[CONTRIBUTION FROM THE NAVAL STORES RESEARCH SECTION][1]

The Effect of Strained Rings on Ultraviolet Absorption Spectra

BY R. N. MOORE AND G. S. FISHER

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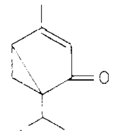
On the basis of ultraviolet spectral data obtained on various derivatives of the pinenes, it is suggested that Woodward's rule for the prediction of the position of ultraviolet absorption maxima in conjugated dienes and enones be amended to provide the addition of 15 mμ when part of the chromophoric system is included in a bicyclo[3.1.1]heptyl ring.

The various rules for prediction of the position of the ultraviolet absorption maxima for compounds containing conjugated double bond systems[2] have been applied with notable success to acyclic compounds and cyclic compounds containing six-membered rings. However, anomalies have been observed in the case of cyclopentenones[3] and in compounds containing a cyclopropane ring attached to the chromophoric system.[4] Little work has been available on the spectral characteristics of chromophoric systems having a cyclobutyl substituent, or of systems including a portion of a highly strained bicyclic ring.

In the course of work on the autoxidation of turpentine, several pinene derivatives containing a cyclobutane ring attached to a double bond were prepared.[5] As shown in Table I, and Fig. 1, these compounds exhibit anomalous ultraviolet absorption maxima, in that there is a bathochromic shift of 15 ± 3 mμ from the predicted value. It is suggested that in predicting the positions of ultraviolet absorption maxima using the existing rules,[2] 15 mμ should be added if part of the chromophoric system is in a bicyclo[3.1.1]heptyl ring.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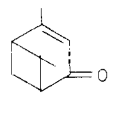
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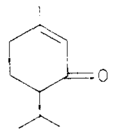
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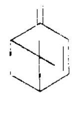
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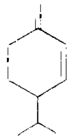
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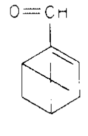
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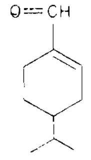
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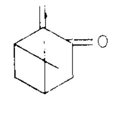
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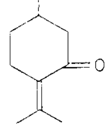
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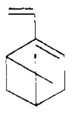
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TABLE I

BATHOCHROMIC EFFECT OF THE PINENE RING

	Compound	$(\lambda_{\max}^{\text{alc}}$ mμ) Predicted[2]	Obsd.	Dev.	$\epsilon_{\max}$	Ref.
I	Umbellulone	235	265	+30	3,290	6
II	Verbenone	235	253	+18	6,840	
III	Piperitone	235	235.5	+ 0.5	17,780	4
IV	Verbenene	232	245.5	+13.5	10,550	
V	β-Phellandrene	232	231.2	− 0.8	19,300	7
VI	Myrtenal	230	247	+17	8,900	
VII	Phellandral	230	228.5	− 1.5	18,600	8
VIII	Pinocarvone	230	242	+12	5,240	
IX	Pulegone[10]	252	252	0	6,500	9
X	Nopadiene	227	243	+16	15,200	

A similar shift of 30 mμ has been observed[4] in umbellulone (I), which is a cyclopropyl analog of verbenone (II). After studying a number of other cyclopropyl compounds, Eastman[6] has concluded that this shift is due to a conjugative effect when the cyclopropyl ring is at the end of a chain of conjugation, not to cross conjugation as suggested by Gillam and West.[4]

This explanation cannot be applied in the present case since the cyclobutane ring is not in a position to extend conjugation in myrtenal (VI), pinocarvone (VIII) or nopadiene (X). The cyclobutane ring is cross-conjugated with the chromophoric system in all cases; that is, it is attached to one of the two central carbon atoms of the conjugated system. However, the limited amount of data given by Fieser[11] indicates that cross conjugation of a carbon–carbon double bond with the keto group of an enone has no effect on the position of the absorption maximum while similar conjugation with a homoannular diene results in a hypsochromic shift. Hence, it seems very unlikely that the observed bathochromic shift can properly be attributed to cross conjugation, particularly since the cyclobutyl group in methyl cyclobutyl ketone produces no more bathochromic shift than the isobutyl group in methyl isobutyl ketone.[12]

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(1) One of the laboratories of the Southern Utilization Research Branch, Agricultural Research Service, U. S. Department of Agriculture.

(2) (a) R. B Woodward, THIS JOURNAL, **63**, 1123 (1941); **64**, 72, 76 (1942); (b) L. K. Evans and A. E. Gillam, *J. Chem. Soc.*, 565 (1943).

(3) (a) A. E. Gillam and T. F. West, *ibid.*, 811 (1941); (b) 483, 486 (1942).

