# Alicyclic Syntheses. II. Diels–Alder Adducts Derived from 1-(α-Styryl)cyclohexene and 3-(α-Styryl)-$\Delta^2$-cyclohexenone

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The synthesis of 1-(α-styryl)cyclohexene (XII) and 3-(α-styryl)-$\Delta^2$-cyclohexenone (VII) and the Diels–Alder reactions of these dienes with a variety of dienophiles, maleic and citraconic anhydrides, and quinone, are described. Of particular interest is the reaction with 5-*p*-tolylthiotoluquinone (XXI). Angularly methylated polycarbocyclic systems have been stereospecifically obtained as models for steroid synthesis. The stereochemistry of the various adducts and their transformation products is discussed.

In our initial publication[1b] in this series of studies on the use of the Diels–Alder reaction in the synthesis of angularly methylated polycarbocyclic ring systems approaching steroid proportions, we presented our general theme on the potential utility of incorporating styryl moieties in an alicyclic system at the site(s) of potential oxygen functions. The general purpose of this diene addition scheme, as well as the orientational course of the reaction with unsymmetrical addends of the types necessary to the proposed scheme, was studied earlier in the simpler systems of 2-phenyl-1,3-butadiene (I) and citraconic anhydride (II) yielding *cis*-1-methyl-4-phenyl-1,2,3,6-tetrahydrophthalic acid anhydride (III).[1b]

We now wish to report on an extension of this approach to larger size ring systems in both the diene and the dienophilic components.

The possibility of employing a system such as 3-(α-styryl)-$\Delta^2$-cyclohexenone (VII) as the diene appeared initially attractive, since Diels–Alder products therefrom could be envisioned as models for C-ring oxygenated steroids. Cyclohexenones of the general type VII are readily available as shown by the work of Woods on the reaction of phenylmagnesium bromide on dihydroresorcinol enol ethers.[2] More recently announcements from three laboratories, those of Eschenmoser,[3] Nazarov,[4] and Normant,[5] report the successful addition of acetylene and the vinyl Grignard reagent[6] to the enol ethers of dihydroresorcinols affording 3-ethinyl- or 3-vinyl-$\Delta^2$-cyclohexenones. In strict analogy, α-styrylmagnesium bromide (IV)[7] was treated with dihydroresorcinol methyl ether (V) followed by acid hydrolysis of the reaction intermediate VI to produce the desired dienone VII, albeit in a yield reduced considerably by resinification. In fact, although an adduct, 8-oxo-4-phenyl-1,2,3,5,6,7,8,8a-octahydronaphthalene-1,2-dicarboxylic acid (VIII), was obtained from VII and maleic anhydride, further attempts to utilize VII in additions with citraconic anhydride (II) and 5-methoxytoluquinone[8] (X) were fruitless as a result of its extreme instability under the more drastic and driving conditions required generally in Diels–Alder reactions with the methylated dienophiles. Such sensitivity was noted also for the related vinyl cyclohexenones cited previously.[4] Although it was possible to obtain a yellow dinitrophenylhydrazone derived from structure VIII, mixtures of dinitrophenylhydrazones were obtained varying in color from yellow to reddish orange indicating considerable mobility of the styryl double bond (β,γ to the carbonyl) into conjugation with the carbonyl. Such facile isomerization contraindicated the desirability of further preoccupation with structures of the type VIII for our intended purposes, requiring the preservation of the styryl function. Concerning the stereochemical configuration of adduct VIII, *vide infra.*

Attention was next directed at the desoxo system, 1-(α-styryl)cyclohexene, to ascertain whether or not the geometrical factors obtaining in a bulky diene of this degree of substitution were still compatible with successful addition to dienophiles of the citraconic and, ultimately, a blocked toluquinone type. Considerably more success was achieved along these lines.

The addition of α-styrylmagnesium bromide (IV) to cyclohexanone afforded 1-(α-styryl)cyclohexanol (XI) in satisfactory yield, but attempts to dehydrate the latter by azeotropic distillation of water formed by mild oxalic acid or iodine[9] catalysis did not meet with complete success. More vigorous conditions employing thionyl chloride and pyridine resulted in a product contaminated with halogen-containing material.[10] Dehydration of the carbinol XI to 1-(α-styryl)cyclohexene (XII) ultimately was accomplished successfully by heating with fused potassium bisulfate.

The diene XII was induced to react with a variety of dienophiles, including maleic anhydride, citraconic anhydride, and *p*-benzoquinone. The adduct from maleic anhydride, XIII, was characterized additionally as the diacid 4-phenyl-1,2,3,5,6,7,8,8a-octahydronaphthalene-1,2-dicarboxylic acid (XIIIa), and that from citraconic anhydride was best characterized as 1-methyl-4-phenyl-1,2.3.5,6,7,8,8a-octahydronaphthalene 1,2-dicarboxylic acid (XVI) (concerning the position of the methyl group *vide infra*). Quinone yielded the adduct 1,4-dioxo-9-phenyl-1,4,4a,4b,5,6,7,8,10,10a-decahydrophenanthrene (XVIII).

Concerning the stereochemistry of the Diels–Alder adducts described herein, the following discussion is

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[1] (a) Department of Chemistry, Tufts University, Medford 55, Mass.; (b) V. Georgian and J. Lepe M., paper I of this series, *J. Org. Chem.*, **29**, 40 (1964).

[2] G. F. Woods, *J. Am. Chem. Soc.*, **69**, 2549 (1947); G. F. Woods and I. W. Tucker, *ibid.*, **70**, 2174 (1948).

