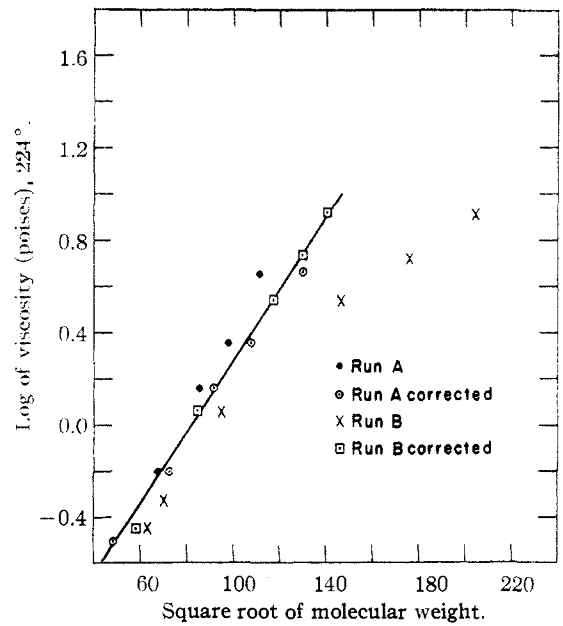

Fig. 5.—Viscosity-molecular weight relationship, polyester from dilinoleic acid with dilinoleyl glycol.

that the ester present in the glycol would be reactive by glycolysis and should be allowed for in calculating the required amount of acid to be used. The viscosity-molecular weight relationships of samples taken during this run indicated that an excess of glycol was present, and since no catalyst was present, it would appear that the ester had not reacted. When the results of both runs were corrected for the excess of acid or glycol present, assuming that the ester is unreactive, the points for both runs showed the same linear relationship of log of viscosity to square root of molecular weight. All corrections were calculated using Flory's equation for approximate percentage error.[14] In the first run, 34.42 g. (0.1214 equivalent) of dilinoleic acid (from soybean oil; neutral equivalent, 283.8) and 32.76 g. (0.1193 equivalent, based on OH no.) of hydrogenated dilinoleyl glycol reacted at 224°. In the second run, 31.14 g. (0.1098 equivalent) of dilinoleic acid and 31.09 g. (0.1131 equivalent) of the same glycol reacted at 224°. The results for viscosity molecular weight relationship are identified as Run A and Run B, respectively, in Fig. 5. The corrected values lie on the same straight line, and again indicate linear superpolyesters of molecular weights up to 20,000. Final samples from both runs were soluble in chloroform.

Summary

Superpolyesters were prepared from an unsaturated dibasic acid, dilinoleic acid, with ethylene, decamethylene and hydrogenated dilinoleyl glycols.

Loss and decomposition of ethylene glycol at reaction temperatures occurred and therefore superpolyesters were not obtained when an equivalent amount of ethylene glycol was used. Superpolyesters from ethylene glycol were obtained when excess of glycol was used and the final stages of the reaction were effected by glycolysis. Superpolyesters having molecular weights of 20,000 or more were obtained by direct esterification when decamethylene and hydrogenated dilinoleyl glycols were used.

A study of the variation of viscosity with molecular weight showed a straight line relationship between log of viscosity and square root of molecular weight up to molecular weights of 10,000 on certain polyesters. Direct comparison of superpolyesters from dilinoleic acid and from hydrogenated dilinoleic acid demonstrated that reaction conditions can be controlled so that non-conjugated unsaturation does not cause crosslinking of chains.

PEORIA, ILLINOIS RECEIVED SEPTEMBER 14, 1943

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

Spectroscopic Evidence for Conjugation in Cyclopropane Systems

BY IRVING M. KLOTZ

The properties of molecules composed of a cyclopropane ring adjacent to a carbonyl group have been studied for some time, and considerable chemical evidence has been accumulated to show that such structures behave as conjugated systems.[1] Recently similar behavior has been observed in molecules containing a cyclopropane ring adjacent to an olefinic double bond.[2] That these systems are indeed conjugated can be shown also by direct physical evidence, for with recent progress in the theory of absorption spectra[3] it is now possible to interpret ultraviolet spectra in terms of molecular structure.

