Tetrahedron, 1959, Vol. 5, pp. 70–89. Pergamon Press Ltd. Printed in Northern Ireland

THE MECHANISM OF THE DIELS–ALDER REACTION

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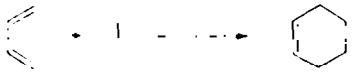
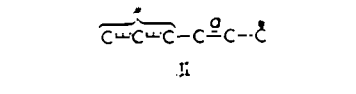
(*Received* 4 *August* 1958)

THE combination (I) of the termini of a system of two conjugated double bonds with those of a single unsaturated center– universally known as the Diels–Alder reaction –



I

is one of the most useful of synthetic reactions.[1] In systems activated by appropriate substitution, the reaction proceeds smoothly, often spontaneously, and is little affected by extramolecular circumstances. This fact, and the very nature of the change, ensure that a detailed understanding of the course of the reaction must involve questions of much subtlety. None the less, if only because the reaction constitutes one of the simplest of known bond-forming processes, its detailed mechanism deserves, and has gotten, much attention. The views which have been put forward fall into one or the other of two categories. In the one, the central thesis is that the reaction takes place in *two* steps, the first of which is rate-controlling, and comprises the formation of one single bond (*a* in the intermediate II) between appropriate atoms of the reaction partners; the process is then completed by subsequent formation of a second bond.[2]



II

Those who hold the alternative view maintain that the combination involves the simultaneous formation of the two new single bonds which appear in the product.[3]

[1] J. A. Norton, *Chem. Rev.* **31**, 319 (1942); M. C. Kloetzel, *Organic Reactions* Vol. IV, p.1. Wiley, New York (1948); H. L. Holmes, *Ibid.* Vol. IV, p. 60; L. W. Butz and A. W. Rytina, *Ibid.* Vol. V, p. 136 (1949); K. Alder, *Newer Methods of Preparative Organic Chemistry* p. 381. Interscience, New York (1948); K. Alder and Marianne Schumacher, *Fortschr. Chem. Naturstoffe* **10**, 1 (1953).

[2][a] R. Robinson, *Outline of an Electrochemical (Electronic) Theory of the Course of Organic Reactions* p. 29. The Institute of Chemistry of Great Britain and Ireland, London (1932); [b] G. B. Kistiakowsky and J. R. Lacher, *J. Amer. Chem. Soc.* **58**, 123 (1936); [c] J. B. Harkness, G. B. Kistiakowsky and W. H. Mears, *J. Chem. Phys.* **5**, 682 (1937); [d] G. B. Kistiakowsky and W. W. Ransom, *Ibid.* **7**, 725 (1939); [e] E. C. Coyner and W. S. Hillman, *J. Amer. Chem. Soc.* **71**, 324 (1949); [f] W. E. Bachmann and N. C. Deno, *Ibid.* **71**, 3062 (1949); [g] C. W. Smith, D. G. Norton and S. A. Ballard, *Ibid.* **73**, 5273 (1951); [h] J. S. Meek, B. T. Poon, R. T. Merrow and S. J. Cristol, *Ibid.* **74**, 2669 (1952).

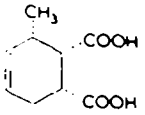
[3][a] K. Alder and G. Stein, *Angew. Chem.* **50**, 510 (1937); [b] A. Wassermann, *Trans. Faraday Soc.* **34**, 128 (1938); [c] A. Wassermann, *Ibid.* **35**, 841 (1939); [d] B. J. F. Hudson and R. Robinson, *J. Chem. Soc.* 715 (1941); [e] A Wassermann, *Ibid.* 612 (1942); [f] F. Bergmann and H. E. Eschinazi, *J. Amer. Chem. Soc.* **65**, 1405 (1943); [g] R. B. Woodward and H. Baer, *Ibid.* **66**, 645 (1944); [h] H. Henecka, *Z. Naturf.* **4B**, 15 (1949); [i] K. Alder, Marianne Schumacher, and O. Wolff, *Liebigs Ann.* **564**, 79 (1949); [j] W. Rubin and A. Wassermann, *J. Chem. Soc.* 2205 (1950); [k] K. Alder, *Liebigs Ann.* **571**, 157 (1951); [l] R. D. Brown, *Quart. Rev.* **6**, 63 (1952); [m] B. Eisler and A. Wassermann, *J. Chem. Soc.* 979 (1953); [n] C. K. Ingold, *Structure and Mechanism in Organic Chemistry* p. 711. Cornell University Press, New York (1953).

The evidence which has been brought forward in support of these proposals is of three kinds. Above all, the magnificent systematic investigations of Alder[3(a,i,k)] established a series of remarkable stereochemical generalizations which have led most chemists to favor the single-step mechanism. Then, the kinetic and thermodynamic investigations, especially those of Wassermann,[3(b,c,e,i,m)] have usually been adduced in favor of a similar choice. On the other hand, the effects brought about by substituents attached to the reacting unsaturated centers have generally been regarded as providing support for the two-step mechanism.[2]

It is the purpose of the present paper to put forward a novel view of the mechanism of the Diels-Alder reaction, which circumvents the difficulties while incorporating the features of merit of each of the previous proposals.

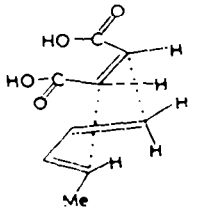
STERIC CONSIDERATIONS

The stereochemical factors attendant upon the Diels-Alder reaction may be summarized in two principles. (1) The stereometrical relationships of groups attached to the diene and to the olefin are, as nearly possible, maintained in the product. (2) If two modes of combination, leading to different steric results, are possible, that one is favored which results from maximum accumulation of unsaturated centers in the presumed activated complex. To exemplify, when *trans* piperylene combines with maleic acid, the reaction proceeds to give the product (III). In accordance with principle (1), the carboxyl groups of the product are on the same side of the newly

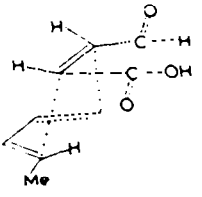


III

formed six-membered ring, as they were on the same side of the double bond in the reactant. Further, in accordance with principle (2), the product is that which would result from the union of the components in the sense (IV), rather than (V). Similarly,

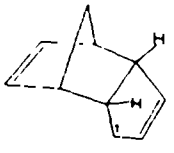


IV

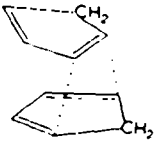


V.

the dimerization of *cyclo*pentadiene, under mild conditions, gives only the *endo* product (VI), through an assumed complex (VII). It should be emphasized at this



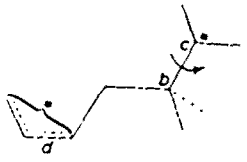
VI



VII

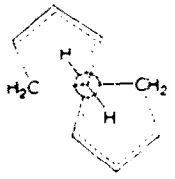
point that while the principle of maximum accumulation of unsaturated centers is in the first instance empirical, it has been given physical meaning through the proposal[3(c),4] that electrostatic and electrodynamic attractive forces associated with the mobile electronic systems not directly involved in the bond-forming processes lower the energy of intermediates such as (IV) and (VII), as compared with the alternatives of the type (V). A very great number of cases have been investigated, and the virtually universal predictive success of the above principles, applied as exemplified here, has been the major factor in bringing about acceptance of the one-step mechanism for the Diels-Alder reaction.

By contrast, the two-step mechanism, in the form in which it has been discussed previously, seems quite incapable of accomodating the stereochemical observations. For, once the initial barrier has been traversed, and the intermediate (VIII) reached,



VI

free rotation about the bond *bc* would permit dissolution of the original stereometrical relationships of the groups attached to the atoms *b* and *c*. Furthermore, if the repulsive forces of steric demand are alone operative in determining which of the available conformations will be assumed at the barrier in the initial bond-forming process, we may not doubt that in the case of *cyclo*pentadiene, for example, the activated complex will possess the structure (IX). This array leads uniquely to the



IX

X

exo dimer (X), rather than to the observed *endo* product (VI).

