polymer) of acetone 2,4-dinitrophenylhydrazone was isolated.

The residual solution after removal of acetone was evaporated and taken up in ether. The ether solution was washed, dried and the solvent removed. The residual polymeric solid was only partially soluble in methanol. It was dissolved in benzene and the polymeric residue was precipitated by pouring this solution into methanol. About 1.2 g. of polymeric material was recovered. This had an infrared spectrum much like polyalloöcimene except there was a pronounced absorption at 1260 cm.$^{-1}$ (epoxide).

The methanolic solution was poured into water and a yellowish resin was precipitated. This was taken up in benzene and reprecipitated by pouring the benzene solution in heptane. After five solutions and reprecipitations the substance was freeze-dried to yield 0.87 g. of a white substance, m.p. 90–93°. This polymer gave a strong band in the infrared at 1725 cm.$^{-1}$ (aldehyde) and a medium band at 2720 cm.$^{-1}$. The yield of polymeric aldehyde was 37% based on the oxidized polymer; carbon methyl calcd. for 2 C-CH_3 per C_5 unit 35.7, found 34.8. The inherent viscosity (0.191 g. in 100 ml. of benzene at 25°) is 0.05.

Anal. Calcd. for $(C_5H_8O)n$: C, 71.4; H, 9.5. Found: C, 71.9; H, 9.1.

The water washings of the original ether solution and the water used to precipitate the polymer from methanol was treated with 2,4-dinitrophenylhydrazine and a derivative was obtained. Recrystallization from pyridine gave a product melting at 304° which showed a slight melting point depression when mixed with an authentic glyoxal derivative.

Aging Polyalloöcimene in Air.—A sample of polymer which was a white, fibrous solid melting at 128-145° and with an inherent viscosity of 1.0 was allowed to stand in a closed bottle in the laboratory for six weeks. It then was a yellow, sticky solid which showed some solubility in alcohol, whereas the original polymer was alcohol insoluble. The degraded polymer had an inherent viscosity of only 0.12 and it softened at 110° and seemed to decompose at 140°. The degraded polymer gave very little ultraviolet absorption at 245 (ϵ 3120) and had weak bands in the infrared at 1710 and 1670 cm.$^{-1}$ which were not present in the spectrum of the original polymer.

Another sample of polymer which stood for five months changed into a sticky, yellow solid. This product had a medium strong band in the infrared at 3415 cm.$^{-1}$ and a strong wide band at 1720–1715 cm.$^{-1}$ which were absent in the spectrum of the original polymer. The oxidized polymer showed a medium band at 905 cm.$^{-1}$ which is present in the original polymer, but all other bands below 1300 cm.$^{-1}$ in the original polymer seemed to have disappeared or to be obscured by broad absorption (Fig. 2).

Acknowledgments.—The microanalyses were performed by Mr. Jozsef Nemeth of the University of Illinois. Carbon methyl determinations were made by Clark Microanalytical Laboratory, Urbana, Ill. The infrared spectra were determined by Mr. Paul McMahon, University of Illinois, and Mr. J. Chiu determined the ultraviolet spectra.

URBANA, ILL.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, POLYTECHNIC INSTITUTE OF BROOKLYN]

Synthesis and Polymerization of Methyl Substituted Vinylcyclohexanes[1]

BY C. G. OVERBERGER AND J. E. MULVANEY[2]

RECEIVED MARCH 13, 1959

The synthesis of the *cis* or *trans* isomers of 2-methyl-, 3-methyl- and 4-methylvinylcyclohexanes are described. The latter two compounds were polymerized to linear crystalline high polymers using aluminum triisobutyl and titanium tetrachloride in heptane.

A number of crystalline α-olefin polymers have now been reported using Ziegler[3]–Natta[4] catalyst systems, and a comparison of their physical properties has been reported. In a series proceeding from polypropylene to polypentene-1, the melting point of the crystalline polymer decreases with increasing size of the side chain up to polyhexene-1 which is completely amorphous.[3] However, a six-carbon and even a seven-carbon α-olefin can be obtained crystalline if the side chain is branched as in the case of 3-methylhexene-1 and 4-methylpentene-1.[3] Another interesting aspect of the α-olefin polymers is that branched side chains usually result in higher melting points than their linear side-chain counterparts. Thus, for example, polypentene-1 melts at 80° whereas poly-3-methylbutene-1 melts at 245°.[3]

A crystalline polymer has also been prepared from a racemic monomer, 4-methylhexene-1. The polymer of this material is isotactic as far as the carbon atoms of the main chain are concerned. With respect to the asymmetric centers on the side chain, further cases of stereoisomerism are possible depending upon this order of steric regularity. Natta has suggested that the high solubility and the poor definition in X-ray photographs indicates a statistical distribution of the asymmetric side-chain molecules.[3]

X-ray diffraction data,[4,5] obtained on Natta's polypropylene, polybutene-1 and polystyrene, as well as the crystalline vinyl isobutyl ether prepared by Schildknecht,[6] showed a distinct identity period along the chain of 6.5-6.7 Å. Both Bunn[7] and Natta[4,5] concluded that this repeating unit for polypropylene involved three monomer units linked exclusively by head to tail orientation. Other α-olefin polymers give repeat distances of variable size. The polymer chain backbones exist in skew conformations which lead to helical chains in the isotactic configuration.[4,5,7]

