

deposited (IX) in black needles on cooling. When crystallized from butyl acetate the compound IX melts at 255°. With cold concentrated sulfuric acid the compound gives a red-violet color; on heating a change to blue-violet, rose and finally yellowish-green occurs.

Anal. Calcd. for C₂₉H₁₈O: C, 91.1; H, 4.7. Found: C, 91.2; H, 4.9.

Summary

α -(9-Phenanthryl)- α,β -diphenylethanol yields

two geometrically isomeric ethylenes upon dehydration. In the addition of alkali metal to these isomers two sterically different metal-organic compounds are formed. A probable steric formula is ascribed to each of the two "stilbenylphenanthrenes" based upon the products of the alkali metal addition reaction.

REHOVOTH, PALESTINE RECEIVED FEBRUARY 10, 1941

[CONTRIBUTION FROM THE CONVERSE MEMORIAL LABORATORY OF HARVARD UNIVERSITY]

Structure and Absorption Spectra. III. Normal Conjugated Dienes

BY ROBERT BURNS WOODWARD

It is now clearly recognized¹ that the conjugated diene chromophore may manifest absorption in one of two broad regions, according to whether the two double bonds comprising the absorbing system are or are not present in a single ring. The former class as a whole absorbs sufficiently far to the red (255–290 m μ) to necessitate the postulation of a first order environmental effect, comparable in magnitude with the linear introduction of an additional double bond.² The second class, however, may be considered normal, and the variations (215–250 m μ) within the group are certainly the result of second order environmental effects similar to those discussed in connection with α,β -unsaturated ketones in the first paper of this series.³ This communication is concerned with the substitution-type classification of these normal dienes.⁴

Inspection of the position of the band maxima for a number of dienes reveals immediately that simple substitutive effects cannot be the sole factor in causing variations within the group, since in some cases dienes of the same substitution

type, *e. g.*, 1,1'-dicyclohexenyl (Table I, compound 6) and 2-hydroxy- α,β -dicyclohexylideneethane (Table I, compound 7) have different values of λ_{\max} , while in other cases compounds of different substitution type, *e. g.*, allylidene-cyclohexane (Table II, compound 4) and zingiberene (Table II, compound 6) have identical maxima. These facts indicate clearly that one or more positional factors are superimposed upon the expected substitutive effect.

The nature of this positional factor is discernible without difficulty. It has been⁵ pointed out that the introduction of strain into a given chromophore will labilize the electronic system with a consequent shift toward the red of the absorption band associated with the system. It is well known that a double bond exocyclic to a six-membered ring is unstable by *ca.* 3.5 k. c. with respect to the corresponding endocyclic compound.⁶ Further evidence of the strained character of such bonds may be found in the very high reactivity of cyclohexanone, and in the equilibrium data for systems of the type Δ^1 -cyclohexenyl-1-acetic acid \rightleftharpoons cyclohexylideneacetic acid.⁷ It is therefore reasonable to assume that a diene chromophore containing such exocyclic linkages would absorb nearer the red than the corresponding system lacking such linkages, but of the same substitution type.

In actual fact, this assumption is amply justified. Table I lists the symmetrical dienes⁸ of known structure whose absorption characteristics

(1) Fieser and Campbell, *THIS JOURNAL*, **60**, 160 (1938); Bergmann and Hirschmann, *J. Org. Chem.*, **4**, 40 (1939); Callow, *J. Chem. Soc.*, 462 (1936).

(2) Possibly the electrons of the single bond which is α,β to each of the double bonds of the diene chromophore are sufficiently labilized to permit oscillations approximating those of a conventional six-



electron system such as that of the trienes.

(3) Woodward, *THIS JOURNAL*, **63**, 1123 (1941).

(4) Booker, Evans and Gillam, *J. Chem. Soc.*, 1453 (1940), in an excellent paper containing valuable new data have classified dienes into several groups, *e. g.*, acyclic, acyclic with a cyclic substituent, semicyclic, bicyclic, etc. It will be evident from the sequel that the presence or absence of a ring in a normal diene has no intrinsic effect on the position of λ_{\max} , except in so far as the structure is such that the ring exerts a normal substitutive or positional effect.

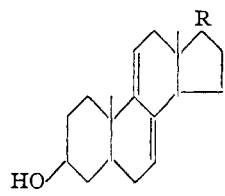
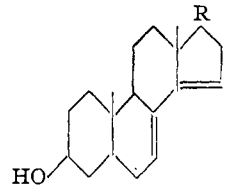
(5) Lewis and Calvin, *Chem. Rev.*, **25**, 273 (1939).

(6) Cf. Hückel, "Theoretische Grundlagen der organischen Chemie," 2nd edition, p. 72.

(7) Linstead, *J. Chem. Soc.*, 1603 (1930).

