served differences in ultraviolet absorption of the derivatives are in accord with this interpretation.[31]

Benzyl *t*-Butyl Ketone (IIId).—To an ethereal solution of benzylmagnesium chloride, prepared from 99.0 g. (0.783 mole) of benzyl chloride and 19.2 g. (0.790 g.-atom) of magnesium, was added, in portions with stirring over a period of 30 min., 19.7 g. (0.195 mole) of trimethylacetamide. The resulting solution was refluxed with stirring for 22 hr. and then poured into a mixture of ice and hydrochloric acid. The neutral products, isolated in the usual way, were subjected to a series of fractional distillations, the course of the distillation being followed by gas chromatography. After the separation of 0.119 g. of unchanged amide, m.p. 152–153°, and 1.94 g. of bibenzyl, m.p. 50–51.5° (lit.[32] 52.5–53.5°), the yield of pure ketone, b.p. 130–131° (21 mm.), $n^{29}\mathrm{D}$ 1.4984–1.4989, amounted to 8.52 g. (25%).

Anal. Calcd. for $C_{12}H_{16}O$: C, 81.77; H, 9.15. Found: C, 81.72; H, 9.08.

The infrared spectrum[21] of the product has a band at 1711 cm.$^{-1}$ (C=O); the ultraviolet spectrum[23] has a maximum at 258 mμ (ε 220) with a molecular extinction of 121 at 244 mμ.

The ketone formed a 2,4-dinitrophenylhydrazone which separated from ethanol as yellow needles, m.p. 139.3–140.3°, yield 70%. An additional recrystallization raised the melting point to 140.1–140.8°. The ultraviolet spectrum[20] has a maximum at 365 mμ (ε 25,200).

Anal. Calcd. for $C_{18}H_{20}N_4O_4$: C, 60.66; H, 5.66; N, 15.72. Found: C, 60.52; H, 5.76; N, 15.52.

CAMBRIDGE, MASS.

[31] F. Ramirez and A. F. Kirby, THIS JOURNAL, **76**, 1037 (1954).

[32] F. D. Greene, W. A. Remers and J. W. Wilson, *ibid.*, **79**, 1416 (1957).

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

Polymerization of Higher α-Diolefins with Metal Alkyl Coordination Catalysts[1]

BY C. S. MARVEL AND W. E. GARRISON, JR.

RECEIVED FEBRUARY 14, 1959

The α-diolefins of the general formula $CH_2{=}CH(CH_2)_nCH{=}CH_2$ where *n* is equal to 4, 5, 6, 7, 8, 9, 10, 11, 12, 14 and 18, have been prepared and polymerized with the system aluminum triisobutyl–titanium tetrachloride. The polymers obtained consist of both soluble and insoluble, cross-linked fractions. The results of quantitative infrared and bromination determinations indicate that the soluble polymers possess cyclic units, open chain units containing terminal unsaturation as is present in the monomer, and open chain units containing internal unsaturation resulting from a rearrangement of the double bond from the terminal position.

In a recent publication,[2] was described the polymerization of 1,5-hexadiene and 1,6-heptadiene by means of the aluminum triisobutyl–titanium tetrachloride catalyst system to yield polymers which contained repeating cyclic units separated by methylene bridges. The present paper reports a study of the action of the coördination catalysts on longer chain α-diolefins.

The preparation of 1,7-octadiene (I) and 1,13-tetradecadiene (II) was carried out by allowing the appropriate ω-unsaturated alkylenemagnesium bromide to react with allyl bromide.

$$\mathrm{CH_2{=}CH(CH_2)_nMgBr} \xrightarrow{\mathrm{CH_2{=}CHCH_2Br}} \mathrm{CH_2{=}CH(CH_2)_{n+1}CH{=}CH_2}$$

I, $n + 1 = 4$
II, $n + 1 = 10$

The use of allyl chloride has been reported to yield only 15% of 1,7-octadiene,[3] but our yields were about 65%. Also the preparation of 1,13-tetradecadiene only in low yields in a manner similar to that described here has been reported[4] before.

The use of the appropriate α,ω-alkylenedimagnesium halides afforded good yields of 1,11-dodecadiene (III) (72%),[5] 1,14-pentadecadiene (IV) (54%) and 1,15-hexadecadiene (V) (56%). In addition to the main products, small amounts of α-diolefins containing an increased number of carbon atoms were isolated. From the synthesis of 1,14-pentadecadiene and 1,15-hexadecadiene were isolated, respectively, 1,23-tetracosadiene (VI) (12%) and 1,25-hexacosadiene (VII) (11%). These are new compounds and represent the longest known members of the straight-chain α-diolefin series.

$$\mathrm{Br(CH_2)_nBr} \xrightarrow{\mathrm{Mg}} \xrightarrow{\mathrm{CH_2{=}CH{-}CH_2Br}} \mathrm{CH_2{=}CH(CH_2)_{n+2}CH{=}CH_2} +$$

III, $n + 2 = 8$
IV, $n + 2 = 11$
V, $n + 2 = 12$

$$\mathrm{CH_2{=}CH(CH_2)_{2n+2}CH{=}CH_2}$$

VI, $2n + 2 = 20$
VII, $2n + 2 = 22$

1,14-Pentadecadiene has not been previously reported in the literature. 1,15-Hexadecadiene has been obtained only as a by-product from the reaction of 1,5-pentanedimagnesium bromide with allyl bromide.[6] The constants for these compounds reported earlier do not agree with those obtained here and they are not consistent with those expected in the α-diolefin series.

1,12-Tridecadiene (IX) has not been previously reported in the literature. The Boord olefin synthesis provided an easy route to this diolefin from undecylenyl bromide. The intermediate, α-(10-undecenyl)-β-bromoethyl ethyl ether (VIII), was obtained in 75% yield by allowing the Grignard reagent of undecylenyl bromide to react with α,β-dibromoethyl ethyl ether. However, it was difficult to find conditions which would permit formation and isolation of 1,12-tridecadiene from this

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[1] The work discussed herein was sponsored by a grant (NSF-G-2626) from the National Science Foundation.

[2] C. S. Marvel and J. K. Stille, THIS JOURNAL, **80**, 1740 (1958).

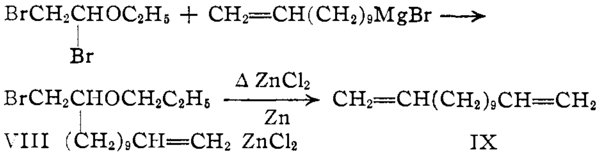
[3] R. Ya. Levina and E. A. Viktorova, *Vestnik, Moscov. Univ.*, **6**, No. 2, *Ser. Fiz.-Mat. i Estestven. Nauk*, No. 1, 89 (1951); *C. A.*, **46**, 8605 (1952).

[4] L. Canonica, M. Martinolli and T. Bacchotti, *Atti. accad. nazl. Lincei. Rend., Classe sci. fis, mat. e nat.*, **13**, 61 (1952); *C. A.*, **47**, 11131 (1953).

[5] A. D. Petrov and M. A. Cheltsova, *Bull. Acad. sci. U.S.S.R.. Classe sci. chim.*, 267 (1940); *C. A.*, **35**, 4730 (1941).

