

Hazura procedure recommended by Hilditch⁶ gave 0.57 g. of solid tetrahydroxystearic acids. Hilditch states that the tetrahydroxy acids were "separated by fractional crystallization from ethyl acetate." We used absolute ethyl acetate and found that the lower melting acid could be extracted and recrystallized from this solvent but that the higher melting acid was too insoluble to be recrystallized from it. After extraction of the lower melting acid with absolute ethyl acetate, the higher melting acid was recrystallized from 95% alcohol. There was obtained in this way 0.28 g. of tetrahydroxystearic acid, m. p. 156–157° and 0.07 g., m. p. 172–175°. When 1.0 g. of the synthetic acid was treated in exactly the same way there was obtained 0.40 g. of a sticky product from which was isolated only 0.08 g. of m. p. 151–154° and 0.02 g., m. p. 174–175°. Mixed melting points with the corresponding acids from natural α -linoleic acid were 152–155° and 173–175°.

A solution of 1.536 g. (0.00548 mole) of synthetic acids in 20 cc. of absolute ethyl acetate was ozonized and the solution decomposed with zinc dust and water according to the procedure of Whitmore and Church¹⁰ without removal of the solvent. After distillation and extraction of the aqueous layer with ethyl acetate the formaldehyde was estimated iodimetrically.¹¹ A blank run was made in which 20 cc. of ethyl acetate was ozonized for the same length of

time and decomposed in the same manner as the sample. The amount of formaldehyde from the sample, corrected by the blank, was 0.000883 mole, indicating the presence of 16% of 11-*n*-amyl-9,12-tridecadienoic acid. Pure undecylenic acid, however, gave only 44% of the calculated amount of formaldehyde under the same conditions. The water-zinc dust decomposition of the ozonides does not seem to be very satisfactory for compounds giving water insoluble products since the latter tend to coat the zinc dust and cause it to agglomerate.

The formaldehyde was identified positively by conversion into the 2,4-dinitrophenylhydrazone which after four crystallizations from methyl alcohol melted at 158–162°. The mixed melting point with pure formaldehyde-2,4-dinitrophenylhydrazone (m. p. 166–167°) was 159–163°.

An attempt to isolate the *n*-hexoic and *n*-heptoic acids which also should be formed on ozonation of the synthetic product gave a small amount of mixed acids distilling at 200–260° but conversion to the anilides gave an oil which could not be made to crystallize.

Summary

A series of reactions has been carried out which led to the synthesis of a mixture of linoleic acid and 11-*n*-amyl-9,12-tridecadienoic acid.

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(10) Whitmore and Church, *THIS JOURNAL*, **54**, 3712 (1932).

(11) Feinberg, *Am. Chem. J.*, **49**, 89 (1913).

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF THE UNIVERSITY OF CALIFORNIA AT LOS ANGELES]

Studies of Absorption Spectra. I. Crotonaldehyde and Acrolein

BY FRANCIS E. BLACET, WILLIAM G. YOUNG AND JACK G. ROOF

In connection with problems in photochemistry and in the synthesis of pure stereoisomeric compounds, a quantitative study of the absorption spectra of crotonaldehyde and acrolein in the vapor phase has been made. The object of this investigation was (1) to determine the types of absorption in different regions of the spectrum, (2) to compare the absorption of these two closely related compounds, and (3) in the case of crotonaldehyde, to test by spectroscopic means for the presence of *cis*-crotonaldehyde in the purified commercial product.

Although a number of investigators have studied these compounds,¹ the work for the most part was done with solutions in which the band structure of absorption, as shown by the vapors, was not observed. However, two exceptions to

this generalization should be mentioned. Lüthy^{1c} reported the fine structure but did not attempt to calculate extinction coefficients from studies of the vapor phase. Eastwood and Snow^{1h} also have done nothing with extinction coefficients, but by means of a 21-foot (6.3 meter) grating have shown that some of the prominent maxima of acrolein may be resolved into very narrow bands which they attribute to rotational levels in the molecule.

Experimental Part

Purification and Treatment of Samples.—In an attempt to detect the presence of *cis*-crotonaldehyde in the purified commercial product, samples were prepared in two different ways and their absorption spectra studied. The first of these, which is hereafter called the "original" sample, was made in such a way that any mixture of the *cis* and *trans* forms would be preserved. The second or "irradiated" sample was treated with hydrochloric acid and sunlight by a procedure which is known to cause similar compounds to be converted into the *trans* form.²

(1) (a) Bielecki and Henri, *Ber.*, **46**, 3627 (1913); (b) Purvis and McClelland, *J. Chem. Soc.*, **103**, 433 (1913); (c) Lüthy, *Z. physik. Chem.*, **107**, 284 (1923); (d) Henri, *Compt. rend.*, **178**, 844 (1924); (e) Purvis, *J. Chem. Soc.*, **127**, 9 (1925); (f) Henri, *Compt. rend.*, **199**, 849–851 (1934); (g) Thompson and Linnett, *Nature*, **134**, 937 (1934); (h) Eastwood and Snow, *Proc. Roy. Soc. (London)*, **A149**, 446 (1935).

