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Final Report

SYNTHESIS OF OLEFINS FOR USE IN PREPARATION OF DETERGENT ALKYLATES

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SUMMARY

The dimerization of selected hexenes and heptenes has been studied.

Polyphosphoric acid has been shown to be an effective catalyst for this purpose.

The dimers thus prepared can be used in the alkylation of benzene to produce detergent alkylates.

INTRODUCTION

The alkylaryl hydrocarbon most widely used for the manufacture of dodecylbenzene (detergent alkylate) is a mixture of dodecenes obtained by alkylation of benzene by propylene tetramer.¹ Detergents produced by sulfonation of this detergent alkylate have been found to be unsatisfactory in many respects.² Perhaps the most serious shortcoming of these detergents is their resistance to bacterial degradation in sewage disposal plants.³ Such resistance results in carry through of undegraded detergent and, particularly in areas where the recycle rate of river water is high, serious foaming problems have been encountered.

At present, no completely adequate theory to account for this resistance to degradation has been put forward. One suggestion involves the idea that either during the course of the polymerization of propylene or the subsequent alkylation of benzene by the tetramer, extensive rearrangements occur with the formation of quaternary carbon atoms in the alkyl side chain. It is felt that the bacteria used in the disposal plants require hydrogen attached to carbon to degrade the detergent and that the presence of quaternary carbon atoms thus blocks degradation. In any event, it is evident that availability of medium molecular weight olefins other than tetrapropylene might provide alkylates which are biodegradable.

One attempted solution to this problem involves the use of propylene pentamer obtained by polymerization of propylene with 117-122% phosphoric acid at 170-300°F and 200-1800 psi.² In the present work it was decided to investigate the dimerization of representative hexenes and heptenes carrying a terminal double bond in order to provide a biodegradable detergent. The dimerization of a hexene obtained by dimerization of propylene has also been studied.

The literature contains very little information on dimerization of olefins higher than the amylenes.⁴ Sulfuric acid of various concentrations has been used to polymerize the amylenes but in most instances the products were not

actually isolated. Dimerization of 5-methyl-1-hexene with 85% sulfuric acid has been reported to yield a C₁₂ olefin, b.p. 220-224°C, in about 33% yield.⁵

Ziegler and Gellert⁶ have used aluminum alkyl catalysts to dimerize 1-pentene and 1-hexene. The dimers are reported to be preponderantly 2-propyl-1-heptene and 2-butyl-1-octene, respectively. Similar catalysts are reported to give the same dimer from either 1-heptene and 3-heptene,⁷ but the nature of the dimer is not mentioned.

Irradiation of 1-hexene with high-energy electrons and gamma rays gives polymeric material in addition to hydrogen, light olefins, 1-hexene, and n-hexane.⁸ Fractional distillation of the polymer gave a dimer fraction which appeared to be about 90% monoolefin with some saturated hydrocarbons and some diolefin. Infrared data indicated 27% terminal, 57% trans nonterminal, and 3% vinylidene-type double bonds.

DISCUSSION AND RESULTS

When 1-hexene was stirred at room temperature with an equimolar amount of 85% sulfuric acid, the mixture became homogeneous after several hours, and within 24 hours an upper layer appeared. The upper layer was collected at 24-hour intervals until it no longer appeared (about 8 days). The combined upper layers were distilled to give 8.7% of dimer, 12.4% of trimer, and 6.5% residue. The acid reaction mixture was diluted with water and extracted with ether. Distillation of the ether extract gave about a 30% yield of carbinol and 10% of higher boiling material which contained only a very small amount of dimer. In a similar experiment, in which the upper layer was not removed until the end of 7 days, only 4.7% of dimer were obtained and the yields of the other fractions were about the same. From 1-heptene under conditions of the first experiment 6.2% dimer, 5.8% trimer, 3.7% residue, and 22% carbinol were obtained.