[6] J. N. Reformatsky, E. Grischkewitsch-Trochimowsky and A. Semensow, *Ber.*, **44**, 1885 (1911).

intermediate. Treatment of VIII with zinc dust in isopropyl alcohol for 24 hours followed by distillation resulted in the formation of a tar. Next, attention was turned to a method which would permit removal of the diolefin as it was formed. Since the distillation would have to take place under reduced pressure, the use of a high-boiling solvent was necessary. The use of "Carbowax 600" polyethylene glycol as a solvent together with a short Vigreux column at a pressure of 1–2 mm. produced the diolefin in 96% yield from the β-bromo ether.



$$\underset{|\atop \text{Br}}{\text{BrCH}_2\text{CHOC}_2\text{H}_5} + \text{CH}_2{=}\text{CH(CH}_2)_9\text{MgBr} \longrightarrow$$

$$\underset{\text{VIII}\quad|\atop (\text{CH}_2)_9\text{CH}{=}\text{CH}_2\ \text{ZnCl}_2}{\text{BrCH}_2\text{CHOCH}_2\text{C}_2\text{H}_5} \xrightarrow[\text{Zn}]{\Delta\ \text{ZnCl}_2} \underset{\text{IX}}{\text{CH}_2{=}\text{CH(CH}_2)_9\text{CH}{=}\text{CH}_2}$$

The reaction of undecylenyl bromide with sodium produced 1,21-docosadiene (X) in 61% yield. Canonica, *et al.*,[4] have reported the synthesis of this compound in 27% yield by the action of potassium on undecylenyl bromide.

$$CH_2{=}CH(CH_2)_9Br \xrightarrow[\text{ether}]{\text{Na}} CH_2{=}CH(CH_2)_{18}CH{=}CH_2$$

X

Synthetic methods for the remainder of the diolefins were based on the elimination of the elements of water from the appropriate diol or ω-unsaturated alcohol. The pyrolysis of the corresponding acetate was the method of choice. The diols were obtained by hydrogenolysis of the appropriate esters, and converted to the diacetoxy compounds, using acetyl chloride in ether. Undecylenyl acetate (XIX) was prepared by the action of acetyl chloride on the alcohol in ether–pyridine. The pyrolysis of this acetate yielded 1,10-undecadiene (XX).

$$CH_3COO(CH_2)_nOCOCH_3 \xrightarrow{565°}$$

XI, $n = 9$
XII, $n = 10$
XIII, $n = 18$

$$CH_2{=}CH(CH_2)_{n-4}CH{=}CH_2 +$$

XIV, $n - 4 = 5$
XV, $n - 4 = 6$
XVI, $n - 4 = 14$

$$CH_3COO(CH_2)_{n-2}CH{=}CH_2$$

XVII, $n - 2 = 7$
XVIII, $n - 2 = 16$

$$CH_2{=}CH(CH_2)_9OCOCH_3 \xrightarrow{565°}$$

XIX

$$CH_2{=}CH(CH_2)_7CH{=}CH_2$$

XX

The polymerization of these higher α-diolefins yielded low molecular weight polymers made up of soluble and insoluble portions. It was observed that a 1:1 molar ratio of aluminum triisobutyl to titanium tetrachloride gave a higher conversion to polymer than did a 3:1 ratio, and the viscosity of the polymer was not significantly affected by this change in catalyst. It was also noticed that reproducible results could be obtained only if the monomer concentrations were low, and a high catalyst to monomer ratio were used.

All of the insoluble polymers possess similar characteristics. They were insoluble in benzene, but upon treatment with benzene at room temperature swelled to form a thin gel. When sufficient benzene was present, the gels possessed the appearance of a sirupy solution. However, this gel would not pass through a filter, and filtration left a swollen polymer on the filter. When the dilute gels were subjected to freeze-drying, the polymer possessed the shape of the container. These observations indicated that the insoluble polymer possessed a low degree of crosslinking. This was further substantiated by the infrared spectra of the insoluble polymers, which indicated a high degree of unsaturation. The expected analyses, calculated for the monomers, were obtained for the insoluble polymers.

All of the soluble polymers obtained from the diolefins possess a very low molecular weight as evidenced by their sticky semi-solid appearance and their inherent viscosities, which are in the range of 0.1. This low molecular weight is not surprising since chances of ring formation of a size larger than six are not great and crosslinkages will form before a high degree of polymerization is attained.

The infrared spectra of the soluble polymers together with quantitative measurements of unsaturation by infrared spectroscopy and by bromination indicate that they are mixtures of several types of units. Since the total unsaturation in the soluble polymers is considerably less than one double bond per monomer unit, some cyclization has occurred. It cannot be ascertained whether this cyclization is within one monomer unit, or whether several monomer chains are involved in the cyclization process.

The polymer possesses unreacted vinyl groups, as well as internal unsaturation, resulting from a rearrangement of the double bond during or following the polymerization process. In the case of poly-1,7-octadiene, the situation is further complicated by the presence of considerable vinylidene unsaturation ($R_2C{=}CH_2$) detectable in the infrared spectrum at 1366 and 885 cm.$^{-1}$. Since the molecular weight of poly-1,7-octadiene is very low, this type of unsaturation is probably due to the presence of this type of end group. The following scheme using 1,7-octadiene as an example can account for the formation of simple cyclic units, as well as vinyl and internal unsaturation and vinylidene end groups. Such a scheme is similar to that proposed by Natta for the stereospecific polymerization of vinyl monomers.[7] The rearranged unit is represented here as a 2-olefin, although the position of the unsaturation has not been established. Recent work in this Laboratory indicates that a mixture of various olefins may be present. This type of rearrangement with metal coördination catalysts has been reported in one patent[8] covering the polymerization of 1,5-hexadiene but does not seem to have been recognized in other cases.

This rearrangement could involve abstraction of an allylic hydrogen atom by an anion, followed

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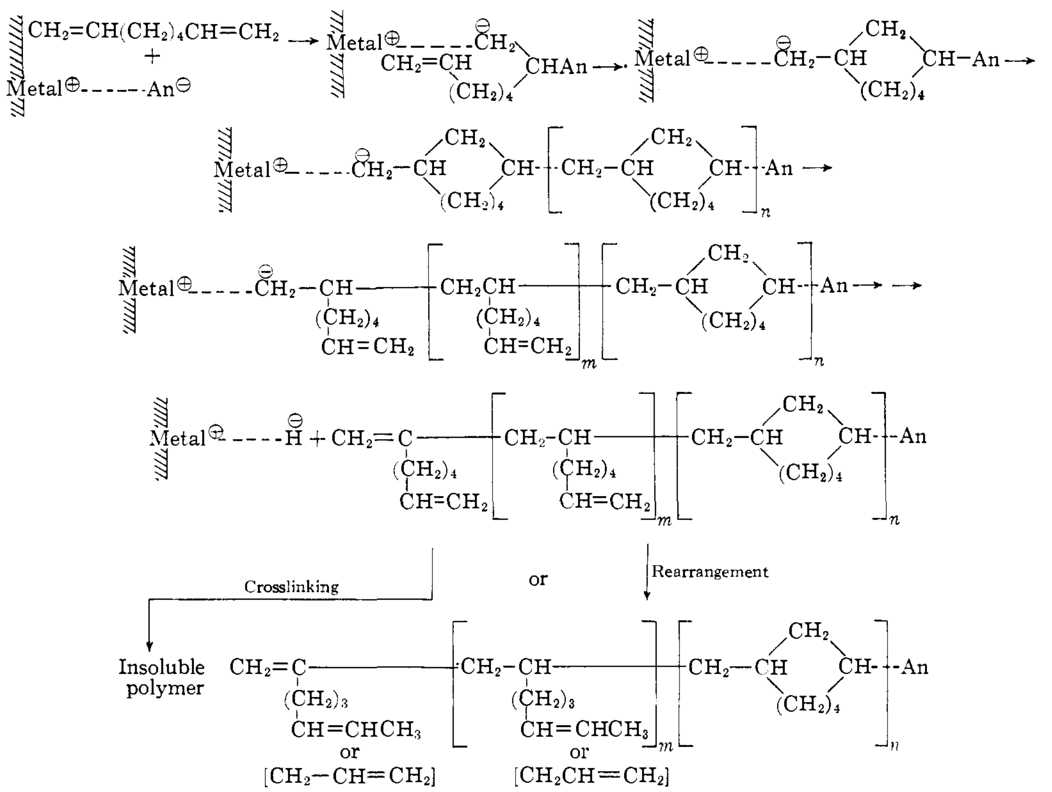
[7] G. Natta, *Makromol. Chem.*, **16**, 213 (1955).

