parison with those from similar reactions will be deferred.

Behavior of Methyl 2,4,6-Trimethoxybenzoate.—Examination of the spectrum of the methyl ester in perchloric acid at 10° (Fig. 3) show it to be essentially unchanged between 2 and 41.9% perchloric acid. There is presumably no ionization in this region and thus the methyl ester appears to be a weaker base than the corresponding carboxylic acid. In greater than 42% and up to 58.6% acid only a single ionization step is apparent. Although the new peak appears at about the same wave length as the peak for $RCO^{\oplus}$, this cannot be ionization to $RCO^{\oplus}$ in view of the following fact: the rate of decline of the spectrum in 52.9, 55.6 and 58.6% perchloric acid at 10° is extremely slow, much slower than for the carboxylic acid in the same medium at the same temperature. If the ester were appreciably converted to $RCO^{\oplus}$ (either directly or *via* hydrolysis to the acid) during the measurement of the spectrum, instant equilibration with rapidly decarboxylated species would have occurred.[16] The change in spectrum with acid percentage in this region thus must correspond to ester conjugate acid formation.[17] In 60.0% perchloric acid at 10° there is a slow induction period in the rate of spectral change. The rate then increases appreciably but does not follow first-order kinetics and does not attain the rate of decline in spectrum of the carboxylic acid in the same medium. The final spectrum is that of 1,3,5-trimethoxybenzene. Ionization to acylonium ion therefore does occur in 60% acid but it is slow, and is incomplete at the first spectral reading (ϵ = 19.14 at 295 mμ). The decline in spectrum is a consequence of rapid equilibration of the $RCO^{\oplus}$ formed with $RCO_2H_2^{\oplus}$ and RCO_2H followed by decarboxylation. A spectrum taken in 60% perchloric acid at −10° (Fig. 3, ϵ = 16.38 at 295 mμ) did not change with time and is presumed to contain no acylonium ion. In 80% sulfuric acid the spectrum is very intense and the same at first reading as that of the carboxylic acid in the same medium. The rate of decline of this spectrum is the same as for the carboxylic acid. Therefore, in 80% sulfuric acid, the ester has been converted rapidly and completely to acylonium ion.

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(16) Reversal of the equilibrium $RCO_2CH_3H^{\oplus} \rightleftarrows RCO^{\oplus} + CH_3OH$ would be negligible due to the low concentration of methanol compared with water.

(17) Whereas $RCO_2CH_3H^{\oplus}$ and $RCO^{\oplus}$ have about the same λ_{max} although the intensities differ greatly, the presumed $RCO_2H_2^{\oplus}$ has a lower λ_{max} (Fig. 2) than does $RCO^{\oplus}$.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF WASHINGTON]

The Effect of Ring Strain on the Ultraviolet Spectra of α,β-Unsaturated Carbonyl Compounds

BY W. M. SCHUBERT AND W. A. SWEENEY[1]

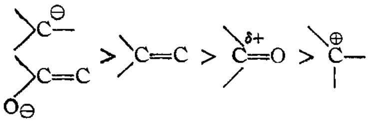
RECEIVED JULY 30, 1954

A qualitative correlation has been made of λ_{max} values for α,β-unsaturated carbonyl compounds in which there is strain in one part of the chromophore. The excitation energy has been found to be lower for compounds in which the electron displacement in the spectrally excited state is away from a site of strain; it is generally greater for compounds in which the electron displacement is toward a site of strain.

The following general rule is enunciated to correlate and explain the effect of ring size on the λ_{max} values for the E-band (excitation to a state with greater contribution of dipolar forms[2]) of compounds such as listed in Table I. If a conjugated chromophore is "strained" in one part, then excitation to a dipolar type excited state will occur at longer wave length (lower energy) relative to the corresponding unstrained molecule if electron displacement in the excited state is away from the region of strain. Conversely, absorption will occur at a shorter wave length if displacement is toward that region. This rule can be expected to hold only when the chromophores being compared have the same configuration and in the absence of appreciable steric inhibition of conjugation.

One fundamental assumption of the rule is that during excitation of a chromophore by light absorption, there is no time for the movement of nuclei. This assumption, though often overlooked, is involved in the Franck-Condon principle and is commonly invoked.[3] It is then presumed that removal of electrons from a site of strain in the excitation by light decreases the strain energy in the excited state over that in the ground state. Conversely, addition of electrons to a site of strain increases the strain energy in the excited state over that of the ground state. Care must be exercised in comparing relative ultraviolet excitation energies with rate or equilibrium data. In the latter instances, a re-orientation of atomic nuclei, both in the reacting molecules and surrounding solvent, can take place from ground to transition state or final state.