Attempts with 85% sulfuric acid at 100°C in a sealed tube, 98% sulfuric acid at 0°C, or 75% sulfuric acid at room temperature and 1-hexene all gave less satisfactory results. Use of 85% orthophosphoric acid at room temperature or at 100°C in a sealed tube with 1-hexene resulted in nearly quantitative recovery of the hexene.

The successful use of polyphosphoric acid (PPA) as an acid catalyst in many organic reactions⁹ suggested its application in these dimerizations. When 1-hexene was stirred with an excess of PPA at room temperature for about 20 hours, a 51% yield of dimer was obtained. The boiling range and infrared spectrum of this material were identical with those of the dimer resulting from the action of sulfuric acid on 1-hexene. In addition a 32% yield of trimer and no carbinol were obtained. The ratio of PPA to 1-hexene was varied from 4.6 to 6.1 to 1 and a slightly higher yield of dimer was obtained at the

higher ratio. The yield does not vary significantly with time once the reaction mixture has become essentially homogeneous (generally about 24 hours).

The dimer boiled in the range generally reported for various dodecenes and analyzed correctly for carbon and hydrogen. Treatment of the dimer with alcoholic bromine solution by the Kaufmann method¹⁰ confirmed the assignment of a dimeric structure. Attempts to isolate a dibromo derivative from the action of ethereal bromine solution on the dimer gave a material, b.p. 72-77°C (0.3-0.5 mm), which decomposed very rapidly and could not be analyzed. Ozonolysis of the dimer under conditions required for aldehyde or ketone formation gave materials the boiling range of which indicates C₄ to C₇ fragments. Infrared curves have been submitted to Esso Research and Engineering Company for interpretation in view of their extensive experience in interpretation of such curves. Representative curves for this dimer as well as the others prepared are given in Figs. 1-4.

4-Methyl-1-pentene, 1-heptene, and a mixed C₆ olefin from the dimerization of propylene were similarly treated with PPA. The results are summarized in Table I.

It was found that PPA catalyzed the alkylation of benzene with 1-hexene to give a slightly higher yield of hexylbenzene than that reported when sulfuric acid is the catalyst.¹¹ However, addition of benzene and additional PPA to the PPA-1-hexene mixture after allowing sufficient time for the dimerization to occur did not lead to dodecylbenzene.

Alkylation of benzene with the 1-hexene dimer using aluminum chloride as described by Sharrah and Feighner¹ gave a 25% yield of material boiling in the dodecylbenzene range. With sulfuric acid the yield of dodecylbenzene was 32% and recyclization of the forerun, which boiled in the dimer range, increased the yield to 47%. Similar alkylations of benzene with the other dodecenes and tetradecenes gave material boiling in the dodecyl- and tetradecylbenzene range in 51-54% yield. These results are summarized in Table II.

An attempted alkylation of toluene with the dimer from 4-methyl-1-pentene gave a product boiling in the dodecyltoluene range but which showed an abnormal infrared spectrum. The bands at 1610 and 1506 cm⁻¹ present in the other alkyl benzenes were absent and a band at 1525 cm⁻¹ and a very weak band at 1650 cm⁻¹ were present.

All the dodecylbenzenes and the tetradecylbenzene showed a strong infrared band at 758-760 cm⁻¹, indicating a substituent on the alpha position of the allyl side chain.¹² The toluene product showed a weak band at 755-760 cm⁻¹.

A single attempt to alkylate benzene with the 1-hexene trimer under conditions which were successful with the dimer was unsuccessful.

Samples of the various alkylates prepared have been submitted to Esso Research and Engineering Company for evaluation in the manufacture of detergents.

EXPERIMENTAL*

MATERIALS

1-Hexene and 1-heptene were prepared either by the Boord olefin synthesis or by the reaction of an appropriate Grignard reagent with allyl bromide. The latter method appears to be the method of choice for the synthesis of a terminal olefin. Representative preparations are given below. 1-Hexene and 4-methyl-1-pentene were also purchased from Phillips Petroleum Company. The propylene dimer was supplied by Esso Research and Engineering Company. Infrared analysis of this material indicates the following distribution: trans olefin, 9.4-12.9%; alpha olefin, 1.3-4.2%; tertiary olefin, 8.4-12.7%; 2-methyl-2-pentene, 24.4-30.8%; 3-methyl-cis-2-pentene, 16.3-21.2%; 3-methyl-trans-2-pentene, 12.2-14.6%; tetra-substituted ethylenes, 8.2-13.2%.

