Further Evidence for Nonconjugated Chromophoric Interactions in Certain Polyenes[1,2]

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In an effort to account for the unique tendency for 1,6-dienes to undergo cyclization, it has been proposed that a homoconjugative interaction occurs between the unconjugated ethylenic bonds, thus providing an energetically favorable path from diene to cyclic product. Certain evidence, consisting of bathochromic shifts in ultraviolet absorption maxima, of three series of compounds which were derivatives of butadiene, styrene, and methacryclic acid, has been presented. This paper consists of the synthesis of three tetraenes, 1,3,9,11-dodecatetraene, 1,3,6,8-nonatetraene, and 3,6-dimethylene-1,7-octadiene, and a spectral study of these compounds in an effort to further test the above proposal. For comparison, the corresponding 1,3-dodecadiene, 1,3-nonadiene, and 3-methylene-1-octene were prepared and their spectral properties compared with the respective tetraenes. All of the dienes absorbed in the rather narrow range of 224.7–226.5 mμ while the tetraenes exhibited absorption maxima over the wide range of 221.8–272.1 mμ. The dodecatetraene exhibited an absorption maximum at 228 mμ, which represents a bathochromic shift of 2.7 mμ when compared to the dodecadiene. The nonatetraene exhibited an absorption maximum at 237.1 mμ, representing a bathochromic shift of 10.6 mμ when compared to the nonadiene. In addition two new absorption peaks not shown by the diene were found at 261.0 and 272.1 mμ. 3,6-Dimethyl-1,7-octadiene exhibits an absorption maximum at 221.8 mμ compared to a maximum at 224.7 mμ for 3-methylene-1-octene. This represents a hyposchromic shift of 2.9 mμ. All of the tetraenes show extinction coefficients considerably greater than the dienes, but not twice as great. The dodecatetraene gave an extinction coefficient 41% greater than the dodecadiene, while that of the nonatetraene was only 11.7% greater than the nonadiene, and that of the dimethyleneoctadiene was 71% greater than the methyleneoctene. If there were no interaction between the butadienyl groups, each tetraene should have an extinction coefficient twice that of its corresponding diene. These data are interpreted as a strong indication that interactions do occur.

In a recent paper from this laboratory[3] evidence was presented which is suggestive of nonconjugated interactions in certain dienes and trienes which are functionally capable of undergoing cyclopolymerization. Other instances where data are suggestive of such a phenomenon have been summarized.[4] Such nonconjugated interactions were proposed[4] in an effort to account for the unique tendency of 1,5- and 1,6-dienes to cyclopolymerize. More recent evidence supporting these proposed interactions has been published.[5,6] In addition many examples of excited-state interactions similar in nature to that observed in cation-initiated polymerization[7] have been cited.[8]

This paper represents an extension of the above-described concept to a series of tetraenes in an effort to provide further evidence for nonconjugated interactions. For the purposes of this work, it was necessary to have compounds with nonconjugated double bonds located in such positions that they could interact interspatially with concomitant formation of six-membered ring conformations. Since instrumental limitations prevented the use of simple dienes which absorb at too short a wave length in the ultraviolet, it was decided to synthesize derivatives of butadiene as model compounds. Derivatives of butadiene would be expected to absorb at wave lengths longer than 217 mμ, which places them in a region easily accessible with available ultraviolet spectrophotometers.

The compounds chosen for synthesis and study were 1,3,9,11-dodecatetraene, 1,3,6,8-nonatetraene, and 3,6-dimethylene-1,7-octadiene. The ultraviolet spectra of these compounds were obtained and compared with the spectra of the closely analogous dienes, 1,3-dodecadiene, 1,3-nonadiene, and 3-methylene-1-octene. Thus we have a series of dibutadienyl compounds and a series of analogous monobutadienyl compounds.

In seeking a method of preparation for the olefins, we turned our attention to the Wittig[9] reaction, which seemed to offer a ready path to these compounds. This reaction, in brief, is a route to olefins through reaction of triphenylphosphoranes with carbonyl compounds. The final step of this synthesis is usually accomplished by refluxing at *ca.* 70° for a period of several hours. Early attempts to prepare the dodecatetraene using published techniques with hexamethylenebis(triphenylphosphonium bromide) and acrolein yielded no distillable product. However, by use of reaction conditions[10] which involved addition of acrolein to the phosphorane at 5–10°, satisfactory yields of the tetraene could be obtained.

