phosphate (b.p. 46-47°/0.3 mm., n_D^{20} 1.4058, quantitative yield).

Anal: Calcd. for $C_6H_{15}O_4P$: P, 17.0%; Found: P, 17.0%.

The *t*-butyl alcohol was identified as the 3,5-dinitrobenzoate ester (melting point and mixture melting point 139.5–140.0°).

Acknowledgments. The authors wish to thank Dr. W. Nudenberg for his invaluable suggestions and discussions during the course of the work.

CHICAGO, ILL.

[CONTRIBUTION FROM THE PIONEERING RESEARCH DIVISION, TEXTILE FIBERS DEPARTMENT,
E. I. DU PONT DE NEMOURS & CO., INC.]

Intermolecular-Intramolecular Polymerization of 2,6-Diphenylheptadiene-1,6

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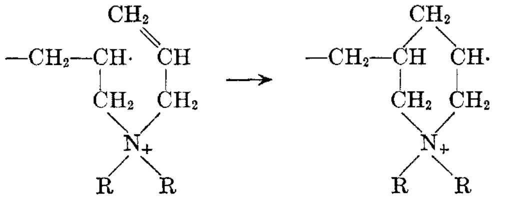
Received December 18, 1959

The synthesis of 2,6-diphenylheptadiene-1,6 from 1,3-dibenzoylpropane was accomplished in good yield utilizing the Wittig reaction. It was polymerized using free radical, cationic, anionic, and Ziegler-type initiation to give in all cases soluble polymers of essentially the same structure with few or no double bonds detectable in the infrared spectrum. This is the first example of a diene on which all known general types of initiation have led to intermolecular-intramolecular polymerization.

In order to explain the solubility of polymers obtained from diallyl quaternary ammonium salts, Butler and Angelo[1] proposed an intermolecular-intramolecular propagation mechanism in the free radical polymerization, the intramolecular step producing piperidinium units:

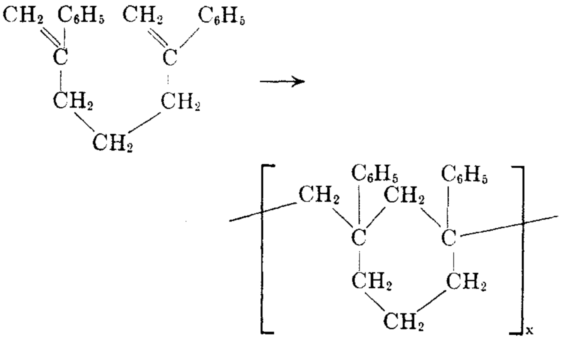


(1)

Strong evidence for this mode of polymerization is seen in Marvel's results on the polymerizations of 2,6-dicarboxyheptadiene-1,6 and its esters.[2] High molecular weight soluble polymers with no detectable residual unsaturation were obtained. For example, 2,6-dicarbomethoxyheptadiene-1,6 was polymerized using free radical initiation in an emulsion system to give polymer with an intrinsic viscosity in chloroform of 0.73. It was soluble in a number of organic solvents and showed no carbon-carbon double bonds in the infrared spectrum.

A number of examples of intermolecular-intramolecular polymerization have since appeared. These include, in addition to the free radical variety discussed above, Ziegler-type,[3] anionic,[4] and cationic.[5]

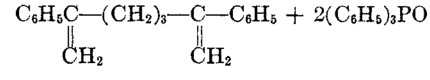
This paper reports the preparation of 2,6-diphenylheptadiene-1,6 and its polymerization. All the known general types of initiation mentioned above were employed and resulted only in intermolecular-intramolecular polymerization. To our knowledge, this is the first example of a diene which responds in this fashion:



(2)

