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Estimation by Bond-Additivity Schemes of the Relative Thermodynamic Stabilities of Three-Membered-Ring Systems and Their Open Dipolar Forms

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Some aspects of the chemistry of cyclopropanones, α-lactones, α-lactams, and diaziridinones are discussed in terms of thermodynamic and kinetic stabilities. Semiempirical quantum chemical methods fail for the parent systems, and *ab initio* calculations of substituted systems are limited by practical considerations. Bond-additivity schemes are shown to provide useful estimates of thermal stabilities of the ring systems discussed. Further, they allow formulation of intuitive models which facilitate comparison with experiment. These schemes are used to estimate heats of formation of cyclopropanone, α-lactone, α-lactam, diaziridinone, and related isomers, as well as the open dipolar forms of the first three compounds. The relationships of these structures to methylenecyclopropane, carbon trioxide, and diaziridine imine, and the corresponding open forms are briefly discussed. The heats of decarbonylation of cyclopropanone, α-lactone, α-lactam, and diaziridinone as well as a brief discussion of the role of hyperconjugative stabilization of open forms are included.

Some of the decomposition pathways of α-lactones, α-lactams, and cyclopropanones, the ring systems **1–3**,[1] are explained as proceeding *via* highly reactive, open dipolar intermediates. Difficulty in obtaining these intermediates increases in the above order, namely **1–3**, as will be substantiated in this paper. These compounds are subject to decarbonylation, another contributor to thermal instability, and attack by chemical agents (*e.g.*, nucleophiles and electrophiles) which relates to kinetic stability. The utility of the differentiation of thermodynamic and kinetic stabilities becomes apparent when one considers that a thermodynamically stable, kinetically unstable system may be rendered reasonably unreactive through attachment of substituents which block entry of reagents to reactive sites. The diaziridinone system, **4**, decomposes through radical chain processes and decarbonylation. No reactions invoking the corresponding open forms have been reported to date. The relative propensities of compounds **1–4** to react through the corresponding dipolar forms **5–8** may be explained in the simplified manner depicted in Table I.

While it is possible to compare the above systems to methylenecyclopropanes, diaziridinimines, and carbon trioxide (**14–16**), discussion of these is deferred until the last section. The reason for the separation is that the corresponding open forms (**17–19**) have potential threefold symmetry, which should significantly decrease their dipolar nature relative to **5–8**.

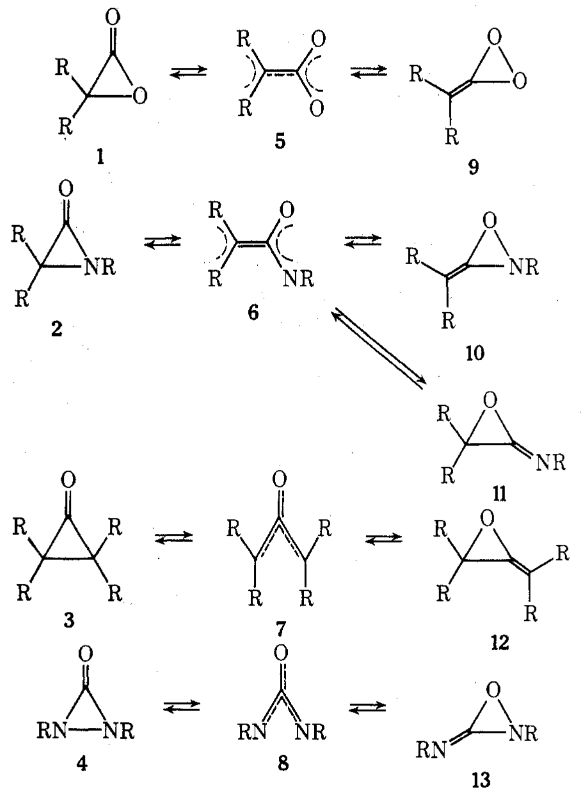
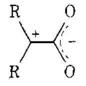
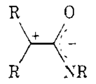
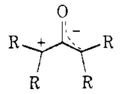
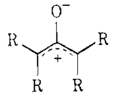
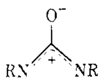
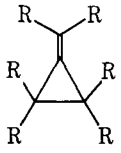


Table I
Factors Determining the Relative Stabilities of the Dipolar Forms Corresponding to Cyclic Compounds 1–4

Dipolar structure	Relative stability	Negative portion	Positive portion
 **5**	Most stable	Strong resonance stabilization	Stabilization by two substituents
 **6**	Moderately stable	Appreciable resonance stabilization	Stabilization by two substituents
 **7a**	Less stable than **6**	Little resonance stabilization	Stabilization by two substituents
 **7b**	Less stable than **7a** More stable than **8**	No stabilization	Allylic system stabilized by four substituents
 **8**	Least stable	No stabilization	1,3-Diazaallylic system less stable than allylic; two substituents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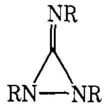
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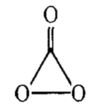
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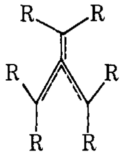
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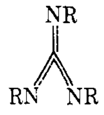
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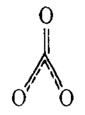
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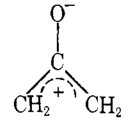
Cyclopropanones and Allene Oxides. While some substituted cyclopropanones undergo cycloaddition reactions, the parent compound has not been induced to react in this manner.[2] These observations are explicable in terms of the barriers to conversion to the corresponding oxyallyl isomers, which are presumably the reacting species. An estimate of the energy difference between cyclopropanone and oxyallyl may be obtained through the use of the bond additivity schemes expressed in eq 1–5 (see ref 3 for the literature source of the heats of formation employed in this paper as well as the rationale for use of this particular source). Such schemes might allow calculation of substituent effects which would otherwise be highly expensive to calculate by computer.[4] They also allow formulation of intuitive models which facilitate comparison with experiment.

