TABLE VII

"WING" CORRECTIONS FOR ABSORPTION AREAS (METHOD III)

$og_e(I_0/I)\nu_{max}$	4	5	6	7	8	9	10	11	12	13	14	15
2.0	29.9	22.9	18.6	15.6	13.4	11.8	10.6	9.4	8.6	7.9	7.3	6.8
1.8	28.7	22.0	17.9	15.0	13.0	11.4	10.2	9.1	8.3	7.6	7.0	6.5
1.6	27.5	21.1	17.2	14.4	12.5	11.0	9.8	8.8	8.0	7.4	6.8	6.3
1.4	26.3	20.2	16.5	13.8	12.0	10.6	9.4	8.5	7.7	7.1	6.6	6.1
1.2	25.0	19.3	15.7	13.2	11.5	10.1	9.0	8.1	7.4	6.8	6.3	5.8
1.0	23.8	18.4	15.0	12.6	11.0	9.7	8.6	7.8	7.1	6.5	6.0	5.6
0.8	22.6	17.5	14.3	12.0	10.5	9.3	8.3	7.5	6.8	6.3	5.8	5.4
0.6	21.4	16.6	13.6	11.5	10.0	8.8	7.9	7.2	6.5	6.0	5.5	5.2
0.4	20.3	15.8	12.9	10.9	9.5	8.4	7.5	6.8	6.2	5.7	5.3	5.0
0.2	19.3	15.0	12.3	10.5	9.1	8.1	7.2	6.5	5.9	5.4	5.0	4.7

$(\nu - \nu_0)/b.$

far as the initial assumptions are valid, the two methods are mathematically equivalent.

Acknowledgments.—The author is indebted to Dr. R. Norman Jones for constant encouragement and discussion throughout the course of the work. He is indebted to Dr. G. Herzberg and Dr. G. B. B. M. Sutherland for much helpful criticism and for suggestions concerning the manuscript. He also wishes to acknowledge helpful discussions with colleagues at the National Research Council.

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The Intensities of Carbonyl Bands in the Infrared Spectra of Steroids[1]

BY R. NORMAN JONES, D. A. RAMSAY, D. S. KEIR AND KONRAD DOBRINER

The application of the methods which are described in the previous paper to the determination of the intensities of C=O stretching bands in steroids is illustrated. Correlations between band intensities and molecular structures have been established on the basis of measurements on 55 steroids. The integrated absorption intensities of different types of carbonyl groups vary by a factor of four but the intensity for a given type of carbonyl group is sensibly constant in different compounds. The ketone intensity does not vary appreciably with the position of the carbonyl group in the steroid nucleus, but is significantly different when the carbonyl group is in a side chain. Systematic changes in intensity are observed when the carbonyl group is conjugated or when a halogen atom is introduced at a vicinal methylene group. In the di- and polycarbonyl compounds investigated the carbonyl intensities were found to be additive within the limits of experimental error. Such measurements permit the number of carbonyl groups in a compound to be determined even where the bands overlap completely, and have been applied to the elucidation of the structure of steroids isolated from natural sources. Integrated absorption intensities are found to give more satisfactory structural correlations than maximal molecular extinction coefficients.

Introduction

The infrared absorption band associated with the stretching vibration of the carbonyl group normally occurs between 1650 and 1800 cm.$^{-1}$. In solution the exact position of the band maximum is influenced by the solvent and by the molecular structure in the immediate environment of the carbonyl group. Characteristic band positions have been established for different types of carbonyl functions in steroid[2] and from observation of the number and position of the carbonyl bands it is often possible to determine both the number and the location of the carbonyl groups present in a steroid molecule.[2,3]

Ambiguity can arise in the interpretation of such bands, as certain different carbonyl groups absorb near the same frequency. For example, the acetates of 3-, 6-, 7-, 11-, 12-, 17- and 20-steroid alcohols absorb between 1735 and 1745 cm.$^{-1}$ in carbon disulfide solution, and from the band position alone it is possible neither to distinguish among these structures nor to determine how many acetate groups are present in the molecule. The carbonyl bands of the 17-ketone and the δ-lactone groups also absorb in the same range and may be obscured in the spectra of acetylated derivatives.

The characterization of certain types of di- and polyketosteroids from the infrared spectrum is also rendered impossible because of the superposition or extensive overlap of the bands. Ketosteroids containing carbonyl groups at position 3-, 6-, 7-, 11-, 12- and 20- all absorb between 1706 and 1720 cm.$^{-1}$ in carbon disulfide solution, and, although two maxima have been resolved in the spectrum of one 3,20-diketosteroid,[3] the other diketosteroids involving these positions give one band only.

A distinction between carbonyl systems giving overlapping bands might be achieved from an analysis of the band intensities, and a general study

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[1] Published as Contribution No. 2566 from the Laboratories of the National Research Council of Canada, and No. XI in the series "Studies in Steroid Metabolism," Presented, in part, at a Symposium on Molecular Spectroscopy held at the Ohio State University, June, 1948, and at the Pittsburgh Conference on Analytical and Applied Spectroscopy, March, 1951. In this paper frequent references are made to the tables in the preceding paper, and this is indicated by an asterisk, *viz.*, for Table I* see page 75 and for Table I see page 83.

[2] R. N. Jones, P. Humphries and K. Dobriner, THIS JOURNAL, **72**, 956 (1950), and earlier publications.

[3] R. N. Jones and K. Dobriner, *Vitamins and Hormones*, **7**, 293 (1949).

of methods for the evaluation of band intensities, was initiated; an account of this work is given in the preceding paper.[4]

Definitions

The quantity selected as a criterion of band intensity in the present work is the *true integrated absorption intensity* (A) given by

$$A = \frac{1}{cl}\int \log_e \left(\frac{I_0}{I}\right)_\nu \mathrm{d}\nu \qquad (1)$$

where c is the concentration of the solute in gram moles per liter, l is the path length in cm., I_ν and $I_{0\nu}$ the intensities of the incident and transmitted *monochromatic* radiation of frequency ν.

Because the slit widths presently employed in infrared spectrophotometry are of the same order as the widths of the absorption bands, the absorption curve observed experimentally differs from the true absorption curve. The quantity derived from the area under the experimental curve is the *apparent integrated absorption intensity* (B) defined by

$$B = \frac{1}{cl}\int \log_e \left(\frac{T_0}{T}\right)_\nu \mathrm{d}\nu \qquad (2)$$

where T_ν and $T_{0\nu}$ are the intensities of the incident and transmitted radiation *when the spectrometer is set at frequency* ν *and the radiation is not assumed to be monochromatic.*

The peak intensities of the true and apparent bands are designated by $\log_e (I_0/I)\nu_{\max}$ and $\log_e (T_0/T)\nu_{\max}$, respectively. $\Delta\nu^t_{1/2}$ and $\Delta\nu^a_{1/2}$ denote the true and apparent half-band widths, *i.e.*, the intervals between the frequencies at which $\log_e (I_0/I)_\nu$ and $\log_e (T_0/T)_\nu$ are equal to half their maximal values. It is convenient to denote $\Delta\nu^t_{1/2}$ by $2b$. The effective slit width, s, is given by equation (8) of the preceding paper.[4] Relations between $\log_e(I_0/I)\nu_{\max}$, $\log_e(T_0/T)\nu_{\max}$, $\Delta\nu^t_{1/2}$, $\Delta\nu^a_{1/2}$ and s are given in Tables I* and II* (see footnote 1).