DISCUSSION

Monomer synthesis. A powerful synthetic tool for unequivocal olefin formation is the Wittig reaction[6] in which a carbonyl group is converted to an ethylenic group via the action of a triphenylphosphinemethylene. *The ethylenic linkage is reported to form only at the point* where the carbonyl group existed originally. This reaction was conducted by us on 1,3-dibenzoylpropane to give 2,6-diphenylheptadiene-1,6 in 65% yield based on starting diketone:



$$2(C_6H_5)_3PCH_2 + C_6H_5CO(CH_2)_3COC_6H_5 \longrightarrow C_6H_5\underset{CH_2}{\underset{\|}{C}}-(CH_2)_3-\underset{CH_2}{\underset{\|}{C}}-C_6H_5 + 2(C_6H_5)_3PO \quad (3)$$

The structure of the diene was confirmed by oxidation to the starting dione in 76% yield using sodium periodate and osmium tetroxide.[7]

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(1) G. B. Butler and R. J. Angelo, *J. Am. Chem. Soc.*, **79**, 3128 (1957).

(2) C. S. Marvel and R. D. Vest, *J. Am. Chem. Soc.*, **79**, 5771 (1957).

(3) C. S. Marvel and J. K. Stille, *J. Am. Chem. Soc.*, **80**, 1740 (1958).

(4) J. F. Jones, *J. Polymer Sci.*, **33**, 7 (1958).

(5) J. F. Jones, *J. Polymer Sci.*, **33**, 513 (1958).

(6) G. Wittig and E. Schollkopf, *Ber.*, **87**, 1308 (1954).

(7) R. Pappo, D. S. Allen, R. V. Lemieux, and W. S. Johnson, *J. Org. Chem.*, **21**, 478 (1956).

In general, the reaction was conducted in two steps. The ylide was prepared by adding a solution of phenyllithium or butyllithium in diethyl ether to a suspension of triphenylmethylphosphonium bromide in an appropriate medium. This step was followed by the addition of the dione. In the course of a number of synthetic attempts, glycol dimethyl ether (Ansul) was found to give good results as the reaction medium. It served as an excellent solvent for the large concentrations of ylide prepared and permitted a higher reaction temperature than could be obtained by using diethyl ether in conventional equipment.[8]

The main shortcoming in the use of glycol dimethyl ether in the reaction was the problem of separating the triphenylphosphine oxide formed. This was overcome by replacing the solvent with diethyl ether in which triphenylphosphine oxide-lithium bromide complex is insoluble.[6] Use of phenyllithium instead of butyllithium in the ylide-forming step gave better yields of crude diene but added a purification difficulty in the removal of biphenyl by-product probably formed in the preparation of the phenyllithium.

Polymerization. The monomer was polymerized using radical, cationic, anionic and Ziegler-type initiators. In all cases the polymers obtained were soluble in a number of solvents. Infrared spectra were run on polymers representing each mode of polymerization and found to be essentially the same. Only the lower molecular weight polymers (having low polymer melt temperatures[9]) showed a slight absorption in the carbon-carbon double bond region.

Thermal polymerizations without initiator were run at 100° and 180°. Only the latter temperature afforded any appreciable polymer. The reaction was slow and the highest inherent viscosity, ηinh, $\left(\frac{\ln \eta\text{rel.}}{\text{concn.}}\text{ at } 0.5\%\text{ concentration at } 30.0°\right)$ in benzene was 0.23. When cumene hydroperoxide was used as a free radical initiator, polymerization at 100° was slow, five days being required to give a 35% yield of polymer with an inherent viscosity of 0.35 and polymer melt temperature of 265°.

Cationic polymerizations were run in a number of solvents. When boron trifluoride was used as the initiator in hexane or carbon disulfide, the polymers could be prepared either in high conversion and low molecular weight or low conversion and high molecular weight. On the other hand, in methylene chloride, conditions leading both to high and low conversions gave polymers having the same polymer melt temperatures (~250°). Boron trifluoride etherate as initiator led only to very low molecular weight polymers (polymer melt temperatures ~125°).

Polymerization with a Ziegler-type catalyst from aluminum triisobutyl and titanium tetrachloride proceeded slowly, four days being required to give a 71% yield of polymer with a polymer melt temperature of 140°. An increase in the ratio of monomer to catalyst by a factor of about 50 gave a polymer with a somewhat higher molecular weight, the polymer melt temperature rising to 190°.

