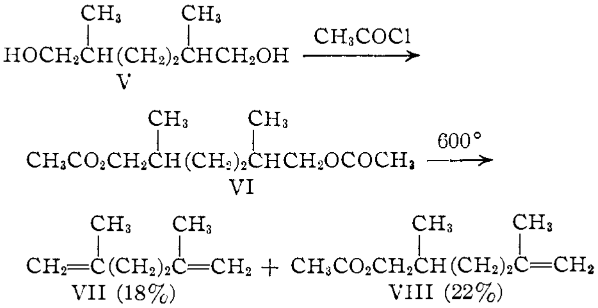
Attention recently has been drawn to the fact that non-conjugated diolefins do not always produce crosslinked polymers. Butler[2] has shown that diethyldiallylammonium bromide can be polymerized to yield a soluble polymer. Marvel and Vest[3] have succeeded in obtaining soluble polymers containing cyclic recurring units from a series of 2,6-disubstituted-1,6-heptadienes by free radical initiation. Since unsubstituted α-olefins do not usually polymerize readily with free radical initiation, it seemed best to attempt the polymerization of these α-diolefins with metal alkyl coördination catalysts of the type described by Ziegler.[4,5] A patent[6] describes the polymerization of non-conjugated diolefins by coördination catalysts but does not describe the structure of the product. We have succeeded in obtaining soluble polymers by the polymerization of three α-diolefins, 1,6-heptadiene, 1,5-hexadiene and 2,5-dimethyl-1,5-hexadiene. The last hydrocarbon is a monomer type which has heretofore failed to polymerize with metal alkyl coördination catalysts. The polymers obtained are all believed to contain cyclic recurring units in the polymer chain.

1,6-Heptadiene was first prepared by the hydrogenation of 1,6-heptadiyne as has been previously described.[7] However, in order to obtain a monomer of high purity the diacetate of heptamethylene glycol[8,9] was pyrolyzed to afford a 62% yield of 1,6-heptadiene (III) and a 21% yield of 7-acetoxy-1-heptene (V).

$$\underset{\text{I}}{HO(CH_2)_7OH} \xrightarrow{CH_3COCl} \underset{\text{II (97\%)}}{CH_3CO_2(CH_2)_7OCOCH_3} \xrightarrow{570°}$$

$$\underset{\text{III (62\%)}}{CH_2{=}CH(CH_2)_3CH{=}CH_2} + \underset{\text{IV (21\%)}}{CH_3CO_2(CH_2)_5CH{=}CH_2}$$

The 2,5-dimethyl-1,5-hexadiene used for the polymerization studies was prepared by the coupling reaction of methallyl chloride[10,11] and by pyrolysis of the acetate VI of 2,5-dimethyl-1,6-hexanediol (V) to 2,5-dimethyl-1,5-hexadiene (VII) and the half acetate VIII.



$$\underset{\text{V}}{HOCH_2\overset{\overset{CH_3}{|}}{C}H(CH_2)_2\overset{\overset{CH_3}{|}}{C}HCH_2OH} \xrightarrow{CH_3COCl}$$

$$\underset{\text{VI}}{CH_3CO_2CH_2\overset{\overset{CH_3}{|}}{C}H(CH_2)_2\overset{\overset{CH_3}{|}}{C}HCH_2OCOCH_3} \xrightarrow{600°}$$

$$\underset{\text{VII (18\%)}}{CH_2{=}\overset{\overset{CH_3}{|}}{C}(CH_2)_2\overset{\overset{CH_3}{|}}{C}{=}CH_2} + \underset{\text{VIII (22\%)}}{CH_3CO_2CH_2\overset{\overset{CH_3}{|}}{C}H(CH_2)_2\overset{\overset{CH_3}{|}}{C}{=}CH_2}$$