By use of this technique, yields for 1,3,9,11-dodecatetraene and 1,3,6,8-nonatetraene [from trimethylenebis(triphenylphosphonium bromide) and acrolein] were 6–8% in diethyl ether and 12% in diglyme. The low yields of olefin were attributed to anion-initiated polymerization of the acrolein with formation of a polymer with pendant carbonyl groups. These carbonyl groups, not being conjugated, are more polar than that in acrolein, and presumably more reactive with the phosphorane, thus decreasing the yield of the desired product. 1,3,9,11-Dodecatetraene and 1,3,6,8-nonatetrane prepared by this method were quite pure. The former absorbed 3.98 moles of hydrogen when hydrogenated over a platinum oxide catalyst, while the latter absorbed 4.01 moles. 1,3-Dodecatetraene was prepared through use of the Wittig reaction between the phosphorane derived from allyltriphenylphosphonium bromide and nonanal. 1,3-Nonadiene was

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[1] This work was supported by the Petroleum Research Fund, American Chemical Society, under Grant No. 470A. Taken from the Ph.D. Dissertation of M. A. Raymond, University of Florida, Dec. 1962.

[2] Presented before the Division of Organic Chemistry, 146th National Meeting of the American Chemical Society, Denver, Colo., Jan. 1964.

[3] G. B. Butler and T. W. Brooks, *J. Org. Chem.*, **28**, 2699 (1963).

[4] G. B. Butler, *J. Polymer Sci.*, **48**, 279 (1960).

[5] R. E. Ireland and P. W. Schiess, *J. Org. Chem.*, **28**, 6 (1963).

[6] R. C. Cookson, J. Hudec, S. A. Knight, and B. R. D. Whiter, *Tetrahedron*, **19**, 1955 (1963).

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

[8] P. D. Bartlett, *Ann. Chem.*, **653**, 45 (1962).

[9] G. Wittig and U. Scholkepf, *Chem. Ber.*, **97**, 1318 (1954).

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

prepared by reaction of the phosphorane derived from *n*-hexyltriphenylphosphonium bromide and acrolein and was purified on a preparatory g.l.c. column.[10]

3,6-Dimethylene-1,7-octadiene was prepared by dimerization of 2-(bromomethyl)butadiene with magnesium. 2-(Bromomethyl)butadiene was prepared by the method of Krug and Yen.[11] The structure of the tetraene was supported by analytical, infrared, and n.m.r. data. The diene analog of this compound, 3-methylene-1-octene, was obtained by reaction of 2-(bromomethyl)butadiene with *n*-butylmagnesium bromide.

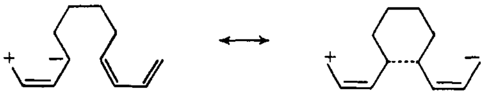
The data from the ultraviolet spectra of the compounds are summarized in Table I. It is seen that the dienes all absorb in a narrow range: 1,3-nonadiene at 226.5 mμ, 1,3-dodecadiene at 225.3 mμ, and 3-methylene-1-octene at 224.7 mμ. In contrast, the tetraenes show rather marked deviations in the position of maximum absorption from their corresponding dienes. The dodecatetraene exhibits an absorption maximum at 228 mμ, which represents a bathochromic shift of 2.7 mμ compared to the dodecadiene. This corresponds to an energy lowering of 1.6 kcal./mole in the $\pi-\pi^*$ transition. The lowering of the energy required for this transition can be due to a higher energy ground state, a lower energy excited state, or a combination of these.

