Linear Polymers from Triene Monomers by the Cyclopolymerization Mechanism. VIII. Nonconjugated Chromophoric Interactions Related to Cyclopolymerization

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Three series of compounds which are derivatives of (1) butadiene, (2) styrene, and (3) methacrylic acid have been studied spectrophotometrically in the region of the ultraviolet spectrum extending from 190 to 270 mμ. The butadiene derivatives studied were the *cis* and *trans* isomers of 1,3,8-nonatriene and 1,3,7-octatriene. The ultraviolet absorption maxima for these compounds were shifted bathochromically from the position calculated by Woodward's rule. The styrene derivatives studied were 2-phenyl-1-hexene (I), 2-phenyl-1,5-hexadiene (II), and 2,5-diphenyl-1,5-hexadiene (III). In a polar solvent the absorption intensities increased in the order I < II < III. The compounds studied in the methacrylate series were the ethyl, allyl, and methallyl esters of methacrylic acid and finally methacrylic anhydride. The anhydride exhibits a band which is shifted bathochromically 5 mμ from those of the esters. These data are taken as evidence for unconjugated interactions of the 1,6- and possibly the 1,5-ethylenic bonds in the excited state. Such interactions account at least partially for the tendency of certain 1,5- and 1,6-dienes to undergo polymerization by the intra–intermolecular mechanism leading to linear saturated polymers. The *trans* isomer of 1,3,8-nonatriene was polymerized with a Ziegler-type initiator to yield a soluble polymer. The infrared spectrum of this polymer was compatible with the structure which would be expected to result from cumulative 1,2- and 1,4-additions during the propagation steps of the polymerization.

Cyclopolymerization or intra–intermolecular polymerization is a phenomenon observed with certain 1,5- and 1,6-dienes by which a polymer is formed having cyclic recurring units. Recent summaries[1,2] of work in this area include numerous references. In an effort to account for the unique tendency of the diene systems under consideration to cyclopolymerize, it has been proposed that a homoconjugative interaction may occur between the unconjugated ethylenic bonds. It does not seem unlikely that such a phenomenon would have a stabilizing influence on the excited state of the molecule, thus providing an energetically favorable path from diene to cyclic product. This subject will be developed further and evidence to support such an interaction will be presented.

For many years it was believed a fundamental principle of ultraviolet spectroscopy that chromophores separated by two or more single bonds were additive in their absorption of light,[3] although some notable exceptions to this principle have been published.[4] Attempts to interpret the nonadditive ultraviolet absorption of certain chromophoric systems gave rise to two schools of thought. Ingold, Shoppee, and Parekh[5,6] offered the first interpretation, an interspacial interaction of the olefinic bonds in 1,5-dienes, even though it was based largely on chemical rather than spectral observations. A second interpretation came about as a result of X-ray and ultraviolet spectral studies on the same compounds.[7,8] It was found that the X-ray pattern was incompatible with a *cis* configuration in the crystalline state, and, on this basis, it was concluded that Ingold's hypothesis was incorrect. Instead, all the data were interpreted in terms of a hyperconjugative effect involving the entire carbon framework of the molecule. In more recent years, however, there has been a growing tendency for theoreticians to favor the interspacial resonance interpretation. A number of systems have been found which exhibit chemical and physical properties indicative of such a phenomenon.[9,10]

A systematic investigation of π-bond interactions and the attending chemical consequences in 1,6-dienoid systems has never been undertaken, although a number of instances where data are suggestive of such a phenomenon has been pointed out.[2] Aside from the many cyclic polymers which have been characterized there is one piece of physical evidence which gives direct support to the postulated interactions of 1,6-dienes. Mikulasova and Hvirik[11] found the total activation energy for the polymerization of diallyldimethylsilane to be 9 kcal. per mole per double bond lower than for allyltrimethylsilane. This represented a decrease in the over-all activation energy of some 30%. It has been shown by Field[12] that the second double bond of 2,6-diphenyl-1,6-heptadiene reacts many times more rapidly with either a free radical, a carbonium ion, or a carbanion generated at the site of the first double bond than the double bond of a neighboring molecule. Thus, he was able to obtain a high polymer containing recurring cyclohexane units by all three types of initiators.

