methyl isopropyl ketone, the diisobutylenes, 2,3,4,4-tetramethyl-1-pentene and other nonenes, have been found along with the chief products of the reaction, the two decenes, 3,4,5,5-tetramethyl-2-hexene and 3,5,5-trimethyl-2-heptene.

3. 3,5,5-Trimethyl-3-heptanol has been prepared and dehydrated. Dehydration with copper sulfate and with sulfuric acid give different ratios of the isomers. The relation of this dehydration to the structure of the polymers is considered.

4. Methyl and ethyl Grignard reagents would not add to 4,5,5-trimethyl-3-hexanone and 3,4,4-trimethyl-2-pentanone, respectively.

STATE COLLEGE, PA. RECEIVED FEBRUARY 6, 1941

[CONTRIBUTION FROM THE CONVERSE MEMORIAL LABORATORY OF HARVARD UNIVERSITY]

Structure and the Absorption Spectra of α,β-Unsaturated Ketones

BY ROBERT BURNS WOODWARD*

Henri,[1] working with mesityl oxide, first observed the absorption spectrum which is now accepted as characteristic in general outline of all simple α,β-unsaturated ketones. A strong absorption band ($\log \epsilon = 4.1$, $\lambda_{\text{max.}} = 236$ mμ) as well as a weak band ($\log \epsilon = 1.9$) at 315 mμ was evident. Scheibe[2] confirmed and extended this work, showing that the exact position of the wave length of maximum absorption was to some extent dependent on the solvent used. On changing to a relatively more polar solvent, the intense band was shifted toward the red, while the weak band was shifted toward the violet.

Menschick, Page and Bossert,[3] investigating cholestenone and pulegone, the latter known to be an α,β-unsaturated ketone, pointed out the similarity of the spectra of these substances to that of mesityl oxide, and adduced the resemblance as evidence of the α,β-unsaturated carbonyl character of the steroid ketone. These investigators further indicated that in general the presence of an α,β-unsaturated carbonyl system in a given compound could be correlated with intense selective absorption in the region 230–250 mμ. The anticipation that this effect would be a powerful tool in the determination of structure has been amply justified in the interim, in that the presence in a large number of compounds, of this structural feature has been adduced as a consequence of absorption in this region (*cf.* Tables II, III and IV). In the steroid series alone, more than fifty substances have been investigated, in all of which $\lambda_{\text{max.}}$ for the intense band is in the region 220–260 mμ.

In this communication it is shown that the position *within this region* of the wave length of maximum absorption may be rigidly correlated with the extent of substitution of the carbon–carbon double bond in the α,β-unsaturated carbonyl system and that consequently the determination of this physical property throws a very considerable light upon the structure of the compound under examination. In Tables II, III and IV are listed the wave lengths of maximum absorption for the intense band in the absorption spectra of all α,β-unsaturated ketones of unequivocal structure whose absorption characteristics have been measured to date. It must be emphasized that in order that the spectra of different substances shall be exactly comparable, the absorption characteristics must be determined in a single solvent, or the observed values must be corrected to a given solvent. That the mass of data now available has not previously been amenable to classification is in large part a consequence of the fact that the use of a variety of solvents for the determinations has resulted in a general diffuseness of the published values of $\lambda_{\text{max.}}$. The values of the latter in the sequel are for spectra in absolute ethanol, the published values, in case this solvent was not used, being corrected as indicated in Table I. The corrections are average values deduced from a considerable number of cases in which the shifts have been measured experimentally.[2]

TABLE I

Solvent	To correct to EtOH add
CH_3OH	-1 mμ
$CHCl_3$	± 0
$(C_2H_5)_2O$	$+6$
Hexane	$+7$

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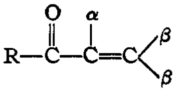
[1] Bieleski and Henri, *Ber.*, **47**, 1690 (1914).

[2] Scheibe, Rössler and Backenköhler, *ibid.*, **58**, 586 (1925).

[3] Menschick, Page and Bossert, *Ann.*, **495**, 233 (1932).

Each of these substances contains the system I.

I 

$$R-\overset{\overset{\displaystyle O}{\|}}{C}-\overset{\alpha}{\overset{|}{C}}=C\Big\langle{}^{\beta}_{\beta}$$

Those in Table II have a single substituent, either in the α- or the β-position, the two remaining positions being occupied by hydrogen atoms.