TABLE I

ABSORPTION OF BUTADIENE DERIVATIVES

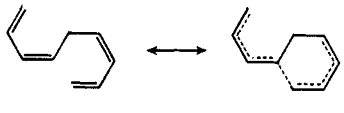
Compd.	$\lambda_{\max}^{\mathrm{EtOH}}$, mμ	log ε
1,3,9,11-Dodecatetraene	228	4.62
1,3-Dodecadiene	225.3	4.47
1,3,6,8-Nonatetraene	237.1	4.51
	261.0	3.91
	272.1	3.76
1,3-Nonadiene	226.5	4.44
3,6-Dimethyleneoctadiene-1,7	221.8	4.55
3-Methyleneoctene-1	224.7	4.31

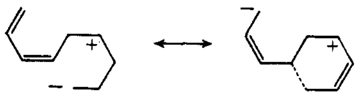
If we consider that in the ground state there is a homoconjugative interaction between the double bonds (measurements on models indicate a closest distance of approach of about 3 Å.), then in the electronically activated state, the double bonds may interact in a dipole–dipole manner. The homoconjugative interaction between the double bonds should provide a lowering in the electronic energy level of the molecule in the ground state; however, the interaction in the activated state is between dipoles (or between a dipole and an induced dipole), which is a stronger interaction. The net result is a lowering of the energy for the $\pi-\pi^*$ transition.



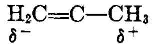
The shift in the ultraviolet absorption maximum may be explained without postulating a ground-state interaction because, statistically, a certain number of the molecules will have the double bonds close enough[12] to interact in the activated state. However, the results of the probability calculation for cyclic polymerization[13] show that, if the cyclic conformation were merely sterically controlled, the high degree of cyclization during polymerization cannot be accounted for; therefore, on the basis of this evidence, the statement that there is an interaction in the ground state as well as in the activated state appears highly justified.

1,3,6,8-Nonatetraene presents a more complex case. The ultraviolet absorption spectra of this compound and 1,3-nonadiene are shown in Figure 1. The position of maximum absorption occurs at 237.1 mμ, representing a bathochromic shift of 10.6 mμ when compared to $\lambda_{\max}$ of 1,3-nonadiene. The energy for the $\pi-\pi^*$ transition has been lowered by 5.5 kcal./mole. As in the case of the dodecatetraene, we may picture a ground state stabilized by homoconjugative interaction between the double bond systems as follows. The electronically activated state may then be stabilized by dipole–dipole (or dipole–induced dipole) interaction.





The net effect here is a greater lowering of the energy for the $\pi-\pi^*$ transition than in the case of the dodecatetraene. This may be explained by considering the direction of the dipoles within each of the tetraenes. The normal polarization of an alkyl-substituted double bond is illustrated as follows. In nonatetraene we



$$\underset{\delta^-}{\mathrm{H_2C}}{=}\mathrm{C}{-}\underset{\delta^+}{\mathrm{CH_3}}$$

may have both butadienyl groups polarized in this manner during the interspatial interaction in the electronically excited state. However, in the case of the dodecatetraene, we may have only one of the butadienyl groups polarized in this manner. It would seem reasonable on the basis of this that the activated state in the nonatetraene is at a lower energy than the activated state in the dodecatetrane. The ground states should be on comparable energy levels, the result being in agreement with the observed shift in absorption maximum.

Nonatetraene has a methylene group joining the two butadienyl groups. Because of this, the hydrogens should be very susceptible to hyperconjugation. It may be expected that this would influence the ultraviolet spectrum in some way. Consideration of some comparable compounds may give an indication of how this active methylene group may affect the spectrum. The ultraviolet spectrum of 1,4-pentadiene has been determined[14] in gas phase and it shows absorption at 170 mμ (log ε 4.1), 176 (4.2), 181 (4.2). This may be compared to 1-pentene, which has the following absorption maxima: 164.3 mμ (sh) (log ε 3.91), 177 (4.22), 181.3 (4.14), and 187.1 (sh) (3.65). The differences between the spectra are the disappearance of the high-intensity shoulder at 164.3 mμ, and the low-

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(11) R. C. Krug and T. F. Yen, *J. Org. Chem.*, **21**, 1082 (1956).

(12) S. Glasstone, "Textbook of Physical Chemistry," D. Van Nostrand Co., Inc., Princeton, N. J., 1958, p. 524.

(13) G. B. Butler and M. A. Raymond, *J. Polymer Sci.*, in press.

(14) "Organic Electronic Spectral Data," Vol. II, H. E. Ungnade, Ed.; Interscience Publishers, Inc., New York, N. Y., 1960.