Three series of compounds, (1) butadiene, (2) sytrene, and (3) methacrylate derivatives, were studied spectrophotometrically in the region of the ultraviolet spectrum extending from 190 to 270 mμ. The butadiene derivatives synthesized were the *cis* and *trans* isomers of 1,3,8-nonatriene and 1,3,7-octatriene. *cis*-1,3,8-Nonatriene was obtained by reaction of 3-butenylmagnesium bromide with *cis*-1-chloro-2,4-pentadiene. 1,3,7-Octatriene and 1,3,8-nonatriene are monomers which are unique in that they are potentially capable of undergoing cyclopolymerization by a cumulative 1,2- and 1,4-addition during the propagation steps. The *trans* isomer was obtained by the Wittig[13] reaction of 5-hexenyltriphenylphosphonium bromide with acrolein. Synthesis of *cis*-1,3,7-octatriene was accomplished *via* the Wittig reaction between triphenylphosphorus al-

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(1) C. S. Marvel, *J. Polymer Sci.*, **48**, 101 (1960).

(2) G. B. Butler, *ibid.*, **48**, 279 (1960).

(3) E. A. Braude, *Ann. Rept. Progr. Chem.* (Chem. Soc. London), **42**, 105 (1945).

(4) L. Zechmeister, *Chem. Rev.*, **34**, 267 (1944).

(5) C. K. Ingold and C. W. Shoppee, *J. Chem. Soc.*, 364 (1928).

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(7) L. Bateman and G. A. Jeffrey, *ibid.*, 211 (1945).

(8) L. Bateman and H. P. Koch, *ibid.*, 216 (1945).

(9) P. D. Bartlett and E. S. Lewis, *J. Am. Chem. Soc.*, **72**, 1005 (1950).

(10) S. Winstein, *ibid.*, **83**, 1516 (1961).

(11) O. Mikulasova and A. Hvirik, *Chem. Invest.*, **11**, 641 (1957).

(12) N. D. Field, *J. Org. Chem.*, **25**, 1006 (1960).

(13) G. Wittig and U. Schollkopf, *Chem. Ber.*, **97**, 1318 (1954).

lylide and 4-pentenal. The *trans* isomer of 1,3,7-octatriene was obtained from the reaction of the ylide derived from 4-pentenyltriphenylphosphonium bromide with acrolein.

Syntheses of the styrene derivatives for this study were accomplished by reaction of the appropriate Grignard reagent (*n*-propyl, allyl, and 2-phenylallyl) with 2-phenyl-3-bromopropene.[14]

Data for the ultraviolet absorption spectra of *cis*- and *trans*-1,3,8-nonatriene are found in Table I. The calculated absorption maxima were determined according to Woodward's rule,[15] for the prediction of ultraviolet absorption maxima of alkyl-substituted butadienes. Included in Table I are several selected examples reported in the literature which serve as comparators for the compounds studied in this work.

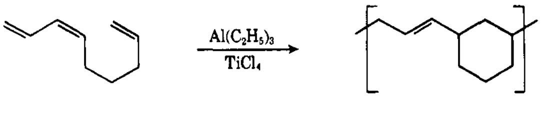
TABLE I

SELECTIVE ABSORPTION OF BUTADIENE DERIVATIVES[a]

Compound	λ_{max}, calcd.[b]	λ_{max}, obsd.	$\epsilon \times 10^4$
Piperylene[c]	222	223.5	2.30
Isoprene[d]	222	222	2.39
Myrcene[e]	222	224.5	1.70
cis-1,3,8-Nonatriene	222	225.5	2.03
trans-1,3,8-Nonatriene	222	227	2.10

[a] All data were determined in ethanol except for isoprene which was determined in hexane. [b] Wave lengths are in mμ. [c] H. Booker, L. K. Evans, and A. E. Gillam, *J. Chem. Soc.*, 1458 (1940). [d] A. Smakula, *Angew. Chem.*, **47**, 657 (1934). [e] R. T. O'Connor and L. A. Goldblatt, *Anal. Chem.*, **26**, 1727 (1954); E. D. Parker and L. A. Goldblatt, *J. Am. Chem. Soc.*, **72**, 2151 (1950).

The *cis* and *trans* isomers of 1,3,8-nonatriene exhibit distinct departures from Woodward's rule. Myrcene also exhibits a bathochromic shift of 2.5 mμ. It is significant, therefore, that during the course of this work, Marvel and Hwa[16] reported polymerizing this compound to a soluble, apparently cyclic polymer. In the cases of *cis*- and *trans*-1,3,8-nonatriene the shifts amount to 3.5 and 5.0 mμ, respectively. The *trans* isomer has been polymerized by a Ziegler catalyst initiator to yield a polymeric product approximately half of which is soluble and exhibits the properties expected for a cyclic polymer, produced by the following mechanism.



