

# The Carbonium Ion of *all-trans*-Retinyl Acetate. Spectroscopic Detection and Identification of Absorbing Species. Effect of Environment on Spectral Properties<sup>1,2</sup>

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**Abstract:** The retinyl cation was investigated spectroscopically as a model compound to furnish a basis for the evaluation of this species as the chromophore in visual pigments. Low temperatures and rapid handling techniques led to the detection of the retinyl cation from retinol and retinyl acetate. This cation was observed in a number of solvent-acid systems and absorbs at  $598 \pm 14 \text{ m}\mu$ . The retinyl cation was shown to be pentaenylic by comparison with the anhydroretinyl cation which is pentaenylic. The  $\epsilon_{\text{max}}$  of the cation is solvent dependent and has values between 44,000 and 113,000. Spectral properties are discussed in terms of a free-electron model.

A study of carbonium ions of highly conjugated polyenes was begun when it was realized that their spectral properties are similar in some respects to the unexplained behavior of visual pigments. For example, Wassermann<sup>3</sup> reported that retinyl acetate absorbs at about  $300 \text{ m}\mu$  in benzene, whereas its cation was reported to absorb at  $650 \text{ m}\mu$  in a benzene solution acidified with trichloroacetic acid. A similar bathochromic shift occurs when retinal is complexed with a visual protein. The polyene aldehyde absorbs maximally in the ultraviolet, whereas when it is complexed with a visual protein it absorbs in the visible.<sup>4</sup> The polyene is bound to the protein by a Schiff base linkage which is formed between the aldehyde of the polyene and an amino group of the protein.<sup>5,6</sup> However, incorporation of nitrogen into the conjugated sequence does not cause a bathochromic shift. Consequently, the protein must exert additional forces upon the  $\pi$ -electron cloud in order to cause further delocalization. Two mechanisms have been postulated to explain these shifts;<sup>7</sup> the one advanced by Blatz<sup>8</sup> invokes carbonium ions. Unfortunately, only meager spectral and chemical evidence relating to carbonium ions of highly conjugated polyenes has been available, and consequently, it has been impossible to determine the role, if any, played by these ions in visual pigments. The work presented here was undertaken in order to understand more clearly the nature of the bathochromic shift in model carbonium ions with the hope that their behavior could then be compared with that of visual pigments.

At the very beginning of our work it became clear that the previously reported absorption spectrum<sup>3</sup> of the retinyl cation prepared from retinyl acetate had been in error.<sup>9</sup> In this article we present data

which shows that the retinyl cation has been directly observed, the structure of the absorbing species has been identified, and the effect of environment upon the spectral properties has been determined.

## Results and Discussion

**Absorption of Retinyl Acetate Cation.** By using low temperature and rapid handling, we were able to record the visible spectrum 30 sec after retinyl acetate (I)<sup>10</sup> was mixed with an acid solution. Depending on the specific conditions, we could observe (see Figure 1) a single, nearly symmetrical band that had a maximum at about  $600 \text{ m}\mu$ , a very high molar absorptivity, and a narrow half-band width. Simultaneous with the disappearance of this band, new absorption bands were formed. Table I shows the  $\lambda_{\text{max}}$  exhibited by the

**Table I.** Initial and Later  $\lambda_{\text{max}}$  Values of Retinyl Acetate<sup>a</sup> in Solvents Acidified with Trichloroacetic Acid<sup>a</sup>

Solvent	Init	Later absorp $\lambda_{\text{max}}, \text{m}\mu$	Temp, °C
	absorp <sup>b</sup> $\lambda_{\text{max}}, \text{m}\mu$		
Chloroform	605	553, 635, 945	4
Carbon tetrachloride	603	863	5-6
1,2-Dichloroethane	594	887	4-5
Cyclohexane	603	871	5-6
<i>n</i> -Heptane	596	844	5-6
Isooctane	594	864	4-5
Benzene	612	560, 628	7-8
Toluene	610	560, 617	7-8
Acetic anhydride	583	~810	4-5

<sup>a</sup> Retinyl acetate  $2.4 \times 10^{-4} \text{ M}$ , trichloroacetic acid  $4.4 \times 10^{-4} \text{ M}$  in all solvents except 1,2-dichloroethane where it is  $4.4 \times 10^{-2} \text{ M}$ .

