and with the optically pure amine (*vide infra*), 3300–3400 cm.$^{-1}$ (OH, NH), no carbonyl band, $[\alpha]_D^{23}$ −20.0° (ethanol, *c*, 2.48, 53.5% active). The total yield of amine was 30%; lit.[21,26] m.p. for halostachine, 43–45°, $[\alpha]_D$ −47.03° (no solvent given).

Resolution of (±)-*halostachine.* A solution of 2.3 g. of (±)-halostachine in acetone was added to an acetone solution containing 3.48 g. of (+)-10-camphorsulfonic acid (total volume = 60 cc.). On addition of ether, 3.64 g. of crystalline salt was obtained, m.p. 109–112°, $[\alpha]_D^{23}$ +28.21° (acetone, *c*, 1.74). Three recrystallizations from acetone-ether gave 0.65 g. of pure salt, m.p. 132–134°, $[\alpha]_D^{23}$ +49.41°.

The amine (IX) was obtained from the salt by passage over ethyl acetate-washed Merck alumina using chloroform as solvent and 10% ethanol-chloroform as eluent. From 650 mg. of salt 64.2 mg. of pure amine, $[\alpha]_D^{25}$ +37.43° (ethanol, *c*, 2.37), was obtained. R. D. (Fig. 5) in ethanol: $[\alpha]_{650}$ 30.21°, $[\alpha]_{589}$ 37.43°, $[\alpha]_{314}$ 172°, $[\alpha]_{306}$ 176°, $[\alpha]_{295}$ 203°, $[\alpha]_{292}$ 193°, $[\alpha]_{288}$ 219°, $[\alpha]_{280}$ 182°, $[\alpha]_{276}$ 187°, $[\alpha]_{271}$ 41°. A = +18.0. A total of 151 mg. (74%) of the base was recovered from the salt.

The hydrochloride of IX melted at 108–111°, $[\alpha]_D^{25}$ +53.20° (water, *c*, 0.750): lit.[26] m.p. 113–114°, $[\alpha]_D$ +52.46°. R. D. (Fig. 4) in ethanol (*c*, 1.57): $[\alpha]_{650}$ 48.6°, $[\alpha]_{589}$ 59.1°, $[\alpha]_{292}$ 362°, $[\alpha]_{290}$ 346°, $[\alpha]_{284}$ 392° (sh.), $[\alpha]_{274}$ 447°, $[\alpha]_{272}$ 411°. A = +34.9.

Acknowledgment. The author is grateful to Dr. A. W. Ingersoll, Dr. G. D. Wessinger of Sterling-Winthrop, and Dr. Edwin Shepard of Eli Lilly and Co. for samples of some of the materials used in this study.

DURHAM, N. H.

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

Intramolecular-Intermolecular Polymerizations of Some Phenyl Substituted Nonconjugated Diolefins[1]

C. S. MARVEL AND E. J. GALL

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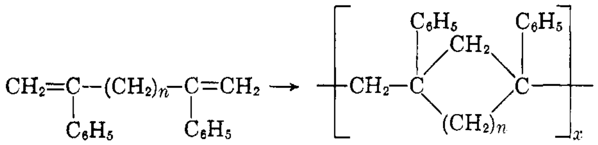
The three hydrocarbons 2,5-diphenylhexadiene-1,5, 2,6-diphenylheptadiene-1,6 and 2,7-diphenyloctadiene-1,7 have been synthesized and polymerized to yield polymers with cyclic recurring units. The evidence indicates that five- and seven-membered rings form less readily than does the six-membered ring in such polymerization reactions.

The work reported here was undertaken to determine whether phenyl substituted nonconjugated diolefins of the type shown in formula I would undergo the intramolecular-intermolecular polymerization reaction which has been successfully applied in a number of instances.[2] While the work was in progress, we learned of the work of Field,[3] who has found that the heptadiene derivative (Ib) readily yields a polymer with a cyclic recurring unit (IIb) by all standard types of initiation. We have confirmed his experience.



Ia. *n* = 2
Ib. *n* = 3
Ic. *n* = 4

IIa. *n* = 2
IIb. *n* = 3
IIc. *n* = 4

The two homologous dienes (Ia and Ic) have been synthesized from the corresponding diketones by application of the Wittig reaction.[3,4] They polymerize to yield soluble, powdery solids which are rather low melting and have low inherent viscosities. These polymers show very little absorption in the infrared in the carbon-carbon double bond region. It seems obvious that these are low molecular weight polymers of the cyclic structures expected (IIa and IIc). It is quite evident however, that there is less tendency to yield five-or seven-membered recurring units than is the case for six-membered recurring units.