It can be seen from Table II that two effects seem to be operative in the light absorption properties of the styrene derivatives. A marked steric effect is observed when comparing styrene and α-methylstyrene in that a hypsochromic shift of the K-band for styrene is produced when the α-position is substituted with a methyl group. The nature of this effect is fully discussed in the literature.[17]

TABLE II

SELECTIVE ABSORPTION OF STYRENE DERIVATIVES

Compound	Solvent	λ_{max}, K-band[a]	$\epsilon \times 10^4$
Styrene[b,c]	Ethanol	248	1.40
α-Methylstyrene[c]	Ethanol	243	1.15
2-Phenyl-1-hexene	Ethanol	239	0.80
	Isooctane	239	0.90
2-Phenyl-1,5-hexadiene	Ethanol	238	1.09
	Isooctane	239	0.90
2,5-Diphenyl-1,5-hexadiene	Ethanol	238	1.85
	Isooctane	238	1.80

[a] Wave lengths are in mμ. [b] D. J. Cram and D. I. Wilkinson, *J. Am. Chem. Soc.*, **82**, 572 (1960). [c] C. G. Overberger and D. Tanner, *ibid.*, **77**, 371 (1955).

The second effect is more subtle in that it manifests itself only in the intensities of the maxima and band broadness and not in their location. In going from 2-phenyl-1-hexene to 2-phenyl-1,5-hexadiene and 2,5-diphenyl-1,5-hexadiene, the intensities of the K-band increase and considerable band broadening occurs when the spectra are measured in ethanol. In the nonpolar solvent, isooctane, there is almost perfect additivity. This trend in the intensities and band widths is roughly in the same order as would be expected for the tendencies of these models to cyclopolymerize. Since the magnitude of the absorption intensities are, at least to a degree, dependent upon the polarity of the excited state,[18] it seems conceivable that any effect which tends to enhance this polarity (such as an interspacial interaction of the absorbing chromophore with a neighboring chromophore) also might enhance the intensity. That this effect is observed in a solvent with a high dielectric constant and not in isooctane might be expected if the effect arises purely from the polar condition of the excited state.

In the methacrylate series it is again seen that the spectral data follow the same trend that would be expected for the tendencies of the models to undergo cyclopolymerization. A bathochromic shift of the maximum with methacrylic anhydride is observed and an enhancement of the extinction coefficients is seen to occur in going from the monoolefin to the diolefins. The spectral data for the methacrylate models are shown in Table III.

TABLE III

SELECTIVE ABSORPTION OF METHACRYLATE DERIVATIVES IN ISOOCTANE

Compound	λ_{max}[a]	$\epsilon \times 10^4$
Ethyl methacrylate	206	0.72
Allyl methacrylate	205	0.85
Methallyl methacrylate	204.5	0.95
Methacrylic anhydride	210	1.50

[a] Wave lengths are in mμ.

It is felt that the spectral data shown and discussed here are significant evidence for the unconjugated electronic interactions previously (2) proposed as an explanation for the propensity of certain unconjugated diolefins to undergo cyclopolymerization. The bathochromic shifts and enhanced absorption intensities all follow a pattern which would be expected for such electronic effects. The chemical consequences of this

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(15) R. B. Woodward, *ibid.*, **63**, 1123 (1941); **64**, 72, 76 (1942).

(16) C. S. Marvel and C. L. Hwa, *J. Polymer Sci.*, **45**, 25 (1960).

(17) A. E. Gillam and E. S. Stern, "An Introduction to Electronic Absorption Spectroscopy in Organic Chemistry," Edward Arnold (Publishers) Ltd., London, 1958, p. 98.

(18) L. N. Ferguson, *Chem. Rev.*, **43**, 394 (1948).

interaction and the attending stabilizing effect are revealed in the phenomenon of cyclopolymerization. In view of Winstein's[10] studies in nonclassical carbonium ion systems it is believed that this effect is either peculiar to the excited (or activated) state of the reacting molecules or to the radical or ionic transient intermediates produced during the propagation step of the polymerization.

Experimental

Source and Purification of Materials.—Ethylene oxide, allyl bromide, vinylmagnesium chloride, 5-hexen-1-ol, titanium tetrachloride, and triphenylphosphorus were obtained from Peninsular ChemResearch, Inc. The allyl bromide was distilled before use and the vinylmagnesium chloride, which was obtained as an approximately 3.5 *M* solution in tetrahydrofuran, was analyzed for concentration by the double titration method. Dihydropyran was obtained from the Chemicals Division of The Quaker Oats Co. and was used as received. Tetrahydrofuran-2-methanol and acrolein were obtained from Carbide and Carbon Chemicals Co. The tetrahydropyran-2-methanol was distilled before use and the acrolein was used as received. Acetyl chloride, α-methylstyrene, and N-bromosuccinimide were obtained from the Distillation Products Industries Division of Eastman Kodak Co. and were used as received. *n*-Propyl bromide was obtained from Columbia Organic Chemicals Co. and was distilled before use. Allyl methacrylate, ethyl methacrylate, and methacrylic anhydride were obtained from Monomer-Polymer Laboratories, Chemicals Division, Borden Co. Gas chromatography indicated these compounds to be sufficiently pure for ultraviolet spectral measurements. Triethylaluminum was obtained as a 25% solution in heptane from Hercules Powder Co. and was used as received.

