adian and Messrs. Thomas Slauson, Howard Bishop and Donald Page for some of the intermediates employed in this work and to Messrs. Donald Sepplin and Leon Duprey and Miss Dorothy Fort for the toxicity determinations.

RENSSELAER, NEW YORK

[CONTRIBUTION FROM THE INSTITUTO DE QUÍMICA DE LA UNIVERSIDAD NACIONAL AUTÓNOMA DE MÉXICO]

Structure and Properties of Cyclic Compounds. V.[1] Strain Effects in the Ultraviolet Light Absorption of Cyclic Compounds

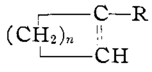
BY OWEN H. WHEELER

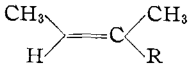
RECEIVED APRIL 19, 1955

New and previous data on the ultraviolet light absorption of cyclic systems containing double bonds are discussed in terms of strain effects in the rings. Simple α,β-unsaturated amides and nitriles have, in general, absorption similar to that of the corresponding acids.

It has been observed by a number of workers that the presence of a carbon ring in, or at the end of a conjugate chromophore, affects the characteristic wave length of absorption of that chromophore.[2] In this investigation the absorption of a series of cyclic acids and amides, with both endo- and exocyclic double bonds, has been measured under standard conditions, and these results, together with previous literature data, are discussed in terms of the strain effects produced by these endo- and exocyclic double bonds.

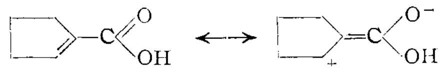
Compounds with Endocyclic Double Bond.—The ultraviolet light absorption of cycloalkenylcarboxylic acids (I, R = CO_2H), carboxamides (I, R = $CONH_2$) and nitriles (I, R = CN) of ring size 5 to 7 carbon atoms (I, n = 3 to 5), has been measured and is given in Table I, together with published data on the corresponding carboxaldehydes (I, R = CHO) and methyl ketones (I, R = $COCH_3$). It is seen that the cyclopentenyl and cycloheptenyl derivatives all absorb at higher wave lengths than the cyclohexenyl compounds, and that the latter absorb at similar wave lengths to the acyclic analogs (*cf. cis*-α,β-dimethylacrylic acid (tiglic acid) (II, R = CO_2H) and amide (II, R = $CONH_2$)).


I


II

The absorption of light by a molecule in the near ultraviolet region of the spectrum results in electronic transitions from a hybrid ground state, in which ionic resonance forms normally play little part, to an excited state to which ionic resonance forms make a large contribution.[3] If there is a structural change in the molecule which raises the energy of the excited state more than that of the ground state, then the energy of the transition will be increased and absorption will take place at lower wave length. Such effects are well known in sterically hindered molecules,[4] where there is inhibition of resonance stabilization in the excited state. However, if some effect in the molecule raises the energy level of the ground state with little effect on the energy level of the excited state, the energy of the absorption transition will be lowered, and the absorption peak displaced to a longer wave length. It is proposed that this last effect offers an explanation of the spectral differences in cycloalkenyl compounds.

The presence of a double bond in a cyclopentane ring leads to considerable strain in the ring, since the angles about the double bond are considerably compressed.[5] However, when the double bond is exocyclic to the ring, this angle strain is greatly relieved.[5] As a result of this the endocyclic double bond in cyclopentenylcarboxylic acid (III) makes this a strained molecule, relative to its acyclic analog (II, R = CO_2H), and increases the energy level of its ground state. Absorption of light causes a transition to a higher energy level, to which polar resonance forms (*e.g.* IV) contribute. Resonance of this type (III–IV) will give some single bond character to the endocyclic double bond, and produce a partial double bond exocyclic to the ring. This leads to a delocalization of the endocyclic double bond with relief of strain in the ring and the energy level of the excited state will be lowered relative to that of an unstrained molecule. Hence the energy level of the ground state is raised and that of the excited state lowered, decreasing the energy of the transition and causing absorption at longer wave length. It can be seen (Table I) that cyclopentenylcarboxylic acid (I, n = 3; R = CO_2H) shows a bathochromic shift over its acyclic strainless analog, tiglic acid (II, R = CO_2H). A similar explanation holds for the other cyclopentenyl compounds (I, n = 3, R = $CONH_2$, CN, CHO, $COCH_3$).