Polyphosphoric acid (PPA) was purchased from Victor Chemical Company.

1-HEPTENE

A. By the Boord Synthesis.—To the Grignard reagent from 210.6 g (1.4 mole) of n-amyl bromide, 24.32 g of magnesium, and 300 ml of anhydrous ether were added 325 g (1.4 mole) of α,β -dibromo-ethyl ether.¹³ The β -bromo ether¹⁴ (50% yield) from this reaction was refluxed with 250 g of zinc dust in n-propyl alcohol to give after treating in the usual manner¹⁴ 15.2 g (22%) of a liquid, b.p. 91-93°, reported¹⁵ b.p. 93.5-94.5°.

B. Using a Grignard Reagent.—To the Grignard reagent formed by reacting 18.2 g of magnesium and 95.9 g (0.7 mole) of n-butyl bromide in 350 ml of anhydrous ether was slowly added, at 0°, with stirring 83.5 g (0.69 mole) of allyl bromide in 80 ml of ether. The mixture was stirred an additional 4 hours at 0° and then brought to room temperature. After decanting the liquid from the solids, the liquid was washed with cold concentrated hydrochloric acid until the volume remained constant. After standing over sodium ethoxide in ethanol, the mixture was diluted with water. The organic layer was washed with concentrated hydrochloric acid, water, a sodium carbonate solution, and water. After drying (CaCl_2), distillation gave 22.8 g (34%) of liquid, b.p. 92.5-93.5°.

REACTION OF OLEFINS WITH POLYPHOSPHORIC ACID

1-Hexene.—A mixture of 500 g of polyphosphoric acid and 84 g (1 mole) of 1-hexene was stirred at room temperature for 18 hours and poured onto ice. The

*All boiling points are in °C and are uncorrected. Microanalyses by Spang Microanalytical Laboratory, Ann Arbor, Michigan.

aqueous mixture was extracted with ether and the dried (sodium sulfate) extract was distilled to give 43.3 g (51.5%) of liquid, b.p. 81-91° (20 mm) and 39.15 g (46.6%) of residue.

Anal. Calcd. for $C_{12}H_{24}$: C, 85.63; H, 14.37. Found: C, 85.53; H, 14.68.

Treatment of this material with alcoholic bromine¹⁰ gave a molecular weight of 166.2. Calcd. for $C_{12}H_{24}$: 168.3.

In another run the residue from distillation of the dimer was found to contain about 68% of a liquid, b.p. 77-83° (0.06-0.07 mm).

Anal. Calcd. for $C_{18}H_{36}$: C, 85.63; H, 14.37; mol. wt. 252.5. Found: C, 85.69; H, 14.12; mol. wt. 262.

1-Heptene.—By the same procedure 590 g of PPA and 98 g (1 mole) of 1-heptene gave 58% of dimer and 9% of trimer.

4-Methyl-1-Pentene.—By the same procedure, 515 g of PPA and 84 g (1 mole) of isohexene gave 58.9% of dimer and 20% of trimer.

Propylene Dimer. The yield of dimer was 51.7% along with 21% of trimer.

These results are summarized in Table I.

ALKYLATION REACTIONS

2-Phenylhexane. PPA Method.—A mixture of 78 g (1 mole) of benzene and 42 g (0.5 mole) of 1-hexene was added at room temperature with stirring to 275 g of PPA. After stirring for 21.5 hours, the mixture was poured onto ice and the aqueous mixture was extracted with benzene. Distillation of the dried (calcium chloride) extract gave 52.47 g (65.8%) of 2-phenylhexane, b.p. 85-94° (18 mm). The infrared spectrum had a strong band at 760 cm^{-1} for an alpha substituted alkyl benzene.¹²

Sulfuric Acid Method.—Addition of 1-hexene to a mixture of sulfuric acid and benzene at 0° gave a 53% yield of 2-phenylhexane the infrared spectrum of which was identical with that prepared by the PPA method.