[8] E. I. du Pont de Nemours and Co., British Patent 776,326 (1957).



by an allylic shift and subsequent abstraction of a hydrogen atom by the rearranged allylic anion from another species as illustrated

$$An^- + CH_2{=}CHCH_2R \longrightarrow CH_2{=}CH\overset{\ominus}{C}HR + AnH$$

$$CH_2{=}CH\overset{\ominus}{C}HR \longleftrightarrow \overbrace{CH_2 \cdots CH \cdots CHR}^{\ominus} \longleftrightarrow \overset{\ominus}{C}H_2CH{=}CHR$$

$$^-CH_2CH{=}CHR + RH \longrightarrow CH_3CH{=}CHR + R^-$$

In an attempt to identify the catalyst species responsible for this rearrangement, 1,10-undecadiene was treated in heptane solution with aluminum triisobutyl and with titanium tetrachloride. However, the monomer was recovered unchanged in both cases. Apparently the combination of the aluminum isobutyl and titanium tetrachloride is needed to produce the rearrangement.

The results of polymerization at varying dilutions of the monomer show an interesting relationship. The data in Table XIII clearly indicate that the amount of terminal unsaturation decreases considerably with a higher dilution of the monomer, while the internal unsaturation, due to rearrangement, is much less affected. The simplest explanation of this phenomenon would be that a cyclization process takes place, and a higher degree of cyclization would be favored in a more dilute solution.

It is impossible to determine the exact extent of cyclization in the polymerization of these dienes since there is no method of estimating the extent to which cyclic units occur in the crosslinked polymer. It would seem reasonable to believe that the ratio of open chain units to cyclic units in this insoluble fraction was about the same as it was found to be in the low molecular weight soluble polymer since the crosslinking undoubtedly occurs as these polymers continue to grow. A rough estimate of the percentage of cyclic units which occur in the soluble polymers can be made by using the data on total unsaturation of these polymers and their yields. The amount of cyclization is related to the dilution with the maximum amount of cyclization occurring at the greatest dilution used in polymerization experiments.

By using the data for a series of polymerizations carried out at approximately 0.2 molar or less concentration the maximum yield of the smallest possible ring size has been calculated and the figures are listed in Table I. It must be emphasized that these are estimates rather than accurate determinations since some uncertain assumptions are made in the calculations.

TABLE I

ESTIMATED MAXIMUM YIELD OF SMALLEST POSSIBLE RING SIZE

Possible ring size	% cyclic units in soluble polymer	Possible ring size	% cyclic units in soluble polymer
7	25	12	11
8	9	14	15
9	6	15	15
10	10	17	4
11	11	21	8

These percentages of cyclization correspond roughly to those which have been realized in other cyclization reactions. Seven-membered rings form fairly readily, the intermediate ring sizes with greater difficulty, the larger rings (14–15) are easier to obtain, and finally the yields drop again with the higher ring sizes.

Holt and Simpson[9] determined the degree of cyclization which occurred in the free radical initiated polymerization of diallyl esters of dibasic acids. They concluded that for ring sizes of nine or greater the degree of cyclization decreases as the distance between the unsaturated groups increases. They observed unexpectedly high values for cyclization in the case of diallyl succinate which would yield an eleven-membered ring.

Experimental

1,7-Octadiene (I).—The Grignard reagent was prepared from 224 g. (1.50 moles) of 5-bromo-1-pentene[10] and 37 g. (1.52 moles) of magnesium in 600 ml. of ether under a nitrogen atmosphere. The solution of the Grignard reagent was heated with stirring under reflux for 45 minutes, and allowed to cool. Then 218 g. (1.8 moles) of redistilled allyl bromide was added over a period of one hour. After the completion of the addition the resulting mixture was heated and stirred for 14 hours and then poured slowly into an ice–water mixture and acidified with hydrochloric acid. The ether layer was separated, washed with water, dried over potassium carbonate, and distilled. The yield of 1,7-octadiene was 109 g. (66%), b.p. 112–120°.[2] The octadiene was further purified by two redistillations under nitrogen from sodium through a Fenske column, b.p. 116–118°, $n^{20}\text{D}$ 1.4236.[3] The infrared spectrum[11] of this material showed absorption maxima for C=C (1641 cm.$^{-1}$) and =CH (995 and 913 cm.$^{-1}$).

Anal. Calcd. for C_8H_{14}: C, 87.19; H, 12.81. Found[12]: C, 87.51; H, 12.90.

1,9-Nonanediol.—Commercial azelaic acid, obtained from Armour and Co., was decolorized and recrystallized from water until a constant melting point, 105.0–105.9°, was obtained. The purified acid was esterified with ethanol, and the diethyl ester was hydrogenated according to the procedure described for 1,6-hexanediol.[13] The diol was isolated by distillation, b.p. 147–150°[14] (2 mm.), and solidified upon standing at room temperature.

1,9-Diacetoxynonane (XI).—To a slurry of 160 g. (1.00 mole) of 1,9-nonanediol in 250 ml. of dry ether was added, with stirring, 190 ml. (2.6 moles) of acetyl chloride at a rate sufficient to keep the mixture at a gentle reflux. The resulting mixture was heated under reflux for 6 hours and stirred overnight. Distillation of the mixture yielded 230 g. (94%) of 1,9-diacetoxynonane, b.p. 110° (0.30 mm.), $n^{25}\text{D}$ 1.4347.[15]

1,8-Nonadiene (XIV).—The pyrolysis of 227 g. (0.93 mole) of 1,9-diacetoxynonane at 565°, according to the method described by Marvel and Stille[2] for the preparation of 1,6-heptadiene, yielded 56.9 g. (56%) of 1,8-nonadiene, b.p. 140–144°, and 22.1 g. (13%) of 9-acetoxy-1-nonene, b.p. 100–113° (13 mm.). The nonadiene was digested over sodium wire at 80° for 14 hours and distilled under nitrogen through a Fenske column, b.p. 141–142°, $n^{25}\text{D}$ 1.4248.[15] The infrared spectrum of this material was similar to that for 1,7-octadiene.

9-Acetoxy-1-nonene (XVII).—The 9-acetoxy-1-nonene obtained above was redistilled through a Holtzman column, and a fraction was obtained which boiled at 78.3° (2.3 mm.), $n^{25}\text{D}$ 1.4325. The infrared spectrum of this compound showed absorption maxima for ester C=O (1745 cm.$^{-1}$), C=C (1644 cm.$^{-1}$), C–O (1240 cm.$^{-1}$) and =CH_2 (995 and 908 cm.$^{-1}$).

Anal. Calcd. for $C_{10}H_{20}O_2$: C, 71.69; H, 10.94. Found: C, 71.54; H, 11.03.

