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

The Formation of a Cyclic Recurring Unit in Free Radical Polymerization[1]

BY C. S. MARVEL AND R. D. VEST

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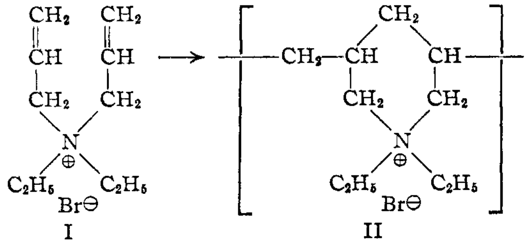
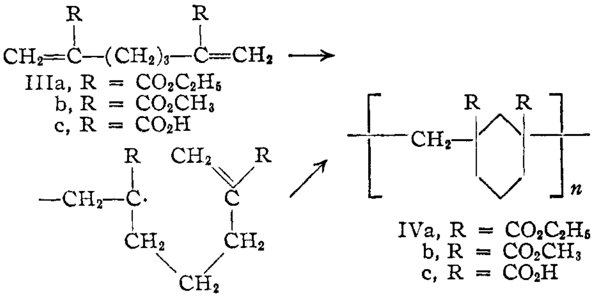
α,α'-Dimethylenepimelic acid and its methyl and ethyl esters have been polymerized in free radical systems to produce soluble polymers which are essentially free of unsaturation. These polymerizations are examples of an alternating intramolecular-intermolecular polymerization reaction.

When non-conjugated diolefins are polymerized under free radical conditions, cross-linked polymers are the expected products.[2] However, Butler[3] has observed that diethyldiallylammonium bromide (I) gives soluble polymers and has explained that this is an "alternating intermolecular–intramolecular" reaction which produces recurring piperidine units II.



I II

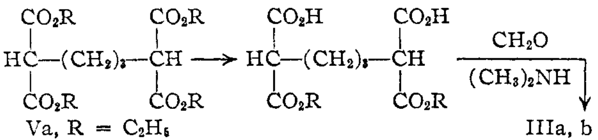
We have now extended this discovery to the case of the formation of a six-membered carbon ring. Three 2,6-disubstituted 1,6-heptadienes (IIIa, b, c) have been prepared and polymerized by free radical initiation. Based on the evidence given in this paper, the structure of these polymers must be cyclic (IVa, b, c).



IIIa, R = $CO_2C_2H_5$
b, R = CO_2CH_3
c, R = CO_2H

IVa, R = $CO_2C_2H_5$
b, R = CO_2CH_3
c, R = CO_2H

The two diesters (IIIa, b) were prepared by the series of reactions



Va, R = C_2H_5
b, R = CH_3

IIIa, b

These diolefins polymerize readily in bulk, solution or in emulsion systems to produce polymers which are readily soluble in such solvents as chloroform or benzene and show no infrared absorption in the carbon–carbon double bond region; thus both olefinic groups must have been involved in the polymerization reaction to produce the cyclic recurring unit. The other alternative would be the formation of a highly cross-linked polymer which would be insoluble.

Occasionally, a small amount of insoluble polymer was obtained from samples of polydiethyl α,α'-dimethylenepimelate, and, furthermore, the polymers produced had an intrinsic viscosity of only 0.1. A careful investigation of the impurities in this monomer led to the isolation of two compounds (VI and IX) which indicates the presence of two monoölefins (VII and VIII). These monoölefins were not completely removed from the major product IIIa by distillation as is borne out by its analysis.

Dimethyl α,α'-dimethylenepimelate (IIIb), a crystalline substance, is easily purified and polymerized to produce soluble polymers having an intrinsic viscosity of 0.73. No data are available for correlating viscosity to molecular weight for polymers of these structures; however, for a linear polymer with related functional groups (polymethyl methacrylate), a viscosity of 0.7 corresponds to a molecular weight of between 200,000 and 300,000.

The ester polymers (IVa and IVb) resemble polymethyl methacrylate while the polymeric acid IVc resembles polymethacrylic acid.

When heated to temperatures above 250°, the polymeric ethyl ester loses ethylene and carbon dioxide and forms a glassy material which is soluble in organic solvents. The infrared spectrum of this product indicates that it is a mixture containing some anhydride groups.

Two polymers (IVa, IVc) have been partially dehydrogenated with potassium perchlorate. The spectral data indicate the presence of aromatic rings in the dehydrogenated material which is in direct support of the idea that the polymerization reaction proceeds by a cyclic mechanism. The infrared spectrum of the dehydrogenated polymer indicates the presence of aromatic double bonds (1620, 1595, 1500 cm.$^{-1}$), and the ultraviolet spectrum has an absorption maximum at 255 mμ and strong generalized absorptions below 240 mμ.