BENZENE AND 1-HEXENE DIMER

Aluminum Chloride Method.¹—To a mixture of 78 g (1 mole) of benzene, a drop of water, and 1.33 g of aluminum chloride, 42 g (0.25 mole) of 1-hexene dimer was added slowly so as to keep the temperature below 55°. During the addition of the dimer, 0.67 g of aluminum chloride was added in two portions. After stirring for an additional 30 minutes, the reaction mixture was washed with

two 20-ml portions of 5% sodium hydroxide solution and one 10-ml portion of water and dried over calcium chloride. Distillation gave 19.7 g (47%), b.p. 76-96° (17 mm) (dimer range); 15.7 g (25.5%) of dodecylbenzene, b.p. 76-100° (0.3 mm); and 6.5 g (15.5%) of residue.

Sulfuric Acid Method.—To a mixture of 232 g (2.97 mole) of benzene and 53 ml of concentrated sulfuric acid at 0° was added with stirring 66 g (0.393 mole) of 1-hexene dimer during one hour. After stirring at 0° for 1.25 hours, the mixture was washed successively with 50 ml of water, two 50-ml portions of 5% sodium hydroxide, and 50 ml of water. After drying over calcium chloride, distillation gave 18.8 g (28.5%) of unreacted dimer, 30.8 g (32.1%) of dodecylbenzene, b.p. 97-127° (0.9-1.0 mm), and 10.75 g (16.3%) of residue.

Anal. Calcd. for $C_{18}H_{30}$: C, 87.73; H, 12.27. Found: C, 87.39; H, 12.56.

When the forerun and residue were recycled in another run, the yield of dodecylbenzene, b.p. 72-99° (0.15 mm), was raised to 46.6%.

BENZENE AND 4-METHYL-1-PENTENE DIMER

By the sulfuric acid method, alkylation of benzene with isohexene dimer gave 16.2% of recovered dimer, 51% of dodecylbenzene and 12.4% of residue. In this case recycle of the forerun and residue did not increase the yield of dodecylbenzene.

TOLUENE AND 4-METHYL-1-PENTENE DIMER

By the sulfuric acid method, alkylation of toluene with isohexene dimer gave 14.3% of recovered dimer, 53% of dodecyltoluene (see above for discussion of infrared data), and 9% of residue.

Anal. Calcd. for $C_{19}H_{32}$: C, 87.61; H, 12.39. Found: C, 87.49; H, 12.36.

BENZENE AND 1-HEPTENE DIMER

By the sulfuric acid method, there was obtained 11.6% of recovered dimer, 53.9% of tetradecylbenzene, and 9.3% of residue.

BENZENE AND THE DIMER OF PROPYLENE DIMER

By the sulfuric acid method, there was obtained 21.8% of recovered dimer, 52% of dodecylbenzene, and 17.4% of residue.

Anal. Calcd. for $C_{18}H_{30}$: C, 87.73; H, 12.27. Found: C, 87.58; H, 12.47.

The results obtained are summarized in Table II.

We acknowledge the assistance of James Smith in the preparation of some of the starting olefins.

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TABLE I

REACTION OF OLEFINS WITH POLYPHOSPHORIC ACID

Olefin	Yield of Dimer (%)	b.p., °C (mm Hg)	Yield of Trimer (%)	b.p., °C (mm Hg)
1-Hexene	51.5	81-91 (20)	32	77-83 (0.06-0.07)
1-Heptene	58.0	102-112 (14)	9	60-80 (0.3)
4-Methyl-1-pentene	58.9	66-89 (18)	20	50-80 (0.3)
Dipropylene dimer	51.7	63-98 (21)	21	59-89 (0.2-0.3)

TABLE II

ALKYLATIONS WITH THE DIMERS (SULFURIC ACID METHOD)

