

Ionization constants of the hydroquinones K_1 and K_2 were calculated from the ultraviolet spectra at various pH values. A 10^{-3} M solution of the desired hydroquinone was prepared with deaerated water. Some hydroquinones are slow to dissolve in water, so they were first dissolved in a small volume of alcohol and this solution was added to water. The alcohol was never more than 0.5% of the total volume of the reaction solution. The hydroquinone solution was mixed in the volume ratio of 1:1 with various phosphate buffers or KOH solutions in a flow machine¹⁰ and the ultraviolet absorption spectra were measured in the region of 220 to 400 m μ . A flow system was not actually necessary for this phase of the study since all of the hydroquinone species are stable at high pH. However, the apparatus was convenient in these cases since the deaerated solutions could be kept from contact with the air until the spectra were measured.

The pK values could be determined from plots of log (singly ionized hydroquinone/hydroquinone) or log (doubly ionized hydroquinone/singly ionized hydroquinone) vs. pH. However, we used the ratios of density differences instead of the ratios of concentrations¹² of the species. The analyses were made at wave lengths at which the difference in density between the two species was greatest.

The use of strong alkali necessary for the complete ionization of some hydroquinones had to be avoided in order to protect the quartz optics of the flow machine. Where pK₂ was very large, then, it was calculated along with K' from analysis of the pH dependence of K , as described in another section.

(12) C. A. Bishop and L. K. J. Tong, *J. Phys. Chem.*, **66**, 1034 (1962).

Semiquinone Formation Data. The semiquinones were produced in a jet mixing machine¹³ by partial oxidation of a deaerated solution of hydroquinone with ferricyanide solutions of predetermined concentrations. The hydroquinone, ferricyanide, and buffer (or KOH) solutions were mixed in volume ratio of 1:1:2 and examined 16 msec. after mixing by measuring the per cent transmission through an interference filter at 420 or 430 m μ in a 0.25-cm. cell. In the time scale we used, the equilibrium according to eq. 1 was established instantaneously. No change in semiquinone concentration could be detected in the interval 16–100 msec., showing that irreversible side reactions were negligible.

The hydroquinone stock solutions were made up by dissolving 2×10^{-3} mole in 1 l. of water, so that the initial hydroquinone concentration, $[R_0]$, was 5×10^{-4} M after mixing in the flow machine. In most cases, the concentration was checked by showing that the maximum occurred in the D vs. per cent oxidation curve when precisely one-half of the calculated amount of oxidant required to oxidize R_0 completely was added. In a few cases, e.g., the hydroquinonesulfonates, the solid hydroquinone was hydrated, so the weighed amount was something less than 2×10^{-3} mole. In these cases, the maxima in the D vs. per cent oxidation curves occurred when less than the expected amount of oxidant was added, but from the normality of the oxidant and the amount added at the maximum, the precise value of $[R_0]$ was calculated.¹⁴

(13) W. R. Ruby, *Rev. Sci. Instr.*, **26**, 460 (1955).

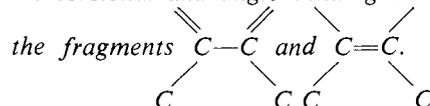
(14) NOTE ADDED IN PROOF. A similar treatment for *p*-phenylenediamines has appeared recently: L. K. J. Tong and M. C. Glesmann, *Phot. Sci. Eng.*, **8**, 319 (1964).

Strain Effects. I. The Hydroxymethylene Ketone–Aldo Enol Equilibrium

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Directions of enolizations of α -formyl cyclic ketones relative to the cyclohexyl system (K_n/K_6) have been estimated by considering strain energy differences between I and II. The good qualitative agreement between the calculated and observed values of K_n/K_6 that is found suggests that the major effects that influence the relative directions of enolizations of α -formyl cyclic ketones are the torsional and angle bending strains associated with



The effects of strain on chemical reactivities and equilibria are most pronounced in cyclic structures

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where molecular geometry takes on various forms of constraint. An understanding of the fundamental origin of reactivity of equilibrium differences in ring systems requires knowledge of the structures of the systems being compared, and this is a most formidable requirement particularly for the medium-sized and seven-membered rings whose basic structures might be expected to depend largely on the degree and nature of substitution.

The concept of I-strain^{2,3} has led in some instances to rather quantitatively striking correlations between relative reactivities of chemically divergent processes involving a common change in carbon hybridization

(2) H. C. Brown and M. Gerstein, *J. Am. Chem. Soc.*, **72**, 2926 (1950).

