mately 70° a vigorous evolution of gas was observed and after heating for 17 hr. at 90°, the reaction mixture was cooled, and the excess thionyl chloride was decomposed with ice. The upper layer was separated and combined with ether extracts of the lower layer, washed successively with cold saturated sodium bicarbonate solution (three times) and with water (once), dried over anhydrous magnesium sulfate, and distilled to give (+)-1-chloro-2-phenylbutane, b.p. 74–75° (4 mm.), 110.4 g. (81%), $[\alpha]^{28}_{\text{D}}$ +5.75 ± 0.01° (neat, l = 1), 97.7% optically pure based on its conversion to (+)-2-phenylbutane.

Asymmetric Reductions.—The Grignard reagent was prepared under purified nitrogen from (+)-1-chloro-2-phenylbutane in anhydrous ether (or tetrahydrofuran) in the usual manner[3,4] using highly purified magnesium.[16] An aliquot of this Grignard solution (about 0.06 mole of an 0.2 M solution) was added dropwise with stirring to the solution of alkyl phenyl ketone (about 0.06 mole in 25 ml. of ether or tetrahydrofuran) maintained in water bath at the specified temperature. The runs reported in Table I in ether solvent, with the exception of the first, used (+)-1-chloro-2-phenylbutane described earlier, $[\alpha]^{28}_{\text{D}}$ +5.75° (neat, l = 1). The runs in tetrahydrofuran were made with a sample of (+)-1-chloro-2-phenylbutane with $[\alpha]^{27.5}_{\text{D}}$ +5.55°. A suitable correction for the optical purity of the Grignard reagent, as determined by conversion to the (+)-2-phenylbutane, is made in the calculated per cent asymmetric reduction. After 18 hr., the reaction mixture was hydrolyzed with an ice-cold ammonium chloride solution. The ether layer was combined with several ether extracts of the aqueous layer and dried over magnesium sulfate. The ether extracts were fractionated through a short column, and the fractions were analyzed with an Aerograph A-90 vapor phase chromatograph. The carbinol fraction was then purified on a Beckman Megachrom preparative gas chromatograph fitted with a 12-ft. 10% Ucon Polar column, using helium as the carrier gas. Under a vacuum of less than 1 mm. the carbinol was distilled from the collection trap into a specially designed centrifuge tube. The purity of the alcohol was then established on an Aerograph A-90 gas chromatograph. The results are summarized in Table I.

(+)-**2-Phenylbutane.**—An aliquot of the prepared Grignard reagent from (+)-1-chlorophenylbutane (0.04 mole) was added to an ice-cold solution of ammonium chloride, and the mixture extracted with ether. The ether extracts were washed with saturated brine, dried over anhydrous magnesium sulfate, and distilled to give (+)-2-phenylbutane, b.p. 31–33° (4 mm.), 4.11 g., $[\alpha]^{26}_{\text{D}}$ +23.76 ± 0.02° (neat, l = 1).[17] Analysis by gas chromatography failed to detect any impurity.

Acknowledgment.—We are indebted to Professor Kurt Mislow for valuable discussions concerning these experiments.

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[16] We gratefully acknowledge a gift from Dow Chemical Co. of sublimed magnesium with the following upper limits of elemental impurities in parts per million: Al, 1; Cu, 1; Fe, 4; Mn, 2; Ni, 4; Pb, 10; Si, 10; Sn, 10; Zn, 100; Ba, 1; Ca, 18; K, 5; Na, 6; Sr, 1.

[17] This value is 97.7% of the maximum value of $[\alpha]^{28}_{\text{D}}$ 24.3° (neat, l = 1) reported by Cram.[11] Based on this hydrocarbon value the Grignard reagent and the chloride from which it was prepared will be considered 97.7% optically pure.

Alicyclic Syntheses. I. The Diels–Alder Reaction of 2-Phenylbutadiene with Citraconic Anhydride and 5-*p*-Tolylthiotoluquinone

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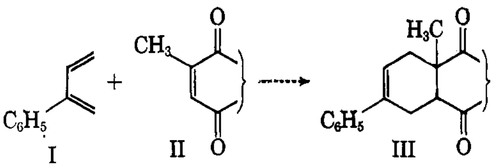
The identity of the adduct of 2-phenyl-1,3-butadiene and citraconic anhydride has been established as *cis*-1-methyl-4-phenyl-1,2,3,6-tetrahydrophthalic acid (IV), contrary to what would have been predicted from a consideration of polar factors. The significance of this and related Diels–Alder reactions is discussed and a mechanism to account for the results is propounded. The stereochemical configurations of the hydrogenation products VII and IX of the adduct IV and of its *trans* isomeride VIII, respectively, have been assigned on the basis of a conformation analytical argument. Use of an arylthiotoluquinone X has been made in an analogous addition to phenylbutadiene to force the generation of angularly methylated decalin systems XI, XII, XIII. Substance XI was desulfurated and reduced in one operation with zinc–acetic acid. Substances XII and XIII were desired as models in the synthesis of steroids lacking ring B.