(2) (a) Wislicenus, *Ann.*, **248**, 341 (1889); (b) Blaise, *Ann. chim. phys.*, [8] **11**, 116 (1907).

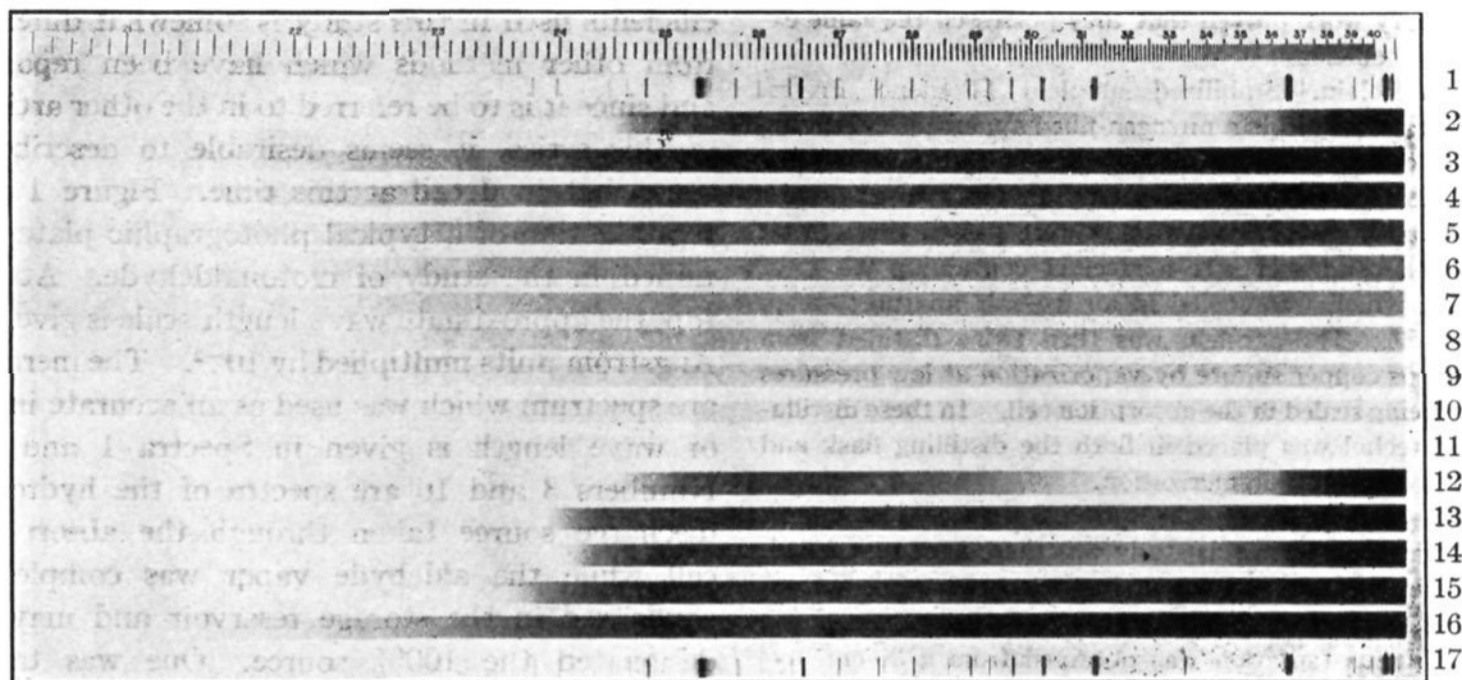


Fig. 1.—Reproduction of a typical spectrogram obtained in the study of crotonaldehyde.

(a) **Crotonaldehyde (Original).**—The crotonaldehyde obtained from the Niacet Chemical Corporation was purified by distillation through a 90-cm. Claisen-head column full of cut glass rings and equipped with a Hopkins condenser. The fraction boiling between 101–102° (750 mm.) was dried over anhydrous copper sulfate and redistilled in an atmosphere of nitrogen through a 30-cm. Vigreux column, b. p. 102.6–102.8°; d_{25}^{25} 0.8495; n_{20}^{20} 1.4356. Other drying agents such as calcium chloride and magnesium perchlorate caused more or less polymerization of the aldehyde.

(b) **Crotonaldehyde (Irradiated).**—One hundred cc. of the freshly distilled commercial crotonaldehyde, b. p. 101–102°, was placed in a Pyrex flask with 4 cc. of 6 *N* hydrochloric acid and exposed to strong sunlight for five hours.