The polymerization of 1,6-heptadiene by use of a catalyst prepared by the reduction of titanium tetrachloride with aluminum triisobutyl gave a white, tough polymer which was soluble in benzene, had a capillary melting point of 210–230°, and formed a transparent film on evaporation of its benzene solution. When a catalyst formed from a 1:1 molar ratio of aluminum triisobutyl to titanium tetrachloride was employed, a dilute solution viscosity of 0.2 was obtained, but when the ratio was increased to 3:1, the viscosity of the polymer was 0.4. This is not surprising, since it has been shown that the most effective catalyst is that in which the average valence of titanium is two, and that this average valence state is achieved with a catalyst ratio of 3:1.[12] The viscosity of the polymer seemed to be independent of the polymerization temperature and the amount of solvent, but a higher conversion was obtained with larger amounts of solvent. A quantitative comparison of this polymer with 1,6-heptadiene by use of infrared techniques showed that there were between 4 and 10% of the monomer units incorporated in the polymer chain which still retained one double bond.

In an attempt to elucidate the structure of poly-1,6-heptadiene, dehydrogenation reactions were carried out. Dehydrogenation by use of palladium and platinum catalysts were unsuccessful. It is believed that the inability to isolate the dehydrogenated polymer from the dehydrogenation catalyst may have been the real difficulty since very little product of any type was obtained on extraction of the reaction mixture. Chemical dehydrogenation with potassium perchlorate[3,13] was,

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[1] The work discussed herein was performed as a part of the polymer research project sponsored by the National Science Foundation.

[2] G. B. Butler and R. J. Angelo, THIS JOURNAL, **79**, 3128 (1957).

[3] C. S. Marvel and R. D. Vest, *ibid.*, **79**, 5771 (1957).

[4] K. Ziegler and H. Martin, *Makromol. Chem.*, **19**, 186 (1956).

[5] K. Ziegler, *Chem. Techn.*, **27**, 230 (1955).

[6] E. I. du Pont de Nemours and Co., British Patent 776,326 (published June 5, 1957).

[7] A. L. Henne and K. W. Greenlee, THIS JOURNAL, **65**, 2020 (1943).

[8] A. H. Blatt, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1953, p. 155.

[9] W. F. Huber, THIS JOURNAL, **73**, 2730 (1951).

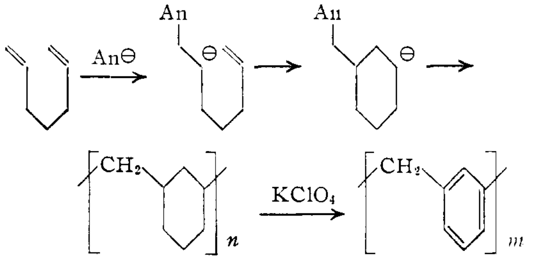
[10] M. Tamele, C. J. Ott, K. E. Marple and G. H. Hearn, *Ind Eng. Chem.*, **33**, 120 (1941).

[11] O. Schales, *Ber.*, **70**, 119 (1937).

[12] Private communication, D. B. Ludlum, A. W. Anderson and C. E. Ashby, Polychemicals Department, Research Division, E. I. du Pont de Nemours and Co.

[13] S. Patai and L. Rabenbuch, THIS JOURNAL, **73**, 862 (1951).

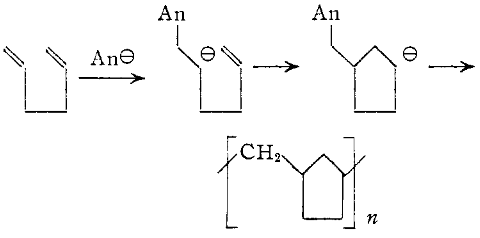
however, successful as evidenced by the presence of aromatic and *meta* substitution absorption maxima by the dehydrogenated polymer in the infrared region and an aromatic absorption maximum in the ultraviolet region of the spectrum. This evidence, in addition to the facts that the polymer is completely soluble in benzene and there is very little unsaturation in the polymer, indicates that the polymer contains the cyclic recurring unit IX as its main structural feature and proceeds by an alternating intermolecular–intramolecular mechanism. Whether the mechanism of this polymerization is cationic, anionic or free radical is indeed uncertain. It has been established that a divalent titanium compound is the effective catalyst.[14] In the mechanism which is proposed an anionic mechanism has been chosen in order to illustrate the cyclopolymerization process.