$$\begin{array}{lllll} \Delta H_f(\mathbf{3}, R = H) & = \Delta H_f(\overset{+}{\Delta}) & + \Delta H_f(CH_3COCH_3) & - \Delta H_f[(CH_3)_2CH^+] & (1) \\ -3\ \text{kcal/mol} & = (239) & + (-51.8) & - (190) & \end{array}$$

$$\begin{array}{lllll} \Delta H_f(\mathbf{3}, R = H) & = \Delta H_f(\mathbf{14}, R = H)\text{[5]} & + \Delta H_f(CH_3COCH_3) & - \Delta H_f[CH_2{=}C(CH_3)_2] & (2) \\ 0\ \text{kcal/mol} & = (48) & + (-51.8) & - (-4.04) & \end{array}$$

Although the assumptions in eq 1 and 2 are quite different, the values are in close agreement, and an average value of −1.5 kcal/mol will be used as the heat of formation of cyclopropanone. Decarbonylation of cyclopropanone is calculated to be exothermic by 12.5 kcal/mol (see Table V).

Evaluation of oxyallyl requires consideration of dipolar form **20** and diradicals **21** and **22**. Similarities in the effects of methyl substituents in cycloaddition reactions of cyclopropanones and solvolyses of cyclopropyl tosylates are cited[6] as evidence favoring **20** as the structure of oxyallyl. Dipolar form **20** and diradical **21** are of different orbital symmetry and total wave function symmetry, and thus one cannot assume that they are resonance structures of the same species.[7] Equations 3, 4, and 5 estimate heats of formation of **20**, **21**, and **22**, respectively.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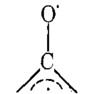
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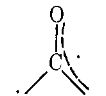
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$$\begin{array}{llllll} \Delta H_f(\mathbf{20}) & = \Delta H_f(\text{allyl cation}) & + \Delta H_f(CH_3O^-) & + E_{\text{coul}} & - \Delta H_f(CH_4) & (3) \\ 53\ \text{kcal/mol} & = (216) & + (-37.3) & + (-144) & - (-17.88) & \end{array}$$

$$\begin{array}{lllll} \Delta H_f(\mathbf{21}) & = \Delta H_f(\text{allyl radical}) & + \Delta H_f(CH_3O\cdot) & - \Delta H_f(CH_4) & (4) \\ 47\ \text{kcal/mol} & = (30) & + (-0.5) & - (-17.88) & \end{array}$$

$$\begin{array}{lllll} \Delta H_f(\mathbf{22}) & = \Delta H_f(CH_3COCH_2) & + \Delta H_f(CH_3\cdot) & - \Delta H_f(CH_4) & (5) \\ 43\ \text{kcal/mol} & = (-7.7) & + (33.2) & - (-17.88) & \end{array}$$

Estimation of the coulombic energy term (E_{coul}) in (3) is based on the following assumptions.

(a) Assumption of a point charge model with the charges localized on the nuclei. Two unit, but opposite, charges at a distance of 1 Å attract each other with a net stabilization of 14.4 eV = 332.1 kcal/mol.

(b) Charge on oxygen = −1; charges on allylic C_1 and C_3 = +½. No C_1–C_3 repulsion is incorporated in this model since it is implicit in the experimental value of the heat of formation of allyl cation.

(c) Carbon–oxygen bond length = 1.20 Å;[8] carbon–carbon bond length = 1.466 Å.[8]

(d) The value ($E_{\text{coul}} = -144$ kcal/mol) corresponds to the idealized $C_1C_2C_3$ angle of 120°.

The value for the heat of formation of methoxide used in eq 3 has only recently become available. The ion cyclotron resonance determination of equilibrium 6 in the gas phase yields a value for $\Delta G°$ of 1.9 kcal/mol.[9]

$$CH_3O^- + C_2H_5OH \rightleftharpoons CH_3OH + C_2H_5O^- \qquad (6)$$

Assuming $\Delta S° \cong 0$ and equal O–H bond dissociation energies for methanol and ethanol, the electron affinity of ethoxy radical is 1.9 kcal/mol greater than that of methoxy radical. The bond dissociation energy assumption is valid in this case, as is apparent from comparison of eq 7 and 8.

$$\begin{aligned} &\text{Dissociation energy } (CH_3O\text{–}H = \Delta H_f\,(CH_3OH) - \\ &\quad -99.6\ \text{kcal/mol} \qquad = \quad (-47.96) \\ &\qquad\qquad \Delta H_f(CH_3O) - \Delta H_f\,(H) \qquad (7) \\ &\qquad\qquad -(-0.5) \quad - \quad (52.10) \end{aligned}$$

$$\begin{aligned} &\text{Dissociation energy } (C_2H_5O\text{–}H) = \Delta H_f\,(C_2H_5OH) - \\ &\quad -99.7\ \text{kcal/mol} \qquad = \quad (-56.19) \\ &\qquad\qquad \Delta H_f\,(C_2H_5O) - \Delta H_f\,(H) \qquad (8) \\ &\qquad\qquad -(-8.5) \quad - \quad (52.10) \end{aligned}$$

A published value[10] of the electron affinity of ethoxy radical (1.68 eV) allows assignment of an electron affinity of 36.8 kcal/mol to methoxy radical and thus the heat of formation of methoxide is −37.3 ± 0.5 kcal/mol.

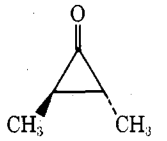
The dipolar oxyallyl intermediate **20** is about 54 kcal/mol higher in energy than cyclopropanone. The intermediates **21** and **22** are, respectively, 49 and 45 kcal/mol higher in energy than cyclopropanone. This is contrary to the expectation that **20** is the structure of the open form. This is a deficiency in the method, probably in large part due to the coulombic term, which appears, at present, to relegate the method to comparison of dipolar forms and the closed rings. In any case, the energy difference between **20** and **22** is not large. Agreement between the above values (*ca.* 50 kcal/mol) and the *ab initio* value of 83 kcal/mol[8] does not appear to be very good. However, the *ab initio* calculation predicts a slightly bonding unoccupied molecular orbital in oxyallyl. A calculation which included partial configuration interaction would lower the energy of oxyallyl and yield an energy difference in closer agreement with the value calculated here. The energy difference between cyclopropanone (unsubstituted) and oxyallyl would appear to preclude cycloaddition reactions unless a concerted mechanism (no intermediacy of oxyallyl) were operative.