The true and apparent maximal molecular extinction coefficients are defined as

$$E^t = \frac{1}{cl}\log_{10}\left(\frac{I_0}{I}\right)_{\nu_{\max}} \text{ and } E^a = \frac{1}{cl}\log_{10}\left(\frac{T_0}{T}\right)_{\nu_{\max}} \qquad (3)$$

It will be shown that under the experimental conditions described below, the differences between A and B are small ($\sim$2%) but E^t may exceed E^a by as much as 20%.

Experimental

The carbonyl bands of 55 steroids were measured using a Perkin-Elmer Model 12C infrared spectrometer with a 7-cycle G.M. type amplifier and Brown Elektronik pen recorder. A calcium fluoride prism was used in most of the experiments although a sodium chloride prism was employed in some of the earlier measurements.

The absorption cell was of conventional type, consisting of two rock salt plates separated by a brass spacer of approximately 1-mm. thickness and held together by Benolite cement. The spacer was fitted with two tightly fitting tapered stoppers. The cell thickness was measured at several positions by focusing a traveling microscope on each of the inside surfaces of the cell in turn. In this manner the thickness was determined to ±0.01 mm. and the cell was found to be uniform in thickness to within these limits. The total volume of the cell was 250 cu. mm.

Solutions of steroids were prepared by weighing 0.5–2.0 mg. in a platinum boat on a microbalance and dissolving in a weighed quantity (400–1200 mg.) of carbon disulfide or carbon tetrachloride. The total weight of steroid commonly required for measurement at three or four concentrations was 3–6 mg.

The absorption curves were measured over a frequency range of approximately 50 cm.$^{-1}$ on either side of the band center and the solvent background curve was determined immediately beforehand, using the same cell. A glass shutter was used to determine the energy zeros; the amount of scattered energy was estimated as less than 0.5%. The curves were measured at frequency intervals of 2 cm.$^{-1}$, the atmospheric water bands being used for calibration purposes. During the measurements a constant stream of dry nitrogen was swept through the spectrometer to maintain the intensity of the water vapor absorption bands in the background below a maximum of 20% absorption.

Calculation of Results

A. **Monocarbonyl Compounds.**—The true integrated absorption intensities of the single carbonyl bands were calculated by each of the three methods discussed in the preceding paper.[4] These methods assume that the shape of the true absorption band may be represented by a Lorentz curve, *viz.*

$$\log_e \left(\frac{I_0}{I}\right)_\nu = \frac{a}{(\nu - \nu_0)^2 + b^2} \qquad (4)$$

where a and b are constants and v_0 the frequency of the band center.

Method I. **The Method of Direct Integration.**—The true integrated absorption intensity, A, is obtained from the apparent absorption curve by means of the equation

$$A = \frac{K}{cl} \times \log_e \left(\frac{T_0}{T}\right)_{\nu_{\max}} \times \Delta\nu^a_{1/2} \qquad (5)$$

where K is a constant dependent on the resolving power and to a lesser extent on the peak intensity of the band (see Table III*).[1]

EXAMPLE 1. Etiocholanol-3α-one-17 in CCl_4 solution: Prism NaCl; slit width, s = 0.040 mm. = 7.2 cm.$^{-1}$ (from equation (8) of the preceding paper); cell thickness, l = 0.104 cm.

Soln.	Concn., moles per liter, $\times 10^{-3}$	$\log_e \left(\frac{T_0}{T}\right)_{\nu\max}$	$\Delta^a_{1/2}$ (cm.$^{-1}$)	K from Table III*	A from equation (5) mole.$^{-1}$ liter. cm.$^{-2}$ $\times 10^4$
A	10.58	1.34	14.5	1.55	2.74
B	7.21	0.93	14.3	1.51	2.68
C	3.78	0.52	14.7	1.47	2.86
D	2.08	0.29	14.8	1.45	2.88

Mean value of A = 2.80 × 10^4 moles.$^{-1}$ liter. cm.$^{-2}$ = 2.80 intensity units.

The numerical values of the intensities lie between 1 × 10^4 and 9 × 10^4 and it is convenient to designate 1 × 10^4 mole.$^{-1}$ liter. cm.$^{-2}$ as one *intensity unit*.[5]

Method II. **The Method of Wilson and Wells.**—In this method the apparent integrated absorption intensity B, is determined at a series of concentrations or path lengths. Extrapolation of B to zero concentration or path length gives the true integrated absorption intensity A. If the true shape of the absorption band is given by a Lorentz curve and B is plotted against $\log_e (T_0/T)\nu_{\max}$ the extrapolation is linear with a slope $A\theta$ dependent on the slit width used. Values of θ for various values of $s/\Delta\nu^t_{1/2}$ are given in Table IV*.

The absorption curve is plotted as $\log_e (T_0/T)\nu$ against ν in cm.$^{-1}$ (Fig. 1) and the area under the curve determined for a frequency interval $\nu - \nu_0$ on both sides of the band center. This area may be evaluated by several methods, *viz.*, by planimeter, by counting squares, by cutting out the band and weighing it or, most conveniently, by the use of Simpson's rule.[6] A correction is applied for the area under the "wings" of the absorption band. To do this the quantity $(\nu - \nu_0)/b$ is evaluated[7] and the correction obtained from Table V*, expressed as a percentage of the measured band area.

The apparent integrated absorption intensity B is calculated from equation (2) and plotted against $\log_e (T_0/T)\nu_{\max}$. The best straight line with intercept A and slope $A\theta$ is found by trial and error, θ being obtained from Table IV*.

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(4) D. A. Ramsay, THIS JOURNAL, **74**, 72 (1952).

(5) This differs from the unit used in a preliminary account of this work reported in ref. 3. For conversion, the data given in Tables IV and V of ref. 3 should be divided by 3 × 10^{10}.

(6) See "Handbook of Chemistry and Physics" 31st edition, published by Chemical Rubber Publishing Co., Cleveland, Ohio, 1949, p. 288. In applying this rule the curve was divided into sections of 2-cm. $^{-1}$ intervals.

(7) Note that in this expression b = half the *true* half intensity band width. This may be derived from the *apparent* half intensity band width by the use of Table II.*

EXAMPLE 2.—Etiocholanol-3α-one-17 in CCl_4 solution:

Soln. (see ex. 1)	$\int_{1710}^{1776} \log_e \left(\frac{T_0}{T}\right)_\nu d\nu$ (cm.$^{-1}$)	Wing correction: $\Delta\nu^a_{1/2}$ (cm.$^{-1}$)	$\frac{s}{\Delta\nu^a_{1/2}}$	$\Delta\nu^t_{1/2}$ (cm.$^{-1}$) from Table II*	$\frac{\nu - \nu_0}{b}$	Correction from Table V*, %	Total area (cm.$^{-1}$)	Apparent integrated absorption intensity B mole.$^{-1}$ liter. cm.$^{-2}$ × 10^4
A	24.2	14.5	0.50	11.5	5.7	13	27.3	2.49
B	16.1	14.3	.50	11.1	5.9	12	18.0	2.41
C	9.8	14.7	.49	11.3	5.8	12	11.0	2.81
D	5.4	14.8	.49	11.3	5.8	12	6.0	2.78

s = 7.2 cm.$^{-1}$ and the mean value of $s/\Delta\nu^a_{1/2}$ = 0.64, hence from Table IV, θ = −0.03. The best straight line (Fig. 2) with intercept A and slope $A\theta$ has an intercept $A = 2.68 \times 10^4$ mole.$^{-1}$ liter. cm.$^{-2}$ and a slope $A\theta = 2.68 \times (-0.03) = -0.08 \times 10^4$ mole.$^{-1}$ liter. cm.$^{-2}$. Note that the method of least squares gives an intercept equal to 2.90×10^4 mole.$^{-1}$ liter. cm.$^{-2}$.