IX

A correlation between the intrinsic viscosity and the molecular weight of this type of polymer has not been determined. However, an approximate calculation of the molecular weight using an intrinsic viscosity of 0.38 and the values for K and a, as determined for polyisobutylene in benzene at 24°,[15] gives a molecular weight of the order of 200,000.

The polymerization of 1,5-hexadiene gave a white, tough, rubbery polymer, about 40% of which was soluble in benzene. A catalyst formed by a 1:1 molar ratio of aluminum triisobutyl to titanium tetrachloride was not effective in this polymerization, but a catalyst ratio of 3:1 gave high conversion. The best conversion to a soluble polymer was obtained by using a 3:1 catalyst ratio at room temperature with a high ratio of polymerization solvent to monomer. The soluble portion of this polymer had a dilute solution viscosity of 0.23, and a capillary melting point of 85–90°. A quantitative comparison of the soluble portion of this polymer with 1,5-hexadiene by use of infrared techniques showed that between 5 to 8% of the monomer units which were incorporated in the polymer chain retained one double bond. The most probable structure for the principal recurring unit of this polymer is structure X, resulting from the intermolecular–intramolecular polymerization mechanism. There is one other possible structure, XII, which would fit the experimental observations, but it is not consistent with any expected mechanism since it would require the formation of the less stable intermediate carbanion XI (carbonium ion or free radical as the case may be). The true polymerization process with this heterogeneous catalyst is most likely a much more complex process in which the classical carbanion (carbonium ion, free radical) does not exist as such, but that a clearer picture of the mechanism could be written as shown in XIII.



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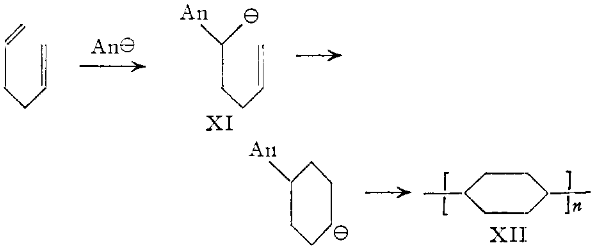

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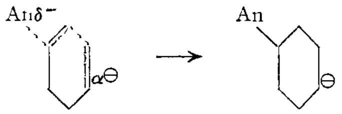
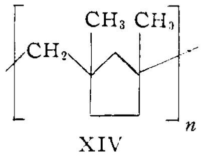
XII

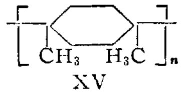


XIII

In contrast, the polymerization of 2,5-dimethyl-1,5-hexadiene gave a white, low molecular weight polymer which melted at 80–85° (capillary), and had a dilute solution viscosity of 0.1. This polymer was very soluble in benzene, ether, and chloroform. The best conversions and highest molecular weight polymers were obtained with a 1:1 catalyst ratio at room temperature with the minimum amount of solvent. It is interesting that a catalyst prepared from a 3:1 molar ratio of aluminum triisobutyl to titanium tetrachloride did not bring about polymerization. A quantitative infrared analysis of this polymer compared with 2,5-dimethyl-1,5-hexadiene showed that 3 to 13% of the monomer units retained one double bond during polymerization. This evidence supports the proposed structure XIV as the main structural feature, but also is consistent with the unlikely structure XV, in which the same polymerization mechanisms could be postulated to account for these structures as were postulated for the polymerization of 1,5-hexadiene. This polymerization was not cationically initiated, as titanium tetrachloride alone failed to produce polymer.



XIV



XV

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[14] E. I. du Pont de Nemours and Co., British Patent 777,588 (published June 26, 1957).

[15] P. J. Flory, "Principles of Polymer Chemistry," Cornell University Press, Ithaca, N. Y., 1953, p. 312.