[3] A. Eschenmoser, J. Schreiber, and S. A. Julia, *Helv. Chim. Acta*, **36**, 482 (1953).

[4] I. N. Nazarov, I. V. Torgov, and G. P. Verkholetova, *Dokl. Akad. Nauk SSSR*, **112**, 1067 (1957); *Chem. Abstr.*, **51**, 14, 647 (1957).

[5] C. Crisan and H. Normant, *Bull. soc. chim. France*, 1451 (1957).

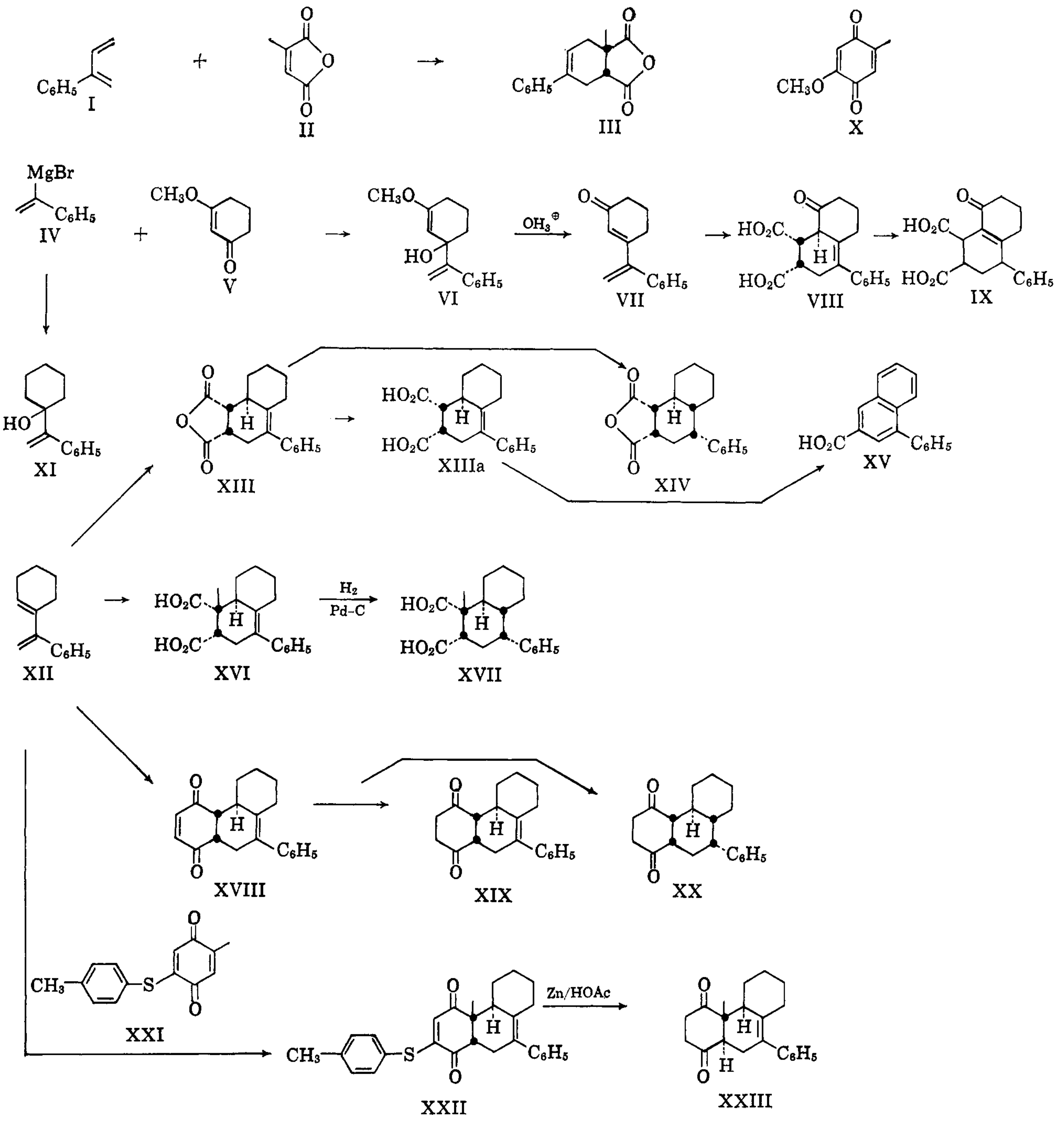
[6] For a general review with collection of references on the vinyl Grignard in synthesis, see H. Normant, *ibid.*, 1764 (1959).

[7] For an earlier application of this Grignard reagent, see K. Alder and J. Haydn, *Ann.*, **570**, 201 (1950).

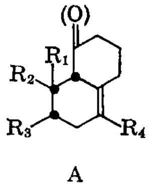
[8] Kindly supplied by Dr. W. S. Knowles, Monsanto Chemical Co., St. Louis, Mo.

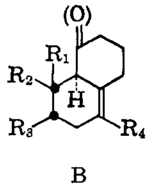
[9] H. Hibbert, *J. Am. Chem. Soc.*, **37**, 1748 (1915); P. A. Robins and J. Walker, *J. Chem. Soc.*, 3249 (1956); 177 (1957).