1,10-Decanediol.—Diethyl sebacate (903 g., 3.5 moles) was hydrogenated as decribed for 1,6-hexanediol.[13] After hydrolysis of the residual ester and removal of the ethanol as usual, the hot, oily residue was poured, with stirring, into cold water. The precipitated diol was collected on a filter, washed well with cold water, and dried. The dry material was dissolved in six liters of hot benzene, decolorized with Darco, filtered hot, and allowed to cool, yielding a mass of white crystals. These were filtered off, washed with ether, and dried, yielding 440 g. (72%) of 1,10-decanediol, melting at 71.4–72.5°. Further recrystallizations from benzene raised the melting point to 72.3–72.9°.[14]

1,10-Diacetoxydecane (XII).—From 174 g. (1.0 mole) of 1,10-decanediol and 177 ml. (2.5 moles) of acetyl chloride, using 300 ml. of ether, as described for the preparation of 1,9-diacetoxynonane, was obtained 244 g. (95%) of 1,10-diacetoxy-decane, b.p. 118–120° (0.4 mm.).[16]

1,9-Decadiene (XV).—The pyrolysis of 242 g. (0.94 mole) of 1,10-diacetoxydecane as described for the preparation of 1,8-nonadiene yielded 428 g. (33%) of 1,9-decadiene, b.p. 164–165° (760 mm.), and 13.5 g. (7%) of 10-acetoxy-1-decene, b.p. 120–125° (14 mm.), $n^{25}\text{D}$ 1.4350.[17] The diene was redistilled from sodium, under nitrogen through a Fenske column, b.p 164.7–165.0°, $n^{25}\text{D}$ 1.4302, d^{18}_4 0.7478.[18]

11-Acetoxy-1-undecene (Undecylenyl Acetate) (XIX).—Undecylenyl alcohol of greater than 98% purity was obtained from Givaudan–Delawanna, Inc., and 170 g. (1.0 mole) of this material was dissolved in 109 ml. (1.35 moles) of dry pyridine and 300 ml. of ether. The resulting mixture was cooled in an ice-bath and 89 ml. (1.25 moles) of acetyl chloride was added over 45 minutes. The reaction mixture was stirred for 9 hours and poured into an ice–water mixture. The ether layer was separated and washed with water, 5% hydrochloric acid, water, and saturated sodium bicarbonate, and dried over magnesium sulfate. Distillation of the ether solution yielded 190 g. (90%) of 11-acetoxy-1-undecene, b.p. 96–98° (1.8 mm.), $n^{25}\text{D}$ 1.4380.[19]

1,10-Undecadiene (XX).—The pyrolysis of 11-acetoxy-1-undecene was carried out as described for the preparation of 1,8-nonadiene. When a rate of 0.9 g. per minute and a temperature of 565° was used, 73.6 g. (57%) of 1,10-undecadiene and 15.8 g. (9%) of recovered reactant were obtained. The diene was digested for 17 hours over sodium wire at 70° and redistilled under nitrogen through a Fenske column, b.p. 119–120° (95 mm.), $n^{25}\text{D}$ 1.4347, d^{28}_0 1.7572.[6] The infrared spectrum of this material was identical to that of 1,7-octadiene.

Anal. Calcd. for $C_{11}H_{20}$: C, 86.76; H, 13.24. Found: C, 86.53; H, 13.50.

1,11-Dodecadiene (III).—The Grignard reagent was prepared from 97.6 g. (0.4 mole) of hexamethylene dibromide and 21.9 g. (0.9 mole) of magnesium by the addition of the dibromide over a period of 3 hours to the magnesium in 300 ml. of ether. The Grignard reagent, insoluble in excess ether, was stirred for 30 minutes, filtered through glass wool, and added slowly, with rapid stirring, to a solution of 121 g. (1.0 mole) of redistilled allyl bromide in 250 ml. of ether. The resulting mixture was stirred overnight and then hydrolyzed with 40 ml. of 20% acetic acid followed by 300 ml. of water. The ether layer was separated, washed with saturated sodium bicarbonate solution, then with saturated sodium chloride solution, dried over sodium sulfate, and distilled. The yield of 1,11-dodecadiene was 47.8 g. (72%), b.p. 91–95° (14 mm.). The diene was purified by digestion over sodium followed by distillation under nitrogen through a Fenske column, b.p. 117–118° (40 mm.), $n^{25}\text{D}$ 1.4371, d^{28}_4 0.7614.[5]

Anal. Calcd. for $C_{12}H_{22}$: C, 86.66; H, 13.34. Found: C, 86.73; H, 13.43.

11-Bromo-1-undecene. (Undecylenyl Bromide).—Undecylenyl alcohol (425 g., 25 moles) was dissolved in a mixture of 700 ml. of dry toluene and 67 ml. of pyridine, and the solution was cooled to −10° and kept at −5 to −10° while a solution of 271 g. (1.0 mole, 95.3 ml.) of phosphorus tribromide in 700 ml. of dry toluene was added over a period of two hours. Then the reaction mixture was allowed to warm to room temperature and heated on a steam-bath for two

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(9) T. Holt and W. Simpson, *Proc. Roy. Acad.* (*London*), **A238**, 154 (1956).

(10) P. Gaubert, R. P. Linstead and H. N. Rydon, *J. Chem. Soc.*, 1971 (1937).

(11) The infrared spectra were determined by Mr. Paul McMahon and Miss Mary DeMott. The spectra were obtained from a Perkin-Elmer model 21 spectrometer.

(12) The microanalyses were performed by Mr. Joszef Nemeth, Miss Claire Higham, Miss Jane Liu and Mrs. Ruby Ju, University of Illinois.

(13) W. A. Lazier, J. W. Hill and W. J. Amend, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., p. 325 (1943).

(14) R. H. Manske, *ibid.*, p. 154.

(15) A. J. Van Pelt, Jr., and J. P. Wibaut, *Rec. trav. chim.*, **60**, 55 (1941).

(16) R. Scheuble, *Monatsh.*, **24**, 618 (1903).

(17) L. Alberti and B. Smieciuszewski, *ibid.*, **27**, 411 (1906).

(18) J. L. Everett and G. A. R. Kon, *J. Chem. Soc.*,31 31 (1950).

(19) J. Colonge and M. Reymermier, *Bull. soc. chim.*, *France* 1531 (1955).

hours with stirring. The liquid was decanted from the yellow solid material, and the solid was washed with a small amount of toluene. The washings were added to the liquid layer and the toluene was removed under reduced pressure. The residue was distilled rapidly without a column at 0.1–0.3 mm. until no further distillation occurred and copious fuming appeared in the pot. The distillate was diluted with an equal volume of ether, and the solution was washed with water, saturated sodium bicarbonate, saturated sodium chloride, dried over sodium sulfate, and distilled. A yield of 390 g. (67%) of colorless 11-bromo-1-undecene was obtained, b.p. 95–98° (2 mm.), n^{25}_{D} 1.4667.[20]

α-(10-Undecenyl)-β-bromoethyl Ethyl Ether (VIII).—The Grignard reagent was prepared from 128 g. (0.55 mole) of 11-bromo-1-undecene and 14.6 g. (0.60 mole) of magnesium in 400 ml. of ether, heated under reflux for one hour, and filtered under nitrogen through glass wool into a dry, nitrogen-filled flask. The filtrate was cooled in an ice-bath, and then 116 g. (0.50 mole) of α,β-dibromoethyl ethyl ether[21] was added, with rapid stirring, over a period of two hours. The resulting mixture was heated under reflux for 90 minutes, stirred overnight, and then hydrolyzed with 10 ml. of 20% acetic acid followed by 150 ml. of water. The ether layer was separated, washed with saturated sodium bicarbonate and saturated sodium chloride solution, and dried over sodium sulfate. Distillation of the ether solution yielded 113 g. (75%) of α-(10-undecenyl)-β-bromoethyl ethyl ether, b.p. 118–122° (0.3 mm.), n^{25}_{D} 1.4631. The infrared spectrum of this material showed absorption maxima for C═C (1638 cm.$^{-1}$), C—CH$_3$ (1372 cm.$^{-1}$), C—O—C (1100 cm.$^{-1}$) and =CH$_2$ (992 and 907 cm.$^{-1}$).

