Organic and Biological Chemistry

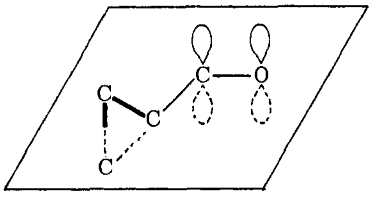
The Ultraviolet Spectra of Cyclopropyl Conjugated Ketones[1]

William G. Dauben and Gilbert H. Berezin

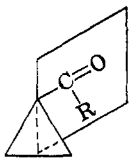
Contribution from the Department of Chemistry, University of California, Berkeley, California 94720. *Received February 3, 1967*

Abstract: A series of bicyclo[*n*.1.0]alkan-2-ones and spiro[*n*.2]alkan-2-ones were prepared and the ultraviolet spectra of the materials measured. The effects of ring size (*n*), of number and of position of alkyl substituents, of the dihedral angle relationship between the π orbitals of the carbonyl group and the formal bonds of the cyclopropane ring, and of the relationship of the planes of the π orbitals of the carbonyl group and the cyclopropane ring on the spectra were evaluated. A general rule for the prediction of the spectral maxima in bicyclic systems has been postulated.

The conjugative ability of a cyclopropane ring has been recognized for many years and the steric circumstances required for maximum electron delocalization in the electronically excited state have been postulated by various investigators.[2-5] These requirements are (1) the plane of the π bonds of a neighboring unsaturated system and the plane of the cyclopropane ring should be orthogonal to the same plane (*i.e.*, the so-called parallel relationship shown in **1**) and (2) the plane of the atoms of the π-bonding system should bisect the cyclopropane ring, *i.e.*, the π bonds of the unsaturated system should be symmetrically arranged with respect to the cyclopropane ring so that overlap occurs with two of the three bonds of the ring as shown in **2**. Experimental support for these generalizations have been given by Cromwell and Hudson,[4] and by Kosower and Ito.[5]



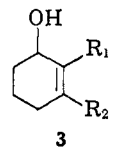
1



2

Recently, Goodman and Eastman[6] have studied conjugative effects in various phenylcyclopropane derivatives and they have concluded there is no preferred geometry for conjugation of a cyclopropane ring with a benzene ring, a conclusion opposite to one arrived at by the earlier workers in the case where a cyclopropane ring was conjugated with a carbonyl group. In order to obtain a better evaluation of the importance of the earlier defined steric requirements for appreciable overlap in the system with the more electronegative carbonyl group as well as the role played by inductive and strain effects, a series of related compounds containing the cyclopropane–carbonyl conjugative system has been prepared.

The general synthetic procedure employed, as illustrated below with the bicyclo[4.1.0]heptan-2-one (**5**), was to allow the Simmons–Smith reagent (iodomethylzinc iodide) to react with a cyclic allyl alcohol **3** and to oxidize the resulting cyclopropyl carbinol **4** to the related ketone **5**.[7,8] The ultraviolet spectra of the ketones were obtained using a Beckman DK-2A far-ultraviolet spectrometer under conditions where previously it has been shown that the spectrometer gives the true, not a spurious, maximum.[9]



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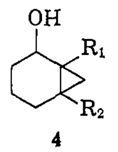

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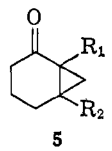
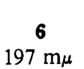
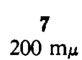
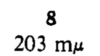


5

The ultraviolet spectra of **6**, **7**, and **8**, when compared with the spectra of their related α,β-unsaturated ketones,[10] indicate that the π–π^* transition energy (K band) is about 17–19 kcal/mole larger for the cyclopropyl conjugated system. The difference probably is mostly due to a higher energy of the electronic excited state. These data also indicate there is a small bathochromic variance in the position of the absorption band as the size of the carbonyl-containing ring changes from five to seven, a somewhat smaller difference than is found in the related enones.







	6	**7**	**8**
$\lambda_{max}^{H_2O}$	197 mμ	200 mμ	203 mμ
ϵ_{max}	5400	6000	5000

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[1] This work was partially supported by Grant No. GP 3890 from the National Science Foundation.

[2] A. D. Walsh, *Trans. Faraday Soc.*, **45**, 179 (1949).

[3] J. F. Music and F. A. Matsen, *J. Am. Chem. Soc.*, **72**, 5256 (1950).