[10] K. Alder and J. Haydn[7] successfully converted an α-styryl *sec*-carbinol to the corresponding chloride with hydrochloric acid.



germane. In strict compliance with the Alder–Stein rules,[11] a *cis–syn* configuration, represented in A, would have to be assigned, arising from *endo* addition accounted for by maximum accumulation of unsaturation in the transition state of the Diels–Alder complex.[12]


A


B

However, the situation at hand has been rendered sufficiently complicated by the forcing reaction conditions (higher reaction temperatures, prolonged heating periods, lower yields than those obtaining in cleaner-cut cases unencumbered by geometrical factors) as to warrant a reappraisal of such an assignment. Thus, Ansell and Brooks[13] assigned a *cis–syn* configuration to the adduct from maleic anhydride and 1-(1-acetoxyvinyl)cyclohexene (A, $R_1$ = H; $R_2$, $R_3$ = anhydride; $R_4$ = OAc), which was obtained under *mild* conditions (room temperature) and which obviously differed from a liquid adduct obtained in addition thereto by Nazarov[14] under more forcing conditions (8 hr., boiling benzene) to which the latter investigator assigned a *cis–anti* configuration (B, $R_1$ = H; $R_2$, $R_3$ = anhydride; $R_4$ = OAc). This case is quite closely comparable with our own. Similar results have been encountered with 1-vinylcyclohexene and maleic anhydride. Cook

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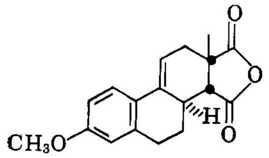
[11] K. Alder and G. Stein, *Angew. Chem.*, **50**, 510 (1937).

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

[13] M. F. Ansell and G. T. Brooks, *J. Chem. Soc.*, 4518 (1956).

[14] I. N. Nazarov, V. F. Kucherov, V. M. Andreyev, and G. M. Segal, *Dokl. Akad. Nauk SSSR*, **104**, 729 (1955); *Chem. Abstr.*, **50**, 11, 304 (1956).

and Lawrence[15] obtained an adduct under mild conditions (in solvent, room temperature) undoubtedly of *cis–syn* configuration (A, $R_1 = R_4 = H$; $R_2$, = $R_3$ = anhydride), whereas Nazarov[16] using somewhat more forcing conditions (exothermicity of reaction without solvent, or low temperature and long reaction time) obtained the *cis–syn* adduct and an isomeric one as well, undoubtedly the *cis–anti* adduct (B, $R_1 = R_4 = H$; $R_2 = R_3$ = anhydride). Moreover, the former substance was isomerized to the latter on heating. While assigning a *cis–syn* configuration to their acetoxyvinylcyclohexene–maleic anhydride adduct, Ansell and Brooks[13] were careful to consider the possibility of a departure from the *endo* addition principle in their diene addition of acetoxyvinylcyclohexene and 2,6-xyloquinone, which was conducted under more strenuous conditions (*i.e.*, 21 hr., boiling benzene or ethanol). Perhaps even more closely related to our case at hand is that of the addition of citraconic anhydride to 1-(1-acetoxyvinyl)cyclohexene which required rather elevated temperatures and which was shown to yield a *cis–anti* adduct (B, $R_1 = CH_3$; $R_2 = R_3$ = anhydride; $R_4$ = OAc).[17a] Finally, it may be recalled that Heer and Meischer[17b] established that one of the adducts from citraconic anhydride and 6-methoxy-1-vinyl-3,4-dihydronaphthalene under not especially forcing conditions (overnight, cold and short heating period) had a *cis–anti* configuration. The foregoing examples make it abundantly obvious that whereas the Alder–Stein rule for *endo* addition may be applied with confidence in those cases where low temperatures and not too long reaction periods are employed, quite clearly an opportunity is presented for *exo* addition where forcing conditions obtain. We feel that this latter qualification more accurately represents the situation prevailing in our case at hand and suggest tentatively that a *cis–anti* configuration, *viz.*, B, is possessed by our initially isolated adducts.



Hydrogenation of the styryl function in substances XIII and XVI was smoothly effected over palladium–charcoal to yield XIV and XVII, respectively, and, in the case of XVIII, a di- as well as a tetrahydro derivative was obtained, XIX and XX. The configurational assignment at the newly established ring junctures in these hydrogenation products will be discussed subsequently.

Although the anhydride XIII did not yield any recognizable product on palladium–charcoal dehydrogenation, the dimethyl ester of XIIIa afforded, after dehydrogenation and saponification, a monocarboxy-4-phenylnaphthalene of m.p. 261–263°. This acid is not 4-phenyl-1-naphthoic acid (m.p. 172–173°)[18] and, from its origin, must be assigned the structure 4-phenyl-2-naphthoic acid (XV) by exclusion. An acid of this melting point, but of undefined structure, had been reported previously by Wagner-Jauregg[19] in addition to a carboxyphenylnaphthalene of m.p. 172–173° in a series of degradation products from the adduct of two moles maleic anhydride and 1,1-diphenylethylene. The reported analysis for the Wagner-Jauregg acid, 261.5–263.5°, suggests that it is a monocarboxyphenylnaphthalene, and from its mode of genesis it is very likely identical with our acid XV.