<sup>b</sup> Spectrum measured in a 1-cm cell approximately 30 sec after solutions were mixed.

retinyl cation in a number of solvents. Solvents have only a small effect on the  $\lambda_{\text{max}}$  of the retinyl cation, although they greatly influence both the number and location of absorption bands which develop later. For example, in 1,2-dichloroethane at  $4.5^\circ$ , the retinyl cation exhibits a sharp, narrow band that appears at  $594 \text{ m}\mu$  and reaches maximum absorption in 83 sec. As this band decreases, it maintains its narrow width

(10) The numbering system used here is that generally used for carotenoids and retinyl compounds.

(1) This investigation was supported by PHS Research Grant No. GM-12616 and NB-6712.

(2) This investigation was supported in part by Public Health Service Fellowship GM-31,379 to D. L. P.

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

(4) H. J. A. Dartnall, "The Eye," Vol. 2, H. Davson, Ed., Academic Press Inc., New York, N. Y., 1962, pp 427-471.

(5) S. Ball, F. D. Collins, P. D. Dalvi, and R. A. Morton, *Biochem. J.*, **45**, 304 (1949).

(6) R. Hubbard, D. Bounds, and T. Yoshizawa, *Cold Spring Harbor Symp. Quant. Biol.*, **30**, 301 (1965)

(7) A. Kropf and R. Hubbard, *Ann. N. Y. Acad. Sci.*, **74**, 266 (1958).

(8) P. E. Blatz, *J. Gen. Physiol.*, **48**, 753 (1965).

(9) P. E. Blatz and D. L. Pippert, *Tetrahedron Letters*, 1117 (1966); see footnote 18.

and gives rise to broad absorption from 700 to 1000  $m\mu$  with a broad maximum at 887  $m\mu$ . In benzene at 6° where the behavior of the retinyl cation is slightly different, a narrow band is produced first at 613  $m\mu$ . For certain acid concentrations, this band disappears simultaneously with the rise of a doublet at 560 and 628  $m\mu$ . When the acid concentration is increased and the reaction is allowed to proceed at room temperature, the longer wavelength band is favored and the  $\lambda_{\max}$  is shifted to values near 650  $m\mu$ . This band is extremely broad and of low molar absorptivity. There are no further maxima up to 1000  $m\mu$ . Retinyl acetate exhibits similar behavior in other acidified solvents, and these absorption bands which appear later are attributable to some anomalous cyclization or polymerization product.

Further studies of the spectral properties of the retinyl cation substantiate this postulate. In the remainder of the first part of this paper, we compare the spectral properties of the retinyl cation with those of cations reported by Sorensen.<sup>11</sup> He synthesized a number of polyenes which give rise to symmetrical carbonium ions when placed in acid solution, and he determined the structure of these ions by nmr, electronic, and infrared spectroscopy. We first set out to determine the value of the molar absorptivity of the retinyl cation. For various experimental reasons, the cation could not be stabilized in hydrocarbon and chlorohydrocarbon solvents to the degree necessary for the determination of the molar absorptivity. Examination of the recording obtained by repetitively scanning the spectrum at short time intervals showed that the rates of formation and decay of the retinyl cation were nearly equal. The absorbance obtained from these recordings gave low values of molar absorptivity. It was not until alcohol-sulfuric acid solvent systems were employed that significantly higher molar absorptivities were obtained. Greater stability in these solvents was indicated by rapid formation of a cation with relatively slow decomposition. Table II shows the variation in  $\lambda_{\max}$  and the maximum molar

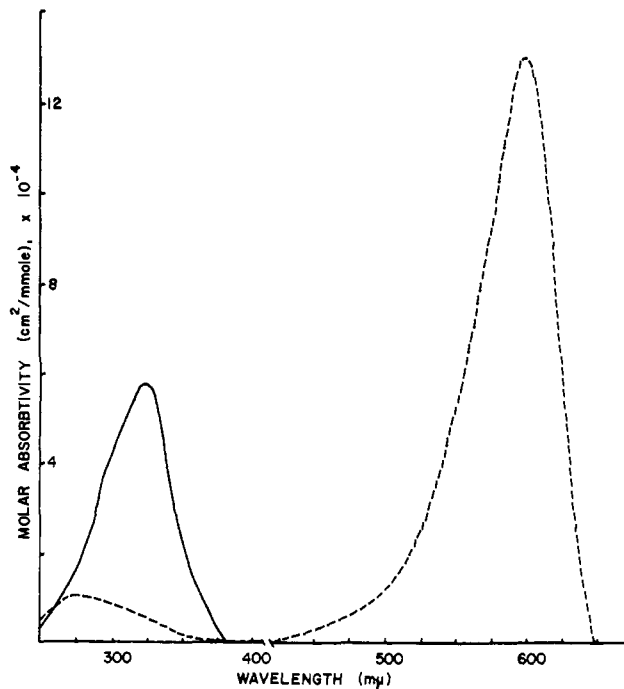
**Table II.** Variation of  $\lambda_{\max}$  and  $\epsilon_{\max}$  of the Retinyl Cation<sup>a,b</sup> as a Function of the Mol % Sulfuric Acid in Methanol