The intense absorption bands of single ethylenic linkages lie in the region near 1800 Å., and if the carbon atoms are highly substituted, strong absorption may extend somewhat beyond 2000 Å.[4] However, when two double bonds are conjugated to each other a pronounced shift in the absorption toward the red end of the spectrum is observed. Wave-mechanical considerations[3] have shown that high intensity ultraviolet absorption spectra are due to transitions from a neutral ground state of the molecule to an ionic excited state. Conjugation permits the existence of a number of ionic structures which contribute appreciably to the resonance in

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(1) R. C. Fuson, "Organic Chemistry, An Advanced Treatise," Vol. I, second edition, edited by H. Gilman, John Wiley and Sons, Inc., New York, 1943, p. 102.

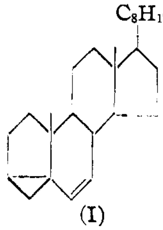
(2) B. Riegel, M. F. W. Dunker and M. J. Thomas, THIS JOURNAL, **64**, 2115 (1942).

(3) R. S. Mulliken, *J. Chem. Phys.*, **7**, 121 (1939); **7**, 339 (1939).

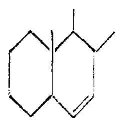
(4) A. Lüthy, *Z. physik. Chem.*, **107**, 285 (1923).

the excited state, but not to that in the ground state, and hence lower the energy of the former relative to that of the latter.

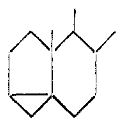
Since it is now recognized that conjugation may also occur between a saturated group and a double bond (hyperconjugation[3]) it would be expected that a compound such as Δ^6-*i*-cholestadiene (I) should have an ultraviolet absorption spectrum much farther toward the red than either 6-cholestene (II) or *i*-cholestene (III).



(I)

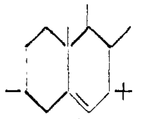


(II)

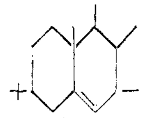


(III)

For in *i*-cholestadiene the structures (IV) and (V) are possible in addition to those which exist even when the cyclopropane ring is isolated from the olefinic linkage, and these new structures will contribute appreciably to the stabilization of the excited state of the molecule.

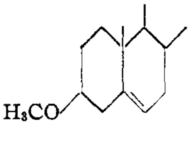


(IV)

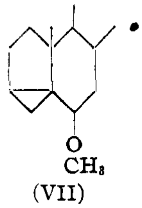


(V)

This prediction has been confirmed by an examination of the ultraviolet absorption spectra of Δ^6-*i*-cholestadiene (I), cholesteryl methyl ether (VI) and *i*-cholesteryl methyl ether (VII).



(VI)



(VII)

The two methyl ethers show no significant absorption, when examined in thickness and concentration comparable with Δ^6-*i*-cholestadiene (I), as low as 2230Å., the limit of our present instrument. These latter compounds correspond to structures (II) and (III) except for slight, non-influential differences in the position of the double bond and in the presence of a methoxy group. The *i*-cholestadiene, on the other hand, shows appreciable absorption below 2500Å. and gives strong indications of a peak near 2100Å. The spectrum of the compound has been plotted in Fig. 1 in conjunction with some mono- and diolefins for comparison. The unconjugated diolefin absorbs far to the left of *i*-cholestadiene, as is predicted by quantum mechanics.[3] Cyclopropane absorbs at even shorter wave lengths. Cholestadiene, on the other hand, absorbs in a region farther toward the red than even *i*-cholestadiene, for hyperconjugation is a second order effect compared to ordinary conjugation.[5] The position of the maximum of absorption of conjugated dienes is a function of the degree of substitution of the carbon atoms,[6] but for any cholestadiene, the absorption is much farther toward the red than that of *i*-cholestadiene.