Successful addition to styrylcyclohexene having been accomplished with citraconic anhydride and quinone, it was desired to effect appendage of an additional ring-bearing angular methylation. Toward this end, 5-methoxytoluquinone (X) was attempted in the diene addition, but, in spite of previous successes with this dienophile,[20a] no crystalline product could be isolated. Nevertheless, the efficiency of employing a toluquinone in the Diels–Alder reaction rather than commencing with the citraconic adduct and constructing the next ring therefrom by laborious means compelled a search for other appropriate quinone dienophiles. Such was found in 5-*p*-tolylthiotoluquinone (XXI), which is readily prepared from *p*-toluquinone and *p*-thiocresol, and which bears a gross electronic similarity to the methoxytoluquinone, known to undergo diene addition on the methylated side.[20a] Addition of styrylcyclohexene to the thio-substituted toluquinone XXI proceeded after long reflux in benzene, or preferably toluene, and the adduct is formulated on the basis of the discussion on stereochemistry (*vide supra*) as *cis–anti*-1,4-dioxo-4a-methyl-9-phenyl-2-*p*-tolylthio-1,4,4a,4b,5,-6,7,8,10,10a-decahydrophenanthrene (XXII). The thio ether function having served the purpose of directing addition toward angular methylation[20b] (for a discussion on the position of the methyl *vide infra*), it was next desired to desulfurize, reduce the dioxoethylenic bond while preserving the styryl double bond, and isomerize the *cis* ring juncture to *trans*. The usual method of desulfurization by means of Raney nickel did not prove particularly adaptable. The results were erratic and over-reduction of the carbonyl and styryl functions could not be cleanly avoided. A method which was devised to overcome this difficulty, and which served uniquely to accomplish the three desired purposes just specified, consisted of refluxing for 8 hr. with zinc in acetic acid. Thus, *trans–anti*-1,4-dioxo-4a-methyl-9-phenyl-1,2,3,4,4a,-4b,5,6,7,8,10,10a-dodecahydrophenanthrene (XXIII) was produced from XXII by this means, which has been applied in other series of our investigations, and which will be reported in greater detail in subsequent

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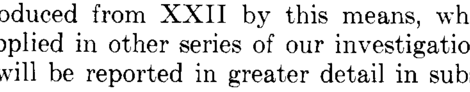
[15] J. W. Cook and C. A. Lawrence, *J. Chem. Soc.*, 58 (1938).

[16] I. N. Nazarov, V. F. Kucherov, and V. M. Andreyev, *Dokl. Akad. Nauk SSSR*, **102**, 751 (1955).

[17] (a) F. Winternitz and C. Balmossiere, *Tetrahedron*, **2**, 100 (1958); I. N. Nazarov, V. F. Kucherov, and V. M. Andreyev, *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, **67**, 77 (1955); *Chem. Abstr.*, **50**, 1713 (1956). (b) J. Heer and K. Meischer, *Helv. Chim. Acta*, **31**, 219 (1948); **32**, 1572 (1949).

[18] J. v. Braun and E. Anton, *Ber.*, **67B**, 1051 (1934).

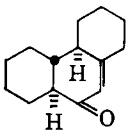
[19] T. Wagner-Jauregg, *Ann.*, **491**, 1 (1931).



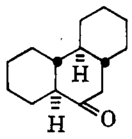
acid (171.5–173.5°) + acid (261.5–263.5°)

[20] (a) 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). (b) This course of the Diels–Alder reactions with alkylthio-substituted quinones has been firmly established in several other cases and, for a disclosure of these results, see V. Georgian and L. L. Skaletzky, *ibid.*, **29**, 51 (1964).

publications. The *trans* ring juncture is postulated on the basis of findings by Robins and Walker[21] and our own investigations on zinc–acetic acid reductions of Diels–Alder products from quinone and 3,20-diacetoxypregna-5,16,20-triene.[22] Short treatment of a few minutes' duration without heat of a *cis*-1,4-dioxo-$\Delta^2$-octalin with zinc–acetic acid usually permits the reduction of the ethylenic bond with survival of the *cis* ring juncture. Prolonged treatment supplemented by heating results in reduction concomitant with isomerization to a *trans* ring fusion. Moreover, whereas *cis*-$\alpha$ decalone isomerizes only extremely slowly to *trans*-$\alpha$-decalone at room temperature,[23] *cis*-1,4-dioxodecalins have been found to be considerably less stable with respect to their *trans* isomerides.[24] The conditions employed in the reduction of XXII to XXIII, *i.e.*, 8-hr. refluxing, ensure that the stereochemistry of XXIII is almost certainly *trans–anti*. This assignment is further corroborated by the proof in the case of a similar desulfurization of the adduct of butadiene and 5-*p*-tolylthiotoluquinone. The angularly methylated *trans* ring fusion is clearly evident by the single strong infrared absorption at 1450 cm.$^{-1}$ [25] of the resulting 8a-methyl-$\Delta^2$-octalin. Such a result is in consonance with the greatest stability of the *trans–anti–trans* form of perhydrophenanthrenes (*cf.* W. S. Johnson[26]). A *trans–anti* configuration has been elucidated experimentally in a closely related case for the condensation product XXIV of sodiocyclohexanone and 1-acetylcyclohexene.[27]

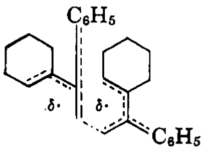


XXIV

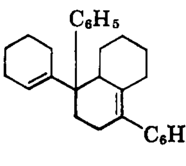


XXV

The Diels–Alder reaction between styrylcyclohexene and mesaconic acid yielded only a heavy acidic oil from which no identifiable product could be obtained. When the reaction was attempted with fumaric acid, the product isolated, m.p. 198–200°, was found on elemental analysis to contain no oxygen and appeared to be simply a Diels–Alder dimer of the diene to which structure XXVII is provisionally assigned. This structure is based on a consideration of the principles governing the orientational course of the diene reaction between unsymmetrical addends presented and discussed in detail in our first paper of this series,[1b] in which the phenyl–methyl relationship in III was elucidated. Application of those principles in the addition of citraconic anhydride and 5-*p*-tolylthiotoluquinone to styrylcyclohexene leads to the suggested structures XVI and XXII for these adducts. By way of brief recapitulation it may be stated that *the gross structural character of the adduct will be determined by an association of the addends in the transition state (of possibly a spin-paired nature)*[28a] *generating greatest electron delocalization.*