Mol % H <sub>2</sub> SO <sub>4</sub>	Retinyl cation	
	$\lambda_{\max}$ , $m\mu^a$	$\epsilon_{\max}$ , ( $\text{cm}^2 \text{mmol}^{-1}$ ) $\times 10^{-4}$
21.4	No color	
28.2	588	2.4
35.4	588	3.7
43.0	589	2.4
47.0	591	4.3
51.1	589	4.4
55.5	591	4.2
59.8	592	4.2
68.8	~580, ~535	1.5

<sup>a</sup> Measured at about -46° within 30 sec after mixing. <sup>b</sup> Retinyl acetate  $9.01 \times 10^{-6}$  M.

absorptivity of the cation as a function of increasing acid concentration in methanol-sulfuric acid. Up to a certain acid concentration, the molar absorptivity increases with increased acid but the  $\lambda_{\max}$  shows little variation. Absorption is sharp, narrow, and almost

(11) T. S. Sorensen, *J. Amer. Chem. Soc.*, **87**, 5075 (1965).



**Figure 1.** Spectra of retinyl acetate in 1-butanol (—) and in a 1-butanol-sulfuric acid mixture (---).

symmetrical in this concentration range (see Figure 1). The point of maximum absorption coincides roughly with an equimolar mixture of alcohol and acid. After this amount has been exceeded, the molar absorptivity decreases and the spectrum may break into a number of absorption bands. Only limited precision is obtained in measuring molar absorptivity; poor mixing caused by the highly viscous solvent at -45° is the main reason for this. However, low temperature is necessary to retard the rate of reaction of the cation. The highest observed value of 44,000 at 51.1 mol % sulfuric acid is taken as the molar absorptivity in methanol. Molar absorptivities were determined in other alcoholic solvents by the same technique as given above. These data are given in Table III. The lowest value of 44,000

**Table III.** Variation of the  $\lambda_{\max}$  and  $\epsilon_{\max}$  of the Retinyl Cation as a Function of Solvent

Solvent	Mol % <sup>a</sup> H <sub>2</sub> SO <sub>4</sub>	Retinyl Cation	
		$\lambda_{\max}$ , $m\mu$	$\epsilon_{\max}$ , ( $\text{cm}^2 \text{mmol}^{-1}$ ) $\times 10^{-4}$
Methanol	51.1	589	4.4
Ethanol	52.0	594	8.6
1-Propanol	50.3	595	6.8
2-Propanol	58.7	594	6.7
1-Butanol	66.6	600	11.3

<sup>a</sup> Mol % acid at which  $\epsilon_{\max}$  is greatest.

is obtained in methanol, whereas the highest value of 113,000 is obtained in 1-butanol. The molar absorptivity values reported here are in good agreement with those of Sorensen who gave values of 150,000 and 80,000 for the 2,10-dimethylundecatetraenylic cation and 170,000 and 220,000 for the 2,12-dimethyltridecapentaenylic cation in water-sulfuric acid and heptafluorobutyric acid, respectively.

