411. *Reactions of Cyclic Hydrocarbons. Part II. The Polymerisation of* cyclo*Hexene and* 1-*Methyl*cyclo*pentene.*

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*cyclo*Hexene is polymerised by 97% sulphuric acid at 0°, the polymerisation being accompanied by change in ring-size and disproportionation, resulting in the formation of two series of polymeric oils, one almost completely saturated and insoluble in the acid layer, and the other consisting of diolefins soluble in the acid layer. The saturated dimeric fraction contains 1-*cyclo*hexyl-2-methyl*cyclo*pentane and 1-*cyclo*hexyl-3-methyl*cyclo*pentane, whereas the unsaturated dimeric fraction appears to contain diolefins derived from *cyclo*hexyl-methyl-*cyclo*-pentane.

1-Methyl*cyclo*pentene is dimerised by 87% sulphuric acid, but with 97% acid gives rise to products similar to those from *cyclo*hexene.

THE action of sulphuric acid on olefins has received considerable attention since Brookes and Humphrey (*J. Amer. Chem. Soc.*, 1918, **40**, 822) found that the acid polymerises, hydrates, and sulphates olefins. Nametkin and Abakumovskaya (*Ber.*, 1933, **66**, 358) treated *cyclo*hexene with sulphuric acid, and obtained two series of polymers: saturated acid-insoluble and unsaturated acid-soluble. The latter authors found that the former series consisted principally of the dimer and trimer which were completely saturated, and suggested that they were di- and tri-*cyclo*hexyl respectively, but were unable to dehydrogenate them to the corresponding aromatic compounds. *cyclo*Hexene has been polymerised by a number of other reagents, including hydrogen fluoride (McElvain and Langston, *J. Amer. Chem. Soc.*, 1944, **66**, 1759), aluminium chloride (Waterman *et al.*, *Rec. Trav. chim.*, 1935, **54**, 245), boron trichloride (Hoffmann, *Chem. Ztg.*, 1933, **57**, 5), and benzoyl peroxide (Farmer and Michael, *J.*, 1942, 513; Hermans and Van Eyk, *J. Polymer Sci.*, 1946, **1**, 407), but, with the exception of those from aluminium chloride, the products differed from those obtained with sulphuric acid.

Whereas sulphuric acid of concentrations less than 90% sulphates and hydrates *cyclo*hexene at 0°, 97% acid gives, as principal products, two series of polymeric oils, one insoluble in the acid layer and consisting almost entirely of saturated hydrocarbons, and the other soluble in the acid layer and consisting of highly unsaturated reactive polymers. These two series were separated and then fractionated, and the properties of the fractions examined.

The acid-insoluble polymers consisted principally of the dimer and trimer fractions, which were completely saturated. The tetrameric fraction, however, contained approximately 30% of olefinic hydrocarbons. The dimeric fraction could be separated into two components, whose physical properties approximated to those of 1-*cyclo*hexyl-2-methyl*cyclo*pentane (Orchin and Feldman, *J. Amer. Chem. Soc.*, 1946, **68**, 2737), and 1-*cyclo*hexyl-3-methyl*cyclo*pentane (Zelinsky and Titz, *Ber.*, 1925, **58**, *B*, 2755). They resisted dehydrogenation over palladised charcoal at 340°, under which conditions di*cyclo*hexyl readily yields diphenyl, but they were readily dehydrogenated to the corresponding phenylmethyl*cyclo*pentane at 410°.

The unsaturated series of polymers differed from the saturated series in containing only a small amount of dimer, somewhat larger amounts of trimer and tetramer, and an undistillable residue containing polymers of higher molecular weight. The last-named were highly reactive diolefins, but the dimers appeared to be derivatives of *cyclo*hexyl-methyl-*cyclo*pentane. The diolefins reacted vigorously with bromine in carbon tetrachloride by substitution, absorbed atmospheric oxygen, decolorised potassium permanganate, reduced silver nitrate to silver, and ferric to ferrous salts, and formed coloured complexes with mineral acids; they absorbed ultra-violet light very strongly, reacted abnormally with maleic anhydride, and were hydrogenated in the presence of Raney nickel, giving colourless saturated hydrocarbons whose properties approached those of the corresponding saturated polymer. The hydrogenated dimer could be dehydrogenated by palladised charcoal at 410°. In addition, the diolefins reacted with perbenzoic acid, the trimer and tetramer absorbing two atoms of oxygen per molecule. Sulphonation of the diolefins with dioxan–sulphur trioxide complex (Suter *et al.*, *J. Amer. Chem. Soc.*, 1938, **60**, 538) produced a range of sulphonic acids, whose barium salts could be partly separated by addition of alcohol to an aqueous solution. Those salts containing between 3 and 4 sulpho-groups per molecule were readily precipitated, those remaining in solution consisted principally of sulphated hydroxy-sulphonic acids containing one sulpho-group per molecule. They decolorised potassium permanganate and bromine water, but only a trace of barium sulphate was precipitated by the latter reagent.