Energy differences between open and closed forms of cyclopropanone as well as methyl-substituted cyclopropanones (**23**–**28**) are tabulated in Table II. The calculated energy differences between methyl-substituted cyclopropanones and their oxyallyl counterparts are probably underestimated. The reason for this is the fact that the heat of formation of the carbonium ion takes charge delocalization into account implicitly, while the coulombic term employed here assumes charges localized at the atomic centers. Explicit correction of this term would decrease coulomic stabilization of the oxyallyl isomer and increase the energy difference between the open and the closed form.

Table II
Energy Differences between Corresponding Oxyallyls and Cyclopropanones Employing Same E_{coul} as in Eq 3 in All Cases

Species	Energy difference, kcal/mol
Oxyallyl[11] − cyclopropanone	+54
24[a] − **23**	+38
26 − **25**[b]	+35
28[c,d] − **27**[e]	+29

[a] Steric interaction in **24** taken as twice the enthalpy difference between *cis*- and *trans*-2-pentene (1 kcal/mol). [b] Steric interaction in **25** taken as difference in strain energy between *cis*-1,2-dimethylcyclopropane and cyclopropane (2.7 kcal/mol).[12] [c] Steric interaction in **28** is obtained from k_{rel} (150°) of solvolysis of *cis,cis*-2,3-dimethylcyclopropyl tosylate and *trans,trans*-2,3-dimethylcyclopropyl tosylate.[13] The value obtained ($\Delta\Delta H^* \cong \Delta\Delta G^* = 7.1$ kcal/mol) is due to steric interactions in the transition states. An energy difference (strain in **28**) between allylic cations of 10 kcal/mol is assumed. [d] ΔH_f (1,1,3,3-tetramethylallyl cation) = 160 kcal/mol is obtained by comparison of allyl cation (ΔH_f = 216) with 1,3-dimethylallyl cation (ΔH_f = 182) and 1,1-dimethylallyl cation (ΔH_f = 184). The average difference (−33 kcal/mol) represents the substitution of two methyl groups. Thus, four methyl groups introduce a factor of −66 kcal/mol and an additional 10 kcal/mol steric factor (note *c*) relative to allyl cation. Addition of ΔH_f (1,1,3,3-tetramethylallyl cation) to ΔH_f (CH_3O^-) and E_{coul} (−144 kcal/mol) and subtraction of ΔH_f (CH_4) yield a value for ΔH_f (**28**) of −3.4 kcal/mol. [e] Steric interaction in **27** taken as 2 × 2.7 = 5.4 kcal/mol.



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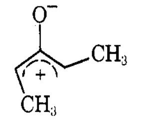

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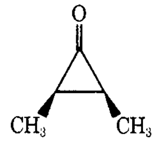

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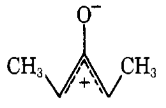

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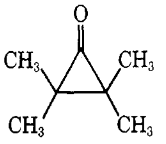

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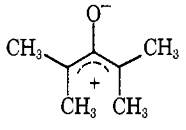
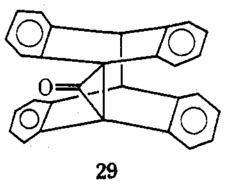


28

Curiously, the only phenyl-substituted cyclopropanone isolated to date is **29**,[14] although diphenyl-substituted cyclopropanones have been generated, for example, as intermediates in syntheses of cyclopropenones.[15-17] Compound **29** does not allow conjugation of phenyl rings in the oxyallyl form and is, therefore, stable to ring opening. Unfortunately, heats of formation of phenyl-substituted allylic cations are presently not available. However, monophenyl- and diphenylcyclopropanones may be isolable. Triphenyl- and tetraphenylcyclopropanones may also be stable in the closed forms, since steric interactions limit the extent of conjugative stabilization of oxyallyl isomers.



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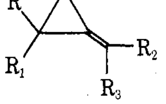
Allene oxide (**12**, R = H) has not been isolated. Its energy relative to cyclopropanone may be calculated through comparison of eq 9 or 10 with eq 2. The average energy

$$\begin{array}{llll} \Delta H_f(\mathbf{12}, \mathrm{R} = \mathrm{H}) = \Delta H_f(\mathbf{14}, \mathrm{R} = \mathrm{H})^5 + & & & \\ 23 \text{ kcal/mol} \quad = \quad (48) \quad + & & & \\ & \Delta H_f(\overset{\mathrm{O}}{\triangle}) & - \ \Delta H_f(\Delta) & (9) \\ & (-12.58) & - \ (12.74) & \end{array}$$

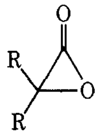
$$\begin{array}{llll} \Delta H_f(\mathbf{12}, \mathrm{R} = \mathrm{H}) = \Delta H_f(\mathbf{14}, \mathrm{R} = \mathrm{H})^5 + & & & \\ 20 \text{ kcal/mol} \quad = \quad (48) & & & \\ & \Delta H_f(\mathrm{CH_3OCH{=}CH_2}) & - \ \Delta H_f(\text{1-butene}) & (10) \\ & +(-27.7) & - \ (-0.03) & \end{array}$$

difference between cyclopropanone and allene oxide of 23 kcal/mol is in excellent agreement with *ab initio* calculations.[8] Furthermore, comparison with eq 3 suggests that allene oxide is quite stable to ring opening to oxyallyl. Its failure to be isolated must be due to kinetic instability. Allene oxides **30**,[18] **31**,[19] and **32**[20] have been generated but not isolated because of kinetic instability. Highly hindered allene oxides **33**[21] and **34**[22] have been isolated.