(8) *I. e.*, symmetrical in so far as the substitutive and positional factors about the double bonds are concerned.

TABLE I

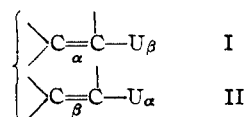
Substance	Formula	$\lambda_{\max.}(\text{calcd.})$	$\lambda_{\max.}(\text{obs.})$
Butadiene ^a	$\text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2$..	217 $\text{m}\mu$
β,γ -Dimethylbutadiene ^b	$\text{CH}_2=\text{C}(\text{CH}_3)-\text{C}(\text{CH}_3)=\text{CH}_2$	227 $\text{m}\mu$	226
$\Delta^{2,4}$ -Hexadiene ^c	$\text{CH}_3-\text{CH}=\text{CH}-\text{CH}=\text{CH}-\text{CH}_3$	227	227
1,6-Diacetoxy- $\Delta^{2,4}$ -hexadiene ^c	$\text{AcOCH}_2-\text{CH}=\text{CH}-\text{CH}=\text{CH}-\text{CH}_2\text{OAc}$	227	228
1,6-Diethoxy- $\Delta^{2,4}$ -hexadiene ^c	$\text{EtOCH}_2-\text{CH}=\text{CH}-\text{CH}=\text{CH}-\text{CH}_2\text{OEt}$	227	228
1,1-Dicyclohexenyl ^c	$\text{CH}_2(\text{C}_6\text{H}_{11})\text{CH}=\text{C}(\text{C}_6\text{H}_{11})-\text{CH}(\text{C}_6\text{H}_{11})\text{CH}_2$	237	236
2-Hydroxy- α,β -dicyclohexylideneethane ^d	$\text{HO}-\text{CH}(\text{C}_6\text{H}_{11})_2\text{C}=\text{CH}-\text{CH}=\text{C}(\text{C}_6\text{H}_{11})_2\text{CH}_2$	247	248
2,5-Dihydroxy-2-methyl- α,β -dicyclohexylideneethane ^c	$\text{HO}-\text{C}(\text{CH}_3)(\text{C}_6\text{H}_{11})_2\text{C}=\text{CH}-\text{CH}=\text{C}(\text{C}_6\text{H}_{11})_2\text{CH}_2$	247	245
2,5-Dihydroxy- α,β -dicyclohexylideneethane-2-acetic acid ^e	$\text{HO}-\text{C}(\text{CH}_2\text{COOH})(\text{C}_6\text{H}_{11})_2\text{C}=\text{CH}-\text{CH}=\text{C}(\text{C}_6\text{H}_{11})_2\text{CH}_2$	247	247
2-Hydroxy-5-acetoxy- α,β -dicyclohexylideneethane-2-acetic acid ^e	$\text{HO}-\text{C}(\text{CH}_2\text{COOH})(\text{C}_6\text{H}_{11})_2\text{C}=\text{CH}-\text{CH}=\text{C}(\text{C}_6\text{H}_{11})_2\text{CH}_2$ $\text{HOOC}-\text{CH}_2$ OAc	247	246
Cholestadienol D-acetate ^f		247	245
Cholestadienol B ₃ -acetate ^f		247	246

^a Smakula, *Angew. Chem.*, **47**, 657 (1937). ^b Scheibe, *Ber.*, **59**, 1333 (1926). ^c Booker, Evans and Gillam, *J. Chem. Soc.*, 1453 (1940). ^d Dimroth and Jonssen, *Ber.*, **71**, 2658 (1938). ^e Aldersley, Burkhardt, Gillam and Hindley, *J. Chem. Soc.*, 10 (1940). ^f Windaus, Linsert and Eckhardt, *Ann.*, **481**, 119 (1938).

have been determined. The values of $\lambda_{\max.}$ (calcd.) were obtained by adding to the base value (butadiene, $\lambda_{\max.} = 217 \text{ m}\mu$) 5 $\text{m}\mu$ for each substituent, and 5 $\text{m}\mu$ for each exocyclic bond present in the diene system. It will be seen that the agreement is in every case excellent.

The shift ($\Delta\lambda_s = 5 \text{ m}\mu$) accompanying the introduction of a single substituent into a conjugated diene system seems at first thought very low in comparison with the shift⁹ ($\Delta\lambda_s = 10-11 \text{ m}\mu$) in the α,β -unsaturated carbonyl system. Since, however, this displacement is actually 5 $\text{m}\mu$ for the whole diene system, the actual shift, referred to one carbon-carbon bond, is 10 $\text{m}\mu$, *i. e.*, the substitutive effect is almost identical in the two systems. This point may be clarified by the following example. In order to effect a comparison

with the α,β -unsaturated carbonyl system a diene containing two double bonds, α and β , may be considered as a composite of the type



where U_α and U_β correspond to the carbonyl group. The position of $\lambda_{\max.}$ for the two components will be $\lambda_0 + n_I \Delta\lambda$, $\lambda_0 + n_{II} \Delta\lambda$, and $\lambda_{\max.}$ for an actual diene will be the average of the component values.¹⁰ For 1,1'-dicyclohexenyl (Table I, compound 6), $n_I = n_{II} = 2$, $\lambda_{\max.} = 236 \text{ m}\mu$, whence $\Delta\lambda = 10 \text{ m}\mu$.