(4) A. E. Gillam and T. F. West, *ibid.*, 95 (1945).

(5) R. N. Moore, C. Golumbic and G. S. Fisher, THIS JOURNAL, **78**, 1173 (1956).

(6) R. H. Eastman, *ibid.*, **76**, 4115 (1954).

(7) J. B. Davenport, M. D. Sutherland and T. F. West, *J. Applied Chem.* (*London*), **1**, 527 (1951).

(8) R. G. Cooke and A. K. Macbeth, *J. Chem. Soc.*, 1408 (1938).

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

(10) Since no ultraviolet spectral data for an authentic methylene or ethylidene cyclohexanone was found in the literature, the isopropylidene compound is included as the closest analog to pinocarvone.

(11) L. F. Fieser and M. Fieser, "Natural Products Related to Phenanthrene," 3rd Ed., Reinhold Publ. Corp., New York, N. Y., 1949, pp. 187, 193.

(12) A. E. Gillam and E. S. Stern, "An Introduction to Electronic Absorption Spectroscopy in Organic Chemistry," Arnold, London, 1954, p. 48.

A bathochromic shift of similar magnitude with respect to the predicted position has been observed by Bailey and Lawson[13] for dimethylenebicyclo[2.2.1]heptane. In this case the cyclohexyl analog exhibits a major hypsochromic shift.[14] The shifts are attributed to rigid coplanarity in the bicyclo compound and non-coplanarity in the cyclohexyl compound. Leonard and Mader[15] have used the same explanations for hypsochromic shifts in cyclic α-diketones and a bathochromic shift to 466 mμ for camphorquinone. Acyclic α-diketones which are not highly substituted absorb below about 435 mμ[16] and are presumably nearly coplanar.

Although most of the compounds studied in the present investigation are not free to rotate about the central bond of the chromophore and may be assumed to have a rigidly coplanar chromophore, myrtenal (VI) and nopadiene (X) are as free to rotate about this bond as are the monocyclic analogs. Furthermore, a high degree of coplanarity should be accompanied by a high molecular extinction coefficient.[9] In all cases the compounds of the pinene series have lower coefficients than their monocyclic analogs. Hence, the observed spectral characteristics of the pinene derivatives cannot be explained on the basis of rigid coplanarity.

Since the spectra of the corresponding *p*-menthene derivatives are entirely normal, the observed shift is obviously associated with the closure of the cyclobutane ring. The major effect of such closure is to introduce strain in the molecule. On the basis of the combustion data of Hawkins and Erikson[17] this strain amounts to about 25 kcal./mole. Obviously much of this energy is used in stretching the C–C bonds and distorting the C–C–C bond angles of the cyclobutane ring; but distortion of the length of the bond or bonds which link this ring to the chromophore and of the bond angles involving these bonds is also to be expected. Lewis and Calvin[18] have pointed out that strain moves some electron pairs to positions where less energy is required for excitation. Hence, it seems reasonable to assume that the observed bathochromic shifts in the pinene derivatives are due to localization of part of the strain energy of the bicyclic ring in such a manner as to reduce the energy of excitation of the chromophore by about 7.7 kcal./mole. This might occur through shortening of the single bond of the chromophore, but final determination of the mechanism by which the strain produces the reduction in energy of excitation can probably not be made until the various force constants, bond lengths and bond angles have been determined for members of the pinane series.

The explanation of the bathochromic shift reported for bicyclo[2.2.1]heptanes[13,15] on the basis of rigid coplanarity is not entirely satisfactory. If it is correct, one would expect a similar shift for dimethylenecyclopentane, and for dimethylenecyclohexenes, which should also have a coplanar chromophore. However, Bailey and co-workers[19] have studied the ultraviolet spectra of these compounds and observed a hypsochromic shift which is even larger than that observed for dimethylenecyclohexane. In both camphorquinone, and dimethylenebicyclo[2.2.1]heptane, the two central carbon atoms of the chromophore are attached to a strained ring, and the decrease in energy of excitation in going from the cyclohexyl analog to the bicycloheptane is very nearly the same in both cases. Hence it is suggested that, as in the pinenes, the observed shifts are a consequence of the bicyclic ring strain. The inadequately explained hypsochromic shift in the monocyclic dimethylene compounds complicates any quantitative treatment of the bathochromic shift. If the absorption maximum predicted by Woodward's rule is used as the reference point, there is an 11 mμ shift in the dimethylenebicyclo[2.2.1]heptane, which is slightly less than that observed in the pinenes; but if the absorption maximum for dimethylenecyclohexane is the reference point, the shift is 28 mμ.