It was desired to acquire an understanding of the mode of addition of 2-phenyl-1,3-butadiene to unsymmetrical dienophiles of the type II as an introduction to projected syntheses of substances incorporating part structure III. Such structures bearing a 1,4-arylmethyl relationship were desired in projected syntheses[2] of 19-nor steroidal compounds lacking ring B.



Subsequent to the inception of this work, there have appeared disclosures of similar activity from other laboratories aimed at the synthesis of such substances,[3] and one case, that of estrone and estradiol lacking ring B,[4] was shown to possess considerable estrogenic activity.

2-Phenyl-1,3-butadiene[5] was treated with citraconic anhydride, and the product was isolated in good yield more conveniently as the diacid. The orientation of the angular methyl group and the identity of the adduct as *cis*-1-methyl-4-phenyl-1,2,3,6-tetrahydrophthalic acid (IV) were established as follows.

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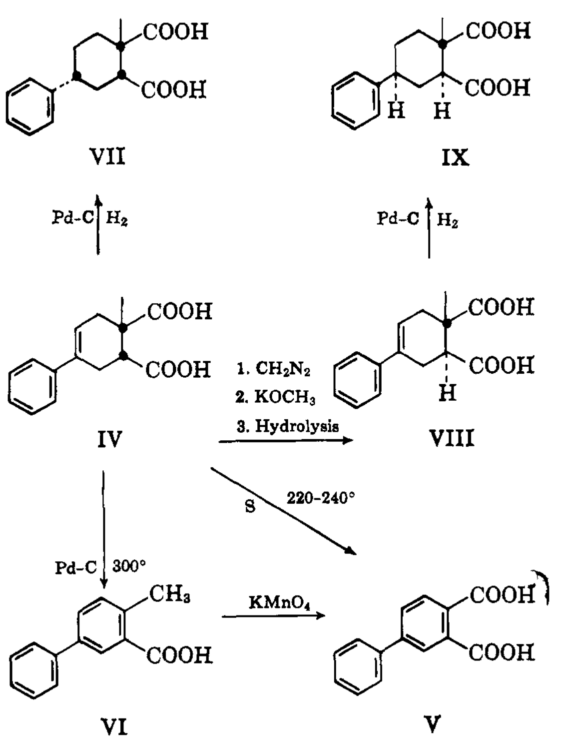
[2] Additionally, polycyclic substances containing styryl moieties and available by Diels–Alder reactions were desired to test the acid-catalyzed benzyl hydroperoxide transformation of such to oxo derivatives in another synthetic problem. The facile conversion of α-methylstyrene or the derived tertiary alcohol or chloride therefrom to phenol and acetone by Kharasch and co-workers, *J. Org. Chem.*, **15**, 748 (1950), and later papers [see also H. Kwart and R. T. Keen, *J. Am. Chem. Soc.*, **81**, 943 (1959), for a related transformation] suggested the possibility of utilizing such a sequence in synthetic work to introduce carbonyl groups at sites suitably earmarked initially as styryl functions. This scheme, an additional portion of which is presented in paper II of this series, V. Georgian and J. Lepe M., *J. Org. Chem.*, **29**, 45 (1964), is under investigation.

[3] A. J. Birch, E. Pride, and H. Smith *J. Chem. Soc.*, 4688 (1958); R. H. Jaeger, *Tetrahedron*, **2**, 326 (1958).

[4] F. C. Novello, U. S. Patent 2,886,589 (May 12, 1959).

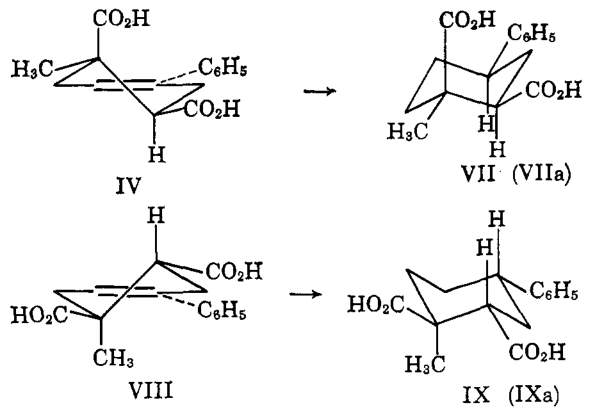
[5] C. C. Price, F. L. Benton, and C. J. Schmidle, *J. Am. Chem. Soc.*, **71**, 2860 (1949).