We now turn to the unsymmetrical dienes, listed in Table II. Under $\lambda_{\alpha\alpha}$ and $\lambda_{\beta\beta}$ are listed the

(10) It will be evident from the sequel that this may be rigidly true only in symmetrical case.

(9) Woodward, *This Journal*, **63**, 76 (1941).

TABLE II

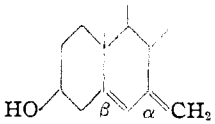
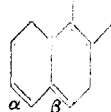
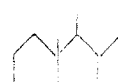
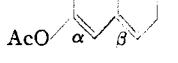
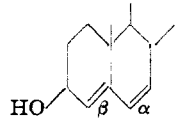
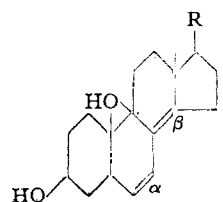
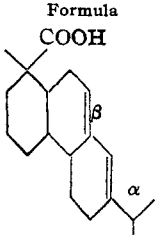
Substance	Formula	$\lambda_{\alpha\alpha}$	$\lambda_{\beta\beta}$	$(\lambda_{\alpha\alpha} + \lambda_{\beta\beta})/2$	$\lambda_{\max. (obs.)}, m\mu$
Piperylene ^a	$\text{CH}_2\text{CH}=\underset{\beta}{\text{C}}\text{H}-\underset{\alpha}{\text{C}}\text{H}=\text{CH}_2$	217	227	222	223.5
Isoprene ^b	$\text{CH}_2=\underset{\beta}{\text{C}}(\text{CH}_3)-\underset{\alpha}{\text{C}}\text{H}=\text{CH}_2$	217	227	222	220
Myrcene ^a	$\text{CH}_2=\underset{\beta}{\text{C}}(\text{CH}_2\text{CH}_2\text{CH}=\text{C}(\text{CH}_3)_2)-\underset{\alpha}{\text{C}}\text{H}=\text{CH}_2$	217	227	222	224.5
Allylidene-cyclohexane ^a	$\text{CH}_2(\text{CH}_2)_4\underset{\beta}{\text{C}}=\text{CH}-\underset{\alpha}{\text{C}}\text{H}=\text{CH}_2$	217	247	232	236.5
γ -(2-Dimethylaminomethylcyclohexylidene)- $\Delta\alpha$ -propene ^c	$(\text{CH}_3)_2\text{NCH}_2\text{CH}(\text{CH}_2)_4\underset{\beta}{\text{C}}=\text{CH}-\underset{\alpha}{\text{C}}\text{H}=\text{CH}_2$	217	247	232	236
Zingiberene ^a	$\text{CH}_2\text{CH}=\underset{\beta}{\text{C}}(\text{CH}_2)_2\text{CH}(\text{CH}_3)\text{CH}(\text{CH}_3)\underset{\alpha}{\text{C}}\text{H}=\text{CH}-\underset{\beta}{\text{C}}\text{H}=\text{C}(\text{CH}_3)_2$	227	237	232	235.5
Δ^1 -Cyclohexenylethylene ^a	$\text{CH}_2(\text{CH}_2)_3\underset{\beta}{\text{C}}\text{H}=\text{C}-\underset{\alpha}{\text{C}}\text{H}=\text{CH}_2$	217	237	227	230
$\Delta^{3,8(9)}$ - <i>nor</i> -Menthadiene ^a	$\text{CH}_2(\text{CH}_2)_3\underset{\beta}{\text{C}}\text{H}=\underset{\alpha}{\text{C}}(\text{CH}_3)=\text{CH}_2$	227	237	232	242
Menthadiene ^a	$\text{CH}_2\text{CH}_2\text{CH}(\text{CH}_3)\text{CH}_2\underset{\beta}{\text{C}}\text{H}=\underset{\alpha}{\text{C}}(\text{CH}_3)=\text{CH}_2$	227	237	232	235
β -Phellandrene ^a	$\text{CH}_2\text{CH}_2\text{CH}(\text{CH}_3)\text{CH}=\underset{\alpha}{\text{C}}\text{H}-\underset{\beta}{\text{C}}\text{H}=\text{CH}_2$	227	237	232	232
2-Methyl- Δ^1 -cyclohexenylethylene	$\text{CH}_2(\text{CH}_2)_3\underset{\beta}{\text{C}}(\text{CH}_3)=\underset{\alpha}{\text{C}}\text{H}=\text{CH}_2$	217	247	232	233
7-Methylenecholesterol ^d		237	247	242	236 ⁱ
$\Delta^{3,6}$ -Cholesta- diene ^e		227	247	237	235
Testosterone di- acetate ^e		237	247	242	240
Cholestenone enolacetate ^e		237	247	242	240
$\Delta^{4,6}$ -Cholestadi- enol ^h		227	247	237	238
9-Oxycholestadi- enol ⁱ		227	257 ^k 267	242 ^k 247	248