It seemed that it would be of interest to compare the properties, *e.g.*, melting point, crystallinity, of some vinylcycloalkanes with the linear or branched-chain α-olefins. Early work in these laboratories has shown that vinylcyclohexane may be polymerized, using aluminum triisobutyl–titanium tetrachloride, to a high molecular weight crystalline polymer. It was decided, therefore, to prepare

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(1) This is the 18th in a series of papers on new monomers and polymers. For the previous paper in this series see C. G. Overberger and P. V. Bonsignore, THIS JOURNAL, **80**, 5431 (1958).

(2) Abstracted in part from the Doctoral Thesis of J. E. Mulvaney, Polytechnic Institute of Brooklyn, June, 1959.

(3) G. Natta, *Angew. Chem.*, **68**, 393 (1956).

(4) G. Natta, *Makromol. Chem.*, **16**, 213 (1955).

(5) G. Natta, THIS JOURNAL, **77**, 1708 (1955).

(6) C. E. Schildknecht, *Ind. Eng. Chem.*, **40**, 2104 (1948).

(7) C. W. Bunn and E. R. Howells, *J. Polymer Sci.*, **16**, 307 (1955).

some of the stereoisomers of 2,3 and 4-methylvinylcyclohexane. The 2- and 3-methyl compounds exist as *cis–trans* racemates, whereas 4-methylvinylcyclohexane has a plane of symmetry and exists only in the *cis* or *trans* form.

Preparation of Monomers.—Two routes leading to the syntheses of the methylvinylcyclohexanes have been investigated: the acetate cracking procedure[8,9] and the amine oxide route.[10] A general outline of the two procedures is

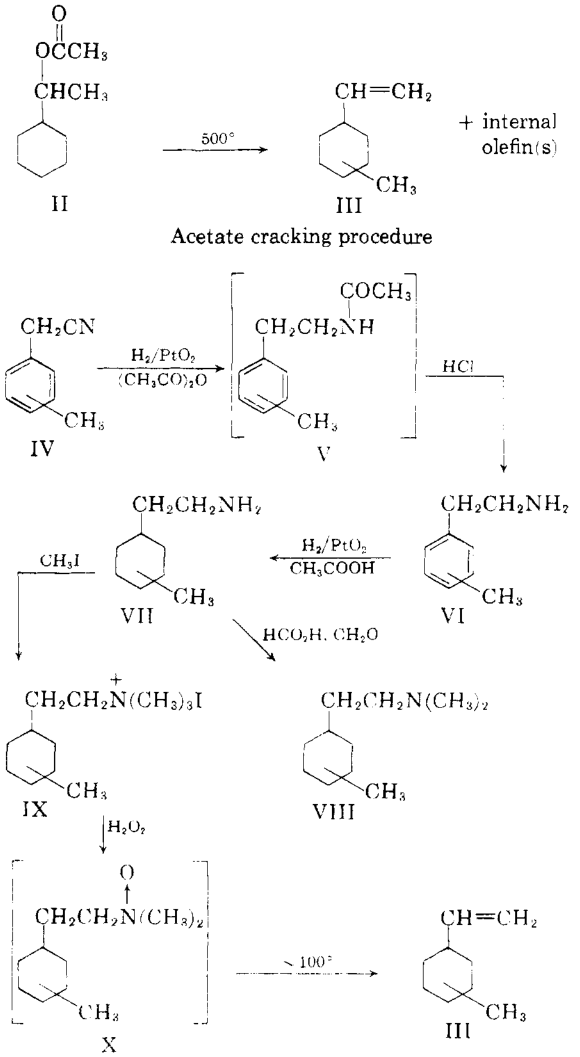

Fig. 1.

Throughout this paper lower case letters a, b, c, following the roman numerals of the compounds, will be used to indicate, 2-, 3- and 4-methyl derivatives, respectively.

Because we were not able to reduce the nitrile IV directly to the cyclohexylamine VII, the amine oxide route requires several more steps than the acetate cracking procedure. However, the former procedure is still useful for two principal reasons. On the basis of Cope's work,[10] it would appear that pyrolysis of amine oxide X should lead exclusively to the formation of terminal olefin, whereas we found that pyrolysis of acetate IIc leads to a mixture of terminal and internal olefin(s). Furthermore, amine XIII exists as a pair of *cis–trans* isomers which could be separated by fractional crystallization of picrates.

cis- or *trans*-4-methylvinylcyclohexane was prepared *via* the acetate cracking route in the following way. Treatment of the Grignard derivative of 4-methylcyclohexyl bromide gave a 55% yield of 1-(4-methylcyclohexyl)-ethanol (Ic) which upon acetylation with acetyl chloride yielded 75% of 1-(4-methylcyclohexyl)-ethyl acetate (IIc).