EXPERIMENTAL

Melting points are uncorrected.

Monomers: 2,6-Diphenylheptadiene-1,6 (Ib). This monomer was prepared according to the procedure reported by Field[3] and previously reported by us.[5]

2,7-Diphenyloctadiene-1,7 (Ic). 1,4-Dibenzoylbutane was prepared according to the procedure reported by Fuson and Walker.[6]

The conversion of 1,4-dibenzoylbutane to 2,7-diphenyloctadiene-1,7 (Ic) was similar to that described earlier for the preparation of 2,6-diphenylheptadiene-1,6 (Ib). Phenyllithium was prepared in the usual way from 86.4 g. (0.55 mole) of bromobenzene and 9.7 g. (1.4 g.-atoms) of lithium metal in dry diethyl ether in 94.5% yield. A solution of 0.455 mole of phenyl lithium was added to a slurry of 146 g.

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[1] This work was carried out under the sponsorship of Contract AF-33(616)-5486 with the Materials Laboratory of Wright Air Development Center, Wright-Patterson Air Force Base, Ohio. This paper may be reproduced for any purpose of the United States Government.

[2] G. B. Butler and R. J. Angelo, *J. Am. Chem. Soc.*, **79**, 3128 (1957); C. S. Marvel and R. D. Vest, *J. Am. Chem. Soc.*, **79**, 5771 (1957); **81**, 984 (1959); C. S. Marvel and J. K. Stille, *J. Am. Chem. Soc.*, **80**, 1740 (1958); J. F. Jones, *J. Poly. Sci.*, **33**, 15 (1958) and others.

[3] N. D. Field, *J. Org. Chem.*, **25**, 1006(1960).

[4] G. Wittig and U. Schöllkopf, *Ber.*, **87**, 1318 (1954).

[5] C. S. Marvel and E. J. Gall, *J. Org. Chem.*, **24**, 1494 (1959).

[6] R. C. Fuson and J. T. Walker, *Org. Syntheses*, **Coll. Vol. II**, 169 (1943).

(0.414 mole) of methyltriphenylphosphonium bromide in 600 ml. of dry 1,2-dimethoxyethane. To the resulting yellow-brown solution was added a solution of 1,4-dibenzoylbutane (50 g.; 0.188 mole) in 450 ml. of dry 1,2-dimethoxyethane, and the mixture was stirred and heated under gentle reflux for 20 hr. After the usual work-up, the product isolated was a yellow-red colored solid. This solid was extracted with hot *n*-pentane, the insoluble material was isolated by filtration, and the pentane filtrate was evaporated to dryness. The yellow solid was recrystallized twice from ethanol to give 34.2 g. (71%) of a white, crystalline solid (shiny plates), m.p. 47.5–48.5°. The infrared spectrum (10% in chloroform) showed a small amount of absorption at 1685 cm.$^{-1}$, indicating a small amount of ketonic impurity. Consequently, the solid product was treated with Girard's T reagent, and recrystallized twice more from methanol. The crystalline material purified in this manner melted at 51.0–52.0°. The infrared spectrum[7] (10% in carbon tetrachloride) showed the following important absorption maxima: 700 cm.$^{-1}$ (C_6H_5—); 895 cm.$^{-1}$ ($CR_1R_2{=}CH_2$); 1025 cm.$^{-1}$ (C_6H_5—); 1625 cm.$^{-1}$ (C_6H_5— conjugated $>C{=}C<$); 1800 cm.$^{-1}$ (overtone of 895 cm.$^{-1}$). The NMR spectrum[8] (20% in carbon tetrachloride) was consistent with the structure of the expected diene.

Anal.[9] Calcd. for $C_{20}H_{22}$: C, 91.55; H, 8.45. Found: C, 91.19; H, 8.82.

2,5-Diphenylhexadiene-1,5 (Ia). 1,2-Dibenzoylethane was prepared according to a procedure reported by Weygand and Meusel.[10]

Phenyllithium was prepared in the usual manner. From 70.7 g. (0.45 mole) of bromobenzene and 8.3 g. (1.2 g.-atoms) of lithium metal, there was obtained 320 ml. of 1.24*M* ethereal solution.

