

methyl cinnamate is a direct measure of the acylation reaction.⁹ Application of the classical kinetic formulation for two consecutive first-order reactions¹⁰ to this system leads to a quantitative fit of the absorbance *vs.* time curve. Using the independently determined rate constants for acylation ($2.66 \times 10^{-3} \text{ sec.}^{-1}$) and deacylation of the acyl-enzyme, I ($11.1 \times 10^{-3} \text{ sec.}^{-1}$), together with the independently determined molar absorptivities at 310 $m\mu$ of methyl cinnamate ($\epsilon = 3.27 \times 10^3$), I ($\epsilon = 1.096 \times 10^4$) and cinnamate ion ($\epsilon = 1.00 \times 10^3$ under experimental conditions), one calculates t_{max} for the absorbance *vs.* time curve as 105 seconds (observed, $100 \pm 10 \text{ sec.}$), and $A_{\text{max}} = 0.496$ (observed, 0.470). Thus, both qualitatively and quantitatively the increase in absorbance in the enzyme-catalyzed hydrolysis of methyl cinnamate can be accounted for on the basis of the formation of the highly absorbing intermediate, *trans*-cinnamoyl- α -chymotrypsin.¹¹

For benzyl cinnamate, the absorbance *vs.* time curve also shows a maximum, again indicating the formation of the acyl-enzyme intermediate. However, in this case, one obtains the rate of deacylation of I from the first-order portion of the curve. For example, the rate constant obtained under the conditions specified in Table I is $5.31 \times 10^{-3} \text{ sec.}^{-1}$. The rate constant for the deacylation of I under identical conditions is $5.24 \times 10^{-3} \text{ sec.}^{-1}$. Deacylation is therefore the slow step in the hydrolysis of this ester under the experimental conditions.

Thus the acyl-enzyme hypothesis achieves generality for α -chymotrypsin-catalyzed hydrolyses of both labile and non-labile substrates. However, a discrepancy still exists between these results and those of Bernhard, *et al.*,⁴ for the specific substrate, methyl hippurate and those of Bender and Glasston⁵ for the specific substrate, N-acetyl-L-phenylalanine methyl ester.

(9) The values of the acylation and deacylation rate constants for methyl cinnamate are several orders of magnitude smaller than those of specific substrates of α -chymotrypsin, but there is no reason to believe that the reactions reported here are qualitatively different from those of specific substrates.

(10) The acylation may be considered to be a pseudo first-order process since the enzyme is in great excess.

(11) Preliminary experiments with β -phenylethyl and cyclohexyl cinnamates show behavior very similar to that found for the methyl ester.

(12) Alfred P. Sloan Foundation Research Fellow.

DEPARTMENT OF CHEMISTRY
NORTHWESTERN UNIVERSITY
EVANSTON, ILLINOIS

MYRON L. BENDER^{1,2}
BURT ZERNER

RECEIVED MARCH 22, 1961

PREPARATION OF 1,2,4,4-TETRAMETHYL-3,5-DIMETHYLENOCYCLOPENTENE; THE MAGENTA SPECIES DERIVED FROM IT BY PROTONATION AND FROM HEXAMETHYLCYCLOPENTADIENE BY HYDRIDE ABSTRACTION

Sir:

An intensely magenta solution is obtained from hexamethylcyclopentadiene¹ (I) upon treatment with trityl perchlorate² in acetonitrile; $\lambda_{\text{max}} 552$

(1) L. de Vries, *J. Am. Chem. Soc.*, **82**, 5242 (1960); *J. Org. Chem.*, **25**, 1838 (1960).

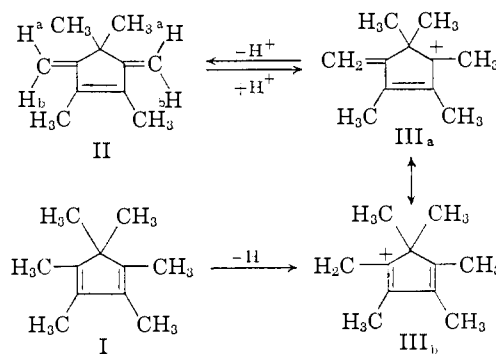
(2) H. J. Dauben, *J. Am. Chem. Soc.*, **79**, 7557 (1957); *J. Org. Chem.*, **25**, 1442 (1960).

$m\mu$, $\epsilon_{\text{max}} 10^4$ (in 2 minutes). Hydride abstraction was proved by recovery of triphenylmethane from the pentane extracts.

It became desirable to attempt the preparation of 1,2,4,4-tetramethyl-3,5-dimethylenecyclopentene (II) so as to determine whether protonation of II also leads to the magenta species.