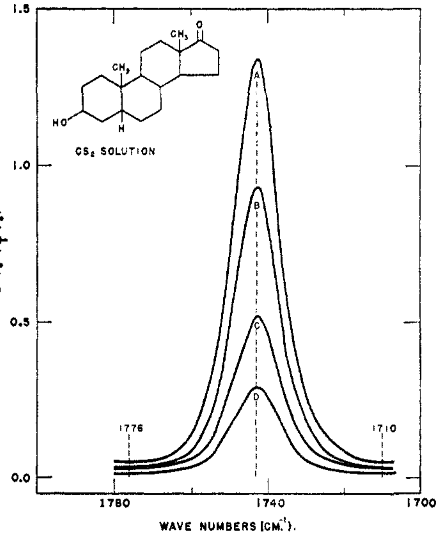

Fig. 1.— C=O stretching band of etiocholanol-3α-one-17 in CS_2 solution. Concentrations in moles per liter × 10^{-3}: A, 10.58; B, 7.21; C, 3.78; D, 2.08. Limits of integration 1710–1776 cm.$^{-1}$; band center(ν_0) at 1743 cm.$^{-1}$.

Method III. The Method of Absorption Areas.—The experimental absorption band is plotted as fractional absorption, $(T_0 - T)/T_0$, against ν in cm.$^{-1}$ and the area under the band for a frequency interval $\nu - \nu_0$ on both sides of the band center determined.[8] A correction is applied for the area under the "wings" of the absorption band (see Table VII*) and the total area A' under the absorption band computed.

The true integrated absorption intensity A is then obtained from the equation

$$A = \phi \frac{A'}{cl} \qquad (6)$$

where ϕ is a function of $\log_e (I_0/I)\nu_{max}$ and is obtained from Table VI*.

EXAMPLE 3.—Etiocholanol-3α-one-17 in CCl_4 solution:

Soln. (see ex. 1)	$\int_{1710}^{1776} \left(\frac{T_0 - T}{T}\right)_\nu d\nu$ (cm.$^{-1}$)	Wing correction: $\frac{\nu - \nu_0}{b}$ from Ex. 2	$\log_e \left(\frac{T_0}{T}\right)_{\nu max}$	$\log_e \left(\frac{I_0}{I}\right)_{\nu max}$ from Table I*	Correction from Table VII,* %	Total area A' (cm.$^{-1}$)	ϕ from Table VI*	$A = \phi A'/cl$, mole.$^{-1}$ liter. cm.$^{-2}$, × 10^4
A	17.1	5.7	1.34	1.66	19	20.3	1.405	2.59
B	12.3	5.9	0.93	1.15	16	14.3	1.284	2.45
C	8.5	5.8	.52	0.64	14	9.7	1.164	2.87
D	5.0	5.8	.29	0.35	13	5.6	1.087	2.81

Mean value of $A = 2.68 \times 10^4$ mole.$^{-1}$ liter. cm.$^{-2}$ = 2.68 intensity units.

B. **Polycarbonyl Compounds.**—The procedures described above are strictly applicable only to single isolated bands such as the carbonyl stretching bands of monocarbonyl compounds. They may also be applied in good approximation to systems in which two or more bands are coincident and symmetrical, *e.g.*, di- and triacyl acetates.

For partially overlapping band systems, Method I cannot be used. Methods II and III are still valid, but the slopes of the extrapolations cannot be calculated. Moreover attempts to fit extrapolation lines by the method of least squares[9] can result in considerable errors unless a large number of observations are carried out (see Fig. 2).

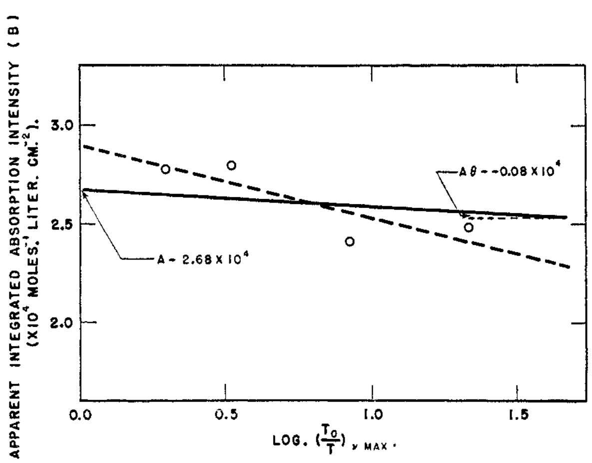

Fig. 2.—Etiocholanol-3α-one-17: —, extrapolation curve for method II; - - -, extrapolation curve for method of least squares.

In the examples of single absorption bands which have been studied (Table I) the extrapolation slope in Method II is quite small, and the true integrated absorption intensities exceed the mean values for the corresponding apparent integrated intensities by only 2%. The uncertainty in the evaluation of the extrapolation slope for a polycarbonyl band system is likely to exceed this considerably and it is sufficient to estimate the true integrated absorption intensity by adding 2% to the mean of the values obtained by method II for the apparent integrated intensity.

Of greater numerical significance than the finite slit factor is the wing correction. In initial measurements on dicarbonyl compounds the wing correction was estimated by assuming values for the true half-band widths of the component bands and for the positions of the component maxima. Separate wing corrections were then computed for each half

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[8] If the spectrum is determined on a double beam spectrometer with a linear wave number scale, this area may be obtained conveniently by cutting out the area under the curve from the experimental chart and weighing it.

[9] See ref. 6, p. 278.

of each component band, and the mean for the four values so obtained was applied. If the areas were measured to 40 cm.$^{-1}$ from the band centers (Fig. 3) the wing corrections so evaluated were all found to lie close to 10%. In subsequent work therefore the latter procedure was adopted and a wing correction of 10% applied.

EXAMPLE 4.—Estradiol diacetate in CS_2 solution: absorption curve, Fig. 3; prism CaF_2; slit width (s) = 0.160 mm. = 4.1 cm.$^{-1}$ (from equation (8) of preceding paper); cell thickness 0.099 cm.

Soln.	Concentration (moles per liter) × 10^{-3}	$\int_{1696}^{1810} \log_e \left(\frac{T_0}{T}\right)_\nu d\nu$ (cm.$^{-1}$)	Wing correction, %	Corrected area (cm.$^{-1}$)	Apparent integrated absorption intensity (B) (mole.$^{-1}$ liter. cm.$^{-2}$) × 10^4
A	10.86	55.8	10	61.4	5.71
B	9.05	48.4	10	53.2	5.94
C	6.32	35.1	10	38.6	6.17
				Mean	5.94

The mean value of B is increased by 2% to give 5.94 × 1.02 = 6.06 intensity units for the true integrated absorption intensity (A).