30, $\mathrm{R = R_1 = R_2 = R_3 = CH_3}$
31, $\mathrm{R = R_1 = CH_3;\ R_2 = C(CH_3)_3;\ R_3 = H}$
32, $\mathrm{R = R_1 = C(CH_3)_3;\ R_2 = R_3 = H}$
33, $\mathrm{R = R_2 = C(CH_3)_3;\ R_1 = R_3 = H}$
34, $\mathrm{R = R_1 = R_2 = C(CH_3)_3;\ R_3 = H}$

α-Lactones. The α-lactones are in marked contrast to cyclopropanones in their thermal stabilities. To date, only **35** has been isolated.[23] Dialkyl α-lactones **36**-**41** have been generated at low temperatures (≤−78°) and, with the exception of **36**, react immediately upon formation.[24-26] The α-lactone **36** is stable at −60° and polymerizes at the relatively high temperature of −20° as the result of kinetic stability afforded by the bulky substituents.[24] Diphenyl α-lactone (**42**) appears to exist as the dipolar form at −100°.[24]

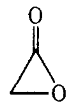


35, $\mathrm{R = CF_3}$	**40**, $\mathrm{R + R = (CH_2)_3}$
36, $\mathrm{R = C(CH_3)_3}$	**41**, $\mathrm{R + R = (CH_2)_4}$
37, $\mathrm{R} = n\text{-}\mathrm{C_4H_9}$	**42**, $\mathrm{R = C_6H_5}$
38, $\mathrm{R = CH_3}$	**43**, $\mathrm{R = H}$
39, $\mathrm{R + R = (CH_2)_2}$	

The heat of formation of α-lactone is calculated in eq 11. The subtraction of the π resonance energy (*RE*) in eq 11 requires comment. The rationale for this approximation will be further substantiated in the sections concerned with α-lactams and diaziridinones.

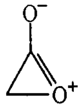
$$\begin{array}{llll} \Delta H_f(\mathbf{43}) = \Delta H_f(\mathbf{3}, \mathrm{R} = \mathrm{H}) + & & & \\ -31 \text{ kcal/mol} = \quad (-1.5) & & & \\ \Delta H_f(\mathrm{CH_3COOCH_3}) & - \ \Delta H_f(\mathrm{CH_3COC_2H_5}) & - \ RE^{27} & (11) \\ +(-99.2) & - \ (-58.4) & - \ (-11) & \end{array}$$

At this point it is worthwhile to note the relative strain energies (in analogy to the hydrocarbons methylenecyclopropane and cyclopropene[12]) in resonance contributors A and B. Thus, the dipolar contribution should be much smaller in α-lactones than in esters or the unstrained δ-lactones.



A

Relative strain = 41 kcal/mol
(methylenecyclopropane[12])

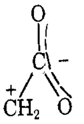


B

Relative strain = 54 kcal/mol
(cyclopropene[12])

Additional evidence may be adduced from the carbonyl stretching frequency of α-lactones (*ca.* 1900 cm^{-1}).[26] The carbonyl frequency of δ-lactone is about 20 cm^{-1} greater than that of cyclohexanone, following the usual relationship between esters and ketones.[28] However, the carbonyl frequencies of α-lactones are 70-85 cm^{-1} greater than those of cyclopropanones.[2]

One might consider two open dipolar isomers of α-lactone. The most probable dipolar structure, **44**, is assigned



44

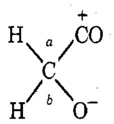
the following geometry: (a) all angles are 120°; (b) carbon-carbon bond length = 1.466 Å;[8] (c) carbon-oxygen bond length = 1.27 Å.

The heat of formation of **44** is calculated in eq 12.

$$\begin{array}{llll} \Delta H_f(\mathbf{44}) = \Delta H_f(\mathrm{C_2H_5^+}) + \Delta H_f(\mathrm{CH_3CO_2^-}) + & & & \\ -23 \text{ kcal/mol} = (219) \quad + \quad (-122) & & & \\ & E_{\mathrm{coul}} & - \ \Delta H_f(\mathrm{C_2H_6}) & (12) \\ & +(-140) & - \ (-20.24) & \end{array}$$

The coulombic attraction is calculated using the point-charge model and a separation of 2.37 Å. The heat of formation of acetate anion used in eq 12 is obtained from the heat of formation of acetoxy radical (−45 ± 4 kcal/mol)[29] and the electron affinity (3.36 ± 0.05 eV = 77.5 ± 1.2 kcal/mol;[30] 78.2 kcal/mol[31]) of this radical.

The second dipolar form, **45**, might be more stable than **44** in cases where electron-withdrawing substituents are



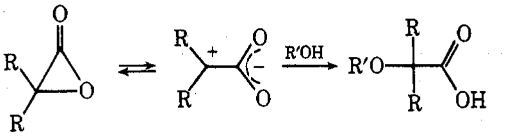
45

attached. It is assigned the following geometry: (a) angle (CO)-C-O = 109.5°; (b) bond length *a* = 1.51 Å (analogy to $\mathrm{CH_3{-}CHO}$); (c) bond length *b* = 1.43 Å (usual C-O bond length).

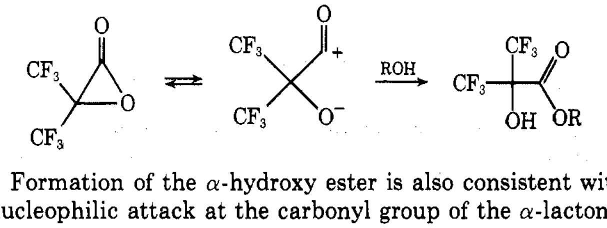
The heat of formation of **45** is calculated in eq 13. Thus, **44** would normally be the lowest energy dipolar form of

$$\begin{array}{llll} \Delta H_f(\mathbf{45}) = \Delta H_f(\mathrm{C_2H_5CO^+}) + & & & \\ -12 \text{ kcal/mol} = (143) \quad + & & & \\ \Delta H_f(\mathrm{CH_3O^-}) & + \ E_{\mathrm{coul}} & - \ \Delta H_f(\mathrm{C_2H_6}) & (13) \\ (-37.3) & + \ (-138) & - \ (-20.24) & \end{array}$$

an α-lactone. This is consistent with the reactions of most α-lactones with alcohol.[24-26]



However, the perfluoroalkyl derivative, **35**, appears to favor open form **45** to **44** as the result of strong electron withdrawal by the substituents, and it reacts with alcohols in the following manner.[23]



Formation of the α-hydroxy ester is also consistent with nucleophilic attack at the carbonyl group of the α-lactone. Facile decarbonylation[23] of **35** may be indicative of the intermediacy of open form **45**.