The basic assumption that the difference in energy between a "strained" and unstrained molecule decreases as the electrons are removed from the site of strain has a corollary. This is that the energy required for a certain angular displacement of attached bonds decreases in the following order



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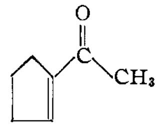
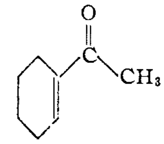
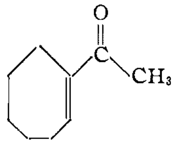
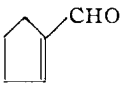
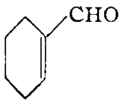
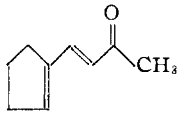
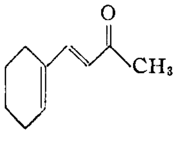
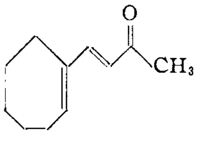
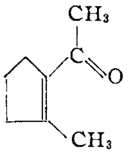
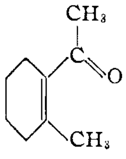
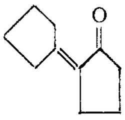
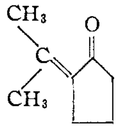
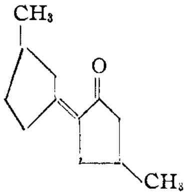
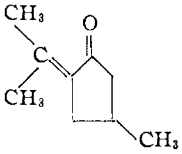
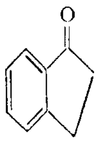
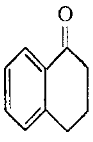
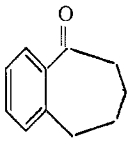
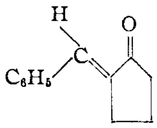
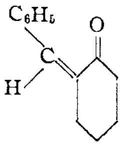
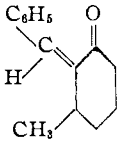
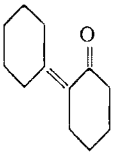
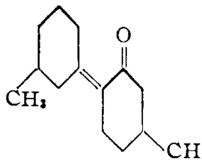
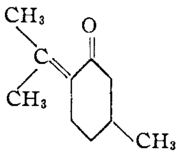
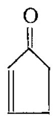
(1) Proctor and Gamble Fellow, 1952–1953.

(2) See, *e.g.*, K. Bowden and E. A. Braude, *J. Chem. Soc.*, 1068 (1952).

(3) See *e.g.*, N. S. Bayliss, *J. Chem. Phys.*, **18**, 292 (1950).

TABLE I

THE λ_{max} ($m\mu$) OF THE ULTRAVIOLET ABSORPTION OF SEVERAL CYCLIC α,β-UNSATURATED CARBONYL COMPOUNDS[a]

					
Cpd. no.	1	2	3	4	5
λ_{max}	239	232, 233, 233.5	236 240[b]	237	229
ϵ_{max}	13000	13000, 12500, 9650	10000 9000	12000	12000
Ref.	5	5, 9, 10	5	5	5
					
Cpd. no.	6	7	8	9	10
λ_{max}	281	281 273[b]	282 289[b]	253	249
ϵ_{max}	21000	21000 18500	16500 15000	10010	6890
Ref.	5	5	5	6	6
					
Cpd. no.	11	12	13	14	15
λ_{max}	259	252	259	254	244
ϵ_{max}	10790	3630?	10070	9950	12300
Ref.	7	7, 6	7	7	8
					
Cpd. no.	16	17	18	19	20
λ_{max}	248	247	298.5	290	288, 289
ϵ_{max}	12200	8600	17000	11300	15850
Ref.	8	8	7	7	11
					
Cpd. no.	21	22	23	24	25
λ_{max}	255, 257.5	254	253, 252, 245,[d] 242.5,[d] 245[e]	218	224.5
ϵ_{max}	6300, >800[c]	6750	6920, 6500, 5130, 8910, 5170	9500	10300
Ref.	7, 12	6	14, 15, 17, 13, 16, 17, 18	19	19

[a] All spectra in alcohol except as noted. [b] Inflection point. [c] Predominance of an unconjugated isomer suggested.[12] [d] In hexane. [e] In cyclohexane.

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(4) A. D. Walsh, *Disc. Faraday Soc.*, **2**, 18 (1947).

(5) I. Heilbron, E. R. H. Jones, J. B. Toogood and B. C. L. Weedon, *J. Chem. Soc.*, 1827 (1949).