III IV

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[1] (a) Part IV, *J. Org. Chem.*, **20**, 1672 (1955); (b) Part III, O. H. Wheeler and I. Lerner, THIS JOURNAL, **78**, 63 (1956).

[2] (a) A. E. Gillam and T. F. West, *J. Chem. Soc.*, 811 (1941); (b) H. S. French and L. Wiley, THIS JOURNAL, **71**, 3702 (1949); (c) H. S. French, *ibid.*, **74**, 514 (1952); (d) R. B. Woodward, *ibid.*, **63**, 1123 (1941); **64**, 72, 76 (1942); (e) L. Dorfman, *Chem. Revs.*, **53**, 47 (1953).

[3] A. L. Sklar, *J. Chem. Phys.*, **5**, 669 (1937); R. S. Mulliken, *Rev. Mod. Phys.*, **14**, 265 (1942); A. Maccoll, *Quart. Rev. Chem. Soc.*, **I**, 16 (1947).

[4] E. A. Braude, W. F. Forbes and F. Sondheimer, *Nature*, **173**, 117 (1954).

[5] H. C. Brown, J. H. Brewster and H. Shechter, THIS JOURNAL, **76**, 467 (1954).

TABLE I

ABSORPTION OF COMPOUNDS WITH ENDOCYCLIC DOUBLE BONDS[a]

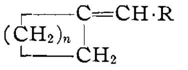
I	R = CO_2H[b]	R = $CONH_2$[b]	R = CN[b]	R = CHO	R = $COCH_3$
$n = 3$	222(9,500)[c]	220(9,850)	217(9,900)	238(13,500)[g]	239(12,000)[i]
$n = 4$	216(9,800)[d]	213(10,300)	212(11,200)[e]	229(12,100)[h]	232(13,000)[i]
$n = 5$	222(9,900)[i]	218(11,100)	216(10,500)	....	236(10,500)[i]
II	214(12,800)[f]	214(12,100)	....	....	....

[a] Wave lengths (λ) in mμ, molar extinction coefficients (ε) in parentheses. All values are for ethanolic solution. [b] Present work. [c] E. A. Braude and W. F. Forbes, ref. 18a, give λ_{max} 211 mμ, ε 9300. [d] H. E. Ungnade and I. Ortega, ref. 20, give λ_{max} 218 mμ, ε 8700; E. A. Braude and J. A. Coles, ref. 18c, give λ_{max} 212 mμ, ε 11,000. [e] E. A. Braude and W. F. Forbes, ref. 18b, give λ_{max} 213 mμ, ε 11,200. [f] R. Adams and B. L. von Duuren, THIS JOURNAL, **75**, 4631 (1953), give λ_{max} 212 mμ, ε 13,500. [g] J. B. Brown, H. B. Henbest and E. R. H. Jones, *J. Chem. Soc.*, 3634 (1950). [h] I. M. Heilbron, E. R. H. Jones, R. W. Richardson and F. Sondheimer, *ibid.*, 737 (1949). [i] I. M. Heilbron, E. R. H. Jones, J. B. Toogood and B. C. L. Weedon, *ibid.*, 1827 (1949).

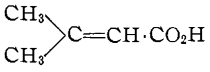
The presence of a double bond in a cyclohexane ring, however, produces little strain, since folding of the ring in a "half chair" conformation relieves angle strain, and thus cyclohexenylcarboxylic acid (I, $n = 4$, R = CO_2H) absorbs at similar wave lengths to tiglic acid (II, R = CO_2H). The absorption of cyclohexenyl compounds, in general, also shows a hypsochromic shift from the absorption of the cyclopentenyl analogs.