Table III lists energy differences between open (44) and closed forms of α-lactone, dimethyl α-lactone, and diphenyl α-lactone using the format of eq 12 and the same coulombic term in all cases. The parent compound should exist in the closed form but not be much more stable than the open form. Dialkyl α-lactones would appear to be most stable in the open form. The energy differences are not very large and it is easy to envision cases in which steric or strain factors might make the closed form more stable. Diphenyl α-lactone certainly appears to be considerably more stable in the open form, although the energy difference in Table III is probably exaggerated. That is, while the experimental heat of formation of the appropriate substituted carbonium ion contains implicit delocalization of the positive charge, such charge delocalization would have to be accounted for explicitly in calculating a better coulombic energy using the method advanced here. For example, if the charges on the open diphenyl compound were separated by an average distance of 3.0 Å instead of 2.4 Å, as in 44, then $E_{\text{coul}} = -111$ kcal/mol and the open form of **42** would be 33 kcal/mol more stable than **42** itself.

The isolation[23] of cyclic **35** is not surprising when one considers the strongly dominant destabilizing inductive effect of trifluoromethyl groups on **44** which apparently (*vide infra*) has the effect of making **45** more stable. Data for evaluation of the heats of formation of perfluoro open forms are not yet available. However, if one assumes that the inductive stabilizing and destabilizing effects of trifluoroalkyl groups on **45** are about equal, then **35** is more stable than its open dipolar form by about 19 kcal/mol (compare eq 11 and 13).

The heat of formation of **9** (R = H) is calculated in eq 14. This compound is considerably less stable than the open dipolar forms.

$$\begin{array}{l}\Delta H_f(\mathbf{9}, \mathrm{R}=\mathrm{H}) = \Delta H_f\,(\mathrm{CH_3OOCH_3})^{32} + \Delta H_f\,[\mathrm{CH_2{=}C(OCH_3)_2}]^{33} - 2\Delta H_f\,(\mathrm{CH_3OCH_3}) + \text{strain}\,(\mathbf{14}, \mathrm{R}=\mathrm{H})^{12} \quad (14)\\ +36\ \text{kcal/mol} = (-23) + (-70.4) - 2(-44) + (41)\end{array}$$

Decarbonylation of α-lactone is calculated to be exothermic by 23.4 kcal/mol (Table V).

Table III
Energy Differences between Corresponding Open (*i.e.*, 44) and Closed Forms of Some α-Lactones

Closed form	Energy difference, kcal/mol (open − closed)
43	+8
38	−18
42	−62

α-Lactams.[34] The tendency for α-lactams to ring open appears to be intermediate between that of α-lactones and cyclopropanones. The heat of formation of α-lactam (**46**) is estimated in eq 15. In eq 15, as in eq 11, the π resonance energy normally ascribed to amides is excluded.

$$\begin{array}{l}\Delta H_f(\mathbf{46}) = \Delta H_f(\mathbf{3}, \mathrm{R}=\mathrm{H}) + \Delta H_f\,(\mathrm{CH_3CONH_2}) - \Delta H_f\,(\mathrm{CH_3COC_2H_5}) - RE^{27} \quad (15)\\ +13\ \text{kcal/mol} = (-1.5) + (-55) - (-58.37) - (-11)\end{array}$$

The rationale for this approximation is as follows.

(a) Carbonyl absorption in simple ketones is 20–60 cm^{-1} higher than in the corresponding amides, but that of cyclopropanone is *ca.* 20 cm^{-1} lower than that of α-lactam.[35] This effect is similar to that observed in quinuclidone-2.[35]

(b) X-Ray study of 1,3-diadamantyl α-lactam (**47**) shows that the substituents attached to nitrogen are not coplanar as they are in amides.[36]

(c) As mentioned previously, π resonance in α-lactams would involve an increase in strain energy of about 13 kcal/mol (*i.e.*, cyclopropene *vs.* methylenecyclopropane).[12]

Decarbonylation of **46** is calculated to be exothermic by 13.2 kcal/mol (see Table V).

The heat of formation of the open dipolar form of α-lactam, **56**, is obtained from eq 16 with the following assumptions: (a) all angles are 120°; (b) carbon–carbon bond length = 1.466 Å;[8] (c) carbon–oxygen and carbon–nitrogen bond lengths are similar enough so that E_{coul} remains at −140 kcal/mol as in eq 12.

$$\begin{array}{l}\Delta H_f(\mathbf{56}) = \Delta H_f\,(\mathrm{C_2H_5^+}) + \Delta H_f\,(\mathrm{CH_3CONH{-}}) + E_{\text{coul}} - \Delta H_f\,(\mathrm{C_2H_6}) \quad (16)\\ +41\ \text{kcal/mol} = (219) + (-58) + (-140) - (-20.24)\end{array}$$

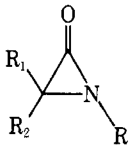
The value for ΔH_f ($\mathrm{CH_3CONH^-}$) used in eq 16 is obtained from pK ($\mathrm{CH_3CONH_2}$) $\cong$ 16,[37] pK ($\mathrm{CH_3CO_2H}$) $\cong$ 5,[37] ΔH_f ($\mathrm{CH_3CONH_2}$) = −54 kcal/mol, ΔH_f ($\mathrm{CH_3CO_2H}$) = −103.31 kcal/mol, and ΔH_f ($\mathrm{CH_3CO_2^-}$) = −122 kcal/mol (*vide infra*). The use of liquid phase pK's in this approach is subject to justified criticism. In the absence of gas-phase values for the heat of formation and electron affinity of $\mathrm{CH_3CONH}$, this crude approximation must suffice. Thus, the energy difference favoring the closed form of α-lactam is predicted to be 28 kcal/mol compared with 54 kcal/mol for cyclopropanone and 8 kcal/mol for α-lactone.