Equipment and Data.—Temperatures reported in this paper are uncorrected and are recorded in degrees centigrade.

Infrared data were obtained with a Perkin-Elmer Infracord double-beam infrared recording spectrophotometer or a Perkin-Elmer Model 21 double-beam infrared recording spectrophotometer.

Ultraviolet data were obtained with a Bausch and Lomb Spectronic 505 double-beam recording ultraviolet-visible spectrophotometer equipped with an IP28 photomultiplier and an air-cooled hydrogen lamp–tungsten lamp combination light source.

Gas–liquid chromatographic analyses were made with a Wilkens Aerograph Model A-90-C gas chromatographic instrument using helium for the eluent gas. Unless otherwise indicated, gas chromatographic analyses were made on a 5-ft. column packed with 20% silicone GE SF-96 on firebrick. (Reference to this technique is abbreviated g.l.c. in this paper.)

Nuclear magnetic resonance data were obtained with a Varian V-4302 high resolution nuclear magnetic resonance spectrometer.

Intrinsic viscosity measurements were made with a Cannon-Ubbelohde semimicro dilution viscometer.

Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tenn.

1-Bromo-3-butene.—3-Buten-1-ol was prepared in yields of 60–70% from vinylmagnesium chloride and ethylene oxide according to the method of Ramsden, *et al.*,[19] and converted to the bromide in 55% yield by the general method of Gaubert, Linstead, and Rydon,[20] b.p. 96–99°, n^{20}_D 1.4652 (lit. b.p. 98.5–99°, n^{20}_D 1.4621).

2,4-Pentadienyl Chloride.—2,4-Pentadienyl chloride was synthesized in six steps by the method of Woods and Lederle[21] as modified by Crombie, Harper, and Thompson,[22] b.p. 46–47° (54 mm.), n^{20}_D 1.4951 [lit.[22] b.p. 80–82° (240 mm.), n^{20}_D 1.492–1.493].

1,3,8-Nonatriene.—The Grignard reagent of 1-bromo-3-butene was prepared in the usual way by adding a solution of 20 g. (0.15 mole) of the halide in 35 ml. of absolute ethyl ether to a mixture of 3.5 g. (0.14 g.-atom) of magnesium sand and 25 ml. of absolute ethyl ether. A solution of 10.0 g. (0.10 mole) of 2,4-pentadienyl chloride in 25 ml. of absolute ether was then added dropwise to the stirred Grignard solution at such a rate as to cause gentle refluxing of the ether. Shortly after addition of the chloride was completed the reaction mixture became a slurry and was heated to a gentle reflux for 30 min. longer. The mixture was then cooled in an ice–water bath and decomposed by careful addition of chilled dilute hydrochloric acid until all of the solid material was dissolved. The ethereal layer was separated, the aqueous layer extracted with 25 ml. of ether, and the two ethereal portions combined. The ether solution of crude product was washed with 10% sodium bicarbonate solution and distilled water and dried over anhydrous sodium sulfate. The ether was removed by distillation and the residual liquid was distilled at reduced pressure through a 23-plate spinning band column. The fraction collected at 65–67° (41 mm.) was refractionated to yield 3.0 g. (25%) of the desired product b.p. 67° (41 mm.), n^{20}_D 1.4694, d^{20}_4 0.891. The compound, which was found to be 99+% pure by the g.l.c. analysis, took up 3.18 moles of hydrogen per mole of sample. The infrared spectrum had the following absorption bands assignable to the proposed structure[23]: 1640 ($C{=}C$, nonconjugated), 1000 ($—CH{=}CH_2$), 913, 900 cm.$^{-1}$ ($—CH{=}CH_2$). An n.m.r. spectrum of the compound gave an integrated peak area ratio for sp^2 to sp^3 hydrogens of 4:3. Data on the ultraviolet spectrum are found in Table I.

Anal. Calcd. for C_9H_{14}: C, 88.45; H, 11.55. Found: C, 88.26; H, 11.39.