TABLE II

Substance	$\lambda_{max.}$, mμ
Δ^3-Pentenone-2	220[a]
4-Isopropyl-Δ^2-cyclohexenone-1	226[b]
Δ^1-Cholestene-3-one	$\leqslant$230[c]
Δ^1-Coprostene-3-one	$\leqslant$228[d]
Δ^1-Androstenedione-3,17	$\leqslant$230[c]
Δ^1-*allo*-Pregnenedione-3,20	$\leqslant$230[c]

[a] Dimroth, *Angew. Chem.*, **52**, 545 (1939). [b] Cooke and Macbeth, *J. Chem. Soc.*, 1408 (1938). [c] Butenandt, *et al.*, *Ber.*, **72**, 1617 (1939). [d] Inhoffen and Huang-Minlon, *ibid.*, **71**, 1720 (1938).

It is evident that $\lambda_{max.}$ for all of these substances is below 230 mμ. Although the experimental limitations often in the case of this class of compounds do not permit the absolute determination of $\lambda_{max.}$, the conclusion is none the less inescapable that a singly substituted α,β-unsaturated ketone may be characterized by strong absorption in the region 225 ± 5 mμ.

The compounds in Table III, representing the most extensively studied class, are all disubstituted, the two substituents being either in the α,β- or β,β-positions, the remaining position being occupied by hydrogen.

TABLE III

Substance	$\lambda_{max.}$, mμ
Mesityl oxide	236[a]
2-Methyl-5-isopropenyl-Δ^2-cyclohexenone-1	235[b,c]
3-Methyl-6-isopropyl-Δ^2-cyclohexenone-1	235[b]
Cyclohexylidene acetone	242[d]
9-Keto-Δ^{10}-dodecahydrophenanthrene	238[e]
Δ^4-Cholestene-3-one	242[f]
Δ^4-Cholestene-3-one-6-sulfonic acid	237[g]
Fucostenone	240[h]
$\Delta^{4,7}$-Ergostadienone-3	240[i]
Δ^4-Androstenedione-3,17	240[j]
6-Bromo-Δ^4-androstenedione-3,17	244[k]
Testosterone	240[j]
17-Ethyltestosterone	243[l]
16-Hydroxytestosterone	240[m]
16-Hydroxytestosterone-16,17-acetonide	240[m]
Progesterone	240[n]
17-Isoprogesterone	242[o]
$\Delta^{4,20}$-Pregnadienol-17-one-3	242[p]
Andrenosterone	235[q]
Corticosterone	240[r]
Desoxycorticosterone	240[s]
Desoxycorticosterone acetate	240[s]
17-Hydroxy-11-desoxycorticosterone	236[r]
Δ^{16}-Pregnenedione-3,20	239[t]
3-Hydroxy-$\Delta^{5,16}$-pregnadiene-20-one	240[u]
3-Acetoxy-$\Delta^{5,16}$-pregnadiene-20-one	240[u]
3-Keto-Δ^4-bisnorcholenic acid	240[v]
3,12-Diketo-Δ^4-cholenic acid	236[w]
2,3-Diketocholestane enol acetate-I	238[x]
2,3-Diketocholestane enol acetate-II	237[x]
3-Hydroxy-Δ^4-cholestene-6-one	239[y]
3-Acetoxy-Δ^4-cholestene-6-one	236[y]
3,17-Dihydroxy-Δ^5-androstene-7-one	238[z]
3-Acetoxy-Δ^5-cholestene-7-one	240[aa]
12-Keto-Δ^9-cholenic acid methyl ester	240[bb]
3-Hydroxy-7-keto-Δ^5-cholenic acid	238[cc]