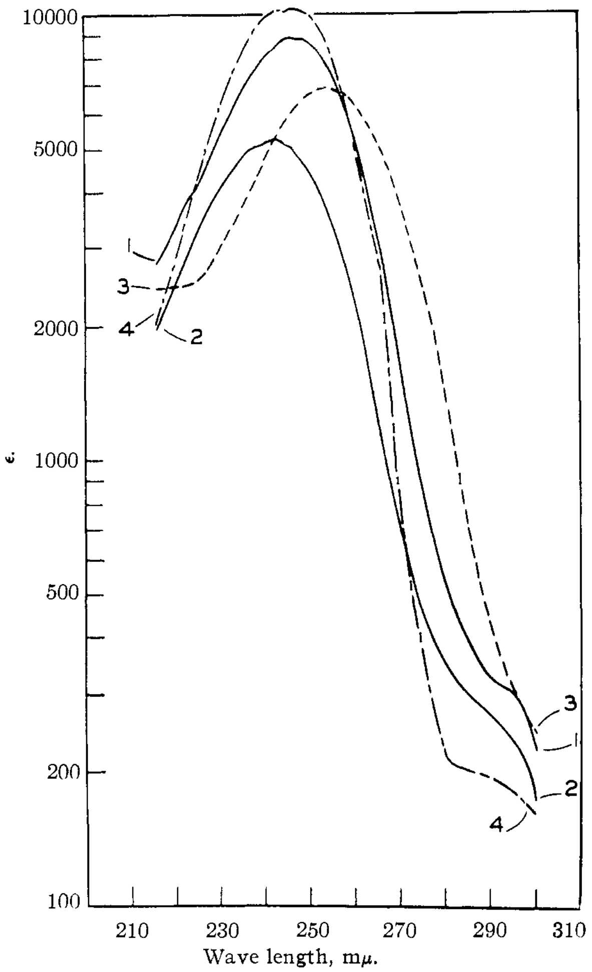

Fig. 1.—Ultraviolet absorption spectra in ethanol: 1, myrtenal; 2, pinocarvone; 3, verbenone; 4, verbenene.

Similarly, it seems probable that at least part of the bathochromic shift in umbellulone is due to

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[13] W. J. Bailey and W. B. Lawson, THIS JOURNAL, **77**, 1607 (1955).

[14] W. J. Bailey and H. R. Golden, *ibid.*, **75**, 4780 (1953).

[15] N. J. Leonard and P. M. Mader, *ibid.*, **72**, 5394 (1950).

[16] N. J. Leonard, H. A. Laitinen and E. H. Mathis, *ibid.*, **75**, 3303 (1953).

[17] J. E. Hawkins and W. T. Erikson, *ibid.*, **76**, 2669 (1954).

[18] G. N. Lewis and M. Calvin, *Chem. Revs.*, **25**, 273 (1939).

[19] (a) W. J. Bailey and W. R. Sorenson, THIS JOURNAL, **76**, 5421 (1954); (b) W. J. Bailey and J. Rosenberg, *ibid.*, **77**, 73 (1955); (c) W. J. Bailey, J. Rosenberg and L. J. Young, *ibid.*, **77**, 1163 (1955).

bicyclic ring strain. Eastman and Freeman[20] have recently shown that the cyclopropane ring does not transmit conjugation when it connects a vinyl group with a carbonyl group. As yet no monocyclic compounds of the type $(CH_2)_n$—C═C—C═, in which n is 3 or 4, have been studied; so the effect (if any) of a strained substituent on an acyclic chromophore is not known. Hence, it is not certain whether the bicyclic structure is required to produce the bathochromic shift or whether the strained ring substituent is sufficient.

Experimental

Verbenone.—Verbenone was obtained from autoxidized α-pinene[21] by fractional distillation and subsequent purification through the semicarbazone, m.p. 208–209°. Hydrolysis of the semicarbazone by phthalic acid gave *l*-verbenone, $n^{20}\text{D}$ 1.4961, d^{20}_4 0.9731, $[\alpha]^{25}\text{D}$ −253.5°.

Verbenene.—Redistillation of the lower boiling fractions from autoxidized *l*-α-pinene gave *d*-verbenene, $n^{20}\text{D}$ 1.4997, d^{20}_4 0.8818, $[\alpha]^{25}\text{D}$ +94.2°.[22] Its identity was confirmed by comparison of the infrared spectrum with the spectrum of verbenene prepared by dehydration of verbenol by acetic anhydride.[23]

Pinocarvone.—Treatment of β-pinene in ethanol with selenium dioxide[24] gave an oil from which pinocarvarone was separated by way of the sodium bisulfite addition compound. Its identity is correct in accordance with the findings of Schmidt.[25]

The ultraviolet spectra were obtained on ethanol solutions using the Beckman Model DU spectrophotometer.