1-Methyl*cyclo*pentene was dimerised by 87% sulphuric acid at 5° (Bearse and Leonard, U.S.P. 2,419,668). The dimer contained one double bond and was dehydrogenated to phenylmethyl*cyclo*pentane by passage over palladised charcoal at 410°, indicating that it consisted of *cyclo*hexenyl-methyl-*cyclo*pentane. Treatment of the dimer with 97% sulphuric acid at 10° gave saturated acid-insoluble and unsaturated acid-soluble polymers. The properties of the mixed saturated dimeric fraction were almost identical with those of the mixed saturated dimeric fraction obtained by the sulphuric acid polymerisation of *cyclo*hexene. Unlike 1-methyl*cyclo*pentene, *cyclo*hexene could not be dimerised by 88% sulphuric acid.

EXPERIMENTAL.

(B. p.s are corrected.)

cyclo*Hexene.*

Preparation and Separation of the Two Series of Polymers.—*cyclo*Hexene (300 g.) was added slowly during 5 hours to 97% sulphuric acid (750 g.), the reaction temperature being maintained at 0°. The mixture was then stirred for a further hour, being kept blanketed all the time by a current of purified nitrogen. As the reaction proceeded, the acid layer became orange in colour but no sulphur dioxide was evolved. After the reaction, the mixture was blanketed with carbon dioxide and set aside overnight in the refrigerator at −25°. The lower, acid layer was then separated from a pale yellow oil (110 g.), containing the saturated series of polymers.

To the lower, acid layer was added an equal weight of ice while the mixture was cooled in a freezing mixture. A greenish viscous oil was precipitated and was extracted with light petroleum (b. p. 40—60°) and then washed free from acid with sodium sulphate solution, the colour changing from bluish- to brownish-green and finally to light orange at complete neutrality. The light petroleum was then removed under reduced pressure. The residual viscous oil (155 g.) contained the unsaturated polymers. In processing the unsaturated polymers, care must be taken to exclude oxygen by blanketing with nitrogen or carbon dioxide.

Distillation of Saturated Polymers.—91 G. of the saturated polymeric oils were distilled at 4 mm. and fractionated through a 3-ft. column, 1 inch in diameter, packed with glass helices, and equivalent to 15 theoretical plates. The following fractions were obtained: (i) b. p. 73—79°/4 mm. (26·04 g., 28·6%), dimer; (ii) b. p. 138—146°/4 mm. (10·36 g., 11·4%), mixed dimer–trimer; (iii) b. p. 146—148°/4 mm. (25·25 g., 27·7%) trimer; (iv) b. p. 148—192°/4 mm. (8·93 g., 9·8%), mainly trimer; (v) b. p. 255—265°/15 mm. (4·89 g., 5·4%), a pale yellow viscous oil, tetramer; and a residue (10·0 g., 11·0%), a light-brown very viscous oil. Fractions (i)—(iv) were colourless, odourless oils. See also Table I.

TABLE I.

Saturated series of polymers.	Mixed dimer.	Trimer.	Tetramer.
n_{20}^{D}	1·4749	1·4965	1·5088
d_4^{20}	0·8771	0·9189	0·9360
Molecular weight	165	249·5	335
Aniline point	49·5°	69·0°	82·9°
Bromine no.	0	0	14·5
Carbon, found	86·04%	86·24%	—
Hydrogen, found	12·96%	12·63%	—

Unsaturated series of polymers.	Dimer.	Trimer.	Tetramer
n_D^{20}	1·5011	1·5200	1·5287
d_4^{20}	0·9173	0·94607	0·96423
Molecular weight	161·5	245	330
Aniline point	—	33·2°	46·0°
Bromine no. (I.P. Method)	77·6	−10·3	−8·1
Total Br/100 g.	200	180·3	153·2
HBr/100 g.	62·5	96·1	81·6
Bromine no. (Wijs)	—	182	155·0
Bromine no. (A.S.T.M.)	—	110·5	93·8
Carbon, found	86·85%	87·00%	87·04%
Hydrogen, ,,	11·35%	11·57%	1·24%
Sulphur, ,,	1·635%	0·97%	0·51%

Carbon and hydrogen contents were determined by Drs. Weiler and Strauss, Oxford.

