[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

Spectral Properties of Medium- and Large-ring Carbocyclic Compounds: α-Bromoketones, Enol Acetates and Unsaturated Ketones

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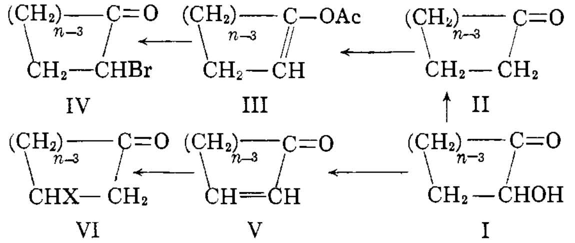
A study of the spectra of medium- and large-ring carbocyclic 2-bromoketones, ketone–enol acetates and unsaturated ketones has provided interesting information concerning their stereochemistry. In particular, the infrared shifts observed for the carbonyl maximum in going from the cyclic ketone to the corresponding 2-bromoketone indicate that the average conformations of 2-bromocycloöctanone, 2-bromocyclononanone and 2-bromocyclodecanone fit a *syn*-skew model; the absence of an appreciable infrared shift for the ketone–2-bromoketone pairs having eleven through fifteen members in the ring is indicative of a C—Br/C=O angle near 90°. In contrast with the infrared findings, the ultraviolet absorption spectra indicate that the 2-bromine produces almost the same shift toward longer wave length and higher molar extinction coefficient regardless of ring size. The α,β-unsaturated carbonyl grouping shows chemical and ultraviolet spectral anomalies in rings of medium size which disappear in the larger rings without steric-repulsion strain. Transannular interaction between C=C and ketone C=O has been detected in the anomalous ultraviolet spectrum of cyclodec-5-en-1-one.

A search for trends and anomalies in the spectral properties of medium- and large-ring ketonic derivatives continues to provide interesting research impetus in a number of laboratories. Our present contribution[2] reports the spectra of series of cyclic α-bromoketones, their cyclic ketone–enol acetate precursors, and cyclic unsaturated ketones, including examples of α,β-unsaturation and "transannular" unsaturation.

The cyclic ketones of nine members and larger were made by the reduction with zinc and hydrochloric acid in acetic acid[3-5] of the corresponding cyclic acyloins (I).[3,4,6-10] Our over-all yields of cyclic ketones from diesters merit recording since they represent optimum yields which were reproducible in this Laboratory: cyclononanone, 27%; cyclodecanone, 54%; cyclohendecanone, 53%; cyclododecanone, 68%; cyclotridecanone, 59%; cyclotetradecanone, 75%.[11] The ketones II were converted efficiently to the enol acetates III by heating with excess isopropenyl acetate in the presence of *p*-toluenesulfonic acid.

Enol Acetates.—The enol acetates of ring size seven through ten members were identified by analysis and infrared spectra, and those of larger ring size were characterized by spectra alone. Despite possible contamination of the enol acetates of ring size eleven through fifteen members with the corresponding ketones, certain variations of infrared spectra with ring size were detectable. Practically invariant for the series (III, $n = 6$–15) was the absorption maximum at 1755–1760 cm.$^{-1}$ (carbon tetrachloride solution) due to the ester carbonyl,[12,13] whereas in the C–H deformation region, a maximum at 840–875 cm.$^{-1}$, observed for III, $n = 6$–10, was absent from the spectra for the compounds where $n = 11$–15. It seems likely, on the basis of the data available for the cycloölefins,[14-21] that the first group of enol acetates, through cyclodec-1-en-1-yl acetate, have the *cis* configuration. By contrast, the *trans* configurational isomer can be expected to make an important contribution to the enol acetates formed from the 11- to 15-membered ketones. The C=C stretching frequency also underwent a suggestive change at $n = 10$, 11 as follows: $n = 6$, 1695; 7, 1690; 8, 1687; 9, 1688; 10, ~1694, 1701; 11, ~1695, ~1712; 12, 1714; 13, 1714; 14, 1715; 15, 1715 cm.$^{-1}$.[22]



2-Bromoketones.—The enol acetates were converted to the 2-bromoketones IV by the method of Bedoukian,[23] consisting of bromination in carbon tetrachloride at −20 to −40°, followed by methanolysis. This method was advantageous because rapid bromination could be effected even

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[1] Eli Lilly and Co. Fellow, 1954–1956. Sinclair Refining Co. Fellow, 1957; work done under the sponsorship of the Sinclair Research Laboratories, Inc.

[2] For earlier studies see, for example, (a) N. J. Leonard, J. C. Little and A. J. Kresge, THIS JOURNAL, **79**, 6436 (1957); (b) N. J. Leonard and P. M. Mader, *ibid.*, **72**, 5388 (1950).

[3] V. Prelog, L. Frenkiel, M. Kobelt and P. Barman, *Helv. Chim. Acta*, **30**, 1741 (1947).

[4] A. T. Blomquist, R. E. Burge, Jr., and A. C. Sucsy, THIS JOURNAL, **74**, 3636 (1952).

[5] A. C. Cope, J. W. Barthel and R. D. Smith, *Org. Syntheses*, **36**, 14 (1956).

[6] V. L. Hansley, U. S. Patent 2,228,268; *C. A.*, **35**, 2534 (1941).

[7] M. Stoll and J. Hulstkamp, *Helv. Chim. Acta*, **30**, 1815 (1947).

[8] M. Stoll and A. Rouvé, *ibid.*, **30**, 1822 (1947); M. Stoll, *ibid.*, **30** 1837 (1947).

[9] V. Prelog, K. Schenker and H. H. Günthard, *ibid.*, **35**, 1598 (1952).

[10] N. L. Allinger, *Org. Syntheses*, **36**, 79 (1956).

[11] See also N. J. Leonard and C. W. Schimelpfenig, Jr., *J. Org. Chem.*, in press.

[12] R. N. Jones, P. Humphries, F. Herling and K. Dobriner, THIS JOURNAL, **74**, 2820 (1952).

[13] R. N. Jones and C. Sandorfy, Chap. IV in "Technique of Organic Chemistry," Vol. IX, Interscience Publishers, Inc., New York, N. Y., 1956, p. 483.