[4] N. H. Cromwell and G. V. Hudson, *ibid.*, **75**, 872 (1953); R. S. Mohrbacher and N. H. Cromwell, *ibid.*, **79**, 401 (1957).

[5] E. M. Kosower and M. Ito, *Proc. Chem. Soc.*, 25 (1962).

[6] A. L. Goodman and R. E. Eastman, *J. Am. Chem. Soc.*, **86**, 908 (1964).

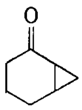
[7] W. G. Dauben and G. H. Berezin, *ibid.*, **85**, 468 (1963).

[8] W. G. Dauben, P. Laug, and G. H. Berezin, *J. Org. Chem.*, **31**, 3869 (1966).

[9] R. A. Micheli and T. H. Applewhite, *ibid.*, 27, 345 (1962). We are indebted to these investigators for some of the spectral results reported in this paper.

[10] The spectral values for Δ^2-cyclopentenone, Δ^2-cyclohexenone, and Δ^2-cycloheptenone are $\lambda_{max}^{H_2O}$ 224 mμ, 233 mμ, and 234 mμ, respectively.

The effect of the position and number of substituents in the bicyclo[4.1.0]heptan-2-one system is summarized in the following chart.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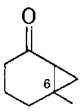
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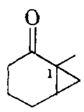
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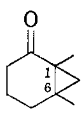
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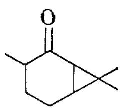
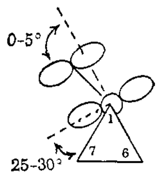
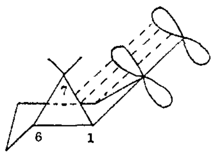

12

	7	9	10	11	12
$\lambda_{\max}^{H_2O}$	200 mμ	203 mμ	207 mμ	210 mμ	217 mμ
$\epsilon_{\max}$	6000	6300	5800	5600	5400

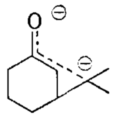
These data show that there is a substituent effect which varies with position. The effect is somewhat additive, *i.e.*, the bathochromic shift obtained with a 1,6-dialkyl derivative is about equal to the sum of the separate alkyl effects. Such a positional effect calls attention again to the role of preferred geometry and not just inductive factors in the conjugative ability of a cyclopropane ring with an adjacent carbonyl group. Of particular interest is the large effect of the geminal grouping on C-7 of the cyclopropane ring. In the fused ring system of the bicyclo[4.1.0] type where the larger ring assumes a twist conformation, C-1 and C-6 lie practically in the same plane (0–5° variance) as the atoms of the carbonyl group (see **13a**), and the π bonds of the carbonyl group form a dihedral angle of 25–30° with the C-1 and C-7 formal bond of the cyclopropane ring.[11] The centers of the bent bonds would be expected to form an angle of 15–20° with the formally written bonds.[12] With this arrangement of atoms, the C-1–C-7 bond of the cyclopropane ring overlaps the π orbitals of the carbonyl group better than the C-1–C-6 bond of the ring does (see **13b**). Since in the π–π* excited state, the α,β-unsaturated system is polarized so as to make the carbonyl oxygen more negative than the β-carbon (see **13c**) and since the cyclopropane ring acts as an electron donor[13] in such a system, it would be expected that substituents on C-7 which are electron donating would bring about a maximal bathochromic shift. Also, a substituent on C-1 would be expected to have a larger effect than a similar substituent on C-6, and this effect has been found.



13a

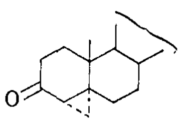


13b



13c

These spectral results also show that there is significant conjugative overlap between the cyclopropane ring and an adjacent unsaturated center when only one bond of the cyclopropane ring is involved, the so-called unsymmetrical arrangement. The position of the absorption maximum is also dependent upon the nature of the ring system into which the cyclopropyl conjugated ketone is incorporated. This effect is illustrated by consideration of the spectra of 4α,5- and 4β,5-methanocholestan-3-ones (**14** and **15**) in relation to the spectrum of the more flexible **9**. These spectra are reported in ethanol and, as shown with **9**, a hypsochromic shift of −7 mμ from the value in water was found, a value similar to that reported for α,β-unsaturated ketones.[14,15] The two more rigid steroids have maxima 4–8 mμ higher than the flexible **9** of similar substitution. For the lack of a better term, this bathochromic shift will be equated to a "rigidity effect" of +5 mμ later in the discussion. The difference in absorption maxima between **14** and **15** may be due, in part, to a greater rigidity of the conformation of **14**. However, in these two steroids the near-planar arrangement of the atoms of the carbonyl group and C-4 and C-5 of the steroid nucleus imposes a 30° dihedral angle relationship between the π bond of the carbonyl group and the formal bond (C-4 and C-4′) of the cyclopropane ring in **14** whereas in **15** the angle is reduced to 10°. If the degree of conjugative overlap is related to this dihedral angle relationship, then this could also be a factor contributing to the larger bathochromic shift found in **14**. At this time, this factor cannot be evaluated separately from the "rigidity effect" which might be due to release of ring strain in the excited state.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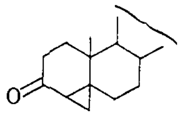
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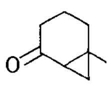
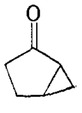