Anal. Calcd. for $C_{15}H_{29}OBr$: C, 59.01; H, 9.57. Found: C, 58.79; H, 9.54.

1,12-Tridecadiene (IX).—A flask was equipped with a mechanical stirrer with a ball-joint seal and an 8-inch Vigreux column to which was attached a head and condenser for vacuum distillation. A mixture of 61.2 g. (0.20 mole) of α-(10-undecenyl)-β-bromoethyl ethyl ether, 140 ml. of "Carbowax 600" polyethylene glycol (Union Carbide Chemical Co.), 52 g. (0.8 g. atom) of zinc dust and 0.4 g. of anhydrous zinc chloride. The system was heated under a pressure of 1.4 mm., so that the diene distilled slowly and the head temperature did not rise above 90°. The distillate was essentially 1,12-tridecadiene, and 34.6 g. (96%) was obtained, n^{25}_{D} 1.4418. This material was digested over sodium at 100° for 20 hours and distilled through a Fenske column. Pure 1,12-tridecadiene was obtained as a colorless liquid, b.p. 111.4–111.8° (17 mm.), n^{25}_{D} 1.4400. The infrared spectrum of this material was similar to that of 1,7-octadiene, and an unsaturation determination with Hanus solution[22] gave a value of 1.98 double bonds per molecule.

1,13-Tetradecadiene (II) was synthesized in the same manner as that described for 1,7-octadiene. From 69.8 g. (0.30 mole) of 11-bromo-1-undecene, 7.28 g. (0.30 mole) of magnesium and 39 ml. (0.45 mole) of allyl bromide was obtained 46.9 g. (81%) of 1,13-tetradecadiene, b.p. 90° (3.3 mm.). This material was purified by digestion over sodium, followed by distillation under nitrogen, b.p. 131.2–131.4° (17 mm.), n^{25}_{D} 1.4427, d^{28}_{4} 0.7761.[4] The infrared spectrum of this material was similar to that of 1,7-octadiene, and bromination with Hanus solution gave a value of 1.97 double bonds per molecule.

Anal. Calcd. for $C_{14}H_{26}$: C, 86.51; H, 13.49. Found: C, 86.67; H, 13.42.

1,14-Pentadecadiene (XIV).—The procedure used was essentially that described for 1,11-dodecadiene. From 143 g. (0.5 mole) of 1,9-dibromononane,[23] 26.7 g. (1.1 g. atoms) of magnesium and 112 ml. (1.3 moles) of allyl bromide was obtained 56.2 g. (54%) of pure, 1,14-pentadecadiene, b.p. 120° (4.3 mm.), n^{25}_{D} 1.4443, d^{28}_{4} 0.7810, and 10.2 g. (12%) of 1,23-tetracosadiene, b.p. 175–180° (0.3 mm.). The infrared spectrum of 1,14-pentadecadiene was similar to that of 1,7-octadiene, and bromination with Hanus solution gave a value of 1.99 double bonds per molecule.

Anal. Calcd. for $C_{15}H_{28}$: C, 86.46; H, 13.54. Found: C, 86.23; H, 13.45.

1,23-Tetracosadiene (VI).—The material described was redistilled, b.p. 74–76° (0.3 mm.), m.p. 40.1–40.5°. The infrared spectrum of this material was similar to that of 1,7-octadiene, and a quantitative bromination with Hanus solution gave a value of 1.99 double bonds per molecule.

Anal. Calcd. for $C_{24}H_{46}$: C, 86.14; H, 13.86. Found: C, 85.75; H, 13.81.

1,15-Hexadecadiene (V).—The procedure for the preparation of 1,14-pentadecadiene was followed. From 150 g. (0.50 mole) of 1,10-dibromodecane,[23] 26.7 g. (1.10 g. atoms) of magnesium and 112 ml. (1.3 moles) of allyl bromide was obtained 62.6 g. (56%) of 1,15-hexadecadiene, b.p. 118.6–118.8° (2.8 mm.), n^{25}_{D} 1.4463, d^{28}_{4} 0.7859, and 9.8 g. (11%) of 1,25-hexacosadiene, b.p. 189° (0.4 mm.). The infrared spectrum of 1,15-hexadecadiene was similar to that of 1,7-octadiene, and a quantitative bromination with Hanus solution gave a value of 1.98 double bonds per molecule.

Anal. Calcd. for $C_{16}H_{30}$: C, 86.40; H, 13.60. Found: C, 86.31; H, 13.78.

1,25-Hexacosadiene (VII).—The 1,25-hexacosadiene described above was recrystallized twice from absolute ethanol, and obtained as waxy white platelets, m.p. 47.9–48.4°. The infrared spectrum of this compound was similar to that of 1,7-octadiene, and a quantitative bromination with Hanus solution gave a value of 1.98 double bonds per molecule.

Anal. Calcd. for $C_{26}H_{50}$: C, 86.10; H, 13.90. Found: C, 86.34; H, 14.14

1,18-Octadecanediol.—Dimethyl hexadecane-1,16-dicarboxylate[24] (137 g.) was hydrogenated over 5 g. of copper chromium oxide without solvent at 260° and 3500 p.s.i. The solid material in the bomb was dissolved in hot benzene and the solution was filtered hot and allowed to cool. The crystallized diol was collected on a filter and heated under reflux with a solution of 30 g. of potassium hydroxide in 1200 ml. of 95% ethanol for two hours. The ethanol was distilled until about 500 ml. of solution remained, and this was diluted with an equal volume of water. A white solid separated, and this was collected on a filter, dried, and dissolved in one liter of hot benzene. The benzene solution was filtered hot to remove the salts, and the filtrate was allowed to cool to room temperature. The crystallized glycol was collected on a filter and dried in a vacuum desiccator; yield, 65 g. (57%), m.p. 97–98°.[25]

1,18-Diacetoxyoctadecane (XIII).—The acetylation of 63 g. of 1,18-octadecanediol in ether–pyridine was carried out as described for the preparation of 11-acetoxy-1-undecene. The ether solution was washed as usual, and the solvent was removed under reduced pressure. The residue was recrystallized from methanol; yield 72.1 g. (89%), m.p. 59.4–60°.[25]

1,17-Octadecadiene (XVI).—Seventy grams of 1,18-diacetoxyoctadecane was pyrolyzed at 565°, as described for the preparation of 1,8-nonadiene. The pyrolyzate was distilled under reduced pressure, yielding 25.3 g. (55.2%) of 1,17-octadecadiene, b.p. 96.5° (0.015 mm.), n^{20}_{D} 1.4513,[5] and 7 g. (11%) of the monoacetoxy olefin, b.p. 121° (0.025 mm.). The infrared spectrum of the octadecadiene was similar to that of 1,7-octadiene, and a quantitative bromination with Hanus solution gave a value of 1.97 double bonds per molecule.

Anal. Calcd. for $C_{18}H_{34}$: C, 86.31; H, 13.69. Found: C, 86.67; H, 13.69.

18-Acetoxy-1-octadecene (XVIII).—The monoacetoxy olefin mentioned above slowly solidified upon standing at room temperature, and its infrared spectrum showed absorption maxima for C=O (1740 cm.$^{-1}$), C=C (1638 cm.$^{-1}$), C–O (1235 cm.$^{-1}$) and =CH$_2$ (990 and 905 cm.$^{-1}$).

Anal. Calcd. for $C_{20}H_{38}O_2$: C, 77.36; H, 12.34. Found: C, 77.91; H, 12.22.