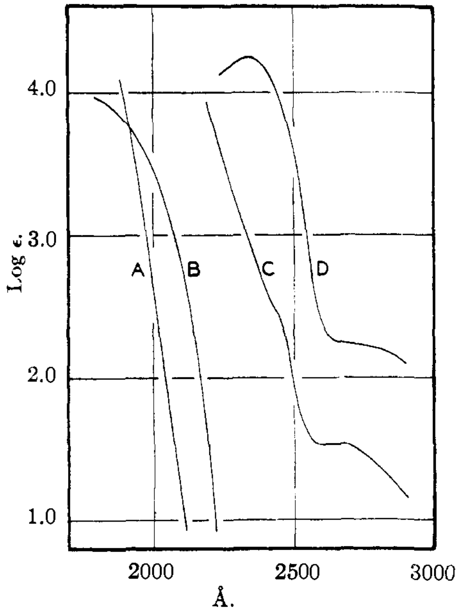


Fig. 1.—Absorption spectra of diallyl, A, trimethylethylene, B, Δ^6-*i*-cholestadiene (I), C, and cholestadiene, D. A and B from G. Scheibe and R. Pummerer, *Ber.*, **60**, 2163 (1927), and D from E. L. Skau and W. Bergmann, *J. Org. Chem.*, **3**, 166 (1938).

The considerations leading to an explanation of the spectrum of a conjugated cyclopropane ring–olefin system are also applicable to structures consisting of a cyclopropane ring adjacent to a carbonyl group. In these cases, however, it is necessary to recognize that all carbonyl compounds show a small absorption maximum near 3000Å., but are relatively transparent below this wave length unless some degree of conjugation exists. Thus 3-cholestanone (VIII) exhibits a maximum at 2860Å. (Fig. 2), a position quite close to that for acetone despite the great bulk of the former molecule. Below 2860Å. there is a decrease in the absorption of cholestanone down to about 2600Å. and a slight rise thereafter. In contrast, 3-cholestenone (IX), which has a conjugated olefinic and carbonyl group, shows, in addition to the carbonyl peak

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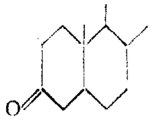
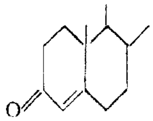
(5) R. S. Mulliken, C. A. Rieke and W. G. Brown, THIS JOURNAL **63**, 41 (1941).

(6) R. B. Woodward, *ibid.*, **64**, 72 (1942).

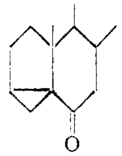


(VIII)



(IX)

at 3100Å., a second and very pronounced maximum at approximately 2410Å. This second maximum is due to stabilization of the excited state of the molecule by resonance between the two double bonds. Since the position of the peak for various α,β-unsaturated ketones depends on the degree of substitution of the carbons in the olefinic bond,[7] the spectrum of 3-cholestenone has been chosen for comparison because its degree of substitution is similar to that of *i*-cholestenone (X). In *i*-cholestenone, the conjugation of cyclopropane ring and carbonyl group introduces a number of ionic structures, in addition to those possible when the groups are isolated, which stabilize the excited state sufficiently to produce the spectrum shown in Fig. 2.



(X)

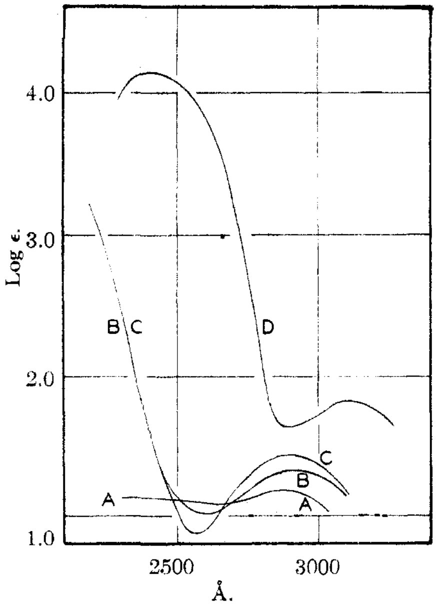
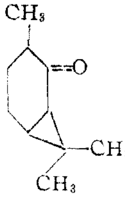


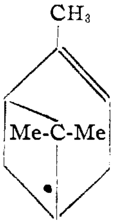
Fig. 2.—Absorption spectra of 3-cholestanone (VIII), A, carone (XI), B, *i*-cholestenone (X), C, and Δ^4-3-cholestenone, D. D is from H. Mohler, *Helv. Chim. Acta*, **20**, 289 (1937).