The Diels–Alder product as the free acid, when dehydrogenated with sulfur at 220–240°, was found to have lost the angular methyl group with the production of 4-phenylphthalic acid (V).[6] The methyl group was retained, however, when the dehydrogenation was conducted at 300° over 10% palladium–charcoal,[7] and a phenyltoluic acid of m.p. 211–212° was obtained. This was not identical with the known 2-methyl-4-phenylbenzoic,[6] which would have arisen had the diene addition proceeded in the alternative manner. The structure VI for this acid was confirmed on conversion to 4-phenylphthalic acid (V) by permanganate oxidation.

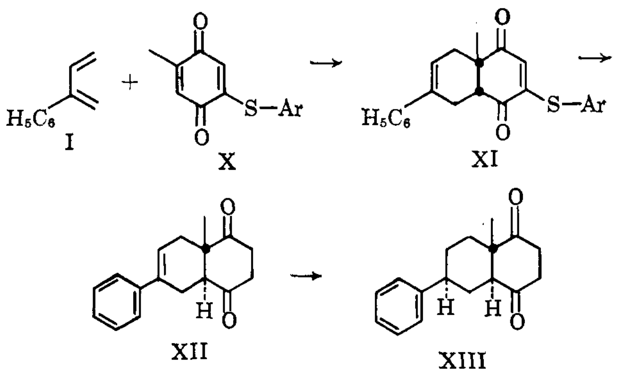
In addition to the correspondence of structure IV to partial structure III, another desirable feature of the former is its ability to be transformed to a *trans* oriented diacid, which could serve as a point of departure in syntheses of steroidal models lacking ring B and requiring *trans* C/D (homo) ring fusion. Indeed, the dimethyl ester of IV was isomerized on being refluxed with potassium methoxide,[8] and subsequently hydrolyzed to yield about 70% of the *trans*-1-methyl-4-phenyl-1,2,3,6-tetrahydrophthalic acid (VIII). Approximately 20% of the *cis* compound (IV) was recovered.

Each of the unsaturated acids IV and VIII was hydrogenated over palladium–charcoal to the corresponding methylphenylhexahydrophthalic acids VII and IX. Although no rigorous proof is available for the stereochemical configurations of the hydrogenation products, those depicted in formulas VII (VIIIa) and IX (IXa) are suggested as reasonble and are derived from a consideration in each case of the most favorable conformation offering least steric hindrance to the catalyst surface. For the cyclohexene systems, the minimum energy half-chair conformations[9] are selected bearing the smallest number of axial substituents (other than hydrogen) with catalyst approach from the least hindered side.[10]



To approach closer to the objectives set forth earlier in this paper, attention was next focused on an addition of 2-phenylbutadiene to a dienophile of an analogous electronic and geometric character to citraconic anhydride but containing a preformed carbocyclic ring system. A toluquinone, of such substitution as to force formation of an angular methylated adduct with the diene, was the required precursor, and specifically a 5-(or 6-)arylthiolated toluquinone was considered to fulfill the added requirement of affording an adduct, permitting easy removal of the protecting group.

A *p*-tolylthiotoluquinone X (Ar = *p*-C_7H_7), most likely bearing the sulfur substitution at position 5, was prepared from *p*-toluenethiol and excess toluquinone,[11] and caused to undergo addition with 2-phenylbutadiene. An adduct resulted which is represented as XI by analogy on the one hand to the known course of diene addition to the electronically similar 5-methoxytolu-



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[6] K. v. Auwers and W. Jülicher, *Ber*, **55**, 2167 (1922).

[7] For examples of decarboxylation–dehydrogenation of α-methylcycloalkanoic acids see: W. E. Bachmann and J. M. Chemerda, *J. Am. Chem. Soc.*, **70**, 1468 (1948); A. Butenandt, H. A. Weidlich, and H. Thompson, *Ber.*, **66**, 601 (1933); J. Heer and K. Miescher, *Helv. Chim. Acta*, **31**, 219, 229 (1948); J. Alder, J. Haydn, and B. Krüger, *Ber.*, **86**, 1372 (1953).

[8] W. Hückel and E. Goth, *ibid.*, **58**, 447 (1925); J. Heer and K. Miescher, *Helv. Chim. Acta*, **32**, 1572 (1949).

[9] D. H. R. Barton and R. C. Cookson, *Quart. Rev.* (London), **10**, 44(1956).

[10] The transition states thus may be envisioned as incorporating no 1,3-nonbonded diaxial interactions between any of the substituents (other than hydrogen) on the cyclohexene ring and catalyst-H, considered as an axial substituent in the transition state. Inspection of the half-chair conformations alternate to those shown previously will reveal such diaxial interferences.