TABLE I

PYROLYSIS OF 1,7-DIACETOXYHEPTANE

Diacetate		Rate of addition,	Unchanged ester		Half-acetate		1,6-Heptadiene		Total recovery,
Wt., g.	Mole	g./min.	Wt.	Yield, %	Wt.	Yield, %	Wt.	Yield, %	%
70	0.324	2	54.0	77.1	6.3	12.5	..	..	89.6
74.3	.344	1	7.0	9.5	17.4	32.5	13.6	..	83.2
132.2	.610	1	5.5	2.6	20.2	21.2	36.2	61.8	85.6
54	.250	1	..	..	..	..	10.0	41.7	41.7

Since the metal alkyl coördination catalyzed polymerizations of 1,1-disubstituted ethylenes have not been successful, it was of interest to determine whether the polymerization techniques employed for the polymerization of 2,5-dimethyl-1,5-hexadiene could be applied to the polymerization of the 1,1-disubstituted ethylene, 2-methyl-1-pentene. When these techniques were applied, a low molecular weight oil was obtained in a low conversion. Ebullioscopic measurements showed a molecular weight of 424, or five monomer units, and its infrared spectrum showed that there was no unsaturation in the molecule. This seems to indicate that the intermolecular–intramolecular cyclic polymerization process of the 1,1-disubstituted ethylene, 2,5-dimethyl-1,5-hexadiene, acts as a driving force in the polymerization process.

Experimental

Tetraethyl 1,1,5,5-Pentanetetracarboxylate. — The method used for the preparation of tetraethyl 1,1,5,5-pentanetetracarboxylate has been described by Marvel and Vest.[3] It was found that the yield could be increased to 89% by heating the reaction mixture under reflux for only nine hours after the addition of the 1,3-dibromopropane was complete.

Diethyl Pimelate.—The method for the semihydrolysis of tetraethyl 1,1,5,5-pentanetetracarboxylate is the same as that described for other dibasic esters.[16,17] The procedure used by Marvel and Vest[3] was followed. The dipotassium diethyl 1,1,5,5-pentanetetracarboxylate, which was obtained from 108.2 g. (0.03 mole) of tetraethyl 1,1,5,5-pentanetetracarboxylate, was dissolved in water and the aqueous solution was washed once with diethyl ether in order to remove any unhydrolyzed tetraester. The aqueous solution was then cooled to 0° in an ice–salt-bath, and concentrated hydrochloric acid was added dropwise as rapidly as possible while the temperature was maintained at 0° until the solution reached a *p*H of 1. During acidification, a yellow oil separated, which was removed from the aqueous layer, and the aqueous layer was extracted with ether. The ether extracts were added to the oil, the organics were dried and the diethyl dihydrogen 1,1,5,5-pentanetetracarboxylate was then decarboxylated thermally at 100° for six hours. The product was distilled under diminished pressure (85° (0.35 mm.)) yielding 40 g. (71%) of diethyl pimelate and 8.6 g. (18%) of ethyl hydrogen pimelate (110° (0.25 mm.)).

Diethyl pimelate was converted to 1,7-heptanediol by reduction with sodium in ethanol[8] and lithium aluminum hydride.[9]

1,7-Diacetoxyheptane.—To 83 g. (0.63 mole) of 1,7-heptanediol was added slowly 118.59 g. (1.51 moles) of freshly distilled acetyl chloride under anhydrous conditions at 0°. The mixture was then stirred for ten hours at room temperature after which time the hydrogen chloride and excess acetyl chloride were removed and the product was distilled under reduced pressure (75° (0.20 mm.)) yielding 132.2 g. (97.1%) of 1,7-diacetoxyheptane. The infrared spectrum[18] of this product showed absorption maxima for CH_2 (2930 cm.$^{-1}$), CH_3 (2860 cm.$^{-1}$), ester C=O (1740 cm.$^{-1}$) and ester -C–O (1247 cm.$^{-1}$).

Anal. Calcd. for $C_{11}H_{20}O_4$: C, 61.08; H, 9.32. Found[19]: C, 61.09; H, 9.10.

1,6-Heptadiene (III).—The apparatus described by Bailey and King[20] was used for the pyrolysis of 1,7-diacetoxyheptane (Table I). The crude pyrolyzates yielded 1,6-heptadiene (b.p. 90° (75 mm.)), 7-acetoxy-1-heptene (b.p. 82° (18 mm.)), and starting material. Purification of the 1,6-heptadiene was effected by distillation from sodium through a Fenske column under a nitrogen atmosphere, n^{26}D 1.4142.[7] The infrared spectrum of this product showed absorption maxima for C=C (1647 cm.$^{-1}$) and =CH (998 and 915 cm.$^{-1}$). Gas chromatography showed the product was free from impurities.