In some experiments the irradiated mixture was then treated with sodium bicarbonate and distilled through a 30-cm. Vigreux column. The water together with a small amount of aldehyde distilled between 90–95°. The temperature then rose rapidly and a chloride-free fraction was collected between 101.5–102.5°. This product was dried over anhydrous copper sulfate and distilled, b. p. 102.6–102.8°, n_{20}^{20} 1.4358. In other experiments the irradiated mixture was distilled at once; the large portion of the hydrochloric acid coming over in the first fraction, b. p. 90–101.5°. The main distillate, b. p. 101.5–102.5°, n_{20}^{20} 1.4356, was essentially chloride free. It was likewise dried and fractionated, b. p. 102.6–102.8°, n_{20}^{20} 1.4356. The crotonaldehyde samples prepared by both of these procedures are referred to as the “irradiated” sample since

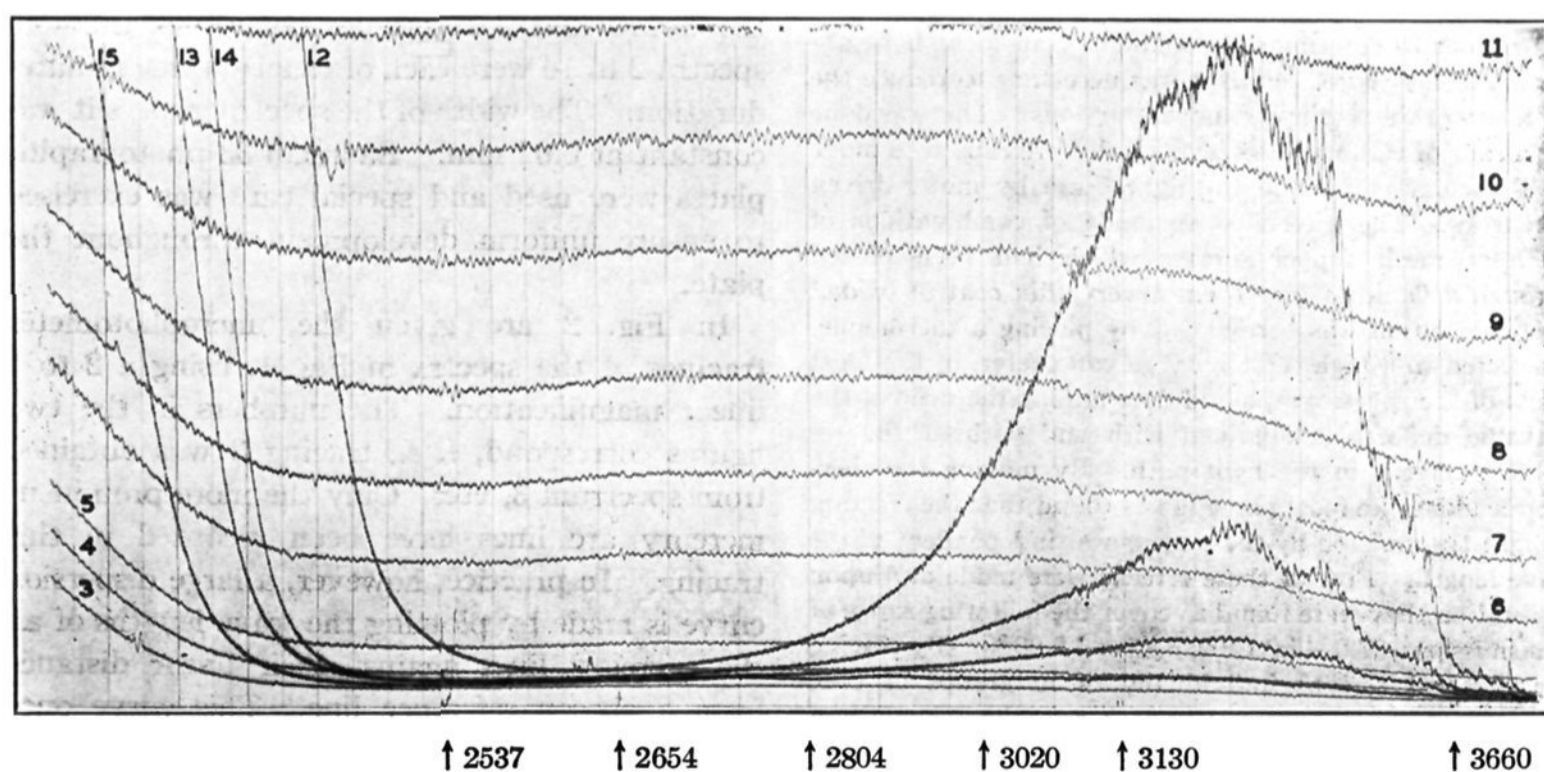


Fig. 2.—Microphotometer tracings of the spectra shown in Fig. 1. The numbers in the two figures correspond, *i. e.*, tracing 3 was obtained from spectrum 3, etc. The positions of the more prominent mercury arc lines are indicated.

preliminary work proved that they possessed the same extinction coefficients.