Experimental

Tetraethyl 1,1,5,5-Pentanetetracarboxylate.—The tetraester was prepared by the method of Bailey and Sorenson.[4] From 303 g. (1.5 moles) of redistilled 1,3-dibromopropane and 2320 g. (14.5 moles) of diethyl malonate was obtained 330 g. (61.5%) of tetraethyl 1,1,5,5-pentanetetracarboxylate, b.p. 160–170° (0.3 mm.), n^{25}_D 1.4409. The literature reports b.p. 259–262° (100 mm.).[5]

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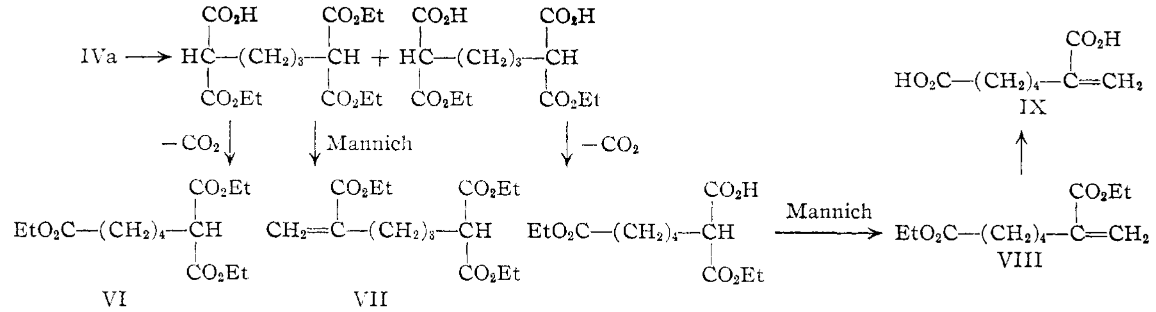
[1] This work was initiated under the synthetic rubber project sponsored by the National Science Foundation and completed under the sponsorship of Contract AF 33(616)-3772 with the Materials Laboratory of Wright Air Development Center, Wright-Patterson Air Force Base, Ohio; Lt. L. E. Coleman, project engineer.

[2] H. Staudinger and W. Heuer, *Ber.*, **67**, 1159 (1934).

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

[4] W. J. Bailey and W. R. Sorenson, *ibid.*, **76**, 5421 (1954).

[5] W. H. Perkin, Jr., *J. Chem. Soc.*, **51**, 242 (1882).



Diethyl α,α'-Dicarboxypimelate.—This semi-hydrolysis was effected by a modified procedure reported[6] for the same reaction on diethyl malonate. To a stirred solution of 39.5 g. (0.6 mole) of potassium hydroxide in 1060 ml. of absolute ethanol was added 106.8 g. (0.3 mole) of tetraethyl 1,1,5,5-pentanetetracarboxylate under anhydrous conditions, and the solution was then heated under reflux for 24 hr. During this time the dipotassium salt precipitated. The ethanol was removed under diminished pressure and the resulting solids dissolved in 650 ml. of distilled water. The alkaline solution was extracted with ether to remove any unhydrolyzed tetraester and then cooled in a continuous extraction apparatus. At −5° the solution was simultaneously extracted with ether and acidified with 50% hydrochloric acid to a *p*H 2. Removal of the ether under diminished pressure at room temperature yielded 97 g. (theor. 91 g.) of a yellow oil, $n^{25}\mathrm{D}$ 1.441. Purification of this unstable oil has not been successful. Infrared analysis[7] indicated a 1:1 ratio of acid: ester groups.

A small sample of this oil was decarboxylated and distilled to yield diethyl pimelate, b.p. 107–119° (1.2–1.5 mm.), $n^{25}\mathrm{D}$ 1.4300 (lit. 112° at 1.0 mm., 1.4305). The distillate was hydrolyzed with 10% aqueous potassium hydroxide and acidified to yield pimelic acid, m.p. and mixed m.p. with known sample 102–104° (lit. 103°). This procedure suggests itself as a good synthetic route to pimelic acid.

Triethyl 1,1,5-Pentanetricarboxylate.—In subsequent work on a larger scale, small amounts of this triester, b.p. 130–140° (1.0 mm.), $n^{19.5}\mathrm{D}$ 1.4405, were isolated from the hydrolysis reaction mixture.