THERMODYNAMIC CONSIDERATIONS

Although the great difficulties associated with calculating the entropy of activated states having incompletely known geometric and other properties has led to a certain amount of controversy,[2(d),3(e)] the burden of the kinetic and thermodynamic studies on the Diels-Alder reaction is that the relatively small non-exponential term in the rate expression for the reaction requires a highly special orientation of the reactants, while the normal frequency factor for the reverse reaction indicates that the geometry of the activated complex is similar to that of the adduct.[3(n),5] It is at once clear that the one-step mechanism is in harmony with these requirements, and scarcely less so

[4] A. Wassermann, *J. Chem. Soc.* 825, 1511 (1935); 432 (1936).
[5] C. Walling, *Free Radicals in Solution* Footnote, p. 188. Wiley, New York (1957).

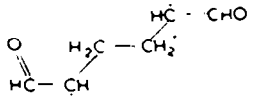
that the simple two-step mechanism is not. Since no conformational specificity is associated with the initial bond-forming process in the latter case, the requirement of similar geometry at the barrier and in the product is clearly violated, and further, it may be doubted that the frequency factor for the forward reaction should be as low as that observed.

THE EFFECTS OF SUBSTITUENTS

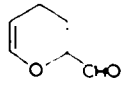
The attachment of groups of various kinds to any of the three unsaturated centers which take part in the Diels-Alder reaction exerts a marked effect upon the ease of the reaction, and upon its sense in unsymmetrical cases. Indeed, the reaction of a simple olefin with a diene takes place only with very great difficulty, and the olefinic components in those reactions which proceed smoothly and rapidly are invariably substances in which the reacting double bond is conjugated with one or more further unsaturated or equivalent groupings. Beyond that, the reaction is especially facilitated when the partners to the union are respectively laden with groups of opposite electrical character. It is easy to comprehend such influences on the basis of the two-step mechanism. For, the delocalization of electrons from each of the unsaturated systems which must be attendant upon the initial bond-forming process leaves on either side electrons which are relatively less stabilized through exchange with their former partners. Clearly, any group which stabilizes these partially freed electrons will facilitate the initial bond-forming process.

By contrast, the one-step mechanism seems ill-adapted to the rationalization of substitutive effects. Indeed, if two electrons from each partner must be simultaneously delocalized in order to participate in two simultaneous bond-forming processes, it might be expected that groups capable of conjugation would render reaction more difficult, in consequence of the demands which they would make upon the electrons necessary for bond formation in the reaction process.

Similarly, directive effects are much more clearly explicable in terms of the two-step mechanism. Thus, to choose an extreme example, it may not be doubted that the combination of two molecules of acrolein in a two-step process would lead initially to (XI),[2(e,g)] and thence to the observed product (XII). On the other hand, were the

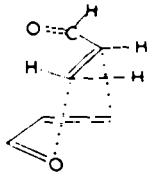


XI

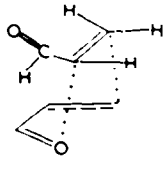


XII

reaction to proceed through a one-step complex such as (XIII) or (XIV), it seems



XIII



XIV

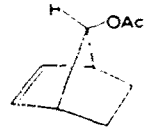
highly probable that the polar forces within such complexes would operate in such wise as to render (XIII) more stable than (XIV).

NEW EVIDENCE

We turn now to new evidence which shows with special clarity that the thermal dissociation of dicyclopentadiene derivatives takes place in two discrete and experimentally separable stages.

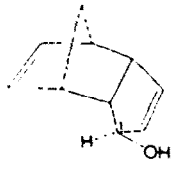
When *endo* dicyclopentadiene (VI) is heated at 200°, it suffers a smooth reverse Diels–Alder reaction, with cleavage to two molecules of cyclopentadiene.[6] The attachment of oxygen at C. 1 of the dicyclopentadiene skeleton does not materially alter the course of the dissociation. When 1-acetoxydicyclopentadiene is heated at 200°, it is converted into cyclopentadiene and acetoxycyclopentadiene. This demonstration is complicated by the lability of acetoxycyclopentadiene, but a simple proof of the course of the reaction is obtained when the decomposition is carried out in the presence of ethylene, which traps the cleavage products, respectively as bicycloheptene (XV) and 7-acetoxybicycloheptene (XVI).[7]

XV

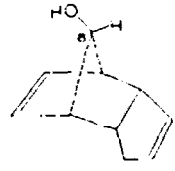


XVI

In sharp contrast to the complete cleavages just described is the behavior of α-1-hydroxydicyclopentadiene (XVII)*[7(a,c),8] when it is heated to the relatively low



XVII



XVIII

temperature of 140°. Under these conditions, the alcohol is smoothly converted, in part, into an isomeric substance, which we have shown possesses the structure (XVIII). Thus, the new alcohol possesses the infrared bands at 3·28 μ, 6·18 μ and 6·37 μ, characteristic of the two double bonds of the dicyclopentadiene system.[9] It forms a toluenesulfonyl derivative whose solvolysis is very sluggish,[10] and is reduced to a

* The prefix α is used arbitrarily to designate the isomer (XVII), while β designates the C. 1 epimer (*vide infra*). The configuration of the α alcohol at C. 1 has not previously been assigned, but follows from our observation that the new β compound is readily converted by very dilute hydrochloric acid in water/acetone to the α isomer. This conversion undoubtedly takes place under equilibrating conditions, and simple steric considerations leave no doubt that (XVII) must be the more stable of the two epimers.

[6] B. S. Khambata and A. Wassermann, *Nature, Lond.* **138**, 368 (1936); G. B. Kistiakowsky and W. H. Mears, *J. Amer. Chem. Soc.*, **58**, 1060 (1936); R. B. Moffett, *Organic Syntheses* Vol. 32, p. 41. Wiley, New York (1952).

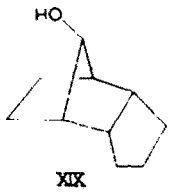
[7(a)] P. Wilder, Jr., Dissertation, Harvard (1950); [(b)] R. E. Vanelli, Dissertation, Harvard (1950); [(c)] C. J. Norton, Dissertation, Harvard (1955); [(d)] S. Winstein, M. Shatavsky, C. Norton and R. B. Woodward, *J. Amer. Chem. Soc.* **77**, 4183 (1955).

[8(a)] M. Rosenblum, *J. Amer. Chem. Soc.*, **79**, 3179 (1957); [(b)] K. Alder and F. H. Flock, *Chem. Ber.* **87**, 1916 (1954).

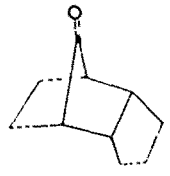
[9] P. von R. Schleyer, Dissertation, Harvard (1956); P. E. Fuchs, Dissertation, Harvard (1955); H. B. Henbest, G. D. Meakins, B. Nicholls and R. A. L. Wilson, *J. Chem. Soc.* 997 (1957).