Pyrolysis of IIc at 500-520° yielded 63% of a mixture of crude olefins; vapor phase chromatography indicated the presence of four components. One would expect two compounds from the exclusive formation of terminal olefin (*cis* and *trans*). The other components are probably isomerized olefins. Careful distillation of the crude olefin mixture through a vacuum-jacketed concentric tube column gave five fractions. Fraction I, b.p. 141.5-144.5°, was redistilled through a 75-plate concentric tube column to give a material, b.p. 142.0-143.0°, which gave only one peak in vapor phase chromatography and showed in the infrared spectrum a strong band at 11.0 μ. This compound is pure *cis-* or *trans*-4-methylvinylcyclohexane (IIIc), although a differentiation between *cis* and *trans* cannot be made at this time.

Another fraction from the concentric tube column fractionation, b.p. 152.3°, gave a single peak upon vapor phase chromatography, decolorized bromine in carbon tetrachloride, and showed no 11.0 μ band in the infrared spectrum. This compound is presumably one of the internal olefins, but positive identification of this compound was not completed. Kooyman[11] has reported that pyrolysis of the acetate of methylcyclopentylcarbinol leads to a mixture of vinylcyclopentane (10%) and (70%) ethylidenecyclopentane. The acetate of methylcyclohexylcarbinol was also pyrolyzed to give a mixture although the olefin isomers were not completely identified.

An attempt to prepare 4-methylvinylcyclohexane (IIIc) *via* the amine oxide route led to a mixture presumably of *cis-* and *trans*-olefins. *p*-Xylene was treated with bromine to give a 40% yield of *p*-xylyl bromide which was converted to *p*-xylyl nitrile (IVc) in 65% yield by the action of sodium cyanide in ethanol. Numerous attempts to reduce IVc directly to the cyclohexylamine VIIc using a platinum oxide catalyst were unsuccessful; therefore the reduction was carried out in two steps. Reduction of IVc with platinum oxide was carried out with acetic anhydride to give the acetylated amine Vc which was not isolated, but hydrolyzed with hydrochloric acid to give a 70% yield of 2-(4-methylphenyl)-ethylamine (VIc). The amine VIc was then further reduced with platinum oxide in glacial acetic acid to give 65% of 2-(4-methylcyclohexyl)-ethylamine (VIIc). An initial attempt to prepare the N,N-dimethyl derivative of VIIc using methyl iodide in al-

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(8) C. G. Overberger, A. Fischman, C. W. Roberts, L. H. Arond and J. Lao, THIS JOURNAL, **73**, 2540 (1951).

(9) W. J. Bailey and C. King, *ibid.*, **77**, 75 (1955).

(10) A. C. Cope, N. A. LeBel, Hiok-Huang Lee and W. R. Moore, *ibid.*, **79**, 4720 (1957).

(11) J. R. van der Bij and E. C. Kooyman, *Rec. trav. chim.*, **71**, 837 (1952).

coholic sodium carbonate led only to a 50% yield of the quaternary ammonium salt IXc. However, when VIIc was treated with formic acid and formalin, there was obtained a 66% yield of N,N-dimethyl - 2 - (4 - methylcyclohexyl) - ethylamine (VIIIc). At this point an attempt was made to separate the *cis–trans* isomers by fractional crystallization of picrates. A picrate was obtained which after several recrystallizations melted at 98-101° and was not increased by further recrystallization. After recovery of the free amine by treatment of the picrate with base the amine was converted to the oxide and pyrolyzed at 100-130° to yield 30% of olefin IIIc. Vapor phase chromatography revealed the presence of two components in the olefin, and therefore the *cis–trans* isomers had apparently not been separated by fractional crystallization of the picrates.

3-Methylvinylcyclohexane (IIIb) was prepared by the acetate pyrolysis procedure as described for the 4-methyl compound IIIc. Starting with 3-bromo-1-methylcyclohexane, a yield of 56% was obtained for the conversion to Ib, 69% for Ib to IIb and 51% for the conversion of IIb to an olefin mixture from which 3-methylvinylcyclohexane (IIIb) was obtained as pure *cis* or *trans* isomer by careful distillation.

cis- or *trans*-2-methylvinylcyclohexane has been prepared *via* the amine oxide route as indicated in Fig. 1. Starting with *o*-xylyl bromide yields of 64% were obtained for the conversion to IVa, 60% for IVa to VIa, 30% for VIa to VIIa and 60% for VIIa to VIIIa. At this point the picrate of VIIIa was fractionally crystallized to yield a material, m.p. 135-137°. Recovery of the amine, followed by conversion to the amine oxide, gave a chromatographically pure compound which was shown to be *cis-* or *trans*-2-methylvinylcyclohexane (IIIa) by infrared spectrum and analysis.

Polymerization of Monomers.—All of the pure isomers of 2-, 3- and 4-methylvinylcyclohexane were polymerized using triisobutyl aluminum and titanium tetrachloride in heptane.

