Anal. Calcd for $C_{10}H_{14}O$: C, 79.96; H, 9.39. Found: **2αN**, C, 80.11; H, 9.47. **2αX**, C, 80.24; H, 9.55.

***endo*-2-Carbo-*sec*-butoxy-*endo*-3-methyl- and *exo*-2-carbo-*sec*-butoxy-*exo*-3-methylbicyclo[2.2.1]hept-5-ene (3cN and 3cX)** were prepared from *sec*-butyl *cis*-crotonate and CPD. The isomeric mixture of **3cN** and **3cX** was analyzed. Nmr spectrum, **3cN**, 0.84 (*endo*-3-CH_3, d, J = 6.8 Hz); **3cX**, 0.96 (*exo*-3-CH_3, d, J = 6.5 Hz); mass spectrum, 208 (mol wt, 208).

Anal. Calcd for $C_{13}H_{20}O_2$: C, 74.96; H, 9.68. Found: C, 74.86; H, 9.70.

***endo*-2-Carbo-*sec*-butoxy-*exo*-3-methyl- and *exo*-2-carbo-*sec*-butoxy-*endo*-3-methylbicyclo[2.2.1]hept-5-ene (3tN and 3tX)** were prepared from *sec*-butyl *trans*-crotonate and CPD. The isomeric mixture of **3tN** and **3tX** was analyzed.

Anal. Calcd for $C_{13}H_{20}O_2$: C, 74.96; H, 9.68. Found: C, 74.90; H, 9.72.

***endo*- and *exo*-2-carbomethoxybicyclo[2.2.1]hept-5-ene (3′N and 3′X)** were prepared from methyl acrylate and CPD and separated by vpc at 150° (retention time, **3′N**, 13.8 min; **3′X**, 12 min). **3′N** was 93.2% pure, contaminated with 5.4% **3′X** isomer and 1.4% DCPD. **3′X** was 90.7% pure, contaminated with 8.5% **3′N** isomer and 0.8% DCPD; nmr spectrum, **3′N**, 3.65 (*endo*-2-OCH_3, s); **3′X**, 3.73 (*exo*-2-OCH_3, s); mass spectrum (same for both isomers), 152 (mol wt 152).

Anal. Calcd for $C_9H_{12}O_2$: C, 71.03; H, 7.95. Found: **3′N**, C, 71.03; H, 8.01. **3′X**, C, 71.06; H, 8.00.

***endo*-2-Carbomethoxy-*exo*-3-methyl- and *exo*-2-carbomethoxy-*endo*-3-methylbicyclo[2.2.1]hept-5-ene (3′tN and 3′tX)** were prepared from methyl *trans*-crotonate and CPD and separated by vpc at 150° (retention time, **3′tN**, 14 min; **3′tX**, 12.5 min). **3′tN** was 94.4% pure, contaminated with 5.6% **3′tX** isomer, and **3′tX** was 79.6% pure, contaminated with 20.4% **3′tN** isomer; nmr spectrum, **3′tN**, 3.66 (*endo*-2-OCH_3, s), 1.22 (*exo*-3-CH_3, d, J = 6.5 Hz); **3′tX**, 3.71 (*exo*-2-OCH_3, s), 0.92 (*endo*-3-CH_3, d, J = 7.0 Hz); mass spectrum (same for both isomers), 166 (mol wt, 166).

Anal. Calcd for $C_{10}H_{14}O_2$: C, 72.26; H, 8.49. Found: **3′tN**, C, 72.31; H, 8.61. **3′tX**, C, 72.30; H, 8.52.

***endo*-2-Carbomethoxy-*exo*-2-methyl- and *exo*-2-carbomethoxy-*endo*-2-methylbicyclo[2.2.1]hept-5-ene (3′αN and 3′αX)** were prepared from methyl methacrylate and CPD and separated by vpc on 1,2,3,4-tetrakis(2-cyanoethoxy)butane at 120° (retention time, **3′αN**, 23 min; **3′αX**, 20 min). **3′αN** was 59.8% pure, contaminated with 32.9% **3′αX** isomer and 7.3% DCPD. **3′αX** was 75.7% pure, contaminated with 21.2% **3′αN** isomer and 3.1% DCPD; nmr spectrum, **3′αN**, 3.70 (*endo*-2-OCH_3, s), 1.10 (*exo*-2-CH_3, s); **3′αX**, 3.62 (*exo*-2-OCH_3), 0.92 (*endo*-2-CH_3); mass spectrum (same for both isomers), 166 (mol wt, 166).