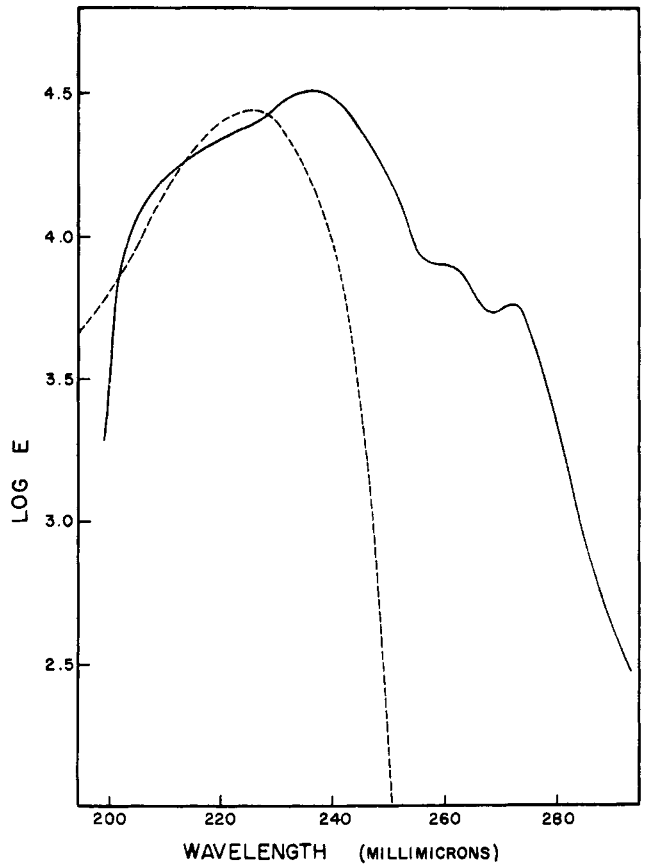


Figure 1.—Ultraviolet absorption spectra of (a) 1,3,6,8-nonatetraene, ———; and (b) 1,3-nonadiene, - - - -.

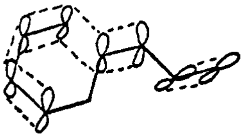
intensity shoulder at 187.1 mμ in the case of the pentene, and the appearance of a high intensity band at 170 mμ in the pentadiene.

Two other comparisons may be made. The spectrum[15] of allylbenzene is almost identical with that of 3-butenylbenzene, showing no change in the position of maximum and only slight increase in the intensity of the absorption of shorter wave lengths than the maximum. The spectrum of diphenylmethane,[15] when compared to that of 1,2-diphenylethane, exhibits the same features, *i.e.*, no change in position or intensity of maximum absorption, but there is an increase in intensity of absorption on the short wave length side of the maximum.

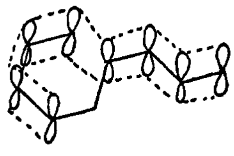
On the basis of the above three examples, it may be possible to ascribe the shoulder on the short wave length side of the maximum for nonatetraene to participation of the methylene group in the excited state.

If the above assignment for the participation of the 5-methylene group in the excited state is correct, it can then be assumed that the unassigned peaks of moderate intensity at 261.0 and 272.1 mμ are not due to participation of this group. The origin of these peaks must be the result of the presence of the two butadiene moieties within a single molecule. These two unpredicted absorption maxima are unquestionably the result of electronic transitions not possible or, at least, not observable in the corresponding diene. Several structural features of 1,3,6,8-nonatetraene should be considered in attempting to assign these absorptions to specific electronic transitions. 1,4-Dienes are capable of undergoing isomerism to 1,3-dienes. Consequently, it may be assumed that 1,3,6,8-nonatetraene exhibits some tendency to undergo isomerism particularly in the presence of bases, *e.g.*, *n*-butyllithium used in its synthesis. Indeed, 1,3,5,7-nonatetraene was isolated as an impurity in the 1,3,6,8-nonatetraene preparation. The conjugated tetraene was removed from the 1,3,6,8-nonatetraene by preparative gas chromatography and was identified by infrared and ultraviolet spectrometery. The spectrum shown in Figure 1 is therefore that for pure 1,3,6,8-nonatetraene. In addition to possible rearrangement, three geometric isomers of 1,3,6,8-nonatetraene are possible, namely the *cis,cis*, the *cis,trans*, and the *trans,trans* isomers. Although these three geometrical isomers were not isolated and identified, nor was evidence obtained that the chromatographically pure sample was a mixture of geometric isomers, the infrared spectrum indicated the presence of absorptions characteristic of both *cis* and *trans* double bonds in the compounds. On this basis, the structural requirement for the proposed across-space electronic interaction to occur, specifically that at least one of the internal double bonds have the *cis* configuration, appears to be substantiated.