1,21-Docosadiene (X).—Eleven grams (0.48 g. atom) of sodium metal was pressed into 1 mm. wire and received directly into 250 ml. of sodium-dried ether. The system was cooled in an ice–salt-bath, and 83.8 g. (0.36 mole) of 11-bromo-1-undecene was added portionwise over 45 minutes. Stirring was continued while the mixture was kept at 0° for

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[21] D. Grumitt, E. P. Budewitz and C. C. Chudd, *Org. Syntheses*, **36**, 60 (1956).

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[24] W. S. Greaves, R. P. Linstead, B. R. Shephard, S. L. S. Thomas and B. C. L. Weedon, *J. Chem. Soc.*, 3326 (1950).

[25] O. C. Musgrave, J. Stark and F. S. Spring, *ibid.*, 4393 (1952).

five hours and allowed to warm to room temperature overnight. The excess sodium was decomposed by the cautious addition of 20 ml. of methanol followed by sufficient water, with cooling, to dissolve the salts. The ether layer was separated, washed with saturated sodium bicarbonate and saturated sodium chloride solutions, dried over magnesium sulfate, and distilled. 1,21-Docosadiene was collected at 151–152° (0.25 mm.), yield 33.8 g. (61%). This material was digested over sodium and distilled through a Fenske column, b.p. 127.5° (0.04 mm.)-129.0° (0.05 mm.), m.p. 29.8–30.7°, d^{55}_4 0.7879.[4] The infrared spectrum of this material is similar to that of 1,7-octadiene, and a quantitative bromination with Hanus solution gave a value of 1.98 double bonds per molecule.

Anal. Calcd. for $C_{22}H_{42}$: C, 86.20; H, 13.80. Found: C, 86.11; H, 13.61.

Polymerization Studies.—The catalyst was made up in a dry, nitrogen-filled bottle sealed with a rubber serum cap. The heptane solvent was introduced and then the required amount of aluminum triisobutyl solution was injected through the cap, and finally the titanium tetrachloride was likewise introduced. The monomer was then injected and the bottle was allowed to stand at room temperature for 48 hours (unless otherwise stated in the tables). At this time the contents of the bottle were emptied into a large excess of methanol. The precipitated polymer was transferred to a paper thimble and extracted in a Soxhlet apparatus with methanol for two days and then with benzene for an additional two days. The benzene extract was freeze-dried to yield the soluble polymer. The white, insoluble polymer remaining in the thimble was freeze-dried to remove the benzene. The inherent viscosity of the soluble polymers was determined at 25° at a concentration of 0.25% in benzene. Determinations of unsaturation were also made on the soluble polymers. The insoluble polymers swelled in benzene to produce a thin gel. The results of the polymerization of the higher α-diolefins are shown in Table II–XII.

TABLE II

POLYMERIZATION OF 1,7-OCTADIENE

Run no.	Total vol., ml.	Monomer, g.	Molar concentration Monomer	Al-$(iBu)_3$	$TiCl_4$	Conversion, % Insoluble	Soluble	Inherent viscosity
1	6	1.10	1.80	0.107	0.107	21	53	0.082
2	8	1.10	1.20	.072	.072	23	52	.055
3	50	1.10	0.20	.012	.012	12	35	.049
4	17	1.10	0.60	.072	.072	19	56	.040
5[a]	6	1.10	1.80	.107	.107	29	49	.047
6[a]	17	1.10	0.60	.072	.072	21	41	.035
7	50	1.10	.20	.100	.100	2	54	.048
8	100	1.10	.10	.050	.050	0	26	.044
9	200	1.10	.05	.025	.025	0	0	...
10	200	1.10	.20	.075	.075	0	0	...
11	50	1.10	.20	.100	.100	0	60	.067[b]

Anal. Calcd. for $(C_8H_{14})x$: C, 87.19; H, 12.81
Found, soluble polymer: C, 86.97; H, 12.59
Found, insoluble polymer: C, 84.98; H, 12.78

[a] Polymerization was carried out at −70° for 48 hours. Then the mixture was allowed to warm to room temperature and decomposed in the usual fashion. [b] An ebullioscopic molecular weight determination in benzene gave a value of 567 for this soluble polymer. Ebullioscopic molecular weight determinations were performed by the Clark Microanalytical Laboratory, Urbana, Ill.

Treatment of 1,10-Undecadiene with Triisobutylaluminum.—To a solution of ten millimoles of triisobutylaluminum in 90 ml. of dry *n*-heptane was added 7.65 g. (10.1 ml.) of 1,10-undecadiene by means of a hypodermic syringe. The resulting solution was allowed to stand at room temperature for 48 hours, and then poured into 200 ml. of methanol. The methanol and heptane were distilled on a steam-bath, and the residual liquid was filtered. The infrared spectrum of the filtrate was identical to that of 1,10-undecadiene.

TABLE III

POLYMERIZATION OF 1,8-NONADIENE

Run no.	Total vol., ml.	Monomer, g.	Molar concentration Monomer	Al-$(iBu)_3$	$TiCl_4$	Conversion, % Insoluble	Soluble	Inherent viscosity
1	6.6	1.24	1.50	0.10	0.10	46	18	0.065
2	10	1.24	1.00	.10	.10	44	15	.077
3	20	1.24	0.50	.10	.10	41	19	.071
4	50	1.24	.20	.10	.10	40	20	.14
5	100	1.24	.10	.050	.050	31	19	.079
6	200	1.24	.05	.025	.025	24	17	.054

Anal. Calcd. for $(C_9H_{16})_x$: C, 87.02; H, 12.98
Found, soluble polymer: C, 87.02; H, 13.16
Found, insoluble polymer: C, 86.58; H, 13.41

TABLE IV

POLYMERIZATION OF 1,9-DECADIENE

Run no.	Total vol., ml.	Monomer, g.	Molar concentration Monomer	Al-$(iBu)_3$	$TiCl_4$	Conversion, % Insoluble	Soluble	Inherent viscosity
1	6.7	1.38	1.5	0.10	0.10	42	17	0.089
2	10	1.38	1.0	.10	.10	42	17	.14
3	20	1.38	0.5	.10	.10	44	20	.10
4	50	1.38	.2	.10	.10	38	18	.12
5	100	1.38	.1	.05	.05	45	14	.13
6	200	1.38	.05	.025	.025	36	13	.14
7	100	4.14	.3	.05	.05	33	10	.35

Anal. Calcd. for $(C_{10}H_{18})_x$: C, 86.88; H, 13.12
Found, soluble polymer: C, 86.66; H, 13.23
Found, insoluble polymer: C, 86.68; H. 13.38

TABLE V

POLYMERIZATION OF 1,10-UNDECADIENE

Run no.	Total vol., ml.	Monomer, g.	Molar concentration Monomer	Al-$(iBu)_3$	$TiCl_4$	Conversion, % Insoluble	Soluble	Inherent viscosity
1	6.7	1.53	1.50	0.10	0.10	29	12	0.16
2	10	1.53	1.00	.10	.10	29	10	.23
3	20	1.53	0.50	.10	.10	34	16	.12
4	50	1.53	.20	.10	.10	41	25	.058
5	100	1.53	.10	.05	.05	38	20	.065
6	200	1.53	.05	.025	.025	30	22	.050
7	100	4.59	.30	.05	.05	33	10	.13
8	100	1.53	.10	.05	.05	35	18	.075
9[a]	100	1.53	.10	.05	.05	22	17	.079
10[b]	100	1.53	.10	.05	.05	45	9	.13

Anal. Calcd. for $(C_{11}H_{20})_x$: C, 86.76; H, 13.24
Found, soluble polymer: C, 86.80; H, 13.56
Found, insoluble polymer: C, 86.82; H, 13.43

[a] Polymerization was carried out in a freezer at −27°. [b] Polymerization was carried out in a water-bath at 47°.