Using a 2:1 molar ratio of aluminum to titanium there was obtained a 42% conversion to polymer with 3-methylvinylcyclohexane. The polymer was a white solid, capillary m.p. 276-355°, completely soluble in benzene and tetralin with an intrinsic viscosity of 0.75 in benzene. An X-ray powder diagram revealed crystallinity (greater than 20%) in the polymer. A 0.25-g. portion of the polymer was extracted with ether, heptane and benzene which dissolved 0.17 g., 0.03 g. and 0.02 g. in that order.

Polymerization of 4-methylvinylcyclohexane using a 1.4:1 ratio of aluminum triisobutyl to titanium tetrachloride for 40 hours at 75-85° gave a 30% conversion to polymer. The polymer was completely soluble in ether as well as benzene and had an intrinsic viscosity of 0.45. Although a powder diagram of the material initially showed no crystallinity, the sample was oriented by treatment with boiling butanol-1 and thereupon gave a crystalline diffraction pattern.

2-Methylvinylcyclohexane was polymerized using a 1.8:1 ratio of aluminum triisobutyl to titanium tetrachloride and after 68 hours at 75-85° there was obtained a 63% yield of polymer. This material, however, was almost completely insoluble. The longer reaction period used in this polymerization may have resulted in some cross-linking.

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Grateful acknowledgement is also made to Mr. Ned Weinshenker for valuable help in the synthesis of 2-methylvinylcyclohexane.

Experimental[12]

Materials and Technique.—Polymerizations were carried out in a thoroughly dry, air-free semi-micro reaction flask under a stream of prepurified nitrogen or helium. Catalyst components were added by means of a hypodermic syringe.

Heptane, when used as solvent for the polymerizations, was refluxed with sulfuric acid, followed by washing with bicarbonate and water, drying over magnesium sulfate, distillation from and storage over sodium under nitrogen.

Aluminum triisobutyl (Hercules) and titanium tetrachloride were distilled under nitrogen prior to use.

Vapor phase chromatographies were carried out on a Perkin–Elmer model 154-B apparatus using an "A" column.

1-(4-Methylcyclohexyl)-ethanol (Ic) and 1-(4-Methylcyclohexyl)-ethyl Acetate (IIc).—1-(4-Methylcyclohexyl)-ethanol was prepared essentially according to the method of van Woerden,[13] who did not completely characterize this compound. There was obtained from 221 g. (1.25 moles) of 4-methylcyclohexyl bromide (Columbia Organic Chemicals), 106 g. (55%) of 1-(4-methylcyclohexyl)-ethanol (Ic), b.p. 69° (2.6–2.4 mm.), $n^{25}\text{D}$ 1.4590, d^{25}_4 0.9058.

Anal. Calcd. for $C_9H_{18}O$: C, 76.00; H, 12.75; $M\text{D}$, 42.93. Found: C, 76.35; H, 12.68; $M\text{D}$, 43.10.

The acetate of Ic was prepared in the usual manner by treating 106 g. (0.75 mole) of Ic with 98 g. (1.25 moles) of acetyl chloride. After washing with water and drying over magnesium sulfate there was obtained 104 g. (75%) of acetate, b.p. 66–63° (3.0 mm.). A redistilled analytical sample had a b.p. 60–61° (2.0 mm.), $n^{25.0}\text{D}$ 1.4426, d^{25}_4 0.9270; $M\text{D}$ (calcd.) 52.65, $M\text{D}$ (found) 52.47 [from acetic anhydride and 1-(4-methylcyclohexyl)-ethanol, no yield reported, b.p. 90° (11 mm.)].[14]

Pyrolysis of 1-(4-Methylcyclohexyl)-ethyl Acetate (IIc).—The acetate of IIc (87 g., 0.47 mole) was dropped slowly through a 30-cm. tube packed with Pyrex glass helices over a period of three hours at temperatures ranging from 498 to 520° according to the general procedure.[8,9] The product was made basic with aqueous potassium hydroxide and washed with water. The aqueous layer was extracted with ether and the organic layers combined and dried over magnesium sulfate. Two distillations through a 10-cm. Vigreux column yielded 36 g. (63%) of crude olefin, b.p. 48–53° (2.3 mm.), $n^{25.0}\text{D}$ 1.4472. Vapor phase chromatography of the crude olefin mixture revealed the presence of four components.

Careful fractionation of the mixture through a concentric tube column yielded five fractions ranging in b.p. from 141.5 to 152.3°. Fraction I, b.p. 141.5–144.5°, was redistilled through a concentric tube column, and there was obtained 5.6 g. of pure terminal olefin, 4-methylvinylcyclohexane (IIIc) (*cis* or *trans*), b.p. 142.3°, $n^{26.0}\text{D}$ 1.4403, d^{25}_4 0.7912.

Anal. Calcd. for C_9H_{16}: C, 87.01; H, 12.98; $M\text{D}$, 41.11. Found: C, 86.83; H, 12.95; $M\text{D}$, 41.40.

A strong band at 11.0 μ in the infrared spectrum and a single peak upon vapor phase chromatography indicated the purity and position of the double bond.

Fraction V, b.p. 152.3°, $n^{26.0}\text{D}$ 1.4541, also had a single peak in the vapor phase chromatogram, but the absence

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[12] Analyses were performed by the Schwarzkopf Microanalytical Laboratory, Woodside 77, N. Y. All melting points and boiling points are uncorrected.