Distillation of Unsaturated Polymers.—140 G. of the unsaturated polymers were distilled at 3 mm. to give the following fractions: (i) b. p. 60—121°/3 mm. (14·32 g., 9·9%), mixed dimer–trimer; (ii) b. p. 126—136°/3 mm. (30·11 g., 20·8%), trimer; (iii) b. p. 168—178°/3 mm. (7·17 g., 5·0%), mixed trimer–tetramer; (iv) b. p. 182—200°/3 mm. (23·60 g., 16·3%), tetramer; residue (62·0 g., 42·7%), a brown resin. Fractions (i)—(iv) were yellow oils of terpinic odour. See also Table I.

The preparation of the polymeric oils was repeated by treating 450 g. of peroxide-free *cyclo*hexene with 1125 g. of 97% sulphuric acid at 0° and yielded 140 g. of saturated polymers and 285 g. of unsaturated polymers. The distillates obtained were similar to those from the first preparation except that the saturated dimer could be separated into two fractions, and that approx. 9% of an unsaturated dimer could be obtained from the unsaturated polymers. Two dimeric fractions were obtained: b. p. 224·5—225°/760 mm., d_4^{20} 0·8712, n_D^{20} 1·4719, aniline point 48°; b. p. 231—232°/760 mm., d_4^{20} 0·8793, n_D^{20} 1·4760, aniline point 48·5°.

Reactions of Saturated Series.—Dehydrogenation. (i) *Palladised charcoal.* The method employed was based on that of Zelinsky (*Ber.*, 1924, **57**, 150; 1926, **59**, 2580). 1 G. of oil was vapourised per hour in a current of carbon dioxide and passed over heated 10% palladised charcoal. The dehydrogenated product was condensed, the carbon dioxide was absorbed in alkali, and the hydrogen formed was collected and measured. The amount of dehydrogenation was determined by ascertaining the change in physical properties and by the hydrogen evolved. The amount of undehydrogenated matter in the product could be measured by noting the volume of residual oil on treatment with 20% oleum.

Di*cyclo*hexyl was readily dehydrogenated to diphenyl at 340°, whereas 1-*cyclo*hexyl-2-methyl*cyclo*pentane, a sample of which was kindly supplied by Dr. M. Orchin, U.S. Bureau of Mines, was dehydrogenated at 410° giving, in a single pass, 79% of 1-phenyl-2-methyl*cyclo*pentane and 21% of residual 1-*cyclo*hexyl-2-methyl*cyclo*pentane. This mixture solidified on cooling in solid carbon dioxide–alcohol and melted sharply on rewarming, whereas a 3 : 1 mixture of diphenyl and 1-*cyclo*hexyl-2-methyl*cyclo*pentane melted at 55°. The 1-phenyl-2-methyl*cyclo*pentane was readily absorbed by 20% oleum.

The changes in physical properties of the dimeric hydrocarbons obtained by dehydrogenation are described in Table II.

TABLE II.

	B. p.	d_4^{20}.	n_D^{20}.	Aniline point.	Vol. (%) insoluble in oleum.
1-*cyclo*Hexyl-2-methyl*cyclo*pentane	222·4°/ 760 mm.	0·8683	1·4705	—	—
do. after dehydrogenation *	—	0·91325	1·5167	13·6°	38·0
*cyclo*Hexene saturated dimer, fraction (i)	224·5—225°/ 760 mm.	0·8712	1·4719	48·0	—
do. after dehydrogenation *	—	0·9257	1·5277	−12·0	21·0
*cyclo*Hexene saturated dimer, fraction (ii)	231—232°/ 760 mm.	0·8793	1·4760	48·5	—
do. after dehydrogenation *	—	0·9185	1·5168	7·0	25·0
Hydrogenated *cyclo*hexene unsaturated dimer	—	—	1·4855	—	—
do. after dehydrogenation *	—	—	1·5080	—	—
1-Methyl*cyclo*pentene dimer (hydrogenated)	224—229°/ 752 mm.	0·8790	1·4798	46·0	—
do. after dehydrogenation *	—	0·9230	1·5253	−10·0	22·0
1-Phenyl-2-methyl*cyclo*pentane (by extrapolation)	—	0·941	1·5430	< −20	—

* The substance was passed over the catalyst once only.