I with N-bromosuccinimide in carbon tetrachloride at 0° gave an unstable bromination product, which was dehydrobrominated readily with trimethylamine in 12 hours at 25°. Preparative vapor phase chromatography of the product yielded a new hydrocarbon, presumably 1,2,4,4-tetramethyl-3,5-dimethylenecyclopentene, (II) *y.*, 29%, $n_{\text{D}}^{20} 1.5181$, mass spec. mol. wt., 148. *Anal.* Calcd. for $\text{C}_{11}\text{H}_{16}$: C, 89.10; H, 10.90. Found: C, 88.96; H, 10.79. The structure assignment is based on these data: (a) infrared bands: $\bar{\nu}$ ($\text{C}=\text{CH}_2$) 3090 cm.^{-1} (m); 1726 cm.^{-1} (w) (overtone of 860); 1395 cm.^{-1} (m); 860 cm.^{-1} (vs); $\bar{\nu}$ ($\text{H}_2\text{C}=\text{C}-\text{C}=\text{C}-\text{C}=\text{CH}_2$) 1618 cm.^{-1} (vs). (b) λ_{max} isoöctane 285.4 (sh), 275.0, 265.6, ϵ_{max} 16750, 25150, 21400. This agrees well with the spectrum of 3,6-dimethylenecyclohexene.³ (c) n.m.r. spectrum (40 M.c.) in c.p.s. rel. to $\text{Si}(\text{CH}_3)_4$ solvent: -43.5 rel. area 6 (*gem*-dimethyl); -72.3, rel. area 6 (two vinyl methyl groups); -185.8 and -190.0 rel. area 2 each (two exocyclic methylene groups). The doublet is ascribed to unequal diamagnetic shielding of the a and b vinyl hydrogen atoms,⁴ which do not split each others resonances further due to the low spin-spin coupling constants.⁵

An intensely magenta solution ($\lambda_{\text{max}} 552 m\mu$) could be obtained instantaneously: (1) upon addition of methanesulfonic acid (to conc. $5 \times 10^{-2} M$) to an initially colorless acetic acid solution of II ($6.4 \times 10^{-5} M$), $\epsilon_{\text{max}} 23,500$; (2) upon addition of a drop of the bromination solution of I to an ionizing solvent, such as acetic acid, formic acid or aq. HCl ($> 3 M$). In both cases the color is discharged upon addition of sodium acetate in acetic acid, regenerated upon addition of methane sulfonic acid.



Protonation of II gives undoubtedly III (III_a \longleftrightarrow III_b). III is also the expected product from I by hydride abstraction. Since dehydrobromination of the bromination product of I gives II, it

(3) R. E. Benson and V. E. Lindsey, *J. Am. Chem. Soc.*, **81**, 4250 (1959); W. J. Bailey and R. Barclay, *ibid.*, **81**, 5393 (1959).

(4) See n.m.r. of longifolene, S. Dev, *Tetrahedron*, **9**, 1 (1960).

(5) J. A. Pople, W. G. Schneider and H. J. Bernstein, "High Resolution N.m.r.," McGraw-Hill Book Co. Inc., New York, N. Y., 1959, pp. 238-246.

must contain bromo-I, which although originally covalent, may ionize in appropriate solvents to give III.

For cations obtained by protonation of carotenoids an upper limit for λ_{\max} has been calculated by Wassermann.⁶ For two double bonds, conjugated with a positive charge, this limit is 484 m μ , indicating that III is not itself the magenta species, but rather a precursor to it.

From the magenta solutions three dimeric hydrocarbons are recovered, with ultraviolet spectra, characteristic of polyenes. Each upon protonation regenerates the magenta color instantaneously with high ϵ . This indicates that in its simplest form the magenta species is also dimeric. The absence of chromophores of different length, corresponding to progressive extension, follows from the observation of only a single peak at 552 m μ .

The acetic acid solvent was evaporated *in vacuo* at 25° from a magenta solution obtained by protonation of II. The remaining viscous magenta residue was triturated repeatedly with pentane so as to extract all but the most strongly protonated compounds. Ice cold aqueous potassium hydroxide then was added. Extraction of the resulting suspension with pentane, then evaporation of the solvent, gave an orange viscous residue. Sublimation at 0.1 mm. (Dry Ice in condenser) yielded: (1) at 80°, a yellow hydrocarbon (VI), after resublimation, partially crystallizable from a minimum of pentane at -10° to give yellow needles, m.p. 66-75° (prob. impure with VII). *Anal.* C, 88.85; H, 11.03; mass spec. mol. wt., 296 (C₂₂H₃₂). $\lambda_{\max}^{\text{isooctane}}$, 333.6, 370.0, 390.0 (sh) m μ ; $\epsilon_{\max} \times 10^{-4}$, 2.165, 3.020, 2.890, 0.627; $\lambda_{\max}^{\text{CH}_3\text{COOH}, \text{CH}_3\text{SO}_3\text{H}(0.05 M)}$, 552 m μ ; ϵ_{\max} 48,800. Carr-Price reaction,⁸ $\lambda_{\max}^{\text{CHCl}_3, \text{SbCl}_5}$, 563, 602 m μ . (2) at 100-110°, an orange hydrocarbon (VII); after resublimation and recrystallization from pentane at -10°, orange needles m.p. 140-145°. *Anal.* C, 89.03; H, 10.97; mass spec. mol. wt., 296 (C₂₂H₃₂). $\lambda_{\max}^{\text{isooctane}}$, 350.0, 369.0, 390.0 m μ ; $\epsilon_{\max} \times 10^{-4}$, 1.88, 2.66, 2.32. $\lambda_{\max}^{\text{CH}_3\text{COOH}, \text{CH}_3\text{SO}_3\text{H}(0.05 M)}$, 552 m μ ; ϵ_{\max} 49,600. Carr-Price reaction: $\lambda_{\max}^{\text{CHCl}_3, \text{SbCl}_5}$, 563, 602 m μ . (3) at 130°, an orange hydrocarbon (VIII); after resublimation and crystallization from pentane at -10°, m.p. 151-153°, orange needles. *Anal.* C, 89.23; H, 10.72; mass spec. mol. wt., 296 (C₂₂H₃₂). $\lambda_{\max}^{\text{isooctane}}$, 350.0, 369.0, 390.0 m μ ; $\epsilon_{\max} \times 10^{-4}$, 1.88, 1.27, 1.66, 1.41; $\lambda_{\max}^{\text{CH}_3\text{COOH}, \text{CH}_3\text{SO}_3\text{H}(0.05 M)}$, 552 m μ ; ϵ_{\max} 49,300. Carr-Price reaction; $\lambda_{\max}^{\text{CHCl}_3, \text{SbCl}_5}$, 563, 602 m μ .