(6) R. B. Turner and D. M. Voitle, THIS JOURNAL, **73**, 1403 (1951).

(7) H. S. French and L. Wiley, *ibid.*, **71**, 3702 (1949).

(8) Measured in these laboratories in a Beckman DU instrument.

(9) K. Dimroth and O. Lüderitz, *Chem. Ber.*, **81**, 242 (1948).

(10) A. E. Gillam and E. S. Stern, "An Introduction to Electronic Absorption Spectroscopy," Edward Arnold Ltd., London, 1954, p. 90 ff.

(11) H. S. French and M. E. T. Holden, THIS JOURNAL, **67**, 1239 (1945).

(12) L. K. Evans and A. E. Gillam, *J. Chem. Soc.*, 815 (1941).

(13) R. G. Cooke and A. K. MacBeth, *ibid.*, 1408 (1938).

(14) Y. R. Naves and G. Papazian, *Helv. Chim. Acta*, **25**, 1023 (1942).

(15) W. Menschick, I. H. Page and K. Bossert, *Ann.*, **495**, 225 (1932).

(16) J. Savard, *Bull. soc. chim.*, **43**, 524 (1928).

(17) A. E. Gillam, J. I. Lynas-Gray, A. R. Penfold and J. L. Simonsen, *J. Chem. Soc.*, 60 (1941).

(18) T. M. Lowry, D. M. Simpson and C. B. Allsopp, *Proc. Roy. Soc.* (*London*), **A163**, 486 (1937).

(19) H. J. Dauben, Jr., E. A. Youngman and H. Ringold, private communication.

The carbonyl group is so placed because the carbonyl carbon has a partial plus charge. This order is in agreement with Walsh's idea[4] that greater electronegativity is associated with greater s-character to the carbon valences and hence with less directional bonds.

Strain in C=C.—A comparison of the cyclopentene *vs.* the cyclohexene derivatives of Table I (compare compounds 1 and 2, 4 and 5, 6 and 7, 9 and 10) discloses that all the cyclopentene derivatives absorb at distinctly longer wave lengths than the cyclohexene derivatives. This is in agreement with the rule since the olefinic system is strained in the cyclopentene derivatives and presumably relatively free of strain in the cyclohexene derivatives.[20] Compounds 1 through 8 are assumed to be in the s-*trans* configuration since (a) this is an energetically more favorable configuration for the pure chromophore and (b) steric hindrance to coplanarity of the chromophore parts would appear to be greater, if anything, in the s-*cis* than the s-*trans* configuration.[6,21] Compounds 9 and 10, indicated to be in the s-*cis* configuration,[6] follow the rule equally well. There may be slight steric inhibition of resonance in 9 and particularly 10, but when inhibition is small it is thought to have little effect on the wave length of absorption.[6]

The rule also is followed in a comparison of 11 and 12 and 13 and 14. In these compounds there is, of course, an electron displacement in the excited state toward a site of strain (the carbonyl group of the five-membered ring), but this portion of the chromophore is being kept structurally the same. Steric inhibition of resonance may be playing a role in the displacements of $\lambda_{\max}$ between 11 and 12. The low ϵ of 12 is indicative of steric inhibition of resonance, but appears anomalous when compared to the ϵ of 14.

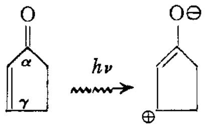
If the general rule is valid, it would appear that there would be some strain in the seven-membered rings of compound 3, 8 and possibly 17. While a double bond (or carbonyl group) located in a five-membered ring would be strained, it is not so obvious for seven-membered rings. No clear cut data could be found concerning the presence or absence of strain in cycloheptene compounds. Examination of Fisher–Taylor–Hirschfelder models is a poor substitute for experimental data; nevertheless, the models do indicate the degree of hydrogen crowding is much more pronounced in the cycloheptene than in the cyclohexene derivatives. This crowding, if it exists, may be enough to cause deformation of the normal bond angles about the double bond.

Changing Strain in C=O.—A thorough literature search revealed no exception to the correlation that strain in the olefinic portion of α,β-unsaturated carbonyl compounds is associated with lower excitation energy. That strain in the carbonyl portion is associated with higher excitation energy is not as firmly established. However, in agreement with the rule, indanone (compound 15) absorbs at a lower wave length than α-tetralone (compound 16). In indanone the electron displacement on excitation is toward a site of strain (the carbonyl group). There is also some relief of strain at the 9-position since this site becomes more positive in the excited state. However, the positive charge in the excited state is well distributed to other sites and thus the relief of strain at the 9-position is presumed small in comparison to the increase in strain at the carbonyl.