[10] *Cf.* S. Winstein and E. T. Stafford, *J. Amer. Chem. Soc.* **79**, 505 (1957), who observed the relatively slow solvolysis of *syn*-7-norbornenyl toluenesulfonate.

tetrahydro derivative (XIX). The latter is oxidized to the corresponding ketone (XX),



XIX



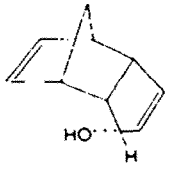
XX

whose infrared spectrum possesses a carbonyl band of characteristic high frequency (5·65 μ),[7(c)] and which is reducible by the Wolff–Kishner method to the known *endo*tetrahydrodi*cyclo*pentadiene (XXI).[11]

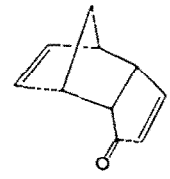
XXI

The conversion of α-1-hydroxydi*cyclo*pentadiene (XVII) into *syn*-8-hydroxydi*cyclo*pentadiene (XVIII) is an equilibrium reaction. When either alcohol is heated at 140°, it is converted into the same equilibrium mixture of (XVII) and (XVIII). The reaction is very smooth, it is accompanied by substantially no ancillary decomposition, and a careful search of the equilibration reaction mixtures reveals the presence of no substantial amounts of other isomers, or other products. The equilibrium constant for the reaction is approximately 1. Since the 8-alcohol is substantially more volatile than the 1-alcohol, the conversion of the latter into its isomer may be effectuated in almost quantitative yield by slow distillation.

Precisely similar phenomena are observed in the case of the new β-1-hydroxydi*cyclo*pentadiene (XXII) (see footnote p. 74), which is obtained by reduction of 1-ketodi*cyclo*pentadiene (XXIII)[8] by lithium aluminum hydride. When the β alcohol

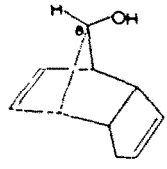


XXII



XXIII

is heated at 140°, it too is converted into an isomeric substance, which in this case has been shown to be *anti*-8-hydroxydi*cyclo*pentadiene (XXIV). The new alcohol again possesses the characteristic infrared bands at 3·28 μ, 6·18 μ and 6·37 μ.[9] Its



XXIV

[11] J. Pirsch, *Chem. Ber.* 67, 101 (1937).

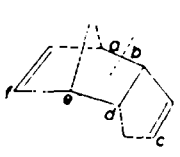
toluenesulfonyl derivative undergoes very ready solvolysis*[12] to give *anti*-8-acetoxydi*cyclo*pentadiene as sole product. It is reduced to a tetrahydro derivative, which is oxidized to the same 8-ketotetrahydrodi*cyclo*pentadiene (XX) which is obtained from the isomer (XIX). As in the case of the α isomer, the isomerization of the β alcohol (XXII) into *anti*-8-hydroxydi*cyclo*pentadiene (XXIV) is an exceptionally smooth reaction. Here again no secondary reactions of by-products are observed. In this case too, an equilibrium reaction is no doubt involved, but as would be expected on the basis of simple steric conditions, the equilibrium here lies strongly in favor of the 8-substituted alcohol (XXIV).

It is of particular significance that complete stereochemical integrity is maintained in both of the reactions just described. In the isomerization of 1-α-hydroxydi*cyclo*pentadiene only *syn*-8-hydroxydi*cyclo*pentadiene and no *anti*-8-hydroxydi*cyclo*pentadiene is formed. In the isomerization of 1-β-hydroxydi*cyclo*pentadiene, only *anti*-8-hydroxydi*cyclo*pentadiene and nc *syn*-8-hydroxydi*cyclo*pentadiene is produced.

How do these reactions proceed? We consider first, and reject at once, the possibility that the alcohol undergoes reversion of the Diels–Alder reaction, to give *cyclo*pentadiene and hydroxy*cyclo*pentadiene, which recombine to give the observed products. For, in that event, the observed stereochemical specificity of the reactions would be inexplicable. Lest an attempt be made to circumvent this argument with the proposal that the reversion does occur, and that the components are trapped in some kind of cage which ensures their recombination with approximate retention of the relevant original stereometrical relationships, we have converted the already very impressive stereochemical demonstration into a dramatic one. Thus, *the α and β alcohols,* (XVII *and* XXII), *were each resolved, and submitted to the isomerization reactions, with complete retention of optical integrity.* It would be a remarkable cage indeed which would permit to its captives the molecular motions required for the isomerization, while at the same time preventing those displacements which would lead to the symmetrical array (XXV), and thence to racemization.

XXV

It is now clear that the isomerizations which we have observed involve the scission of the bond *ab* of the di*cyclo*pentadiene skeleton (XXVI), and the constitution of a

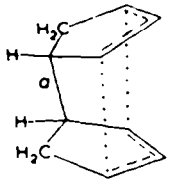


XXVI

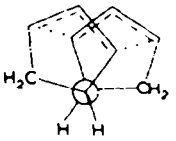
* Winstein *et al.*[18] observed the exceptionally rapid solvolysis of *anti*-7-norbornenyl toluenesulfonate. The difference in solvolytic behavior of the *syn* and *anti* 8-toluenesulfonyloxydi*cyclo*pentadienes is dramatic. The half-life of the *anti* compound in acetic acid at 25° is 8·45 min, while the *syn* isomer was unchanged under similar conditions for thirty days.

[18] S. Winstein, M. Shatavsky, C. Norton and R. B. Woodward, *J. Amer. Chem. Soc.* 77, 4183 (1955); S. Winstein and M. Shatavsky, *Ibid.* 78, 592 (1956).

new bond between *c* and *f*, while the integrity of the bond *de* is maintained. The molecules, in undergoing the transformation, must pass through a stage (XXVII → XXVIII), in which one bond is in process of formation while another is suffering



XXVII



XXVIII

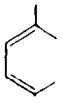
cleavage.*[13]

We now know that cleavage of one bond of the di*cyclo*pentadiene molecule, with conversion to (XXVII), takes place relatively readily. We know further that if (XXVII) is more highly energized, a second bond, at *a*, breaks, and two molecules of *cyclo*pentadiene are produced. These facts lay the basis for presumption that in the *combination* of two molecules of *cyclo*pentadiene, (1) the rate-controlling process is the formation of a single bond between termini of the conjugated systems of the reacting molecules, and (2) after passage of the barrier, reaction proceeds to the same array (XXVII), and thence, with relatively facile formation of a second bond, to the product.

A NEW THEORY

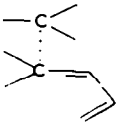
We now generalize the conclusion of the preceding section, and propose that the Diels–Alder reaction takes place in the following way.

(1) The diene assumes, if it does not already have, the *quasi cis* conformation (XXIX).

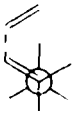


XXIX

(2) The rate-controlling process consists in the formation of a single bond between one terminus of the diene system and one of the unsaturated centers of the olefin. Accordingly, the diene and the olefin approach one another initially in parallel planes, orthogonal to the direction of the bond about to be formed (cf. XXX-XXXI).



XXX

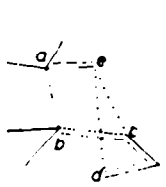


XXXI

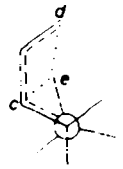
* The reaction is of course a special case of the Cope rearrangement.

[13] *Cf.* E. G. Foster, A. C. Cope and F. Daniels, *J. Amer. Chem. Soc.* **69**, 1893 (1947), and earlier papers.