(ii) *Nickel chromite.* 2·1 G. of saturated dimer in 20 ml. of benzene were heated with 2 g. of reduced nickel chromite at 250° for 5 hours under nitrogen, the charging pressure being 50 atmospheres, according to the method described by McElvain and Langston (*J. Amer. Chem. Soc.*, 1944, **66**, 1759) and by Adkins *et al.* (*ibid.*, 1941, **63**, 1320). The dimer was unchanged.

Reactions of Unsaturated Series.—(a) *Reaction with bromine.* The bromine numbers determined by the I.P. method ("Standard Methods for Testing Petroleum and its Products," p. 46, Institute of Petroleum, 1948) were unsatisfactory as the reaction appeared to proceed predominantly by substitution. With Wijs's reagent, a solution of iodine monochloride in acetic acid, the reaction appeared to proceed to the same extent as with bromine in carbon tetrachloride. More satisfactory results were obtained with the A.S.T.M. Method ("A.S.T.M. Standards on Petroleum Products and Lubricants," p. 328, American Society for Testing Materials, 1946) in which a mixed potassium iodide–iodate reagent is used, approx. 4 atoms of halogen reacting per molecule of unsaturated polymer.

5·94 G. of unsaturated tetramer were dissolved in 50 ml. of dry carbon tetrachloride, and the solution was cooled to −10°. 12 G. of bromine in 50 ml. of carbon tetrachloride were run in rapidly with stirring, the temperature being maintained at −10°. The product was washed with aqueous sodium hydrogen sulphite, followed by water, and finally shaken with calcium carbonate until free from mineral acid. The carbon tetrachloride layer was separated, dried (Na_2SO_4), and filtered, and the bulk of the solvent removed under reduced pressure. The product was a golden-brown resinous oil which decomposed when kept or heated, evolving hydrogen bromide and changing in colour to dark green. The carbon tetrachloride could not be completely removed without decomposition of the product. The product contained 14·65% of carbon tetrachloride and the bromine content of the brominated tetramer was 37·0% (after correction for carbon tetrachloride present); the molecular weight (cryoscopic in benzene) was 524. The bromine content corresponded to the addition of 3·2 atoms of bromine per tetramer molecule, the calculated molecular weight of the tribromide being 590. When the product was heated on the steam-bath for several hours, the colour changed to dark olive-green and a hard resin resulted, having bromine content, 28·84%, *M*, 719, indicating that it was formed by condensation of two molecules of brominated tetramer with the loss of four atoms of bromine.

(b) *Oxidation.* (i) *Atmospheric.* 0·8643 G. of unsaturated tetramer was placed in a 100-ml. CO_2 flask open to the air. The oil gradually darkened and increased in weight by 0·0639 g. in 63 days. The product was then treated with light petroleum to precipitate asphaltic matter (0·103 g.). The increase in weight corresponds to an addition of 1½—2 atoms of oxygen per tetramer molecule. The oxidised oil had molecular weight (cryoscopic in benzene) of 382 (calc. for addition of 2O : 360). Though the oil liberated iodine from potassium iodide after exposure to the atmosphere for a few days, it did not do so after 63 days.

(ii) *Perbenzoic acid.* A 0·178N- solution of perbenzoic acid in chloroform was prepared by treating benzoyl peroxide with sodium methoxide at 0°. 20 Ml. of the solution were added to a weighed sample of the unsaturated polymer in a stoppered glass bottle and maintained for 48 hours at −20°, light being excluded. A blank determination was also carried out. After the reaction, the residual perbenzoic acid was determined by potassium iodide, and the liberated iodine titrated. Results were:

	Unsaturated dimer.	Unsaturated trimer.	Unsaturated tetramer.
Wt. of sample, g.	0·1108	0·1163	0·2064
0·1N-Thiosulphate, ml.	19·75	19·85	24·65
Oxygen absorbed, g./mol.	23·1	33·4	32·0

(iii) *Potassium permanganate.* Unsaturated dimer (1·1 g.) was treated with a dilute solution of potassium permanganate in 1% aqueous sodium carbonate at 0°. No organic matter could be extracted from the product after acidification.