[14] R. B. Turner and W. R. Meador, THIS JOURNAL, **79**, 4133 (1957).

[15] R. B. Turner, Abstracts of Papers, 133rd Meeting of the American Chemical Society, San Francisco, Calif., April, 1958, p. 23N.

[16] N. L. Allinger, *ibid.*, p. 29N.

[17] A. T. Blomquist and A. Goldstein, THIS JOURNAL, **77**, 1001 (1955).

[18] A. T. Blomquist, L. H. Liu and J. C. Bohrer, *ibid.*, **74**, 3643 (1952).

[19] K. Ziegler and H. Wilms, *Ann.*, **567**, 1 (1950).

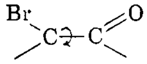
[20] N. L. Allinger, THIS JOURNAL, **79**, 3443 (1957).

[21] N. L. Allinger, *ibid.*, **80**, 1953 (1958).

[22] Indistinguishable from the C=O maximum of any ketone which might be present for $n = 12$–15.

[23] P. Z. Bedoukian, THIS JOURNAL, **67**, 1430 (1945).

at low temperature and formation of dibromoketone was minimized through the use of the enol acetate. The determination of the infrared absorption spectra of the 2-bromoketones was of special interest because of the possibility of assigning the average conformation of the



moiety from the magnitude of the frequency shift of the carbonyl stretching maximum in going from the ketone to the corresponding 2-bromoketone.[24–38] Thus, it has been amply demonstrated[25–33,36–38] in six-membered ring ketones that, with the introduction of an α-bromo substituent, the C=O absorption band is shifted to higher frequency (Δν = 15–22 cm.$^{-1}$) when the carbon–bromine and carbon–oxygen bonds are approximately in the same plane (equatorial) and is not shifted appreciably when these bonds are approximately perpendicular (axial). Consistent with this picture has been the finding that for an intermediate C—Br/C=O angle, as in the α-bromocyclopentanone series, the frequency shift (Δν = 8–14 cm.$^{-1}$) reflects the *syn*-skew geometry.[27,34,35] The values of the infrared carbonyl maxima for the cyclic ketones and 2-bromoketones of ring size six to fifteen (Table I) were obtained in carbon tetrachloride solution. The recent Allinger study[36] has indicated the dependence of the equilibrium, equatorial ⇄ axial conformation of 2-bromocyclohexanone, on the nature of the solvent, the equilibrium constant varying from about 3 in non-polar solvents such as carbon tetrachloride to near 1 in dimethyl sulfoxide. Whereas resolution of the six-membered ring ketone band was possible (in carbon tetrachloride as well as in the other solvents employed), this was not generally possible for the larger rings. Our findings for the seven-membered ring compounds corroborate the earlier infrared results of Corey in this Laboratory.[27] The shoulder at 1703 cm.$^{-1}$ (Δν = 1 cm.$^{-1}$) which we observed for 2-bromocycloheptanone indicates the presence of some Br-axial conformer together with the *syn*-skew form or forms represented by the maximum at approximately 1712 cm.$^{-1}$ (Δν = 10 cm.$^{-1}$).[39] The rather broad carbonyl band for 2-bromocycloöctanone was unsymmetrical but was not resolvable, thus representing a mixture of conformers having an average *syn*-skew geometry. Allinger, in concurrent investigations, also has concluded from infrared and dipole moment data that 2-bromocycloöctanone is a mixture of energetically similar conformers.[40] The carbonyl absorption bands obtained for the 2-bromoketones of ring size nine through fifteen were slightly broader than the bands for the unsubstituted ketones of the same ring size. Above n = 9 (IV), the bands were symmetrical in addition to the maxima being sharp. It is apparent that the average conformations of 2-bromocyclononanone and 2-bromocyclodecanone also fit a *syn*-skew model. The departure from this model in the 2-bromoketones of ring size greater than ten is indicated by the absence of an appreciable frequency shift, Δν, for the remaining pairs listed in Table I. We conclude that in the 2-bromoketones of n = 11–15 (and greater), the C—Br/C=O angle is close to 90° (quasi-axial). As a corollary, we also conclude that this conformation of the α-bromocarbonyl moiety is favored electronically,[32,36] for when steric repulsions, which act in the rings of size up through ten members to constrain C—Br/C=O to an acute angle, are removed the angle approaches the perpendicular.

TABLE I

INFRARED ABSORPTION MAXIMA OF CARBOCYCLIC KETONES AND 2-BROMOKETONES

Compound	$C=O_{max.}$, cm.$^{-1a,f}$	Effect of α-Br Δν, cm.$^{-1a}$
Cyclohexanone	1714	
2-Bromocyclohexanone	1719, 1732^b	5, 18^c
Cycloheptanone	1702	
2-Bromocycloheptanone	1712^d	10^e
Cycloöctanone	1701	
2-Bromocycloöctanone	1710	9
Cyclononanone	1702	
2-Bromocyclononanone	1711	9
Cyclodecanone	1702	
2-Bromocyclodecanone	1712	10
Cyclohendecanone	1709	
2-Bromocyclohendecanone	1712	3
Cyclododecanone	1710	
2-Bromocyclododecanone	1713	3
Cyclotridecanone	1713	
2-Bromocyclotridecanone	1714	1
Cyclotetradecanone	1712	
2-Bromocyclotetradecanone	1714	2
Cyclopentadecanone	1712	
2-Bromocyclopentadecanone	1713	1

[a] Spectra obtained in carbon tetrachloride (50 mg./ml.). The estimated error is ±2 cm.$^{-1}$. [b] Shoulder. [c] Reported Δν: 4 and 18 cm.$^{-1}$ [27]; 0 and 12 cm.$^{-1}$.[36] [d] Slight shoulder at 1703 cm.$^{-1}$. [e] Reported[27] Δν: 8 cm.$^{-1}$. [f] Recognition is given to the cyclanone infrared frequencies (also half-widths and integrated absorption intensities) as measured by T. Bürer and Hs. H. Günthard, *Helv. Chim. Acta*, **39**, 356 (1956). It was considered important in the present study to provide directly comparable values for ketones and 2-bromoketones.

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(24) H.-C. Cheng, *Z. physik. Chem.*, **26**, 288 (1934).