In a 2-l., three necked, round bottomed flask fitted with stirrer, dropping funnel, condenser, and nitrogen inlet tube was placed a slurry of 120.8 g. (0.338 mole) of methyltriphenylphosphonium bromide in 500 ml. of dry 1,2-dimethoxyethane. Over a period of about 45 min. a solution of 0.372 mole of phenyllithium in dry diethyl ether was added with stirring under nitrogen. As a considerable amount of the salt appeared not to have undergone reaction, the mixture was stirred and heated under gentle reflux overnight. A solution of 37.6 g. (0.158 mole) of 1,2-dibenzoylethane in 300 ml. of dry 1,2-dimethoxyethane was then added dropwise with stirring over a period of about 40 min. After stirring and heating under gentle reflux for an additional 20 hr., the solvents were removed to near dryness by distillation, and 1000 ml. of *n*-pentane was added to the oily red residue. The mixture was thoroughly shaken, the pentane solution was decanted, washed thoroughly with water, and dried over anhydrous sodium sulfate. The solvent was removed from the dried solution, leaving 12.0 g. of a mixture of red-colored liquid and yellow solid. Approximately 1000 ml. of water was added to the residue remaining after extraction with pentane, and the resulting aqueous solution was extracted three times with pentane. This pentane solution was treated as described above, and, after the solvent had been removed, there was obtained 2.7 g. of a mixture of red-colored liquid and yellow solid.

The two mixtures were combined, 100 ml. of dry *n*-pentane was added, and the solution obtained was purified by chromatography on a column prepared from 270 g. of silicic acid (B and A Reagent, Code 1169). The solid obtained was recrystallized three times from methanol to give 2.77 g. (7.9%) of a white, crystalline solid (shiny plates), m.p. 51.0–51.8°. The infrared spectrum (10% in carbon tetrachloride) showed the following important absorption maxima: 895 cm.$^{-1}$ ($CR_1R_2{=}CH_2$); 1495 cm.$^{-1}$, 1570 cm.$^{-1}$, 1600 cm.$^{-1}$ (C_6H_5—); 1625 cm.$^{-1}$ (C_6H_5— -conjugated $>C{=}C<$); and 1795 cm.$^{-1}$ (overtone of 895 cm.$^{-1}$). There was no infrared absorption in the region 1675–1750 cm.$^{-1}$. The NMR spectrum was consistent with the structure of the expected diene.

Anal. Calcd. for $C_{18}H_{18}$: C, 92.26; H, 7.74. Found: C, 92.08; H, 7.96.

Polymers. Polymer melting points were obtained by the capillary tube method. The lower temperature given is that at which the polymer begins to soften. The higher temperature is that at which the polymer is a clear, flowing liquid. Yields are based on the amount of monomer allowed to react. Inherent viscosities were obtained in reagent grade benzene solution at concentrations of *ca.* 0.25 g. of polymer per 100 ml. of solution. The amounts of residual unsaturation in the polymers were roughly determined by comparing the intensities of the absorption maxima at 895–900 cm.$^{-1}$ in the polymer and monomer infrared spectra, both measured in solution at the same concentrations. The spectra of all the polymers of each monomer were essentially alike. No attempts were made at quantitative infrared analysis.

Polymers of 2,6-diphenylheptadiene-1,6. (1) *Cationic initiation:boron trifluoride.* A solution of monomer (1.0 ml.) in 10 ml. of methylene chloride was placed in a 50-ml. flask equipped with a stirrer and gas inlet tube, and protected from moisture by a calcium chloride drying tube. The flask was cooled in a Dry Ice–acetone bath while the system was flushed well with nitrogen. While the solution was stirred, boron trifluoride gas was slowly bubbled in for about 2 min. The mixture under nitrogen was stirred at the cold temperature for 1 hr. more and was then slowly poured into methanol. The white solid obtained was reprecipitated twice more from benzene into methanol to give 0.67 g. (67%) of a white, amorphous solid, m.p. 240–270°, $[\eta]_{\text{inherent}} = 0.145$. The presence of a small amount of residual unsaturation (3–5%) was shown by infrared absorption at 900 cm.$^{-1}$. There was no absorption at 1625 cm.$^{-1}$.

Anal. Calcd. for $(C_{19}H_{20})_x$: C, 91.88; H, 8.12. Found: C, 91.55; H, 8.37.