In a cycloheptane molecule folding of the ring will produce both angle and hydrogen opposition strain effects, since the ring cannot assume a symmetrical form. Thus the strained cycloheptenyl derivatives (I, $n = 5$) absorb at a higher wave length than the cyclohexenyl compounds (I, $n = 4$).[6]

Compounds Containing Exocyclic Double Bonds.—The absorption spectra of a series of cycloalkylideneacetic acids (V, $n = 3$ to 5, R = CO_2H) and their acyclic analog β,β-dimethylacrylic acid (VI) have been measured (Table II). All of the three cycloalkylidene acetic acids show a bathochromic shift in wave length of absorption from that of the β,β′-dimethylacrylic acid, but this is smaller for the cyclohexane acid.



V



VI

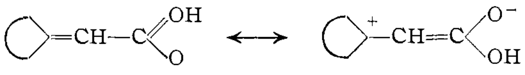
TABLE II

ABSORPTION OF CYCLOALKYLIDENE ACETIC ACIDS[a]

		λ_{max}[b]	ε
V,	$n = 3$	224	12,500
R =	$n = 4$	219	16,100
CO_2H	$n = 5$	224	12,600
VI		216[c]	11,300

[a] Present work. Determinations in ethanolic solution. [b] Wave length of absorption maxima in mμ. [c] H. E. Ungnade and I. Ortega, ref. 20, give λ_{max} 216 mμ, ε 10,000.

A double bond exocyclic to a cyclohexane ring produces strain due to interaction with the α-ring hydrogen atoms.[5] Thus for cyclohexylideneacetic acid (V, $n = 4$, R = CO_2H) the energy of the ground state of the molecule will be higher than that of an unstrained molecule (*e.g.* VI). Ionic resonance forms (*e.g.* VIII) will contribute largely to the excited state of the molecule, and this will give partial single bond character to the exocyclic double bond, leading to a delocalization of the electrons at the ring junction and hence to relief of strain in the ring. Due to these two effects the energy of the transition will be lower than that of an unstrained molecule and cyclohexylideneacetic acid absorbs at a higher wave length than β,β′-dimethylacrylic acid.



VII VIII

For cyclopentylideneacetic acid (V, $n = 3$, R = CO_2H) the exocyclic double bond produces some strain in the system, though less than in the corresponding cyclohexane compounds,[5] but in addition the formation of ionic resonance forms (*e.g.* VIII) will be favored since formation of a trigonal carbon atom will decrease ring hydrogen-interaction strain effects.[7] Thus this acid will have a bathochromic shift of wave length of maximum absorption relative to that of an unstrained unsaturated acid. Similarly, for cycloheptylideneacetic acid the formation of ionic resonance forms in the excited state will be favored, since unfavorable ring constellations will be reduced,[7] and this acid too shows a bathochromic shift.

In a correlation of the ultraviolet light absorption of cyclic compounds, Woodward[2d,c] made the empirical observation that for dienes or α,β-unsaturated ketones which contain a double bond exocyclic to a cyclohexane ring, an extra 5 mμ must be added to the expected wave length based on acyclic analogs. This is in agreement with the above bathochromic shifts resulting from ring strain, and the shift for the cyclohexane acids is similar (+3 mμ).

Amides and Nitriles.—There are few data in the literature on the light absorption of simple α,β-unsaturated amides. The –CO–NH– group itself has a maximum at 185 mμ.[8] From Table I it can be seen that the acid amides absorb at similar wave lengths to the corresponding carboxylic acids. β,β′-Dimethylacrylamide and β,β′-dimethylacrylic acid absorb at λ_{max} 215 and 216 mμ, respectively.[9] The presence of alkyl groups on the nitrogen atom, however, leads to bathochromic shifts; N,N′-diethyl crotonamide and N-isobutylcrotonamide have

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(6) D. H. R. Barton, R. C. Cookson, W. Klyne and C. E. Shoppee, *Chemistry and Industry*, 21 (1954). Since this paper was submitted for publication a similar explanation of strain effects in the light absorption of endocyclic α,β-unsaturated carbonyl compounds has been given; W. M. Schubert and W. A. Sweeney, THIS JOURNAL, **77**, 2297 (1955).