Anal. Calcd for $C_{10}H_{14}O_2$: C, 72.26; H, 8.49. Found: **3′αN**, C, 71.99; H, 8.52. **3′αX**, C, 72.49; H, 8.56.

***endo*- and *exo*-2-formylbicyclo[2.2.1]hept-5-ene (4N and 4X)** were prepared from acrolein and CPD. The reaction products were oxidized with Ag_2O–NaOH followed by methylation by diazomethane to give **3′N** and **3′X**. The vpc analysis indicated the identity of these reaction products with **3′N** and **3′X**.

***endo*-2-Formyl-*exo*-3-methyl- and *exo*-2-formyl-*endo*-3-methylbicyclo[2.2.1]hept-5-ene (4tN and 4tX)** were prepared from *trans*-crotonaldehyde and CPD. The reaction products were treated as above and confirmed as such from the identity of the derived compounds with **3′tN** and **3′tX**.

***endo*-2-Formyl-*exo*-2-methyl- and *exo*-2-formyl-*endo*-2-methylbicyclo[2.2.1]hept-5-ene (4αN and 4αX)** were prepared from methacrolein and CPD. The reaction products were treated as above and confirmed from the identity of the derived compounds with **3′αN** and **3′αX**.

***endo*-2-Carboxy-*endo*-3-methyl- and *exo*-2-carboxy-*exo*-3-methylbicyclo[2.2.1]hept-5-ene (5cN and 5cX)** were prepared from *cis*-crotonic acid and CPD. The reaction mixture was esterified with diazomethane. The isomeric mixture of methyl esters of **5cN** and **5cX** was analyzed.

Anal. Calcd for $C_{10}H_{14}O_2$: C, 72.26; H, 8.49. Found: C, 72.30; H, 8.51.

***endo*- and *exo*-2-carboxybicyclo[2.2.1]hept-5-ene (5N and 5X)** were prepared from acrylic acid and CPD. The reaction mixture was esterified with diazomethane. The vpc analysis indicated the identity of these reaction products with **3′N** and **3′X**.

***endo*-2-Carboxy-*exo*-3-methyl- and *exo*-2-carboxy-*endo*-3-methylbicyclo[2.2.1]hept-5-ene (5tN and 5tX)** were prepared from *trans*-crotonic acid and CPD. The reaction mixture was treated as above and identified.

***endo*-2-Carboxy-*exo*-2-methyl- and *exo*-2-carboxy-*endo*-2-methylbicyclo[2.2.1]hept-5-ene (5αN and 5αX)** were prepared from methacrylic acid and CPD. The reaction mixture was treated as above and identified.

The Thermochemistry of 1,2-Dioxetane and Its Methylated Derivatives. An Estimate of Activation Parameters

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Abstract: Thermochemical data and activation parameters are calculated for the thermal decomposition of 1,2-dioxetane and its methylated derivatives. The calculations, based on a two-step mechanism, give a log A value of 12.4 for 3,3,4-trimethyl-1,2-dioxetane, which is in excellent agreement with the reported value of 12.2. The calculations indicate that increased methyl substitution increases the stability of 1,2-dioxetanes. The lifetime of 1,2-dioxetane is estimated to be 10 sec at 60° compared to 2.3 hr for tetramethyl-1,2-dioxetane at the same temperature. Light emission, associated with the decomposition of 1,2-dioxetanes, is discussed with respect to the calculated thermochemical data.