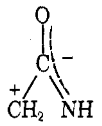
A large number of substituted α-lactams have been synthesized and these exhibit a considerable range of stability.[36,38,39] Sterically hindered 1,3-dialkyl α-lactams such as **47** and **48** are quite stable,[36] while **49** is kinetically unstable.[36] Diaryl and triaryl α-lactams in which an aromatic ring is attached to nitrogen (*e.g.*, **51–53**) have not been isolated.[36,38] The compound **50** is quite stable,[39] since it is sterically hindered and matches a substituent which strongly stabilizes the dipolar form with one that strongly

Table IV[a]
Energy Differences between Corresponding Open and Closed Forms of Some α-Lactams

Closed form	Energy difference, kcal/mol (open − closed)
46	+28
49	+2
52[41]	−49
55	−42

[a] The effects of substituents attached to C_3 of α-lactams is assumed to be equal to those in α-lactones (Table III). Steric effects are not included.





56

46, $R = R_1 = R_2 = H$
47, $R = R_1$ = adamantyl
48, $R = R_1 = C(CH_3)_3$; $R_2 = H$
49, $R = R_1 = CH_3$; $R_2 = H$
50, $R = C(CH_3)_3$; $R_1 = CF_3$; $R_2 = C_6H_5$
51, $R = R_1 = C_6H_5$; $R_2 = H$
52, $R = R_1 = R_2 = C_6H_5$
53, $R = 2,6\text{-}(CH_3)_2C_6H_3$; $R_1 = C_6H_5$; $R_2 = H$
54, $R = C(CH_3)_3$; $R_1 = R_2 = C_6H_5$
55, $R = H$; $R_1 = R_2 = C_6H_5$

destabilizes it. Surprisingly, **54** has been isolated and exists in the cyclic form.[36]

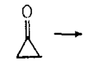
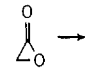
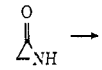
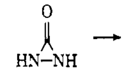
Table IV lists energy differences between open and closed forms of some α-lactams. It is readily apparent that the use of liquid phase p*K*'s has the effect of yielding energies for open dipolar forms that are too low. The thermal stability of **49** is too low and the predicted favoring of the open form of **55** is erroneous. This latter error is also the result of overestimation of the coulombic stabilization of the open form of **55** as stated previously. Conjugative interaction between the α-lactam ring and phenyl substituents[40] is not included.

The heat of formation of **10** (R = H) is estimated in eq 17. The heat of formation of **11** (R = H) is not estimated

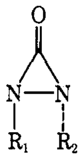
$$\Delta H_f(\mathbf{10}, R = H) = \Delta H_f(\mathbf{14}, R = H) + \Delta H_f(CH_3ONHCH_3)^{42} - \Delta H_f(n\text{-}C_4H_{10}) \quad (17)$$
$$+74 \text{ kcal/mol} = (48) + (-4) - (-30.15)$$

here since heats of formation of nonresonance-stabilized imines are not experimentally available. It is probably a few kilocalories per mole less stable than **46** (**2**, R = H). Derivatives of **11** have been postulated as intermediates in fragmentation reactions of some α-lactams.[36]

Table V
Calculated Heats of Decarbonylation of Small-Ring Systems

Compd	Products	ΔH_0, kcal/mol
	$CH_2{=}CH_2 + CO$	−12.5
	$CH_2O + CO$	−23.4
	$CH_2{=}NH^{49} + CO$	−13.2
	$HN{=}NH + CO$	−12.6

Diaziridinones. The dialkyldiaziridinones **57**–**61** have been prepared and are quite stable.[43–45] No cycloaddition products of these compounds have been observed.[35] This is attributed[35] to either or both steric hindrance to cycloaddition of the open form or negligible presence of the open form.



57, $R_1 = R_2 = C(CH_3)_3$
58, $R_1 = R_2$ = *tert*-amyl
59, $R_1 = R_2$ = *tert*-octyl
60, $R_1 = R_2 = C(CH_3)_2CH_2C_6H_5$
61, $R_1 = C(CH_3)_3$; R_2 = *tert*-octyl
62, $R_1 = R_2 = H$

The heat of formation of the unsubstituted ring system, **62**, is calculated in eq 18. Here again, as in the cases of α-lactones and α-lactams, the π resonance energy normally associated with urea is omitted. Evidence supporting this assumption consists of the observation of noncoplanarity of groups attached to nitrogen,[35] and the observation of carbonyl frequencies of diaziridinones which are 15–65 cm^{-1} higher than those of cyclopropanones, while carbonyl bands of ureas are 15–50 cm^{-1} lower than those of the corresponding ketones.[35] Decarbonylation of **62** is estimated to be exothermic by 12.6 kcal/mol (Table V).

$$\Delta H_f(\mathbf{62}) = \Delta H_f(CH_3NHNHCH_3) + \Delta H_f(\text{urea})^{46} +$$
$$+34.9 \text{ kcal} = (21.6) + (-58.7)$$

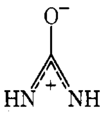
strain ()^{12} $- 2\,\Delta H_f(CH_3NH_2) - RE^{47}$ (18)

$$+ (41) - 2(-5.49) - (-20)$$

The poor tendency for cycloaddition of diaziridinones may be accounted for by steric and/or electronic effects. Since the diaziridinones reported in the literature possess bulky substituents, the reluctance for cycloaddition may be steric in origin. An electronic explanation rests upon comparison of dipolar structure **63** and oxyallyl. The negative portions are similar, but the positive part of **63** (1,3-diazaallylic carbonium ion) should be much less stable than the allylic carbonium ion. Unfortunately, the heat of formation of the 1,3-diazaallylic carbonium ion is not available and only extremely crude estimates are possible.