(3) *Conformational specificity about the newly-forming bond is determined by secondary attractive forces involving the electrons not directly associated with the primary bonding process* (cf. XXXII–XXXIII).* Thus, as electrons at *c*, *d* and *e* are

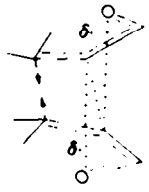


XXXII

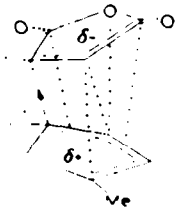


XXXIII

progressively freed of their involvement with their former partners at *a* and *b*, attractive electrostatic, electrodynamic, and even to some extent exchange forces (dotted lines *ed* and *ec* in XXXII–XXXIII) stabilize the conformation shown as compared with other *a priori* available alternatives. It should be noted that by necessity the spins of all the electrons involved in these processes are appropriately coupled at all times. Conjugating substituents at *e*, *c* and *d* will be expected in general to facilitate reaction, through direct interaction with the mobile and partially freed electrons at the positions to which the groups are attached. Further, such groups will have the following important effects: (i) they will determine which termini of the reacting systems are involved in the primary bond-forming process; (ii) their specific nature will determine the extent to which the electronic displacements accompanying the primary bond formation are polarized; (iii) their mobile electrons will make additional contributions to the secondary attractive forces, and in that way determine which of the *a priori* possible orientations of diene with respect to olefin leads to the activated

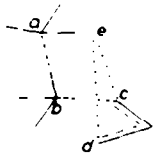


XXXIV

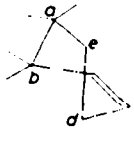


XXXV

complex of lowest energy. All of these effects of substituents will become clear on scrutiny of the activated complexes for the dimerization of acrolein (XXXIV), and for the addition of maleic anhydride to piperylene (XXXV).



XXXVI



XXXVII

(4) After passage of the barrier, formation of the single bond at *ab* is first completed (cf. XXXVI), and the reaction proceeds to its conclusion with the relatively

* In this and subsequent formulae, solid lines represent σ bonds, broken lines symbolize partial bonds, and dotted lines delineate secondary attractive forces.

facile construction of a second full bond at *ed* (XXXVII). The latter process could be opposed by a further, relatively low, barrier, since the change involves substantial, though not great, geometrical displacements, and the attendant strains need not be fully compensated at all times by the stabilization accompanying the growth of the new bond. But it should be pointed out explicitly that we beg the question whether ours is a one-step or a two-step mechanism, that is, whether such a second, lesser barrier must be passed after traversal of the first. Certainly it is a *two-stage* mechanism, in that the formation of two bonds takes place in separable, even if overlapping, processes, discretely delineated in structural terms, and displaced in time. It is entirely possible, indeed likely, that a second, low barrier will be involved in some specific cases, and not in others. In any event, it must be emphasized that for virtually all predictive and explicative purposes, resolution of the extremely subtle problems associated with defining the precise topography of the energy surface for the reaction after passage of the first barrier is irrelevant.

In conclusion, we note that the theory of the Diels–Alder reaction here put forward possesses at one and the same time the divers favorable attributes which have hitherto been considered separately and exclusively characteristic of the one or the other of the previously proposed mechanisms. It shares with the two-step mechanisms the favorable predictive capacity in respect to the effects of substituent groups on ease and sense of reaction. Further, in common with the one-step mechanism, it readily accommodates the kinetic and thermodynamic evidence, since it assumes an activated complex which is relatively rigid, whose geometry is not markedly different from that of the product, and whose formation requires a highly special orientation of the reacting molecules. Finally, it is entirely in consonance with stereochemical observations, since the relative rigidity of the molecular species involved throughout reaction ensures that stereometrical relationships inherited from the reactants are maintained, and since, as compared with previous theories, it lends similar, but expanded physical meaning to the empirical principle of maximum accumulation of unsaturated centers.

EXPERIMENTAL

Melting points, unless otherwise stated, were taken in capillary tubes, and are corrected.

α-1-*Hydroxydi*cyclo*pentadiene* (XVII)

The alcohol was prepared according to the procedure of Rosenblum[8(a)] and Norton[7(c)] with some modifications. Freshly distilled di*cyclo*pentadiene (186 g) was dissolved in 500 ml dioxane in a one-liter three-necked flask equipped with a Hershberg stirrer and reflux condenser. Water (50 ml) and potassium dihydrogen phosphate (20 g) were added, and, while the solution was stirred and heated on a steam-bath, selenium dioxide (80 g, freshly prepared and sublimed[14]) was added. After 3 hr the mixture was cooled, the precipitated selenium was filtered immediately with suction, and the precipitate was washed with ether. The filtrate was shaken with 1 l. of saturated NaCl solution. The aqueous solution was drawn off and washed three times with 300 ml portions of ether. The combined organic solutions were then washed with 250 ml of 5 per cent aqueous sodium hydroxide and 500 ml of saturated

[14] N. Rabjohn, *Organic Reactions* Vol. V, p. 345. Wiley, New York (1949).

brine. The emulsion which formed was broken by filtration through Supercel. The organic phase was washed twice more with brine and dried over sodium sulfate. The solvent was removed at reduced pressure, and the residual oil was distilled (b.p. 67° at 0·1 mm) to yield 132 g (63%) of slightly yellow, waxy crystals. After redistillation this material was sufficiently pure for use in all the following experiments. The alcohol could be obtained by recrystallization from pentane as white crystals, m.p. 36·6–37·4°. It is reported by Rosenblum[8(a)] and Norton[7(c)] to be an oil and by Alder[8(b)] as a waxy mass, m.p. 40–50°.

A phenylurethan was prepared in the usual way; m.p. 139·6–140·0° (reported,[8(b)] m.p. 142°).

The thermal isomerization of α-1-*hydroxydi*cyclo*pentadiene* (XVII)

When the α alcohol is heated to a temp. in the neighborhood of 135–150°, a ready isomerization takes place. At temp. well below 135°, the isomerization does not occur noticeably. Thus, for example, refluxing the alcohol in benzene solution for two days results in no isomerization, and the starting material is recovered unchanged. Above 150°, cracking[8(a,b),15] and polymerization occur. That the isomerization is in fact an equilibration was demonstrated as follows. Pure α-1-hydroxydi*cyclo*pentadiene (162 mg) was placed in a Pyrex tube, which was then evacuated and sealed. Similarly, a sample of the pure *syn*-8-hydroxydi*cyclo*pentadiene (153 mg, *vide infra*) was sealed into an evacuated tube. The two tubes were placed in a round-bottomed flask partially filled with xylene and set for reflux. By refluxing the xylene around the tubes, a temp. of 138° was maintained for 6 hr. The tubes were then quickly cooled, opened, and the infrared spectra of the contents examined. The two samples had superimposable spectra, which, when compared with the spectra of known mixtures of the two alcohols indicated that this equilibrium mixture consists of 53 ± 5% *syn*-8-hydroxydi*cyclo*pentadiene and 47 ± 5% α-1-hydroxydi*cyclo*pentadiene.

Syn-8-*hydroxydi*cyclo*pentadiene* (XVIII)

α-1-Hydroxydi*cyclo*pentadiene was distilled slowly at a pressure of 35 mm through a jacketed distilling column (11·5 mm × 125 cm packed with ⅛ in. Pyrex glass helices). The still-pot was heated in an oil bath kept at 165–175°, and the column was maintained at 131–132°. The product which distilled (b.p. 126° at 35 mm) crystallized immediately, and precautions had to be taken to prevent its freezing in the still-head and fraction collector. The crude distillate consists almost entirely of *syn*-8-hydroxydi*cyclo*pentadiene contaminated with some of the starting material. The yield is limited only by the hold-up of the apparatus and by a very small amount of polymerization which occurs in the pot. If the same distilling column is used from one run to the next, the hold-up of the column no longer affects the yield. Typical results follow.

Fifty grams of the α-1-hydroxydi*cyclo*pentadiene were distilled through the column under the conditions described above. The distillate was collected in three fractions: the first, before the column was completely equilibrated, consisted of 6 g; the main fraction comprised 40 g; and a final few drops (ca. 1 g) were collected. Thus, the total recovery was 47 g (94%). The infrared spectra of the first two fractions were compared with the spectra of known mixtures of *syn*-8-hydroxydi*cyclo*pentadiene and

[15] K. Alder and F. H. Flock, *Chem. Ber.* **89**, 1732 (1956).