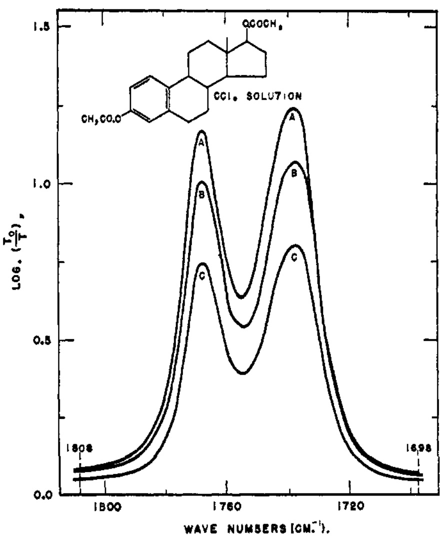


Fig. 3.— C=O stretching bands of estradiol diacetate. The maximum at 1736 cm.$^{-1}$ is due to the acyl ester carbonyl group and that at 1768 cm.$^{-1}$ to the phenolic ester group. Concentrations in moles per liter × 10^{-3}: A, 10.87; B, 9.05; C, 6.32.

Results

The true integrated absorption intensities of the carbonyl stretching band for a selection of steroid monoketones and monoacetates have been evaluated by each of the methods described above (Table I). The intensities as evaluated by methods II and III agree to within 2% (~0.06 unit). The values derived by method I in most cases agree with these to within 5% (~0.15 unit), though in a few cases differences up to 10% are observed. The averaged values for each compound are given in column 7 of Table I and representative values for each type of carbonyl group in Table II. Figures are also given in Table I for true and apparent maximal molecular extinction coefficients, the true and apparent band widths at half maximal intensity and for the mean values of the apparent integrated absorption intensities as determined by method II. The results for a series of measurements on some di- and polycarbonyl compounds are listed in Table III.

TABLE I

INTEGRATED ABSORPTION INTENSITIES OF CARBONYL STRETCHING VIBRATIONS IN STEROID MONOKETONES AND MONOACETATES

Compound[a]	Source[b]	Integrated absorption intensity[c]: Method I	Method II A	Method II B	Method III	Mean	ν_{max}, cm.$^{-1}$	s, cm.$^{-1}$	E^t_{max}	E^a_{max}	$\Delta\nu^t_{1/2}$ cm.$^{-1}$	$\Delta\nu^a_{1/2}$ cm.$^{-1}$
3-Ketone												
Androstanone-3	11	2.60	2.65	(2.62)	2.65	2.63	1715	5.0	540	500	13.2	14.6
Androstanol-17β-one-3 (NaCl prism)	11	2.40	2.44	(2.40)	2.40	2.41	1720	6.9	485	420	13.5	16.2
Androstanol-17β-one-3 (CaF_2 prism)	11	2.43	2.35	(2.33)	2.40	2.39	1720	4.4	490	460	13.2	14.4
Cholestanone-3*	4	2.63	2.63	(2.59)	2.60	2.62	1718	7.4	505	440	14.3	17.4
7-Ketone												
Pregnanone-7	10	2.07	2.20	(2.13)	2.23	2.17	1710	5.1	535	470	10.6	12.2
Cholestanone-7	5	2.07	2.17	(2.13)	2.20	2.15	1710	3.5	550	515	10.3	11.1
12-Ketone												
Pregnanone-12	10	2.23	2.27	(2.16)	2.30	2.27	1705	5.1	670	560	9.2	11.0
16-Ketone												
$\Delta^{1,3,5;10,6,8}$-Estrapentaene-one-16	14	2.83	2.70	(2.60)	2.70	2.74	1749	4.1	735	670	10.6	11.9
17-Ketone												
Androstanol-3α-one-17 (androsterone)	8	2.57	2.50	(2.42)	2.50	2.52	1744	7.2	670	530	10.7	13.9
Etiocholanol-3α-one-17*	9	2.80	2.68	(2.62)	2.68	2.72	1743	7.2	675	545	11.2	14.6
Etiocholanol-3β-one-17	9	2.90	2.77	(2.70)	2.77	2.81	1742	5.7	690	595	11.6	13.5
Δ^5-Androstenol-3β-one-17* (dehydroisoandrosterone)	11	2.57	2.67	(2.60)	2.67	2.64	1744	7.2	740	570	9.2	13.1
α-Equilenone-17	14	2.65	2.50	(2.44)	2.47	2.54	1741	4.1	680	620	10.8	12.0
3-Methoxy-*dl*-equilenin	6	3.03	2.87	(2.84)	2.83	2.91	1744	4.1	660	620	12.6	13.6
3-Methoxy-*dl*-isoequilenin	6	2.77	2.67	(2.64)	2.63	2.69	1741	4.1	650	610	11.6	12.8
20-Ketone												
Pregnanol-3α-one-20*	8	1.70	1.77	(1.72)	1.77	1.75	1707	5.0	595	485	7.9	10.2
Δ^5-Pregnenol-3β-one-20*	12	1.77	1.87	(1.85)	1.87	1.84	1707	6.7	460	380	10.7	13.9

TABLE I (*Continued*)