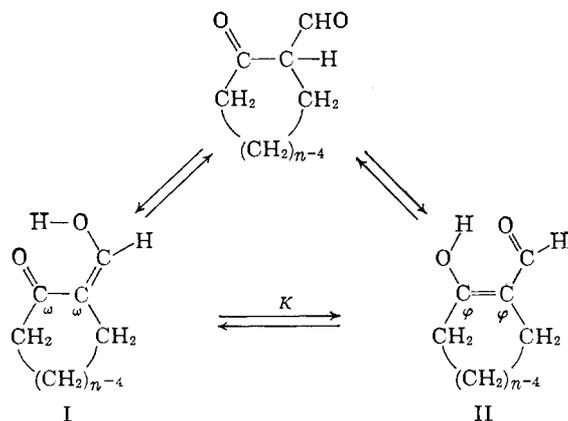
(3) E. L. Eliel, "Stereochemistry of Carbon Compounds," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p. 265 ff; J. Sicher, "Progress in Stereochemistry," Vol. 3, P. B. D. De la Mare and W. Klyne, Ed., Butterworth, and Co. (Publishers) Ltd., London, 1962, Chapter 6

of the ring skeleton.³ However, identification of the specific strains cumulatively considered as I-strain and which supposedly lead to the observed differences in relative reactivities in many reactions of medium-sized cyclic systems has not been attempted.³ Recent attempts to estimate relative solvolysis rates by considering the influence of strain have met with high orders of success.⁴

In this paper, an attempt will be made to identify the principal strains that appear to influence the directions of enolizations of α -formyl cyclic ketones.⁵ It is hoped ultimately that a more comprehensive understanding of the I-strain concept as directed to this equilibrium system will be realized.

Results

The Hydroxymethylene Ketone–Aldo Enol Equilibrium. The directions of enolizations (K) of α -formyl cyclic ketones as determined by nuclear magnetic resonance⁵ are found to vary markedly. The percentages of I as a function of ring size and for the bicyclo[2.2.1]heptyl⁶ and bicyclo[2.2.2]octyl systems are shown in Figure 1. Variation of the percentage of I with ring structure was not foretold and indeed an



explanation of the trends appears to be subtle. The geometries of I and II are predicted to be nearly identical because of the constraint imposed about the endocyclic trigonal carbons by the intramolecular hydrogen bonded ring system and because of π -electron delocalization. As a result, all nonbonded interactions in I are duplicated closely in II and cancel approximately in the difference.

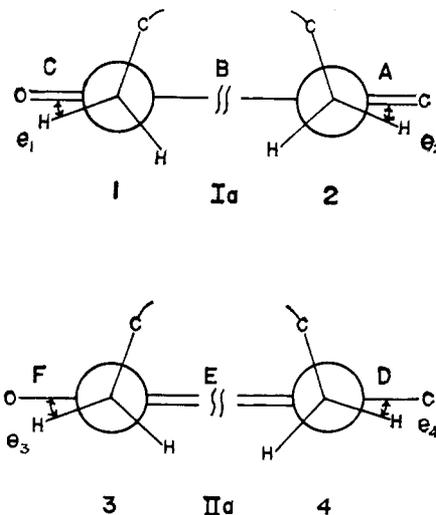
(4) C. S. Foote, *J. Am. Chem. Soc.*, **86**, 1853 (1964); P. von R. Schleyer, *ibid.*, **86**, 1854, 1856 (1964).

(5) E. W. Garbisch, Jr., *ibid.*, **85**, 1696 (1963).

(6) For 3-formylcamphor, the percentage of I at equilibrium with II is taken to lie between 98 and 99. The olefinic proton resonance of 3-hydroxymethylenecamphor is invariant over the temperature range of 25 to -100° , indicating that the aldo enol tautomer concentration must be negligible. When $n = 6$ (2-formylcyclohexanone), $\log K$ varies linearly with $1/T$ over this temperature range, with a change in the chemical shift of the vinylaldehyde proton resonance of 0.15 p.p.m. A finite concentration of the aldo enol form of 3-formylcamphor must be present at equilibrium, as Dr. Richer (University of Montreal) has kindly informed the author that the diazomethane methylation of 3-formylcamphor leads to several per cent of the O-methyl aldo enol (*Can. J. Chem.*, in press). Originally,⁵ the enol form of 3-formylcamphor was taken as the model for 100% I. Using the more realistic percentages above, a finite value of $\Delta\Delta G$ is obtained for the bicyclo[2.2.1]heptyl system and the $\Delta\Delta G$ values for the other systems are not changed significantly from those obtained using the originally reported equilibrium constants (K). Therefore, an adjustment of the originally reported⁵ value of K is made for the bicyclo[2.2.1]heptyl system and values of K for the other systems are not changed.

Bond stretching deformations are too energetic to contribute to minimizing the total strain of a system, in general, and consequently are not likely to contribute to the strain energy difference between I and II.