(iv) *Nitric acid.* Unsaturated dimer (1 g.) reacted with nitric acid (*d* 1·28) at 80°; 0·0994 g. of fatty acid (equiv., 261·5) was obtained.

(v) *Alcoholic silver nitrate.* Unsaturated trimer (1·4988 g.) was heated under reflux with excess of alcoholic silver nitrate for 1 hour under carbon dioxide. A silver mirror was produced, with 0·8705 g. of a grey precipitate containing 95·5% of silver.

(vi) *Ferric chloride.* A few drops of the unsaturated trimer were shaken with an aqueous solution of ferric chloride and potassium ferricyanide. A deep-blue colour and precipitate were formed, whilst a blank sample of reagent itself remained unchanged.

(c) *Hydrogenation.* Before dehydrogenation, the unsaturated dimer was subjected to desulphurisation by heating its alcoholic solution under reflux for 4 hours with 20 g. of Raney nickel (Mozingo *et al., J. Amer. Chem. Soc.*, 1943, **65**, 1013). After removal of the solvent, the sulphur content was almost unchanged (1·615%). The "desulphurised oil" (5 g.) in ethyl alcohol (30 ml.) was hydrogenated with Raney nickel (5 g.) for 3 hours at 160° with a hydrogen pressure of 1500 lb./sq. in. The product, after removal of solvent and catalyst, was a pale yellow oil which still reacted with bromine by substitution (15·9 g. of bromine per 100 g.; 7·5 g. of HBr evolved per 100 g.). The oil was shaken with an excess of concentrated sulphuric acid, and the acid-insoluble oil was washed with water, treated with a little absorbent clay, and filtered. The purified oil was saturated and colourless. The unsaturated trimer and tetramer were hydrogenated by the same procedure. The properties of the hydrogenated products were:

	Dimer.	Trimer.	Tetramer.
d_4^{20}	—	0·9281	0·952
n_D^{20}	1·4855	1·4998	1·5125
Aniline point	—	59·6°	58·0°

(d) *Dehydrogenation.* (i) *Selenium.* The unsaturated dimer (4·102 g.) and selenium (9·8 g.) were heated at 270° for 20 hours, after which the temperature was raised to 330°. 1·1559 G. of hydrogen selenide were collected in absorption tubes. The product was purified by extraction with benzene and redistillation over sodium. The product was an oil which gave no picrate, nitro-, or aroylbenzoic acid derivative. The amount of hydrogen selenide produced was only 10% of that required for complete dehydrogenation of the naphthenic to aromatic rings. Similar results were obtained with the unsaturated trimer.

(ii) *Palladised charcoal.* When passed over palladised charcoal at 410°, the hydrogenated unsaturated dimer was partly dehydrogenated. Little of the sample was available, but the change in *n* was determined (see Table II).

(e) *Ultra-violet light absorption.* There was a broad maximum with its centre at 2512·5 A. ($E_{1\,\text{cm.}}^{1\,\%}$ 5000). The absorption decreased at shorter wave-lengths with a minimum at 2325 A. ($E_{1\,\text{cm.}}^{1\,\%}$ 4350). The intensity of absorption indicates the presence of conjugated double bonds, but is not a reliable guide to the number of double bonds present.

(f) *Reaction with maleic anhydride.* The unsaturated trimer (1·488 g.) in benzene (5 ml.) was heated with maleic anhydride (2·0 g.) in a sealed tube for 24 hours at 100°. After removal of the benzene and residual maleic anhydride, the adduct was hydrolysed and isolated as a water-insoluble fatty acid. After purification, the product was a pale yellow resin having an equivalent weight of 299. The molecular weight of the dicarboxylic acid would thus be 598, which indicates the reaction of two molecules of trimer with one of maleic anhydride. The acid was soluble in light petroleum and insoluble in water, decolorised potassium permanganate, and reacted with 74 g. of bromine per 100 g. The residual oil (42%) had n_D^{20} 1·5142, and reacted with 74 g. of bromine per 100 g. The acid was converted into the barium salt (Found: Ba, 16·6; *M*, 826·5. Calc.: Ba, 18·5%); *M*, 741).