The proximity of the absorption peak at 261.0 mμ to that normally observed for conjugated trienes suggests that the electronic transition occurring at this wave length in the 1,3,6,8-nonatetraene is associated with that fraction of the molecular population in which one conjugated system assumes coplanarity with the internal double bond of the other double bond system, but the terminal double bond is not coplanar, as follows. Conjugated trienes absorb in the region 265–275 mμ.[16] Although the observed maximum in this case is below that observed for conjugated trienes, this characteristic is usual for interspacial electronic interactions.[17] Furthermore, since the maximum is below the range expected for conjugated trienes, the evidence that a pure sample of 1,3,6,8-nonatetraene is under observation is further substantiated.



In a similar manner the absorption peak at 272.1 could possibly arise from that fraction of the molecular population which attains the necessary energy state so that the two isolated double bond systems may approach coplanarity throughout as shown below.



Again, the observed maximum is considerably below the region in which conjugated tetraenes absorb (285–295 mμ) and the arguments presented earlier apply here also.

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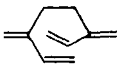
(15) Ramart-Lucas, *Bull soc. chim. France*, **51**, 289 (1932).

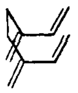
(16) A. E. Gillam and E. S. Stern, "Electronic Absorption Spectroscopy," E. Arnold Ltd., London, 1958.

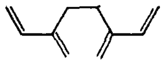
(17) S. Winstein, L. de Vries, and R. Orloski, *J. Am. Chem. Soc.*, **83**, 2020 (1961).

3,6-Dimethyleneoctadiene-1,7 does not fall nicely in line with nonatetraene and the dodecatetraene. It exhibits absorption at 221.8 mμ compared to 3-methylene-1-octene at 224.7 mμ. This represents a hypsochromic shift of 2.9 mμ, or an increase in the energy for electronic transition of 1.3 kcal./mole.

Examination of the model of 3,6-dimethylene-1,7-octadiene, shows that the two conjugated systems are capable of approaching each other in several ways.

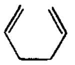






It is possible that the ground state of the molecule is stabilized to a great extent by interspatial interaction of the double bonds in the above conformations. If the excited state then were not stabilized to the same extent, this would account for the hypsochromic shift.

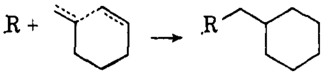
1,5-Hexadiene is a compound which is similar to 3,6-dimethylene-1,7-octadiene. This compound absorbs[18] at 177 mμ (log ε 4.4). The corresponding monoolefin shows maximum absorption at 179 mμ (log ε 4.0) and 189 mμ (sh) (log ε 3.5). Hexadiene is another compound in which the double bonds can interact in different ways as shown. The interaction in the first conformation would be of the π-type; in the second conformation, it would be of the σ-type. Here again the hypsochromic shift may be due to a greater stabilization of the ground state than the excited state.



If there were no interaction between the butadienyl groups, each tetraene should have a molar extinction coefficient twice that of its corresponding diene. All of the tetraenes show extinction coefficients considerably greater than the dienes, but not twice as great. Dodecatetrane has an extinction coefficient 41% greater than dodecadiene. The extinction coefficient of nonatetraene is 11.7% greater than that of nonadiene. Finally, 3,6-dimethylene-1,7-octadiene has an extinction coefficient 71% greater than that of 3-methylene-1-octene.

Nonatetraene shows the broadest ultraviolet spectrum and also shows the least increase in extinction coefficient. The broadness of the absorption band is an indication of the number of possible electronic transitions and the extinction coefficient is an indication of the probability of transition. As the number of possible transitions increases, the probability for any given transition decreases. Hence, nonatetraene with its broad band has a lower extinction coefficient than dodecatetraene or 3,6-dimethylene-1,7-octadiene with their narrow absorption bands.