Compound[a]	Source[b]	Integrated absorption intensity[c]: Method I	Integrated absorption intensity[c]: Method II A	Integrated absorption intensity[c]: Method II B	Integrated absorption intensity[c]: Method III	Integrated absorption intensity[c]: Mean	ν_{max}, cm.$^{-1}$	s, cm.$^{-1}$	E^t_{max}	E^a_{mxa}	$\Delta\nu^t_{1/2}$ cm.$^{-1}$	$\Delta\nu^a_{1/2}$ cm.$^{-1}$
β,γ-Unsaturated ketone												
Δ^5-Cholestenone-3	4	2.80	2.90	(2.90)	2.93	2.88	1721	5.2	525	490	14.6	16.1
$\Delta^{1,3,5:10,6,8,14}$-3-Methoxyestrahexaene-one-17	6	3.23	2.97	(2.82)	2.92	3.04	1752	5.7	540	500	15.8	17.5
α,β-Unsaturated ketone												
Δ^4-Androstenone-3	11	3.60	3.70	(3.61)	3.70	3.67	1678	3.5	730	700	13.6	14.3
Δ^4-Androstenol-17β-one-3* (testosterone)	12	4.07	4.00	(3.99)	4.00	4.02	1678	6.9	610	560	18.5	20.5
Δ^4-17-Methylandrostenol-17β-one-3 (methyltestosterone)	11	3.17	3.47	(3.37)	3.53	3.39	1678	5.4	765	670	11.4	13.2
Δ^4-17-Vinylandrostenol-17β-one-3	11	3.27	3.60	(3.47)	3.67	3.51	1678	5.2	700	630	12.4	13.9
$\Delta^{1,3,5;10,6,8,14}$-Estrahexaene-one-17	6	3.70	3.63	(3.36)	3.67	3.67	1715	5.5	1086	880	9.0	11.2
$\Delta^{1,4}$-Cholestadiene-one-3	2, 14	3.70	3.70	(3.58)	3.70	3.70	1666	4.5	1335	1130	7.5	9.2
$\Delta^{4,6}$-Cholestadiene-one-3	8	4.13	4.10	(4.07)	4.10	4.11	1666	5.3	615	590	18.6	19.6
Halogenated-3-ketone												
2-Bromoandrostanol-17-β-one-3	2	1.93	1.87	(1.85)	1.90	1.90	1733	5.1	360	340	15.3	16.7
2-Bromocholestanone-3	2, 14	1.80	1.90	(1.84)	1.93	1.88	1733	3.6	360	350	13.4	14.2
2-Iodocholestanone-3	1	2.00	1.96	(1.96)	2.00	1.99	1724	3.4	335	325	16.7	17.3
4-Bromocoprostanone-3	2	1.83	1.90	(1.78)	1.87	1.87	1723	4.9	360	340	14.2	15.5
2,2-Dibromocholestanone-3	2	1.73	1.83	(1.82)	1.83	1.80	1735	4.9	350	325	13.6	15.0
2,4-Dibromocholestanone-3	2, 14	1.13	1.23	(1.25)	1.23	1.20	1756	3.4	340	315	9.2	10.2
Δ^4-2-Bromocholestanone-3	2	2.70	2.73	(2.71)	2.73	2.72	1691	5.1	465	440	15.5	16.8
Acyl acetate												
Δ^5-17-Ethynyl-androstenediol-3β-17β-acetate-3	5	3.10	3.17	(3.16)	3.17	3.15	1734	3.4	645	620	13.2	14.0
Cholestanol-3β-acetate	8	3.13	3.03	(2.98)	3.03	3.06	1732	7.2	630	540	13.4	16.3
Cholestanol-3β-acetate*	8	3.27	3.07	(3.02)	3.07	3.14	1733	7.2	585	520	15.6	17.9
Ergostanyl acetate	4	3.27	3.27	(3.24)	3.27	3.27	1732	3.4	690	655	10.7	11.4
Lumistanyl acetate	4	3.47	3.37	(3.33)	3.33	3.39	1736	3.4	860	810	11.1	11.8
Δ^5-Androstenediol-3β-17β-acetate-17	9	3.53	3.37	(3.32)	3.33	3.41	1737	3.4	575	560	17.0	17.6
Carbomethoxy ester												
3α-Hydroxycholanic acid methyl ester	3	3.15	3.20	(3.18)	3.19	3.18	1742	3.1	580	560	15.1	15.6
3α,12α-Dihydroxycholanic acid methyl ester	3	2.98	3.14	(3.12)	3.15	3.09	1742	3.1	520	505	15.9	16.4

[a] An asterisk after the name of the compound indicates carbon tetrachloride solvent: in all other cases the solvent was carbon disulfide. The configuration of the 17-hydroxyl group is designated β when it is the same as in testosterone. [b] (1) C. Djerassi, Syntex, S.A., Mexico City, Mexico; (2) C. Djerassi and C. R. Scholz, Ciba Pharmaceutical Products, Inc., Summit, N. J.; (3) T. F. Gallagher, Sloan-Kettering Inst., New York, N. Y.; (4) Sir I. M. Heilbron, Imperial College, London, England; (5) J. R. Jamieson and E. Lozinski, Charles E. Frosst and Co., Montreal, P. Q.; (6) W. S. Johnson, University of Wisconsin, Madison, Wisconsin; (7) O. Kamm, Parke, Davis and Co., Detroit, Mich.; (8) S. Lieberman, Sloan-Kettering Inst., New York, N. Y.; (9) R. E. Marker, Pennsylvania State College, State College, Pa.; (10) T. Reichstein, University, Basel, Switzerland; (11) C. R. Scholz, Ciba Pharmaceutical Products, Inc., Summit, N. J.; (12) E. Schwenk, The Schering Corp., Bloomfield, N. J.; (13) R. Turner, Harvard University, Cambridge, Mass.; (14) A. L. Wilds, University of Wisconsin, Madison, Wisconsin. [c] Intensity units. 1 intensity unit = 10^4 moles^{-1}. liter. cm.$^{-2}$. The figures in parentheses are the mean values of the *apparent* integrated absorption intensities determined in Method II; the mean values for the *true* integrated absorption intensities as determined by all three methods are given in column 7.

Discussion of Methods and Accuracy

The accuracy of the above intensity measurements depends on several factors, *viz.*, (i) frequency and intensity reproducibility of the spectrometer, (ii) amount of scattered light present, (iii) weighing errors in the preparation of the solutions, (iv) evaporation losses on transfer and on standing, (v) uniformity of the cell thickness and the accuracy of its measurement, (vi) purity of the sample, (vii) assumptions inherent in the methods used.

Intensities could be reproduced with an accuracy of ± 0.5% absorption and the amount of scattered light in the region of the carbonyl bands using a glass shutter was less than 0.5%. The effect of these factors on the accuracy of measurement of band areas depends on the peak intensity of the band, being greater for weak bands than for strong bands. The errors in weighing for both solute and solvent may readily be kept < 0.5% but loss of solvent by evaporation is a serious source of error particularly when volatile solvents are used and the quantities involved are small. These losses may be minimized by using well fitted stoppers and by transferring the solutions under a hood in an atmosphere of solvent vapor.

By using a cell of thickness 1 mm. or greater the errors due to the non-uniformity of the cell and measurement of its thickness may be kept below 1%. The purity of the samples used in the present investigations were probably better than 98–99%. These latter two factors only affect the absolute magnitudes of the experimental intensities obtained.

In the calculation of "true" quantities from "apparent" quantities additional errors due to the assumptions inherent in the methods are involved. Nevertheless true maximal molecular extinction coefficients calculated from measurements on different solutions and at different slit widths agree to ± 3% and corresponding measurements on true half-intensity band width agreed to ± 1–2%. The latter are not dependent on weighing errors and evaporation losses.

TABLE II

AVERAGED VALUES FOR INTEGRATED ABSORPTION INTENSITIES OF CARBONYL STRETCHING BANDS IN STEROIDS

Carbonyl type	True integrated absorption intensity (units)	Number of compounds examined	ν_{max},[a] cm.$^{-1}$
Saturated ketones			
3-Ketone	2.55	3	1715–1719
7-Ketone	2.16	2	1715–1719
11-Ketone[b]	2.21	1	1710–1716
12-Ketone	2.27	1	1706–1710
16-Ketone	2.74	1	1749
17-Ketone	2.69	7	1742–1745
20-Ketone	1.79	2	1706–1710
β,γ-Unsaturated ketones			
Δ^5-3-Ketone	2.88	1	1715–1719
Δ^{14}-17-Ketone	3.04	1	1754
α,β-Unsaturated ketones			
Δ^4-3-Ketone	3.65	4	1674–1677
Δ^{15}-17-Ketone	3.67	1	1716
Di-unsaturated ketones			
$\Delta^{1,4}$-Diene-one-3	3.70	1	1663–1666
$\Delta^{4,6}$-Diene-one-3	4.11	1	1666–1669
Halogenated ketones			
2-Bromo-3-ketone	1.89	2	1735
2-Iodo-3-ketone	1.99	1	1724
4-Bromo-3-ketone	1.87	1	1735
2,2-Dibromo-3-ketone	1.80	1	1737
2,4-Dibromo-3-ketone	1.20	2	1756–1758
Δ^4-2-Bromo-3-ketone	2.72	1	1697
Ester carbonyl			
Acyl acetate	3.24	6	1735–1742
Phenolic acetate[b]	2.75	2	1764–1767
Cholanate methyl ester	3.13	2	1737–1742

[a] These values based on measurements of a larger number of compounds (see ref. 2). [b] These intensities based on subtraction from measurements on di- and polycarbonyl compounds.