9

The other steric relationship which has been mentioned as a requirement for maximum electron delocalization in this system is that the plane of the π bonds of the carbonyl group and the plane of the cyclopropane ring should be orthogonal to the same plane ("parallel relationship"). In the endocyclic fused ring system discussed earlier, the plane of one of the groupings is tilted ∼15° from that of the other. However, when the cyclopropane ring is spiro to the ring containing the carbonyl group the orthogonality relationship is met. In support of this parallel or orthogonality requirement, Kosower and Ito[5] have reported the spiro[4.2]heptyl ketone **16** possessed a maximum 9 mμ higher than the related fused-ring analog **6**, an increase in interaction in the excited state estimated to be as much as 7–9 kcal/mole over the nonorthogonal arrangement. The spiro ketone **16**, however, also possesses a different dihedral angle relationship of the π orbitals of the carbonyl group and the cyclopropane ring than does the fused ring ketone **6**, and the contribution of this effect to the total bathochromic shift has now been evaluated. In this present work, the two spiro analogs in the cyclohexanone series as well as **16** were prepared. Ketones **17** and **18** possess the same orthogonality relationship of the planes of the orbitals as found in **16**, but the geometry (*i.e.*, the dihedral angle) of the overlap between the cyclopropane ring and the carbonyl group is similar to that found in the fused ring system. In the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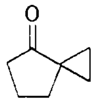
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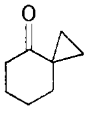
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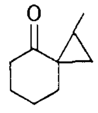
18

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(11) These angles were obtained using Dreiding models and should be viewed as rough approximations.

(12) C. A. Coulson and R. H. Goodwin, *J. Chem. Soc.*, 2851 (1962); 3161 (1963).

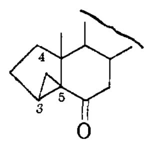
(13) L. A. Strait, R. Ketchum, D. Jambotkar, and V. P. Shah, *J. Am. Chem. Soc.*, **86**, 4682 (1964).

(14) L. F. Fieser and M. Fieser, "Steroids," Reinhold Publishing Corp., New York, N. Y., 1959, pp 15–16.

(15) It has been found, using 0.1-mm path length cells, that the limit of reliable measurement in ethanol is 193 mμ and in water is 183 mμ.

spiro[5.2]octane ketone **17**, a bathochromic shift of the same magnitude as reported by Kosower and Ito[5] for the lower homolog **16** was found, and in **18**, the expected substituent effect was noted. Thus, as pointed out by the earlier workers,[5] an orthogonal relationship of the planes of the orbitals appears to maximize conjugative overlap.

Although it has now been shown that there is significant conjugative overlap between the cyclopropane ring and the adjacent carbonyl group when the system has the unsymmetrical arrangement, the relationship between the dihedral angle formed between the plane of the π bonds of the carbonyl group and the formal bond of the cyclopropane ring and the extent of conjugation has not been fully evaluated. An indication of the potential importance of this angular relationship is obtained from the spectra of the two isomeric 3,5-cyclo-6-ketosteroids **19** and **20**. The ultraviolet maximum of **19**, after correcting for the solvent effect, is in good agreement with that of the similarly substituted simple model compound **18**. The ketone **20**, however, showed no maximum down to 193 mμ, the spectroscopic limiting value for ethanol under our operating conditions. In this latter compound the dihedral angle relationship of the π orbitals of the carbonyl group and the overlapping C-4–C-5 bond is 0–5°. In **19**, the dihedral angle with the overlapping C-3–C-5 bond is 30°, the same value found in the simple analog **18**.