The preceding data on the ultraviolet spectra of the dienes and tetraenes is taken to be an indication that in the tetraenes, the butadienyl systems interact with each other. On the basis of this evidence, it seems likely that in the polymerization of 1,6-dienes the double bonds are placed in a conformation suitable for cyclopolymerization by a ground-state interaction between the double bonds. Thus the polymerization would involve attack of an initiating species on a molecule which is already in the cyclic conformation. This would explain the great tendency of 1,6-dienes to cyclopolymerize.



Experimental

Source and Purification of Materials.—Triphenylphosphorus was obtained from Peninsular ChemResearch, Inc. A 15% solution of *n*-butyllithium in hexane was obtained from Foote Mineral Co. Distillation Products Industries Division of Eastman Kodak Co. furnished the 1,3-dibromopropane and the acrolein that were used. Nonaldehyde was obtained from Chemical Procurement Laboratories. Aldrich Chemical Co. furnished the 1,6-dibromohexane used. Fisher Scientific Co. supplied N-bromosuccinimide and *n*-butyl bromide. Samples of 3-bromo-2,5-dihydrothiophene 1,1-dioxide were obtained from Phillips Chemical Co. The materials were used without further purification.

Equipment and Data.—Temperatures reported in this paper are uncorrected. Infrared data were obtained with a Perkin-Elmer Infracord recording spectrophotometer. Ultraviolet data were obtained with a Cary Model 14 recording spectrophotometer. Gas-liquid chromatographic analyses were made with a Wilkens Aerograph Model A-110-C gas chromatographic instrument using helium as the eluent gas. Unless otherwise stated, g.l.c. analyses were made on a 5-ft. column packed with diethylene glycol succinate on firebrick. N.m.r. data were obtained with a Varian DP-60 n.m.r. spectrometer at a frequency of 56.4 Mc. Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tenn.

Synthesis of 1,3,9,11-Dodecatetraene.—1,3,9,11-Dodecatetraene was prepared by the method of Hauser, *et al.*,[10] yield 12%, b.p. 71–73° (2 mm.), $n^{20}\text{D}$ 1.5043, $d^{20}{}_4$ 0.862. The compound exhibited the following absorptions in the infrared: 3100 (m), 3040 (m), 2970 (s), 2880 (m), 1680 (m), 1580 (m), 1460 (m), 1440 (m), 1370 (w), 1290 (w), 1250 (w), 998 (s), 962 (m), 950 (m), 905 (s), and 787 (m) cm.$^{-1}$.

1,3-Dodecadiene was prepared *via* the Wittig synthesis as follows. A stirred slurry of 37.8 g. (0.1 mole) of allyltriphenylphosphonium bromide in 1 l. of ethyl ether was treated with 62 ml. (0.1 mole) of *n*-butyllithium in hexane. This was stirred 2.5 hr. under a nitrogen atmosphere. The mixture was cooled in an ice bath and 14.2 g. (0.1 mole) of nonylaldehyde in 100 ml. of ethyl ether was added in 30 min. A yellow color persisted when all the aldehyde had been added. Ammonium chloride (5.5 g.) in 150 ml. of water was added, and the mixture was stirred while it warmed to room temperature. The ether layer was separated, washed with water, dried over magnesium sulfate, and distilled through a 25-cm. stainless steel packed column. The residue was distilled through a 50-cm. spinning-band column, yield 2.5 g., b.p. 56° (1 mm.). The diene was purified on a silicone preparatory column by g.l.c. The yield of pure compound was 1.5 g. (0.015 mole, 15%), b.p. 56° (1 mm.), $n^{20}\text{D}$ 1.4594, $d^{20}{}_4$ 0.778; lit.[19] b.p. 101° (13 mm.), $n^{20}\text{D}$ 1.4612, $d^{20}{}_4$ 0.7803. Comparative ultraviolet data for the diene and tetraene are shown in Table I.

Anal.[19] Calcd. for C_9H_{16}: C, 86.7; H, 13.3. Found: C, 86.89; H, 13.16.