(c) **Acrolein.**—Stabilized acrolein (Poulenc Frères, Paris) was distilled in a nitrogen-filled apparatus consisting of a 90-cm. column, containing glass rings and equipped with a Hopkins reflux condenser. In order to avoid the formation of disacryl the vapors were passed through an ice-cooled condenser into a receiver containing 0.5 g. of catechol which was cooled in an ice-salt mixture; b. p. 53.0–53.2°. The acrolein was then twice distilled from anhydrous copper sulfate by vaporization at low pressures before being sealed in the absorption cell. In these distillations catechol was placed in both the distilling flask and receiver to avoid polymerization.

Method of Study of Absorption Spectra.—The quartz spectrograph used in this study was the Hilger type E316. It is primarily an ultraviolet instrument, having a focal plane of 18 cm. in length between λ 2000 and 4000 Å.

Continuous radiation was obtained from a 30-cm. hydrogen discharge between water-cooled iron electrodes. Purified hydrogen was pumped through the discharge tube at a constant rate during the exposures. The pressure in the tube was regulated by observing the structure of the discharge. A blue double herring bone structure was used since it is very sensitive to pressure change and also gives a source with the minimum number of lines due to atomic hydrogen.

The aldehyde vapors were studied in a fused silica absorption cell 40 cm. in length, 3 cm. in diameter and having plane parallel windows. A mercury manometer of 8 mm. inside diameter and a small reservoir for storing the liquid to be studied were connected to the tube by silica-to-Pyrex graded seals. The aldehyde was introduced into the reservoir in the following manner: the system was first flushed out with nitrogen and then about 3 cc. of the aldehyde was distilled at low pressure into the reservoir which contained 0.1 g. of catechol. While the reservoir was still cooled by means of solid carbon dioxide the system was evacuated, and sealed off.

In order to determine the amount of incident light absorbed at any wave length it was necessary to reduce the intensity of the source by known fractions. This was done by means of calibrated screens which were caused to move in a circular manner in the light beam by motor-driven eccentrics. The screens were made of combinations of different mesh copper screens which had been passed through a flame to give them a very thin coat of oxide.³ The calibration was carried out by placing a thermopile, connected to a high sensitivity galvanometer, in the focal plane of the spectrograph and determining the ratio of the galvanic deflections obtained with and without the revolving screens in the light path. By moving the thermopile along the focal plane it was found that the fraction of light transmitted by the screens was independent of the wave length. Five of these screens were made and upon calibration they were found to cover the following range of transmission: 67.0, 45.0, 22.2, 5.85 and 2.90%. By placing the different screens individually or in groups of two, moving out of phase with one another, in the light path, a large variation in transmission could be obtained.

Since the method of obtaining extinction co-

efficients used in this study is somewhat different from other methods which have been reported and since it is to be referred to in the other articles of this series, it seems desirable to describe it somewhat in detail at this time. Figure 1 is a reproduction of a typical photographic plate obtained in the study of crotonaldehyde. At the top, the approximate wave length scale is given in Ångström units multiplied by 10^{-2} . The mercury arc spectrum which was used as an accurate index of wave length is given in Spectra 1 and 17. Numbers 3 and 16 are spectra of the hydrogen discharge source taken through the absorption cell while the aldehyde vapor was completely condensed in the storage reservoir and may be designated the 100% source. One was taken before and the other after all of the other spectra were taken in order to afford a check on the constancy of the source. If in any case it was found that the 100% source had changed in intensity during the time exposures were being made, the entire plate was discarded. Numbers 4, 5, 6, 7, 8, 9, 10 and 11 were taken in like manner except that rotating screens were placed in the path of light so that the intensity of the source was diminished, respectively, to 67, 45, 22.2, 14.9, 10.0, 5.85, 3.92 and 2.90% of the original intensity. Numbers 2, 12, 13, 14 and 15 are absorption spectra of crotonaldehyde taken with pressures in the cell of 42.5, 42.5, 12.0, 23.0 and 5.0 mm., respectively. These pressures were maintained by controlling the temperature of the liquid in the reservoir. Exposure times of spectra 2 to 16 were each of exactly three minutes duration. The width of the spectrograph slit was constant at 0.02 mm. Eastman 33 photographic plates were used and special care was exercised to ensure uniform development throughout the plate.