(7) H. C. Brown and M. Borkowski, *ibid.*, **74**, 1894 (1952).

(8) J. S. Ham and J. R. Platt, *J. Chem. Phys.*, **20**, 335 (1952).

(9) Determinations are from the present work.

λ_{max} 215[10] and 227 mμ,[11] respectively, whereas crotonic acid has λ_{max} 208 mμ.[12]

The absorption of α,β-unsaturated nitriles (Table II) is also very similar to that of the corresponding acids. Braude[13] reported that 1-cyanocyclohexene had λ_{max} 230 (ϵ 1,600) and 261 mμ (ϵ 60). These values seem most unlikely for a simple chromophore consisting of two unsaturated groups in conjugation. Frank, Berry and Shotwell[14] reported that 1-cyano-4-isopropylcyclohexene has λ_{max} 212 (ϵ 8,900) and 271 mμ (ϵ 102). The first maximum agrees with that found in the present work for 1-cyanocyclohexene (I, n = 4, R = CN) but a second maximum was not detected. The cyanoisopropylcyclohexene probably contained some aromatic[15] impurities, since it was prepared by a pyrolytic method.

Experimental

The samples of acids and nitriles were those prepared in part III.[1b]

The acid amides were prepared by heating the acids under reflux with excess thionyl chloride for 0.5 hours, distilling off the unreacted thionyl chloride, and adding the crude acid chloride carefully to excess ammoniacal ether solution. The amides were recrystallized from water or aqueous methanol.

β,β'-Dimethylacrylamide had m.p. 109° (lit. m.p. 110°[16]); tiglamide, m.p. 78° (lit. m.p. 77°[17]); cyclopentenylcarboxamide, m.p. 204° (lit. m.p. 205°[18a]); cyclohexenylcarboxamide, m.p. 135° (lit. m.p. 136°[18c]) and cycloheptenylcarboxamide, m.p. 158° (lit. m.p. 157°[18b]). The ultraviolet light absorption determinations were carried out using freshly prepared solutions in 95% ethanol, with a Beckman DU spectrophotometer. The alcohol was purified by distilling from zinc dust, and had good transmission to 205 mμ. The determinations were carried out in duplicate or triplicate, and no departure from Beer's law was observed. The error in wave length was ±500. The results[19] for the cycloalkenyl acids are in better agreement with those of Ungnade and Ortega[20] than those of Braude and co-workers.

Acknowledgment.—This work was supported by grants from the Rockefeller Foundation, New York.

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[10] K. Bowden, E. A. Braude and E. R. H. Jones, *J. Chem. Soc.*, 948 (1946).

[11] L. Crombie, *ibid.*, 2997 (1952).

[12] I. I. Rusoff, J. R. Platt, H. B. Klevens and G. O. Burr, THIS JOURNAL, **67**, 678 (1945).

[13] E. A. Braude, *Ann. Rept. Chem. Soc.*, **42**, 105 (1945).

[14] R. L. Frank, R. E. Berry and O. L. Shotwell, THIS JOURNAL, **71**, 3889 (1949).

[15] Phenyl cyanide has λ_{max} *ca.* 270 mμ; G. Scheibe, *Ber.*, **59**, 2617 (1926).

[16] R. Kuhn, F. Kohler and L. Kohler, *Z. physiol. Chem.*, **247**, 197 (1937).

[17] H. Sutter, F. Rottmayrand and H. Porsch, *Ann.*, **521**, 189 (1936).

[18] (a) E. A. Braude and W. F. Forbes, *J. Chem. Soc.*, 1755 (1951); (b) *ibid.*, 2202 (1953); (c) E. A. Braude and J. A. Coles, *ibid.*, 2014 (1950).