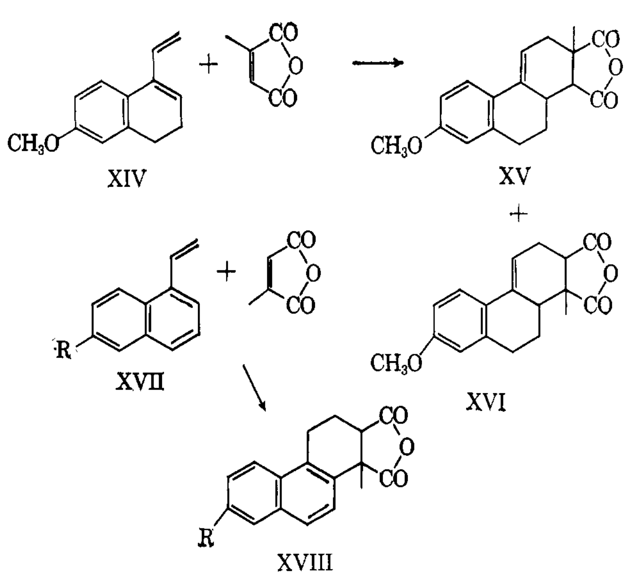
[11] For analogous quinone–sulfide formations see: T. Posner, *Ann.*, **336**, 85 (1904); J. M. Snell and A. Weissberger, *J. Am. Chem. Soc.*, **61**, 450 (1939); A. Schöberl and A. Wagner, "Methoden der Organischen Chemie," Vol. 9, Houben-Weyl, Ed., 4th Ed., Georg Thieme Verlag, Stuttgart, 1955, p. 130. For the ensuing purposes of our *p*-tolylthiotoluquinone the exact position, 5 or 6, of sulfide substitution is not critical.

quinone on the methylated side,[12] and on the other hand to the course of addition of phenylbutadiene with citraconic anhydride established previously. Such an assignment is available from a more detailed study of Diels–Alder additions of alkylthiotoluquinones.[13] Adduct XI was isolated only in a noncrystalline condition, but after desulfuration–reduction a crystalline substance XII was afforded albeit in small over-all yield from components I and X.

The usual Raney nickel desulfuration method failed in the latter transformation as erratic over reductions ensued. A new method, though probably unique for the system in XI, consisted in refluxing XI with zinc dust in acetic acid for a few hours.[13] The *trans* ring juncture in XII is postulated on the basis of the investigations of Robins and Walker[14] on the course of zinc–acetic acid reductions of Diels–Alder products from quinone. Prolonged treatment together with heating results in the reduction of the dioxoethylenic system concomitant with isomerization of the initially produced *cis* ring juncture to *trans*. The conditions of our desulfuration–reduction are those which almost certainly ensure the more stable *trans* ring fusion in XII.[15] Compound XII was readily reduced to XIII by means of hydrogenation over palladium–charcoal, this result being in contradistinction to a comparable situation elsewhere.[16] The stereochemical representation of XIII is the reasonable one resulting from catalyst-H approach from the least hindered side, *vide supra* for representation of the analogous hydrogenation process (VIII → IX).

Note on the Orientational Course of the Diels–Alder Addition.—We wish to draw attention to two points on the orientational aspects of the Diels–Alder reaction observed herein, which are germane to the methanistic considerations of this reaction. (a) The diene addition leading to IV has proceeded *contrary to the direction predictable purely on electrostatic grounds.*

(b) There is a variation in the methyl–phenyl relationship in the adducts resulting from the additions of citraconic anhydride to dienes of the phenylbutadiene type, *e.g.*, phenylbutadiene (I), 1-vinyl-6-methoxy-3,4-dihydronaphthalene (Dane's diene[17] XIV), and 1-vinylnaphthalenes (XVII, R = H or OCH_3), in which the phenylbutadiene moiety is incorporated in a dialin and a naphthalene ring system, respectively. It has been shown[18] that Dane's diene (XIV) yields a portion of adduct XVI (1-3 methyl-"phenyl" orientation) in addition to adduct XV[19] (1-4 methyl-"phenyl" orientation). However, the vinylnaphthalenes (XVII, R = H or OCH_3) gave good yields of only adducts XVIII (R = H, OCH_3) (1-3 methyl-"phenyl" orientation).[20] These results show a definite transition from the 1-4 methyl-phenyl orientation observed as the preponderant if not sole course of our addition, *viz.* IV, with phenylbutadiene itself.[21] We feel this variation as well as the orientational course of our diene addition are readily explicable on the basis of the theory for the Diels–Alder reaction[22,23a] propounded by Woodward.



The transition state leading to the establishment of the initial bond[23b] (in a two-step process) between the termini of unsymmetrical addends will control the gross structure of the adduct. The transition state of lowest energy will be determined by the extent of electron delocalization and a cogent argument may be made in favor of that transition state among the various ones *a priori* possible that avails as sites for electron delocalization in decreasing order of stability: benzyl or α to center of polarizable electrons > tertiary >

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[12] R. B. Woodward, F. Sondheimer, D. Taub, K. Heusler, and W. M. MacLamore, *J. Am. Chem. Soc.*, **74**, 4223 (1952); M. Orchin and L. W. Butz, *J. Org. Chem.*, **8**, 509 (1943).