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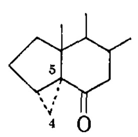


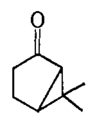
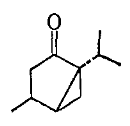
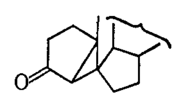
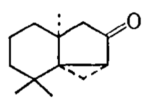
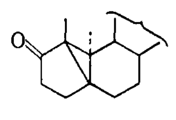
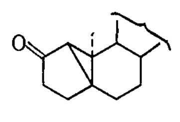
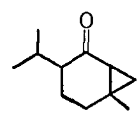
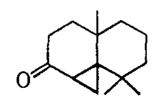
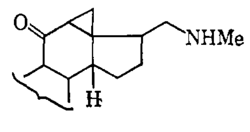
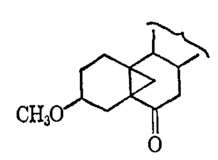
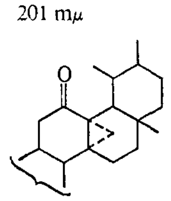
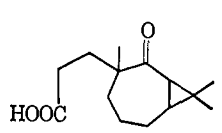
20

The foregoing spectral studies establish the fact that the degree of conjugation between a cyclopropane ring and a carbonyl group is related to the steric orientation of the groupings. From the few spectral data in the literature for the [n.1.0]alkan-2-one systems (the data are summarized below in Table I) it appears that the geometry of the more complex systems is related sufficiently close to that of the simple models discussed above to permit the generality in Table I for the estimation of the spectral maxima to be postulated.

In practically all the cases listed in Table II, the generalizations do predict the ultraviolet maxima with the same degree of reliability as do the related rules for conjugated unsaturated ketone absorption,[14,16] and these present rules are of particular value, diagnostically, for the α and β′ substituents whose bathochromic contributions are large.

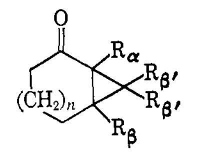
In all the cases quoted above, only those examples having alkyl groups on the cyclopropane ring were chosen. The importance of this limitation is illustrated by consideration of the spectrum of dihydrolumisantonin (**21**).[17] This material, which possesses the basic structure of its analogs in the steroid series, has been reported to have its absorption maximum at 212 mμ (ε 4700), a hypsochromic shift of 8 mμ from the steroids. This shift must be related to the presence of the lactone

Table I. Recorded and Calculated Ultraviolet Maxima for Cyclopropane Conjugated Ketones

			
λ_{max}^{EtOH}	207 mμ (ε 5430)[a]	202 mμ (ε 3550)[b]	207 mμ (ε 8100)[c]
λ_{max}^{calcd}	204 mμ	197 mμ	207 mμ
			
λ_{max}^{EtOH}	198 mμ (ε 5700)[d]	220 mμ (ε 4700)[e]	212 mμ (ε 6000)[f]
λ_{max}^{calcd}	198 mμ	219 mμ	212 mμ
			
λ_{max}^{EtOH}	196 mμ (ε 6300)[g]	201 mμ (ε 5400)[h]	202 mμ (ε 5600)[i]
λ_{max}^{calcd}	196 mμ	201 mμ	201 mμ
			
λ_{max}^{EtOH}	210 mμ (ε 4230)[j]	214 mμ (ε 5500)[k]	213 mμ (ε 2950)[l]
λ_{max}^{calcd}	208 mμ	208 mμ	210 mμ

[a] O. L. Chapman, T. A. Rettig, A. A. Griswold, A. I. Dutton, and P. Fitton, *Tetrahedron Letters*, 2049 (1963). [b] The spectrum was measured in this laboratory using a sample kindly supplied by Professor R. H. Eastman, Stanford University. [c] D. H. R. Barton and W. C. Taylor, *J. Am. Chem. Soc.*, **80**, 244 (1958). [d] The spectrum was measured in this laboratory using a sample kindly supplied by Professor T. Nozoe. [e] K. Weinberg, E. C. Utzinger, D. Arigoni, and O. Jeger, *Helv. Chim. Acta*, **43**, 236 (1960). [f] H. Dutler, C. Ganter, H. Ryt, E. C. Utzinger, K. Weinberg, K. Schaffner, D. Arigoni, and O. Jeger, *ibid.*, **45**, 2346 (1962); B. A. Shoulders, W. W. Kwie, W. Klyne, and P. D. Gardner, *Tetrahedron*, **21**, 2973 (1965). [g] See Experimental Section. [h] W. G. Dauben and A. C. Ashcraft, unpublished result. [i] J. F. Kerwin, M. E. Wolff, F. F. Owings, B. B. Lewis, B. Blank, A. Magnini, C. Karash, and V. Georgian, *J. Org. Chem.*, **27**, 3628 (1962). [j] J. Tadanier, *ibid.*, **31**, 2124 (1966). [k] J. M. Beaton, J. D. Easton, M. M. Macauther, F. S. Spring, and R. Stevenson, *J. Chem. Soc.*, 3992 (1955). [l] M. Palmede and G. Ourisson, *Bull. Soc. Chim. France*, 886 (1958).