In Fig. 2 are given the microphotometer tracings of the spectra in Fig. 1, using a 2 to 1 linear magnification. The numbers in the two figures correspond, *i. e.*, tracing 3 was obtained from spectrum 3, etc. Only the more prominent mercury arc lines have been recorded in this tracing. In practice, however, a large dispersion curve is made by plotting the wave lengths of all the mercury lines against their linear distance from a chosen reference line. This curve once made may be used to determine the wave length of all points on any tracing having this 2 to 1 ratio to an original spectrogram. By placing the

(3) G. R. Harrison, *J. Opt. Soc. Am.*, **18**, 492 (1929).

tracings on thin millimeter cross-section paper over a ground glass illuminating table, the linear distance of any point from the reference line may be obtained with sufficient accuracy to give the wave length in the ultraviolet to within one or two Ångström units.

In calculating ϵ , the molecular extinction coefficient, Lambert-Beer's law

$$\epsilon = \frac{l}{d} \log \frac{I_0}{I} \quad (1)$$

is used in the form

$$\epsilon = \frac{RT}{pl} \left(2 - \log \frac{100I}{I_0} \right) \quad (2)$$

R is the gas constant in liter-atmospheres per mole per degree, T the absolute temperature, p the pressure of the gas in atmospheres, l the length in centimeters of the light beam in the absorbing medium, I_0 the intensity of the incident beam and I the intensity of the transmitted light. Since for a given spectrum T , p and l are measurable constants, it is obvious that wherever the ratio I/I_0 can be determined, ϵ may be calculated. In Fig. 2, tracings 3 to 11 inclusive are lines of known values of I/I_0 . Hence wherever a tracing of an absorption spectrum crosses one of these lines the extinction coefficient may be determined. In regions of continuous absorption these points may be sufficient in number to give a satisfactory curve of extinction coefficients.

However, in regions of discontinuous absorption it is not always easy to estimate the point of intersection; furthermore, there are maxima and minima which do not strike any of the source tracings. To eliminate this difficulty an interpolation curve for a given wave length may be made by plotting $\log 100 I/I_0$ against the perpendicular distance from an arbitrary base line. This gives a smooth curve and by measuring from this line the height of an absorption tracing at the wave length in question, $\log 100 I/I_0$ may be obtained from the graph. For convenience a tracing representing zero transmission of the plate was used as the base line. In regions in which the source tracings are approximately horizontal, the same interpolation curve may be used for a considerable range of wave lengths. When this is not the case, a new curve must be

plotted for each wave length at which extinction coefficients are desired. However, this is not a very tedious process since all curves have the same source values for $\log 100 I/I_0$ and it is only necessary to read off the heights of the tracings and record them on the graph. The microphotometer used in this study has been described elsewhere and has been shown to have constant sensitivity and to give reproducible results.⁴

It may be recognized that because of over-exposure between wave lengths 2450 and 2900 Å. and above 3600 Å., Figs. 1 and 2 are of no value in calculating extinction coefficients. In order to bring out these regions, some spectrograms were taken with the time of exposure reduced

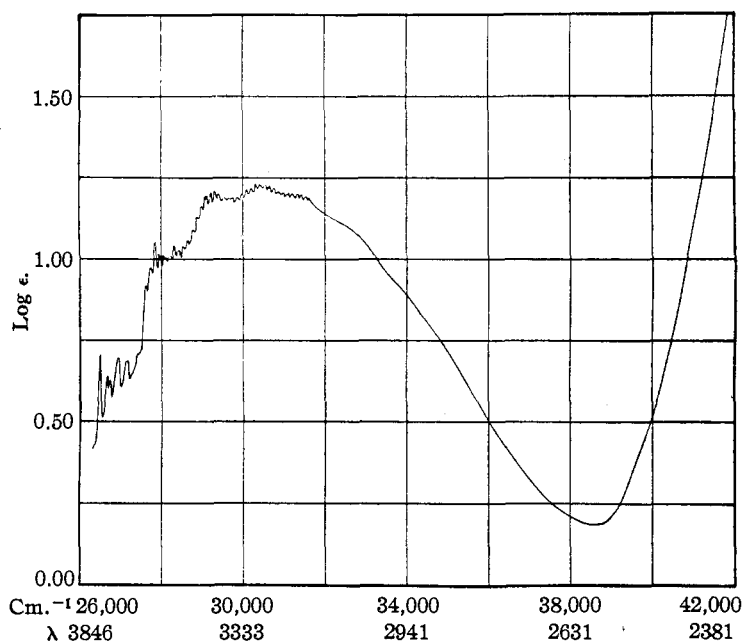


Fig. 3.—Logarithms of the molecular extinction coefficients of crotonaldehyde vs. wave numbers, cm^{-1} and wave lengths, λ , in Ångström units.

to sixty seconds, while still others had the spectrograph slit width reduced from 0.02 mm. to 0.01 mm. as well. As far as it could be ascertained, by studying overlapping regions, these variations had no effect upon the value of the extinction coefficients.