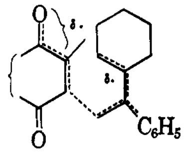


XXVI



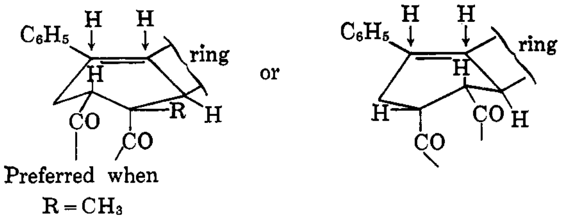
XXVII

We may envision as illustrative of this principle the transition state XXVI, as the precursor to XXVII, resulting in electron delocalization involving both aromatic rings, tertiary benzyl and secondary ring carbon atoms. Alternate association of the components to that depicted in XXVI would lead to higher energy transition states. Analogous transition states may be constructed as intermediates in the formation of XVI and XXII, such states (XVIa and XXIIa synoptic forms) being of lower energy than those leading to the adducts inverse to XVI and XXII.[28b]



XVIa and XXIIa

Finally, an account may be in order on the configurational assignments at the ring junctures established on hydrogenation to the products XIV, XVII, and XX. The complete configurations have been assigned as *cis–anti–trans–cis* by analogy to the hydrogenation of XXIV to *trans–anti–trans* 9-oxoperhydrophenanthrene (XXV).[27,29] This assignment of configuration may be reinforced by a conformational analysis in which the most favorable half-chair conformations are selected bearing the smallest number of axial substituents (other than hydrogen) with catalyst approach invoked from the least hindered side.[30] Such a picture, illustrated in C, compels the stereochemical arrangement indicated in the previous formulas:



C

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

[22] V. Georgian and Lupe T. Georgian, *J. Org. Chem.*, **29**, 58 (1964).

[23] W. Hückel, *Ann.*, **441**, 1 (1925).

[24] R. M. Lukes, G. I. Poos, and L. H. Sarett, *J. Am. Chem. Soc.*, **74**, 1401 (1952).

[25] Paper III in this series; *cf.* also, R. H. Baker, L. S. Minckler, and A. S. Hussey, *J. Am. Chem. Soc.*, **81**, 2379 (1959).

[26] W. S. Johnson, *Experientia*, **8**, 315 (1951).

[27] R. P. Linstead, S. B. Davis, and R. R. Whetstone, *J. Am. Chem. Soc.*, **64**, 2009 (1942).

[28] (a) Recent evidence has accumulated which indicates that, while the Diels–Alder reaction may involve transient intermediates in which one bond has been formed [ref. 12 of C. Walling and J. Peisach, *ibid.*, **80**, 5819 (1958); R. P. Lutz and J. D. Roberts, *ibid.*, **83**, 2198 (1961)], the intermediacy of a triplet biradical has been ruled out [N. J. Turro and G. S. Hammond, *ibid.*, **84**, 2841 (1962)]. (b) See also F. Winternitz and C. Balmossiere, *Tetrahedron*, **2**, 100 (1958); L. D. Bergelson (reporting on I. N. Nazarov's work), *ibid.*, **6**, 161 (1959); M. F. Ansell and G. T. Brook, *J. Chem. Soc.*, 4518 (1956), for additional experimental evidence corroborating the orientational course of Diels–Alder reactions involving addends of the general type discussed in this publication.

[29] See also P. A. Robins and J. Walker, *ibid.*, 642 (1952).

[30] R. P. Linstead W. E. Doering, S. B. Davis, P. Levine, and R. R. Whetstone, *J. Am. Chem. Soc.*, **64**, 1985 (1942).

## Experimental[31]

**α-Bromostyrene.**—To a solution of 528 g. of styrene dibromide in 1200 ml. of ethanol there was added with stirring 112 g. of potassium hydroxide in the minimum amount of ethanol. The addition was made in a thin stream, and the reaction was maintained at room temperature with occasional cooling. Immediate precipitation of potassium bromide followed and, after addition was complete, stirring was continued until neutrality was reached. Water was added and the product was taken up in ether. The ether solution was washed with water, dried over magnesium sulfate, and distilled to yield α-bromostyrene, 236 g. (64%), b.p. 80–85° (10 mm.), lit.[32] b.p. 77° (9 mm.).

**Dihydroresorcinol methyl ether (V)** was prepared by methylating dihydroresorcinol[33] (111 g.) in 1 l. of acetone with 111 g. of anhydrous potassium carbonate, and 93 ml. of dimethyl sulfate. The reaction mixture was stirred at ordinary temperature for 12 hr. The solids were filtered, the acetone was distilled, and the product, 75 g., was distilled at 105–111° (11 mm.).

**3-(α-Styryl)-Δ²-cyclohexenone (VII) and *cis-anti*-8-oxo-4-phenyl-1,2,3,5,6,7,8,8a-octahydronaphthalene-1,2-dicarboxylic Acid (VIII).**—A solution of α-styrylmagnesium bromide (IV)[7] was prepared by the addition of 104 g. of α-bromostyrene in 500 ml. of anhydrous ether to 13 g. of magnesium turnings (under nitrogen) in the usual manner for the preparation of a Grignard reagent. After the addition of the halide was complete, the reaction was stirred for 0.5 hr. longer and then refluxed 10 min.

