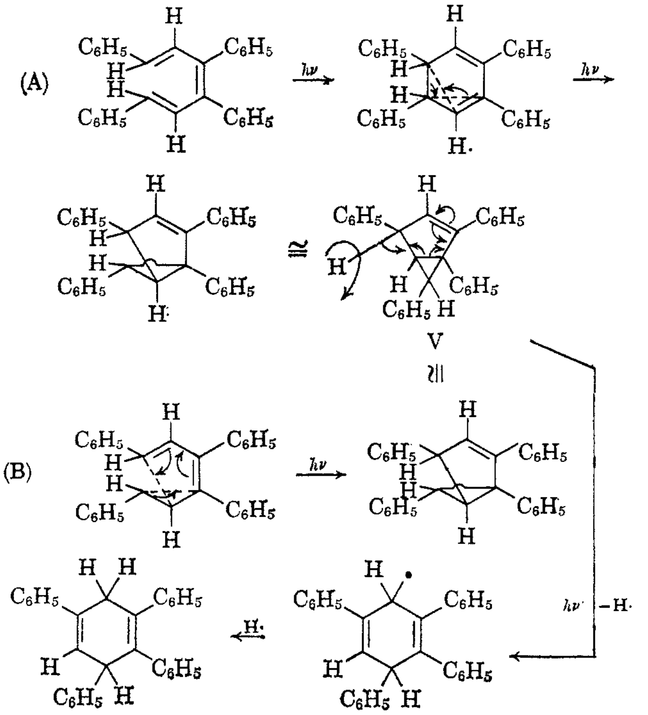
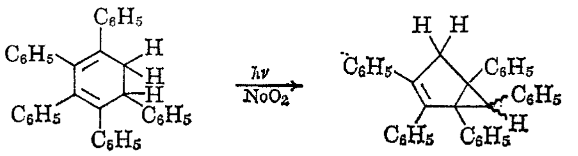
Scheme II



Evanega[12] has reported the photochemical rearrangement of 1,2,3,4,5-pentaphenyl-1,3-cyclohexadiene to produce a compound analogous with the proposed intermediate V, but which apparently was stable to further irradiation. The driving force for further reaction of the proposed intermediate V may be the formation of the conjugated stilbene moiety in the product.



Experimental Section

Preparation of 1,3,4,6-Tetraphenylhexatriene.—2,3-Diphenyl-2,3-butanediol was prepared by the reaction of benzil with 2 equiv of methylmagnesium iodide according to the procedure of Johlin.[13] The butanediol was converted into 2,3-diphenylbutadiene by vacuum distillation from potassium hydrogen sulfate.[14]

2,3-Diphenylbutadiene was then brominated to yield bisbromomethyl stilbene according to the method of Allen.[15]

A mixture of 6.0 g (0.016 mole) of bisbromomethylstilbene and 5.5 g (0.033 mole) of triethylphosphite was heated to a slow reflux for 1 hr. A small amount of ethyl bromide was then distilled off, and the pot temperature was raised to 190–200° for 1 additional hr. The yellow solution was cooled to room temperature, 40 ml of dimethylformamide was added, and the contents of the flask were poured into a 125-ml flask containing 1.9 g of sodium methoxide (0.035 mole). The deep red solution formed was cooled in an ice bath with swirling for 5 min. Benzaldehyde (3.5 g, 0.033 mole) was added dropwise with continued cooling. The reaction flask was then allowed to stand at room temperature for 25 min. A solution of 10 ml of methanol and 20 ml of water was then added to the reaction mixture and the flask was shaken for 1 min. The resulting yellow solid was filtered, washed with water and methanol, and recrystallized from methylcyclohexane to yield 3.7 g (48% based on bisbromomethyl stilbene) of pale yellow crystals, mp 176–178°.

Anal. Calcd for $C_{30}H_{24}$: C, 93.71; H, 6.29; mol wt, 384. Found: C, 93.61; H, 6.13; mol wt (osmometer, diphenyl mercury in monoglyme standard), 350, 361.

The ultraviolet absorption spectrum in *p*-dioxane showed λ_{max} 247 mμ (ε 13,6000), 253 (13,300), 270 (14,600), 353 (49,000), 368 (65,600), and 386 (50,000).