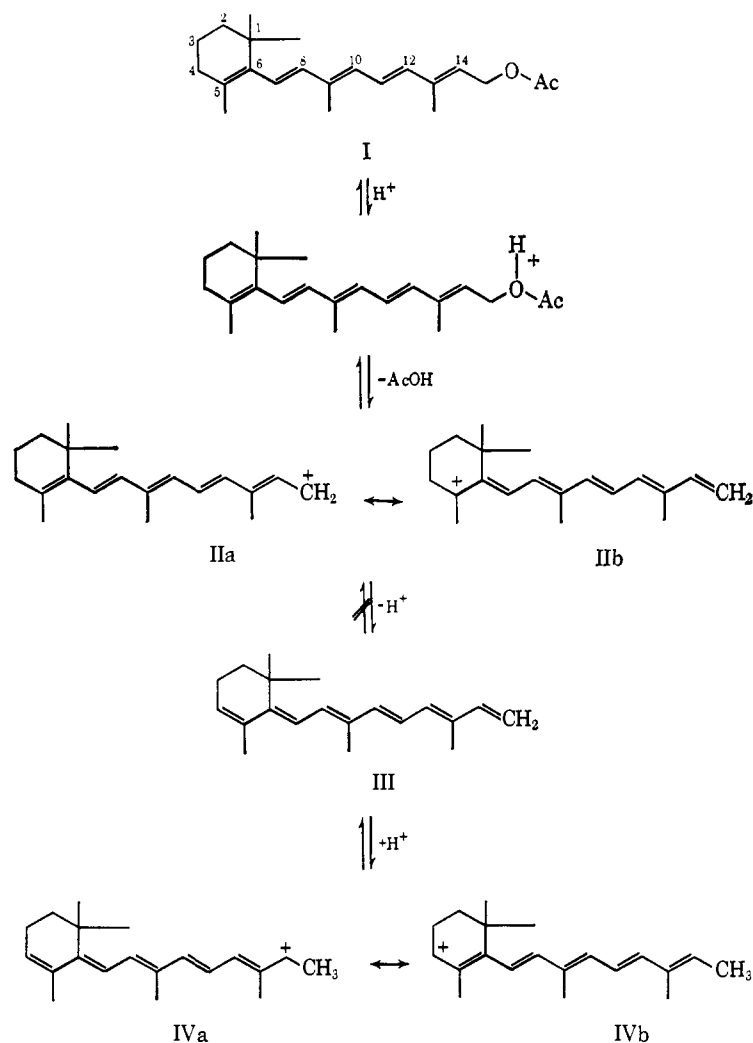


Figure 1 shows the spectra of retinyl acetate in 1-butanol and also the retinylic cation in 1-butanol-sulfuric acid. The acetate absorbs only in the uv, whereas the cation absorbs only in the visible. Sorensen<sup>11</sup> reported similar spectral behavior for 2,10-dimethyl-1,3,5,7,9-undecapentaene and its carbonium ion. The half-band width of  $1900\text{ cm}^{-1}$  reported here is in reasonable agreement with the half-band width of  $1200\text{ cm}^{-1}$  reported for the 2,10-dimethylundecatetraenylic cation.

We showed previously<sup>9</sup> that retinyl acetate does undergo polymerization in acid solution. Retinyl acetate was mixed with trichloroacetic acid in both benzene and 1,2-dichloroethane as solvents. Neutralization of the acid quenched the polymerization, and the organic polyenes were extracted and dried. The average molecular weight of the extract was determined in a Mechrolab vapor osmometer. When benzene is used as a polymerization solvent, the molecular weight is  $1076\text{ g/mol}$  or about 3.3 times that of retinyl acetate; when 1,2-dichloroethane is used, the molecular weight is  $1470\text{ g/mol}$  or about 4.5 times the initial value.

After consideration of the agreement between the spectral and chemical results presented here and those of known carbonium ions, one must conclude that the species reported here is the retinylic cation.

**Identification of Absorbing Species.** We set out to determine whether the retinylic cation is tetraenylic or pentaenylic. The question was resolved by preparing

anhydroretinol (III), which contains six double bonds, and measuring the  $\lambda_{\text{max}}$  of its carbonium ion under similar conditions. This carbonium ion can only be formed by direct addition of the proton to the polyene chain. The resulting cation must be pentaenylic, and its  $\lambda_{\text{max}}$  is compared with values of other cations in Table IV. The  $\lambda_{\text{max}}$  values of the anhydroretinylic and retinylic cations are in good agreement, separated only by  $14\text{ m}\mu$ . A wavelength separation of approximately  $75\text{ m}\mu$  is found in cations of polyenes which differ by one double bond. Consequently, if the retinylic cation is pentaenylic it would be expected to absorb near  $600\text{ m}\mu$  and if it is tetraenylic near  $530\text{ m}\mu$ . The values reported here are also in agreement with those of Sorensen<sup>11</sup> which, however, were not available to us at the time these studies were conducted. He reported a value of  $625\text{ m}\mu$  for a particular pentaenylic and  $550\text{ m}\mu$  for a tetraenylic cation. One must conclude that the retinylic cation reported here is pentaenylic.