[13] S. van Woerden, *Rec. trav chim.*, **45**, 124 (1929).

[14] H. Rupe and Fr. Kuenzy, *Helv. Chim. Acta*, **14**, 701 (1913).

of a band at 11.0 μ and a very weak band at 6.05 μ indicated that this compound contained an internal double bond.

Anal. Calcd. for C_9H_{16}: C, 87.01; H, 12.98. Found: C, 86.68; H, 13.15.

***p*-Xylyl Bromide.**—*p*-Xylyl bromide was prepared according to the procedure of Radziszewsky.[15] From 212 g. (2.0 moles) of *p*-xylene there was obtained 147 g. (40%) of *p*-xylyl bromide, b.p. 85–89° (5.0 mm.), m.p. 35–37° [b.p. 218–220° (740 mm.), m.p. 35.5°[15]].

***p*-Xylyl Cyanide (IVc).**—To 65 g. (1.0 mole) of potassium cyanide in 65 ml. of water and 100 ml. of ethanol was added 147 g. (0.79 mole) of *p*-xylyl bromide in 200 ml. of ethanol. After refluxing for 4.5 hours the solids were removed by filtration and the product was distilled through a short Vigreux column to give 67 g. (65%) of *p*-xylyl cyanide (IVc), b.p. 85° (12 mm.), $n^{25.0}_{D}$ 1.5160 [b.p. 242–245°, by treatment of *p*-xylyl bromide with alcoholic potassium cyanide[16]]. The infrared spectrum showed a sharp band at 4.45 μ.

2-(4-Methylphenyl)-ethylamine (VIc).—To *p*-xylyl cyanide (IVc) (45 g., 0.34 mole) in 120 ml. of acetic anhydride was added 1.5 g. of platinum oxide. After 48 hours and the addition of another 0.7 g. of catalyst, the reaction mixture had taken up 0.75 mole of hydrogen at pressures of 20–50 p.s.i.g. After filtration, most of the acetic anhydride was removed under reduced pressure leaving wet crystals of acetylated amine. These crystals were dissolved in 120 ml. of concentrated hydrochloric acid and refluxed for 6 hours. After making the solution basic with aqueous potassium hydroxide, the organic layer was separated, the aqueous layer was extracted with ether and the combined organic layers were dried over sodium carbonate. Distillation yielded 29 g. (70%) of 2-(4-methylphenyl)-ethylamine (VIc), b.p. 71–74° (1.7 mm.), $n^{25.0}_{D}$ 1.5221 (the compound absorbs carbon dioxide from the air) [no yield given from *p*-xylyl cyanide and sodium in ethanol, b.p. 214.5°, n^{18}_{D} 1.524, also reported absorption of carbon dioxide from the air[17]]. A picrate was obtained by treatment of the compound with a saturated solution of picric acid in ether, m.p. 153–155° (m.p. 155°).[18]

2-(4-Methylcyclohexyl)-ethylamine (VIIc).—To 29 g. (0.21 mole) of 2-(4-methylphenyl)-ethylamine (VIc) was added 150 ml. of glacial acetic acid and 1.5 g. of platinum oxide. The reaction mixture took up 3.0 moles of hydrogen in 48 hours after occasionally adding 0.5 g. quantities of platinum oxide when the reaction slowed down. After filtration most of the acetic acid was removed under reduced pressure, the resulting sirup made basic with aqueous potassium hydroxide, and the organic layer was separated, dried over sodium carbonate and distilled through a 7.5-cm. Vigreux column; there was obtained 18 g. (65%) of 2-(4-methylcyclohexyl)-ethylamine (VIIc), b.p. 67° (4.7 mm.), $n^{25.0}_{D}$ 1.4612. After redistillation, an analytical sample boiled at 62.5° (3.9 mm.), $n^{25.0}_{D}$ 1.4612. This compound absorbs carbon dioxide from the atmosphere.

Anal. Calcd. for $C_9H_{19}N$: C, 76.52; H, 13.56; N, 9.92. Found: C, 76.78; H, 13.67; N, 9.70.

N,N,N-Trimethyl-2-(4-methylcyclohexyl)-ethyl Ammonium Iodide (IXc).—To 4.4 g. (0.03 mole) of 2-(4-methylcyclohexyl)-ethylamine (VIIc), 50 ml. of absolute ethanol and 8.5 g. (0.061 mole) of anhydrous potassium carbonate was added 9.2 g. (0.065 mole) of methyl iodide while maintaining the temperature at 50°. At the completion of the addition (1 hour) the temperature was gradually raised to reflux temperature and kept at that level for 16 hours. After filtration most of the ethanol was removed under reduced pressure, leaving behind a white, water-soluble solid. The solid gave a precipitate with ethanolic silver nitrate and upon recrystallization from water gave 3.4 g. (46% based on methyl iodide) of N,N,N-trimethyl-2-(4-methylcyclohexyl)-ethyl ammonium iodide (IXc), m.p. 208–211°. Two recrystallizations from absolute ethanol raised the m.p. to 216–217°.