(25) R. N. Jones, D. A. Ramsay, F. Herling and K. Dobriner, THIS JOURNAL, **74**, 2828 (1952).

(26) R. N. Jones, *ibid.*, **75**, 4839 (1953).

(27) E. J. Corey, *ibid.*, **75**, 2301 (1953).

(28) E. J. Corey, *ibid.*, **75**, 3297 (1953).

(29) E. J. Corey, *ibid.*, **75**, 4832 (1953).

(30) E. J. Corey, *ibid.*, **76**, 175 (1954).

(31) E. J. Corey, T. H. Topie and W. A. Wozniak, *ibid.*, **77**, 5415 (1955).

(32) E. J. Corey and H. J. Burke, *ibid.*, **77**, 5418 (1955).

(33) R. G. Cummins and J. E. Page, *J. Chem. Soc.*, 3847 (1957).

(34) F. V. Brutcher, Jr., T. Roberts, S. J. Barr and N. Pearson, THIS JOURNAL, **78**, 1507 (1956).

(35) F. V. Brutcher, Jr., and N. Pearson, *Chemistry & Industry*, 1295 (1957).

(36) J. Allinger and N. L. Allinger, *Tetrahedron*, **2**, 64 (1958).

(37) N. L. Allinger and J. Allinger, THIS JOURNAL, in press. We wish to express our appreciation to the authors for allowing us to read this article in manuscript form.

(38) C. Djerassi, J. Osiecki, R. Riniker and B. Riniker, *ibid.*, **80**, 1216 (1958).

(39) Corey[27] suggested that the sterically least-strained conformations of α-bromocycloheptanone had C—Br/C=O angles of approximately 80°, 30° and 25°.

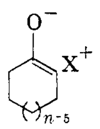
(40) Dr. N. L. Allinger, Wayne State University, private communication.

TABLE II

ULTRAVIOLET ABSORPTION MAXIMA OF CARBOCYCLIC KETONES AND 2-BROMOKETONES

	λ_{max}^{EtOH}, mμ	ϵ_{max}	$\Delta\lambda_{max}$, mμ	$\Delta\epsilon$
Cyclohexanone	282	16		
2-Bromocyclohexanone	308	70	26	54
Cycloheptanone	285	20		
2-Bromocycloheptanone	304	84	19	64
Cycloöctanone	283	17		
2-Bromocycloöctanone	305	86	22	68
Cyclononanone	280	16		
2-Bromocyclononanone	307	95	27	79
Cyclodecanone	283	15		
2-Bromocyclodecanone	306	109	23	94
Cyclohendecanone	283	18		
2-Bromocyclohendecanone	306	98	23	80
Cyclododecanone	284	17		
2-Bromocyclododecanone	303	108	19	91
Cyclotridecanone	283	25		
2-Bromocyclotridecanone	304	110	19	85
Cyclotetradecanone	279	26		
2-Bromocyclotetradecanone	303	109	24	83
Cyclopentadecanone	282	21		
2-Bromocyclopentadecanone	302	112	20	91

The ultraviolet spectral data for the cyclic 2-bromoketones are given in Table II. They indicate clearly that the effects of α-halogen substitution on the infrared and ultraviolet spectra of ketones are *not* necessarily complementary. Cookson[41] has shown that in steroid ketones and camphor derivatives when an α-bromine is equatorial, the wave length shift is about -5 mμ and when the α-bromine is axial, the shift is about $+28$ mμ, with an attendant large hyperchromic shift in extinction. The concept holds generally for α-bromocyclohexanones[36,37] and, with modified values of the wave length and extinction shifts, for α-chlorocyclohexanones.[32] It is now apparent (Table II) that ring size (six and above) causes no significant difference in the wave length of the ultraviolet absorption maxima of either the ketones or the 2-bromoketones and that the 2-bromine produces almost the same shift toward longer wave length and higher molar extinction coefficient regardless of ring size. Moreover, no sharp ultraviolet spectral difference was found in going from a 10- to an 11-membered ring analogous to the frequency-shift values in the infrared. Instead, it was observed that the 2-bromine causes a bathochromic shift of 23 ± 4 mμ from the normal N→A transition band of the cyclic ketone in every case. Corey and Burke[32] have indicated that the observation that an axial halogen in an α-halocyclohexanone produces a bathochromic shift in the ultraviolet whereas an equatorial halogen does not is consistent with a greater contribution of resonance from VII, $n = 6$, when halogen is axial. It now appears that when the halogen is not coplanar with the carbonyl group (*i.e.*, conformations other than equatorial) a bathochromic shift results because of the greater contribution of hyperconjugative forms such as VII to the excited state. Thus, while infrared spectral analysis is suitable for the estimation of the average C—Br/C=O angle in cyclic α-bromoketones because the effect being observed is operative in the ground state, ultraviolet absorption data are not as generally suitable for this purpose because of the added effect of hyperconjugative resonance in the excited state.



VII

α,β-Unsaturated Ketones.—The acyloins (I, $n = 10, 12, 13, 14$) were dehydrated to the corresponding α,β-unsaturated ketones V by a modification of the procedure of Stoll,[8] distillation at 4 mm. pressure through a mixture of alumina and asbestos heated to 320–350°, in yields of 60–80%. The infrared spectra (carbon tetrachloride) of the unsaturated ketones thus obtained (V, $n = 10, 12, 13, 14$) showed strong normal carbonyl absorption at 1700–1705 cm.$^{-1}$, low intensity conjugated carbonyl maxima at 1670–1675 cm.$^{-1}$ and C=C stretching maxima (weakest for V, $n = 10$) at 1625–1630 cm.$^{-1}$,[42] suggesting the preponderance of conformations in which the C=O and C=C (presumed α,β, see below) are not coplanar. A low intensity band at about 3000–3020 cm.$^{-1}$ present in the spectrum of each compound was indicative of =C—H stretching, and in the spectra of the unsaturated ketones of larger ring size than cyclodec-2-en-1-one (V, $n = 10$), the maximum in the 975–985 cm.$^{-1}$ region (*trans* double bond) was of much greater intensity than the absorption in the 695–725 cm.$^{-1}$ region (*cis* double bond).[4,17,21,43] The location of the unsaturation α,β in the ketones here synthesized was indicated by their ultraviolet absorption spectra, as obtained in ethanol solution (see Table III). The short wave length maxima for cyclodec-2-en-1-one through cyclotetradec-2-en-1-one are in the correct region for an α,β-unsaturated ketone with one β-substituent, according to Woodward's empirical rules.[44] The value of the molar extinction coefficient of the *ca.* 227 mμ maximum observed for the 13- and 14-membered ring α,β-unsaturated ketones is diminished by about 37% for the 12-membered and by 63% for the 10-membered ring compound. The probability of N→V transitions occurring is thus markedly decreased in going from the large rings to the 12-, (11)- and 10-membered rings, and is related to the increasing steric resistance to coplanarity of the C=C—C=O system. Since Blomquist and Goldstein[43] have reported that the ultraviolet spectrum of *cis,cis*-1,3-cyclodecadiene shows no maximum in the region 215–230 mμ expected for a conjugated diene and that of *cis-trans*-1,3-cyclodecadiene exhibits a broad maximum at 222 mμ, log ε 3.86, or at lower extinction than normal,[44] there