Numerous reports of 1,2-dioxetane intermediates have appeared in the literature.[1] In most instances, 1,2-dioxetanes were viewed as transient intermediates. Recently isolation of these four-ring peroxides has been reported.[1b,c,2,3] In carbon tetra-

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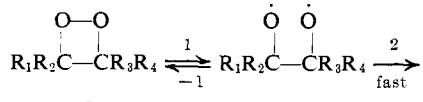
(1) (a) E. H. White, J. Wiecko, and D. F. Roswell, *J. Amer. Chem. Soc.*, **91**, 5194 (1969); (b) R. K. Razdan and V. V. Kane, *ibid.*, **91**, 5190 (1969); (c) K. R. Kopecky and C. Mumford, *Can. J. Chem.*, **47**, 709 (1969); (d) W. Fenical, D. R. Kearns, and P. Radlick, *J. Amer. Chem. Soc.*, **91**, 3396 (1969); (e) F. McCapra and R. A. Hann, *Chem. Commun.*, 422 (1969); (f) K. R. Kopecky, J. H. van de Sande, and C. Mumford, *Can. J. Chem.*, **46**, 25 (1968); (g) C. S. Foote, *Accounts Chem. Res.*, **1**, 104 (1968); (h) C. S. Foote and J. W-P Lin, *Tetrahedron Lett.*, 3267 (1968); (i) A. W. Berger, J. N. Driscoll, J. S. Driscoll, J. A. Pirog, and H. Linschitz, *Photochem. Photobiol.*, 7, 415 (1968); (j) F. McCapra, *Chem. Commun.*, 155 (1968); (k) H. H. Wasserman, K. Stiller, and M. B. Floyd, *Tetrahedron Lett.*, 3277 (1968); (l) D. M. Lemal, "The Chemistry of the Amino Group," S. Patai, Ed., Interscience, New York,

chloride, the activation parameters for the thermal decomposition of 3,3,4-trimethyl-1,2-dioxetane (If) to give acetone and acetaldehyde[1c] are $E = 23.7$ kcal/mol and $\log A = 12.2$.[2] The first-order rate coefficient for the decomposition of If in benzene is reported to be 5.5×10^{-4} sec^{-1} at 60°, which corresponds to a half-life of about 20 min at this temperature.

Two mechanisms may be considered for the thermal decomposition of a 1,2-dioxetane—a concerted process[5] and a two-step biradical sequence (eq 1). If the 1,2-dioxetane decompositions are mechanistically analogous to other saturated four-membered ring compound reactions, then concertedness seems improbable. For example, the activation parameters observed for both the isomerizations and decompositions of cyclobutane derivatives can be estimated to within the experimental error limits (*i.e.*, to within a factor of two in A and ±1.5 kcal/mol in E) by employing *a priori* thermochemical methods[6-8] based on the biradical mechanism. Furthermore, the lack of stereospecificity in the thermal decomposition of substituted cyclobutanes or 1,2-cycloaddition reactions of two olefins is consistent with a two-step biradical mechanism.[6,9] It seemed of some interest, therefore, to make similar transition-state estimates of the kinetic parameters for decomposition of 1,2-dioxetane and its methylated derivatives, and to compare the calculated parameters with those obtained experimentally,[1c,12] The agreement between the observed and calculated data, which are demonstrated below, should not be interpreted as "proving" that the 1,2-dioxetane decompositions *are* biradical processes, but rather only that the observed data are consistent with such a mechanism.

The thermochemistry of the reactants[13] (I) and biradicals[14] (II) for the 1,2-dioxetane decomposition (eq 1) is given in Table I. The most questionable value



I II $R_1R_2CO + R_3R_4CO$ (1)

a, $R_1 = R_2 = R_3 = R_4 = H$
b, $R_1 = CH_3$; $R_2 = R_3 = R_4 = H$
c, $R_1 = R_2 = CH_3$; $R_3 = R_4 = H$
d, $R_1 = R_3 = CH_3$; $R_2 = R_4 = H$, trans
e, $R_1 = R_3 = CH_3$; $R_2 = R_4 = H$, cis
f, $R_1 = R_2 = R_3 = CH_3$; $R_4 = H$
g, $R_1 = R_2 = R_3 = R_4 = CH_3$

in Table I is the strain energy attributed to the cyclic peroxide since, of course, no experimental value is available. It is seen from Table II that there is little change in strain energy produced by replacement of one methylene group with one oxygen. The change in strain energy may be somewhat more pronounced to

Table I. Thermochemistry of 1,2-Dioxetanes (I) and Biradicals (II)