[13] V. Georgian and L. L. Skaletzky, *J. Org. Chem.*, **29**, 51 (1964). Additional examples of such additions are also to be found in paper II of this series.

[14] P. A. Robins and J. Walker, *J. Chem. Soc.*, 642, 1612 (1952); 3960 (1954).

[15] This point is proved definitely in the study on the simpler system resulting from butadiene and quinone X: L. L. Skaletzky, Ph.D. dissertation, Northwestern University (1959); paper III of this series; *cf.* also R. H. Baker, L. S. Minckler, and A. S. Hussey, *J. Am. Chem. Soc.*, **81**, 2379 (1959), and paper II of this series.

[16] A. J. Birch, E. Pride, and H. Smith, *J. Chem. Soc.*, 4688 (1958).

[17] E. Dane and J. Schmitt, *Ann.*, **537**, 246 (1939).

[18] W. E. Bachmann and J. M. Chemerda, *J. Am. Chem. Soc.*, **70**, 1468 (1948); J. Heer and K. Miescher, *Helv. Chim. Acta*, **31**, 219 (1948).

[19] Isomeric adducts with the same gross structure as XV and XVI, but with the double bond in the 4a,10a-position in the hexahydrophenanthrene skeleton, were obtained [W. E. Bachmann and J. Controulis. *J. Am. Chem. Soc.*, **73**, 2636 (1951)], but the argument presented subsequently with respect to the orientational course of these Diels–Alder reactions is not changed, inasmuch as the double bond isomers are transformation products subsequent to the original diene addition.

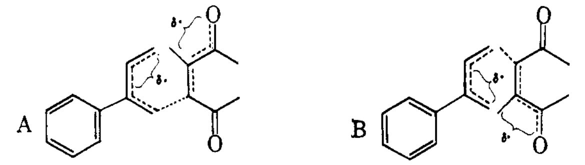
[20] W. E. Bachmann and L. B. Scott, *ibid.*, **70**, 1462 (1948), who also observed that mesaconic acid gave adducts of the type XVIII, *trans* carboxyls.

[21] For an extensive study on the Diels–Alder reaction between unsymmetrical addends consult the series of papers by K. Alder and coworkers: *Ann.*, **564**, 79, 109, 120 (1949); **570**, 201, 214, 230 (1950); **571**, 157 (1951); *Ber.*, **86**, 1302, 1312, 1364, 1372 (1953). In a related study, J. S. Meek, R. T. Merrow, D. E. Ramey, and S. J. Cristol, *J. Am. Chem. Soc.*, **73**, 5563 (1951), showed that the addition of 2-phenyl-1,3-butadiene to monosubstituted ethylenic dienophiles yielded 1,4-disubstituted adducts as major products. See also E. Buchta and G. Satzinger, *Ber.*, **92**, 449 (1959), for a study of the addition of 2-phenyl-1,3-butadiene to substituted acrylic acids.

[22] R. B. Woodward and T. J. Katz, *Tetrahedron*, **5**, 70 (1959).

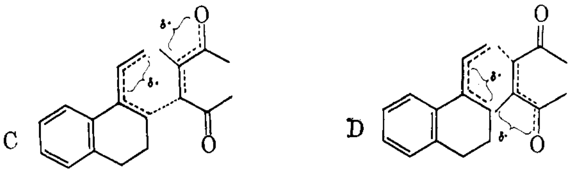
[23] (a) Significant observations and predictive suggestions also have been recorded by C. Walling and J. Peisach, *J. Am. Chem. Soc.*, **80**, 5819 (1958); J. A. Berson, R. D. Reynolds, and W. M. Jones, *ibid.*, **78**, 6049 (1956); and G. Stork, S. S. Wagle, and P. C. Mukharji, *ibid.*, **75**, 3197 (1953). In footnote 2 of the later reference there is formulated in canonical form an electron delocalized single-bonded intermediate for the diene addition process. (b) For recent suggestions that the Diels–Alder reaction may involve transient intermediates in which one bond has formed, see R. B. Woodward and T. J. Katz, *Tetrahedron*, **5**, 70 (1959); C. Walling and J. Peisach, *J. Am. Chem. Soc.*, **80**, 5819 (1958); and R. P. Lutz and J. D. Roberts, *ibid.*, **83**, 2198 (1961).

Scheme I
Transition States



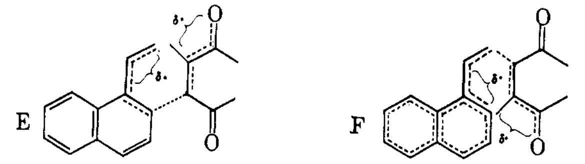
A: benzyl, primary; tertiary, α to carbonyl

B: secondary, primary; tertiary, α to carbonyl



C: benzyl, primary; tertiary, α to carbonyl

D: secondary, secondary; tertiary, α to carbonyl



E: primary, interrupted naphthalene resonance; tertiary, α to carbonyl

F: α-naphthyl; tertiary, α to carbonyl

secondary > primary. We may thus postulate as transition states for the cases under discussion those depicted in Scheme I.