Torsional Strain. Torsional strains have been found to contribute sizably to the total strains of molecules⁷⁻⁹ and their inclusion in strain calculations is important. Since torsional potentials are not thought to contain significant contributions from nonbonded interactions,^{10,11} torsional and nonbonded strains are generally considered separately.⁹ Torsional strains in the aliphatic rings of I and II are considered to be the same as a result of the expected equality in conformations of the two tautomers; however, torsional strains in frag-



ments 1 and 2 of Ia and fragments 3 and 4 of IIa would appear to be different. The torsional potential functions for propene,^{8,12} $E_t' = 1 - \cos 3\theta$, and for acetaldehyde,¹³ $E_t'' = 0.60(1 - \cos 3\theta)$, were selected as being appropriate for application to fragments 1-4. The potential function for propene is considered to be adequate for fragment 3, in view of the similarity of the potentials for acetaldehyde, acetyl chloride, acetyl fluoride, and acetonitrile.^{11a} The potentials as applied to each fragment separately must be weighted to account for the fractional π -bond orders of the mobile bonds in the fragment. For example, the potential function for fragment 1 (E_{t1}) is considered to consist of contributions cE_t'' and bE_t' where c and b are the π -bond orders for bonds C and B, respectively, in Ia, and E_t'' and E_t' are given above. The following equations relate potential functions for fragments 1-4.

$$\begin{aligned} E_{t1} &= 0.60(1 - \cos 3\theta_1)c + (1 + \cos 3\theta_1)b \\ E_{t2} &= (1 - \cos 3\theta_2)a + (1 + \cos 3\theta_2)b \\ E_{t3} &= 0.60(1 - \cos 3\theta_3)f + (1 + \cos 3\theta_3)e \end{aligned}$$

(7) K. S. Pitzer and W. E. Donath, *J. Am. Chem. Soc.*, **81**, 3213 (1959).

(8) C. W. Beckett, N. K. Freeman, and K. S. Pitzer, *ibid.*, **70**, 4227 (1948).

(9) J. B. Hendrickson, *ibid.*, **83**, 4537 (1961).

(10) E. B. Wilson, Jr., *Advan. Chem. Phys.*, **2**, 367 (1959).

(11) (a) D. J. Millen, "Progress in Stereochemistry," Vol. 3, P. B. D. De la Mare and W. Klyne, Ed., Butterworth and Co. (Publishers) Ltd., London, 1962, Chapter 4; (b) E. B. Wilson, Jr., *Tetrahedron*, **17**, 191 (1962).

(12) D. R. Lide and E. E. Mann, *J. Chem. Phys.*, **27**, 868 (1957); D. R. Herschbach and L. C. Krisher, *ibid.*, **28**, 728 (1958).

(13) R. W. Kilb, C. C. Lin, and E. B. Wilson, *ibid.*, **26**, 1965 (1957).

$$E_{t4} = (1 - \cos 3\theta_4)d + (1 + \cos 3\theta_4)e$$

$$a = 0.81, b = 0.51, c = 0.68, d = 0.63$$

$$e = 0.69, f = 0.39$$

HMO calculations have been carried out on the two enol tautomers of α -formylpropanone by Forsén¹⁴ employing various models for inclusion of methyl group interaction.¹⁵ The inductive model,¹⁵ taking the Coulomb integral for the carbon attached to the methyl group as $\alpha - 0.5\beta$ and $\alpha_{O-} = \alpha + B$, $\alpha_{O=} = \alpha + 2\beta$, $\beta_{C=O} = \beta_{C=C}$, and $\beta_{C-O} = 0.8$,¹⁵ is considered qualitatively appropriate for I and II. The mobile bond orders (a - f) calculated therefrom are listed above. The derived torsional potential functions for Ia ($E_{t1} + E_{t2}$) and for IIa ($E_{t3} + E_{t4}$) are

$$E_{tIa} = 0.32 + 0.40(1 - \cos 3\theta)/2 \quad (1)$$

$$E_{tIIa} = 1.04(1 + \cos 3\theta)/2 \quad (2)$$

in which angles θ ($-60^\circ \leq \theta \leq 60^\circ$) in 1-4 are taken as being equal.^{16a}

Angles θ in the six- through twelve-membered rings (I and II) probably will correspond closely to the related angles in the parent *cis*-alkenes and alicyclic semiquinones whose angles have been estimated recently by n.m.r.^{16b, 18} and e.p.r.^{17, 18} A microwave study by Rathjens¹⁹ has shown cyclopentene to be nonplanar (C_s) with $\theta \cong 40^\circ$ and with a low (*ca.* 0.6 kcal./mole) barrier to inversion. This is in slight contrast with earlier considerations by Beckett, Freeman, and Pitzer⁵ who concluded that there is a near balance of strains for small rotations from planarity. Although there may be a significant population of cyclopentene in the planar conformation at room temperature, θ taken as about 40° appears more realistic than a value of about 60° .^{16b, 17} Angles θ for bicyclo[2.2.1]heptene and bicyclo[2.2.2]octene are estimated from molecular models to be about 20 and 0° , respectively. E.p.r. hyperfine splittings in benzobicyclo[2.2.1]heptyl-3',6'-semiquinone²⁰ agree with the angle θ taken for bicyclo[2.2.1]heptene. Table I lists the angles θ selected for this work together with the related angles in the *cis* cycloalkenes and alicyclic semiquinones as estimated by n.m.r. and e.p.r.