Anal. Calcd. for $C_{14}H_{24}O_6$: C, 58.31; H, 8.39. Found:[8] C, 58.03; H, 8.35.

Diethyl α,α'-Dimethylenepimelate.—This compound was prepared by a modified Mannich[9] reaction. Gaseous dimethylamine was passed into a stirred suspension of 37.9 g. (0.125 mole) of crude diethyl α,α'-dicarboxypimelate in 100 ml. of distilled water maintained at ice-bath temperature. After 30 minutes the reaction mixture was allowed to warm to room temperature and 45.0 g. (0.5 mole) of 37% aqueous formaldehyde was added. The dimethylamine was passed into the solution for 1 additional hr. and the mixture heated under gentle reflux for 8 hr. The product which formed a second layer was removed *via* a separatory funnel and washed with two 10-ml. portions of concentrated hydrochloric acid. The crude yield was 27.0 g. (90%). The major portion of this product, b.p. 81–82° (0.1 mm.), $n^{25.5}\mathrm{D}$ 1.4470, d^{20}_{20} 0.9990, was fractionated several times to yield a product which contained some impurities. The infrared spectrum (smear) indicated conjugated ester (1720 cm.$^{-1}$), acrylate type double bond (1638, 950 cm.$^{-1}$). The ultraviolet spectrum[10] (Eastman spectro Grade cyclohexane) showed an apparent λ_{max} 208 mμ, ϵ_{max} 15,000. The literature reports λ_{max} 208 mμ, ϵ_{max} 8,400 for 2-methylenehexanoic acid and λ_{max} 218 mμ, ϵ_{max} 8,780 for 2-methylhexenoic acid.[11]

Anal. Calcd. for $C_{13}H_{20}O_4$: C, 64.98; H, 8.39. Found: C, 64.52; H, 8.89.

Polydiethyl α,α'-Dimethylenepimelate. Solution.—Five grams of monomer, 200 ml. of absolute ethanol and 50 mg. of benzoyl peroxide were heated under reflux for 7 hr. The polymer was precipitated by pouring the ethanolic solution into distilled water. The white, powdery polymer (4.8 g.) was purified by dissolving in ethanol and precipitating with water twice, m.p. 125–135°. The infrared spectrum showed no unsaturation and the intrinsic viscosity (0.241 g./100 ml. chloroform) was 0.14.

Anal. Calcd. for $C_{13}H_{20}O_4$: C, 64.98; H, 8.39. Found: C, 64.52; H, 8.53.

α,α'-Dimethylenepimelic Acid.—At room temperature, 70.0 g. (0.290 mole) of crude diethyl α,α'-dimethylenepimelate was stirred for 36 hr. with 23.3 g. (0.582 mole) of sodium hydroxide dissolved in 230 ml. of distilled water. After acidification with hydrochloric acid the solution was cooled in an ice-bath to yield 41.7 g. (80.7%) of crude product. The filtrate was saved for subsequent work. Six recrystallizations from water yielded 11.5 g. (22.4%) of pure α,α'-dimethylenepimelic acid, m.p. 105.0–105.8°. The infrared spectrum showed bands for conjugated acid (1694 cm.$^{-1}$) and acrylic acid structure (1630, 965 cm.$^{-1}$).

Anal. Calcd. for $C_9H_{12}O_4$: C, 58.69; H, 6.57. Found: C, 58.50; H, 6.79.

Poly-α,α'-dimethylenepimelic Acid.—Into a three-ounce polymerization bottle were placed 0.50 g. of the acid and 10 ml. of distilled water and the solution warmed on a steam-bath to dissolve the monomer. Nitrogen was then passed through the solution for several minutes to remove air and the solution warmed to redissolve the monomer which had crystallized. To this warm solution was added 1.0 ml. of 1% potassium persulfate solution, the bottle capped and placed in a 60° bath for 17 hr. The polymer, which precipitated during this time, was removed by filtration and purified by dissolving it in dilute base and precipitating with dilute acid. The yield was 0.27 g. (54%) of a product which decomposed at 460°. The polymer could not be obtained completely free of impurities and gave the following analysis: C, 54.70; H, 6.71. The infrared spectrum (Nujol mull) of this polymer showed acid (1712 cm.$^{-1}$) and no unsaturation.