[a] Scheibe, Rössler and Backenköhler, *Ber.*, **58**, 586 (1925). [b] Cooke and Macbeth, *J. Chem. Soc.*, 1408 (1938). [c] Mohler, *Helv. Chim. Acta*, **20**, 289 (1937). [d] Dimroth, *Angew. Chem.*, **52**, 545 (1939). [e] Linstead and Walpole, *J. Chem. Soc.*, 845 (1939). [f] Menschick, Page and Bossert, *Ann.*, **495**, 227 (1932); Heilbron, Newton and Sexton, *J. Chem. Soc.*, 47 (1928). [g] Windaus and Kuhr, *Ann.*, **532**, 52 (1938). [h] Heilbron, *et al.*, *J. Chem. Soc.*, 739 (1936). [i] Wetter and Dimroth, *Ber.*, **70**, 1665 (1937). It should be noted that Heilbron, *et al.*, *J. Chem. Soc.*, 869 (1938), presumably working with the same compound observed $\lambda_{max.}$ = 230 mμ. The explanation for this discrepancy is not readily discernible. [j] Butenandt and Peters, *Ber.*, **71**, 2690 (1938). [k] Ruzicka, *et al.*, *Helv. Chim. Acta*, **19**, 1147 (1936). This value is somewhat in doubt since the solvent was not reported. [l] Butenandt, Cobler and Schmidt, *Ber.*, **69**, 448 (1936). [m] Butenandt, Schmidt-Thomé and Weiss, *ibid.*, **72**, 417 (1939). [n] Butenandt, *et al.*, *ibid.*, **72**, 182 (1939). [o] Butenandt, Schmidt-Thomé and Paul, *ibid.*, **72**, 1112 (1939). [p] Inhoffen, *et al.*, *ibid.*, **71**, 1024 (1938). [q] Reichstein, *Helv. Chim. Acta*, **19**, 223 (1936). [r] Reichstein, *ibid.*, **20**, 953 (1937). [s] Steiger and Reichstein, *ibid.*, **20**, 1164 (1937). [t] Masch, Diss., Danzig, 1938. [u] Butenandt and Schmidt-Thomé, *Ber.*, **72**, 182 (1939). [v] Butenandt and Mamoli, *ibid.*, **68**, 1854 (1935). [w] Sawlewicz and Reichstein, *Helv. Chim. Acta*, **20**, 949 (1937). [x] Stiller and Rosenheim, *J. Chem. Soc.*, 353 (1938). [y] Heilbron, Jones and Spring, *ibid.*, 801 (1937). [z] Butenandt, Hausmann and Paland, *Ber.*, **71**, 1316 (1938); Dimroth and Paland, *ibid.*, **72**, 187 (1939). [aa] Eckhardt, *ibid.*, **71**, 461 (1938). [bb] Barnett and Reichstein, *Helv. Chim. Acta*, **21**, 926 (1938). [cc] Haslewood, *J. Chem. Soc.*, 224 (1938).

It is apparent that these disubstituted ketones exhibit selective absorption in the region 239 ± 5 mμ.

Finally, Table IV lists those substances in which all three available positions are substituted.

All of these α,β,β-trisubstituted α,β-unsaturated ketones absorb in the region 254 ± 5 mμ.

From an examination of these data we may conclude that the substitution for hydrogen of an alkyl group causes a shift toward the red of approximately 15 mμ, and that the determination of $\lambda_{max.}$ reveals unequivocally the extent of substi-

TABLE IV

Substance	$\lambda_{max.}$, mμ
Pulegone	252[a]
α-Cyperone	252[b]
5-Hydroxy-$\Delta^{8,14}$-ergostenedione-3,7	254[c]
4-Bromo-Δ^4-androstenedione-3,17	254[d]
4-Bromo-Δ^4-cholestene-3-one	256[e]
7-Bromo-Δ^7-cholestenedione-3,6	256[f]
3,4-Diketocholestane enol acetate	249[g]
4,6-Dibromo-Δ^4-cholestene-3-one	254[h]
4,6,6-Tribromo-Δ^4-cholestene-3-one	258[f]

[a] Menschick, Page and Bossert, *Ann.*, **495**, 233 (1932). [b] Gillam, *J. Chem. Soc.*, 676 (1936). [c] Müller, *Z. physiol. Chem.*, **231**, 75 (1935). [d] Dannenberg, *Abhandl. preuss. Akad. Wiss., Math.-nat. Klasse*, No. 21 (1939) (Pub., 1940). [e] Barbow, Diss., Danzig, 1939. [f] Butenandt and Schramm, *Ber.*, **69**, 2289 (1936). [g] Butenandt, *et al.*, *ibid.*, **69**, 2779 (1936). [h] Inhoffen, *ibid.*, **69**, 1702, 2141 (1936); Butenandt, Schramm and Kudsuss, *Ann.*, **531**, 176 (1937).