The fact that the true integrated absorption intensities as calculated by methods II and III for 39 steroids all agreed to within 2% affords good evidence for the equivalence of these methods despite differences in "wing" corrections and extrapolation slopes. These methods are probably more accurate than method I since they depend on measurements over the whole band whereas the latter depends only on measurements at peak and half-peak intensity.

Discussion of Results

Monocarbonyl Compounds.—In reviewing these results it is of interest to consider both the range and the absolute magnitudes of the integrated absorption intensities associated with various types of carbonyl groups as well as effects of molecular structure on the intensity.

The intensities of all the monocarbonyl compounds lie between 1.20 and 4.11 units,[10] the limits for the simple saturated ketones being 1.75 to 2.91. The measurements on the individual compounds in Table I suggest that the intensities for each type of carbonyl function fall within narrow ranges, and specific values have been assigned to each type of carbonyl group in Table II. The number of compounds of any given carbonyl type included in this survey is hardly sufficient to permit limits to be set to these intensity ranges; however, the seven 17-ketones examined all gave intensities between 2.52 and 2.91 and the limits for four Δ^4-3-ketones were 3.39 and 4.02. It is considered that individual variations from the intensity values for different groups given in Table II are not likely to exceed 10% (~0.3 intensity unit). The non-conjugated ketones in which the carbonyl group is in a ring do not show any significant variation in intensity with the position of the carbonyl group. In the 20-ketones however where the carbonyl group is in the side chain the intensity is appreciably lower.

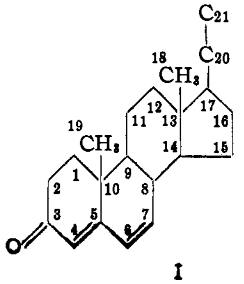
TABLE III

INTENSITIES OF CARBONYL BANDS IN STEROID POLYKETONES AND POLYESTERS

Compounds[a]	Source[b]	True integrated absorption intensity[c] Experimental (units)	Calcd. from Table VIII (units)	Difference, %
Androstanedione-3,17	8	5.19	5.24	1.0
Allopregnanedione-3,20	7	4.45	4.34	2.5
Δ^4-Pregnenedione-3,20 (progesterone)	12	5.90	5.44	7.8
Pregnanetrione-3,11,20	3, 13	6.55	..	...
Pregnanetrione-3,12,20	14	6.93	6.61	4.6
Pregnanediol-3α,20β-diacetate	9	6.21	6.48	4.3
Allopregnanetriol-3α,16,20-triacetate	9	9.05	9.72	7.4
Estradiol diacetate	8	6.06	..	...
Estrone acetate	8	5.40	..	...
Androstanol-3α-one-17 acetate (androsterone acetate)	8	5.66	5.93	4.8
Δ^5-Androstenol-3β-one-17-acetate (dehydroisoandrosterone acetate)	8	5.97	5.93	0.7
3α-Acetoxycholanic acid methyl ester	3	6.21	6.37	2.6
Hecogenin acetate[d]	9	5.71	5.51	3.5
Kammogenin acetate[e]	9	8.47	8.75	3.3

[a,b,c] See corresponding footnotes to Table I. [d] 3-Acetoxy-12-ketone. [e] 2,3-Diacetoxy-12-ketone.

Conjugation of the carbonyl group with an ethylenic double bond raises the intensity of the carbonyl band considerably; the intensity of the 3-ketone band is increased from 2.55 to 3.65 units on introduction of the Δ^4-bond, and the introduction of the Δ^{15}-bond increases the 17-ketone intensity from 2.69 to 3.67 units. The addition of a second



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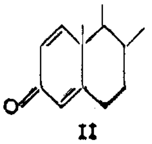

II

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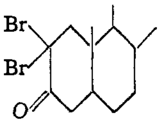
[10] R. E. Richards and W. R. Burton (*Trans. Faraday Soc.*, **45**, 874 (1949)) have made intensity area measurements on a variety of carbonyl compounds. Although their results are not directly comparable with ours, they observe also that the intensities of the weakest and the strongest absorbing groups differ by a factor of about four.

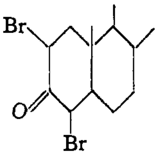
ethylenic double bond in linear conjugation in the $\Delta^{4,6}$-diene-one-3 system (I) produces an additional enhancement of intensity from 3.65 to 4.11 units but the introduction of a second double bond in the cross-conjugated $\Delta^{1,4}$-diene-one-3 (II) system has only a very slight effect on the band intensity (see also end of Col. 2.

The carbonyl group of the acetate esters has a higher intensity than the saturated ketone group, and in Table III a value of 3.23 has been assigned on the basis of measurements on eleven acyl acetates. The intensity of the 3-phenolic acetate is appreciably less.

Systematic intensity changes are induced by bromination of the 2 and 4 methylene groups of 3-ketosteroids. The introduction of one bromine atom at either position 2 or 4 lowers the intensity from 2.55 to 1.87–1.89 units. In the 2,2-dibromo-3-ketones (III) the second bromine atom has a very small effect (1.80 units) but in the 2,4-dibromo-3-ketones (IV) the intensity is further depressed to 1.20 units. The intensity of the Δ^4-3-ketone band is also diminished from 3.65 to 2.72 units by bromination at position 2.



III



IV

These intensity effects of vicinal bromination parallel displacements of the band positions which have been discussed previously[2]; diminution in intensity accompanies displacement of the band maximum to a higher frequency. The carbonyl band intensity in 2-iodocholestanone-3 is 1.99 units which suggests that the effect of vicinal iodination is similar in kind but quantitatively smaller than the effect of vicinal bromination.

Di- and Polycarbonyl Compounds.—With certain well defined exceptions[2,3] the positions of the absorption maxima of the carbonyl stretching bands are not displaced when two or more carbonyl groups occur in the same molecule, and it is of interest to inquire whether the intensities show the same additive property.

The experimentally determined intensities reported in column 3 of Table III may be compared with the figures in column 4 which have been computed by adding the intensities for the separate carbonyl groups in Table II. In all cases there is agreement to within 10% which is the estimated variation for a given carbonyl type from the figures given in Table II.

No intensity measurements have yet been made on di- and polycarbonyl compounds in which the positions of the carbonyl maxima are displaced as a result of interaction effects.[2,3]

Molecular Extinction Coefficients and Band Widths.—The true (E^t_{max}) and apparent (E^a_{max}) maximal molecular extinction coefficients for the monocarbonyl compounds are listed in Table I. In earlier measurements with a sodium chloride prism a slit width of approximately 7 cm.$^{-1}$ was employed, and the apparent maximal extinction coefficients were from 10 to 20% below the true values. With a calcium fluoride prism slits can be reduced to 3–5 cm.$^{-1}$ and the difference between the true and apparent extinction coefficients to 3–10%.