The ultraviolet spectra especially of VI and VII, with three intense maxima, are characteristic of conjugated polyenes with unhindered coplanarity.⁹

II may add to III either as IIIa or IIIb. Dreiding stereomodels¹⁰ indicate that crowding in the primary addition product of II to IIIa is prohibitive in all steric configurations.

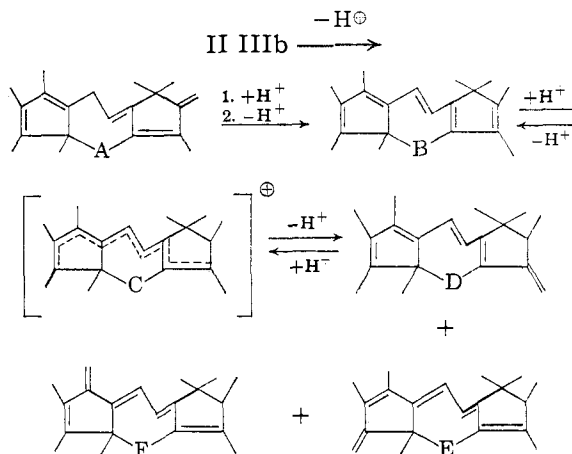
(6) A. Wassermann, *J. Chem. Soc.*, 979 (1959).

(7) Initially the hydrocarbon was dissolved in a minimum of isooctane.

(8) E. H. Carr and E. A. Price, *Biochem. J.*, **31**, 497 (1926).

(9) W. Oroshnik, *et al.*, *J. Am. Chem. Soc.*, **74**, 295 (1952); **76**, 5719 (1959).

(10) Rinco Instrument Company, Greenfield, Illinois.



On the other hand, hindrance is absent in A, the addition product of II to IIIb, as well as in the secondary rearrangement products E and F with double "retro" structure⁹ (B and D show some crowding).

In VI and VII bands at: 858 (mw), 1720 (w) (overtone of 858), 3078 (vw) cm.⁻¹ indicate vinyl-methylene exocyclic to a strained ring such as in II. The low relative intensities indicate a ratio of vinyl-methylene to CH₃ considerably less than half that in II (2:4). A sharp band at 800 cm.⁻¹

(mw) $\left[\begin{array}{c} R \\ \diagdown \\ C=C \\ \diagup \\ R \end{array} \right]$ in VI and VII is absent

in VIII, which instead exhibits a sharp band at 958 cm.⁻¹ (m) $\left[\begin{array}{c} R \\ \diagdown \\ C=C \\ \diagup \\ H \end{array} \right]$ In the 1600-1700

cm.⁻¹ region, all three exhibit complex absorption with a main band at 1620 cm.⁻¹ (s).

These spectra are consistent with the assignments VI = F, VII = E, VIII = B + D. The exceptionally stable magenta species then is presumably the ion C, which is similar to certain carotenoid ions.⁶

Thanks are due to Professor S. Winstein for constructive criticisms.

CALIFORNIA RESEARCH CORPORATION
RICHMOND, CALIFORNIA

L. DE VRIES

RECEIVED MARCH 30, 1961

DIPOLE MOMENTS OF BIS-CYCLOPENTADIENYL TITANIUM AND ZIRCONIUM DICHLORIDES

Sir:

Metal compounds involving π -bonded bis-cyclopentadienyl groups have evoked a great amount of interest in the past decade, and a recent review¹ has critically surveyed the bonding aspects and inorganic and physical chemistry of these materials. The relative positions of the cyclopentadienyl rings have been elucidated by crystal structure and dipole moment determinations for ferrocene and a few other similar materials, but no conclusive evidence as to the structure of bis-cyclopentadienyl

(1) G. Wilkinson and F. A. Cotton in "Progress in Inorganic Chemistry," Vol. I, edited by F. A. Cotton, Interscience Publishers Inc., New York, N. Y., 1959, pp. 1-124.