Spectroscopic evidence of conjugation between a cyclopropane ring and a carbonyl group is not limited to the steroid series. There are a number of terpene molecules which have similar conjugated structures, and we have examined the ultraviolet absorption of one of these substances, carone (XI). This compound exhibits a spectrum extremely similar to that of *i*-cholestenone (Fig. 2). There is very little difference in the spectra of the two substances despite the fact that the cyclopropane ring in the terpene is relatively flexible whereas that in the steroid is locked in very rigidly because it is attached to two other rings. Similarly, the great difference in the bulk of the molecules is not accompanied by a significant difference in the ultraviolet absorption spectra. Apparently the resonance energy due to hyperconjugation is approximately the same in both the steroid and terpene and is influenced but little by the remainder of the molecule.

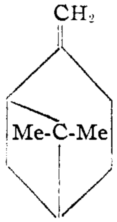


(XI)

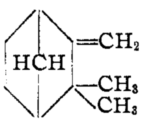
Preliminary data also have been obtained for a number of hydrocarbons, α-pinene (XII), β-pinene (XIII), camphene (XIV) and bicyclo-[2,2,1]-2-heptene (XV), containing a four- or five-membered ring adjacent to an olefinic linkage. In these cases the effect of hyperconjugation (or of strain in the classical point of view) is less than in the cyclopropane compounds and the spectrum should be shifted progressively toward shorter wave lengths. In the compounds examined, the pinenes absorb in the region between the cyclopropane and cyclopentane compounds. The separation between the spectra is rather large, and there are indications that it may be possible to determine ring size in hydrocarbons by examining the spectrum of the compound containing the ring conjugated to an olefinic bond. However, the region farther in the ultraviolet must be investigated, and many more substances must be studied to substantiate this correlation. The necessary work is now in progress.



(XII)



(XIII)



(XIV)

(XV)

Experimental

The ultraviolet absorption spectra were obtained with a Beckmann quartz spectrophotometer. This instrument

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[7] R. B. Woodward, This Journal, **63**, 1123 (1941); **64**, 76 (1942).

uses a hydrogen arc as a source of ultraviolet radiation and a photocell-amplifier combination as a detector. The spectral region covered was from 2230 to 4000Å.

Solutions of known concentration were made by dissolving weighed quantities of solute in ethyl ether in a volumetric flask. At least two different concentrations of solute were used in most cases since a wide range in molecular extinction coefficient was encountered. The solution was poured into one of two matched silica absorption cells and the second cell was filled with solvent. Both cells were then inserted into the spectrophotometer and the intensity of light passing through each of them was recorded. The temperature of the solutions was maintained between 22 and 25°.

Extinction coefficients were calculated from the familiar equation

$$\epsilon = \frac{1}{cd} \log_{10} (I_0/I)$$

where I_0 is the intensity of the light passing through the solvent, I, the intensity of the light passing through the solution, c, the concentration of solute, in moles per liter, and d the thickness of the cell, in centimeters.

The compounds examined were prepared in the following ways.

Cholesteryl Methyl Ether.—The normal ether was prepared by the reaction of cholesteryl *p*-toluenesulfonate with methanol. Repeated crystallization from acetone gave platelets melting at 84–84.5°.

***i*-Cholesteryl Methyl Ether.**—The isomeric methyl ether was prepared from cholesteryl *p*-toluenesulfonate by the method of Stoll.[8] The crude ether was crystallized many times from acetone. Long, thin rods were obtained and melted at 79–79.8°.

***i*-Cholestenone.**—3(α)-Chlorocholestanone-6 was converted into *i*-cholestenone by the method of Windaus and Dalmer.[9] After several crystallizations from methanol, the ketone was sublimed at 75–80° at 10^{-4} mm. Crystallization of the sublimate from methanol gave a product melting at 93–96°. The above compounds were prepared by Dr. Edwin W. Meyer.

3-Cholestanone.—The method used for the preparation of 3-cholestanone was that described by Bruce.[10] The compound was crystallized from dilute ethanol until spectrographically pure. Dr. Irving Allan Kaye prepared this ketone.

Δ^6-*i*-Cholestadiene.—This material melted at 73–73.5° and gave a specific rotation of −60.9°. Its method of preparation and chemical characterization will be described in a publication[11] that will appear shortly.