There remains the consideration of torsional strain

(14) S. Forsén, *Arkiv Kemi*, **20**, 41 (1963).

(15) A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," John Wiley and Sons, Inc., New York, N. Y., 1961, Chapter 5.

(16) (a) Granting the validity of the assumption that the conformations of I and II are nearly identical (see earlier), angles θ in 1 to 4 will be the same in the bicyclo[2.2.1]heptyl, bicyclo[2.2.2]octyl, cyclopentyl, cyclohexyl, and probably the cycloheptyl systems. For the larger membered cyclic systems, angles θ in 1 and 2 (or 3 and 4) may be different. In these cases, time-averaged angles θ as estimated by e.p.r. and n.m.r. are adopted (see ref. 18 and Table I). (b) G. V. Smith and H. Kriloff, *J. Am. Chem. Soc.*, **85**, 2016 (1963).

(17) G. A. Russell and E. T. Strom, *ibid.*, **86**, 744 (1964).

(18) Angles derived by n.m.r.¹⁶ were calculated on the basis that the couplings observed represent averages of the two vinyl-H-allylic-H couplings, assuming rapid interconversions between two rigid and identical conformations (*e.g.*, chair-chair). The angles derived by e.p.r.¹⁷ reflect averages resulting from torsional oscillations from equilibrium conformations or conformational interconversions of small energy barriers. Molecules such as cyclopentene and the medium-sized cycloalkenes are likely to be involved in such rotations and the time-average angle derived by n.m.r. and e.p.r. from a $k \cos^2$ relation will be slightly different from that required for the torsional potential functions.

(19) G. W. Rathjens, *J. Chem. Phys.*, **36**, 2401 (1962).

(20) L. M. Stock (University of Chicago), private communication.

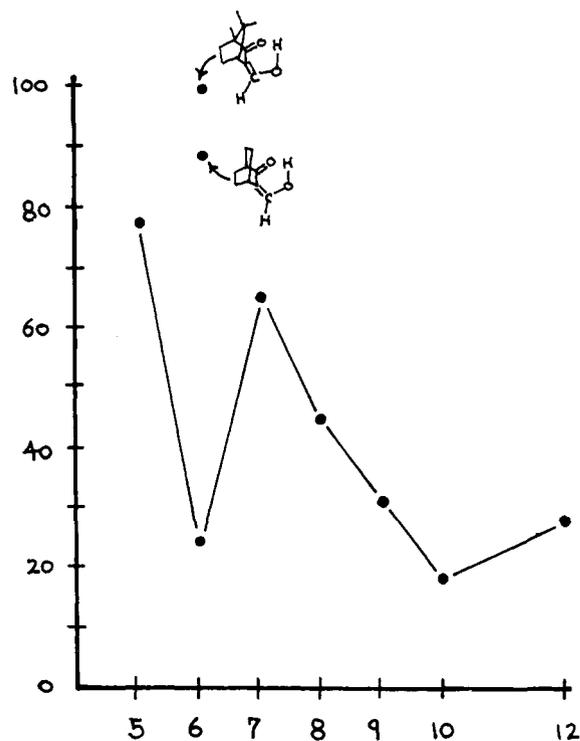


Figure 1. Percent of I as a function of ring size (n).

energy differences between I and II arising from slight rotations about the central bonds B and E in Ia and IIa, respectively. These deformations would not

Table I. Summary of Angles θ Estimated by N.m.r. and E.p.r. and Those Adopted for I and II

Ring system	θ , alkene ^a (n.m.r.)	θ , semiquinone ^b (e.p.r.)	θ , I and II adopted
Bicyclo[2.2.1]-C ₇	20
Bicyclo[2.2.2]-C ₈	0
Cyclo-C ₅	63	63 ^c	40 ^d
Cyclo-C ₆	43	43	40
Cyclo-C ₇	10	20	15
Cyclo-C ₈	15	30	25
Cyclo-C ₉	37	31	35
Cyclo-C ₁₀	15 (50) ^e	~ 0 or (~ 60) ^e or (~ 60 and ~ 0) ^{e, f}	30 ^g
Cyclo-C ₁₂	...	~ 0 or (~ 60) ^e or (~ 60 and ~ 0) ^{e, f}	30 ^g

^a Ref. 16b. ^b Ref. 17. ^c Assumed planar molecule and geometry given in ref. 16b. ^d See text. ^e Parenthetical values fit data. ^f Two different angles θ . ^g From Dreiding models, both angles taken as being 0° or 60° appear to lead to markedly unfavorable ring conformations. The value arbitrarily assigned is compatible with angles θ being different at ~ 60 and $\sim 0^\circ$ (see footnote *f*).

be expected to contribute largely to minimizing ring strain when π -bond orders of bonds B and E are large. For example, in ethene, 0.2, 0.8, and 1.8 kcal./mole are required to twist 5, 10, and 15° , respectively, about the double bond.²¹ The π -bond orders of bonds B and E have been calculated to be 0.51 and 0.69, respectively (see earlier), and therefore small rotations about these bonds may be competitive with other torsional