1-Bromo-5-hexene.—1-Bromo-5-hexene was prepared essentially as described by Butler and Price[24] with the following modifications. The 2-chloromethyltetrahydropyran was prepared according to the procedure of Crombie, *et al.*,[25] and the 5-hexen-1-ol was converted to the alkenyl bromide by the general method of Gaubert, Linstead, and Rydon.[20] With these modifications the yields reported by Butler and Price were improved by approximately twofold (50–60%) and the general method was considerably simplified. The product had b.p. 46° (14 mm.), n^{23}_D 1.4640 [lit.[24] b.p. 76–78° (45 mm.), n^{25}_D 1.4630].

5-Hexenyltriphenylphosphonium Bromide.—This salt was prepared in 95% yield by the procedure of Hauser, *et al.*,[26] m.p. 165–168°. A 500-ml. resin kettle was charged with 105.6 g. (0.65 mole) of 1-bromo-5-hexene, 170 g. (0.65 mole) of triphenylphosphorus, and 200 ml. of anhydrous xylene, and the resulting solution was stirred and refluxed for 10 hr. The mixture was then allowed to cool to room temperature at which time a lower viscous layer of liquid developed and became semisolid on standing. The supernatent liquid was poured from the kettle, and the vessel was evacuated with a water aspirator and heated to drive off most of the remaining xylene. The kettle was then evacuated with a vacuum pump and heated to remove the last traces of xylene, after which the crystalline residue was pulverized, washed with benzene, and vacuum dried in a desiccator over phosphorus pentoxide.

***trans*-1,3,8-Nonatriene.**—The procedure for the preparation of this compound is essentially that devised by Hauser, *et al.*[26] A stirred slurry of 42.4 g. (0.10 mole) of 5-hexenyltriphenylphosphonium bromide in 200 ml. of absolute ethyl ether in a dry nitrogen atmosphere was treated with 85 ml. of an approximately 15% solution of *n*-butyllithium in hexane. The resulting deep orange solution of the triphenylphosphorus-5-hexenylide was cooled to 10° by means of an ice–water bath, and a solution of 6.7 g. (0.12 mole) of acrolein in 25 ml. of absolute ethyl ether was added over a 30-sec. period followed 15 sec. later by 100 ml. of 2 *M* ammonium chloride and finally 100 ml. of water. Addition of the acrolein caused discharge of the orange color and formation of a fine white precipitate. Upon addition of the ammonium chloride solution and the water, the precipitate went into the aqueous layer as a gummy white mass. The liquid layers were poured away from the solid and separated, and the aqueous layer was extracted with 50 ml. of ether. The solid phase of phosphine oxide and lithium bromide was washed with 50 ml. of ether, and the washings combined with the original organic layer and the ether extract. The combined ethereal portions were then dried over anhydrous sodium sulfate, filtered, and inhibited with 0.2 g.

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(24) G. B. Butler and G. D. Price, *J. Org. Chem.*, **24**, 1092 (1959).

(25) L. Crombie, S. H. Harper, F. C. Newman, D. Thompson, and R. J. D. Smith, *J. Chem. Soc.*, 126 (1956).

(26) C. F. Hauser, T. W. Brooks, M. A. Raymond, M. L. Miles, and G. B. Butler, *J. Org. Chem.*, **27**, 372 (1962).

of hydroquinone. The ether and hexane were distilled through a 30-cm. vacuum-jacketed Vigreux column until the pot temperature rose to 70°. The remaining liquid was then distilled through a 23-plate spinning band column under reduced pressure to yield 2.0 g. of a clear, colorless liquid, b.p. 68–69° (43 mm.), $n^{20}\text{D}$ 1.4721, $d^{20}{}_4$ 0.771.

G.l.c. analysis of the product revealed only one component and quantitative hydrogenation resulted in a hydrogen uptake of 3.00 moles per mole of sample. The infrared spectrum of the material showed the following bands assignable to the proposed structure[23]: 1640 (C=C, nonconjugated), 1595 (C=C—C=C), 999 (—CH=CH_2), (—C=C—, *trans*), 900 cm.$^{-1}$ (—CH=CH_2). An n.m.r spectrum of the compound gave an integrated peak area ratio for sp^2 to sp^3 hydrogens of 1:1. G.l.c. analysis of a mixture of this triene and that prepared by the Grignard reaction showed two narrowly spaced peaks. Data on the ultraviolet spectrum are found in Table I.

Anal. Calcd. for C_9H_{14}: C, 88.45; H, 11.55. Found: C, 88.36; H, 11.77.