The small discrepancy in the  $\lambda_{\text{max}}$  values between the anhydroretinylic and retinylic cation gives insight to the exact structure of these species. Protonation of anhydroretinol can give rise to two possible cations. If protonation occurs at C<sub>4</sub> in the ring, the retinylic cation IIa-IIIb (the cation identical with the one formed from retinyl acetate) will be formed. If protonation occurs at C<sub>15</sub> in the side chain the anhydroretinylic cation IVa-IVb (another pentaenylic cation not identical

Table IV. Comparison of Relative  $\lambda_{\max}$  Values<sup>a,b</sup> for Several Pentaenylic Cations

Acid	Cations		Retinylic	
	Symmetrical <sup>d</sup> pentaenylic	Anhydro- retinylic	From retinol	From retinyl acetate
H <sub>2</sub> SO <sub>4</sub>	625.5	607	593	593
HFBA <sup>c</sup>	609	594	586	588

<sup>a</sup> Values in m $\mu$ . <sup>b</sup> Precision  $\pm 2$  m $\mu$ . <sup>c</sup> Heptafluorobutyric acid. <sup>d</sup> 2,12-Dimethyltridecapentaenylic cation.

with II) will be formed. Only the latter event can give rise to the two different values of  $\lambda_{\max}$  which are actually observed. We conclude that retinyl acetate and anhydroretinol both form pentaenylic cations; but the electron distribution and the formal structure of these pentaenylic cations differ. On the other hand, retinyl acetate and retinol would be expected to form the same carbonium ion. Since the cation formed from either compound absorbs at the same wavelength, they are identical. The retinylic cation is unambiguously represented by IIa and IIb, whereas the anhydroretinylic cation is represented by IVa and IVb.

The order of gradually decreasing  $\lambda_{\max}$  values exhibited by the pentaenylic cations suggests that this spectral property may be related to the structure of the ion. It can be assumed<sup>12</sup> that any cation which possesses the greatest coplanarity and whose limiting resonance structures are the most symmetrical should absorb at the longest wavelength. Cation V has no structural substitution to cause steric warping of coplanarity as do ions VI and VII. In addition the  $\pi$ -electron cloud is symmetrical with respect to a plane passing through C<sub>7</sub>. The two major resonance structures of ion V are equivalent and isoenergetic. Because of these observations, ion V would be expected to absorb at the longest wavelength, and it does. The effects of substitution are clearly evident in ions VI and VII, for there is a considerable hypsochromic shift with respect to V. Interestingly enough, although the structures are almost identical, ions VI and VII absorb at different wavelengths. Two explanations for this wavelength difference are possible, and both qualitatively predict the same result. In the first explanation, the contribution of the cyclic structure that is not on the free electron path is neglected. Under these conditions, a plane of symmetry is found at C<sub>9</sub> in ion VI, but none is found in ion VII. Thus ion VI would have resonance structures more nearly isoenergetic and would absorb at longer wavelengths. The second explanation involves the possibility of a shorter free-electron path and therefore a shorter wavelength of absorption. This is caused by the shorter bond distance of the C-H bond found at C<sub>15</sub> in ion VII. Although the relative contributions cannot be separated from the evidence at hand, both mechanisms predict that ion VI should absorb at a longer wavelength than ion VII, and it does.

**Effect of Environment on Spectra.** Although it has been shown that structure strongly affects the  $\lambda_{\max}$  of the absorption band, solvent appears to have little influence on this property. Inspection of Tables I-IV shows the mean  $\lambda_{\max}$  value to be  $598 \pm 14$  m $\mu$ , and this variation is small compared to the total value of the bathochromic shift from 330 m $\mu$  to 598 m $\mu$ . The

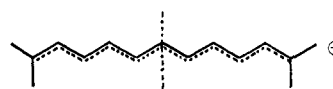
(12) H. Kuhn, *J. Chem. Phys.*, 17, 1198 (1949).

unusual insensitivity toward solvent gives insight into the nature of the ground and excited states of these cations. Platt<sup>13</sup> examined the relationship between spectral properties and structure. A given chromophoric molecule may be represented in terms of its two main resonance structures. In the case at hand, the retinylic cation is represented by structures IIa and IIb. In cases where the two resonance structures are equivalent and isoenergetic, the chromophore will absorb at the longest wavelength—the isoenergetic wavelength  $\lambda_I$ . For these compounds, the dipole moment is the same in the ground and excited states, and solvent will affect each state equally. Consequently solvents will have little or no effect on the placement of the  $\lambda_{\max}$ .