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(41) R. C. Cookson, *J. Chem. Soc.*, 282 (1954).

(42) Complete curves are given in the Ph.D. Thesis of F. H. Owens, University of Illinois, 1958.

(43) A. T. Blomquist and A. Goldstein, THIS JOURNAL, **77**, 998 (1955).

(44) In L. F. Fieser and M. Fieser, "Natural Products Related to Phenanthrene," third edition, Reinhold Publishing Corp., New York, N. Y., 1949, Chap. III, Part 2.

is precedent for the hypochromic and the slight hypsochromic shifts observed for cyclodec-2-en-1-one.[45] The possibility cannot be disregarded, however, that the lower extinction coefficients observed for V, $n = 10, 12$, may be due partially to the reaction of ethanol[48] with the α,β-unsaturated ketonic system. The semicarbazones of the α,β-unsaturated ketones (V, $n = 10, 13, 14$) were obtained in 90–95% yield and appeared to be homogeneous. The two ultraviolet maxima for each of these semicarbazones (Table III) are located at the same wave lengths[49] as cyclodecanone semicarbazone, but both maxima have higher extinction coefficients than those exhibited by the derivative of the saturated ketone. The situation is similar to that reported for pulegone ($\lambda_{\max}$ 252 mμ, ϵ 8130[50] or 6500[51]) and its semicarbazone ($\lambda_{\max}$ 253 mμ, ϵ 11,000).[50]

TABLE III

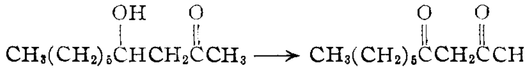
ULTRAVIOLET ABSORPTION MAXIMA OF α,β-UNSATURATED KETONES

	Ketones[42] $\lambda_{\max}^{\text{EtOH}}$, m$\mu$	$\epsilon_{\max}$	Semicarbazones $\lambda_{\max}^{\text{EtOH}}$, m$\mu$	$\epsilon_{\max}$
Cyclodec-2-en-1-one	224	1410	215	14,100
	284	100[a]	232	13,600
Cyclododec-2-en-1-one	227	2400		
	284	450[a]		
Cyclotridec-2-en-1-one	227	3810	215	12,900
	284	150[a]	230	15,500
Cyclotetradec-2-en-1-one	226	3875	215	13,000
	284	150[a]	230	16,000
Cyclodecanone	283	15	215	8,800
(for comparison)			231	13,000

[a] These values may be too high; they are subject to error because the ultraviolet spectra were determined only in dilute solutions, about 4×10^{-4} *M*.

The chemical properties of the α,β-unsaturated ketones under consideration also showed anomaly. All four of the unsaturated ketones (V, $n = 10, 12, 13, 14$) gave a positive color test with tetranitromethane, usually indicative of an unconjugated olefinic bond[52,53]; only the 14-membered ring unsaturated ketone reacted with sodium bisulfite (conjugated ketone). The cyclic α,β-unsaturated ketones (V, $n = 10, 13, 14$) added hydrogen bromide readily, and dehydrobromination of the 3-bromoketones (VI, X = Br) thus obtained did not lead solely to the original α,β-unsaturated ketones. Pyrrolidine reacted with cyclotetradec-2-en-1-one (V, $n = 14$) at room temperature to give 3-(1′-pyrrolidino)-cyclotetradecanone (VI, X = $(CH_2)_4N$–, $n = 14$) in excellent yield.

We were interested in converting the cyclic α,β-unsaturated ketones of varying ring size (V) to the corresponding monocyclic 1,3-diketones for the purpose of defining Bredt's rule[54] with respect to metal chelate formation.[55] Since one approach lay through the oxidation of a 3-hydroxycycloalkanone, (VI, X = OH), possibly obtainable from the unsaturated ketone V or the 3-bromoketone (VI, X = Br), various methods were applied to the oxidation of the open-chain model, decan-4-ol-2-one (VIII): chromic anhydride–sulfuric acid, chromic anhydride–acetic acid, chromic anhydride–pyridine, cyclohexanone–Raney nickel, manganese dioxide in pyridine and in hexane, N-bromosuccinimide, and *t*-butyl hypochlorite in pyridine in carbon tetrachloride and in aqueous dioxane. Only *t*-butyl hypochlorite in aqueous dioxane met with success, an 80% yield of decane-2,4-dione (IX).



$$\underset{\text{VIII}}{CH_3(CH_2)_5\overset{OH}{\overset{|}{C}}HCH_2\overset{O}{\overset{\|}{C}}CH_3} \longrightarrow \underset{\text{IX}}{CH_3(CH_2)_5\overset{O}{\overset{\|}{C}}CH_2\overset{O}{\overset{\|}{C}}CH_3}$$

Since the oxidation studies proved again that a β-ketoalcohol is sensitive to both acid and base, and since Cope and Johnson[56] have shown that displacements involving carbonium ions lead to transannular reactions in medium rings, it was decided to try to effect the conversion of the 3-bromoketones (VI, X = Br) to the 3-hydroxyketones (VI, X = OH) with sodium formate in methanol or aqueous methanol.[57–59] However, all attempts led either to unchanged starting material or to a mixture of ketones, apparently α,β- and β,γ-unsaturated ketones (infrared analysis). Attempted replacement of the bromine with sodium carbonate also failed. These results seem to indicate that either the dehydrohalogenation is faster than the replacement or that the β-ketoalcohol is too unstable to be isolated. Silver chromate in pentane did not react with 3-bromocyclotetradecanone, conditions which converted 3-bromocyclohexene to cyclohex-2-en-1-one.[60] Other routes to the cycloalkane-1,3-diones which failed in model runs were the oxidation of 3-(1′-pyrrolidino)-cyclotetradecanone with mercuric acetate, N-bromosuccinimide and *t*-butyl hypochlorite and the oxidation of the enol acetate of cyclodecanone with selenium dioxide, so that the initial goal remains desirable but unachieved.