The $\lambda_{\max}$ values for compounds 21, 22 and 23 appear to be generally too low in comparison with compounds 12 and 14 to support the rule. However, many, if not all of the samples of 21, 22 and 23 contained varying amounts of other isomers, such as β,γ-unsaturated isomers[12,15,16] (these would lower $\epsilon_{\max}$) and endocyclic α,β-unsaturated isomers[14,17,22] (these would lower $\lambda_{\max}$). The presence of isomers would account for the wide variance in reported spectral data. Complete separation of isomers would be difficult by the methods used, distillation or *via* the bisulfite addition compounds.[13–18] At least partial equilibration with other isomers could occur during the decomposition of a particular bisulfite addition compound under acidic conditions and possibly under basic conditions. Thus, in the case of α-pulegone (compound 23) and its isomers, a trace of acid at room temperature was sufficient to cause isomerization of a mixture rich in β,γ-unsaturated isomer to a mixture rich in α,β-unsaturated isomers.[15]

A comparison of compound 18 with 19 and 20, for purposes of assessing the strain effect, is probably not valid. The difference in $\lambda_{\max}$ is probably due to 18 being the stable *trans* isomer whereas 19 and 20 are probably *cis*. Models indicate the *cis* forms of 20 and particularly 21 are sterically more favored. The unhindered *trans* forms of benzalacetone and benzalacetophenone are more stable than the *cis*, although appreciable *cis*-isomer can be formed with the *trans*-isomer.[22,23] For *trans*-benzalacetophenone in isoöctane, two maxima are given, at 298 mμ (λ 23,700) and at 225 mμ (ϵ 12,200); for the *cis* isomer two maxima also appear, at 289 mμ (8,900) and at 247 mμ (14,000).[24]

Cycloalkenones and Dienes.—Qualitatively, it would be difficult to predict on the basis of strain alone whether cyclopentenone (compound 24) or cyclohexenone (compound 25) would absorb at a higher wave length. In the ground state of the highly strained cyclopentenone, the distribution of the total distortion is difficult to ascertain, although perhaps the angle α is distorted more than γ (see corollary).



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[20] As pointed out by the referee, a difference of 7mμ in $\lambda_{\max}$ between compounds 1 and 2 corresponds to a difference in excitation energy of 3.6 kcal./mole. C. W. Becket, N. K. Freeman and K. S. Pitzer, THIS JOURNAL, **70**, 4227 (1948), recently have calculated the strain energy (including both the bending and the torsional strain) of cyclopentene to be 9.8 kcal./mole, that of cyclohexene, 1.6 kcal./mole.

[21] E. A. Braude, E. R. H. Jones, H. P. Koch, R. W. Richardson, F. Sondheimer and J. B. Toogood, *J. Chem. Soc.*, 1890 (1949).

[22] R. E. Lutz and D. F. H. Hinckley, THIS JOURNAL, **72**, 4091 (1950).

[23] R. E. Lutz, C. R. Bauer and R. H. Jordan, *ibid.*, **72**, 4300 (1950).

[24] L. P. Kuhn, R. E. Lutz and C. R. Bauer, *ibid.*, **72**, 5058 (1950).

In going to the excited state, the energy change relative to an unstrained example would be decreased at γ and increased at α (*i.e.* $=\underset{\alpha}{C}{<}^{O^{\ominus}}$ less easily distorted than $\alpha\ {>}C{=}O$).[25] It can only be guessed whether there would be a net increase or decrease in strain on excitation, compared to cyclohexenone. It would appear difficult, however, to account for the *large* decrease in λ_{max} for cyclopentenone as compared to cyclohexenone mainly on the basis of a net increase in strain for the former. Cyclopentenones in general absorb at a lower wave length than cyclohexenones.[10]

This discussion has assumed that one can estimate which ionic forms are more important in the spectrally excited hybrid state. With dienes, the treatment would be more obscure than with α,β-unsaturated carbonyl compounds. It may be that with dienes or similar chromophores in which polarization may occur with about equal probability in either direction in the excited state, the introduction of strain into one part of the chromophores would produce a splitting of the unstrained absorption band into two bands. One of these bands (at shorter wave length) would correspond to polarization toward the site of strain, and the other (at longer wave length) to polarization away from the site of strain. Splitting of diene absorption bands has been attributed to superimposed vibrational levels.[26a,b]

The possibility that strain in the 1,4-cyclohexadiene ring of 1-acetylcyclohexadiene-1,4 might contribute to the increase in $\lambda(\lambda_{max} = 245, \epsilon\ 4{,}000)$ over that of 1-acetylcyclohexene,[27a,b,c] compound 2, was considered. However, there appears to be little, if any, strain in this ring system.