Acknowledgment.—The authors are indebted to Dr. J. P. Bain for the samples of myrtenal and nopadiene used in this study.

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[20] R. H. Eastman and S. K. Freeman, THIS JOURNAL, **77**, 6642 (1955).

[21] A. Blumann and O. Zeitschel, *Ber.*, **46**, 1178 (1913).

[22] C. Paquot, *Compt. rend.*, **209**, 171 (1939).

[23] A. Blumann and O. Zeitschel, *Ber.*, **54**, 887 (1921).

[24] W. D. Stallcup and J. E. Hawkins, THIS JOURNAL, **63**, 3339 (1941).

[25] H. Schmidt, *Ber. Schimmel & Co., Akt.-Ges.*, 56 (1941).

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The Nitration of Cyclic Ketones with Alkyl Nitrates[1]

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The nitration of cyclic ketones such as cyclopentanone, cyclohexanone, cycloöctanone and α-tetralone with alkyl nitrates in the presence of base affording the salts of cyclic α,α′-dinitro ketones has been investigated. The influence of base, reaction temperature, reaction time and mode of addition on the course of the reaction was studied and the yields of the salts were greatly improved.

The reaction of an alkyl nitrate with an active methylene compound in the presence of an alkali metal (or more frequently, an alkali metal alkoxide) to give the salt of a nitro compound with the nitro group attached to the active methylene group, has been known for many years.[2] However, very little work is reported on this nitration with cyclic ketones. Straus[3] and later Shriner[4] reported the nitration of α-tetralone and Wieland[5] extended the reaction to cyclopentanone and cyclohexanone.

The dinitration of cyclic ketones has been reexamined as part of a program to determine the scope of the reaction. Cyclopentanone was chosen as a model compound for the study of the effect of the reaction variables. This compound offered the advantage that its nitration product dipotassium 2,5-dinitrocyclopentanone (I) is not hygroscopic and can be purified readily. Since the nitration products of the other ketones turned out to be highly hygroscopic and difficult to purify, a suitable derivative had to be found on which the over-all yield could be based and which could be used for all the ketones which were nitrated. Conversion of compounds of type I to cyclic α,α′-dinitro ketones was unsatisfactory because the latter underwent decomposition with the evolution of oxides of nitrogen at room temperatures.[6] The tetrabromodinitro paraffins (II), which result from the reaction[7] of I with bromine in the presence of base, were found to be suitable derivatives. The yields throughout this investigation are expressed as II and are based on the starting ketone.

We found that the ring opening step gave a purer product if freshly prepared potassium hypobromite was employed as the brominating agent.

Compound I also was converted readily to 1,1,-4,4-tetrachloro-1,4-dinitrobutane with calcium hypochlorite.

In preliminary experiments, the nitration of cyclopentanone by the method of Wieland[5] (with ethyl nitrate and potassium ethoxide in a mixture of ethanol and diethyl ether) gave a low yield (7%) of II. The majority of the ketone was lost in the formation of tars, and if too large an excess of ethanol was used, the only product was a tar. These results indicate that the first step in the alkaline nitration reaction of cyclopentanone is the formation of the enolate anion. It seemed probable that the anion is an intermediate for both the nitration reaction and the self-condensation reaction which leads to the formation of tars. If this assumption were correct, it would be advantageous to employ: (1) a non-protonic solvent, (2) to use a stronger base than potassium ethoxide and (3) to

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[1] From the Ph.D. thesis of James W. Shepherd, Purdue University, 1954. Paper presented before the XIVth International Congress of Pure and Applied Chemistry, July 21–27, 1955, Zurich, Switzerland.

[2] For a thorough survey of the literature, reference is made to "The Chemistry of Nitrate Esters" by R. Boschan, R. T. Merrow and R. W. Van Dolah, *Chem. Revs.*, **55**, 485 (1955).

[3] F. Straus and W. Ekhard, *Ann.*, **444**, 146 (1925).

[4] R. L. Shriner and W. H. Horn, THIS JOURNAL, **55**, 4652 (1933).

[5] H. Wieland, P. Garbsch and J. J. Chavin, *Ann.*, **461**, 295 (1928).

[6] 2,5-Dinitrocyclopentanone was stable only at Dry Ice temperature.

[7] K. Klager, *J. Org. Chem.*, **20**, 646 (1955).