In Scheme I only those forms are considered for the dienophilic moiety which involve a tertiary center clearly in preference to the alternate secondary one (each, of course, α to carbonyl). With respect to the diene it may be seen that form A, with electron delocalization involving the aromatic ring, would be of lower energy than B and the product may reasonably be expected to be IV. Similarly, F will be recognized as being of lower energy than E and the product here is solely XVIII. With respect to the situation obtaining in the case of the dialin XIV, transition state C represents the controlling force leading to XV, but now state D, which has an electron (or fraction thereof) delocalized at two secondary sites, represents an energetically more favorable situation than that prevailing in the hypothetical state B, and it may be expected that some product of the 1-3 methyl-"phenyl" orientation, *i.e.*, XVI, would appear as has been observed.[18]

Conformational specificity, obviously important in the more detailed stereochemistry of the polycyclic phenanthrenoid cases XV, XVI and XVIII controlling *exo* or *endo* addition, is neglected in the discussion at hand since it bears no significance to the constitution of the products resulting from the Diels-Alder reaction with 2-monosubstituted butadiene. Attention here has been limited solely to the disposition of methyl and aryl groups in the transition state. It is, of course, understood that the other auxiliary factors characteristic of and contributing to the diene addition process, *e.g.*, cisoid conformation of the diene, parallel biplanar approach of the addends (not shown in perspective in Scheme I), and the electrorestrictive forces leading to a highly circumscribed transition state,[24] will obtain in the present cases also.

Attention was called in the preceding to an apparently "wrong" interplay of polar factors in influencing the orientational course of the Diels-Alder reaction leading to IV (also in the case of XVII → XVIII). Many previously recorded cases involving unsymmetrical addends[21] conform to this same ostensible anomaly. Accordingly, it has proved fruitful in accounting for and predicting products, to treat such cases, even those wherein polar factors[25] appear to suffice, in terms of the single electron delocalization particularized as in Scheme I.

Experimental[26]

2-Phenyl-1,3-butadiene.—The pyrolysis of 4-acetoxy-2-phenyl-1-butene to produce 2-phenyl-1,3-butadiene was conducted essentially as described in the method of Price, Benton, and Schmidle.[5]

***cis*-1-Methyl-4-phenyl-1,2,3,6-tetrahydrophthalic Acid (IV).**—Citraconic anhydride[27] (103 g.) was added to a solution of 120 g. of 2-phenyl-1,3-butadiene in 500 ml. of thiophene-free anhydrous benzene. An exothermicity and the appearance of a yellowish color were noted at this point. After being refluxed for 24 hr., the reaction solution was concentrated by distillation and ultimately was heated at 140° (7–8 mm.) to remove any excess citraconic anhydride. The residual oil was taken up in a solution of 75 g. of sodium hydroxide in 250 ml. of water and extracted twice with ether. The alkaline solution was acidified and the product, *cis*-1-methyl-4-phenyl-1,2,3,6-tetrahydrophthalic acid (IV), separated as a thick oil which soon crystallized. It was filtered, washed with water, and air-dried, yielding 158 g. (66%), m.p. 158–162 (gas evolution). It could be recrystallized (90% recovery) from dilute ethanol, m.p. 174–176° (gas evolution).

Anal. Calcd. for $C_{15}H_{16}O_4$: C, 69.20; H, 6.15. Found: C, 69.17; H, 6.56.

4-Phenylphthalic Acid (V) from Sulfur Dehydrogenation of Adduct IV.—*cis*-1-Methyl-4-phenyl-1,2,3,6-tetrahydrophthalic acid (IV, 3 g.) was mixed with sulfur (1.5 g.) and heated 25 min. at 220–240°. Water and hydrogen sulfide were evolved, and the dark residue was then taken up in hot potassium carbonate solution, filtered (Norit), and extracted twice with ether. Acidification, extraction with ether, and evaporation of the washed and dried ether solution afforded 4-phenylphthalic acid (V), which was recrystallized from acetone–cyclohexane, yielding 580 mg., m.p. 196–197°, lit.[6] 194°.

Anal. Calcd. for $C_{14}H_{10}O_4$: C, 69.42; H, 4.13. Found: C, 69.82; H, 4.51.

The **anhydride of 4-phenylphthalic acid** was prepared from the acid by treatment with acetyl chloride for 60 hr. at room temperature. It was recrystallized from benzene–cyclohexane, m.p. 140–142°, lit.[7] m.p. 135–136°.