The best method for obtaining both high conversion and high molecular weight polymer was anionic polymerization. Lithium naphthalene was used as the initiator and tetrahydrofuran as the solvent. In the best case, an 80% yield of polymer with an inherent viscosity in benzene of 0.49 and a polymer melt temperature of 300° was obtained. In an attempt to obtain this result consistently, polymerizations were run using tetrahydrofuran which had been distilled from lithium naphthalene, nitrogen which had been scrubbed with lithium naphthalene in tetrahydrofuran solution, and in one case treating the monomer with Girard's reagent to remove traces of ketonic material. Attempts to raise the molecular weight by increasing the ratio of monomer to initiator failed. In many cases, lithium metal had to be present as well as lithium naphthalene. In some cases the reaction would not proceed unless a large excess of naphthalene were deliberately added.

Polymer properties. All of the polymers prepared were soluble in tetrahydrofuran, chloroform, and benzene. Clear films were cast from these solvents but these and melt-pressed films prepared in the Carver press were all brittle. Brittle fibers could be drawn from the polymer melts. The most interesting feature of the polymer was its excellent thermal stability. Melts could be held at 300° open to the air for at least a minute without any sign of discoloration, gelation, or depolymerization. This is in marked contrast to the noncyclic analog, poly-α-methylstyrene, which readily depolymerizes under these conditions. By extrapolation of inherent viscosities, the limiting polymer melt temperature of the polymer appears to be about 300°. This high value is interesting in that the polymer does not contain any polar groups and presumably results from a stiff chain structure. This was confirmed by the construction of molecular models which showed little capacity for free rotation.

EXPERIMENTAL

1,3-Dibenzoylpropane. This intermediate was prepared following the procedure of Japp and Mitchie.[10] The synthesis is a two-step one involving the reaction of ethyl benzoyl-

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(8) Wittig's preparations use diethyl ether as the solvent in pressure equipment at temperatures around 65°.

(9) The temperature at which a wet streak is left on a hot metal bar on pressing a sample with a spatula. In any homologous series, the melting point increases with molecular weight to a limiting value. In this study, the polymer melt temperature was used as a relative measure of molecular weight (though it is understood that branching would affect such a relationship).

(10) F. R. Japp and A. C. Mitchie, *J. Chem. Soc.*, **79,** 1016 (1901).

acetate and formaldehyde in the presence of piperidine to give diethyl α,α'-dibenzoylglutarate followed by hydrolysis and decarboxylation to give the dione.

Triphenylmethylphosphonium bromide. In a 1-l. 3-necked flask equipped with thermometer, stirrer, and Dry Ice-acetone condenser, 200 g. (0.76 mole) of triphenylphosphine was dissolved in 400 ml. of dry benzene. To the stirred solution held at −5°, 100 g. (1.06 moles) of methyl bromide was added all at once and the mixture was stirred overnight at room temperature. The cake which formed was broken up, filtered, and washed a number of times with benzene. The yield was 257 g. (95%) and the product, which melted at 233.5–234°, was sufficiently pure for further use.

2,6-Diphenylheptadiene-1,6. In a 2-l., 3-necked flask equipped with a stirrer, dropping funnel, condenser, and nitrogen cover, 120.8 g. (0.338 mole) of triphenylmethylphosphonium bromide was dispersed in 500 ml. of dry glycol dimethyl ether. Over a period of $^3/_4$ hr., a solution of 0.369 mole of phenyllithium in diethyl ether was added. Almost all of the solid appeared to go into solution. A solution of 40 g. (0.158 mole) of 1,3-dibenzoylpropane in 200 ml. of dry glycol dimethyl ether was added dropwise over 1 hr. The solution was then refluxed for 20 hr., following which the solvent was removed under vacuum to near dryness. About 700 ml. of dry diethyl ether was added and the precipitate which formed was separated by filtration. Treatment of the precipitated triphenylphosphine oxide–lithium bromide complex with water gave a 94% yield of triphenylphosphine oxide.