Synthesis of 1,3,6,8-Nonatetraene and 1,3-Nonadiene.—1,3-Nonadiene and 1,3,6,8-nonatetraene were prepared *via* the Wittig reaction according to the procedure of Hauser, *et al.*[10] 1,3-Nonadiene was obtained in 34% yield and exhibited characteristic infrared absorption bands at 1650, 1600, 1000, 955, and 905 cm.$^{-1}$. A single peak was observed upon g.l.c. analysis. 1,3,6,8-Nonatetraene was obtained in 12% yield and the pure compound exhibited characteristic infrared absorption bands as follows: 3100 (m), 3040 (s), 3000 (m), 2940 (m), 1820 (w), 1640 (m), 1580 (w), 1430 (s), 1290 (w), 1260 (w), 996 (s), 975 (s), 963 (m), 940 (s), 828 (w), and 780 (m) cm.$^{-1}$. By g.l.c. analysis, the distilled product was found to have an impurity to the extent of approximately 30%. By use of a silicone preparatory column the two components were separated and identified. The minor

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(18) L. C. Jones, Jr., and L. W. Taylor, *Anal. Chem.*, **27**, 228 (1955).

(19) K. Zeigler, *et al.*, *Ann.*, **551**, 80 (1942).

component was shown by infrared and other physical properties to be 1,3,5,7-nonatetraene, and the major component to be 1,3,6,8-nonatetraene. The pure compound possessed the following physical properties: b.p. 52° (20 mm.), n^{20}_{D} 1.5417, d^{20}_{4} 0.796. Comparative ultraviolet data for these compounds are shown in Table I and Figure 1.

Synthesis of 2-(bromomethyl)butadiene was accomplished in 88% yield according to the procedure of Krug and Yen.[11]

Synthesis of 3,6-Dimethylene-1,7-octadiene.—Magnesium (3.5 g., 0.15 g.-atom, freshly ground under ether) and 20 ml. of ethyl ether were added to a three-necked flask equipped with stirrer, reflux condenser, and constant-pressure addition funnel. The flask was flushed with nitrogen. About 30 ml. of a solution of 30.7 g. (0.21 mole) of 2-(bromomethyl)butadiene in 200 ml. of ethyl ether was added; the mixture was heated to reflux for 15 min. The remainder of the solution was added over a 1.5-hr. period at room temperature. The ether refluxed gently during addition. It was stirred an additional 0.5 hr. The flask was cooled in ice and 27 g. (0.5 mole) of ammonium chloride in 200 ml. of water was added slowly. This was stirred 30 min., and then the ether layer was separated, washed with water, and dried over magnesium sulfate.

The ether layer was distilled through a 25-cm. stainless steel packed vacuum-jacketed column. The residue was distilled through a 50-cm. spinning-band column, yielding 8.8 g. (62%), b.p. 64–65° (22 mm.), n^{20}_{D} 1.4934, d^{20}_{4} 0.7898. Infrared data showed the following absorptions: 3100 (m), 2950 (m), 1790 (m), 1630 (m), 1590 (s), 1460 (m), 1440 (m), 1420 (m), 1390 (m), 1380 (m), 1320 (w), and 1290 (w) cm.$^{-1}$. Ultraviolet data are found in Table I.

Anal. Calcd. for $C_{10}H_{14}$: C, 89.5; H, 10.5. Found: C, 89.72, 89.27; H, 10.43, 10.58.

Synthesis of 3-Methyleneoctene.—Magnesium (4.5 g., 0.19 g.-atom), a small crystal of iodine, and 20 ml. of ethyl ether were placed in a three-necked flask equipped with stirrer, reflux condenser, and a constant-pressure addition funnel. The flask was flushed with nitrogen. A solution (10 ml.) of 27.4 g. (0.2 mole) of *n*-butyl bromide in 180 ml. of ethyl ether was added, and the reaction started easily. The remainder was added over a period of 30 min. at room temperature. Then 14.8 g. (0.1 mole) of 2-(bromomethyl)butadiene in 30 ml. of ethyl ether was added slowly while the flask was cooled in ice water. Ammonium chloride (0.2 mole) in 150 ml. of water was added slowly while the flask was still being cooled. The ether layer was washed with water and dried over magnesium sulfate. The ether was distilled through a 25-cm. stainless steel packed column, and the residue was distilled through a spinning-band column yielding 4.6 g. (37%), b.p. 60° (38 mm.). The infrared spectrum showed the following absorptions: 3100 (m), 2940 (s), 2880 (s), 1790 (w), 1630 (w), 1580 (s), 1470 (m), 1380 (m), 1220 (w), 1110 (w), 1030 (w), 990 (s), 893 (s), 760 (s), and 730 (w) cm.$^{-1}$. Ultraviolet data are found in Table I.