Anal. Calcd. for C_7H_{12}: C. 87.42; H, 12.58. Found: C, 87.44; H, 12.70.

7-Acetoxy-1-heptene (IV).—The infrared spectrum of 7-acetoxy-1-heptene obtained above showed absorption maxima for ester C=O (1747 cm.$^{-1}$), C=C (1647 cm.$^{-1}$) and C–O– (1245 cm.$^{-1}$).

Anal. Calcd. for $C_9H_{16}O_2$: C, 69.20; H, 10.33. Found: C, 69.47; H, 10.65.

1,5-Hexadiene.—Purification of biallyl[21] was accomplished by distillation from sodium wire through a 90-cm. Podbielniak column under nitrogen, b.p. 59.5°, n^{20}D 1.4050. Gas chromatography of this compound showed it to be free from impurities.

2,5-Dimethyl-1,5-hexadiene.—One method which was used for the preparation of 2,5-dimethyl-1,5-hexadiene has been described previously.[10,11] As an alternate method, the diacetate of 73.1 g. (0.5 mole) of 2,5-dimethylhexane-1,6-diol[22] was prepared by the reaction with 94.2 g. (1.2 moles) of freshly distilled acetyl chloride as described for 1,7-diacetoxyheptane, yielding 112.6 g. (97.9%) of a colorless liquid, b.p. 73–74° (0.1 mm.), n^{25}D 1.4310. The infrared spectrum of this diacetate showed absorption maxima for an ester C=O (1745 cm.$^{-1}$) and -C–O (1245 cm.$^{-1}$).

Anal. Calcd. for $C_{12}H_{22}O_4$: C, 62.59; H, 9.56. Found: C, 62.24; H, 9.44.

This diacetate was subjected to pyrolysis[20] at 600° with an addition rate of 1 g./min., and the pyrolyzate was worked up as previously described, yielding 8.9 g. (18%) of 2,5-dimethyl-1,5-hexadiene, 114.3 (760 mm.), 17.4 g. (22.7%) of the half-acetate, b.p. 106–107° (40 mm.), and 14.5 g. (14%) of starting material. The 2,5-dimethyl-1,5-hexadiene was purified by distillation from sodium through a 90-cm. Podbielniak column under nitrogen. Gas chromatography of this compound showed no impurities.

2-Methyl-1-pentene.—Purification of 2-methyl-1-pentene[23] was effected by distillation from sodium through a 90-cm. Podbielniak column under nitrogen. Gas chromatography of this material showed no impurities.

***n*-Heptane** was purified by passing it through a column containing activated silica, heating it under reflux over sodium for 24 hours, and distillation from sodium under a nitrogen atmosphere. The heptane was stored over sodium wire.

Titanium tetrachloride was purified as described by Clabaugh, Leslie and Gilchrist.[24]

Polymerization Studies.—The catalyst for the polymerizations was made up in a dry-box by adding the desired

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(16) M. F. Marguery, *Bull. soc. chim.*, [3] **33**, 541 (1905).

(17) D. S. Breslow, E. Baumgarten and C. R. Hauser, THIS JOURNAL, **66**, 1287 (1944).

(18) The infrared spectra were determined by Mr. James Brader, Mr. Bryan Cloonan and Mr. Paul McMahon, University of Illinois.

(19) The microanalyses were performed by Mr. Jozsef Nemeth, Miss Claire Higham and Mrs. Maria Stingl, University of Illinois.

(20) W. J. Bailey and C. King, THIS JOURNAL, **77**, 75 (1955).

(21) Obtained from Matheson, Coleman and Bell.

(22) Obtained from Carbon and Carbide Chemicals Division.

(23) Obtained from the Phillips Petroleum Co.

(24) W. S. Clabaugh, R. T. Leslie and R. Gilchrist, *J. Research Natl. Bur. Standards*, 261 (1955).