By using the method described above the extinction coefficients of crotonaldehyde and acrolein were obtained. These results are presented graphically in Figs. 3 and 4. As far as it is possible to make a comparison from the information available they are in general agreement

(4) Leighton, Smith and Henson, *Rev. Sci. Instruments*, **5**, 431 (1934).

with those reported by Lüthy.^{1c} It does not seem necessary to give detailed tables of extinction coefficients in addition to the results shown in the

many unsaturated compounds. In order to be sure of the configuration of these products it is of utmost importance to know the exact composition of the crotonaldehyde.

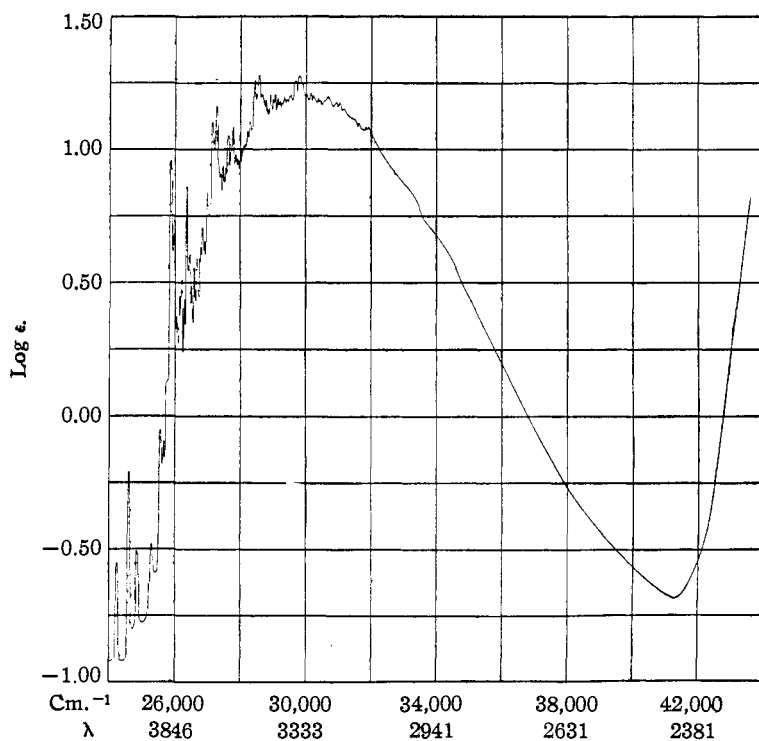


Fig. 4.—Logarithms of the molecular extinction coefficients of acrolein vs. wave numbers, cm.^{-1} and wave lengths, λ , in Ångström units.

figures. However, in Table I are presented some typical results obtained in the comparison study of the original crotonaldehyde and the samples which were irradiated in the manner described above. It may be observed that within the limits of error both in regard to the measurement of wave lengths and the evaluation of the extinction coefficients, there is no difference between the two samples.

TABLE I
WAVE LENGTH AND LOG ϵ OF SOME CHARACTERISTIC ABSORPTION MAXIMA OF THE ORIGINAL AND THE IRRADIATED CROTONALDEHYDES

| Wave length, Å. Original | Irradiated | Log ϵ Original | Log ϵ Irradiated | Difference in log ϵ of original and irradiated | |
|-----------------------------|------------|----------------------------|------------------------------|--|-----------------------------------|
| | | | | of original and irradiated | of two determinations on original |
| 3588 | 3589 | 1.060 | 1.051 | +0.009 | +0.008 |
| 3529 | 3530 | 1.063 | 1.045 | + .018 | - .005 |
| 3422 | 3423 | 1.216 | 1.219 | - .003 | + .009 |
| 3411 | 3412 | 1.216 | 1.221 | - .005 | + .009 |
| 3297 | 3299 | 1.244 | 1.233 | + .011 | + .011 |
| Average | | | | .0060 | .0064 |

Discussion of Results

Composition of Crotonaldehyde.—Crotonaldehyde is the starting material in the synthesis of

the original and irradiated crotonaldehydes. The procedure adopted for the preparation of the irradiated crotonaldehyde takes advantage of the possibility of both photochemical and thermal stereomutation in the presence of hydrochloric acid. Stereomutation of *cis*-crotonic acid by irradiation with sunlight has been reported by Wislicenus.^{2a} Likewise stereomutation of *cis*- α -methylcrotonic acid during distillations at approximately 100° has been reported by Blaise^{2b} and since corroborated.⁶ It was found that during the thermal decomposition of α -methyl- α -hydroxybutyric acid and during the fractional distillation of the decomposition products, it was necessary to avoid even traces of hydrochloric acid in order to obtain a satisfactory yield of *cis*- α -methylcrotonic acid. If appreciable quantities of the catalyst were present only the *trans* isomer could be isolated.