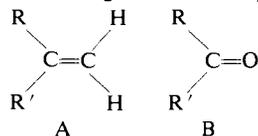
(21) The torsional force constant for ethylene is 3.6×10^{-12} erg radian⁻² (see Herzberg, ref. 26). Angles are the dihedral angles of the CH₂ groups of ethylene about the carbon-carbon axis.

and angular deformations in minimizing total strain. The agreement between angles θ derived from n.m.r. and e.p.r. measurement on the *cis*-cyclic alkenes and the alicyclic semiquinones, respectively, suggests that fragments Ia and IIa probably will be planar to a good approximation. In any event should the signs and magnitudes of small rotations about bonds B and E be about the same for a given enol system, the resulting torsional strains will be comparable because of the similar π -bond orders and will cancel nearly in the difference.

Angle Bending Strain. Examination of both Figure 1 and Table I clearly shows that the torsional strain energy difference between fragments Ia and IIa is not likely to be the sole major explanation of the differences in directions of enolizations of the cyclic α -formyl ketones. Angles θ are taken as being about the same for the five- and six-membered rings, yet I is 1.4 kcal./mole more favored when $n = 5$ than when $n = 6$. Furthermore, the large preference of 3-formylcamphor for I as compared with 2-formylcyclohexanone (3.0–3.4 kcal./mole) is considerably greater than that estimated from eq. 1 and 2 (0.7 kcal./mole).

Particularly for the bicyclo[2.2.1]heptyl, bicyclo[2.2.2]octyl, and cyclopentyl systems, angle bending strain differences associated with the $\text{C} > \text{C} =$ and $\text{C} = \text{C} - \text{C}$ groupings of I and II, respectively, may be important. This expectation may be realized after recalling that equilibrium trigonal bond angles of the type $\text{R} - \text{C} = \text{C}(\text{O})$ appear consistently to be larger than those of the type $\text{R}_2\text{C} =$ (see Table II). Although

Table II.^a Trigonal Bond Angles in Some Acyclic Structures



Structure	R	R'	RCR'	R'CC(O)	Ref.
A	H	H	115.5	122.3	<i>b</i>
B	H	H	118	121	<i>c</i>
A	H	CH ₃	116.7	121.7	<i>d</i>
B	H	CH ₃	117	124	<i>e</i>
A	CH ₃	CH ₃	115.3 (112)	122.3 (124)	<i>f(g)</i>
B	CH ₃	CH ₃	116	122	<i>h</i>
A	H	CHCH ₂	...	122.4	<i>i</i>
B	H	CHO	...	121.9 (123)	<i>j(k)</i>

^a For a summary of additional examples see ref. 10b. ^b L. S. Bartell and R. A. Bonham, *J. Chem. Phys.*, **31**, 400 (1959). ^c R. B. Lawrence and M. W. P. Strandberg, *Phys. Rev.*, **83**, 363 (1951). ^d D. R. Lide, Jr., and D. Christensen, *J. Chem. Phys.*, **35**, 1374, (1961). ^e R. W. Kilb, C. C. Lin, and E. B. Wilson, Jr., *ibid.*, **26**, 1695 (1957). ^f L. H. Scharpen and V. M. Laurie, *ibid.*, **39**, 1732 (1963). ^g L. S. Bartell and R. A. Bonham, *ibid.*, **32**, 824 (1960). ^h J. D. Swalen and C. C. Costain, *ibid.*, **31**, 1562 (1959). ⁱ 1,3-Butadiene: A. Almennings, O. Bastiansen, and M. Traetteberg, *Acta Chem. Scand.*, **12**, 1221 (1958). ^j Glyoxal: G. W. King, *J. Chem. Soc.*, 5054 (1957). ^k J. E. LuValle and V. Schomaker, *J. Am. Chem. Soc.*, **61**, 3520 (1939).

the origin of this trend in trigonal bond angles does not appear to be understood completely,^{10b,22} it is likely that equilibrium angles (ω_e) in ideal²³ I will be some-

(22) L. S. Bartell, *J. Chem. Phys.*, **32**, 827 (1960).

(23) Angles ω_e and φ_e in ideal I and II are the equilibrium angles that

what smaller than the corresponding angles (φ_e) in ideal²³ II (see, for example, butadiene and glyoxal, Table II).