α-Methylenepimelic Acid.—The mother liquors from the above hydrolysis were evaporated to dryness under diminished pressure. To the salt cake thus obtained was added 25 ml. of dry benzene and the whole heated on the steam-bath. The inorganic material was removed by filtration and the filtrate evaporated to dryness under diminished pressure. The residue was dissolved in 100 ml. of distilled water and boiled with 1.0 g. of Darco, filtered and cooled. The white, amorphous solid, m.p. 80–82°, was removed by filtration and recrystallized twice from distilled water; m.p. 83.8–84.2°. The infrared spectrum (Nujol mull) showed conjugated and unconjugated acid (1685–1710 cm.$^{-1}$) and the unsaturation at 1635 cm.$^{-1}$ and 970 cm.$^{-1}$.

Anal. Calcd. for $C_8H_{12}O_4$: C, 55.80; H, 7.03. Found: C, 55.64; H, 7.26.

Tetramethyl 1,1,5,5-Pentanetetracarboxylate.—This compound was prepared by the procedure given above for tetraethyl 1,1,5,5-pentanetetracarboxylate. From 151.5 g. (0.75 mole) of redistilled 1,3-dibromopropane was obtained 155 g. (71%) of the tetramethyl ester, b.p. 165–167° (1.5 mm.), m.p. 44.0–45.0°. Three recrystallizations from low petroleum ether did not change the melting point.

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

(7) The infrared spectra were determined by Mr. James Brader, Mrs. Louise Griffith and S. Portnow. The spectra were obtained from a Perkin-Elmer model 21 spectrophotometer.

(8) The microanalyses were performed by Mr. Jozsef Nemeth, Miss Claire Higham and Mrs. Maria Stingl, University of Illinois; Clark Microanalytical Laboratory, Urbana, Illinois; and Micro-Tech Laboratories, Skokie, Illinois.

(9) C. Mannich and K. Ritsert, *Ber.*, **57**, 1116 (1924).

(10) The ultraviolet spectra were obtained by M. S. Chao and Miss Gerardine Meerman using a Cary model 14m spectrophotometer.

(11) J. Cason and M. J. Kalm, *J. Org. Chem.*, **19**, 1947 (1954).

Anal. Calcd. for $C_{13}H_{20}O_8$: C, 51.31; H, 6.63. Found: C, 51.17; H, 6.60.

Dimethyl α,α'-Dicarboxypimelate.—This compound was prepared by the procedure given above for diethyl α,α'-dicarboxypimelate except that methanol was used as the solvent. From 60.9 g. (0.20 mole) of tetramethyl ester was obtained 56.0 g. (theor. 55.2 g.) of dimethyl α,α'-dicarboxypimelate, m.p. 107–111° dec. Attempts to purify this compound have not been successful. The infrared spectrum of this compound was essentially the same as found for the diethyl analog.

In a manner similar to that used for the diethyl analog, 2.8 g. (0.011 mole) was decarboxylated by heating and hydrolyzed with 10% aqueous sodium hydroxide to yield, on acidification, 1.2 g. (68.5%) of pimelic acid, m.p. 103–104°.

Dimethyl α,α'-Dimethylenepimelate.—The Mannich reaction was carried out on dimethyl α,α'-dicarboxypimelate as described for the diethyl analog above with a slight modification in the workup procedure. The product was extracted from the reaction mixture with low petroleum ether, concentrated and cooled to crystallize the product. From 56.0 g. (0.20 mole) of diester-diacid was obtained 17.3 g. (27%) of dimethyl α,α'-dimethylenepimelate, m.p. 34.0–35.5°. Recrystallization did not change the melting point. The infrared spectrum was essentially the same as that found for the diethyl analog. The yield can probably be significantly increased.

This compound has also been prepared by treating α,α'-dimethylenepimelic acid with diazomethane by standard procedures.[12] The products obtained by both procedures were identical.

Anal. Calcd. for $C_{11}H_{16}O_4$: C, 62.25; H, 7.60. Found: C, 62.33; H, 7.59.

Polydimethyl α,α'-Dimethylenepimelate.—A six-ounce screw-cap polymerization bottle was charged with 4.740 g. of monomer, 8.0 g. of Office of Rubber Reserve soap and 0.5 ml. of a 3% aqueous potassium persulfate solution. The bottle was swept for three minutes with nitrogen, capped, placed in a 50° bath and tumbled for 24 hr. The polymer was precipitated with H_2SO_4–NaCl coagulant and purified by reprecipitation six times in a benzene–methanol system. The yield of polymer was 2.4 g. (64.5% based on unrecovered monomer). The intrinsic viscosity determined in chloroform (0.241 g./100 ml. chloroform) at 25.0° was 0.73 which corresponds to a molecular weight of about 200,000 to 300,000 in a linear polymer system.[13] This polymer was completely soluble in chloroform, benzene and similar organic solvents. No carbon–carbon double bond absorption was observed in the infrared spectrum. This material gives a clear, glassy melt at a temperature of about 300°.