Then, with ice cooling, there was added in a thin stream a solution of 72 g. of dihydroresorcinol methyl ether in 100 ml. of dry ether, and stirring was maintained 5 hr., after which a solution of 350 ml. of water and 35 g. of sulfuric acid was added and agitation was continued 2 hr. longer. The ether layer was separated and, combined with additional ether extracts of the aqueous layer, was washed with water, sodium carbonate solution, water, and saturated sodium chloride solution, and was dried over magnesium sulfate. Evaporation of the ether *in vacuo* with very gentle heat left a residue of 100–110 g. of a dark yellow oil, VII, which could not be distilled without extensive polymerization. In one experiment there was obtained from this size run 15 g. of distillate, VII, b.p. 150–170° (1.0 mm.), whose infrared spectrum indicated the presence of conjugated carbonyl. This material could not be characterized further at this point because of its extreme instability, and it was used forthwith in the diene addition with maleic anhydride.

A solution of 13 g. of the aforementioned product, freshly distilled, and 6.4 g. of maleic anhydride in 100 ml. of toluene was refluxed for 20 hr. The volatiles were then removed *in vacuo* on the steam bath and the residual oil was taken up in 10% sodium hydroxide solution. This alkaline solution was extracted several times with ether, treated with Norit, and acidified. The precipitated gum was taken up in ether, and this solution was washed with water and dried over magnesium sulfate. After the ether solution was evaporated the residual thick oil was allowed to stand for about 1 month when it was noticed that some crystallization had taken place. A little chloroform was added as a thinner, and the crystals were filtered and were recrystallized from acetone and then from ethyl acetate, m.p. 208–210°. Infrared absorption revealed no conjugated carbonyl and thus expression VIII best fits the composition of this substance.

*Anal.* Calcd. for $C_{18}H_{18}O_5$: C, 68.78; H, 5.73. Found: C, 68.85; H, 5.71.

The **dinitrophenylhydrazone of VIII** prepared in the usual fashion was yellow and had m.p. 245–247° (from ethanol).

*Anal.* Calcd. for $C_{24}H_{22}N_4O_8$: C, 58.29; H, 4.45. Found: 57.85; H, 4.61.

Reported recrystallization resulted in orange and reddish products which indicated gradual transformation to the dinitrophenylhydrazone of the conjugated carbonyl tautomer IX.

**Attempted Diels–Alder Addition of VII with Citraconic Anhydride (II) and 5-Methoxytoluquinone (X).**—These additions were attempted by refluxing equimolar quantities of the reactants in anhydrous benzene for 35–38 hr. The experiments with citraconic anhydride, worked up as in the previous case with maleic anhydride, yielded only polymeric tars. In those cases with 5-methoxytoluquinone, the latter was recovered unchanged in 80–90% yield by direct crystallization from the reaction solution after partial evaporation of solvent.

**1-(α-Styryl)cyclohexanol (XI).**—To a solution of α-styrylmagnesium bromide prepared from 126 g. of α-bromostyrene and 17 g. of magnesium turnings in 700 ml. of anhydrous ether there was added with ice-bath moderation of the reaction a solution of 68 g. of cyclohexanone in 500 ml. of anhydrous ether. A yellowish complex gradually precipitated and stirring was continued for 2 hr. with cooling after the addition was complete. Ice (300 g.) and a solution of 50 g. of ammonium chloride in 250 ml. of water were added, and the ether layer was separated and combined with several additional ether extracts of the aqueous phase. The ether solution was washed with water several times and dried over sodium sulfate. The product, 1-(α-styryl)cyclohexanol (XI), was distilled *in vacuo*, yielding 100 g. (72%), b.p. 100–105° (0.1 mm.), $n^{25}D$ 1.5500. A small forerun was rejected. Infrared absorption indicated an hydroxyl band at 2.8–2.9 μ.

*Anal.* Calcd. for $C_{14}H_{18}O$: C, 83.10; H, 8.96. Found: C, 83.32; H, 8.79.

**1-(α-Styryl)cyclohexene (XII).**—A mixture of 35 g. of 1-(α-styryl)cyclohexanol (XI) and 45 g. of fused powdered potassium bisulfate (Mallinckrodt) was heated at 150–155° under the passage of a slow stream of nitrogen for 1 hr. The cooled reaction was taken up in ether and water, and the ether solution was washed with water, bicarbonate solution, water to neutral reaction, and finally with saturated sodium chloride solution. It was dried over sodium sulfate and the product was distilled *in vacuo*, yielding 23 g. (73%) of 1-(α-styryl)cyclohexene (XII), b.p. 100–103° (1.0 mm.), $n^{25}D$ 1.5710. Infrared analysis indicated absence of hydroxyl. This diene could be stored in the cold a short time, but within 2 weeks considerable polymerization was encountered.

*Anal.* Calcd. for $C_{14}H_{16}$: C, 91.30; H, 8.74. Found: C, 90.93; H, 8.89.

**Diels–Alder Adduct of Styrylcyclohexene XII and Maleic Anhydride, *cis-anti*-4-Phenyl-1,2,3,5,6,7,8,8a-octahydronaphthalene-1,2-dicarboxylic Acid (XIIIa) and Anhydride XIII.**—Maleic anhydride (3 g.) and 1-(α-styryl)cyclohexene (XII) (5.4 g.) were heated on the steam bath for 9 hr. A bright yellow color was noted on admixture of the two components. The cooled reaction melt was then taken into benzene and washed with water several times. After being dried over sodium sulfate, the solvent was evaporated leaving 5.5 g. of a crystalline compound, m.p. 112–115°. Recrystallization from benzene–cyclohexane or ethyl acetate–cyclohexane raised the melting point to 119.5-120.3°. This substance, insoluble in bicarbonate solution, possessed infrared absorption at 5.60 μ, diagnostic for the five-membered anhydride carbonyl of adduct XIII.