Table II. Rule for Conjugated Cyclopropane–Carbonyl Absorption in Ethanol Solvent



Bicyclo[4.1.0]heptan-2-one (n = 1)	193 mμ
Increments for	
Alkyl groups, α	+7 mμ
β	+3 mμ
β′	+7 mμ
Rigidity	+5 mμ
Ring size, $n = 0$	−3 mμ
$n = 2$	+3 mμ
Solvent correction, water[a]	+7 mμ
	Calcd λ_{max}^{EtOH} = total

[a] This value for ethanol to water was determined for six compounds.

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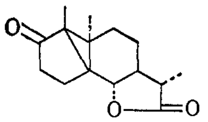

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ring whose atoms must interact in some way with the conjugated system.

In the related spiro[*n*.2]alkan-2-one system, there are too few examples to warrant giving a generalization. However, in the few examples available it does appear that the general substituent effect when applied to the most closely related basic system does predict maxima in the range they have been reported.

Experimental Section[18]

Standard Oxidation Procedure. A solution of the alcohol in acetone (distilled from potassium permanganate) was cooled to 25°, and there was added with stirring over a 5-min period a stock chromium trioxide solution (prepared from 26.72 g of chromium trioxide in 23 ml of concentrated sulfuric acid and diluted to 100 ml with water[19]). Nitrogen was bubbled through all the solvents, reagents, and reaction solution before and during the oxidation. The reaction solution was allowed to stir for an additional 5 min, 10 ml of methanol added to reduce the unused chromium trioxide, the solution decanted from the chromium salts, and the salts were washed with two 150-ml portions of acetone. The acetone was evaporated, the residue dissolved in ether, and the ethereal solution washed twice with saturated sodium chloride solution and dried. The ether was evaporated at reduced pressure and the remaining oil distilled.

Bicyclo[3.1.0]hexan-2-one (6). From 9.8 g (0.1 mole) of bicyclo[3.1.0]hexan-2-ol[7] in 250 ml of acetone and 27.5 ml (0.073 mole) of standard oxidizing solution, there was obtained 5.7 g (59%) of **6**, bp 74-75° (20 mm); n^{25}D 1.4728; $\nu_{\max}^{CCl_4}$ 1728 cm^{-1} [lit.[20] bp 58° (13 mm); n^{25}D 1.4702].

Anal. Calcd for C_6H_8O (96.12): C, 74.97; H, 8.39. Found: C, 75.04; H, 8.62.

Bicyclo[4.1.0]heptan-2-one (7). From 6.0 g (0.053 mole) of bicyclo[4.1.0]heptan-2-ol[7] in 250 ml of acetone and 24.5 ml (0.065 mole) of standard oxidizing solution, there was obtained 3.7 g (63%) of **7**; bp 85° (10 mm); n^{25}D 1.4878; $\nu_{\max}^{CS_2}$ 1695 cm^{-1} [lit.[7] bp 85° (10 mm)].

Bicyclo[5.1.0]octan-2-one (8). From 6.5 g (0.05 mole) of bicyclo[5.1.0]octan-2-ol[7] in 200 ml of acetone and 13.5 ml (0.036 mole) of standard oxidizing solution, there was obtained 3.7 g (59%) of **8**; bp 77° (10 mm); n^{25}D 1.4907; $\nu_{\max}^{CCl_4}$ 1675 cm^{-1} [lit.[21] bp 62° (2.5 mm); n^{25}D 1.4909; $\nu_{\max}^{CCl_4}$ 1675 cm^{-1}].

6-Methylbicyclo[4.1.0]heptan-2-one (9). From 9.0 g (0.071 mole) of 6-methylbicyclo[4.1.0]heptan-2-ol[7] in 200 ml of acetone and 20.0 ml (0.052 mole) of standard oxidizing solution, there was obtained 6.7 g (76%) of **9**; bp 85° (10 mm); n^{25}D 1.4792; $\nu_{\max}^{CCl_4}$ 1692 cm^{-1}.