Anal. Calcd. for C_9H_{16}: C, 87.0; H, 13.0. Found: C, 87.16; H, 13.17.

A Direct Method for the Construction of Benzene Rings

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Reaction of 1,4-diacetoxybutadiene with dienophiles at elevated temperatures yields, in many cases, aromatic products resulting from elimination of acetic acid from the first-formed Diels–Alder adducts. This reaction provides a direct synthesis of benzene rings, especially useful in the synthesis of unsymmetrical biphenyls. Dienophiles used successfully include quinones, β-nitrostyrenes, chalcones, and acetylenes. The reaction of acetylenic dienophiles with 1-acetoxybutadiene also affords aromatic products. The adduct of 1,4-diacetoxybutadiene and benzonorbornadiene did not aromatize below temperatures of 450°, and then only with rearrangement, to yield dibenzocycloheptatriene.

Practical methods for the construction of benzene rings, especially on the base of an existing molecule, are rare and have not played any significant role in the synthesis of complex molecules.

We wish to report a simple and direct method of assembling a benzene ring from a dienophilic double bond, a method which makes possible the synthesis of a variety of aromatic compounds and which is particularly valuable for the preparation of unsymmetrical biphenyls. The synthesis is based on the addition of *trans,trans*-1,4-diacetoxybutadiene (I) to dienophiles. Diels–Alder adducts of structure II might be expected to aromatize readily by thermal elimination of acetic acid; indeed, several observations of such aromatizations have been noted.[2] We have found that heating various dienophiles with I, generally at temperatures of 110–120° for several days, often leads directly to aromatized products[3] (III). Table I lists representative examples.

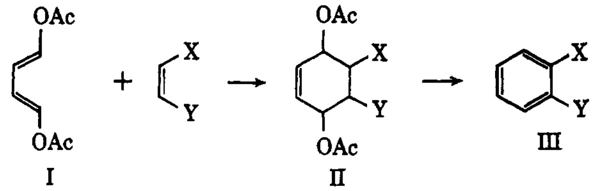

TABLE I

AROMATIC PRODUCTS FROM THE REACTION OF 1,4-DIACETOXYBUTADIENE WITH DIENOPHILES

Dienophile	Product	Yield, %
p-Benzoquinone	1,4-Naphthoquinone	73
	9,10-Anthraquinone	8
1,4-Naphthoquinone	9,10-Anthraquinone	45
β-Nitrostyrene	2-Nitrobiphenyl	20
3,4-Methylenedioxy-β-nitrostyrene	3,4-Methylenedioxy-2′-nitrobiphenyl	45
3,4-Dimethoxy-β-nitrostyrene	3,4-Dimethoxy-2′-nitrobiphenyl	26
Benzalacetophenone	2-Benzoylbiphenyl[a]	24
Benzonorbornadiene	1,2,5,6-Dibenzocycloheptatriene[a]	31
Dimethyl acetylenedicarboxylate	Dimethyl 3-acetoxyphthalate[b]	49
Phenylpropiolic acid	2-Phenyl-3-acetoxybenzoic acid	28

[a] The primary Diels-Alder adduct was isolated in this case and separately aromatized by heating at 575–600°. [b] Isolated as 3-hydroxyphthalic acid.

Quinones.—Quinones react readily with I, as had been noted previously for juglone.[2b] *p*-Benzoquinone, heated with 1 molar equiv. of I, gave a 73% yield of

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[2] (a) R. Criegee, W. Hörauf, and W. D. Schellenberg, *Chem. Ber.*, **86**, 126 (1953); (b) H. H. Inhoffen, J. Heimann-Trosien, H. Muxfeldt, and H. Krämer, *ibid.*, **90**, 187 (1957).

[3] Some of these results have been reported in a preliminary communication: R. K. Hill and R. M. Carlson, *Tetrahedron Letters*, 1157 (1964).