Anal. Calcd. for $C_{12}H_{26}NI$: C, 46.30; H, 8.42; N, 4.50. Found: C, 46.36; H, 8.59; N, 4.50.

N,N-Dimethyl-2-(4-methylcyclohexyl)-ethylamine (VIIIc).—The procedure was the general method of Clarke, Gillespie and Weisshaus.[19] From 18 g. (0.13 mole) of 2-(4-methylcyclohexyl)-ethylamine (VIIc) there was obtained 20 g. (66%) of N,N-dimethyl-2-(4-methylcyclohexyl)-ethylamine (VIIIc), b.p. 76° (4.5 mm.), $n^{26.0}_{D}$ 1.4520, d^{25}_{4} 0.8384.

Anal. Calcd. for $C_{11}H_{27}N$: C, 78.03; H, 13.69; N, 8.28; M_D, 54.76. Found: C, 78.28; H, 13.92; N, 8.54; M_D, 54.48.

Attempted Separation of the *cis*- and *trans*-Picrates of N,N-Dimethyl-2-(4-methylcyclohexyl)-ethylamine (VIIIc). To a saturated solution of wet picric acid (13.5 g. (dry), 0.059 mole) was added 10 g. (0.059 mole) of N,N-dimethyl-2-(4-methylcyclohexyl)-ethylamine (VIIIc). The solution was heated to boiling and after standing overnight in the refrigerator there was obtained 15 g. (64%) of picrate, yellow needles, m.p. 88–95°. After seven recrystallizations from absolute ethanol there was obtained 9 g. of material, m.p. 98–101°, melting point not increased upon further recrystallizations.

Anal. Calcd. for $C_{17}H_{26}N_4O_7$: C, 51.25; H, 6.58; N, 14.06. Found: C, 51.29; H, 6.66; N, 14.33.

The free amine was recovered from the picrate by treatment of 9 g. of picrate (0.021 mole) with 7 g. (0.13 mole) of potassium hydroxide in 100 ml. of water. After stirring and warming, the free amine was extracted from the aqueous suspension of sodium picrate with ether. The ether extract was washed with water, dried over sodium carbonate and distilled through a 5-cm. Vigreux column to yield 3.5 g. (100%) of free amine (VIIIc), b.p. 72° (3.7 mm.), $n^{28.0}_{D}$ 1.4488.

Preparation and Pyrolysis of the N-Oxide Xc of N,N-Dimethyl-2-(4-methylcyclohexyl)-ethylamine (VIIIc).—The amine oxide Xc was prepared and pyrolyzed without isolation according to a procedure used by Cope[20] for the pyrolysis of N,N-dimethylcycloöctylamine. From 3.5 g. (0.021 mole) of N,N-dimethyl-2-(4-methylcyclohexyl)-ethylamine (VIIIc) there was obtained 0.76 g. (30%) of olefin, b.p. 47° (28 mm.), $n^{24.5}_{D}$ 1.4442. Vapor phase chromatography of this material revealed the presence of two distinct peaks indicating that the attempted separation of isomers was unsuccessful.

1-(3-Methylcyclohexyl)-ethanol (Ib).—The method of preparation was the same as that described for 1-(4-methylcyclohexyl)-ethanol (Ic). From 221 g. (1.25 moles) of 3-methylcyclohexyl bromide, there was obtained 100 g. (56%) of crude 1-(3-methylcyclohexyl)-ethanol, (Ib), b.p. 53–68° (2.2 mm.). A sample redistilled for analysis had a b.p. 64–65° (1.9 mm.), $n^{25.0}_{D}$ 1.4605, d^{25}_{4} 0.9081 (no yield reported, b.p. 89.5–94° (13 mm.), no other physical constants or analysis reported).[13]

Anal. Calcd. for $C_9H_{18}O$: C, 76.00; H, 12.75; M_D, 43.10. Found: C, 76.22; H, 12.75; M_D, 42.93.

1-(3-Methylcyclohexyl)-ethyl acetate (IIb) was prepared by the same method described for the preparation of the acetate of 1-(4-methylcyclohexyl)-ethanol (IIc). From 84 g. (0.59 mole) of Ib there was obtained 75 g. (69%) of acetate IIb, b.p. 53–67° (1.8–2.0 mm.), $n^{25.0}_{D}$ 1.4438. A sample redistilled for analysis had a b.p. 73–75° (3.9 mm.), $n^{25.0}_{D}$ 1.4433, d^{25}_{4} 0.9282. The infrared spectrum of this compound showed a strong band at 5.75 μ.

Anal. Calcd. for $C_{11}H_{20}O_2$: C, 71.69; H, 10.94; M_D, 52.47. Found: C, 72.43; H, 11.00; M_D, 52.67.