α-1-hydroxydi*cyclo*pentadiene, as well as with the spectra of *anti*-8-hydroxydi*cyclo*-pentadiene and di*cyclo*pentadiene. The absence of the latter two compounds, as well as ketonic material from cracking, was indicated by the absence of characteristic absorption (e.g., at 5·5–6·0 μ, 9·46 μ, 12·20 μ, 13·80 μ, 13·85 μ, 14·8 μ). In fact, the spectrum of the main fraction was identical with that of a mixture of 93% *syn*-8-hydroxydi*cyclo*pentadiene and 7% α-1-hydroxy*cyclo*pentadiene, while the spectrum of the fore-run was essentially identical with that of a mixture of 11% α-1-hydroxydi*cyclo*pentadiene and 89% *syn*-8-hydroxydi*cyclo*pentadiene.

The first fraction was recrystallized once from pentane, combined with the main fraction, and the combined products recrystallized three times more from pentane. This yielded 36·3 g (73%) of white crystals, m.p. 51·8–52·8°. A sample purified for analysis melted at 52·1–52·9°.

(Found: C, 80·95; H, 8·18; Calc. for $C_{10}H_{12}O$: C, 81·04; H, 8·16%).

The phenylurethan was prepared in the usual way and recrystallized from ligroin to constant melting point: m.p. 113·7–114·3°.

(Found: C, 76·39; H, 6·42; N, 5·06; Calc. for $C_{17}H_{17}O_2N$: C, 76·38; H, 6·41; N, 5·24%).

Oppenauer oxidation of syn-8-*hydroxydi*cyclo*pentadiene* (XVIII)

A solution of *syn*-8-hydroxydi*cyclo*pentadiene (509 mg) and quinone (607 mg) in 75 ml dry benzene was prepared in a 100 ml round-bottomed flask. After removing the last traces of water by distilling out a few milliliters of the solvent, aluminum *t*-butoxide (1 g) was added, and the mixture refluxed for 50 hr. The reaction mixture was cooled, acidified with dilute HCl, and filtered through Supercel. The aqueous phase was drawn off, and the organic phase washed twice with dilute HCl and four times with 5% NaOH. After the solution was dried over K_2CO_3, the solvent was removed at reduced pressure; 482 mg of oil was obtained, which crystallized on seeding with di*cyclo*pentadiene-1-one. The infrared spectrum of the product (300 mg) after two recrystallizations from petroleum ether was compared with that of authentic di*cyclo*pentadiene-1-one (XXIII).[8(a,b)] The two were in every respect identical. Further purification by recrystallization and sublimation afforded material, m.p. 65·3–65·6°; mixed with authentic di*cyclo*pentadiene-1-one (m.p. 65·2–65·6): m.p. 65·3–65·6°.

Tetrahydro-syn-8-*hydroxydi*cyclo*pentadiene* (XIX)

Syn-8-hydroxydi*cyclo*pentadiene (1·013 g) in absolute ethanol (5 ml) was hydrogenated at atmospheric pressure in the presence of 65 mg platinum oxide. 95% of the expected 2 moles of hydrogen was absorbed in 7 hr. The catalyst was filtered, the solvent removed *in vacuo*, and the residue sublimed at reduced pressure to yield 833 mg (80%) of white crystals, m.p. 109·5–109·9°.

On a larger scale, a solution of 20 g of *syn*-8-hydroxydi*cyclo*pentadiene in 200 ml of 95% ethanol was hydrogenated in the presence of 368 mg of platinum oxide in a shaker (initial pressure: 50 lb/in² above atmospheric pressure). After sublimation, 19·4 g (94%) of the tetrahydro derivative were obtained.

Purification was conveniently effected by recrystallization from ligroin. The analytically pure material melts at 110·5–111·5°.

(Found: C, 78·82; H, 10·66; Calc. for $C_{10}H_{16}O$: C, 78·89; H, 10·59%).

*Di*cyclo*pentadiene*-1-*one* (XXIII)

The ketone was prepared according to the procedure of Alder[8(b)] by chromic acid oxidation of α-1-hydroxydi*cyclo*pentadiene. The ketone was purified by recrystallization from ligroin and by sublimation at reduced pressure. The melting point was found to be 65·3–65·6° (reported: 80°[8(b)] and 59·0–59·5°[8(a)]). The 2,4-dinitrophenylhydrazone was prepared and recrystallized from aqueous ethanol, m.p. 199·2–199·5° (dec.) (reported,[8(a)] 203·5–204·0°).

β-1-*Hydroxydi*cyclo*pentadiene* (XXII)

To a stirred solution of lithium aluminum hydride (2·26 g) in anhydrous ether (1 l.) in a 2 l. three-necked flask, equipped with stirrer, condenser, and dropping funnel, a solution of 20·55 g of the above ketone (XXIII) in 200 ml ether was added slowly. The solution was stirred for 15 min after the addition was complete. It was then cooled and treated, with vigorous stirring, successively with 2·3 ml water, 2·3 ml 15% NaOH and 6·8 ml water.[16] The alumina was filtered and the ether removed *in vacuo*. The residue on recrystallization from a mixture of 50 ml ligroin and 150 ml pentane afforded 14·8 g (71%) of the alcohol. For analysis a sample was purified by recrystallization from pentane, from which the alcohol crystallizes as fluffy white needles, and sublimation at 0·05 mm pressure; m.p. 85·0–85·8°.

(Found: C, 81·20; H, 8·34; Calc. for $C_{10}H_{12}O$: C, 81·04; H, 8·16%).

Anti-8-*hydroxydi*cyclo*pentadiene* (XXIV)

A Pyrex bomb-tube partially filled with β-1-hydroxydi*cyclo*pentadiene (8·83 g) was evacuated and sealed. The tube was then placed in a round-bottomed flask and maintained at 135° for 22 hr by refluxing xylene around it. When cool, the tube was opened, and the contents transferred to a sublimation apparatus. The product was sublimed twice at reduced pressure, to yield 7·0 g (80%) of white, slightly oily crystals, which after two recrystallizations from pentane melted at 68·9–70·4°. A sample purified for analysis melted at 66·8–67·4°.

(Found: C, 81·08; H, 8·00; Calc. for $C_{10}H_{12}O$: C, 81·04; H, 8·16%).

The infrared spectrum of a sample of the crude material obtained by sublimation of the contents of the bomb-tube was compared with spectra of *syn*-8-hydroxydi*cyclo*pentadiene and β-1-hydroxydi*cyclo*pentadiene. The absence of these compounds from this material was witnessed by the lack of their characteristic absorption bands. For example, the following absorption bands present in the spectrum of the *syn*-8-ol: 14·10 μ, 14·45 μ, 12·94 μ, 12·81 μ, 9·76 μ, 9·68 μ, and of the β-1-ol: 13·11 μ, 12·82 μ, 11·06 μ, 9·84 μ, 9·70 μ were absent.

The phenylurethan was prepared and recrystallized from ligroin to a constant melting point, m.p. 136·2–136·5°.

(Found: C, 76·53; H, 6·64; N, 5·50; Calc. for $C_{17}H_{17}O_2N$: C, 76·38; H, 6·41; N, 5·24%).

Tetrahydro-anti-8-*hydroxydi*cyclo*pentadiene*

A solution of the above alcohol (XXIV, 931 mg) in absolute ethanol (10 ml) in the presence of 85 mg platinum oxide catalyst absorbed 97% of the theoretical two

[16] V. M. Micović and M. L. Mihailović, *J. Org. Chem.* **18**, 1190 (1953).

moles hydrogen at atmospheric pressure in less than 2 hr. The crystalline residue left after filtration of the catalyst and removal of the solvent *in vacuo* was recrystallized from ligroin to yield 750 mg (81%) of white crystals, m.p. 120·0–120·5°. Further recrystallization and sublimation at reduced pressure afforded the analytically pure material, m.p. 119·8–120·3°.

(Found: C, 78·91; H, 10·72; Calc. for $C_{10}H_{16}O$: C, 78·89; H, 10·59%).