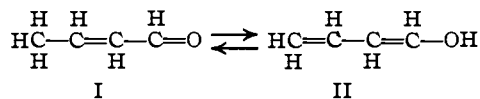
A comparison of results, Table I, indicates that both the extinction coefficients and wave lengths

(5) Young, THIS JOURNAL, 54, 2498 (1932).

(6) Young, Dillon and Lucas, *ibid.*, 51, 2529 (1929).

of characteristic maxima agree within experimental error for both the original and irradiated samples. If the original aldehyde contained an appreciable quantity of the *cis* isomer and the concentration of this isomer were changed by the method adopted, one might expect a shift in the wave length of the characteristic peaks, thus causing a twinning effect or the appearance of small peaks between the larger ones. Likewise, a difference in extinction coefficients might be expected. Since these differences do not appear, it may be reasoned that commercial crotonaldehyde is essentially the pure *trans* isomer just as the oxidation experiments had indicated.⁵ It should be noted that several papers⁷ have appeared on the Raman spectra of crotonaldehyde. However, only Gredy and Piaux reported lines which were attributed to traces of the *cis* isomer. Two possible explanations may be suggested to account for the apparent lack of the unstable stereoisomer in crotonaldehyde. One is the occurrence of

resonance between the forms $\text{H}:\overset{\text{H}}{\underset{\text{H}}{\text{C}}}:\overset{\text{H}}{\underset{\text{H}}{\text{C}}}::\overset{\text{H}}{\underset{\text{H}}{\text{C}}}:\overset{\text{H}}{\underset{\text{H}}{\text{C}}}::\ddot{\text{O}}$ and $\text{H}:\overset{\text{H}}{\underset{\text{H}}{\text{C}}}:\overset{\text{H}}{\underset{\text{H}}{\text{C}}}::\overset{\text{H}}{\underset{\text{H}}{\text{C}}}:\ddot{\text{O}}:$. A second explanation is that crotonaldehyde may consist of a tautomeric system of high mobility.



The aldehyde group is known to be one of the most efficient groups in activating a prototropic system.⁸ The third possible tautomer, vinylacetaldehyde, would not be expected since there is no substitution in the γ -position.⁹

Comparison of Absorption Spectra of Crotonaldehyde and Acrolein.—By an inspection of Figs. 3 and 4, similarities and differences between the absorption spectra of crotonaldehyde and acrolein become obvious. Apparently the fundamental absorption processes are the same in the two compounds and the differences in the spectra result from the variation in length of the carbon chain.

Although the values of $\log \epsilon$ obtained from

(7) (a) Hibben, *Proc. Nat. Acad. Sci.*, **18**, 532 (1932); (b) Gredy and Piaux, *Compt. rend.*, **198**, 1235 (1934); *Bull. soc. chim.*, [5] **1**, 148 (1934).

(8) Baker, "Tautomerism," D. Van Nostrand Company, Inc., New York, N. Y., pp. 44-45.

(9) Ingold, "Annual Reports on the Progress of Chemistry," **24**, 111 (1927).

different spectrograms varied by about 2% in regions of strong absorption by the vapor, the relative values at successive wave lengths can be obtained quite accurately and hence all of the small peaks and valleys appearing in these figures do exist. That is to say, two absorption curves obtained independently have the same characteristic shapes but one may lie above or below the other. $\log \epsilon$ values for all points of inflection shown for both aldehydes are the average values obtained from two or more spectrograms and from two or more pressures recorded on each of these. It was found that extinction coefficients calculated for crotonaldehyde from spectrograms of saturated vapor (42.5 mm. or less) were in substantial agreement with values obtained at lower pressures, indicating that deviations from the perfect gas law were not appreciable under these conditions. For acrolein the pressures used were well below the saturation value. They ranged between 30 and 150 mm. Over this range the values of ϵ reported for the maxima and minima of the discontinuous region are independent of pressure.

The generally accepted interpretation of discontinuous absorption is that the primary act of absorption produces only activated molecules, while, on the other hand, a continuum is thought to signify that dissociation occurs in the primary process. In Fig. 2 it may be observed that the strong lines of the mercury arc are well distributed among the continuous and discontinuous regions of absorption shown by crotonaldehyde. Hence, this aldehyde, as well as acrolein, if studied with the aid of a quartz mercury arc and monochromator, appears to offer an excellent opportunity to correlate these spectral interpretations with photochemical results. Do polymerization or decomposition processes occur in both regions of absorption and, if so, is there a marked change in the quantum yields of these reactions as the studies are shifted from the discontinuous to continuous regions? These questions and related ones are being studied at the present time in this Laboratory.

The authors are indebted to Professor P. A. Leighton for helpful suggestions in regard to this study and for the use of the microphotometer of Stanford University. Substantial aid has been received from Mr. Darrell Osborne in the compilation of experimental data. Likewise, the authors wish to express their appreciation for grants-in-aid from the National Research Council

and the Board of Research of the University of California.