***d*-5-Carone.**—Dihydrocarvone, b. p. 116–118° (17 mm.), was prepared in 62% yield from carvone by the method of Wallach.[12] It was converted to dihydrocarvone hydrochloride by passing in dry hydrogen chloride until 120% of the theoretical amount had been absorbed. This crude product was converted directly to *d*-5-carone by the method of Richter, Wolff, and Presting.[13] The crude *d*-5-carone was dissolved in 5 to 6 volumes of Skellysolve F (petroleum ether, b. p. 30–60°) and the resulting solution was washed with an excess of neutral potassium permanganate solution (20 g. of potassium permanganate and 25 g. of sodium bicarbonate per liter of solution), heated on the steam-bath to remove the Skellysolve F, and distilled under reduced pressure. The yield was 67%, b. p. 115–116° (15 mm.), d^{26}_4 0.933, $[\alpha]^{25}\text{D}$ +155.6° ($\alpha^{25}\text{D}$ 143.3°, *l*, 1 dm.). The *d*-5-carone was prepared and purified by Dr. R. I. Jackson.

α-Pinene.—A commercial product was distilled and a fraction which boiled at 158.5–159.0° was used.

β-Pinene.—A very pure commercial sample was used without further treatment; b. p. 165.8°.

Camphene.—The product examined was obtained from *i*-borneol by dehydration. It had a melting point of 50°.

Bicyclo-[2,2,1]-2-heptene.—This compound was obtained by treating cyclopentadiene and ethylene by the method described by Joshel and Butz.[14] A sample was redistilled and then recrystallized twice from an ethyl alcohol–water mixture. The product melted at 53°.

The samples of α-pinene, β-pinene, camphene and bicyclo-[2,2,1]-2-heptene were supplied by Dr. H. Pines.

Summary

The absorption spectra of a number of compounds containing a cyclopropane ring adjacent to an olefinic or carbonyl group have been examined and have been interpreted in terms of resonance due to hyperconjugation.

EVANSTON, ILLINOIS RECEIVED JULY 8, 1943

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[8] W. Stoll, *Z. physiol. Chem.*, **207**, 147 (1932).

[9] A. Windaus and O. Dalmer, *Ber.*, **52**, 168 (1919).

[10] W. F. Bruce, "Org. Syntheses," Coll. Vol. II, p. 139.

[11] Unpublished results of B. Riegel, G. P. Hager and B. L. Zenitz.

[12] O. Wallach, *Ann.*, **279**, 377 (1894).

[13] F. Richter, W. Wolff and W. Presting, *Ber.*, **64**, 877 (1931).

[14] L. M. Joshel and L. W. Butz, THIS JOURNAL, **63**, 3350 (1941).

[COMMUNICATION NO. 951 FROM THE KODAK RESEARCH LABORATORIES]

Ascorbic and Iso-ascorbic Acids as Photographic Developing Agents

BY T. H. JAMES

Ascorbic and iso-ascorbic acids represent a type of developing agent chemically quite distinct from the conventional aromatic agents. The developer activity of ascorbic acid was first reported by Maurer and Zapf[1] in 1934. Shortly afterwards, Bills[2] published formulas in which ascorbic acid was the active developing agent, and Rzymkowski[3] and Pavolini[4] published similar formulas for iso-ascorbic acid. Reaction mechanism studies have not been reported.

The present paper is concerned chiefly with establishing the general kinetics of development by ascorbic and iso-ascorbic acids, preliminary to using these substances in an investigation of the electric charge effect[5] in development. They show certain definite advantages over the aromatic agents usually employed for this purpose. The most important advantage is that the oxidation products of the ascorbic acids do not

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[1] K. Maurer and G. Zapf, *Ber.*, **67**, 1239 (1934); *Phot. Ind.*, **33**, 90 (1935).

[2] C. E. Bills, *Science*, **81**, 257 (1935).

[3] J. Rzymkowski, *Phot. Ind.*, **33**, 91 (1935).

[4] T. Pavolini, *Il Corr. Fot.*, **32**, 33 (1935).

[5] T. H. James, *J. Phys. Chem.*, **43**, 701 (1939).