1,3,7-Octatriene. A.—A stirred slurry of 38.3 g. (0.10 mole) of allyltriphenylphosphonium bromide in 200 ml. of absolute ethyl ether in a dry nitrogen atmosphere was treated with 75 ml. of 1.6 *M* *n*-butyllithium in hexane. The resulting solution of triphenylphosphorusallylide was cooled to 10°, and 12.7 g. (0.10 mole) of 4-pentenal in 35 ml. of absolute ether was added over a 30-sec. period followed 15 sec. later by 100 ml. of 2 *M* ammonium chloride and 100 ml. of water. The remainder of the procedure described previously for 1,3,8-nonatriene was employed for purification of this compound; yield, 2.1 g. (19.5%); b.p. 115–117°; $n^{20}\text{D}$ 1.4594. The product gave only one peak by g.l.c. analysis and exhibited characteristic infrared absorption bands at 1640, 1600, 1000, and 910 cm.$^{-1}$. The characteristic infrared absorption band at 965 cm.$^{-1}$ for *trans* olefin was absent. The *cis* configuration is assigned to this compound on this basis. The ultraviolet absorption maximum occurs at 225 mμ with an ϵ value of 21,000.

Anal. Calcd. for C_8H_{12}: C, 88.82; H, 11.18. Found: C, 88.48; H, 11.37.

1,3,7-Octatriene. B.—By a procedure similar to that previously described, 41.1 g. (0.10 mole) of 4-pentenyltriphenylphosphonium bromide was treated with 85 ml. of 14.9% *n*-butyllithium in hexane. The resulting ylide was treated with 8.4 g. (0.15 mole) of acrolein to yield 2.6 g. (24%) of 1,3,7-octatriene; b.p. 120–122°; $n^{20}\text{D}$ 1.4704. The product gave two peaks by g.l.c. analysis indicating a mixture of *cis* and *trans* isomers. Combination of the products of several runs and careful redistillation yielded a product of b.p. 124–125°, $n^{20}\text{D}$ 1.4686, $d^{20}{}_4$ 0.77, and which gave a single peak by g.l.c. analysis. This product absorbed 2.98 moles of hydrogen per mole of compound, and exhibited characteristic infrared absorption bands at 1640, 1600, 1000, 965, and 910 cm.$^{-1}$. On the basis of these results, this product is believed to be predominantly the *trans* isomer. A n.m.r. spectrum of the compound gave a ratio of sp^2 to sp^3 bonded hydrogen of 1.9:1 in good agreement with the calculated value of 2:1.

3-Bromo-2-phenylpropene.—Preparation of 3-bromo-2-phenylpropene was accomplished *via* the N-bromosuccinimide bromination of α-methylstyrene according to the procedure of Hatch and Patton.[14] The product had the physical properties reported by these authors, but was contaminated with β-bromo-α-methylstyrene as was found by Pines *et al.*,[27] in their studies of this reaction. Since g.l.c. analysis with available columns failed to resolve the two halides, an estimation of purity was not possible. The impure product was, however, successfully used to prepare desired model compounds in low yields. The properties of the impure product used in this work were b.p. 89–91° (5 mm.), $n^{20}\text{D}$ 1.5869 [lit.[14] b.p. 90° (5 mm.), $n^{20}\text{D}$ 1.5869].

2-Phenyl-1-hexene.—The Grignard reagent of *n*-propyl bromide was prepared in the usual manner from 27.6 g. (0.23 mole) of *n*-propyl bromide in 30 ml. of absolute ethyl ether and 5.1 g. (0.21 g.-atom) of magnesium turnings in 45 ml. of absolute ethyl ether. A solution of 29.6 g. (0.15 mole) of 3-bromo-2-phenylpropene in 30 ml. of absolute ethyl ether was then added dropwise to the Grignard solution at a rate such as to cause gentle refluxing of the ether. When addition of the allylic halide was complete the resulting mixture was refluxed overnight, cooled in an ice-water bath and decomposed by cautiously adding dilute hydrochloric acid. The organic layer was separated, the aqueous layer extracted with ether, and combined organic layer and ether extract washed free of acid with 10% sodium bicarbonate. The ethereal product was then washed with water and dried over anhydrous sodium sulfate; the ether was removed at reduced pressure with a flash evaporator. The residual liquid was then distilled under reduced pressure through a 23-plate spinning band column to yield five fractions boiling from 83–90° (8 mm.) totaling 12 g. (50%) in weight. Each of the fractions was found by g.l.c. and index of refraction measurements to be slightly contaminated with β-bromo-α-methylstyrene. Redistillation of the middle fractions yielded a 1.0 g. fraction of analytical purity, b.p. 89–90° (10 mm.), $n^{20}\text{D}$ 1.5254. Data on the ultraviolet spectrum are shown in Table II.

Anal. Calcd. for $C_{12}H_{16}$: C, 89.94; H, 10.06. Found: C, 89.96; H, 10.10.