*Anal.* Calcd. for $C_{18}H_{18}O_3$: C, 76.60; H, 6.41. Found: C, 77.08; H, 6.58.

The anhydride XIII was taken up in dilute alkali and the **diacid XIIIa** was precipitated on acidification. It could be recrystallized from ethanol, m.p. 215–216° dec.

*Anal.* Calcd. for $C_{18}H_{20}O_4$: C, 72.00; H, 6.66. Found: C, 71.52; H, 6.82.

***cis-anti-trans-cis*-4-Phenyldecahydronaphthalene-1,2-dicarboxylic Acid Anhydride (XIV).**—The anhydride XIII (1.0 g.) was hydrogenated at ordinary temperature and pressure in 40 ml. of ethanol over 100 mg. of 5% palladium–charcoal. One molar equivalent of hydrogen was absorbed. The catalyst was filtered and washed with acetone. The combined organic solutions were evaporated, and the crude crystalline residue was filtered and washed with cyclohexane, yielding 900 mg., m.p. 150–155°. Recrystallization from acetone–cyclohexane afforded pure XIV, m.p. 156–157°.

*Anal.* Calcd. for $C_{18}H_{20}O_3$: C, 76.03; H, 7.12. Found: C, 75.91; H, 7.13.

**4-Phenyl-2-naphthoic Acid (XV).**—The anhydride XIII (2.0 g.) was converted to the diacid XIIIa as described previously, and the crude ether extract of the latter was methylated with an ethereal solution of diazomethane prepared from 4.0 g. of *N*-nitroso-*N*-methylurea. The oily diester resulting from evaporation of the ether was mixed with 500 mg. of 10% palladium–charcoal and heated at 300° for about 1.5 hr., at the end of which all gas evolution had practically ceased. The cooled reaction mixture was extracted with ethanol (Norit) and the residual oil, remaining after evaporation of the ethanol, was treated with 20

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(31) All melting points are uncorrected. Analyses were performed by Miss Hildegarde Beck, Microanalytical Laboratory, Northwestern University. Infrared spectra were determined in chloroform solution on a Baird double beam instrument, Model AB-2.

(32) M. H. Jones, *Can. J. Chem.*, **34**, 108 (1956).

(33) R. B. Thompson, *Org. Syn.*, **27**, 21 (1900).

ml. of 5% alkali and 5 ml. of ethanol on the steam bath for 1 hr. The cooled alkaline solution was filtered (Norit) and extracted with ether a few times and then acidified. The precipitated material was taken up in ether and dried, and evaporation of the ether afforded 4-phenyl-2-naphthoic acid (XV), which was recrystallized from dilute ethanol, m.p. 261–263°.

*Anal.* Calcd. for $C_{17}H_{12}O_2$: C, 82.40; H, 4.88. Found: C, 82.18; H, 4.89.

**Diels–Alder Adduct of 1-(α-Styryl)cyclohexene (XII) and Citraconic Anhydride,** *cis–anti*-**1-Methyl-4-phenyl-1,2,3,5,6,7,8,8a-octahydronaphthalene-1,2-dicarboxylic Acid (XVI).**—A mixture of 12 g. 1-(α-styryl)cyclohexene (XII) and 7.4 g. of citraconic anhydride (II) was heated on the steam bath 1 hr. and then refluxed in 40 ml. of dry benzene for 48 hr. The volatiles were removed *in vacuo* to eliminate also any unchanged citraconic anhydride, and the residue was treated with 10% alkali. The alkaline solution, after being extracted several times with ether, was acidified, and the precipitated material was extracted with ether. The dried (sodium sulfate) ether solution on evaporation deposited 5.4 g. of XVI, m.p. 224–227° dec. Recrystallization from ethanol raised the melting point to 232–233° dec.

*Anal.* Calcd. for $C_{19}H_{22}O_4$: C, 72.61; H, 7.00. Found: C, 73.02; H, 7.13.

*cis–anti–trans–cis*-**1-Methyl-4-phenyldecahydronaphthalene-1,2-dicarboxylic Acid (XVII).**—The hydrogenation of 1.0 g. XVI in 50 ml. ethanol over 100 mg. 5% palladium–charcoal was conducted at ordinary temperature and pressure. One equivalent of hydrogen was absorbed in 6 hr., and the reaction was worked up in the usual way to yield 900 mg. of XVII, m.p. 254–256°, from ethanol. Additional recrystallization from ethanol raised the melting point to 258–259°.

*Anal.* Calcd. for $C_{19}H_{24}O_4$: C, 72.13; H, 7.64. Found: C, 72.34; H, 7.58.

**Diels–Alder Addition of Diene XII with Quinone,** *cis–anti*-**1,4-Dioxo-9-phenyl-1,4,4a,4b,5,6,7,8,10,10a-decahydrophenanthrene (XVIII).**—A solution of 15.0 g. of 1-(α-styryl)cyclohexene (XII) and 26 g. of quinone (large excess) in 100 ml. of dry benzene was refluxed for 7 hr., and the solvent was then evaporated. The residue was maintained *in vacuo* on the steam bath to eliminate any unchanged quinone and was then treated with a minimum quantity of ethanol which induced crystallization of XVIII, 3.0 g. (13%), m.p. 116–118°. The analytical sample was light yellow in color, m.p. 117–118°.

*Anal.* Calcd. for $C_{20}H_{20}O_2$: C, 82.10; H, 6.89. Found: C, 82.60; H, 6.95.