Table VI
Heats of Formation of α-Methyl Substituted Carbonium Ions and Corresponding Alkanes

ΔH_f (Ion), kcal/mol	Registry no.	ΔH_f (Alkane), kcal/mol	Registry no.	(Ion) − (Alkane), kcal/mol
$n\text{-}C_3H_7^+$ (209)	19252-52-9	$n\text{-}C_3H_8$ (−24.82)	74-98-6	234
$i\text{-}C_4H_9^+$ (205)	19252-54-1	$i\text{-}C_4H_{10}$ (−32.15)	75-28-5	237
neo-$C_5H_{11}^+$ (196)	14128-47-3	neo-C_5H_{12} (−39.67)	463-82-1	236



63

It is, therefore, presently impossible to determine whether cyclopropanone or diaziridinone is more stable to ring opening.

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Decarbonylation Reactions and Hyperconjugative Stabilization of Open Dipolar Forms. Table V lists calculated heats of decarbonylation of the ring systems discussed in this paper. Interestingly, omission of resonance energies makes α-lactam and diaziridinone unstable relative to their decarbonylation products. Concerted decarbonylation pathways are prohibited by orbital symmetry.[48]

Hyperconjugative stabilization of open dipolar forms is possible, and the stability conferred onto ring systems by *tert*-butyl groups might be evidence supporting this contention. However, examination of Table VI leads us to conclude that the major effect of the *tert*-butyl groups is steric hindrance to attacking agents, and hyperconjugative stabilization of open forms is relatively minor.

Systems Capable of Threefold Symmetry. Methylenecyclopropane (**14**, R = H), carbon trioxide (**16**), and diaziridinimine (**15**, R = H) are not discussed here since the corresponding acyclic forms (**17**, **19**, **18**) have potential D_{3h}, D_{3h}, and C_{3h} symmetries, respectively. Thus, the dipolar structures advanced in this paper are probably less applicable in discussing these systems.

It is worthwhile to point out that the thermal instability of carbon trioxide[50-53] and diaziridinimines[54] relative to methylenecyclopropanes[55-58] is at least in part due to small resonance contributions in the closed forms of the first two as explained in this paper. Additionally, the special instability of carbon trioxide may be due to the fact that stabilization during ring opening is achieved without movement of attached groups, a necessary feature of the other cyclic systems discussed in this paper.

Conclusions

The bond-additivity schemes proposed in this paper reproduce qualitative trends in thermal stability of the ring systems discussed. Refinement of the calculations to the point where they might be used to make reasonably accurate quantitative predictions must await accurate gas-phase determinations of electron affinities and p*K*'s. Calculation of coulombic terms using point-charge assumptions leads to significant errors when phenyl groups, which disperse charge to a large extent, are involved.

We anticipate that the schemes advanced here will provide intuitively satisfying models and hope that further sophistication of the methods as well as additional data will allow more reliable calculations of related systems.

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Registry No. 1 (R = H), 42879-41-4; 2 (R = H), 34734-31-1; 3 (R = H), 5009-27-8; 4 (R = H), 42879-43-6; 9 (R = H), 42879-44-7; 10 (R = H), 42879-45-8; 12 (R = H), 40079-14-9; 14 (R = H), 6142-73-0.

References and Notes

(1) The open forms **5-8** and **17-19** are normally considered 4π systems. Promotion of lone-pair electrons to the π framework permits **5**, **6**, **8**, **18**, and **19** to be "Y-aromatic" [see P. Gund, *J. Chem. Educ.*, **49**, 100 (1972)]. However, this effect need not be invoked to explain these cases (*vide infra*). Compounds **1-4**, **5-8**, and **9-13** also constitute sets of isoelectronic compounds [for applications of the isoelectronic principle see H. A. Bent, *J. Chem. Educ.*, **43**, 171 (1966), and J. F. Liebman, *ibid.*, **48**, 188 (1971)].

(2) For comprehensive reviews of cyclopropanones see (a) N. J. Turro, *Accounts Chem. Res.*, **2**, 25 (1969); (b) N. J. Turro, R. B. Gagosian, S. S. Edelson, T. R. Darling, and W. B. Hammond, *Trans. N. Y. Acad. Sci.*, **33**, 396 (1971).

(3) All values of ΔH_f [(g) 298°K] are reported in kcal/mol and are obtained from J. L. Franklin, J. G. Dillard, H. M. Rosenstock, J. T. Herron, K. Draxl, and F. H. Field, "Ionization Potentials, Appearance Potentials, and Heats of Formation of Positive Ions," National Standard Reference Data Series, National Bureau of Standards (U. S.), 26, NSRDS-NBS 26, 1969. We acknowledge that this reference is an unusual, and admittedly perhaps not ideally appropriate, source of information for any species other than a positive ion. However, it does provide a single data compendium for cations such as cyclopropyl, stable and "normal" neutral molecules such as acetone, free radicals such as the methoxy radical, and even some anions such as hydroxide. This uniformity of origin for most of our thermochemical data suggests that the implicit biases in the selection of numerical data from experiment are essentially uniform.

(4) Semiempirical methods to date apparently fail for oxyallyl and predict seemingly erroneous substituent effects in the cyclopropanone series [see A. Liberles, S. Kang, and A. Greenberg, *J. Org. Chem.*, **38**, 1922 (1973)].

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(6) S. S. Edelson and N. J. Turro, *J. Amer. Chem. Soc.*, **92**, 2770 (1970).