Aromatic Compound	Dimer from	Yield (%)	b.p., °C (mm Hg)
Benzene	1-Hexene	46.6	72-99 (0.15)
Benzene	4-Methyl-1-pentene	51.0	75-105 (0.3)
Toluene	4-Methyl-1-pentene	53.0	80-112 (0.3)
Benzene	1-Heptene	53.9	84-120 (0.3)
Benzene	Dipropylene	52.0	90-120 (0.6)

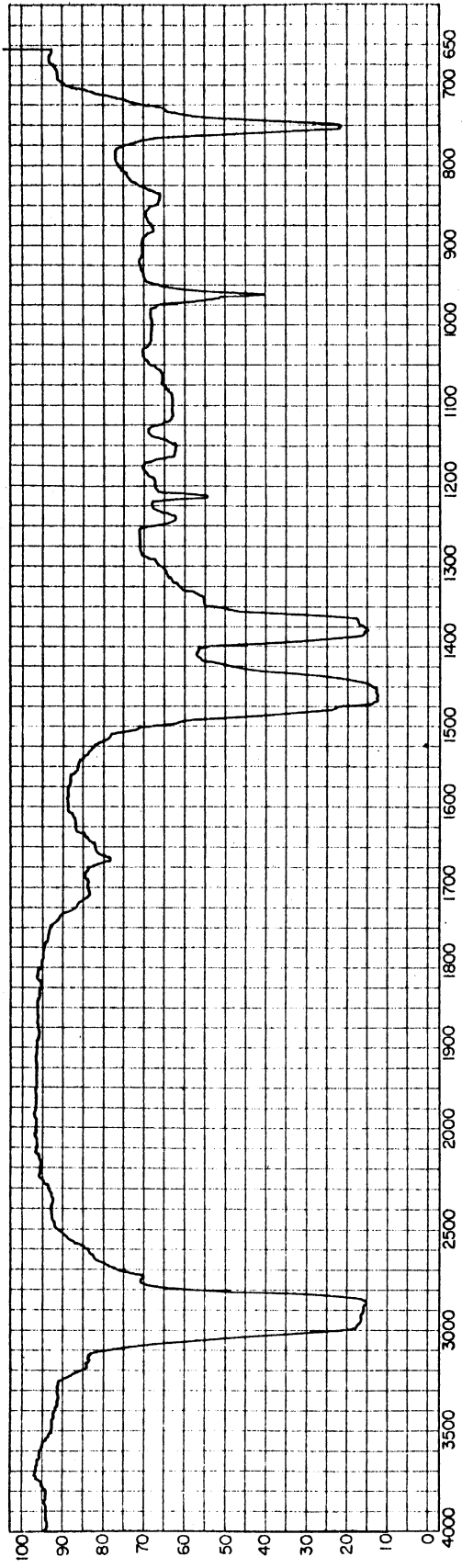


Fig. 1. 1-Hexene dimer.