2-Phenyl-1,5-hexadiene.—The preparation of 2-phenyl-1,5-hexadiene was accomplished according to the method of Pines, *et al.*[27] The product was obtained in analytical purity as described for 2-phenyl-1-hexene, and had b.p. 89–90° (9 mm.), $n^{20}\text{D}$ 1.5361 [lit.[27] b.p. 104° (10 mm.), $n^{20}\text{D}$ 1.5314]. While the rather large discrepancies in physical properties noted here raise a question as to the purity of the sample, g.l.c. analysis as well as infrared and elemental analyses indicate the sample prepared in this work to be of high purity. Data on the ultraviolet spectrum are shown in Table II.

Anal. Calcd. for $C_{12}H_{14}$: C, 91.08; H, 8.92. Found: C, 90.91; H, 8.68.

2,5-Diphenyl-1,5-hexadiene.—A solution of 59 g. (0.3 mole) of 3-bromo-2-phenylpropene in 150 ml. of absolute ethyl ether was added dropwise to a stirred mixture of 5.8 g. (0.15 g.-atom) of magnesium turnings in 50 ml. of absolute ethyl ether over 2 hr. The resulting mixture was then treated with 0.9 g. of anhydrous cobalt chloride[28] causing a mildly exothermic reaction which kept the ether refluxing for approximately 30 min. The resulting black-brown mixture was then refluxed for 2 hr. after which it was cooled in an ice-water bath and decomposed with dilute hydrochloric acid. The organic layer was separated and the aqueous layer extracted twice with 25-ml. portions of ethyl ether. The combined organic layer and ether extracts were washed with 10% sodium bicarbonate and water and dried over anhydrous sodium sulfate. The ether was then removed at reduced pressure in a flash evaporator and the dark brown residual oil distilled at reduced pressure. After a forerun of volatile materials, a fraction came over at 150–160° (1 mm.) which crystallized upon cooling. The solid material, 2.8 g. (8.3%), was crystallized four times from methanol to afford a white crystalline product which had m.p. 48.5–49.0° (lit.[29] m.p. 51.0–51.3°). The infrared spectrum of the product agreed with that reported by Marvel and Gall,[29] and g.l.c. analysis showed only one peak. Data on the ultraviolet spectrum are shown in Table II.

Anal. Calcd. for $C_{18}H_{18}$: C, 92.26; H, 7.74. Found: C, 92.42; H, 7.94.

Methallyl Methacrylate.—The ester was prepared from methacrylic anhydride and methallyl alcohol in the usual manner and was fractionated through a 23-plate spinning band column to obtain an analytically pure sample, b.p. 58° (15 mm.), $n^{20}\text{D}$ 1.4415 [lit.[30] b.p. 63° (17 mm.), $n^{20}\text{D}$ 1.4400]. Data on the ultraviolet spectrum are shown in Table III.

Polymerization of *trans*-1,3,8-Nonatriene.—A screwcap vial was charged by means of a microhypodermic syringe with 0.056 g. (0.15 mmole) of titanium tetrachloride, 0.08 ml. containing 0.013 g. (0.11 mmole) of triethylaluminum, and finally with 3.6 ml. of high purity hexane and 1.0 g. (8 mmoles) of *trans*-1,3,8-nonatriene. All of the operations were carried out in a drybox under an atmosphere of dry nitrogen. The mixture was shaken well and allowed to stand for 40 hr. at 25° after which it was decomposed by pouring into methanol. The gelatinous material was filtered, washed with methanol, and allowed to stand in dry benzene for 10 hr. with occasional vigorous agitation. The remaining undissolved polymer was then filtered, and the filtrate was poured into methanol to afford 0.1 g. of clear colorless tacky polymer, which after a second precipitation from benzene into methanol, had a flow temperature of 50–55° and an intrinsic viscosity of 0.15. The insoluble material, which was a soft

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[28] A. R. Pray, *Inorg. Syn.*, **5**, 153 (1957).

[29] C. S. Marvel and E. J. Gall, *J. Org. Chem.*, **25**, 1784 (1960).

[30] C. E. Rehberg, C. H. Fisher, and L. T. Smith, *J. Am. Chem. Soc.*, **65**, 1003 (1945).

rubbery substance, weighed 0.13 g. for a total conversion of 23%. An infrared spectrum of the soluble polymer (run as a film pressed out from the melt) had the following absorption bands: 2950 (broad); 1650 (w); 1450 (s); 1380 (s); 1070 (w); 965 (s); 910 cm.$^{-1}$.

Anal. Calcd. for C_9H_{14}: C, 88.45; H, 11.55. Found: C, 83.86; H, 9.81; ash, 1.8.