TABLE VI

POLYMERIZATION OF 1,11-DODECADIENE

Run no.	Total vol., ml.	Monomer, g.	Molar concentration Monomer	Al-$(iBu)_3$	$TiCl_4$	Conversion, % Insoluble	Soluble	Inherent viscosity
1	5.6	1.66	1.80	0.11	0.11	52	30	0.057
2	5.6	1.66	1.80	.00	.036	0	0	...
3	10	1.66	1.00	.10	.10	37	17	.14
4	100	1.66	0.05	.025	.025	40	27	.086

Anal. Calcd. for $(C_{12}H_{22})_x$: C, 86.76; H, 13.24
Found, soluble polymer: C, 86.80; H, 13.56
Found, insoluble polymer: C, 86.82; H, 13.43

Treatment of 1,10-Undecadiene with Titanium Trichloride.—To a suspension of 0.16 g. (0.0011 mole) of titanium trichloride in 50 ml. of dry *n*-heptane was added 7.65 g. (10.1 ml.) of 1,10-undecadiene by means of a hypodermic syringe. The immediate appearance of a flocculent brown precipitate was noticed. The mixture was shaken periodi-

TABLE VII

POLYMERIZATION OF 1,12-TRIDECADIENE

Run no.	Total vol., ml.	Monomer, g.	Molar concentration Monomer	Molar concentration Al$(iBu)_3$	Molar concentration $TiCl_4$	Conversion, % Insoluble	Conversion, % Soluble	Inherent viscosity
1	5.6	1.80	1.80	0.11	0.11	37	26	0.035
2	10	1.80	1.00	.10	.10	37	20	.104
3	200	1.80	0.05	.025	.025	36	25	[a]

Anal. Calcd. for $(C_{13}H_{24})_x$: C, 86.58; H, 13.42
Found, soluble polymer: C, 86.33; H, 13.52
Found, insoluble polymer: C, 86.66; H, 13.53

[a] The viscosity was not determined, but the material possessed the usual properties of a low polymer.

TABLE VIII

POLYMERIZATION OF 1,13-TETRADECADIENE

Run no.	Total vol., ml.	Monomer, g.	Molar concentration Monomer	Molar concentration Al$(iBu)_3$	Molar concentration $TiCl_4$	Conversion, % Insoluble	Conversion, % Soluble	Inherent viscosity
1	4.0	1.94	2.50	0.10	0.10	7	9	0.032
2	6.7	1.94	1.50	.10	.10	69	31	.094
3	10	1.94	1.00	.10	.10	48	37	.063
4	20	1.94	0.50	.10	.10	51	32	.052
5	50	1.94	0.20	.10	.10	61	30	.048
6	10	1.94	1.00	.30	.10	29	12	.067
7	50	1.94	0.20	.10	.10	77	20	.059
8	100	1.94	1.10	.05	.05	65	21	.052
9	50	1.94	0.20	.05	.05	29	22	.050
10	200	1.94	0.05	.025	.025	66	12	.073
11	10	1.94	1.00	.10	.10	52	15	.11

Anal. Calcd. for $(C_{14}H_{26})_x$: C, 86.51; H, 13.49
Found, soluble polymer: C, 86.30; H, 13.59
Found, insoluble polymer: C, 86.46; H, 13.59

TABLE IX

POLYMERIZATION OF 1,14-PENTADECADIENE

Run no.	Total vol., ml.	Monomer, g.	Molar concentration Monomer	Molar concentration Al$(iBu)_3$	Molar concentration $TiCl_4$	Conversion, % Insoluble	Conversion, % Soluble	Inherent viscosity
1	10	2.08	1.00	0.10	0.10	27	13	[a]
2	200	2.08	0.05	0.025	0.025	32	38	0.062

Anal. Calcd. for $(C_{15}H_{28})_x$: C, 86.46; H, 13.54
Found, soluble material: C, 86.25; H, 13.71
Found, insoluble material: C, 86.23; H, 13.71

[a] The viscosity was not determined, but the material possessed the usual properties of a low polymer.

TABLE X

POLYMERIZATION OF 1,15-HEXADECADIENE

Run no.	Total vol., ml.	Monomer, g.	Molar concentration Monomer	Molar concentration Al$(iBu)_3$	Molar concentration $TiCl_4$	Conversion, % Insoluble	Conversion, % Soluble	Inherent viscosity
1	6.7	2.22	1.50	0.10	0.10	32	20	0.091
2	10	2.22	1.00	.10	.10	40	19	.11
3	20	2.22	0.50	.10	.10	53	22	.18
4	50	2.22	.20	.10	.10	57	17	.16
5	100	2.22	.10	.05	.05	56	11	.091
6	200	2.22	.05	.025	.025	38	23	.14
7	100	6.66	.30	.05	.05	8	30	.25

Anal. Calcd. for $(C_{16}H_{30})_x$: C, 86.40; H, 13.60
Found, soluble polymer: C, 86.12; H, 13.54
Found, insoluble polymer: C, 86.40; H, 13.75

TABLE XI

POLYMERIZATION OF 1,17-OCTADECADIENE

Run no.	Total vol., ml.	Monomer, g.	Molar concentration Monomer	Molar concentration Al$(iBu)_3$	Molar concentration $TiCl_4$	Conversion, % Insoluble	Conversion, % Soluble	Inherent viscosity
1	5.6	2.50	1.8	0.11	0.11	40	46	0.10
2	17	2.50	0.6	.036	.036	22	40	.055
3	8.4	2.50	1.2	.21	.071	23	32	.080
4	10	2.50	1.0	.10	.10	40	27	.053

Anal. Calcd. for $(C_{18}H_{34})_x$: C, 86.32; H, 13.68
Found, soluble polymer: C, 86.38; H, 13.97
Found, insoluble polymer: C, 86.00; H, 13.63

TABLE XII

POLYMERIZATION OF 1,21-DOCOSADIENE

Run no.	Total vol., ml.	Monomer, g.	Molar concentration Monomer	Molar concentration Al$(iBu)_3$	Molar concentration $TiCl_4$	Conversion, % Insoluble	Conversion, % Soluble	Inherent viscosity
1	5.6	3.07	1.80	0.11	0.11	10	22	0.083
2	5.6	3.07	1.80	.11	.036	13	21	.073
3	10	3.07	1.00	.10	.10	18	9	.126
4	200	3.07	0.05	.025	.025	37	38	.066

Anal. Calcd. for $(C_{22}H_{42})_x$: C, 86.20; H, 13.80
Found. soluble polymer: C, 85.97; H, 13.91
Found, insoluble polymer: C, 85.96; H, 14.05

TABLE XIII

UNSATURATION IN POLY-α-DIOLEFINS

Monomer	Run no.	Average double bonds per monomer unit in the soluble polymer Trans	Average double bonds per monomer unit in the soluble polymer Terminal	Average double bonds per monomer unit in the soluble polymer Total
1,7-Octadiene	8	0.21	0.05	..
	9	.21	.04	..
	11	.23	.11	0.57
				.60
1,8-Nonadiene	1	.16	.51	..
	2	.14	.56	..
	3	.14	.54	..
	4	.12	.53	..
	5	.16	.37	..
	6	.17	.22	.54
1,9-Decadiene	1	.19	.63	..
	2	.15	.64	..
	3	.16	.56	..
	4	.14	.56	..
	5	.10	.45	..
	6	.11	.43	.54
1,10-Undecadiene	1	.16	.70	.83
	2	.14	.69	.84
	3	.15	.63	.82
	4	.20	.38	.67
	5	.20	.33	.57
	6	.20	.21	.55
	8	.20	.41	..
	9	.21	.50	..
	10	.14	.43	..
1,11-Dodecadiene	4	.22	.19	.59
1,12-Tridecadiene	3	.27	.16	.58
1,13-Tetradecadiene	6	.29	.45	..
1,14-Pentadecadiene	2	.23	.17	.54
1,15-Hexadecadiene	1	.20	.71	..
	2	.20	.65	..
	3	.17	.56	..
	4	.16	.47	..
	5	.13	.18	..
	6	.16	.18	.38
				.36
1,17-Octadecadiene	4	.26	.55	.90
1,21-Docosadiene	4	.32	.24	.70

cally for 24 hours and poured into 150 ml. of methanol, whereupon the brown precipitate dissolved. The solvents were distilled, and the residue was filtered. The infrared spectrum of the filtrate was identical to that of 1,10-undecadiene.