[19] The discrepancy may be due to the fact that with the Hilger spectrophotometer the use of too large optical density intervals can give spurious "maxima"; E. A. Braude quoted by J. K. L. H. Allan, E. R. H. Jones and M. C. Whithing, *J. Chem. Soc.*, 1862 (1955). This cannot occur with photoelectric instruments, which were used by Ungnade and Ortega, and in the present work.

[20] H. E. Ungnade and I. Ortega, THIS JOURNAL, **73**, 1564 (1951).

MEXICO 20, D.F.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING OF STANFORD UNIVERSITY]

The Stereochemistry of Raney Nickel Action. VI. Functional Group Hydrogenolyses in the α-Substituted α-Phenylpropionic Acid Series

BY WILLIAM A. BONNER AND JOHN A. ZDERIC

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Optically active methyl and ethyl 2-phenyl-2-hydroxypropionates were dehydroxylated to optically active 2-phenylpropionates by action of Raney nickel in refluxing ethanol. The reaction occurred with predominant configurational retention, but with not quite as high stereospecificity as previously suggested. Methyl D(+)-2-phenyl-2-methoxypropionate was demethoxylated under similar conditions to methyl D(+)-2-phenylpropionate, again with substantial retention of configuration. Ethyl (+)-2-phenyl-2-aminopropionate failed to suffer deamination, but underwent reduction to ethyl (+)-2-cyclohexyl-2-aminopropionate. Methyl 2-phenyl-2-formylaminopropionate failed to undergo any reaction whatever, suggesting that a free amino group is necessary for the observed facile ring reduction. 2-Chloro-2-phenylpropionamide was smoothly cleaved to 2-phenylpropionamide, providing a preliminary example of carbon–chlorine bond hydrogenolysis.

Previous investigations on the stereochemistry of Raney nickel catalyzed hydrogenolyses have indicated that phenylmercapto,[1] benzenesulfinyl,[2] benzenesulfonyl[1] and hydroxyl groups[3] are removed from the α-position of the 2-phenylpropionamide skeleton by the hydrogen adsorbed on Raney nickel[4] with varying stereochemical consequences. Thus the former two functional groups suffer hydrogenolysis with complete racemization of the 2-phenylpropionamide moiety, whereas the benzenesulfonyl and hydroxyl groups are removed with substantial retention of optical activity in the adjacent asymmetric center. While the benzenesulfonyl group departs with apparent inversion of the adjacent carbon atom, hydroxyl group removal results in retention of the starting configuration in the final product. In view of these divergent results it seemed pertinent to investigate other Raney nickel catalyzed functional group hydrogenolyses from, if possible, a stereochemical viewpoint. To this end we herein report new observations regarding hydrogenolyses of hydroxyl, alkoxyl, amino and chlorine functions by the action of excess Raney nickel in refluxing ethanol.

It was previously stated[3] that ethyl D(−)-2-phenyl-2-hydroxypropionate[5] ($[\alpha]^{25}\text{D}$ −20.0°, 87% optically pure) was dehydroxylated to produce ethyl D(+)-2-phenylpropionate, $[\alpha]^{23}\text{D}$ 45.5° (ether), of over 90% optical purity, *i.e.*, with essentially no racemization. The latter figure was

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[1] W. A. Bonner, THIS JOURNAL, **74**, 1034 (1952).

[2] W. A. Bonner, *ibid.*, **74**, 5089 (1952).

[3] W. A. Bonner, J. A. Zderic and G. A. Casaletto, *ibid.*, **74**, 5086 (1952).

[4] W. A. Bonner, *ibid.*, **74**, 1033 (1952).

[5] K. Freudenberg, J. Todd and R. Seidler, *Ann.*, **501**, 199 (1933); E. Eliel and J. Freeman, THIS JOURNAL, **74**, 923 (1952).