If angles ω and φ could be estimated for the ring systems investigated and a reasonable value assigned to φ_e in ideal²³ II, the value of ω_e in ideal I can be estimated assuming that the free energy difference $\Delta G (n = 5) - \Delta G (n = 6)$ for the equilibrium $\text{I} \rightleftharpoons \text{II}$ is due primarily to the difference in trigonal angle bending strain (recall that for these systems the difference $\Delta\Delta E_t$ is thought to be near zero). Angle bending strain for I (E_{bI}) and II (E_{bII}) then may be estimated from eq. 3

$$E_{bI} = k(\omega_e - \omega)^2 \text{ or } E_{bII} = k(\varphi_e - \varphi)^2 \quad (3)$$

where ω and φ are the actual angles in I and II, respectively, ω_e and φ_e are defined above; and the force constants, k , for the in-plane bending of $\text{C} = \text{C} - \text{C}$ and $\text{C} > \text{C} =$ are taken as being the same^{7,8,24,25} and equal to 8×10^{-12} erg radian⁻² (which is equivalent to 35 cal. deg.⁻²).

It is necessary to digress momentarily and discuss the use here of angle bending strain in lieu of angle strain. Angle strain, as generally considered,^{7,8,24} relates a bond angle strain relative to an ideal angle corresponding to the hybridization of the atom which bond angles are bent and is given by eq. 3 where ω_e and φ_e are replaced by 120° for trigonal angles. In actuality, $\text{C} - \text{C} - \text{C}$, $\text{C} = \text{C} - \text{C}$, and $\text{C} > \text{C} =$ angles in simple "unstrained" acyclic molecules rarely exhibit ideal angles as evidenced by the data in Table II and by electron diffraction data²⁶ on the *n*-alkanes that gives average $\text{C} - \text{C} - \text{C}$ angles of 112.4° . Since steric repulsions do not appear to be the dominant origin of these bond angle deformations from ideal values^{11b} (see Table II), $\text{C} = \text{C} - \text{C}$ and $\text{C} > \text{C} =$ fragments in cyclic hydrocarbons would appear to encompass *minimum total strain* when their equilibrium bond angles correspond to the respective equilibrium angles in suitably related "unstrained" acyclic hydrocarbons. Consequently, it may be qualitatively more realistic to estimate strain associated with bent endocyclic $\text{C} = \text{C} - \text{C}$ and $\text{C} > \text{C} =$ angles with reference to their ideal equilibrium values and not to 120° . Ideal equilibrium $\text{C} = \text{C} -$ and $\text{C} > \text{C} =$ angles appear to be about 122 and 116° , respectively. If the associated angle

would be expected for a simple "unstrained" acyclic or cyclic system in which there is no constraint imposed on fragments Ia and IIa by the remaining hydrocarbon ring. It can be shown that any reasonable value for φ_e can be selected without altering significantly the relative strain energy values between I and II.

(24) F. H. Westheimer, "Steric Effects in Organic Chemistry," M. S. Newman, Ed., John Wiley and Sons, Inc., New York, N. Y., 1956, Chapter 12.

(25) Force constants for the $\text{C} = \text{C} - \text{H}$ and $\text{C} > \text{C} = \text{H}$ in-plane bending are 5.7×10^{-12} and 6.4×10^{-12} erg radian⁻², respectively. See G. Herzberg, "Infrared and Raman Spectra of Polyatomic Molecules," D. Van Nostrand Co., Inc., New York, N. Y., 1945, p. 183, and E. B. Wilson, *J. Chem. Phys.*, **9**, 319 (1941). Westheimer²⁴ has suggested a force constant equal to 8×10^{-12} erg radian⁻² as being approximately applicable to CCC bending in general.

(26) R. A. Bonham, L. S. Bartell, and D. A. Kohl, *J. Am. Chem. Soc.*, **81**, 4765 (1959).

Table III. Angles ω and φ Adopted and Summary of Supporting N.m.r. Data

Ring system	Vinyl H,H	J of <i>cis</i> -alkene, c.p.s.			
		Vinyl $^{13}\text{C-H}$ (± 1)	τ O-H I and II ^a	ω (I) adopted	φ (II) adopted
Bicyclo[2.2.1]-C ₇	5.8 ^b	174 ^c	-0.15	107	107
Bicyclo[2.2.2]-C ₈	8.3 ^d	162 ^e	-2.15	115	115
Cyclo-C ₅	5.1 ^f , 5.4 ^g	160 ^e	-1.35	111.5	111.5
Cyclo-C ₆	8.8 ^f , 9.6 ^g	157 \pm 2 ^e	-4.27	120.	120
Cyclo-C ₇	10.8 ^f (10.9 \pm 0.5) ^e	155 ^e	-4.60	119.6 ^g	122 ^g
Cyclo-C ₈	10.3 ^f (10.4 \pm 0.3) ^e	155 ^e	-4.97	119.6	122
Cyclo-C ₉	10.7 ^f		-5.14	119.6	122
Cyclo-C ₁₀	10.8 ^f		-5.11	119.6	122
Cyclo-C ₁₂	...		-5.15	119.6	122

^a Averaged enol proton resonance of I and II. ^b Ref. 27. ^c Ref. 28. ^d 1,3-Cyclohexadiene-TCNE adduct and bicyclo[2.2.2]octene. ^e Present investigation. ^f Ref. 16b. ^g Taken as ideal equilibrium value; see text.

strains (if any) are normalized to zero (in the present work, these strains, if any, cancel upon considering total strains of I and II relative to the six-membered ring) and if the bending force constants are comparable for the different angles,²⁵ bending both angles to 110° leads to a strain in the C=C-C fragment of about 2.5 kcal./mole as compared with 0.6 kcal./mole for the C>C=C fragment (eq. 3). On the other hand, both of these bent angles would be considered to relate the same angle strain (*ca.* 1.7 kcal./mole). In order to avoid confusion with *angle strain*, the strain resulting from bending an angle from its ideal equilibrium value in an "unstrained" acyclic reference is called *angle-bending strain*.