***cis*- or *trans*-3-methylvinylcyclohexane (IIIb)** was prepared the same way as described for IIIc by pyrolysis of IIb at 498–520°. From 66 g. (0.36 mole) of IIb there was obtained 23 g. (51%) of olefin mixture, b.p. 54–70° (35 mm.), $n^{25.0}_{D}$ 1.4473. Distillation through a 75-plate concentric tube column gave 8.0 g. of 3-methylvinylcyclohexane (IIIb) (*cis* or *trans*), b.p. 144.0–145.0°, $n^{24.0}_{D}$ 1.4428, d^{25}_{4} 0.7936 [from dehydration of 1-(3-methylcyclohexyl)-ethanol, b.p. 146°, n^{25}_{D} 1.4513, d_{25} 0.810[21]]. The infrared spectrum of this compound showed a strong band at 11.0 μ indicating

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(16) E. F. J. Atkinson and J. F. Thorpe, *J. Chem. Soc.*, **191**, 1687 (1907).

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(21) M. Mousseron, R. Richard and R. Granger, *Bull. soc. chim.*, 222 (1946).

terminal olefin. Vapor phase chromatography indicated the presence of only one compound.

Anal. Calcd. for C_9H_{16}: C, 87.01; H, 12.98; M_{D}, 41.11. Found: C, 87.13; H, 12.78; M_{D}, 41.45.

***o*-Xylyl cyanide (IVa)** was prepared in the same manner as for the *p*-xylyl cyanide (IVc) except that reflux was continued for 16 hours. From 107 g. (0.58 mole) of *o*-xylyl bromide there was obtained 48 g. (64%) of *o*-xylyl cyanide (IVa), b.p. 74° (0.7 mm.), $n^{25.0}_{\mathrm{D}}$ 1.5260 [86% from *o*-xylyl chloride and sodium cyanide, b.p. 125.5° (14 mm.)[22]]. The infrared spectrum of this compound showed a strong band at 4.45 μ.

2-(2-Methylphenyl)-ethylamine (IVa) was prepared in the same manner as 2-(4-methylphenyl)-ethylamine (VIc). From 48 g. (0.37 mole) of *o*-xylyl cyanide (IVa) in 120 ml. of acetic anhydride there was obtained 30 g. (60%) of 2-(2-methylphenyl)-ethylamine (VIa), b.p. 67–72° (1.5–2.0 mm.), $n^{25.0}_{\mathrm{D}}$ 1.5326. A sample redistilled for analysis had a b.p. 55° (0.5 mm.), $n^{25.0}_{\mathrm{D}}$ 1.5328. This compound also absorbed carbon dioxide from the atmosphere.

Anal. Calcd. for $C_9H_{13}N$: C, 79.95; H, 9.69; N, 10.36. Found: C, 79.75; H, 9.74; N, 10.58.

A picrate was prepared from saturated picric acid in ether. After two recrystallizations from ethanol the picrate had m.p. 175.5–177.5° dec.

Anal. Calcd. for $C_{15}H_{16}N_4O_7$: C, 49.44; H, 4.43; N, 15.38. Found: C, 49.68; H, 4.58; N, 15.65.

2-(2-Methylcyclohexyl)-ethylamine (VIIa) was prepared in the same way as 2-(4-methylcyclohexyl)-ethylamine (VIIc). From 28 g. (0.21 mole) of 2-(2-methylphenyl)-ethylamine (VIa) there was obtained 9 g. (30%) of 2-(2-methylcyclohexyl)-ethylamine (VIIa), b.p. 64° (3.1 mm.), $n^{25.0}_{\mathrm{D}}$ 1.4690. A sample redistilled for analysis had a b.p. of 68° (2.6 mm.), $n^{25.0}_{\mathrm{D}}$ 1.4671. This compound absorbs carbon dioxide from the atmosphere.

Anal. Calcd. for $C_9H_{19}N$: C, 76.52; H, 13.56; N, 9.92. Found: C, 76.28; H, 13.90; N, 9.98.

N,N-Dimethyl-2-(2-methylcyclohexyl)-ethylamine (VIIIa) was prepared in the same way as compound VIIIc. From 7 g. (0.050 mole) of 2-(2-methylcyclohexyl)-ethylamine (VIIa) there was obtained 5.1 g. (60%) of N,N-dimethyl-2-(2-methylcyclohexyl)-ethylamine (VIIIa), b.p. 64° (1.5 mm.), $n^{25.0}_{\mathrm{D}}$ 1.4638, d^{25}_{4} 0.8455.

Anal. Calcd. for $C_{11}H_{27}N$: C, 78.03; H, 13.69; N, 8.28; M_{D}, 55.22. Found: C, 78.22; H, 13.85; N, 8.06; M_{D}, 54.76.

Separation of *cis*- and *trans*-Picrates of N,N-Dimethyl-2-(2-methylcyclohexyl)-ethylamine (VIIIa).—To a saturated ethanolic solution of 17.6 g. (0.077 mole) of pure picric acid was added 13.0 g. (0.077 mole) of N,N-dimethyl-2-(2-methylcyclohexyl)-ethylamine (VIIIa). After refrigeration overnight there was obtained 37 g. of yellow needles, m.p. 130–134°. After five recrystallizations from methanol, 16 g. (52%) of pure picrate was obtained, m.p. 135–137°.