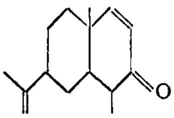
tution of the carbon–carbon double bond in an α,β-unsaturated ketone. It is a striking fact that the substitution, at least in the α-position, of a bromine atom or an acetoxy group has much the same effect as the substitution of an alkyl group.[4] The general position is summarized in Table V. It should be pointed out that the three classes do not overlap, and that the average deviation from the mean position is much less than 5 mμ.

TABLE V

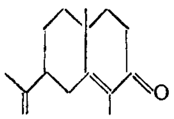
Substitution	$\lambda_{max.}$, mμ
α or β	225 ± 5
$\alpha\beta$ or $\beta\beta$	239 ± 5
$\alpha\beta\beta$	254 ± 5

The use in the determination of structure of the generalizations formulated in this paper may aptly be illustrated by a consideration of the work on the constitution of the sesquiterpene ketone α-cyperone. Simonsen, *et al.*,[5] first ascribed to the substance the formula II. In order to confirm the

II

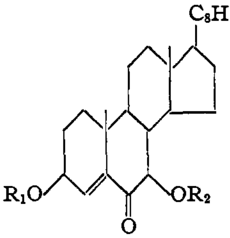


III



character of the compound as an α,β-unsaturated ketone, the absorption spectrum was determined, and revealed an intense band ($\log \epsilon = 4.28$) at 252 mμ. This observation renders structure II inadmissible. Granting the correctness of the carbon skeleton and the position of the carbonyl group, it is evident that only formula III is in conformity with the absorption data. In fact, more recent work[6] has shown the correctness of the latter formulation.

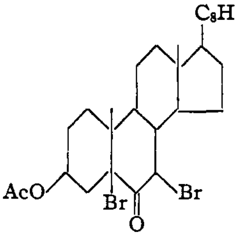
A few substances do not conform with the generalizations outlined above. The simplest and most probable explanation of this apparent anomaly is that the structures at present assigned to those compounds are incorrect. Since the proof of this view will constitute further evidence of the power of the absorption method in the determination of structure, we are at present studying these relatively few anomalous cases. In particular, the three compounds at present represented by IV (a, b and c) all have $\lambda_{max.} \leqslant 230$ mμ,[7] a value well outside the range 239 ± 5 mμ, within which $\lambda_{max.}$ for compounds having structure IV should lie. We suggest tentatively that



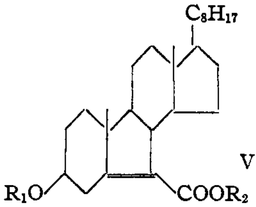
IV

a: $R_1 = H$, $R_2 = H$
b: $R_1 = Ac$, $R_2 = H$
c: $R_1 = Ac$, $R_2 = Et$

these substances, which were prepared by Heilbron, *et al.*,[7] by the action of basic reagents on 5- and 5′,7-dibromo-6-ketocholestanyl acetate (V), are more probably represented by VI (a, b and c),



V



VI

a: $R_1 = H$, $R_2 = H$
b: $R_1 = Ac$, $R_2 = H$
c: $R_1 = Ac$, $R_2 = Et$

a view which not only accords with the absorption data,[8] but is supported by the early work of Wallach[9] on the debromination of simpler dibromocyclohexanones (*e. g.*, VII → VIII), and is equally admissible on the basis of the chemical evidence presented in favor of the alternative structure.

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(4) This interesting observation accords with the accumulating evidence that there is little or no physical basis for the concept of cross-conjugation.

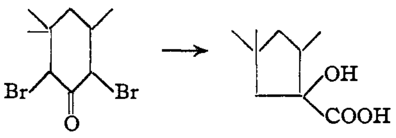
(5) Bradfield, Hegde, Rao, Simonsen and Gillam, *J. Chem. Soc.*, 667 (1936).

(6) Bradfield, Pritchard and Simonsen, *J. Chem. Soc.*, 760 (1937).

(7) Heilbron, Jackson, Jones and Spring, *ibid.*, 102 (1938).

(8) For typical spectra of α,β-unsaturated acids and esters, *cf.* Dimroth, *Angew. Chem.*, **52**, 552 (1939).