Cyclodehydrogenation of 1,3,4,6-Tetraphenylhexatriene.—A mixture of 0.2 g of 1,3,4,6-tetraphenylhexatriene and 0.05 g of 10% palladium–charcoal was refluxed in mesitylene for 20 hr. The solution was filtered and the solvent was evaporated. The solid residue was recrystallized from benzene–methanol to yield 0.12 g of 1,2,4,5-tetraphenylbenzene, mp 270–271°. The melting point, mixture melting point, and ultraviolet absorption spectrum were identical with those of an authentic sample prepared according to the method of Dilthey[8] from 3,4-diphenylcyclopentadienone and diphenylacetylene. The ultraviolet absorption spectrum in *p*-dioxane showed λ_{max} 253 mμ (ε 56,000).

Irradiation of 1,3,4,6-Tetraphenylhexatriene.—A solution of 1.0 g of 1,3,4,6-tetraphenylhexatriene in 400 ml of methylcyclohexane was set in the sunlight in a stoppered Pyrex flask for 8 days during which time the yellow solution became nearly colorless. Evaporation of the solvent yielded a faintly yellow solid which was recrystallized from ethanol to yield 0.82 g of 1,2,3,5-tetraphenyl-1,4-cyclohexadiene as colorless crystals, mp 144–145°. Concentration of the mother liquor yielded an additional 0.05 g of the same material, yield 87%.

Anal. Calcd for $C_{30}H_{24}$: C, 93.71; H, 6.29; mol wt, 384. Found: C, 93.50; H, 6.36; mol wt (osmometer, diphenylmercury in monoglyme standard), 364.

The ultraviolet absorption spectrum in *p*-dioxane showed λ_{max} 238 mμ (ε 23,800). The nmr spectrum (ppm) gave phenyl protons centered about τ 3.0, doublet at 4.3, doublet at 5.9, and a singlet at 7.7; integration 20:1:1:2.

The irradiation was also carried out with a Westinghouse sunlamp for 40 hr, and produced the same results.

Dehyrogenation of 1,2,3,5-Tetraphenyl-1,4-cyclohexadiene.—A mixture of 0.3 g of 1,2,3,5-tetraphenyl-1,4-cyclohexadiene and 0.1 g of 10% palladium–charcoal was refluxed in 15 ml of mesitylene for 17 hr. The solution was filtered and the solvent was evaporated. The residue was taken up in 5 ml of ethanol and warmed to dissolve some dark residue. The remaining tan crystals were filtered and recrystallized from benzene–methanol to yield 0.13 g of 1,2,3,5-tetraphenylbenzene, mp 224–225°. The melting point, mixture melting point, and ultraviolet absorption spectrum were identical with those of an authentic sample prepared according to the methods of Woods.[9]

Acknowledgment.—The authors wish to thank the National Science Foundation for its support and encouragement in the form of Grant GP 1984.

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(13) J. Johlin, *J. Am. Chem. Soc.*, **39**, 291 (1917).

(14) K. Alder and J. Haydn, *Ann.*, **570**, 212 (1950).

(15) C. Allen, C. Eliot, and A. Bell, *Can. J. Res.*, **17B**, 80 (1939).

The Electron Spin Resonance Spectrum of the 9-Nitrotriptycene Anion Radical

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The question of transannular interaction between the benzene rings in triptycene has prompted several workers[1–3] to examine the ultraviolet spectrum of the compound. While an electron spin resonance (esr) spectroscopic study of the triptycene anion radical would have an obvious bearing on this question such a study has not been reported. DeGroot and van der Waals[4] have studied the lowest triplet state of triptycene by magnetic resonance and report that

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

(2) C. F. Wilcox, Jr., *J. Chem. Phys.*, **33**, 1874 (1960).

(3) C. F. Wilcox, Jr., and A. C. Craig, *J. Org. Chem.*, **26**, 2491 (1961).

(4) M. S. DeGroot and J. H. van der Waals, *Mol. Phys.*, **6**, 545 (1963).