TABLE II

POLYMERIZATION OF 1,6-HEPTADIENE

Sample	Heptane, g.	Al(*i*-Bu)$_3$, g.	TiCl$_4$, g.	Moles Al(*i*-Bu)$_3$ / moles TiCl$_4$	Monomer, g.	Temp., °C.	Time, hr.	Polymer wt., g.	Conversion, %	η[a]
1	5	0.10	0.085	1.16	3.57	30	24	2.86	80	0.12
2	1.5	.10	.085	1.16	3.57	30	24	1.64	46	.12
3	1.5	.10	.085	1.16	10	30	24	5.7	57	.12
4	7.5	.05	.048	1.16	5	0	24	2.5	50	.14
5	7.5	.10	.048	2.32	5	30	24	2.8	56	.19
6	7.5	.10	.048	2.32	2.7	30	54	2.0	74	.21
7	7.5	.15	.048	3.0	5	30	44	3.3	66	.38
8	7.5	.15	.048	3.0	5	50	44	3.8	76	.31

[a] All viscosities were run at 0.25 g./100 ml. Extrapolation of the curve obtained by plotting concentration *vs.* viscosity showed that the inherent viscosity was the same as the dilute solution viscosity at this concentration, within experimental error.

TABLE III

POLYMERIZATION OF 1,5-HEXADIENE

Sample	Heptane, g.	Al(*i*-Bu)$_3$, g.	TiCl$_4$, g.	Moles Al(*i*-Bu)$_3$ / moles TiCl$_4$	Monomer, g.	Temp., °C.	Time, hr.	Polymer, wt., g. Sol.	Insol.	Conversion, %	η[a]
1	15	0.10	0.085	1.16	10	60	24	0.40	0.6	10	..
2	15	.10	.085	1.16	10	30	70	.10	..	1	..
3	3.5	.10	.085	1.16	5	30	70	.20	..	4	..
4	3.5	.10	.085	1.16	5	50	70	.60	0.70	26	..
5	2	.15	.048	3.0	4.5	30	50	1.5	2.0	78	0.20
6	2	.15	.048	3.0	4.5	50	50	0.5	3.0	78	.23
7	7.5	.15	.048	3.0	4.5	30	50	1.8	2.1	87	.23
8	7.5	.15	.048	3.0	4.5	50	50	0.7	2.6	73	.22

[a] All viscosities were run at concentrations of 0.25 g./100 ml.

TABLE IV

POLYMERIZATION OF 2,5-DIMETHYL-1,5-HEXADIENE

Sample	Heptane, g.	Al(*i*-Bu)$_3$, g.	TiCl$_4$, g.	Moles Al(*i*-Bu)$_3$ / moles TiCl$_4$	Monomer, g.	Temp., °C.	Time, hr.	Polymer, wt., g.	Conversion, %	η[a]
1	15	0.1	0.085	1.16	10	30	36	1.2	12	0.028
2	15	.1	.085	1.16	10	60	36	4.3	43	.023
3	3.4	.2	.170	1.16	15	0	72	8.6	57	.084
4	3.4	.2	.170	1.16	15	30	72	15.0	100	.107
5	3.4	.2	.170	1.16	15	60	72	14.0	93	.078
6	2	.15	.048	3.0	5	30	50	0.1	2	..
7	2	.15	.048	3.0	5	50	50	..	..	..
8	7.5	.15	.048	3.0	5	30	50	..	..	..
9	7.5	.15	.048	3.0	5	50	50	..	..	..

[a] All viscosities were run at concentrations of 0.25 g./100 ml. in benzene.

amount of a 10% heptane solution of aluminum triisobutyl[25] to the heptane polymerization solvent in a polymerization bottle, and then adding a measured amount of the pure titanium tetrachloride to this mixture. The monomer was then added to the dark brown suspension of catalyst which formed, and the bottles were sealed and removed from the dry-box.

Poly-1,6-heptadiene (IX).—Table II shows the results of the polymerization of 1,6-heptadiene. At the end of the polymerization period, the bottles were opened and their contents were emptied into methanol in order to decompose the catalyst. All polymers were purified by four reprecipitations from a benzene solution by addition to rapidly stirred methanol. The reprecipitated polymers were then subjected to freeze drying from a benzene solution. Sample 7 had a melting point of 210–230°. It formed a clear, tough film on slow evaporation of its benzene solution. Quantitative infrared analyses of standard carbon tetrachloride solutions (5%) of both 1,6-heptadiene and a sample of polyheptadiene were made by comparing the absorption strengths of the C=C stretching frequency at 1650 cm.$^{-1}$ and the vinyl C–H wagging frequency at 920 cm.$^{-1}$. The percentage double bond character was found by a direct comparison of the optical densities. The analysis showed that the polymer contained from 4 to 10% of the monomer units which still had one of the two double bonds unaltered.