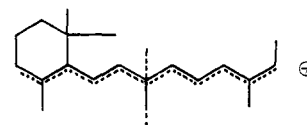
The symmetrical polymethine dyes are a class of compounds which fit the above description.<sup>13</sup> Their spectral properties have been studied extensively both theoretically and experimentally. Their  $\lambda_I$  is almost solvent independent; the bonds in the chromophore have approximately equal lengths with no alternation in either state; there is no vibrational fine structure and they have a single narrow peak with a half-band width of from 900 to 1600 cm<sup>-1</sup>. This description also fits the pentaenylic cations described in this paper, and it is predictable from the free-electron model.<sup>12,13</sup> Thus it can be concluded that solvent insensitivity indicates that the ground state and the excited states of the pentaenylic cations are similar. Solvent dependency increases with asymmetry. Consequently ions V, VI, and VII should be increasingly solvent dependent. This dependency is presently under investigation.

Additionally, Platt was able to show that for polymethine dyes with some degree of asymmetry wavelength and molar absorptivity increases as the amount of pyridine in a pyridine-water solution is increased. The same relationship between wavelength and molar absorptivity is apparent from inspection of the results given in Table III. Because of the small spread in experimental values, they cannot be treated quantitatively, but the qualitative trend is unmistakable.

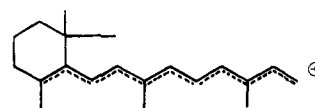
The spectral properties of the carbonium ions disclosed here and the properties of other ions now under investigation can be examined and are meaningful as models of visual pigments. However, comparison with



V,  $\lambda_{\max}$  625 m $\mu$



VI,  $\lambda_{\max}$  607 m $\mu$



VII,  $\lambda_{\max}$  594 m $\mu$

(13) J. R. Platt, *ibid.*, 25, 80 (1956).

visual pigments should await the outcome of present work and will be put forth at some future time.

### Experimental Section

**Polynes.** *all-trans*-Retinyl acetate was obtained crystalline from Distillation Products Industries in vacuum-sealed ampoules which were stored at Dry Ice temperature in the dark. Opened ampoules were stored under nitrogen in the dark at Dry Ice temperature. All studies were performed in red light. *all-trans*-Retinol was treated as given above. Anhydroretinol [3,7-dimethyl-9-(2,6,6-trimethyl-2-cyclohexan-1-ylidene)-1,3,5,7-nonatetraene] was prepared and characterized according to the procedures outlined by Shantz and coworkers.<sup>14</sup>

**Acids.** Sulfuric acid was dried by adding a sufficient amount of fuming sulfuric acid to react with the water.<sup>15</sup> Trichloroacetic acid was purified by recrystallization and was dried in a drying pistol.

**Solvents.** All solvents were dried and stored over molecular sieves in a nitrogen atmosphere. Methanol, ethanol, 1,2-dichloroethane, chloroform, carbon tetrachloride, cyclohexane, *n*-heptane, and isooctane were dried by the methods set forth by Wiberg.<sup>16</sup> Acetic acid was dried by treatment with triacetyl borate which reacts with the water to form acetic acid and insoluble boric acid.<sup>17</sup>

**Generation and Observation of the Retinylic Cation.** Variations in experimental conditions were necessary for the generation and detection of retinylic cations. Conditions were dictated by the acid-solvent system employed and the kind of information sought. Low temperatures were always necessary to stabilize the cation; the exact temperature was determined by solvent and the acid concentration. Also experimental conditions were dependent on whether the  $\lambda_{\max}$  or  $\epsilon_{\max}$  of an absorption band was to be measured.

(14) E. M. Shantz, J. D. Cawley, and N. D. Embree, *J. Amer. Chem. Soc.*, **65**, 901 (1943).

(15) A. I. Vogel, "A Textbook of Practical Organic Chemistry," 2nd ed, Longmans, Green and Co., New York, N. Y., 1951, pp 171-172.

(16) K. B. Wiberg, "Laboratory Techniques in Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1960, pp 240-252.

(17) L. F. Fieser, "Experiments in Organic Chemistry," 3rd ed, D. C. Heath and Co., Boston, Mass., 1955, p 281.