Anal. Calcd for $C_8H_{12}O$ (124.18): C, 77.37; H, 9.74. Found: C, 77.59; H, 9.64.

1-Methylbicyclo[4.1.0]heptan-2-one (10). From 5.0 g (0.04 mole) of 1-methylbicyclo[4.1.0]heptan-2-ol[7] in 150 ml of acetone and 12 ml (0.03 mole) of standard oxidizing solution, there was obtained 4.0 g (80%) of **10**; bp 76° (10 mm); n^{25}D 1.4794; $\nu_{\max}^{CCl_4}$ 1692 cm^{-1}.

Anal. Calcd for $C_8H_{12}O$ (124.18): C, 77.37; H, 9.74. Found: C, 77.06; H, 9.84.

1,6-Dimethylbicyclo[4.1.0]heptan-2-one (11). From 3.0 g (0.021 mole) of 1,6-dimethylbicyclo[4.1.0]heptan-2-ol[7] in 100 ml of acetone and 6.35 ml (0.017 mole) of standard oxidizing solution, there was obtained 2.5 g (85%) of **11**; bp 85° (10 mm); n^{25}D 1.4814; $\nu_{\max}^{CCl_4}$ 1688 cm^{-1}.

Anal. Calcd for $C_9H_{14}O$ (138.19): C, 78.21; H, 10.21. Found: C, 77.97; H, 10.32.

3,7,7-Trimethylbicyclo[4.1.0]heptan-2-one (12). This material was kindly supplied by Professor Richard E. Eastman, Stanford University.

Spiro[2.4]heptan-2-one (16). From 4.2 g (0.039 mole) of spiro[2.4]heptan-2-ol[7] in 100 ml of acetone and 12.0 ml (0.032 mole) of standard oxidizing solution, there was obtained 2.6 g (67%) of **16**; bp 81° (50 mm); n^{25}D 1.4650; $\nu_{\max}^{CCl_4}$ 1732 cm^{-1} [lit.[22] bp 55° (14 mm); $n^{17.5}$D 1.4688; $\nu_{\max}^{CS_2}$ 1729 cm^{-1}].

Anal. Calcd for $C_7H_{10}O$ (110.15): C, 76.32; H, 9.15. Found: C, 76.14; H, 9.24.

Spiro[2.5]octan-2-one (17). From 5.0 g (0.039 mole) of spiro[2.5]octan-2-ol[7] in 100 ml of acetone and 12.0 ml of standard oxidizing reagent, there was obtained 4.0 g (80%) of **17**; bp 71° (20 mm); n^{25}D 1.4712; $\nu_{\max}^{CCl_4}$ 1695 cm^{-1}.

Anal. Calcd for $C_8H_{12}O$ (124.18): C, 77.37; H, 9.74. Found: C, 77.28; H, 9.80.

7-Methylspiro[2.5]octan-2-ones (18). From 2.8 g (0.02 mole) of 7-methylspiro[2.5]octan-2-ol[7] in 100 ml of acetone and 6 ml (0.016 mole) of standard oxidizing solution, there was obtained 2.4 g (86%) of a mixture of the two 7 isomers of **18**; bp 78° (10 mm).

Glpc separation of the product gave two fractions in a ratio of 20:80. The first fraction (*i.e.*, the 20% material) was isolated; n^{25}D 1.4756; $\nu_{\max}^{CCl_4}$ 1695 cm^{-1}; $\lambda_{\max}^{H_2O}$ 215 mμ (ϵ 2500).

Anal. Calcd for $C_9H_{14}O$ (138.20): C, 78.21; H, 10.21. Found: C, 77.66; H, 10.27.

The second fraction (*i.e.*, the 80% material) was isolated; n^{25}D 1.4770; $\nu_{\max}^{CCl_4}$ 1692 cm^{-1}; $\lambda_{\max}^{H_2O}$ 215 mμ (ϵ 3360).

Anal. Found: C, 77.91; H, 10.40.

Ultraviolet Spectra. Spectra were determined with a Beckman Model DK-2A "Extended UV-Range" spectrophotometer under the conditions described by Micheli and Applewhite.[9]

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(18) Analyses by the microanalytical laboratory, College of Chemistry, University of California.

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