Polymerization of *cis*-1,3,8-Nonatriene.—A small serum capped vial was charged by means of a microhypodermic syringe with 0.0028 g. (0.07 mmole) of titanium tetrachloride and 0.08 ml. of heptane containing 0.013 (0.11 mmole) of triethylaluminum in a drybox under a dry nitrogen atmosphere. The vial was further charged with 1.0 ml. of high purity hexane and 0.61 g. (5 mmoles) of the triene, shaken well, and allowed to stand at 25° in the drybox for 72 hr. The mixture was then poured into methanol and filtered on a sintered glass disk, the residue was washed with methanol. The residue was a tough plastic substance which could not be ground up. The material was placed in a Soxhlet extractor and extracted for 2 days with hot benzene. The benzene extract was then poured into methanol causing less than a milligram of solid to be precipitated. The solid which was recovered from the extraction thimble and dried appeared unchanged. A second attempt to polymerize this monomer at a concentration of 10% in hexane gave essentially the same results. The cross-linked material which was insolube in several organic solvents was obtained in the amount of 0.05 g. (8.5%) and was not investigated any further.

One attempt was made to polymerize this monomer in bulk with 0.1% azobisisobutyronitrile and was not successful after 1 week at 80°.

Polymerization of 1,3,7-Octatriene.—This reaction was carried out in the same manner as was described for the nonatriene. The reaction charge consisted of the same molar proportions of catalyst and monomer. The polymerization was conducted for 18 hr. after which the polymer was worked up in the previously described manner. The yield of polymer was 0.5 g. (22.8% conversion), 0.12 g. (24.0%) of which was soluble in hot benzene. The soluble polymer was a soft plastic material which flowed on standing and had an intrinsic viscosity of 0.09 (1.120 and 0.560 g./100 ml. in benzene at 30°).

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Synthesis and Cyclopolymerization of 1,8-Divinylnaphthalene

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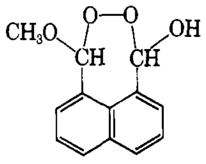
1,8-Divinylnaphthalene has been synthesized and polymerized to give soluble, low molecular weight polymers. The monomer was synthesized by the reaction of 1,8-naphthalenedialdehyde hydrate with triphenylphosphinemethylene. Several other 1,8-naphthalene compounds have been synthesized during the investigation.

It has been shown that nonconjugated diolefins will undergo an intramolecular–intermolecular cyclic propagation during polymerization giving a polymer that contains carbocyclic rings along the backbone of the chain.[1,2] Considering these results and the mechanism proposed for cyclic polymerization,[3] the position of the vinyl groups in 1,8-divinylnaphthalene (I) should be ideally situated for a cyclic propagation reaction since the vinyl groups are held rigidly with a minimum of free rotation. In addition, group interaction in 1,8-naphthalene compounds is very common and formation of a six-membered ring seems to be preferred in cyclopolymerization.[4]

The first approach to the synthesis of 1,8-divinylnaphthalene was through dehydration of 1,8-bis-(1-hydroxyethyl)-naphthalene (II). This compound was synthesized according to the reactions depicted in Chart I. Hydrolysis of 1,2-dibromoacenaphthene (IV) produced a mixture of isomers of 1,2-dihydroxyacenaphthene (V). The reaction of lead tetraacetate with diol V is reported[5] to give 1,8-naphthalenedialdehyde as the hydrate but no yields were given. It was found, however, that when diol V reacts with lead tetraacetate the major product was a polymeric material rather than the crystalline 1,8-naphthalenedialdehyde hydrate (VI). The polymeric material was found to react with *p*-nitrophenylhydrazine to give good yields of the reported hydrazone of VI, while the reaction with base gave a good yield of 1,8-naphthalide (VII).


VIII

Since the reduction of 3-hydroxy-7-methoxy-4,5,6-(1,8-naphtho)-1,2-dioxacycloheptane (VIII) formed from ozonolysis of acenaphthylene (III) has been reported[6] to produce an oil which also affords the same *p*-nitrophenylhydrazone that is obtained from VI, an investigation of this method of the preparation of VI was undertaken.

When III was allowed to react with an ozone–oxygen mixture the major product after reduction was 1,8-naphthaldehydic acid (IX).[6] If the hemiperacetal VIII, which precipitates from the ozonolysis solution, was isolated, and subsequently reduced with potassium iodide in methanol, a 16.5% yield of VI could be obtained after hydrolysis with dilute acid. Ozonolysis of III by ozone in a nitrogen stream[7] afforded a 73.5% yield of VI compared to the 16.5% yield obtained using the oxygen–ozone mixture.

The structure, 2,6-dihydroxy-3,4,5-(1,8-naphtho)oxacyclohexane (VI) was assigned on the basis of the in-

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