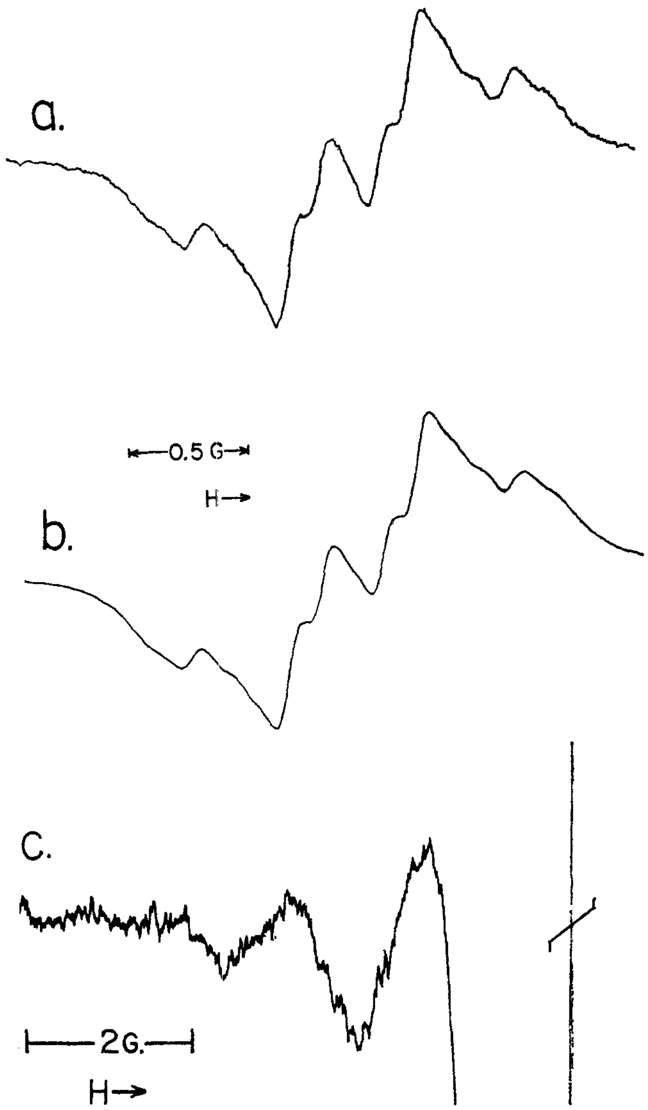
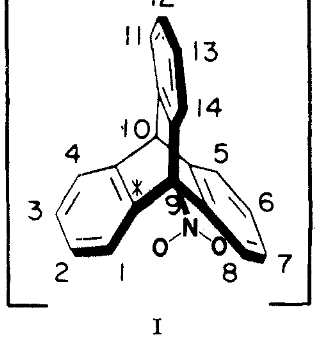


Figure 1.—Esr spectrum. (a) Low-field one-third of esr spectrum of the 9-nitrotriptycene anion radical, approximately 1 m*M*, in dimethylformamide. (b) Computed spectrum based on coupling constants of 0.41 and 0.15 gauss, each for three equivalent protons, and line width of 0.18 gauss (Lorentzian line shape). (c) Low-field one-sixth of esr spectrum of the 9-nitrotriptycene anion radical under conditions of high gain.

intramolecular excitation transfer between the benzene rings occurs at a rate $\gg 10^{10}$ sec^{-1}.

As a matter of ancillary interest, the authors have examined the esr spectrum of the 9-nitrotriptycene anion radical (I) and measured five isotropic hyperfine coupling constants for the radical including two ^{13}C constants.



I

9-Nitrotriptycene undergoes a reversible one-electron reduction in dimethylformamide with $E_{1/2} = -1.31$ v *vs.* aqueous-saturated calomel electrode and a current constant (measured at maximum current) of 2.7 μa mg$^{-2/3}$ sec$^{1/2}$ mM^{-1}. The anion radical I as prepared by *intra muros* electrochemical reduction[5] of 9-nitrotriptycene in dimethylformamide solution was stable for a period of several hours.

The esr spectrum of I in dimethylformamide solution exhibits a predominant ^{14}N splitting of $|25.3| \pm 0.2$ gauss. As is usually the case with nitroaromatic anion radicals, the low-field component of the ^{14}N triplet was better resolved than the remaining components. Proton coupling constants of $|0.41| \pm 0.03$ and $|0.15| \pm 0.02$ gauss, each for three equivalent protons, have been assigned on the basis of the further hyperfine structure shown in Figure 1a. The validity of this assignment is supported by the close agreement of Figure 1a with the simulated spectrum shown in Figure 1b. The ^{13}C satellites, Figure 1c, observed at high gain for a 2.9 m*M* solution were assigned to coupling constants of $|7.5|$ (0.5% as intense as the parent line) and $|4.3|$ gauss (1.5% as intense as the parent line). A signal 0.7% as intense as the parent line was attributed to a ^{15}N coupling constant of $|35.5|$ gauss.