The dependence of the apparent maximal extinction coefficient on the slit width is well illustrated by measurements on androstanol-17β-one-3 made at slit widths of 6.9 cm.$^{-1}$ and 4.4 cm.$^{-1}$ using NaCl and CaF_2 prisms, respectively, (Table I). The values obtained for E^t_{max}, 485 and 490, agree well, but for E^a_{max} the values 420 (NaCl) and 465 (CaF_2) were obtained. The apparent half band widths observed were 16.2 and 14.4 cm.$^{-1}$, respectively, compared with 13.5 and 13.2 cm.$^{-1}$ for the true half-band widths. On the other hand, the effect of slit width on the integrated absorption intensity is much smaller. The apparent integrated absorption intensity mean values are 2.40 (NaCl) and 2.22 (CaF_2) intensity units and the corresponding true integrated absorption intensities 2.44 and 2.35 units.

"Molecular extinction coefficients" have been reported by several investigators for infrared absorption bands.[11–14] Since these measurements are uncorrected for finite slit widths, the above results suggest that they may be as much as 20% below the true values. Such measurements can still be useful as guides to the general order of the intensity but the values obtained by various investigators on different instruments cannot be expected to be consistent.[15] These conclusions are in substantial agreement with the results reported by Philpotts, Thain and Smith.[16]

The true maximal molecular extinction coefficients do not show the same structural correlations as do the true integrated absorption intensities (Fig. 4). Thus the saturated ring ketones, 20-ketones, unsaturated ring ketones and acetates which display characteristic ranges for the integrated absorption intensities give overlapping values for the molecular extinction coefficients. The halogenated 3-ketones which give low values for the true integrated absorption intensities also give low values for the true maximal molecular extinction coefficients.

The true integrated absorption intensity of a band is a better criterion of band intensity than the true maximal molecular extinction coefficient as it takes cognizance of variations in band width as well as in band height. This conclusion is in agreement with expectations from theoretical considerations.[17]

A striking example of reciprocal variations in band height and band width is afforded by comparison of the $\Delta^{4,6}$-diene-one-3 (I) and $\Delta^{1,4}$-diene-one-

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(11) F. W. Rose, Jr., *J. Research Natl. Bur. Standards*, **20**, 129 (1938).

(12) J. A. Anderson, Jr., and W. D. Seyfried, *Anal. Chem.*, **20**, 998 (1948).

(13) R. R. Hampton and J. E. Newell, *ibid.*, **21**, 914 (1949).

(14) L. Marion, D. A. Ramsay and R. N. Jones, This Journal, **73**, 305 (1951).

(15) It is recommended that in reporting "apparent" molecular extinction coefficients the slit width in wave numbers should be included so as to permit repetition of the work under comparable conditions. This can be done conveniently by addition of a superscript to the symbol used for the extinction coefficient (see ref. 14).

(16) A. R. Philpotts, W. Thain and P. G. Smith, *Anal. Chem.*, **23**, 268 (1951).

(17) G. Herzberg, "Infrared and Raman Spectra of Polyatomic Molecules," D. Van Nostrand Co., Inc., New York, N. Y., 1945, p. 261.

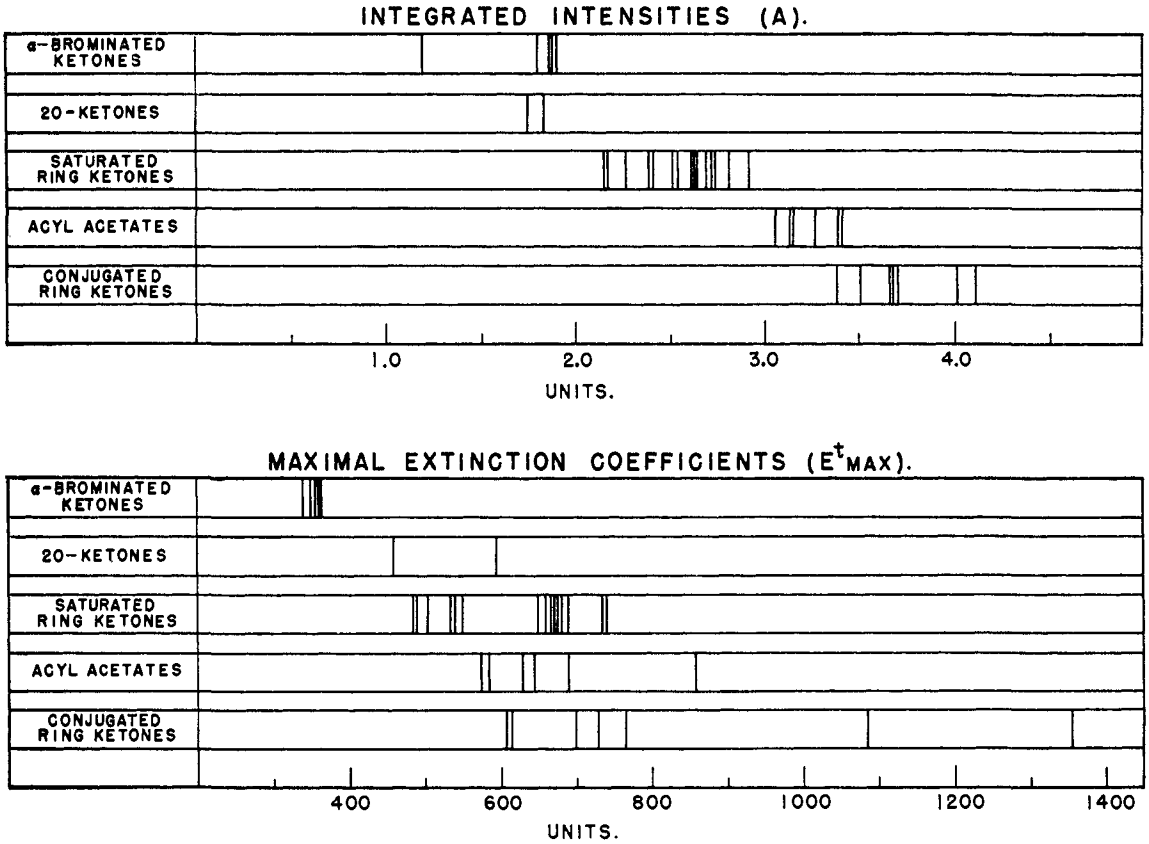

Fig. 4.—Diagram showing relation between maximal molecular extinction coefficients, integrated absorption intensities and molecular structure for carbonyl bands in the infrared spectra of steroids.

3 (II) structures; whereas the former gives a broad band ($\Delta\nu^t_{1/2}$ = 18.6 cm.$^{-1}$) with a small extinction coefficient ($E^t_{\max}$ = 615) the latter gives a narrow band ($\Delta\nu^t_{1/2}$ = 7.5 cm.$^{-1}$) with a large extinction coefficient ($E^t_{\max}$ = 1355).

Application of Intensity Measurements to the Elucidation of Molecular Structure.—In the monocarbonyl compounds the variation of intensity with carbonyl position is small, and the intensities do not aid appreciably in the characterization of the positions of individual carbonyl groups. Thus the 3-, 7- and 12-ketosteroids which cannot be distinguished from the position of the band maxima[2,3] give bands of similar intensity. Where the intensity differences are larger, as between saturated and α,β-unsaturated carbonyl groups the band frequency differences are also characteristic.