The diethyl ether filtrate was evaporated to about 200 ml., washed with water until free of alkali, dried over sodium sulfate, and evaporated to dryness to give 39 g. of a dark yellow oil. After the addition of 0.1 g. of di-*t*-butyl-*p*-cresol, the oil was distilled through a Vigreux column at around 0.1 mm. A small amount of solid forecut identified as biphenyl came over followed by product; yield 25.9 g. (65%).

Carefully distilled monomer is a water-white liquid and has the following properties: b.p. 108°/ca. 0.03 mm., n_D^{25} 1.5801, d_4^{25} 0.998.

Anal. Calcd. for $C_{19}H_{20}$: C, 91.9; H, 8.1. Found: C, 91.8; H, 7.8.

Oxidation of 2,6-diphenylheptadiene-1,6. The method used was essentially that of Pappo, *et al.*[7] A mixture of diethyl ether and water containing 0.62 g. (0.0025 mole) of diene, approximately 0.1 g. osmium tetroxide, and excess sodium metaperiodate was stirred for 3 days. The ether layer was dried over sodium sulfate and the black osmium-containing material was removed from the ether solution by passage through an alumina column. Ether and chloroform were used as eluants. Evaporation gave 0.48 g. (76%) of dione, m.p. 64.5–66.5° (lit.,[10] m.p. 67°). A mixed melting point with known dione showed no depression. The dioxime was prepared, m.p. 162–164° (lit.,[11] m.p. 165–166°). A mixed melting point with the dioxime of the known dione showed no depression.

Polymerization. Polymerization procedures typical of the different types of initiation follow below.

Thermal. One milliliter of monomer was sealed off under nitrogen in a 5-ml. test tube and kept in refluxing *o*-dichlorobenzene for 4 days. The gelled, clear product was dissolved in chloroform and precipitated by pouring the solution into methanol; yield 41%, PMT[9] 280°, ηinh (benzene) 0.23.

Anal. Calcd. for $C_{19}H_{20}$: C, 91.9; H, 8.1. Found: C, 91.5; H, 8.0.

Free radical initiation. One milliliter of monomer containing approximately 40 mg. of cumene hydroperoxide was sealed off under nitrogen in a 5-ml. test tube and kept in boiling water for 5 days. The product was precipitated twice from chloroform into methanol. Yield 36%, PMT 265°, ηinh (benzene) 0.35.

Cationic. In a 50-ml. flask equipped with a stirrer, nitrogen cover, and stopper, boron trifluoride gas was introduced over a solution of 1 ml. of monomer in 5 ml. of methylene chloride maintained at Dry Ice-acetone temperature. An almost immediate viscosity increase occurred. Precipitation with methanol gave a 94% yield of polymer with PMT 255° and ηinh 0.19.

Anionic. In a nitrogen blanketed 50-ml. flask equipped with stirrer and stopper, a small flattened piece of lithium metal was stirred with 5 mg. of naphthalene in 10 ml. of tetrahydrofuran until a faint green color began to appear. At this point, one ml. of monomer was introduced. The color promptly discharged and after a few seconds turned red. The polymer was precipitated into methanol; yield 80%, PMT 300°, ηinh 0.49.

Ziegler-Type. In a 50-ml. flask equipped with a magnetic stirrer, 0.6 ml. titanium tetrachloride ($0.001M$ in Decalin[12] decahydronaphthalene solvent) was dissolved in 6 ml. of Decalin under a nitrogen blanket. One milliliter of $0.001M$ aluminum triisobutyl in Decalin was added with stirring to give an immediate brown-black precipitate. After 10 min., 1.5 ml. of monomer was added. The closed flask was stirred for 4 days and the contents precipitated into ethanol; yield 71%, PMT ~140°.

Acknowledgment. The author is indebted to Dr. R. Zbinden for interpretation of the infrared spectra.

WILMINGTON, DEL.

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[11] M. Milone and G. Venturello, *Gazz. chim. ital.*, **66**, 808 (1936).

[12] Registered du Pont trade-mark.