Anal. Calcd. for $(C_7H_{12})_n$: C, 87.42; H, 12.58. Found: C, 86.61; H, 12.28.

Dehydrogenation of Poly-1,6-heptadiene.—Dehydrogenation attempts with platinum and palladium catalysts failed, probably because of the inability to remove the polymer from the catalyst since the recovery of poly-1,6-heptadiene was extremely low. To 2.6 g. of potassium perchlorate[18] was added 0.5 g. of poly-1,6-heptadiene dissolved in benzene. The benzene was completely removed under reduced pressure, thus depositing a film of polymer on the potassium perchlorate crystals. The reaction tube was sealed and heated to 390° for 16 hours. The contents of the tube were ground and extracted with benzene by use of a Soxhlet extractor for eight hours, and the extract was subjected to freeze drying. A chloroform solution of the product showed absorption maxima for aromatic C–H (3040 cm.$^{-1}$), aromatic C=C (1607 and 1505 cm.$^{-1}$) and C–H for *m*-substitution (815 and 748 cm.$^{-1}$). The ultraviolet spectrum of an ethanol solution of the product showed λ_{max} at 255 mμ.

Poly-1,5-hexadiene (X, XII).—The results of the polymerization are shown in Table III. The soluble portion of these polymers was extracted with benzene. The melting point of the soluble fraction was 85–90°, and a quantitative

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[25] The aluminum triisobutyl was obtained from the Hercules Powder Co. and was reported to analyze for 13.2% Al; calculated is 13.6%.

TABLE V

POLYMERIZATION OF 2-METHYL-1-PENTENE

Sample	Heptane,[a] g.	$Al(i\text{-}Bu)_3$, g.	$TiCl_4$, g.	Moles $Al(i\text{-}Bu)_3$[b] / moles $TiCl_4$	Monomer, g.	Time, hr.	Temp., °C.	Polymer wt., g.	Conversion, %
1	4	0.10	0.085	1.16	10	30	54	1	10
2	3.5	.10	.085	1.16	10	30	54	1.3	13
3	3.5	.10	.085	1.16	10	50	54	1	10

[a] A solvent ratio to monomer of 1.5 (wt. ratio) failed to produce polymer. [b] A catalyst ratio of 3.0 failed to produce polymer.

infrared analysis of carbon tetrachloride solutions of both 1,5-hexadiene and poly-1,5-hexadiene were made by comparing the absorption maxima of the C=C at 1650 cm.$^{-1}$ and the vinyl C–H at 920 cm.$^{-1}$. The analysis showed that the polymer contained from 5.6 to 8.6% of the monomer units which still retained one of the two double bonds. No attempt was made to dehydrogenate this polymer.

Anal. Calcd. for $(C_6H_{12})_n$: C, 87.72; H, 12.24. Found: C, 86.78; H, 12.16.

Poly-2,5-dimethyl-1,5-hexadiene (XIV, XV).—Table IV shows the results of the polymerization of 2,5-dimethyl-1,5-hexadiene. These polymers had melting points of 80–85° and a quantitative infrared analysis of carbon tetrachloride solutions of both 2,5-dimethyl-1,5-hexadiene and its polymer by comparison of the maxima for C=C and vinyl CH showed that from 3.4 to 12.8% of the monomer units retained one double bond during polymerization. No attempt was made to dehydrogenate this polymer.

Anal. Calcd. for $(C_8H_{14})_n$: C, 87.19; H, 12.81. Found: Sample 1: C, 87.43; H, 12.57. Sample 2: C, 87.13; H, 13.21.