The large ^{14}N coupling constant observed for I is closely comparable with the range of nitrogen coupling constants (23.8–25.7 gauss) observed by Piette, Ludwig, and Adams for a series of nitroalkane anion radicals.[6,7] The magnitude of a_N for I is the basis for asserting that almost all of the unpaired spin density is localized on the nitro group.

The assignment of the 7.5-gauss ^{13}C coupling constant to the C_9 atom of I is based on (a) the agreement of the relative line intensity, 0.5%, with a calculated value of 0.55% for a single equivalent carbon atom, and (b) the proximity of the C_9 to the large π-electron spin density on the adjacent nitro group. Unfortunately, similar data for the nitroalkane anion radicals are not available for comparison. This coupling constant appears to be the first measured for an essentially sp^3 hybridized carbon atom bonded directly to a center of substantial π-electron spin density.[8] Although a detailed theoretical analysis has not been done for this case, it is interesting to note that the ^{13}C constant for a hypothetical tetrahedral methyl radical has been estimated at *ca.* 300 gauss.[9]

Assignment of the 4.3-gauss ^{13}C coupling constant to the ring carbon position indicated in I by the asterisk, a position of threefold degeneracy, is consistent with the relative intensity of the ^{13}C line, *i.e.*, 1.5%, as compared with a theoretical value of 1.66%.[10] The theoretical interpretation of ^{13}C coupling constants

(5) D. H. Geske and A. H. Maki, *J. Am. Chem. Soc.*, **82**, 2671 (1960).

(6) L. H. Piette, P. Ludwig, and R. N. Adams, *ibid.*, **83**, 3909 (1961); **84**, 4212 (1962).

(7) Compare also the value of 26.45 gauss for the 2-methyl-2-nitropropane anion radicals as reported by A. K. Hoffman, W. G. Hodgson, and W. H. Jura [*J. Am. Chem. Soc.*, **83**, 4676 (1961)].

(8) The bond angles about C_9 and C_{10} presumably are only slightly distorted from the value for a normal tetrahedron; see W. Theilacker and W. H. Beyer, *Chem. Ber.*, **94**, 2968 (1961).

(9) T. Colé, H. O. Pritchard, N. R. Davidson, and H. M. McConnell, *Mol. Phys.*, **1**, 406 (1958).

(10) This is not an unequivocal assignment since there are five other carbon sites with threefold degeneracy.

proposed by Karplus and Fraenkel[11] would not be applicable to this case.

We do not have an unequivocal basis for assigning the two-proton coupling constants of 0.41 and 0.15 gauss to particular ring positions. *Assuming* that both coupling constants are negative, and taking the value of $Q_{CH}{}^{H}$ as -24 gauss, the unpaired spin density on the three rings totals 0.07. It is interesting to note that protons attached to carbon atoms *two* bonds away from the nitro group in the nitroalkane anion radicals[6] do show splittings of 0.24 gauss.

Experimental Section

The sample of 9-nitrotriptycene used in this work was provided by Professor W. Theilacker.[12] Details of electrochemical and esr instrumentation have been described previously.[13]

Acknowledgment.—The authors acknowledge the preliminary studies of I by Mr. Alan Balch. This work was supported by National Science Foundation grant GP-4906 as well as through GP-1687 for partial support for purchase of the esr spectrometer. P. H. H. was supported in this work as a participant in the National Science Foundation Undergraduate Research Participation Program.

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[11] M. Karplus and G. K. Fraenkel, *J. Chem. Phys.*, **35**, 1312 (1961).

[12] W. Theilacker, U. Berger-Brose, K.-H. Beyer, *Chem. Ber.*, **93**, 1658 (1960). Infrared, ultraviolet, and nmr studies of 9-nitrotriptycene were subsequently reported by W. Theilacker, A. Konrad, and H. Uffman, *ibid.*, **98**, 428 (1965).

[13] K. Kuwata and D. H. Geske, *J. Am. Chem. Soc.*, **86**, 2101 (1964).