(2) *Cationic initiation:titanium tetrachloride.* In the dry box, in an atmosphere of nitrogen, a small amount of titanium chloride (0.12 g.; 0.00063 mole) was dissolved in 3 ml. of anhydrous, purified *n*-heptane, contained in a 2-ounce bottle. The monomer (5.0 ml.) was added to this solution, and the mixture was thoroughly shaken. An almost immediate reaction took place, as heat was liberated, the mixture turned dark brown and became very viscous. After the stoppered bottle had stood at room temperature for 78 hr., 30 ml. of methanol was added to precipitate the polymer and decompose the catalyst. The solid obtained was reprecipitated from benzene into methanol to give 2.6 g. (52%) of a powdery solid, m.p. 115–130°; $[\eta]_{\text{inherent}} = 0.051$. Infrared analysis indicated a small amount of residual unsaturation; approximately 5–10% of that of the monomer.

(3) *Anionic initiation:phenyl lithium.* The diene (2.0 g.) was dissolved in 1,2-dimethoxyethane (6.0 g.) in a 2-ounce bottle. The solution was flushed well with dry nitrogen, and the bottle was stoppered with a serum cap. While the solution was cooled in powdered Dry Ice (−40° to −50°), a solution of phenyllithium in diethyl ether (1 ml. of 0.99*N* solution; 0.99 mmole) was added by means of a hypodermic syringe, and, after thorough shaking, the mixture was cooled for an additional 3.5 hr. At the end of this time, there

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(7) The infrared spectra were obtained from a Perkin-Elmer model 21 spectrophotometer by Mr. P. E. McMahon, Mrs. M. Verkade, Miss C. Luebke, Mr. R. Johnson, and Mr. W. Dalton, University of Illinois.

(8) The NMR spectra were obtained from a Varian 4300-B spectrometer by Mr. B. Shoulders and Mr. O. Norton, University of Illinois.

(9) The microanalyses were performed by Mr. J. Nemeth, Mrs. F. Ju, Miss C. Higham, Miss J. Liu, and Mrs. A. S. Bay, University of Illinois.

(10) C. Weygand and W. Meusel, *Ber.*, **76**, 498 (1943).

was no apparent change in viscosity of the solution. After standing at room temperature for 18 hr., however, the entire mixture had solidified. Methanol (100 ml.) was added, and the white solid (1.9 g.) was isolated by filtration on a Büchner funnel. This solid was completely dissolved in 40 ml. of benzene, and was reprecipitated by filtration into 400 ml. of methanol. There was obtained 1.7 g. (85%) of a white, powdery solid, m.p. 275–290°; $[\eta]_{\text{inherent}} = 0.26$. Residual unsaturation: 5–10%.

(4) *Free radical initiation:cumene hydroperoxide.* The monomer (1.0 ml.) containing approximately 40 mg. of cumene hydroperoxide was sealed off under nitrogen in a small test tube, and was kept in boiling water for 5 days. The polymer obtained was an opaque, nonflowing plastic, which was, however, soft, not brittle, and could easily be scratched. The softening point of this plastic material, taken on a hot stage, was 85°. It was completely soluble in benzene; precipitation into methanol gave 0.56 g. (56%) of a white powder, m.p. 240–270°; $[\eta]_{\text{inherent}} = 0.128$. Residual unsaturation: approximately 3%.

(5) *Thermal polymerization.* The monomer (1.0 ml.) was sealed under nitrogen in a small test tube, and was kept in *o*-dichlorobenzene, heated to its reflux temperature, for 5 days. The polymer obtained was a clear, nonflowing plastic, which, however, was soft and could easily be scratched. Its softening point, taken on a hot stage, was 90°. This plastic solid was completely dissolved in benzene, and was precipitated into methanol to give 0.54 g. (54%) of a white powdery solid, m.p. 260–290°; $[\eta]_{\text{inherent}} = 0.154$. Residual unsaturation: approximately 3%.

(6) *Ziegler-type polymerization.* The catalyst was prepared in a dry box in an atmosphere of nitrogen by adding titanium tetrachloride (0.12 g.; 0.00063 mole) to a solution of aluminum triisobutyl (0.1 g.; 0.0005 mole) in dry *n*-heptane (2.05 g.). The monomer (5.0 g.) was added, and the mixture was allowed to stand under nitrogen in a stoppered bottle at room temperature for 72 hr. After precipitation into methanol, there was obtained 2.79 g. (56%) of a white powdery solid, m.p. 185–200°, $[\eta]_{\text{inherent}} = 0.041$. Residual unsaturation: 5–10%.