The unsaturated tetramer (1·9492 g.) was similarly treated with maleic anhydride (4 g.). The resulting carboxylic acid had a molecular weight of 684 (calc. for reaction of two molecules of tetramer with one of maleic anhydride, 776). The acid reacted with 40·5 g. bromine per 100 g. The residual oil (52%) had n_D^{20} 1·5270, reacted with 108·5 g. of bromine per 100 g., and gave a barium salt (Found: Ba, 14·0%; *M*, 979·5. Calc.: *M*, 911).

(g) *Sulphonation.* (i) *Unsaturated* cyclo*hexene trimer.* This trimer (5·13 g.) was treated with an excess of dioxan–sulphur trioxide complex in ethylene dichloride at 0°. Only a trace of sulphur dioxide was produced, and the product, after dilution and removal of neutral oils, etc., was neutralized with barium hydroxide. The resulting water-soluble barium salts were separated into three fractions by addition of alcohol to the aqueous solution.

Fraction (1) (3·04 g.) was insoluble in 50% alcohol, being precipitated as a viscous oil. The barium content (31·0%) was equivalent to 3·3 sulpho-groups per trimer molecule. It formed uncrystallisable dark brown resins, reduced potassium permanganate, and decolorised bromine water although only a trace of barium sulphate was precipitated. The derived benzylthiuronium derivative was a brown oil which could not be crystallised. The sulphonic acids did not contain any sulphated hydroxy-compounds.

Fraction (2) (1·55 g.) was soluble in 50% alcohol but insoluble in 90% alcohol. The barium content (29·0%) was equivalent to 3·0 sulpho-groups per trimer molecule. The properties were similar to those of fraction (1), but the product was lighter in colour and contained a small percentage of sulphated hydroxy-sulphonic acids.

Fraction (3) (1·32 g.) remained in solution after addition of excess of alcohol to the aqueous solution. The barium content was 24·46%. Hydrolysis showed that these salts were principally sulphated hydroxy-sulphonates containing one sulphated hydroxy-sulphonic acid group per trimer molecule. They were unsaturated and gave oily benzylthiuronium derivatives.

(ii) *Unsaturated* cyclo*hexene tetramer.* This tetramer fraction (3·23 g.) was sulphonated by means of the dioxan–sulphur trioxide complex in a similar manner to the trimer, the barium salts of the resulting sulphonic acids being separated by addition of alcohol to an aqueous solution.

Fraction (1) (1·12 g.), insoluble in 50% alcohol, had a barium content (29·54%) equivalent to four sulpho-groups per tetramer molecule. The properties were similar to those of the corresponding trimer products. Fraction (2) (0·62 g.) had a barium content (28·48%) equivalent to 3·7 sulpho-groups per tetramer molecule. Fraction (3) (0·71 g.) had a barium content of 26·5%. It contained a large proportion of sulphated hydroxy-sulphonic acids, in addition to some polysulphonic acids.

1-*Methyl*cyclo*pentene.*

1-*Methyl*cyclo*pentene Dimer.*—A sample was kindly supplied by Dr. A. E. Bearse, Battelle Memorial Institute, Columbus, Ohio, U.S.A., who prepared it by treating 1-methyl*cyclo*pentene with 87% sulphuric acid at 5° (Bearse and Leonard, U.S.P. 2,419,668). It had b. p. 126—128°/50 mm. d_4^{20} 0·914, n_D^{20} 1·4962, Br no. (I.P. method), 43 g. per 100 g. (substitution, 62 g. of bromine per 100 g.) or (A.S.T.M. method) 111 g. per 100 g. (Calc. : 97·6) (Found : C, 87·2; H, 12·1. Calc. for $C_{12}H_{20}$: C, 87·8; H, 12·2%). After dehydrogenation, the Br no. (A.S.T.M.) was 3·7, indicating that the double bond is present in the *cyclo*hexane and not in the *cyclo*pentane ring.

Hydrogenation.—A solution of the dimer in *cyclo*hexane was hydrogenated for 22 hours at 160°/2500 lbs. per sq. in. The product, treated with sulphuric acid, freed from acid, and distilled, had b. p. 224—229°/752 mm., d_4^{20} 0·8790, n_D^{20} 1·4798, and aniline point 46·0.

Treatment with Sulphuric Acid.—The unsaturated dimer was shaken with an excess of 97% sulphuric acid at 10°, and the acid-insoluble polymers were collected, freed from acid, and distilled; the dimer fraction had b. p. 223—226°/758 mm., d_4^{20} 0·8788, n_D^{20} 1·4774, and aniline point 46·9°. The dimer did not solidify in solid carbon dioxide–alcohol.

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