(7) Resonance structures are governed by both spin and spatial symmetry constraints on a molecule. Normally, this presents no problems. Let us consider the axis colinear with oxygen and carbon and the plane which bisects oxyallyl. The p π orbital of oxygen must be symmetric with respect to this plane. In the zwitterionic structure, **20**, there are two electrons occupying this orbital. The occupied orbital on the allyl cation fragment is symmetric with respect to this plane. Accordingly, all four π electrons are symmetric with regard to this plane. Let us now consider biradical **21**. The single electron on oxygen is again in a symmetric orbital. The allyl radical fragment contains three electrons, of which only two can occupy the previously mentioned symmetric allyl orbital. The remaining electron is presumably in the next higher orbital of the allyl fragment, which, as in the case of the free allyl radical, is antisymmetric with respect to the plane. Accordingly, there are three electrons in symmetric orbitals and one in an antisymmetric orbital and the overall wave function is antisymmetric. Thus, **20**, and **21** are of different wave function as well as orbital symmetry and do not mix.

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(11) There is a temptation to use tropone as a model for **20**. However, the heat of formation of tropone may be accurately accounted for without use of dipolar structures; see also M. J. S. Dewar, *Croat. Chem. Acta*, **42**, 1 (1970).

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(13) (a) P. v. R. Schleyer, G. W. V. Dine, U. Schollkopf, and J. Paust, *J. Amer. Chem. Soc.*, **88**, 2868 (1966); (b) C. H. Depuy, L. G. Schnack, and J. W. Hauser, *ibid.*, **88**, 3343 (1966).

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(20) J. K. Crandall and W. H. Machleder, *J. Amer. Chem. Soc.*, **90**, 7347 (1968).

(21) R. L. Camp and F. D. Greene, *J. Amer. Chem. Soc.*, **90**, 7349 (1968).

(22) J. K. Crandall and W. H. Machleder, *J. Heterocycl. Chem.*, **6**, 777 (1969).

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(26) O. L. Chapman, P. W. Wojkowski, W. Adam, O. Rodriquez, and R. Rucktäschel, *J. Amer. Chem. Soc.*, **94**, 1365 (1972).

(27) Resonance energies of amides and esters are considered to be al-

most equal (L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960, p 197). The Pauling values contain contributions due to π conjugation, hyperconjugation, and changes in hybridization relative to the model compounds. We assume here a value for the π conjugation energy of acetamide of 11 kcal/mol (J. D. Roberts, R. Stewart, and M. C. Caserio, "Organic Chemistry: Methane to Macromolecules," W. A. Benjamin, New York, N. Y., 1971, p 435). This seemingly arbitrary choice represents a presumed contribution due to π conjugation that is a bit more than half of the "total resonance energy" calculated by the Pauling approach. We feel that this value represents a "safe" choice since it is approximately centered between 0 and 100% π contribution to the total resonance energy.

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(32) This value was computed by taking the experimental value of the heat of formation of dimethyl peroxide (S. W. Benson, "Thermochemical Kinetics," Wiley, New York, N. Y., 1968, p 201) and adding to it the cis rotational barrier of hydrogen peroxide, *i.e.*, E (cis H_2O_2, dihedral angle 0°) − E (H_2O_2, dihedral angle at equilibrium 111°), of 7 kcal/mol [R. B. Davidson and L. C. Allen, *J. Chem. Phys.*, **55**, 519 (1971)].

(33) A value of −69 kcal/mol is obtained from ΔH_f ($CH_2{=}CHOCH_3$) = −27.7, ΔH_f (propene) = +0.88, and ΔH_f (isobutene) = −4.04. An alternate value of −71.8 kcal/mol is obtained from ΔH_f ($CH_2{=}CHOCH_3$) = −27.7, ΔH_f ($CH_2{=}CHCl$) = +8.5, and ΔH_f ($CH_2{=}CCl_2$) = +0.58. These two values are averaged to give the final value.

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Base-Promoted Reactions of Bicyclic Mono- and Diquaternary Ammonium Salts[1]

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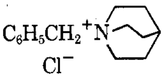
The synthesis and base-promoted reactions of the mono- and diquaternary ammonium salts, 1-benzyl-1-azoniabicyclo[2.2.2]octane chloride (1), 1-benzyl-1-azonia-4-azabiocyclo[2.2.2]octane chloride (2), and 1,4-dibenzyl-1,4-diazoniabicyclo[2.2.2]octane dichloride (3) have been carried out. The acidifying influence of the quaternary nitrogen atom appears to be the controlling factor in determining the reaction pathway. Thus, the most acidic disalt, **3**, leads initially to an elimination product, **11**. Subsequent reaction of **11** leads to both ring expansion and vinyl migration *via* a Stevens rearrangement. Change of a bridgehead carbon atom to a bridgehead nitrogen atom (comparison of 1 and 2) decreases the acidity and removes the elimination pathway while enhancing the Stevens rearrangement product. The novel vinyl Stevens rearrangement was confirmed by the synthesis of benzyldimethylvinylammonium hydroxide (**19**) and its conversion to α-vinylbenzyldimethylamine (**21**).

In recent years a renewed interest has been oriented toward 1,2-anionic rearrangements as new techniques and results have prompted changes in our mechanistic theories.[2] The base-promoted rearrangements of quaternary ammonium salts, the Stevens rearrangement,[3] has received considerable attention in this regard.[4] As a continuation of our interest in this area we have investigated the base-promoted reactions of the bicyclic salts 1-benzyl-1-azoniabicyclo[2.2.2]octane chloride (1) (quinuclidinium salt), 1-benzyl-1-azonia-4-azabicyclo[2.2.2]octane chloride (2) (Dabco monosalt), and 1.4-dibenzyl-1,4-diazoniabicyclo[2.2.2]octane dichloride (3) (Dabco disalt). In contrast to most previous work reported on the Stevens rearrangement, these bicyclic systems introduce stereochemical restraints which could influence the reaction pathways.[5] In addition to the possibility of displacement reactions, the presence of β hydrogen atoms also enables elimination to compete with the rearrangement. Another consideration in the choice of this series of compounds for study was the possibility that intramolecular electronic interactions might be important as one of the bridgehead atoms changes from C to N to N+. Interaction between the nitrogen atoms in Dabco has been observed by esr and uv



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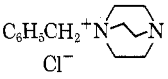

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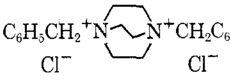

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