Polymers of 2,7-diphenyloctadiene-1,7. (1) *Cationic initiation:boron trifluoride.* The procedure used was the same as that described above for the boron trifluoride–initiated polymerization of 2,6-diphenylheptadiene-1,6. From 1.0 g. of monomer there was obtained 0.06 g. (6%) of solid polymer after two precipitations from benzene into methanol. Polymer m.p. 115–150°; no residual unsaturation (no infrared absorption at 900 or 1625 cm.$^{-1}$); $[\eta]_{\text{inherent}} = 0.021$.

Anal. Calcd. for $(C_{20}H_{22})_x$: C, 91.55; H, 8.45. Found: C, 91.10; H, 8.51.

(2) *Cationic initiation titanium tetrachloride.* Under conditions like those described above for the titanium tetrachloride–initiated polymerization of 2,6-diphenylheptadiene-1,6, this monomer (1.5 g.) was allowed to react with the catalyst (0.12 g.; 0.07 ml.) in 5.5 ml. of purified *n*-heptane for 40 hr. at room temperature. At the end of this time, the reaction was quenched by the addition of 10 ml. of methanol. There was obtained an oily, viscous liquid, insoluble in the solvent. The solvent was carefully decanted, the oil was dissolved completely in benzene, and precipitated into methanol to give 0.70 g. (47%) of a tan-colored powder, m.p. 87–128°; $[\eta]_{\text{inherent}} = 0.039$. Residual unsaturation: approximately 2–5%.

(3) *Ziegler-type polymerization.* The catalyst was prepared as described above. From 2.0 g. of monomer there was obtained 1.5 g. of a white, powdery solid, m.p. 95–157°; $[\eta]_{\text{inherent}} = 0.040$. This polymer possessed no residual unsaturation.

Polymers of 2,5-diphenylhexadiene-1,5. (1) *Cationic initiation:boron trifluoride.* The procedure used was the same as that described above for the boron trifluoride–initiated polymerization of 2,6-diphenylheptadiene-1,6. From 0.4 g. of monomer there was obtained 0.33 g. (83%) of a white powdery solid, m.p. 185–210°; $[\eta]_{\text{inherent}} = 0.083$, after three precipitations from benzene into methanol. Residual unsaturation: 5–10%.

Anal. Calcd. for $(C_{18}H_{18})_x$: C, 92.26; H, 7.74. Found: C, 91.35; H, 7.41.

(2) *Free radical initiation:cumene hydroperoxide.* The monomer (0.50 g.) containing approximately 25 mg. of cumene hydroperoxide was sealed off under nitrogen in a small test tube and was kept in boiling water for 5 days. The tube was then opened, and the contents were poured into 100 ml. of methanol. The white, insoluble solid was isolated and reprecipitated from benzene into methanol to give a very small amount (11 mg.) of white, powdery solid, m.p. 150–170°. The amount isolated was not sufficient for a viscosity measurement. Residual unsaturation: <5%.

(3) *Ziegler-type polymerization.* The catalyst was again prepared by using aluminum triisobutyl and titanium tetrachloride in a mole ratio of 0.8. From 0.5 g. of monomer there was obtained 0.29 g. (58%) of a white, powdery solid, m.p. 157–177°; $[\eta]_{\text{inherent}} = 0.072$. Residual unsaturation: 3–5%.

URBANA, ILL.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF SOUTH CAROLINA]

The Reaction of Free Radicals with Non-benzenoid Aromatic Hydrocarbons. II. 6-Alkylfulvenes and Benzofulvenes

JOHN L. KICE[1] AND FATEMEH TAYMOORIAN

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Kinetic studies of the reactivity of a series of 6,6-dialkylfulvenes and benzofulvenes toward free radicals have provided fairly definite evidence that these substances like their phenyl substituted counterparts undergo radical attack at one of the ring positions and not at the external 6-position. The experimental evidence seems to favor the 2-position as the site of radical attack.

The reactivity of various phenyl substituted fulvenes and benzofulvenes toward free radicals and the site of radical attack on these molecules were the subjects of a previous paper.[2] That study

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(2) J. L. Kice and F. M. Parham, *J. Am. Chem. Soc.*, **80**, 3792 (1958).