Transannular Interaction in a Cyclic Unsaturated Ketone.—In order to supplement our spectral investigation of the cyclic α,β-unsaturated ketones and to detect possible transannular interaction between C=C and C=O when these groups are located opposite each other in a ring of medium size, we determined the ultraviolet spectra of cyclodec-

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(45) While *cis-cis-* and *cis-trans*-1,3-cyclodecadiene failed to form Diels–Alder adducts,[43] it was observed by Wiesner and his colleagues that 1,3-cyclododecadiene ($\lambda_{\max}$ 230 mμ),[46] cyclotridecadiene ($\lambda_{\max}$ 232 mμ),[46] 1,3-cyclotetradecadiene,[47] and 1,3-cycloöctadecadiene[47] formed adducts with maleic anhydride, see also E. A. Braude, *Chemistry & Industry*, 1557 (1954).

(46) M. F. Bartlett, S. K. Figdor and K. Wiesner, *Can. J. Chem.*, **30**, 291 (1952).

(47) R. B. Ingraham, D. M. MacDonald and K. Wiesner, *Can. J. Research*, **28B**, 453 (1950).

(48) C. Sandris and G. Ourisson, *Bull. soc. chim. France*, 958 (1956).

(49) *Cf.* L. Dorfman, *Chem. Revs.*, **53**, 47 (1953).

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

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

(52) E. Heilbronner, *Helv. Chim. Acta*, **36**, 1121 (1953).

(53) L. F. Fieser, "Experiments in Organic Chemistry," third edition, D. C. Heath and Co., Boston, Mass., 1955, p. 71.

(54) F. S. Fawcett, *Chem. Revs.*, **47**, 219 (1950).

(55) R. C. Fox, Ph.D. Thesis, University of Illinois, 1953.

(56) A. C. Cope and H. E. Johnson, THIS JOURNAL, **79**, 3889 (1957).

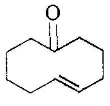
(57) K. v. Auwers, H. Ludewig and A. Müller, *Ann.*, **526**, 143 (1936).

(58) E. B. Reid, R. B. Fortenbaugh and H. R. Patterson, *J. Org. Chem.*, **15**, 572 (1950).

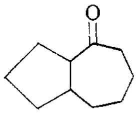
(59) P. A. Levene and A. Walti, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 5.

(60) E. J. Corey and W. A. Remers, private communication.

5-en-1-one (X) and several related compounds, including bicyclo[5.3.0]decan-2-one (XI), *cis*- and *trans*-cyclodecene and *cis*- and *trans*-cyclononene. 6-Acetoxycyclodecanone was prepared according to the method of Holmquist, Rothrock, Theobald and Englund.[61] Saponification yielded 6-hydroxycyclodecanone, which was used to prepare cyclodec-5-en-1-one (X) by the method of Cope and Holzman[62] and bicyclo[5.3.0]decan-2-one (XI) following the directions of Goering, Olson and Espy.[63] Quantitative hydrogenation using palladium-on-charcoal was employed to check the purity of the two ketones, X and XI, and to ensure that the samples of each used for spectral determinations were not contaminated with the structural isomer. The infrared spectrum of cyclodec-5-en-1-one (X) in carbon tetrachloride had a C=O stretching maximum at 1706 cm.$^{-1}$ (1706 cm.$^{-1}$ as a liquid film, 1697 cm.$^{-1}$ in chloroform), strong absorption in the C–H deformation region for *trans*-CH=CH, 993(s) and 960(m) cm.$^{-1}$, and a weak maximum at 704 cm.$^{-1}$ [4] (same frequencies for a liquid film).



X



XI

Whereas the infrared spectrum of cyclodec-5-en-1-one (X) showed no abnormality, the ultraviolet spectrum (Table IV) was a striking departure from the summation of the *trans*-cyclodecene and cyclodecanone curves. Transannular interaction between C=C and C=O in X, which was not detected in the ground state by infrared, was apparent in the excited state from the ultraviolet spectrum. In an earlier ten-membered ring example, 1-methyl-1-azacyclodecan-6-one, an anomalous ultraviolet maximum (at 221 mμ, ε 5600) reflected interaction between $-\underset{|}{N}-$ and C=O.[64] Significantly, the positions of the maxima for cyclodec-5-en-1-one (X) were not shifted in changing solvent from ethanol to cyclohexane. Within either solvent cage the $\Delta^{5,6}$-double bond is essentially the fixed environment of the ketonic carbonyl. In the ten-membered ring these groupings are held close together in conformations which have little strain, according to scale molecular models. The N→A band[65] (n→π* transition)[66] for cyclodecanone shifts 5 mμ to longer wave length in going from ethanol to cyclohexane. By contrast, this band remains at 302 mμ for cyclodec-5-en-1-one in both solvents. The displacement of the N→A band by +14 to 19 mμ in wave length and by about 500% in molar extinction coefficient in comparing cyclodec-5-en-1-one with cyclodecanone as a model suggests an unusual electronic interaction between C=C and C=O, since this band is not shifted in wave length by α,β-unsaturation in the related cyclic compounds listed in Table III. The maximum at 258 mμ (ethanol) for cyclodec-5-en-1-one may be due to N→V transitions made possible by the overlap of the π-electron clouds of the C=C and C=O groupings which are essentially in parallel planes or intersect at an acute angle. It is difficult to predict where such a band would be found, since the N→V transitions for the coplanar CH=CH—C=O grouping occur at about 227 mμ and log ε > 3 and the previously reported cases of non-bonded interaction between C=C and C=O are for compounds in which (at least in the ground state) the planes of these groupings meet in extension at an obtuse angle.[67–70] The possibility that the unusual maximum at 258 mμ for X is due to an N→B transition is more remote even though the intensity is in the correct range, since the carbon–carbon double bond would in this case be called upon to exert an influence that would move this band about 80 mμ to longer wave length.[65,66] It was possible to discount the influence of a strained olefinic bond on the spectrum of cyclodec-5-en-1-one by obtaining the ultraviolet spectra of *trans*- and *cis*-cyclodecene and *trans*- and *cis*-cyclononene, which were kindly furnished by Dr. A. T. Blomquist. These compounds exhibited no maxima above 210 mμ, which was the lower limit of accurate determination. The extinction coefficients for these compounds at 210 and 220 mμ are given in Table IV. It is of special interest to