Anal. Calcd. for $(C_{11}H_{16}O_4)_n$: C, 62.25; H, 7.60. Found: C, 62.37; H, 7.46.

Partial Dehydrogenations.—According to the procedure of Patai and Rajbenback,[14] 0.75 g. of polydimethyl α,α'-dimethylenepimelate was heated with 2.25 g. of potassium perchlorate in a sealed, thick-walled Pyrex tube at 380–395° for 16 hr. After the tube had cooled, it was wrapped in a towel and opened. The dark brown solids were transferred to a Soxhlet extractor and extracted with methylene dichloride for 2.5 days. The extracts fluoresced strongly under the influence of ultraviolet light. The infrared spectrum (CH_2Cl_2) of the concentrated extracts showed acid (3610, 3500, 1695–1715 cm.$^{-1}$), ester (1715–1735 cm.$^{-1}$) and unsaturation in the aromatic region (1620, 1595, 1500 cm.$^{-1}$). The ultraviolet spectrum (CH_2Cl_2) was consistent with aromaticity in this product having a λ_{max} at 255 mμ.

A sample of poly-α,α'-dimethylenepimelic acid was treated in a similar manner with comparable results.

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[12] L. F. Fieser, "Experiments in Organic Chemistry," 2nd Ed., D. C. Heath and Co., New York, N. Y., 1941, p. 378.

[13] J. H. Baxendale, S. Bywater and M. G. Evans, *J. Poly. Sci.*, **1**, 237 (1946).

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

URBANA, ILLINOIS

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

The Synthesis of α-Santalene and of *trans*-$\Delta^{11,12}$-Iso-α-santalene

BY E. J. COREY, S. W. CHOW[1] AND R. A. SCHERRER[2]

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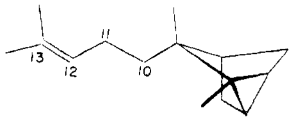
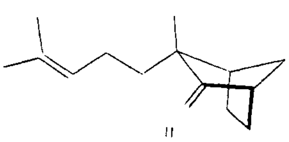
Synthesis of natural α-santalene (I) in six steps and of *trans*-$\Delta^{11,12}$-iso-α-santalene (XV) in nine steps have been carried out starting with (+)-α-bromocamphor.

Among the most noteworthy sesquiterpene hydrocarbons with regard to structure and chemical interest are the two main hydrocarbon components of East Indian sandalwood oil, α-santalene (I) and β-santalene (II). Little is known about the chemistry of these substances beyond the limited number of degradation reactions from which the structures were derived,[3] including the key degradations of α-santalene to teresantalic acid (III) and tricycloekasantalic acid (IV), both of which have been synthesized subsequently.[4,5] An interest in the chemistry of α-santalene, together with the difficulty of obtaining pure material from natural sources and the availability to us of suitable synthetic intermediates from other work in the sesquiterpene field, prompted the investigation of the synthesis of α-santalene which is described herein.



I



II

α-*trans*-π-Dibromo-(+)-camphor (VI), which was prepared directly from α-bromo-(+)-camphor (V) by a modified procedure based on the method of the Takeda workers,[6] was converted to *trans*-π-bromocamphor (VII) by treatment with zinc–hydrogen bromide in methylene chloride[7] and thence to (−)-π-bromotricyclene (VIII) *via* the hydrazone derivative by oxidation. The bromide VIII was

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[1] Alfred P. Sloan Foundation Postdoctoral Fellow, 1956–1957.

[2] Allied Chemical and Dye Corp. Fellow, 1955–1957; Alfred P. Sloan Foundation Summer Fellow, 1956.

[3] Reviewed in (Sir) J. Simonsen and D. H. R. Barton, "The Terpenes," Vol. III, 2nd Ed., University Press, Cambridge, 1952, p. 98

[4] Y. Asahina, M. Ishidate and T. Momose, *Ber.*, **68**, 83 (1935).

[5] P. C. Guha and S. C. Battacharyya, *J. Indian Chem. Soc.*, **21**, 271 (1944).

[6] H. Nishimitsu, M. Nishikawa and M. Hagiwara, *Proc. Japan Acad.*, **27**, 285 (1951).

[7] E. J. Corey and R. A. Sneen, THIS JOURNAL, **78**, 6269 (1956).