*Tetrahydrodi*cyclo*pentadiene*-8-*one* (XX)

(a) *From tetrahydro*-syn-8-*hydroxydi*cyclo*pentadiene* (XIX). The alcohol (2·0 g) and freshly sublimed quinone (2·45 g) were dissolved in dry benzene (85 ml) in a 100 ml round-bottomed flask. To remove the last traces of water a few milliliters of benzene were distilled from the flask. Aluminum *t*-butoxide (4 g) was then added, and the mixture, protected from moisture, was refluxed for approximately 30 hr. After the flask had been cooled, the contents were poured into cold 5% HCl, and the aqueous layer drawn off. The benzene solution was washed once more with cold 5% HCl and three times with 5% NaOH, and then was dried over potassium carbonate. The solvent was distilled at reduced pressure, and the residue sublimed twice to yield 1·57 g (80%) of a slightly yellow camphoraceous product. Purification was effected by recrystallization from pentane. The analytically pure material consisted of colorless waxy crystals, m.p. 65° (Fisher–Johns block), which were too soft to place into a melting point tube.

(Found: C, 79·80; H, 9·48; Calc. for $C_{10}H_{14}O$: C, 79·95; H, 9·39%).

(b) *From tetrahydro*-anti-8-*hydroxydi*cyclo*pentadiene*. The latter (221 mg) and quinone (280 mg) in benzene solution (8 ml) was refluxed with aluminum *t*-butoxide (469 mg) for 40 hr. After the reaction mixture had been cooled and acidified with cold 5% HCl, insoluble material was removed by filtration through a mat of Supercel (which was then washed with pentane). The aqueous layer was drawn off, and the organic phase washed successively with cold water, cold 5% NaOH and cold water. After drying over sodium sulfate, the solvent was distilled at diminished pressure, and the residue sublimed to yield 128 mg (59%) of an oily solid. After purification, as above, by recrystallization from pentane and sublimation, its infrared spectrum was identical with that of the ketone prepared as in (a) (above).

Purified samples of the ketone prepared from the two epimers had identical melting points (65°, Fisher–Johns block) undepressed by admixture of the two. The infrared spectra of the two samples were superimposable. 2,4-Dinitrophenylhydrazones were prepared in the usual way from samples of the ketone prepared by the alternative methods, and these were recrystallized from aqueous ethanol to constant melting points, which follow:

2,4-DNP from tetrahydro-*syn*-8-hydroxydi*cyclo*pentadiene: m.p. 155·4–156·6°

2,4-DNP from tetrahydro-*anti*-8-hydroxydi*cyclo*pentadiene: m.p. 156·2–157·3°

mixed: m.p. 155·9–157·1°

The ultraviolet spectrum of the 2,4-dinitrophenylhydrazone was determined: λ_{max} (ethanol) 357 mμ (log ε · · 4·4).

*Wolff–Kishner reduction of tetrahydrodi*cyclo*pentadiene*-8-*one* (XX)

A solution of the ketone (587 mg) in triethylene glycol (20 ml) was treated with 0·4 ml 95% hydrazine. After the solution had been allowed to stand at room temp.

for 1 hr, benzene (45 ml) was added and water azeotroped from the reaction mixture over a period of 5 hr. KOH (2·5 g) was added, and water again was azeotroped from the mixture. Volatile materials were distilled, and the reaction flask, equipped with a short condenser leading to a fresh receiver, and thermometer extending into the reaction mixture, was heated to 205°. After 20 hr, the temp. was raised to distill out last traces of the reaction products. The distillate was diluted with its own volume of water and extracted twice with pentane. The pentane solutions, after being washed with 5% HCl, water, and 5% NaOH, were dried over K_2CO_3. The residual oil left after the solvent was distilled was freed of polar materials by elution from an alumina column (10 g, Woelm, activity I) with pentane. The eluted material was again placed on an alumina column (100 g, Woelm, activity I) and eluted with pentane. Sublimation of the crystalline residue left after removal of the solvent yielded 273 mg (51%) of the hydrocarbon. After one more chromatographic treatment and resublimation, the hydrocarbon was compared with authentic tetrahydrodi*cyclo*pentadiene.[11] Its melting point (74–76°) was identical with that of the authentic material and was undepressed on admixture with the latter. Its infrared spectrum, though lacking detail, was identical with that of the authentic sample.

*Epimerization of β-1-hydroxydi*cyclo*pentadiene* (XXII)

A mixture of β-1-hydroxydi*cyclo*pentadiene (570 mg) acetone (10 ml) and 30 ml 0·1 M HCl was stirred for 90 min at room temp. The solution was made basic by the addition of saturated K_2CO_3 solution, and 50 ml saturated NaCl solution were added. The mixture was extracted three times with 30 ml portions of pentane. The combined pentane/acetone solutions were washed once with brine and dried over sodium sulfate. The drying agent was filtered, and the solvent removed *in vacuo*, leaving 548 mg (96%) of an oil, the infrared spectrum of which was rich in detail and identical with that of α-1-hydroxydi*cyclo*pentadiene (XVII). The phenylurethan was prepared from this alcohol, and recrystallized twice from ligroin. Its melting point (140·0–140·1°) was undepressed by admixture with the phenylurethan of the alcohol produced by selenium dioxide oxidation of di*cyclo*pentadiene (m.p. 139·9–140·4°).

Syn-8-*tosyloxydi*cyclo*pentadiene*

Syn-8-hydroxydi*cyclo*pentadiene (6 g), dissolved in pyridine (16 ml) was treated with tosyl chloride (8·48 g). The flask was stoppered and shaken until all the solids had dissolved, and was allowed to stand at room temp. overnight.[17] The reaction mixture was poured into cold dilute HCl sufficient to neutralize all the pyridine. The precipitated solid was dissolved by the addition of benzene, and after the two phases were separated, the aqueous phase was extracted twice more with benzene. The combined benzene solutions were washed with dilute HCl and dilute NaOH, dried over K_2CO_3, and the solvent removed *in vacuo*. The tosylate is unstable to heat, and was recrystallized by dissolving it quickly in hot ligroin, cooling rapidly to room temperature, and finally cooling in an ice-bath. After two recrystallizations, 8·85 g (71%) of the tosylate were obtained. A sample purified for analysis melted at 96·4–96·8°.

(Found: C, 67·72; H, 6·08; Calc. for $C_{17}H_{18}SO_3$: C, 67·52; H, 6·00%).

[17] R. S. Tipson, *J. Org. Chem.* **9**, 235 (1944).

Anti-8-*tosyloxydi*cyclo*pentadiene*

Anti-8-hydroxydi*cyclo*pentadiene (995 mg) was dissolved in 5·0 ml dry pyridine (freshly distilled from barium oxide), and the solution, in a 10 ml stoppered flask, was cooled in an ice/salt bath. Tosyl chloride (1·416 g, recrystallized from ether) was added, and the flask securely stoppered and shaken, with cooling, until solution was complete. The flask was then stored for 6 hr in the refrigerator (ca. 8°). The contents were poured into a cold solution of 1·65 ml of conc. H_2SO_4 in 50 ml water. The mixture was extracted three times with 30 ml portions cold benzene, and the combined benzene solutions were washed successively with cold 0·3 N H_2SO_4, cold water, cold 5% $NaHCO_3$, and cold water again. The benzene solution was dried over Na_2SO_4, and the solvent was carefully removed *in vacuo*. The residue was recrystallized by dissolving it in ca. 75 ml ligroin at room temp and cooling to Dry Ice temp. This afforded 1·10 g of white crystals. Concentration of the mother liquors at reduced pressure to half the original volume, and cooling yielded an additional 0·34 g, which after one more recrystallization from 15 ml of ligroin afforded 0·25 g of tosylate. The combined yield (1·35 g) is 66% of the theoretical. The tosylate is unstable at room temp. and above, and turns deep purple on warming. It can, however, be stored for weeks in a freezer.