TABLE IV

ULTRAVIOLET ABSORPTION DATA FOR CYCLODEC-5-EN-1-ONE AND RELATED COMPOUNDS[42]

Cyclic ketones	Solvent	λ_{max}, mμ	ϵ_{max}
Cyclodec-5-en-1-one (X)	Ethanol[a]	258	472
		302	73
	Cyclohexane	260	423
		302	73
Cyclodecanone (II, *n* = 10)	Ethanol	283	15
	Cyclohexane	288	16
1,6-Cyclodecanedione	Ethanol	287	35
	Cyclohexane	292	35
Bicyclo[5.3.0]decan-2-one (XI)	Ethanol	250(?)	46
		288	27
	Cyclohexane	245(?)	53
		290	25
Cyclic olefins	Solvent	ϵ_{210} mμ[b]	ϵ_{220} mμ[b]
trans-Cyclodecene[4,9]	Ethanol	275	110
	Cyclohexane	227	85
cis-Cyclodecene[4,9]	Ethanol	85	42
	Cyclohexane	57	31
trans-Cyclononene[18]	Ethanol[c]	275	75
cis-Cyclononene[18]	Ethanol	85	34
	Cyclohexane	48	28

[a] Minima were observed at 233 mμ (ε 144) and 282 mμ (ε 55). [b] These values do not represent maxima. [c] Not determined in cyclohexane.

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TABLE V

2-BROMOKETONES

2-Bromo-	Yield, %	B.p., °C.	B.p., Mm.	M.p., °C.	$n^{25}D$	Formula	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found
Cyclohexanone		74[a]	3.8		1.5100[a]					
Cycloheptanone		83[b]	3.5		1.5125[b]					
Cycloöctanone	89	51[c]	0.2		1.5150[c]	$C_8H_{13}BrO$	46.85	46.65	6.39	6.51
Cyclononanone	83	54	.15		1.5150	$C_9H_{15}BrO$	49.33	49.80	6.90	6.98
Cyclodecanone	79	56	.06		1.5160	$C_{10}H_{17}BrO$	51.51	51.69	7.35	7.54
Cyclohendecanone	60	83	.25		1.5152	$C_{11}H_{19}BrO$	53.45	52.94	7.75	7.74
Cyclododecanone	61			52–53.5[d]		$C_{12}H_{21}BrO$	55.17	55.23	8.10	8.22
Cyclotridecanone	34	98	.30		1.5140	$C_{13}H_{23}BrO$	56.72	56.94	8.43	8.34
Cyclotetradecanone	54	105	.15	46–47[d]		$C_{14}H_{25}BrO$	58.13	57.83	8.71	8.59
Cyclopentadecanone	55	114[e]	.2		1.5045	$C_{15}H_{27}BrO$	59.40	59.65	8.97	9.10

[a] Reported[27,28] b.p. 74° (3 mm.), $n^{27}D$ 1.5093. [b] Reported[27,28] b.p. 72–73° (1.5 mm.), $n^{25}D$ 1.5130. [c] Reported[56] b.p. 79–81° (1 mm.), $n^{25}D$ 1.5161. [d] Recrystallized from pentane. [e] Reported[77] b.p. 126–134° (0.06 mm.), $n^{25}D$ 1.505.

note that the *trans* isomers, which are less stable,[14,17–21] have higher extinction coefficients than the *cis* isomers, reflecting the greater probability of the former reaching excited states having sp^3 hybridization.

Since a comparison of the infrared and ultraviolet data for cyclodec-5-en-1-one (X) indicated that the transannular interaction in this molecule was an excited-state phenomenon, it seemed worthwhile to check another property indicative of the ground state, namely, the electric moment. Cyclodecanone has a dipole moment (in benzene) of 2.72 D.,[71] and *trans*-cyclodecene has no appreciable moment. Cyclodec-5-en-1-one was found to have μ = 2.57 D. (benzene). Interaction involving enhanced charge separation would have been expected to raise the moment above 2.72.[72,73] The decrease in dipole moment of 0.15 D. in going from the saturated to the unsaturated ketone, if real, is not possible to explain on the basis of charge-separated forms and is of such a low order that its interpretation would be only conjectural (also because of the lack of dipole moment data on non-conjugated unsaturated ketones).

Acknowledgment.—The authors extend warm thanks and appreciation to Dr. A. T. Blomquist of Cornell University for his generous donation of isomerically-pure cycloölefins and to Dr. M. T. Rogers of Michigan State University for the determination of the dipole moment of cyclodec-5-en-1-one.

Experimental[74]

Carbocyclic Acyloins (I) and Ketones (II).—The methods described in "Organic Syntheses"[5,10] were used to effect the acyloin ring closure and the reduction of each acyloin to the corresponding cyclic ketone. The ketones were identified by the physical properties reported previously.[8,75] The over-all yields of ketones from α,ω-diesters have been cited in the Discussion section.

Enol Acetates (III).—The general procedure for the synthesis of the enol acetates of the cyclic ketones is illustrated by the specific directions for the preparation of cyclohex-1-en-1-yl acetate. The properties of the enol acetate are also given below.