(9) Wallach, *Ann.*, **414**, 296 (1918).



VII VIII

Summary

It has been shown that the determination of the position of the wave length of maximum absorption for the intense band in the absorption spectra of α,β-unsaturated ketones reveals the extent of substitution of the carbon–carbon double bond in an α,β-unsaturated carbonyl system.

The power of the method as a tool in structure determinations is indicated and exemplified.

CAMBRIDGE, MASS. RECEIVED JANUARY 15, 1941

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF OREGON STATE COLLEGE AND THE UNIVERSITY OF CALIFORNIA AT LOS ANGELES]

Photolysis of Biacetyl in the Near Ultraviolet

BY JACK G. ROOF AND FRANCIS E. BLACET

Investigations in recent years have shown that biacetyl is a product of the photolysis of various compounds, such as acetone,[1] methyl ethyl ketone,[2] and acetaldehyde.[3] If any of these reactions is allowed to proceed to an appreciable extent, decomposition of the biacetyl formed may tend to obscure the results of the primary reaction. The investigation herein described was undertaken to study quantitatively the photolysis of biacetyl in the vapor state and to make a comparison with results of recent investigations on the thermal decomposition of this compound.[4]

The effect of ultraviolet light on biacetyl has received little attention to date. In aqueous solutions it is reported to give acetaldehyde and acetic acid.[5] In benzene and ether solutions it was found that no gaseous products are evolved.[6] In a qualitative experiment[5] on the vapor at 100° and atmospheric pressure, full exposure to an unfiltered arc gave gases reported to be carbon monoxide and ethane in a volume ratio of 2 to 1. Considering the complexity of the photolysis of the homolog glyoxal,[7] it was felt that the reaction of biacetyl might be more complex than previously supposed. That such is the case is shown by the large percentage of methane found in the products reported in the present paper.

Experimental

The photochemical apparatus was quite similar to the one used in a study of the photolysis of crotonaldehyde at elevated temperatures.[8] Products not condensed at dry-ice temperature were treated with slightly moist potassium hydroxide beads to remove any biacetyl and ketene present. The remaining gases were then analyzed by micro methods. Quantum yields reported are based upon analyses for carbon monoxide in the permanent gas. All results reported represent the averages of from 2 to 5 determinations on aliquot portions of the sample.

Except at the lowest pressures, the reaction was not allowed to proceed more than about 2 or 3% toward completion—as determined from the amount of carbon monoxide produced. It was found that no corrections for thermal decomposition were necessary at these temperatures, in agreement with the observations of Walters,[4b] who could detect no decomposition below 346°.

Beer's law was found to hold within experimental error at room temperature. Assuming that it applies at higher temperatures and that the absorption coefficient is independent of temperature, it was possible to calculate[8] the absorption at elevated temperatures from a measurement of the arc intensity through the cold cell.

Experimental Results

In the present paper quantum yields have been calculated on the basis of molecules of carbon monoxide produced per quantum absorbed. It is recognized that if, as in the thermal decomposition, a molecule such as ketene is produced, not all of the reacting biacetyl molecules are accounted for by the carbon monoxide and Φ is low correspondingly. Usually runs were made in series such that only one factor varied at a time. Fig. 1 shows directly the increase of Φ with rise of temperature. Further, it shows that at any one temperature Φ increases with decreasing wave length.

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(1) Spence and Wild, *Nature*, **138**, 206 (1936); *J. Chem. Soc.*, 352 (1937).

(2) Ells and Noyes, THIS JOURNAL, **60**, 2031 (1938).

(3) Blacet and Blaedel, *ibid.*, **62**, 3374 (1940).

(4) (a) Rice and Walters, *J. Chem. Phys.*, **7**, 1015 (1939); (b) Walters, THIS JOURNAL, **62**, 880 (1940).

(5) Porter, Ramsperger and Steel, *ibid.*, **45**, 1827 (1923).

(6) Bowen and Horton, *J. Chem. Soc.*, 1505 (1934).

(7) (a) Norrish and Griffiths, *ibid.*, 2829 (1928); (b) Blacet and Moulton, THIS JOURNAL, **63**, 868 (1941).

(8) Blacet and LuValle, *ibid.*, **61**, 273 (1939).