**Hydrogenation of XVIII,** *cis–anti*-**1,4-Dioxo-9-phenyl-1,2,3,4,4a,4b,5,6,7,8,10,10a-dodecahydrophenanthrene (XIX) and** *cis–anti–trans–cis*-**1,4-Dioxo-9-phenyltetradecahydrophenanthrene (XX).**—The hydrogenation of adduct XVIII (1.0 g.) was conducted in ethanol (50 ml.) over 100 mg. of 5% palladium–charcoal at ordinary temperature and pressure. One mole equivalent of hydrogen was absorbed fairly quickly (30 min.), and after the usual work-up a white substance of m.p. 145.5–146.5° was obtained by crystallization from acetone–cyclohexane. Infrared examination revealed no conjugated carbonyl and, accordingly, expression XIX fits the composition of this substance. The analytical sample melted at 146–147° (acetone–cyclohexane).

*Anal.* Calcd. for $C_{20}H_{22}O_2$: C, 81.59; H, 7.54. Found: C, 81.56; H, 7.73.

When an analogous hydrogenation of XVIII was conducted so as to ensure the absorption of two molar equivalents of hydrogen (3–4 hr.), there was isolated by crystallization from acetone a substance of m.p. 202–204°, whose composition corresponds to XX. The analytical sample melted at 203–204° (acetone).

*Anal.* Calcd. for $C_{20}H_{24}O_2$: C, 81.04; H, 8.15. Found: C, 80.91; H, 8.08.

**5(or 6?)-*p*-Tolylthiotoluquinone (XXI).**—To a suspension of 122 g. of toluquinone in 200 ml. of absolute ethanol was added 62 g. of *p*-thiocresol. An exothermic reaction ensued, and a clear dark red solution soon resulted, whereupon the reaction was cooled to and maintained at room temperature overnight. The product, 5(6?)-*p*-tolylthiotoluquinone (XXI), was filtered, washed with ligroin (b.p. 86–100°), and recrystallized from benzene–ligroin twice, to give bright orange crystals, 40 g., m.p. 151–153°. The analytical sample had m.p. 154.5–155.5°.

*Anal.* Calcd. for $C_{14}H_{12}O_2S$: C, 68.90; H, 5.00; S, 13.13. Found: C, 69.40; H, 5.00; S, 13.16.

**Diels–Alder Addition of Diene XII with 5-*p*-Tolylthiotoluquinone (XXI),** *cis–anti*-**1,4-Dioxo-4a-methyl-9-phenyl-2-(*p*-tolylthio)-1,4,4a,4b,5,6,7,8,10,10a-decahydrophenanthrene (XXII).**—A solution of 5 g. of 1-(α-styryl)cyclohexene (XII) and 6.6 g. of 5-*p*-tolylthiotoluquinone (XXI) in 50 ml. of toluene containing a trace of hydroquinone was refluxed for 48 hr. The crystalline residue remaining after vacuum removal of solvent was triturated with a few milliliters of ethanol to dissolve some unchanged quinone. The filtered insoluble portion was recrystallized twice from benzene–hexane to yield 3.0 g. of XXII, pale yellowish in color, m.p. 205–208°. The analytical sample was recrystallized once again from ethanol, m.p. 207–209°. The infrared spectrum showed a strong characteristic band at 6.40 μ (thio-substituted enedione) in addition to the usual conjugated carbonyl bands.

*Anal.* Calcd. for $C_{28}H_{28}O_2S$: C, 78.50; H, 6.58. Found: C, 78.88; H, 6.38.

*trans–anti*-**1,4-Dioxo-4a-methyl-9-phenyl-1,2,3,4,4a,4b,5,6,7,8,10,10a-dodecahydrophenanthrene (XXIII).**—To a solution of 1.0 g. of adduct XXII in 50 ml. of acetic acid heated on the steam bath was added 10 g. of zinc dust in small portions with swirling during 15 min. The initial yellow color of the solution disappeared, and the reaction mixture was refluxed 8 hr. The zinc was filtered, most of the acetic acid was removed on the steam bath *in vacuo*, and the residue was taken up in sodium carbonate solution and ether. The ether solution was washed with water until the washings were neutral, dried over sodium sulfate, and evaporated. The residue was crystallized from benzene–hexane to yield XXIII, 525 mg., m.p. 145–147°. Infrared absorption revealed only nonconjugated carbonyl function.

*Anal.* Calcd. for $C_{21}H_{24}O_2$: C, 81.77; H, 7.84. Found: C, 82.03; H, 7.82.

**Attempted Diels–Alder Additions of 1-(α-Styryl)cyclohexene (XII) with Fumaric Acid, Mesaconic Acid, and 5-Methoxytoluquinone (X), to Give 1-(α-Styryl)cyclohexene Dimer (XXVII).**—No successful addition resulted from refluxing diene XII with 5-methoxytoluquinone in toluene or xylene solution for 36–48 hr.; heavy intractable oils resulted. The attempted addition with mesaconic acid (36-hr. reflux in propionic acid solution) resulted in recovery of most of the mesaconic acid.

A solution of 8.5 g. of diene XII and 8.0 g. of fumaric acid in 35 ml. of propionic acid was refluxed 60 hr. After the reaction cooled, a large amount of unchanged fumaric acid was filtered off, and the mother liquors were allowed to stand. A few weeks later it was noted that a small quantity of crystals had deposited, 400 mg., m.p. 195–200°. This substance was crystallized from dilute ethanol, whereupon it melted at 198–200°. Infrared analysis revealed no carbonyl bands, and elemental analysis, while not in excellent agreement with the dimer of XII, suggests strongly that it is indeed the nature of this material for which structure XXVII is advanced.

*Anal.* Calcd. for $(C_{14}H_{16})_2$: C, 91.2; H, 8.74. Found: C, 90.50; H, 8.77.

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