Anal. Calcd. for $C_{14}H_8O_3$: C, 75.00; H, 3.57. Found: C, 74.87; H, 3.58.

2-Methyl-5-phenylbenzoic Acid (VI) from Pd–C Dehydrogenation of Adduct IV.—A mixture of *cis*-1-methyl-4-phenyl-1,2,3,6-tetrahydrophthalic acid (IV, 2.6 g.) and 10% palladium–charcoal (500 mg.) was heated under an initial nitrogen cover at 300° for 30 min. Ether extraction, water washing, drying over sodium sulfate (Norit), and evaporation yielded 2-methyl-5-phenyl-

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(24) Including the coupling of the spins of the electrons involved[22] and overlap of unsaturated centers. For evidence against triplet biradical intermediates in Diels-Alder reactions see N. J. Turro and G. S. Hammond, *J. Am. Chem. Soc.*, **84**, 2841 (1962).

(25) For further discussion eliminating polar structures from consideration as intermediates in the Diels-Alder reaction between the neutral components, diene and dienophile, see C. Walling and J. Peisach, *ibid.*, **80**, 5819 (1958). The startling accelerations of some diene additions between anthracene and dienophiles of the maleic anhydride and quinone types imparted by aluminum chloride present in *one and two molar equivalents* and observed recently by P. Yates and P. Eaton, *J. Am. Chem. Soc.*, **82**, 4436 (1960), may very well be due to an altered nature of one or both components and may not necessarily be used as an argument either supporting or negating the intermediacy of polar structures in the reactions between the noncatalytically (Lewis acids) perturbed components.

(26) All melting points and boiling points are uncorrected. Microanalyses were performed at Northwestern University by Miss Joyce Sorensen.

(27) R. L. Shriner, S. G. Ford, and L. J. Roll, in "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1946, p. 140.

benzoic acid (VI, 810 mg.), m.p. 175–205°, recrystallized from dilute ethanol, m.p. 211–212°.

Anal. Calcd. for $C_{14}H_{12}O_2$: C, 79.24; H, 5.66. Found: C, 79.58; H, 5.85.

Permanganate Oxidation of 2-Methyl-5-phenylbenzoic Acid (VI).—The palladium–charcoal hydrogenation product VI of m.p. 200–211° (780 mg.) was refluxed for 3 hr. with a solution of 3.5 g. of potassium permanganate in 75 ml. of water containing 1 ml. of 10% alkali. The excess permanganate and manganese dioxide were reduced with sodium bisulfite, and the filtered solution was acidified and extracted exhaustively with ether. Solvent removal left 200 mg. of 4-phenylphthalic acid, m.p. 195–197°, undepressed by a sample prepared previously in the sulfur hydrogenation of IV.

***trans*-1-Methyl-4-phenyl-1,2,3,6-tetrahydrophthalic Acid (VIII).**—A suspension of 12 g. of *cis*-1-methyl-4-phenyl-1,2,3,6-tetrahydrophthalic acid (IV) in 200 ml. of ether was treated with an ether solution of diazomethane (prepared from 7 g. of nitrosomethylurea[28]). The excess diazomethane was boiled off after 10 min., the ether solution was washed with bicarbonate solution, water to neutrality, and saturated sodium chloride solution, and dried over magnesium sulfate. After evaporation of the ether, the remaining oil was taken up in dry benzene and boiled down to ensure dryness; the last traces were removed *in vacuo*.

The residual dimethyl ester of acid IV was refluxed 72 hr. in a solution of 1.0 g. of potassium metal in 200 ml. of absolute methanol. Then a solution of 5.0 g. of sodium hydroxide in 250 ml. of water was added and refluxing was continued for 4 hr. The alkaline solution, after being extracted with ether, was acidified and extracted exhaustively with ether. The ether solution was processed in the usual manner after partial evaporation of the ether. Addition of cyclohexane and storage overnight in the cold yielded 8.3 g. (70%) of *trans*-1-methyl-4-phenyl-1,2,3,6-tetrahydrophthalic acid (VIII), m.p. 216–221°. A second fraction, 2.0 g. (17%), m.p. 174–176°, proved to be recovered *cis* diacid IV, and a third fraction, 1.0 g., had m.p. 155–160°. Recrystallization of the *trans* diacid VIII from acetone–cyclohexane raised the melting point to 229–231°.

Anal. Calcd. for $C_{15}H_{16}O_4$: C, 69.23; H, 6.15; neut. equiv., 130. Found: C, 69.69; H, 6.31; neut. equiv., 136.

***cis–syn*-1-Methyl-4-phenylhexahydrophthalic Acid (VII).**—Three grams of 1-methyl-4-phenyl-1,2,3,6-tetrahydrophthalic acid in 50 ml. of absolute ethanol was hydrogenated over 150 mg. of 5% palladium–charcoal. During 1 hr. 280 ml. of hydrogen was absorbed (theoretical, 300 ml.). The catalyst was filtered off and the product, *cis-syn*-1-methyl-4-phenylhexahydrophthalic acid (VII), was crystallized from dilute ethanol, yielding 2.5 g. (83%), m.p. 188.5–189.5°.