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[25] No doubt the strain problem is even more complicated than this; fixing attention only on the change in strain at α and γ is probably an oversimplification.

[26] (a) E. P. Carr, L. W. Pickett and H. Stucklen, *Rev. Mod. Phys.*, **14**, 260 (1942); (b) L. Dorfman, *Chem. Revs.*, **53**, (1953).

[27] (a) D. J. Cram and H. Steinberg, THIS JOURNAL, **73**, 5691 (1951); (b) K. Bowden and E. R. H. Jones, *J. Chem. Soc.*, 52 (1946); (c) E. A. Braude, E. R. H. Jones, F. Sondheimer and J. B. Toogood, *ibid.*, 607 (1950).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF PURDUE UNIVERSITY]

Rates and Isomer Distribution in the Mercuration of Benzene and Toluene. A Proposed Extension of the Quantitative Relationship Governing Isomer Distribution in Aromatic Substitution[1]

BY HERBERT C. BROWN AND CHARLES W. MCGARY, JR.[2]

RECEIVED JUNE 18, 1954

A detailed study has been made of the perchloric acid catalyzed mercuration of benzene and toluene in glacial acetic acid at 25, 50 and 75°. Under the experimental conditions the isomer distribution in toluene changes with time and approaches a statistical distribution of the three tolylmercuric acetates. By extrapolating the data to zero time it has been established that the three isomers are formed at 25° with the distribution: *ortho*, 21.0 ± 0.5; *meta*, 9.5 ± 0.5; *para*, 69.5 ± 1.0%. At 50° the distribution is: *ortho*, 20.0; *meta*, 11.5; *para*, 68.5%. At 75° the observed distribution is: *ortho*, 18.3; *meta*, 12.6; *para*, 69.1%. At 25° both competition experiments and absolute rate measurements lead to a toluene/benzene reactivity of 7.9 ± 0.2. At 50 and 75° this ratio changes to 7.0 and 5.9, respectively. These data are consistent with the linear relationship previously proposed to account for isomer distribution in toluene substitutions and thereby remove a discrepancy provided by the mercuration data previously available. It now has been established that the linear relationship satisfactorily accounts for isomer distribution in toluene substitution for isopropylation, sulfonylation, mercuration, nitration, chloromethylation and chlorination. An extension of the theory is proposed to permit the quantitative correlation of isomer distribution in the substitution of all benzene derivatives.

The high proportion of meta isomer formed in the alkylation of toluene under non-isomerizing conditions has been considered to be an anomalous characteristic of the Friedel–Crafts reaction.[3,4] In an earlier paper it was proposed that no anomaly was involved in this reaction, that the high percentage of *meta* isomer is to be attributed to the high activity and consequent low selectivity of the substituting species.[5] The relative rate of substitution of toluene to benzene was adopted as a measure of the activity or selectivity of the substituting agent. A simple quantitative relationship was then demonstrated for a number of reactions between this activity of a given substituting agent and the relative amounts of substitution in the *para* and *meta* positions of toluene.

However, in the case of mercuration the available data[5,6] neither agreed with each other, nor with the proposed generalization.[7] Klapproth and Westheimer[6] reported that in glacial acetic acid with perchloric acid as catalyst, toluene is mercurated by mercuric acetate to give 6% of the *meta* isomer at 25°. Data from this Laboratory subsequently indicated 12% *meta* under similar conditions.[5] In the former case a radiochemical technique was employed in establishing orientation, whereas infrared analysis was utilized in the latter. Furthermore, the toluene/benzene reactivity of 30, reported in

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[1] Directive Effects in Aromatic Substitution. IV. Previous publications in this series: THIS JOURNAL, **73**, 5605 (1951); **75**, 6292 (1953); **76**, 605 (1954).

[2] American Cyanamid Fellow, 1953–1954.

[3] C. C. Price, "Organic Reactions," Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1946, Chapt. I.

[4] A. W. Francis, *Chem. Revs.*, **43**, 257 (1948).

[5] H. C. Brown and K. L. Nelson, THIS JOURNAL, **75**, 6292 (1953).

[6] W. J. Klapproth and F. H. Westheimer, *ibid.*, **72**, 4461 (1950).

[7] The mercuration of toluene has been carried out under a variety of conditions and the percentage of *meta* isomer formed in these reactions varies from 6 to 21. For a summary of the available data, see ref. 5.