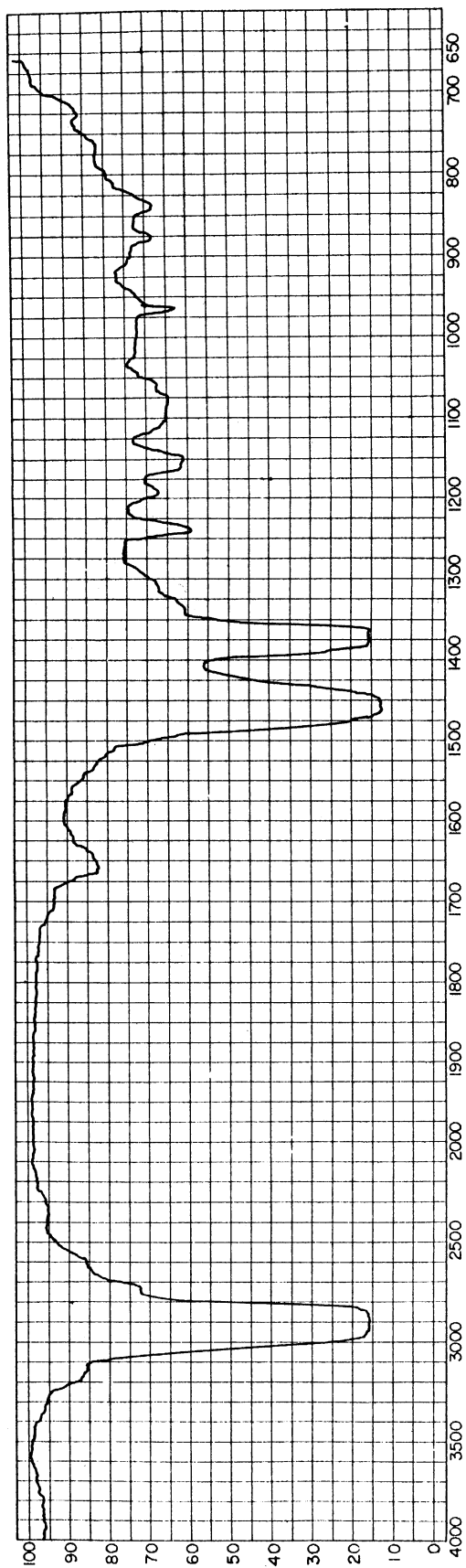


Fig. 2. 4-Methyl-1-pentene dimer.

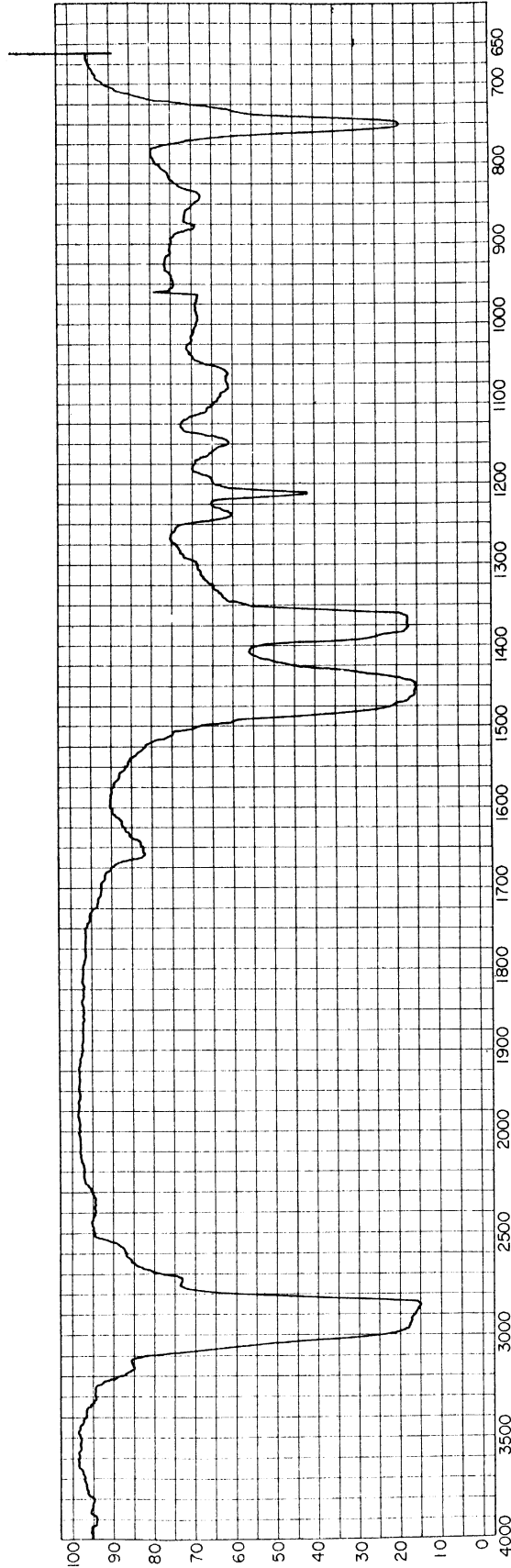


Fig. 3. Dipropylene dimer.