Regressing to the subject matter of this paper, angles φ , which are taken to be equal in a given ring system, are expected to resemble closely the endocyclic trigonal bond angles in the corresponding olefinic hydrocarbons. These bond angles in olefinic hydrocarbons correlate qualitatively with vinyl-H^{16,27} and $^{13}\text{C-H(vinyl)}$ ²⁸ nuclear spin coupling constants. The *cis*-vinyl-H couplings are calculated²⁹ to decrease with increasing C=C-H angle which will increase²⁴ with decreasing C=C-C angle in the *cis* cycloalkenes. $^{13}\text{C-H}$ couplings have been found to increase rather linearly with decreasing C=C-C angles in the *cis* cycloalkenes.²⁸ It is expected also that the average chemical shift of the enol proton of I and II would move to high field with decreasing angles ω and φ , because of the concurrently increasing hydrogen bond distance, $r(\text{O-H}\cdots\text{O})$.³⁰ The above magnetic resonance data are used as a guide in assigning angles φ and ω and are summarized in Table III.

The trigonal bond angle strain in cyclohexene is thought to be near zero³¹ giving bond angles of 120°. The endocyclic trigonal bond angles in *cis*-cyclododecene and *cis*-cyclodecene and, consequently, also in I and II where $n = 10$ and 12 are likely to represent ideal equilibrium angles. From Table II (see particularly butadiene and glyoxal), φ_e is estimated to be 122° and angle ω_e is computed to be 119.6° (see earlier).

(27) P. Laszlo and P. von R. Schleyer, *J. Am. Chem. Soc.*, **85**, 2017 (1963).

(28) P. Laszlo and P. von R. Schleyer, *ibid.*, **86**, 1171 (1964).

(29) M. Karplus, *ibid.*, **85**, 2870 (1963).

(30) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High-Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co. Inc., New York, N. Y., 1959, p. 407 ff.

(31) K. S. Pitzer, *Science*, **101**, 672 (1945).

The data in Table I show that cycloheptene, *cis*-cyclooctene, and *cis*-cyclononene also are expected to bear endocyclic trigonal angles close to the ideal equilibrium values. As before, ω and φ in I and II are assigned the values ω_e and φ_e , respectively. The C₁-C₂-C₃ angle in bicyclo[2.2.1]heptane has been estimated to be 104°. Because of the rigidity of this system, the C-C=C angle in bicyclo[2.2.1]heptene will not be much larger than 104°. This angle in bicyclo[2.2.1]heptadiene was estimated at 109.1° from electron diffraction.³³ In the corresponding monoalkene, this angle should be somewhat closer to 104°, and a value of 107° would seem reasonable. The C=C-C angle in cyclopentene has been estimated to be 111.5° by microwave spectroscopy.¹⁹ The vinyl-H and $^{13}\text{C-H(vinyl)}$ couplings for bicyclo[2.2.2]octene and the τ -values³⁴ for the enol proton of the bicyclo[2.2.2]octyl system (I and II) all are intermediate between the respective parameters for the bicyclo[2.2.1]heptyl and cyclododecyl systems (see Table III). From this information, the C=C-C angle in bicyclo[2.2.2]octene is considered to be about 115°.

Table III summarizes angles ω and φ that will be used for estimations of angle bending strains, together with supporting n.m.r. parameters. Angles ω and φ for the bicycloheptyl, bicyclooctyl, and cyclopentyl rings are assumed to be the same.³⁵

Discussion

Using eq. 1-3 and the appropriate angles from Tables I and III, differences in total strain energies relative to the cyclohexyl system ($\Delta\Sigma\Delta E$) have been estimated for I \rightleftharpoons II and compared with the corresponding observed $\Delta\Delta G$ values. The results are given in Table IV. The close agreement between the calculated and observed values for all the systems in-

(32) H. Krieger, *Suomen Kemistilehti*, **31**, 348 (1959); C. F. Wilcox Jr., *J. Am. Chem. Soc.*, **82**, 414 (1960).

(33) W. G. Woods, R. A. Carboni, and J. D. Roberts, *ibid.*, **78**, 5653 (1956).

(34) It is interesting that a plot of τ -values of the averaged enol proton resonance in I and II listed in Table III vs. φ is closely linear. The low τ -value of this proton resonance for the cycloheptyl system relative to the medium-sized ring systems probably reflects its high percentage in enol form II.