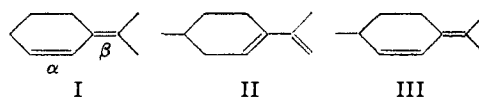
TABLE II (Concluded)

Substance	Formula	$\lambda_{\alpha\alpha}$	$\lambda_{\beta\beta}$	$(\lambda_{\alpha\alpha} + \lambda_{\beta\beta})/2$	$\lambda_{\max.}$ (obs.), $m\mu$
Abietic acid ^f		237	247	242	237.5

^a Booker, Evans and Gillam, *J. Chem. Soc.*, 1453 (1940). ^b Scheibe and Pummerer, *Ber.*, **60**, 2163 (1927). ^c Milas and Alderson, *THIS JOURNAL*, **61**, 2534 (1939). ^d Bann, Heilbron and Spring, *J. Chem. Soc.*, 1274 (1936). ^e Stavely and Bergmann, *J. Org. Chem.*, **1**, 567 (1937); Bergmann and Hirschmann, *ibid.*, **4**, 40 (1939). ^f Kraft, *Ann.*, **520**, 133 (1935). ^g Westphal, *Ber.*, **70**, 2128 (1937). ^h Dane, Wang and Schulte, *Z. physiol. Chem.*, **245**, 80 (1937). ⁱ Windaus and Zühlsdorff, *Ann.*, **536**, 204 (1938). ^j No curve given; inflection (?) reported. ^k This case brings up the important point of the effect of a double bond exocyclic to a five-membered ring. From the meager data available it is not possible to estimate this effect.

calculated values of $\lambda_{\max.}$ for the symmetrical dienes corresponding to the double bonds α and β (as marked). In all cases except that of $\Delta^{3,8(9)}$ -*nor*-menthadiene, $\lambda_{\beta\beta} > \lambda_{\max.} > \lambda_{\alpha\alpha}$, and, in fact, the position of $\lambda_{\max.}$, except in this one case, is within 5 $m\mu$ (average deviation 3 $m\mu$) of the average $(\lambda_{\alpha\alpha} + \lambda_{\beta\beta})/2$. It will be recognized that this latter value for any diene is identical with that which would be obtained by calculating $\lambda_{\max.}$ as was done in the case of the symmetrical dienes. However the unsymmetrical dienes, have been considered in this way, *i. e.*, as composite systems intermediate between two symmetrical systems, since it is not possible at present to determine whether the small discrepancies in $\lambda_{\max.}$ (calcd.) are due to experimental variations, or whether, as is quite possible, subtle constitutive factors shift the maximum slightly toward that characteristic of one or the other of the component systems.

The most probable explanation of the apparently anomalous behavior of $\Delta^{3,8(9)}$ -*nor*-menthadiene is that the structure at present assigned to this compound is incorrect. It is reasonable to assume that the substance is actually largely $\Delta^{2,4(8)}$ -*nor*-menthadiene (I), for which $\lambda_{\beta\beta} = 257 m\mu$, $\lambda_{\alpha\alpha} = 227 m\mu$, $(\lambda_{\alpha\alpha} + \lambda_{\beta\beta})/2 = 242 m\mu$, a view which not only is in excellent accord



with the absorption data, but receives support from the fact that preparations of menthadiene itself (II) usually contain appreciable amounts of $\Delta^{2,4(8)}$ -menthadiene (III).¹¹ We are at present endeavoring to furnish a proof of this assumption in order to provide further evidence of the power of the absorption method in the determination of structure.

Summary

It has been shown that by the use of simple substitutive and positional shifts it is possible to calculate with reasonable accuracy the position of the band maxima in the absorption spectra of normal conjugated dienes, *i. e.*, those dienes which do not contain both double bonds within a single ring.

The use of these generalizations in structure determinations is exemplified, and certain analogies between the diene chromophore and the α,β -unsaturated ketone chromophore are pointed out.

CAMBRIDGE, MASS.

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(11) Indeed, the sample of II used by Booker, Evans and Gillam (ref. 4) in the determination of the absorption spectrum was described as probably containing 23% of the isomer III.