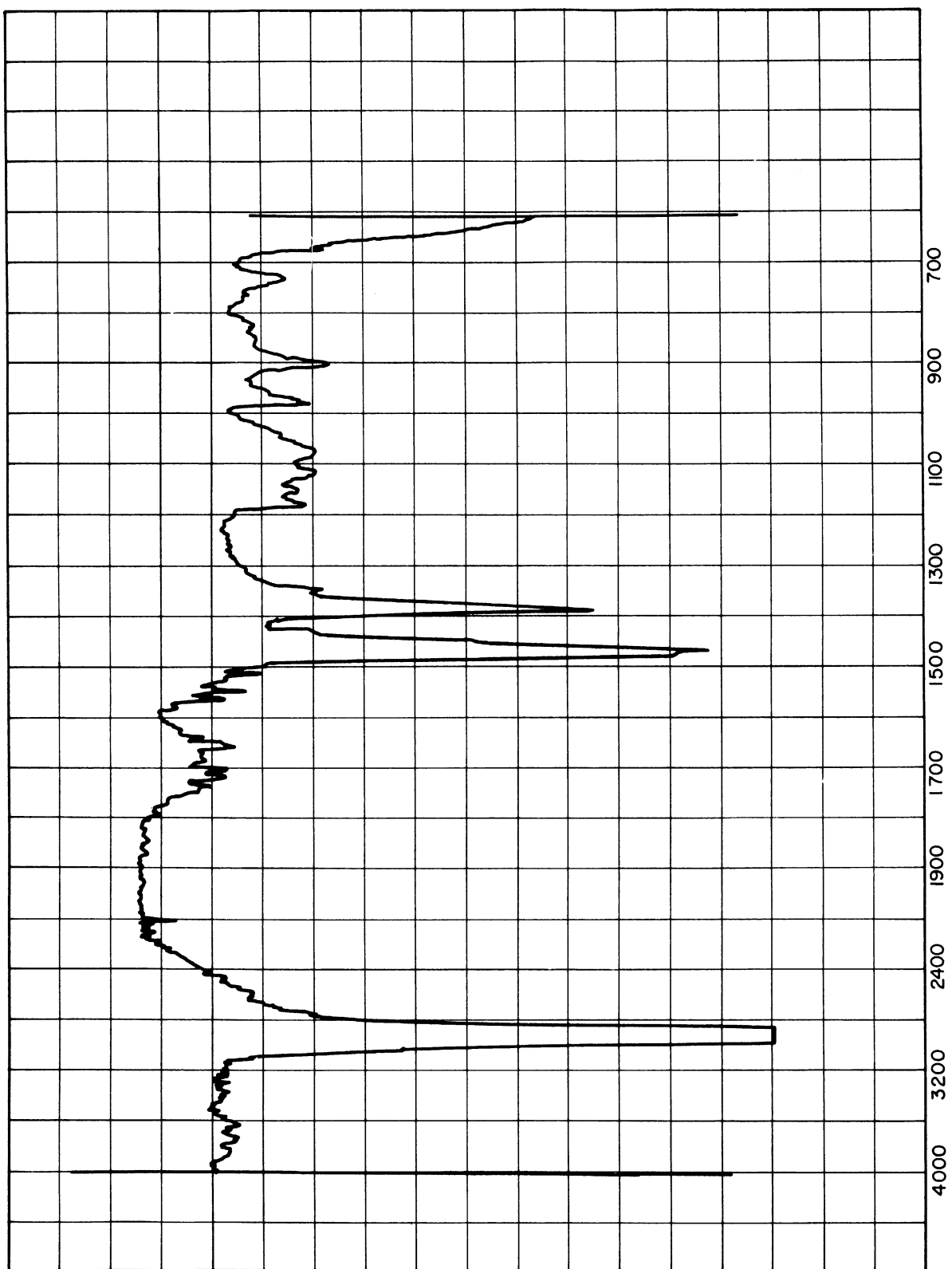


Fig. 4. 1-Heptene dimer.

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