(Found: C, 67·75; H, 6·06; Calc. for $C_{17}H_{18}SO_3$: C, 67·52; H, 6·00%).

Tetrahydro-syn-8-*tosyloxydi*cyclo*pentadiene*

A solution of tetrahydro-*syn*-8-hydroxydi*cyclo*pentadiene (XIX, 1·09 g) in pyridine (3 ml) was cooled in an ice-bath, and tosyl chloride (1·5 g) was added. The flask was stoppered and shaken to effect solution of the solids, and stored in the refrigerator for 2 hr and then overnight at room temp. The reaction mixture was treated with a cold solution of 2·5 ml conc. HCl in 20 ml water, and the product was then extracted twice with ether. The combined ether solutions were washed with dilute HCl, water, and 5% $NaHCO_3$, and then dried over Na_2SO_4. Removal of the solvent left an oil which crystallized on cooling and scratching. One crystallization from petroleum ether afforded 1·9 g of the tosylate, which after recrystallization melted at 46·5–46·8°.

Attempted acetolysis of tetrahydro-syn-8-*tosyloxydi*cyclo*pentadiene*

A solution of the tosylate (500 mg) potassium acetate (173 mg) in acetic acid (15 ml), sealed into an evacuated bomb-tube, was heated in a steam cone for 78 hr. The bomb was cooled, opened, and the contents diluted with water and extracted three times with chloroform. The combined chloroform solutions were washed successively twice with water and twice with $NaHCO_3$ solution, and dried over Na_2SO_4. Removal of the solvent left 485 mg (97% recovery) of the original tosylate, identified by its infrared spectrum, which was identical with that of the starting material.

Attempted acetolysis of syn-8-*tosyloxydi*cyclo*pentadiene*

A solution of 223 mg tosylate (m.p. 95·4–96·3°) and 102 mg potassium acetate in 10 ml acetic acid was allowed to stand at room temp. for 30 days. After dilution with 75 ml water, the mixture was extracted with four 30 ml portions of chloroform, and the combined chloroform solutions were washed successively with 5% NaOH and three times with water. After drying over Na_2SO_4 the solvent was distilled at reduced

pressure, leaving 220 mg (99% recovery) of slightly yellow crystals, m.p. 95·0–96·3°. The infrared spectra of the product and starting material were identical.

Acetolysis of anti-8-*tosyloxydi*cyclo*pentadiene*

(a) *Kinetics.* The rate of acetolysis at 25·03 ± ·02° of the tosylate in the presence of 0·1 M sodium acetate and 1% acetic anhydride was determined by the infinity titer method[18] as follows. The tosylate (294 mg) was weighed into a 10 ml volumetric flask, and the flask was then allowed to equilibrate with the thermostating bath. 10 ml of a solution of sodium acetate (0·1 M) in anhydrous acetic acid containing 1% excess acetic anhydride, previously equilibrated with the bath, were added to the tosylate, and the flask was shaken to effect solution. After about 4 min, the first 1·000 ml aliquot was withdrawn and reaction quenched by running it into petroleum ether in an ice-bath.[19] The amount of the petroleum ether used was varied in such a way that at the end-point of the titration the solution contained twice as much petroleum ether as acetic acid. Five drops of a saturated solution of bromphenol blue in acetic acid was added, and the sodium acetate titrated with 0·02 M perchloric acid in anhydrous acetic acid and 0·02 M sodium acetate in anhydrous acetic acid; excess perchloric acid was added and back-titrated with the sodium acetate solution to determine the titer, V, of the solution in milliliters of perchloric acid solution. A plot of ln $(V-V_\infty)$ against time was found to be a straight line with slope, $k = -1{\cdot}37 \times 10^{-3}\ \text{sec}^{-1}$.

(b) *Product study.* A solution of 74 mg tosylate and 34 mg potassium acetate in 3·3 ml glacial acetic acid was allowed to stand at room temp. overnight. The reaction mixture was diluted with cold water and extracted three times with 15 ml portions of cold pentane. The combined pentane solutions were washed with cold water, cold 5% $NaHCO_3$, and cold water again. After drying over Na_2SO_4, the solvent was removed *in vacuo*, leaving 42 mg (91%) of an oil. Its infrared spectrum was compared with the spectra of the acetates (*vide infra*) of *syn*-8-hydroxydi*cyclo*pentadiene and *anti*-8-hydroxydi*cyclo*pentadiene. The infrared spectrum was identical with that of the *anti*-acetate. No evidence for the presence of the *syn* epimer could be found. Thus, there were no bands at 9·30 μ, 11·94 μ, 13·05 μ, 13·19 μ or 14·08 μ, all of which are present in the spectrum of the *syn*-acetate.

Anti-8-*acetoxydi*cyclo*pentadiene*

Anti-8-hydroxydi*cyclo*pentadiene (498 mg) was dissolved in pyridine (1·0 ml) and the solution cooled in an ice/salt bath. Acetic anhydride (1·1 ml) was added, and the mixture was swirled, stoppered, and allowed to stand at room temp. overnight. After 20 hr, the solution was poured into an ice-cold solution of 0·8 ml of conc. HCl in 20 ml water. The mixture was extracted with 3 ice-cold 20 ml portions of pentane, and the combined pentane solutions washed with cold 2% HCl, cold water, twice with cold 5% $NaHCO_3$, and again with cold water. After drying over Na_2SO_4, most of the pentane was removed at reduced pressure. In order to remove traces of polar impurities, the solution was put on a column of 10 g of Woelm alumina (activity I) and eluted successively with 50 ml portions each of pentane, 5% ether in pentane, and 25% ether in pentane. Removal of the solvents yielded 507 mg (80%) of the acetate,

[18] S. Winstein, C. Hanson and E. Grunwald, *J. Amer. Chem. Soc.* **70**, 812 (1948); S. Winstein, E. Grunwald and L. L. Ingraham, *Ibid.* **70**, 821 (1948).

[19] S. Winstein and D. Trifan, *J. Amer. Chem. Soc.* **74**, 1154 (1952).

a very pleasant-smelling oil. For analysis the product was re-chromatographed on alumina and distilled.

(Found: C, 75·80; H, 7·48; Calc. for $C_{12}H_{14}O_2$: C, 75·76; H, 7·42%).

Syn-8-*acetoxydi*cyclo*pentadiene*

Syn-8-hydroxydi*cyclo*pentadiene (3·75 g) in pyridine (6·0 ml) was treated with acetic anhydride (2·72 ml) and the flask swirled, stoppered, and allowed to remain at room temp. overnight. The reaction mixture was poured into an amount of dilute HCl calculated to neutralize the pyridine, and the product extracted three times with ether. The combined ether solutions were washed with dilute HCl, brine and 5% $NaHCO_3$. After drying over Na_2SO_4, the solvent was removed, and the residual oil was distilled at reduced pressure to yield 2·64 g of a pleasant-smelling oil, b.p. 83° at 0·6 mm. This was purified by chromatography on alumina and redistilled.

Resolution of α-1-*hydroxydi*cyclo*pentadiene* (XVII)

3-β-Acetoxy-Δ^5-etiocholenyl chloride was freshly prepared by allowing freshly recrystallized 3-β-acetoxy-Δ^5-etiocholenic acid* (36·9 g) and thionyl chloride (200 g) to react at room temp. for 4 hr. Removal of the excess thionyl chloride *in vacuo* yielded the crystalline acid chloride, which was dissolved in 300 ml dry pyridine (freshly distilled from barium oxide). The solution was then cooled in an ice-bath. The α-1-hydroxydi*cyclo*pentadiene (17·0 g) dissolved in 50 ml dry pyridine, was added. The flask was stoppered securely, shaken vigorously, and was then allowed to stand at room temp. overnight.