Determination of Unsaturation in the Soluble Poly-α-diolefins. Quantitative Infrared Spectrometry.—Quantitative measurements of the intensity of the absorption due to unsaturation in the soluble polymers were made at 967 cm.$^{-1}$, corresponding to the *trans* form of olefins of the type RCH=CHR′, and at 910 cm.$^{-1}$, corresponding to the vinyl group, $RCH{=}CH_2$.

The measurements were carried out using an automatic-recording Perkin-Elmer single-beam infrared spectrometer, model 12B, modified for double-pass operation and equipped with sodium chloride optics. The methods used were similar to those described by Treumann and Wall.[26] All measurements were carried out in carbon disulfide solution, using a sodium chloride cell of 1.002 mm. inside thickness and a slit width of 0.400 mm.

The system was calibrated at 967 cm.$^{-1}$, using *trans*-4-methylpentene-2[27] as a standard. Measurements of the optical densities of solutions of this compound in carbon disulfide over a concentration range of 0.005 to 0.04 *M* gave a value for the molar absorptivity, ε, of 137 liters/mole-cm. Hampton[28] states a value of 139 for the absorptivity of *trans*-olefins at 967 cm.$^{-1}$.

The calibration of the system at 910 cm.$^{-1}$ was accomplished in the same manner, using 1-octadecene,[29] 1,8-nonadiene, 1,13-tetradecadiene and 1,21-docosadiene as standards. The absorbancy *versus* molarity (of olefin) curves based on these results are superimposable and linear at molarities below 0.04. The molar absorptivity was calculated to be 152 liters/mole-cm. Hampton[28] reports a value of 155 for the absorptivity of terminal olefins at 910 cm.$^{-1}$.

The measurements of *trans* and terminal unsaturation in the soluble polymers was carried out as follows. A solution of the polymer, 0.02–0.07 molar in monomer units, was made up in carbon disulfide. The absorbancy of the solution was measured both at 967 and at 910 cm.$^{-1}$. The molar concentrations of *trans* and of terminal olefin were calculated by dividing the absorbancies measured at 967 and at 910 cm.$^{-1}$ by 13.7 and 15.5, respectively. The average amount of each type of double bond per monomer unit was calculated by dividing the molarity of the polymer solution (expressed in monomer units) into the molar concentration of the appropriate double bond. The results of these determinations are listed in Table XIII.

Quantitative Bromination.—The measurement of total unsaturation in the soluble polymers using iodine monobromide (Hanus solution) was carried out according to the method described by Siggia.[22] The results of these determinations are listed in Table XIII.

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[26] W. B. Treumann and F. T. Wall, *Anal. Chem.*, **21**, 1161 (1949).

[27] The authors are grateful to Dr. John E. Mahan of the Phillips Petroleum Co. for a sample of 99.53% pure *trans*-4-methylpentene-2.

[28] R. R. Hampton, *Anal. Chem.*, **21**, 923 (1949).

[29] The authors are grateful to John Rogers for a sample of pure 1-octadecene.

COMMUNICATIONS TO THE EDITOR

HETEROPOLY TUNGSTOCOBALTATE ANIONS CONTAINING RESPECTIVELY Co(II) AND Co(III) IN CoO_4 TETRAHEDRA. I. 12-TUNGSTOCOBALTOATE AND 12-TUNGSTOCOBALTIATE[1]

Sir:

In a previous paper,[2] a system of four chemically interrelated heteropoly tungstocobaltate anions was reported. The isomorphous structures of $[Co^{+2}Co^{+2}W_{12}O_{42}]^{-8}$ and $[Co^{+2}Co^{+3}W_{12}O_{42}]^{-7}$ were considered in detail. The other two anions[3] are $[Co^{+2}O_4W_{12}O_{36}]^{-6}$ and its isomorph, $[Co^{+3}O_4W_{12}O_{36}]^{-5}$. This paper reports several proofs of the formulas and structure of the two monocobalt anions.

The significant feature of the results lies in the fact that the cobalt atoms are shown conclusively to be located within CoO_4 tetrahedra. So far as we have been able to ascertain, these are: (a) the first complex ions known to contain Co(III) in *any* tetrahedral site and (b) the first complex ions known to contain Co(II) within a tetrahedron of oxygen atoms which is unequivocally perfectly regular.[4]

Because of the electronic configuration of cobalt, these soluble complexes have various interesting implications for ligand field theory. Also, evaluation of the strength of the ligand field produced by oxygen atoms which are simultaneously attached to other atoms (W) of high oxidation state is possible. This facilitates better understanding of heteropoly electrolytes and perhaps of certain oxides.

Both anions have perfect tetrahedral symmetry; therefore no distortion of the central CoO_4 tetrahedra should occur in solution, except insofar as introduced by the electronic structure of the cobalt. Anionic distortion can also be caused by packing forces in some crystals.

We have proven the structure of the anion by several lines of evidence[6]:

(a) A geometrical argument establishes, for $[X^{+v}W_{12}O_{40}]^{-(8-v)}$, that the central atom lies within a tetrahedron of oxygens, provided all tungstens are within octahedra each of which shares at least one oxygen with the central polyhedron.[7] The structure is identical to that deduced by Keggin and others[8] for $[PO_4W_{12}O_{36}]^{-3}$ and similar anions (see point "e"). Formula proof rests upon: (A) analyses, including establishment of oxidation states; (B) potentiometric titrations which establish that each anion contains just 40 oxygen atoms provided neither contains constitutional water; and (C)

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[1] This research was supported in part by the U. S. Atomic Energy Commission, through Contract AT(30-1)-1853.

[2] L. C. W. Baker and T. P. McCutcheon, THIS JOURNAL, **78**, 4503 (1956).

[3] In the earlier paper[2] the obsolete Miolati–Rosenheim formulation was deliberately used for the monocobalt anions because the correct formulas were unknown.

[4] No Jahn–Teller effect is expected for Co(II) in a tetrahedral field, because the ground state is not orbitally degenerate.[5]

[5] C. J. Ballhausen and C. K. Jørgensen, *Acta Chem. Scand.*, **9**, 397 (1955).

[6] Detailed discussion of each of these results and its implications will be included in papers soon to be published.

[7] This condition is assumed because it obtains in every heteropoly tungstate (and molybdate) structure investigated to date.

[8] J. F. Keggin, *Nature*, **131**, 908 (1933); *Proc. Roy. Soc.* (*London*), **A144**, 75 (1934); J. W. Illingworth and J. F. Keggin, *J. Chem. Soc.*, 575 (1935); J. L. Hoard, *Z. Krist.*, **84**, 217 (1933); J. deA. Santos, *Revista Faculdade Cienc.*, *Univ. of Coimbra* (*Portugal*), **16**, 5 (1947); R. Signer and H. Gross, *Helv. Chim. Acta*, **17**, 1076 (1934); L. C. W. Baker, "Properties of Heteropoly Molybdates," Climax Molybdenum Company Information Bulletin Cdb-12 (1956).