Summary

A modified procedure for obtaining molecular extinction coefficients has been described.

Working with the vapor phase, the ultraviolet

absorption spectra of crotonaldehyde and acrolein have been determined quantitatively.

Experiments designed to test for the presence of *cis*-crotonaldehyde in the commercial product gave results which indicate that this form of the aldehyde was not present.

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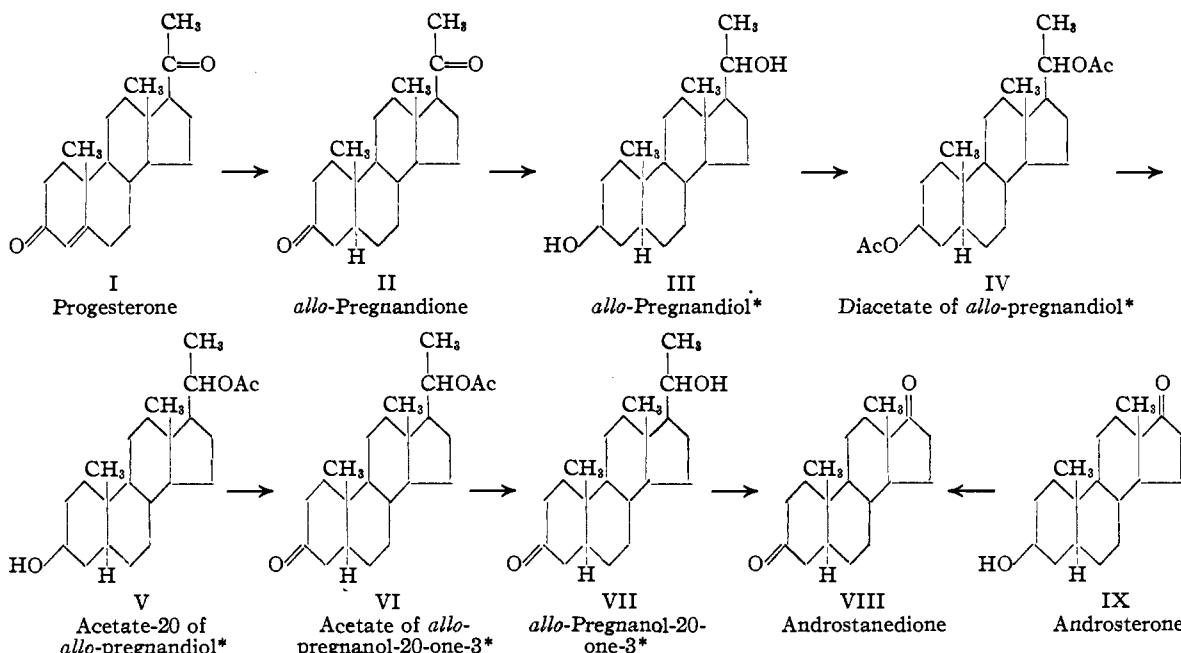
[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY AND PHYSICS OF THE PENNSYLVANIA STATE COLLEGE AND THE PARKE, DAVIS & CO. RESEARCH LABORATORIES]

Sterols. VIII. Preparation of Androstenedione from *allo*-Pregnandiol

BY RUSSELL E. MARKER, OLIVER KAMM, DAVID M. JONES AND THOMAS S. OAKWOOD

The present paper serves to establish a complete structural relationship between the female sex hormone, progesterone (I) and the male sex hormone, androsterone (IX). This has been

oxidizing the mixture, and separating from it pregnandione and *allo*-pregnandione. The reactions involved in our work are illustrated by formulas II-VIII.



* The designation *trans* has been omitted at the suggestion of the referee. It seems to us, however, that such a designation is needed to differentiate our new compounds from previously known isomers.

accomplished by supplementing the known preparation¹ of androstenedione (VIII) by oxidation of androsterone, with a new method of preparation of the same compound starting with *allo*-pregnandione (II). The last mentioned compound has been described previously by Butenandt,² who obtained it by reducing progesterone to a mixture of pregnandiol and *allo*-pregnandiol,

(1) Butenandt and Tscherning, *Z. physiol. Chem.*, **229**, 189 (1934).
 (2) Butenandt and Fleischer, *Ber.*, **68**, 2094 (1935).

allo-Pregnandione (II) was obtained by oxidation with chromic anhydride of the mixture of pregnandiol and *allo*-pregnandiol obtained from concentrates of human pregnancy urine. Crystallization from acetone gave pure *allo*-pregnandione. The latter was reduced in acetic acid at room temperature with platinum oxide and hydrogen to *allo*-pregnandiol (III). This gave a digitonide readily. The diol was converted to the diacetate (IV). The acetyl group in the 3-