Anal. Calcd. for $C_{17}H_{26}N_4O_7$: C, 51.25; H, 6.58; N, 14.06. Found: C, 51.34; H, 6.75; N, 13.98.

The free amine was recovered from the picrate by treatment with 10% aqueous sodium hydroxide. After filtration the reaction mixture was extracted with ether, dried over sodium carbonate and distilled through a 5-cm. Vigreux column to give pure *cis*- or *trans*-N,N-dimethyl-2-(2-methylcyclohexyl)-ethylamine (VIIIa), b.p. 65° (2.3 mm.), $n^{25.0}_{\mathrm{D}}$ 1.4560. This compound showed a single peak on vapor phase chromatography.

Anal. Calcd. for $C_{11}H_{27}N$: C, 78.03; H, 13.69; N, 8.28. Found: C, 78.42; H, 13.80; N, 7.95.

***cis*- or *trans*-2-Methylvinylcyclohexane (IIIa).**—The amine oxide was prepared and pyrolyzed without isolation according to a procedure used by Cope[20] for the pyrolysis of N,N-dimethylcycloöctylamine. From 7.6 g. (0.046 mole) of N,N-dimethyl-2-(2-methylcyclohexyl)-ethylamine there was obtained 3.5 g. (60%) of 2-methylvinylcyclohexane (IIIa), b.p. 149°, $n^{25.5}_{\mathrm{D}}$ 1.4510, d^{25}_{4} 0.8168, pure by vapor phase chromatographic analysis. The infrared absorption showed peaks at 6.05, 10.05, 11.00 μ.

Anal. Calcd. for C_9H_{16}: C, 87.01; H, 12.98; M_{D}, 41.11. Found: C, 86.80; H, 12.95; M_{D}, 40.94.

Polymerization of 3-Methylvinylcyclohexane (IIIb) (Pure *cis* or *trans*).—To 27 ml. of heptane was added 1.6 g. (0.0089 mole) of triisobutylaluminum and 0.86 g. (0.0045 mole) of titanium tetrachloride. The catalyst mixture was preheated to 85° and cooled to room temperature before adding 4.0 g. of 3-methylvinylcyclohexane. All operations were conducted under a nitrogen atmosphere. After heating with stirring for 40 hours at 60–85° the reaction mixture was cooled to room temperature, and the catalyst was decomposed with ethanolic hydrochloric acid. The polymer was collected by filtration and reprecipitated three times from benzene into methanol and dried overnight in a vacuum oven at 65° to yield 1.7 g. of solid polymer, m.p. 276–355° (under nitrogen in sealed capillary).

Anal. Calcd. for $(C_9H_{16})_n$: C, 87.01; H, 12.98. Found: C, 86.73; H, 13.22.

An X-ray powder diagram of this polymer revealed that it was crystalline. The intrinsic viscosity of the polymer was found to be 0.74 in dilute benzene solution at 29.2° using a Ubbelohde viscometer. Extraction in a Soxhlet of 0.25 g. of the polymer for 24-hour periods with ether, heptane and benzene dissolved 0.17 g., 0.03 g. and 0.02 g., in that order.

Polymerization of 4-Methylvinylcyclohexane (IIIc) (Pure *cis* or *trans*).—To 20 ml. of heptane containing 1.6 g. (0.0081 mole) of triisobutylaluminum and 1.1 g. (0.0058 mole) of titanium tetrachloride was added 2.3 g. of *cis*- or *trans*-4-methylvinylcyclohexane. After heating with stirring for 40 hours at 75–85°, the reaction mixture was decomposed with ethanolic hydrogen chloride. After filtration the polymer was reprecipitated twice from benzene into methanol and dried overnight in a vacuum oven to give 0.6 g. (30%) of poly-4-methylvinylcyclohexane, m.p. 225–250° (capillary), $[\eta]$ 0.45 determined as above.

Anal. Calcd. for $(C_9H_{16})_n$: C, 87.01; H, 12.98. Found: C, 87.10; H, 12.82.

Because the original X-ray powder diagram of the polymer showed no crystallinity, a sample was treated overnight in a Soxhlet with refluxing butanol-1. The butanol-1 extracted only a trace of the polymer and the remaining material after overnight drying in a vacuum oven gave a crystalline X-ray diffraction pattern.

Polymerization of 2-Methylvinylcyclohexane (IIIa) (Pure *cis* or *trans*).—To 11 ml. of heptane containing 0.64 g. (0.0032 mole) of triisobutylaluminum was added 0.34 g. (0.0018 mole) of titanium tetrachloride followed by 1.6 g. of *cis*- or *trans*-2-methylvinylcyclohexane (IIIa), and the reaction mixture was heated with stirring for 68 hours. At the end of this time the reaction mixture was decomposed with 20 ml. of ethanol and stirred overnight in 300 ml. of methanolic hydrogen chloride. After filtration there was obtained 1 g. of solid material. This material was insoluble in benzene and almost completely insoluble in boiling tetralin or decalin. The small amount which did dissolve was present in too small a quantity to be characterized.

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(22) M. S. Newman, THIS JOURNAL, **62**, 2295 (1940).