Intensity measurements are valuable for the characterization of carbonyl functions in di- and polycarbonyl compounds, particularly in cases where the individual carbonyl bands overlap more or less completely. Thus mono-, di- and triacyl acetates give intensities in the ratio of 1:2:3 and can be readily distinguished.

Of particular interest from the viewpoint of steroid metabolic studies is the possibility of recognizing the 17-ketone group in the presence of an acetate, as in androsterone acetate and its stereoisomers. The intensity of the superimposed 17-ketone and monoacetate bands is 5.77 units which is readily distinguishable from 3.2 units for the acetate band alone. Confusion with a diacetate of intensity 6.17 units may be resolved by an additional intensity measurement on the acetate band near 1240 cm.$^{-1}$.

For a number of acetates the apparent integrated absorption intensity

$$B = \frac{1}{cl}\int_{1190}^{1290} \log_e \left(\frac{T_0}{T}\right)_\nu d\nu \qquad (7)$$

has been determined at a slit width of approximately 5 cm.$^{-1}$ and found to lie between 3.9 and 4.7 units per acetate group.[18] The absorption of the ketonic carbonyl group is negligible in this region, so that monoacetoxy-, diacetoxy- and polyacetoxy-17-ketosteroids can all be differentiated if the absorption intensities in these two regions of the spectrum are known.

The application of intensity measurements to the characterization of a steroid of unknown structure may be illustrated by measurements on a compound[19] of empirical structure $C_{21}H_{30}O_4$, first obtained by Marker and co-workers[20] from hecogenin. This compound possesses a single carbonyl absorption band at 1714 cm.$^{-1}$ in carbon disulfide solution, and was initially believed to be a monohydrate of a triketone, although subsequent in-

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(18) R. N. Jones, P. Humphries, F. Herling and K. Dobriner, THIS JOURNAL, 73, 3215 (1951).

(19) We are indebted to Dr. R. B. Wagner of Pennsylvania State College for this compound.

(20) R. E. Marker, R. B. Wagner, P. R. Ulshafer, E. L. Wittbecker, D. P. J. Goldsmith and C. H. Ruof, THIS JOURNAL, 69, 2167 (1947).

vestigations cast doubt on this structure.[21] Measurements of the integrated absorption intensity of the carbonyl band gave a value of 4.9 units. The intensities for triketones absorbing near 1714 cm.$^{-1}$ lie in the neighborhood of 6.7 units and for diketones absorbing in the same region between 4.0 and 5.3 units (Table II). A dicarbonyl structure is therefore indicated for this hecogenin derivative.

Concluding Remarks

Integrated absorption intensities are more satisfactory than molecular extinction coefficients as a basis for correlation with molecular structure, particularly where small differences of intensity are involved, *e.g.*, less than a factor of 2–3, or if overlapping band systems are being investigated. The integrated absorption intensity is less dependent on slit width corrections and hence is more suitable for comparing results on different instruments.

In comparing the results obtained by the three methods it has been observed that methods II and III should be more accurate than I, since the latter is dependent on measurements at three points on the curve only. In the practical application, the much greater rapidity of method I is a compensatory factor. Methods II and III are tedious if the absorption curves are plotted point-by-point from the experimental records; this however may be obviated in the case of method II by the use of a logarithmic integrator,[22] or in method III by the use of a double beam spectrometer with a linear wave number scale.[8]

For survey work where an accuracy of 10% is sufficient, apparent integrated absorption intensities as determined by method II are probably adequate. If true integrated absorption intensities are required however, a small correction for the finite slit width may be applied. In this connection it is better to make measurements on strong bands, *e.g.*, peak absorption 70%, than on weak bands for the areas may be measured more accurately and the wing corrections minimized.

Although these investigations have been directed to the solution of certain specific problems in steroid chemistry, the application of infrared intensity measurements to other problems of molecular structure is self-evident. Molecules with chromophoric groups producing isolated absorption bands, *e.g.*, O–H, N–H, S–H, $-C\equiv C-H$, $C=N$, $C=C$, are especially suitable for study as also are molecules with a particular absorption band considerably stronger than the neighboring absorption, *e.g.*, the 1240-cm.$^{-1}$ acyl acetate band. The relative intensities of some C–H, C–D, O–H and O–D stretching bands are at present being investigated in connection with the analysis and structure determination of deuterium-labeled compounds.

Acknowledgments.—The authors wish to thank the several investigators listed individually in a footnote to Table I who kindly made available many of the compounds. The investigation was aided by grants from The Commonwealth Fund, the American Cancer Society (upon recommendation of the Committee on Growth of the (U.S.) National Research Council), and the National Cancer Institute, U.S. Public Health Service.

OTTAWA, CANADA
NEW YORK, N. Y.

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[21] R. B. Wagner, J. A. Moore and R. F. Forker, THIS JOURNAL, 71, 3856, 4159 (1950).

[22] S. A. Francis, *J. Chem. Phys.*, 18, 861 (1950).

[CONTRIBUTION FROM THE GIBBS CHEMICAL LABORATORY, HARVARD UNIVERSITY]

Photochemical Decomposition of Ketene. III

BY G. B. KISTIAKOWSKY AND WALTER L. MARSHALL

Methylene diradicals formed in the photochemical decomposition of ketene have been shown to react readily at room temperature with carbon monoxide forming ketene. The reaction appears to be of third order. A mass spectrographic study of the products of reaction of methylene and *sym*-dideuteroethylene favors the intermediate formation of trimethylene diradical rearranging into propylene. Allene has been identified as one of the products of the reaction of methylene with ketene. The over-all mechanism of the photochemical decomposition of ketene is discussed.

Past work[1] has identified several secondary reactions involved in the photochemical decomposition of ketene, but some of the experimental observations still lack adequate explanation. Thus, the rate of pressure rise decreases more on prolonged illumination than is to be expected on the basis of the proposed reaction mechanism, the dependence of the quantum yield of carbon monoxide on the ethylene to ketene ratio is not correctly reproduced; the postulated polymethylene diradicals are in doubt because of the absence of cycloparaffins among the products and so forth. The research reported here is an attempt to elucidate these matters.

Experimental

The reaction took place in a thermostated, dual cylindrical jacketed quartz cell with a G. E. fluorescent lamp (maximum at 3200 Å.) placed axially in the middle compartment of the cell. The reaction was followed by pressure measurements and by analyses of the products. Pressure measurements were made with the aid of a Pearson-type differential manometer.[2]

The preparation, purification and analysis of ketene were the same as described in the previous paper.[1]

Carbon monoxide from two sources was used, without noting any difference in the results. For earlier runs Mathieson compressed carbon monoxide was passed over hot copper and further purified by condensation in liquid nitrogen. Mass spectrographic analysis indicated that this gas contained a small amount of methane. For later runs

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[1] G. B. Kistiakowsky and N. W. Rosenberg, THIS JOURNAL, 72, 321 (1950).

[2] A. Farkas and H. W. Melville, "Experimental Methods in Gas Reactions," The Macmillan Co., New York, N. Y., 1939.