The cooled reaction mixture was poured into an ice-cold solution of 380 ml of conc. HCl in 2 l. of water. The mixture was shaken vigorously and filtered. The precipitate was washed with more cold dilute HCl and then with cold water to neutrality. Water was removed from the crude reaction product by drying *in vacuo* over calcium chloride. Yield: 47·0 g (94%).

The dried esters were dissolved in 2 l. of hot acetone. The solution was filtered and then concentrated to about 800 ml, at which point crystallization began. Cooling, followed by filtration, yielded 24·5 g of plates, m.p. 191–192·8°. After two more recrystallizations, the yield of the one pure diastereomer was 17·4 g (70%), m.p. 200·0–201·2°.

A sample prepared for analysis melted at 201·9–202·7°, and had $[\alpha]_D^{23}$ −110° ($CHCl_3$, c 1·96).

(Found: C, 78·11; H, 8·46; Calc. for $C_{32}H_{42}O_5$: C, 78·33; H, 8·63%).

A suspension of this ester (17·2 g) in about 1800 ml anhydrous ether was slowly added, with vigorous stirring, to a suspension of lithium aluminum hydride (7 g) in 1200 ml anhydrous ether in a dry three-necked flask set for reflux. The reaction mixture was stirred for 30 min after addition was complete and was then cooled in an ice-bath. With vigorous stirring, 7 ml water were slowly added, followed by 7 ml 15% NaOH, and another 21 ml water. Stirring was stopped after another 5 min, and the reaction mixture filtered through a mat of Supercel. Ether was used to wash the precipitate. The combined solutions were transferred to a separatory funnel and washed twice with 200 ml portions water. Drying (Na_2SO_4), followed by removal of

* We wish to express our warm appreciation to Dr. Eugene P. Oliveto (Schering Corporation, Bloomfield), who kindly provided a generous sample of 3-β-acetoxy-Δ^5-etiocholenic acid.

the ether *in vacuo*, left a residue, which was shaken vigorously with approximately 1 l. of pentane. The steroidal alcohol was filtered, washed with more pentane, and the pentane largely removed from the filtrate. Cooling the concentrated solution precipitated the optically active α-1-hydroxydi*cyclo*pentadiene (3·68 g, 71%) as soft white crystals, m.p. 68–70·3°, $[\alpha]_D^{24}$ 87° ($CHCl_3$, *c* 2·91). The infrared spectrum (CS_2) of this material was superimposable in detail on that of the *dl*-α-1-hydroxydi*cyclo*pentadiene.

*Rearrangement of l-α-1-hydroxydi*cyclo*pentadiene* (XVII)

The optically active α alcohol (519 mg) was sealed into an evacuated Pyrex tube, which had been carefully cleaned to ensure a clean dry neutral surface. The sealed tube was heated in a bath of refluxing xylene (139–140)° for 6 hr. The tube was then quickly cooled and opened. The oily product had $[\alpha]_D^{25}$ −38° ($CHCl_3$, *c* 2·21). The components of the mixture were separated by chromatography on 50 g Florisil. The *syn*-8-hydroxydi*cyclo*pentadiene was eluted by ether/benzene (1:25) and was immediately followed by the α-1-hydroxydi*cyclo*pentadiene. Identical fractions were combined and sublimed, and mixed fractions were discarded.

The *syn*-8-hydroxydi*cyclo*pentadiene thus obtained (127 mg, white needles, m.p. 49·4–51·6°) had $[\alpha]_D^{22}$ +1·1°, $[\alpha]_{400\ m\mu}^{22}$ −32·9° ($CHCl_3$, *c* 9·62). Its infrared spectrum was identical with that of *dl-syn*-8-hydroxydi*cyclo*pentadiene. That the observed rotations were not due to the presence of a trace of the starting material (α-1-hydroxydi*cyclo*pentadiene) was demonstrated by a determination of the rotatory dispersion curve of the latter compound: $[\alpha]_D^{22}$ 86°, $[\alpha]_{400\ m\mu}^{22}$ 248° ($CHCl_3$, *c* 2·21). The rotations of the starting material and product are opposite in sign.

The recovered α-1-hydroxydi*cyclo*pentadiene had m.p. 69·2–70·9° and $[\alpha]_D^{23}$ 85° ($CHCl_3$, *c* 2·21).

*l-Di*cyclo*pentadienone*-1 (XXIII)

l-α-1-Hydroxydi*cyclo*pentadiene (2·35 g) was added to the complex formed from 4·45 g chromic anhydride and 45 ml dry pyridine, according to the procedure of Sarett.[20] After 24 hr at room temp., the mixture was poured into 400 ml water, and benzene was added. Insoluble material was removed by filtration. The layers were separated, and the aqueous phase re-extracted twice more with fresh portions of benzene, filtering as necessary. The combined benzene solutions (ca. 500 ml) were washed twice with water, twice with cold 20% HCl, and then three times with saturated brine to neutrality. The benzene was removed *in vacuo* after drying over potassium carbonate, leaving the crystalline ketone, which was recrystallized from ligroin: yield 1·93 g. After one more recrystallization from a small amount of ligroin, the yield was 1·90 g of white crystals, m.p. 72·6–76·4°. A small sample recrystallized from ligroin melted at 76·8–77·8°, and had $[\alpha]_D^{26}$ −162° ($CHCl_3$, *c* 3·15). Its infrared spectrum was identical with that of *dl*-di*cyclo*pentadienone-1.

*d-β-1-Hydroxydi*cyclo*pentadiene* (XXII)

In a dry three-necked flask, equipped with condenser, dropping funnel and stirrer, a suspension of 317 mg of lithium aluminum hydride in 150 ml dry ether was prepared. While stirring, a solution of the *l*-ketone (1·71 g) in 50 ml dry ether was added, and

[20] G. I. Poos, G. E. Arth, R. E. Beyler and L. H. Sarett, *J. Amer. Chem. Soc.* 75, 422 (1953).

stirring was continued for another 15 min. The reaction mixture was cooled in an ice-bath, and, with vigorous stirring, 0·3 ml water, followed by 0·3 ml 15% NaOH and 0·9 ml water were added. The alumina was filtered through a mat of Supercel and washed with more ether. The combined ether filtrates were washed twice with water and dried (Na_2SO_4). After the removal of the solvent, the residue was twice recrystallized from ligroin and then sublimed: yield 1·09 g. The infrared spectrum of this product was extremely similar to, but not identical with, that of pure β-1-hydroxydi*cyclo*pentadiene. The product was therefore purified by chromatography on aluminum oxide (Merck). The alcohol was eluted with ether/pentane (1:1), and pure fractions were combined and sublimed. The pure product thus obtained had $[\alpha]_D^{25}$ +130° ($CHCl_3$, $c = 1{\cdot}82$) and melted at 83·7–84·8°. Its infrared spectrum (CS_2) was in every respect identical with that of β-1-hydroxydi*cyclo*pentadiene

*Rearrangement of d-β-1-hydroxydi*cyclo*pentadiene* (XXII)

The above alcohol (151 mg) was sealed into an evacuated clean dry Pyrex tube. The sealed tube was heated in a bath of refluxing xylene (140°) for 20 hr. It was then cooled and opened. The crystalline residue was scraped out and sublimed to yield 135 mg (90%) of white crystalline product, m.p. 65·5–67·6°, $[\alpha]_D^{25}$ +22·2° ($CHCl_3$, $c = 12{\cdot}4$). The infrared spectrum (CS_2) was compared with that of *dl-anti*-8-hydroxydi*cyclo*pentadiene. The spectra were superimposable.

Acknowledgment—We wish to express our appreciation of the support provided by the National Science Foundation and the National Institutes of Health.