Cyclohex-1-en-1-yl Acetate.—A mixture of 100 g. (1 mole) of cyclohexanone, 200 ml. (2 moles) of isopropenyl acetate and 1 g. of *p*-toluenesulfonic acid was maintained at reflux for 12 hours. Approximately 100 ml. of solvent was removed *in vacuo*, and 1 g. of sodium carbonate was added. The mixture was distilled through a Holzman column. The first fraction consisted of a mixture of isopropenyl acetate and cyclohexanone. Cyclohex-1-en-1-yl acetate[76] boiled at 84–85° (25 mm.), $n^{25}D$ 1.4555, yield 90%.

Cyclohept-1-en-1-yl acetate was prepared from cycloheptanone (Geigy); b.p. 64° (4 mm.), $n^{25}D$ 1.4620, yield 93%. *Anal.* Calcd. for $C_9H_{14}O_2$: C, 70.10; H, 9.15. Found: C, 70.09; H, 9.15.

Cycloöct-1-en-1-yl acetate[56] was prepared from cyclooctanone (Aldrich); b.p. 73° (3.4 mm.), $n^{25}D$ 1.4705, yield 93%. *Anal.* Calcd. for $C_{10}H_{16}O_2$: C, 71.39; H, 9.59. Found: C, 71.30; H, 9.59.

Cyclonon-1-en-1-yl acetate, b.p. 45° (0.13 mm.), $n^{25}D$ 1.4765, yield 64%. *Anal.* Calcd. for $C_{11}H_{18}O_2$: C, 72.48; H, 9.96. Found: C, 72.92; H, 10.51.

Cyclodec-1-en-1-yl acetate, b.p. 97° (3.5 mm.), $n^{25}D$ 1.4805, yield 90%. *Anal.* Calcd. for $C_{12}H_{20}O_2$: C, 73.43; H, 10.27. Found: C, 73.06; H, 10.36.

Cyclohendec-1-en-1-yl acetate, b.p. 57° (0.1 mm.), $n^{25}D$ 1.4795, yield 73%.

Cyclododec-1-en-1-yl acetate, b.p. 65° (0.1 mm.), $n^{25}D$ 1.4810, yield 67%.

Cyclotridec-1-en-1-yl acetate, b.p. 70° (0.1 mm.), $n^{25}D$ 1.4805, yield 60%.

Cyclotetradec-1-en-1-yl acetate, b.p. 82° (0.1 mm.), $n^{25}D$ 1.4815, yield 50%.

Cyclopentadec-1-en-1-yl acetate, b.p. 97° (0.2 mm.), $n^{25}D$ 1.4815, yield 78%.

2-Bromoketones (IV).—The general procedure for the synthesis of the 2-bromoketones is a modification of that of Bedoukian[23] and is illustrated below in the specific directions for the preparation of 2-bromocycloöctanone. The physical properties and analyses of the 2-bromoketones are shown in Table V, the infrared data in Table I and the ultraviolet data in Table II.

2-Bromocycloöctanone.—To 10 g. (0.06 mole) of cyclooct-1-en-1-yl acetate in 15 ml. of carbon tetrachloride cooled in Dry Ice–acetone mixture was added during 10–15 minutes 9.6 g. (0.06 mole) of bromine in 20 ml. of carbon tetrachloride. Decolorization of the bromine took place almost immediately. Absolute methanol (50 ml.) was added, and the solution was allowed to stand at 25° for 3 days, whereupon it was transferred to a separatory funnel. Carbon tetrachloride (50 ml.) was added, and the solution was washed with 50 ml. of water and was dried over anhydrous magnesium sulfate. The solvent was removed *in vacuo* at room temperature, and the residue was distilled through a Holzman column, b.p. 51° (0.2 mm.), $n^{25}D$ 1.5140, yield 11 g. (89%) (see Table V).

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α,β-Unsaturated Ketones (V).—The general method for the dehydration of acyloins to α,β-unsaturated ketones is illustrated below in the directions for the preparation of cyclodec-2-en-1-one. This method is a modification of the procedure of Stoll.[8] The ultraviolet absorption maxima are given in Table III.

Cyclodec-2-en-1-one.—A flask equipped with a capillary tube for the admission of nitrogen, a thermometer reaching almost to the bottom, and connected to a 30 × 2.5-cm. column packed with a mixture of equal volumes of Alcoa alumina (48–100 mesh) and Gooch grade, medium-fiber asbestos was charged with sebacoin (85 g., 0.5 mole). The system was maintained at a pressure of 4 mm. by connecting the side-arm of the receiving flask to a vacuum system and adjusting the nitrogen flow. The temperature within the column, which was maintained at 330–350°, was measured by means of an ordinary thermometer in the center of the column. Distillation began when the pot temperature reached 180–200° and was continued for 6–7 hours, the final pot temperature reaching 300–320°. The crude distillate was dried over calcium chloride and was distilled through a Holzman column, b.p. 70–73° (1.5 mm.), $n^{20}\text{D}$ 1.4960, yield 48 g. (63%).

A **semicarbazone** was prepared in 92% yield, m.p. 189° after four recrystallizations from methanol.

Anal. Calcd. for $C_{11}H_{19}N_3O$: C, 63.13; H, 9.15; N, 20.08. Found: C, 63.23; H, 9.26; N, 20.06.

Cyclododec-2-en-1-one, b.p. 45–49° (0.04 mm.), $n^{20}\text{D}$ 1.4790 (reported[46] 142–153° (16–18 mm.)), 68% yield. A **semicarbazone** was prepared in 96% yield, m.p. 178° after 4 recrystallizations from methanol.

Anal. Calcd. for $C_{13}H_{23}N_3O$: C, 65.78; H, 9.77; N, 17.71. Found: C, 66.02; H, 9.68; N, 17.41.

Cyclotridec-2-en-1-one, b.p. 85–92° (0.06 mm.), $n^{21}\text{D}$ 1.4970 (reported[46] 119–125° (0.5 mm.), 72% yield. A **semicarbazone** was prepared in 97% yield, m.p. 180° after four recrystallizations from methanol.

Anal. Calcd. for $C_{14}H_{25}N_3O$: C, 66.89; H, 10.03; N, 16.72. Found: C, 66.98; H, 9.90; N, 16.80.