(35) Whereas this assumption only may be valid approximately, angle bending strains computed assuming that the endocyclic trigonal angles decrease linearly from the value given for φ to the value for the saturated hydrocarbon as the ideal endocyclic trigonal angles decrease from 122° to the value for the saturated hydrocarbon (ω_e then becomes smaller than 119.6°) did not differ significantly from the strains estimated taking ω and φ as being the same.

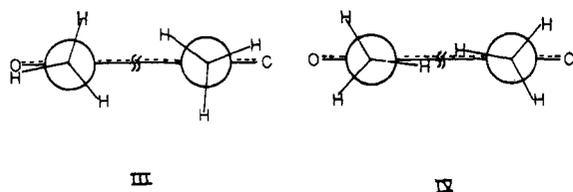
Table IV. Calculated Strain Energy^a and Observed Free Energy^a Differences between I and II Relative to the Six-Membered Ring

Ring system (<i>n</i>) I and II	E_{bI}	E_{bII}	ΔE_b	E_{tIa}	E_{tIIa}	ΔE_t	$\Sigma \Delta E$	$\Delta \Sigma \Delta E_{\text{calcd}}$ ($-1.37 \log K_n/K_6$)	$\Delta \Delta G^{25^\circ}$ _{obsd}
Bicyclo[2.2.1]-C ₇	5.56	7.88	2.32	0.42	0.78	0.36	2.68	2.9	3.0-3.4
Bicyclo[2.2.2]-C ₈	0.74	1.72	0.98	0.32	1.04	0.72	1.70	1.9	1.9
5	2.30	3.86	1.56	0.62	0.26	-0.36	1.20	1.4	1.4 ^b
6	0.0	0.14	0.14	0.62	0.26	-0.36	-0.22	0.0	0.0
7	0.0	0.0	0.0	0.38	0.89	0.51	0.51	0.7	1.1
8	0.0	0.0	0.0	0.47	0.66	0.19	0.19	0.4	0.5
9	0.0	0.0	0.0	0.66	0.47	-0.19	-0.19	0.0	0.2
10	0.0	0.0	0.0	0.52	0.52	0.0	0.0	0.2	-0.2
12	0.0	0.0	0.0	0.52	0.52	0.0	0.0	0.2	0.1

^a Kcal. mole⁻¹. ^b Value was used to estimate ω_e . See text.

investigated suggests that the major effects that influence the directions of enolizations of the α -formyl cyclic ketones relative to the six-membered ring have been accounted for and are torsional and angle bending strains in fragments Ia and IIa. Entropy effects would appear to be small.

The directions of enolizations of simple acyclic α -formyl ketones such as 3-formylbutanone would be expected to favor the hydroxymethylene ketone tautomers to a larger extent than do the six- and medium-membered ring systems on the basis of torsional strain, since the populations of molecules in conformation III are likely to be greater than those in less favorable



conformations such as IV. Angle θ , therefore, is likely to be small, giving a preference for the hydroxymethylene ketone tautomer relative to the six-membered ring (eq. 1 and 2). Angle-bending strain in both tautomers would not be expected to be important (see Table II). This expectation, that the hydroxymethylene ketone tautomers in simple acyclic systems will be more stable relative to that in the six-membered ring, is borne out experimentally.³⁶

The direction of enolizations of α -formyl cyclic ketones promises to be a sensitive probe for detecting deformations from ideal ring conformations resulting from substitution on and ring fusion to cyclic enol rings. Such deformations from ideal conformations would be expected to lead to changes in angles ω , φ ,

(36) E. W. Garbisch, Jr., to be published.

and θ , which in turn would alter the equilibrium composition of I and II relative to the parent systems. Changes in angles ω and φ (taken as being equal) can be qualitatively separated from changes in angles θ , since the chemical shift of the enol proton appears to be crudely linearly related³⁴ to the former angles (see Table III). As a result, qualitative understanding of the nature of ring deformations may be accumulated.³⁶

Experimental

The α -formyl cyclic ketones in Figure 1 were prepared following directions reported in the literature,³⁷ 3-Formylbicyclo[2.2.2]octanone, previously unreported, was prepared similarly from 200 mg. of parent ketone. The distilled product is a colorless liquid, n_D^{25} 1.5290.

Anal. Calcd.: C, 71.02; H, 7.95. Found: C, 70.95; H, 7.80.

N.m.r. spectral data on the α -formyl ketones discussed in this paper have been reported.⁵ The ¹³C-H(vinyl) couplings listed in Table I that were not previously reported and the parenthetical vinyl proton couplings were determined from ¹³C satellite patterns in natural abundance at 60 Mc, using concentrated solutions of alkene in carbon tetrachloride and neat liquids. The vinyl proton couplings in the 1,3-cyclohexadiene-TCNE adduct and bicyclo[2.2.2]octene were determined by partial spectral analysis using the vinyl proton resonances, the details of which will be given in a separate paper.

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