Anal. Calcd. for $C_{15}H_{18}O_4$: C, 68.70; H, 6.87. Found: C, 69.20; H, 7.01.

***trans–syn*-1-Methyl-4-phenylhexahydrophthalic Acid (IX).**—One and one-half grams of *trans* diacid VIII was hydrogenated in 50 ml. of absolute ethanol over 150 mg. of 5% palladium–charcoal. The uptake of hydrogen, 148 ml. (theoretical, 144 ml.), required 20 min. After the usual work-up, there was isolated 1.3 g. of *trans-syn*-1-methyl-4-phenylhexahydrophthalic acid (IX), m.p. 215–225° (acetone–cyclohexane). One more recrystallization (acetone–cyclohexane) afforded 1.10 g. of IX (74%), m.p. 243–245°.

Anal. Calcd. for $C_{15}H_{18}O_4$: C, 68.70; H, 6.78. Found: C, 68.36; H, 7.06.

5(or 6?)-*p*-Tolylthiotoluquinone (X, Ar = *p*-C_7H_7).—*p*-Toluenethiol (31 g.) was added in one portion to a magnetically stirred suspension of 61 g. of toluquinone in 100 ml. of absolute ethanol. A clear dark red solution soon resulted with the evolution of some heat. The reaction was cooled to and maintained at room temperature overnight. The product, 5(6?)-*p*-tolylthiotoluquinone (X, Ar = *p*-C_7H_7), was filtered, washed with ligroin (b.p. 86–100°), and recrystallized from benzene–ligroin twice to yield 20 g. of bright orange crystals, m.p. 151.5–153°. The analytical sample had m.p. 154.7–155.6°.

Anal. Calcd. for $C_{14}H_{12}O_2S$: C, 69.00; H, 4.97; S, 13.15. Found: C, 69.40; H, 5.00; S, 13.16.

***trans*-1,4-Dioxo-6-phenyl-8a-methyl-1,2,3,4,4a,5,8,8a-octahydronaphthalene (XII).**—A solution of 5.2 g. of freshly distilled 2-phenylbutadiene and 9.7 g. of 5-(or 6?)*p*-tolylthiotoluquinone (X, Ar = *p*-C_7H_7) in 250 ml. of toluene was refluxed for 17 hr. The initially dark red solution gradually lightened in color to orange. Much of the toluene was removed *in vacuo* and the residue was diluted with 300 ml. of ether. This solution was then extracted with alternate portions of 10% sodium hydroxide solution and sodium hydrosulfite solution until no more color was removed in the washings. These were followed by washing with water until neutral and then with saturated sodium chloride solution; the organic layer was dried over magnesium sulfate and solvents were evaporated. The oily residue was kept under vacuum on the steam bath until no further change in weight. Approximately 15 g. of a thick yellow oil remained, and this corresponds to adduct XI.

The reaction concentrate obtained was taken up in 300 ml. of glacial acetic acid, 40 g. of zinc dust was added, and the mixture was refluxed with magnetic stirring for 8 hr. The cooled reaction was filtered and the zinc and salts were washed with acetone. The volatile matter was removed under aspirator vacuum on the steam bath, and the residue was taken up in ether, and washed several times with 5% sodium hydroxide solution until no more coloration to the wash liquors. After being washed with water and saturated sodium chloride solution until neutral, the ether solution was dried over magnesium sulfate and evaporated, and the product was distilled evaporatively at 0.2 mm. with a short path distillation apparatus at an oil bath temperature of 210–215°. A distillate of 6.4 g. was obtained which crystallized and was recrystallized from ethanol to yield XII, 4.8 g., m.p. 128–129° (after vacuum drying).

Anal. Calcd. for $C_{17}H_{18}O_2$: C, 80.28; H, 7.13. Found: C, 80.46; H, 7.31.

1,4-Dioxo-6-phenyl-8a-methyldecahydronaphthalene (*cis*-6,4a, *trans*-4a,8a, XIII).—A solution of 500 mg. of XII in 20 ml. of reagent ethyl acetate was hydrogenated over 50 mg. of 5% Pd-C at near atmospheric pressure. The theoretical uptake of hydrogen required only 20 min., and the reaction was worked up in the usual way to yield 420 mg. of the dioxophenylmethyldecahydronaphthalene XIII, m.p. 149–150°. The analytical sample was recrystallized from ethanol, m.p. 152–153°.

Anal. Calcd. for $C_{17}H_{20}O_2$: C, 79.65; H, 7.86. Found: C, 79.44; H, 7.71.

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[28] F. Arndt, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons Inc., New York, N. Y., 1946, p. 166.