Structural Directivity in Diene Syntheses. I. Addition of Monosubstituted Acetylenes to Ethyl 1,3-Cyclohexadiene-1-carboxylate

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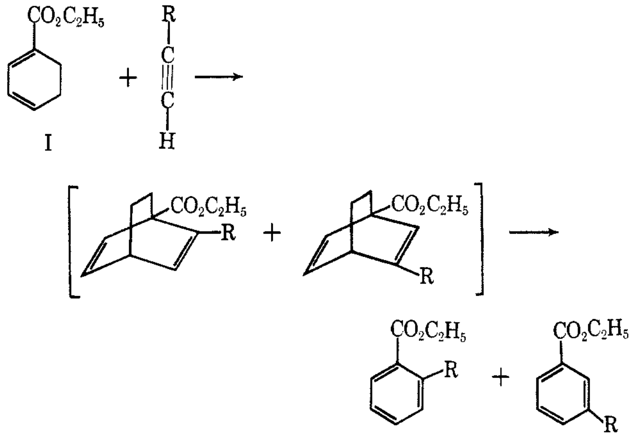
Few data are available on structural directivity in diene syntheses involving cyclic dienes. In the addition of unsymmetrical dienophiles to 9-substituted anthracenes, the ratio of "*ortho*" to "*meta*" products varies from exclusive formation of "*ortho*" isomer to complete predominance of "*meta*" isomer.[2] Completely different ratios of the structural isomers could be obtained even when the substituents in the reactants had similar electronic and steric characteristics. Kazan and Greene[3] have condensed ethyl 1,3-cyclohexadiene-1-carboxylate (I) with ethyl acrylate and obtained all four possible adducts with the "*ortho*" one predominating in a ratio of 35:9. We wish to present some data using monosubstituted acetylenes and I. It was hoped that these additions would provide syntheses of bridgehead-substituted bicyclo[2.2.2]octadienes; however, aromatization occurred at the conditions necessary for reaction.[4]

Compound I added to phenylacetylene, ethyl propiolate, and propyne to give monosubstituted aromatic esters. Mixtures of *ortho* and *meta* isomers were obtained in the following ratios (*ortho*:*meta*): R = C_6H_5, 3.4:1.0; R = $CO_2C_2H_5$, 0.96:1.0; R = CH_3, 1.0:3.2. Kazan and Greene[3] observed predominantly "*ortho*" orientation in the addition of I to ethyl acrylate. The related dienophile, ethyl propiolate, gave almost equal amounts of *ortho* and *meta* isomers. This considerable loss in selectivity is expected since a much higher temperature for reaction was used.



$R = C_6H_5, CO_2C_2H_5, CH_3$

Mechanisms which have been proposed for Diels–Alder reactions are a heterolytic process with polarization orientation of the addends and a homolytic process involving a biradical transition state.[5] An ionic mechanism is improbable since the reactions took place in the vapor phase. A biradical transition state should favor production of *ortho* isomer.[6] Steric repulsion of the substituents in the adduct should favor *meta* orientation.[7] The orienting power observed is determined by an interaction between electronic and steric effects in I and the dienophiles.

Ethyl benzoate was formed during each adduction (evidently due to aromatization of I). Dimer was produced when I was heated in benzene solution. Reversible dimerization probably occurred during each adduction; however, only the irreversibly formed aromatized adducts were isolated.

Experimental Section[8]

Product structures were determined by nmr and vpc comparisons with authentic samples. Product distribution was determined by gas chromatographic analysis.

Diels–Alder Reactions of Ethyl 1,3-Cyclohexadiene-1-carboxylate (I) with Acetylenes.—Solutions of 50 mmoles of I,[9] an

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[1] National Science Foundation Undergraduate Research Participant (Grant No. GY-38).

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[7] I. N. Nazarov, Y. A. Titov, and A. I. Kuznetsova, *Dokl. Akad. Nauk SSSR*, **124**, 586 (1959); *Chem. Abstr.*, **53**, 11268 (1959).

[8] Nmr spectra were obtained with tetramethylsilane as the internal standard using a Varian Model A-60 spectrometer. The gas chromatographic analyses were performed on an F & M Model 500, programmed-temperature gas chromatograph, using a 6-ft silicone gum rubber column. Infrared spectra were obtained from a Perkin-Elmer Model 21 infrared spectrometer. Microanalysis was performed by Spang Microanalytical Laboratory, Ann Arbor, Mich.

[9] C. A. Grob, M. Ohta, E. Renk, and A. G. Weiss, *Helv. Chim. Acta*, **41**, 1191 (1958).