Cyclotetradec-2-en-1-one, b.p. 107–109° (1 mm.), $n^{21}\text{D}$ 1.4949. A **semicarbazone** was prepared in 96% yield, m.p. 165–166° (reported[47] 165–166°), after two recrystallizations from methanol.

Decan-4-ol-2-one (VIII) was prepared according to the procedure of Grignard and Chambret,[78] b.p. 72–74° (0.5 mm.) (reported[78] 130–134° (15 mm.)), 70% yield.

Oxidation of Decan-4-ol-2-one (VIII).—Oxidations were carried out using various reagents and conditions (see Discussion). The products were identified by infrared spectroscopy. The procedure for the successful oxidation using *t*-butyl hypochlorite is given. To a solution of 5.2 g. (0.03 mole) of decan-4-ol-2-one in 80 ml. of dioxane containing 5 ml. of water was added 3.3 g. (0.03 mole) of *t*-butyl hypochlorite.[79] The solution was allowed to stand at room temperature for one hour and in the refrigerator overnight. The dioxane solution then was poured into 100 ml. of water, and the product was extracted with four 50-ml. portions of ether. The ethereal extracts were combined and washed with 50 ml. of water, 50 ml. of a 10% aqueous solution of sodium carbonate and 50 ml. of water. The solvent was removed *in vacuo*, and the residue was distilled through a Holzman column. The first fraction consisted of 0.9 g. of a mixture of starting material and dehydrated product. Decane-2,4-dione (IX) boiled at 50–52° (0.3 mm.) (reported[80] 130–131° (23 mm.)), yield 4.0 g. (80%). The product gave a positive ferric chloride test.

3-Bromocyclotetradecanone.—To a solution of 4.68 g. (0.225 mole) of cyclotetradec-2-en-1-one in 100 ml. of chloroform cooled in a Dry Ice–acetone mixture was added over a period of 30 minutes a saturated solution of hydrogen bromide in chloroform. The solution was allowed to stand in a cooling bath for 1 hour, and the solvent was removed *in vacuo*, allowing the solution to warm slowly to room temperature. The light brown residue was recrystallized from pentane, affording 6.25 g. (96%) of colorless needles, m.p. 75°.

Anal. Calcd. for $C_{14}H_{25}BrO$: C, 58.13; H, 8.71. Found: C, 58.32; H, 8.78.

3-Bromocyclotridecanone.—Prepared from 2.0 g. (0.01 mole) of cyclotridec-2-en-1-one in the same manner as 3-bromocyclotetradecanone, 1.6 g. (60%) yield of off-white crystals, m.p. 42–46°, from pentane, this material decomposed rapidly.

3-Bromocyclodecanone.—Prepared from 7.0 g. (0.046 mole) of cyclodec-2-en-1-one in the same manner, evaporation of the chloroform left a viscous oil which was distilled through a Holzman column, b.p. 95–100° (0.4 mm.), $n^{25}\text{D}$ 1.4980, yield 7.0 g. (65%). The infrared spectrum of a liquid film showed no unsaturation but exhibited a carbonyl absorption maximum at 1700 cm.$^{-1}$ (for cyclodecanone as a liquid film, $\nu_{\max}$ 1698 cm.$^{-1}$).

Attempted conversions of these 3-bromoketones to 3-hydroxyketones and to cycloalkane-1,3-diones were not successful.

3-(1′-Pyrrolidino)-cyclotetradecanone.—Pyrrolidine (2.1 g., 0.03 mole) was added to 4.16 g. (0.02 mole) of cyclotetradec-2-en-1-one. The solution was allowed to stand at room temperature for 6 hours, the excess pyrrolidine was removed *in vacuo*, and the yellow residue was recrystallized from pentane yielding 5 g. (89%) of colorless needles, m.p. 75°.

Anal. Calcd. for $C_{18}H_{35}NO$: C, 77.36; H, 11.90; N, 5.01. Found: C, 77.72; H, 11.82; N, 4.89.

The product appeared to be stable when stored in the refrigerator, but it decomposed rapidly at room temperature. Attempts to form a hydrochloride, hydrobromide or perchlorate yielded only intractable oils. Attempted oxidations to a derivative of cyclotetradecane-1,3-dione were not successful.

Cyclodec-5-en-1-one (X) was prepared from 6-hydroxycyclodecanone[61,62] ($\nu_{\max}^{\text{CHCl}_3}$ 1700 (C=O), 3620 (O–H, sharp), 3470 cm.$^{-1}$ (O–H, bonded)), m.p. 69–71°, by the method of Cope and Holzman,[62] b.p. 74–76° (3.1 mm.), $n^{25}\text{D}$ 1.4941; $\nu_{\max}^{\text{liquid film}}$ 1706, ~1672, 1448, ~1433, 1357, 993, 960, 747, 703 cm.$^{-1}$; $\nu_{\max}^{\text{CHCl}_3}$ 1697, 992, 960 cm.$^{-1}$; $\nu_{\max}^{\text{CCl}_4}$ 1706, 993, 960, 704 cm.$^{-1}$ (selected maxima in each case).

Anal. Calcd. for $C_{10}H_{16}O$: C, 78.89; H, 10.60. Found: C, 78.67; H, 10.74.

Hydrogenation of a 0.149 g. of the analytical sample in 5 ml. of methanol in the presence of 0.115 g. of prereduced palladium-on-charcoal required 99.5% of one molar equivalent of hydrogen.

Bicyclo[5.3.0]decan-2-one (XI) was prepared from 6-hydroxycyclodecanone according to method "B" of Goering, Olson and Espy,[63] b.p. 92–93° (4.5 mm.), $n^{25}\text{D}$ 1.4870. The infrared spectrum (liquid film) had a maximum of 1702 cm.$^{-1}$, but lacked maxima at 1600 and 980 cm.$^{-1}$. Hydrogenation of a 0.142-g. sample in 5 ml. of methanol in the presence of 0.100 g. of prereduced palladium-on-charcoal required no hydrogen, showing that no cyclodec-5-en-1-one was present.

Anal. Calcd. for $C_{10}H_{16}O$: C, 78.89; H, 10.60. Found: C, 78.72; H, 10.43.

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