Poly-2-methyl-1-pentene.—The results of polymerization of 2-methyl-1-pentene are shown in Table V. The oils obtained were combined and distilled under diminished pressure (150° (0.1 mm.)). The infrared spectrum of this hydrocarbon showed no unsaturation was present in the molecule.

Anal. Calcd. for $(C_6H_{12})_n$: C, 84.63; H, 14.37; mol. wt. ($n = 5$), 425.8. Found: C, 85.45; H, 14.13; mol. wt., 424.

URBANA, ILLINOIS

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE UNIVERSITY OF NOTRE DAME]

The Mechanism of Halide Reductions with Lithium Aluminum Hydride. VI. Reduction of Certain Bromohydrins and Epoxides[1,2]

BY ERNEST L. ELIEL AND DAVID W. DELMONTE[3]

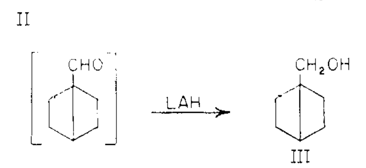
RECEIVED OCTOBER 24, 1957

Lithium aluminum hydride reduction of 1,1-diphenyl-2-bromoethanol yields 2,2-diphenylethanol, in addition to the expected 1,1-diphenylethanol. Similarly, reduction of 1,1,2-triphenyl-2-bromoethanol yields 1,2,2-triphenylethanol, and reduction of 1,1-diphenyl-2-(*p*-chlorophenyl)-2-bromoethanol yields 1-(*p*-chlorophenyl)-2,2-diphenylethanol. The "oxygen shift" observed in these reductions is explained on the basis of an epoxide intermediate. In accordance with this explanation, it has been found that lithium aluminum hydride reduction of unsymmetrically substituted epoxides, $RR'\overset{O}{\widehat{C\text{—}C}}HR''$ *in the presence of aluminum halides* gives rise to the less highly substituted carbinols RR'CHCHOHR", although similar reduction *in the absence of aluminum halides* gives the more highly substituted carbinols $RR'COHCH_2R''$. Tracer studies show that the reduction of styrene oxide and isobutylene oxide in the presence of aluminum halides involves the corresponding aldehydes (phenylacetaldehyde and isobutyraldehyde) as intermediates. The implications of these results on the mechanism of reduction of halohydrins in general are discussed.

In a previous publication[4] it has been shown through tracer studies that lithium aluminum hydride reduction of a halohydrin with tertiary halogen, such as 2-chloro-2-methyl-1-propanol (I), proceeds largely through a hydride shift

$$\underset{\text{I}}{(CH_3)_2CClCH_2OH} \xrightarrow[-HCl]{H^-} (CH_3)_2CHCHO \xrightarrow{LiAlD_4} (CH_3)_2CHCHDOH \quad \text{(i)}$$

It was the original aim of the present work to establish whether a corresponding *alkyl* shift would occur in the reduction of halohydrins of the type $RR'COH\overset{|}{\underset{|}{C}}X$. Isolated instances of alkyl shifts of this kind in lithium aluminum hydride reductions are already on record; thus reduction of the bicyclic bromoketone II gives rise to the alcohol III[5]; in the treatment of *trans*-2-chlorocyclohexanol (IV) with lithium aluminum hydride under drastic conditions some cyclopentaldehyde (V) is ob-



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(1) Presented before the Organic Division of the American Chemical Society at Miami, Fla., on April 11, 1957. For a preliminary communication of part of this work, see THIS JOURNAL, **78**, 3226 (1956); cf. also G. J. Park and R. Fuchs, *J. Org. Chem.*, **21**, 1513 (1956).

(2) Paper V, E. L. Eliel and J. T. Traxler, THIS JOURNAL, **78**, 4049 (1956).

(3) This paper is based on the Ph.D. dissertation of D. W. Delmonte, Shell Research Fellow, 1955–1956.

(4) E. L. Eliel and Th. J. Prosser, THIS JOURNAL, **78**, 4045 (1956).

(5) A. C. Cope, E. S. Graham and D. J. Marshall, *ibid.*, **76**, 6159 (1954). These authors postulate rearrangement at the bromoketone stage, but, reasoning by analogy with the hydride shift in eqn. (i),[4] we prefer to assume that the ring contraction occurs at the bromohydrin stage.