**Absorption Maximum.** The following procedure performed in the dark was used most extensively. Two milligrams of retinyl acetate were weighed, placed in a 10-ml volumetric flask, and diluted to the mark. A 0.3-ml aliquot ( $1.83 \times 10^{-7}$  mol of retinyl acetate) of this solution was mixed quickly with 25 ml of a cooled (approximately  $-35^\circ$ ) sulfuric acid-solvent mixture using a magnetic stirrer. The acid-solvent ratio can be varied considerably; but 10 ml of sulfuric acid and 15 ml of solvent were used most often. After formation of a homogeneous blue color, a portion of the solution at about  $-50^\circ$  was quickly transferred to a 1-cm cuvette and its spectrum was scanned from 800 to 400  $m\mu$ . The spectrophotometer was set to scan this region repetitively at a rapid rate so that spectral changes could be recorded as a function of time.

When trichloroacetic acid was used as the protonating agent, the carbonium ion solution was maintained at a temperature above  $0^\circ$  to avoid precipitation. A constant-temperature cell was employed for most measurements.

**Molar Absorptivity.** Experimental conditions for determination of molar absorptivity of the retinylic cation were chosen to ensure maximum concentration of the cation. Although the same procedure was used as described above, it was necessary to: (1) use acid-solvent proportions known to give the highest absorbance (*i.e.*, 50-60 mol % sulfuric acid), (2) mix the components as completely as possible, and (3) freeze the carbonium ion mixture in Dry Ice-acetone immediately after mixing to retard its decay to other products.

**Measurements.** All spectral measurements in the visible and ultraviolet regions were obtained in 1-cm matched quartz cells with the Beckman DK-2A ratio recording spectrophotometer equipped with a Beckman temperature-regulated cell holder. When lower temperatures were required, the cell holder was cooled either by ice water or by methanol at  $-78^\circ$ . For temperatures lower than  $0^\circ$ , dry nitrogen was flushed across the optics of the spectrophotometer and the cells to eliminate condensation. Because of the rapid scanning speed, it was necessary to add a correction of 8  $m\mu$  to the measured absorptions to compensate for instrument time lag.<sup>18</sup>

(18) The value of 8  $m\mu$  should be added to all values reported in ref 9.

## The Role of Singlet and Triplet Excited States in the Photochemistry of 3,5-Cycloheptadienone<sup>1</sup>

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**Abstract:** The photolysis of 3,5-cycloheptadienone in ethyl ether, hexane, and ethanol solutions gives solely carbon monoxide and a mixture of *cis*- and *trans*-1,3,5-hexatrienes. This reaction cannot be quenched using either piperylene (1,3-pentadiene) or naphthalene. Photolysis of 3,5-cycloheptadienone sensitized by either benzophenone (in ether) or acetone (neat) gives exclusively the valence tautomer, bicyclo[3.2.0]hept-6-en-3-one. Product mixtures were analyzed spectroscopically and by gas-liquid partition chromatography with direct comparison with authentic samples of products and possible intermediates. It is concluded that the direct photolysis occurs exclusively *via* a singlet excited state, and that the efficient concerted fragmentation to carbon monoxide and the hexatrienes, in contrast to facile valence tautomerizations in related systems, can be understood on the basis of the symmetry properties of the dienone. Relationships with the previously proposed modes of fragmentation of diazenes are discussed. The sensitized reaction *via* the triplet state is seen possibly as another example of conversion of a *cis,cis*-1,3-diene to the *cis,trans* isomer followed by thermal conversion to the cyclobutene derivative.

In 1961 and 1962 Chapman and his coworkers reported the photolysis of 3,5-cycloheptadienone (**1a**) and its 2-methyl homolog (**1b**) in ether solution.<sup>4</sup>

(1) Part XIII of a series on the photochemistry of unsaturated ketones in solution. Part XII: D. I. Schuster and D. F. Brizzolara, *Chem. Commun.*, 1158 (1967).

(2) Fellow of the Alfred P. Sloan Foundation.

These ketones on irradiation with a broad spectrum lamp in Pyrex vessels give carbon monoxide (95% in the

(3) Abstracted in part from the A.B. Honors Thesis of B. R. S., University College, New York University, 1967, and the Ph.D. Dissertation of F.-T. H. L., New York University, 1966.

(4) (a) O. L. Chapman and G. W. Borden, *J. Org. Chem.*, **26**, 4185 (1961); (b) O. L. Chapman, D. J. Pasto, G. W. Borden, and A. A. Griswold, *J. Amer. Chem. Soc.*, **84**, 1220 (1962).