Species	$S°$ (intrin)[a]	$\Delta S°_{1,-1}$,[a,b] eu	$\Delta H_f°$[c]	$\Delta H°_{1,-1}$[c,d]	E (strain)[c,e]
Ia	66.9	4	0	13.0[f]	26
IIa	70.0		12.2		0
Ib	76.0	2.7	−8.6	13.2	26
IIb	78.7		4.6		0
Ic	83.8	3.1	−18.3	14.4	26
IIc	86.9		−3.9		0
Id	85.1	2.3	−17.2	14.2	26
IId	87.4		−3.0		0
Ie	86.3	1.1	−16.2	13.2	26
IIe	87.4		−3.0		0
If	94.1	1.4	−25.8	15.2	26
IIf	95.5		−10.6		0
Ig	103.1	0.7	−34.6	16.2	26
IIg	103.8		−18.4		0

[a] Intrinsic entropies are $S°$ (intrinsic) = $S°$ (obsd) + $R \ln \sigma/ng_e$. The biradicals are assumed to be singlets, since by spin conservation rules, only singlets can undergo ring closure. The spin degeneracy term (g_e) is then one. The symmetry number and number of optical isomers are given by σ and n, respectively. [b] $\Delta S°_{1,-1} = (S°_{II} - S°_{I})$. [c] Kilocalories/mole. [d] $\Delta H°_{1,-1} = (\Delta H_f°_{II} - \Delta H_f°_{I})$. [e] Does not include cis repulsions of methyl substituents. The ring-opening endothermicity includes a gauche repulsion consistent with the conformation of the biradical formed on ring opening.

Table II. A Comparison of Strain Energies in Cyclic Hydrocarbons with Corresponding Oxygen Heterocycles[a]

Cyclic hydrocarbon	E (strain),[a] kcal/mol	Oxygen heterocycle	E (strain)[a]
△	27.6		27.6
□	26.2		26.4
⬡	0		2.2
			5.4
			3.4

[a] See ref 13 for literature data sources.

N. Y., 1968, p 701; (m) T. Matsuura and I. Saito, *Tetrahedron Lett.*, 3273 (1968); (n) T. Matsuura, H. Matsushima, and H. Sakamoto, *J. Amer. Chem. Soc.*, **89**, 6370 (1967); (o) T. A. Hopkins, H. H. Seliger, E. H. White, and M. W. Cass, *ibid.*, **89**, 7148 (1967); (p) W. H. Richardson, J. W. Peters, and W. P. Konopka, *Tetrahedron Lett.*, 5531 (1966); (q) E. H. White and M. J. C. Harding, *Photochem. Photobiol.*, **4**, 1129 (1965); (r) F. McCapra, D. G. Richardson, and Y. Chang, *ibid.*, **4**, 1111 (1965); (s) E. H. White and M. J. C. Harding, *J. Amer. Chem. Soc.*, **86**, 5686 (1964); (t) W. H. Richardson and V. F. Hodge, *J. Org. Chem.*, **35**, 1216 (1970); (u) W. Fenical, D. R. Kearns, and P. Radlick, *J. Amer. Chem., Soc.*, **91**, 7771 (1969); (v) R. S. Atkinson, *Chem. Commun.*, 177 (1970).

(2) We thank Dr. K. R. Kopecky for providing us with spectral data and activation parameters for 3,3,4-trimethyl-1,2-dioxetane prior to publication.

(3) To our knowledge the first claimed isolation of a 1,2-dioxetane was made by Blitz.[4] It was reported that chromic acid oxidation of tetrakis(4-nitrophenyl)ethylene at 115–130° gave tetrakis(4-nitrophenyl)-1,2-dioxetane. It appears likely that the product is 4,4′-dinitrobenzophenone which corresponds closely in melting point to the proposed 1,2-dioxetane.

(4) H. Blitz, *Ann.*, **296**, 238 (1897).

(5) (a) D. R. Kearns and A. U. Khan, *Photochem. Photobiol.*, 10, 193 (1969); (b) D. R. Kearns, *J. Amer. Chem. Soc.*, **91**, 6554 (1969).

(6) S. W. Benson and H. E. O'Neal, NSRDS-NBS, 21, U. S. Government Printing Office, Washington, D. C., 1970, p 20402.

(7) S. W. Benson, "Thermochemical Kinetics," Wiley, New York, N. Y., 1968.

(8) H. E. O'Neal and S. W. Benson, *J. Phys. Chem.*, **72**, 1866 (1968).

(9) One stereospecific, and therefore presumably concerted, 1,2-cycloaddition reaction to form a cyclobutane has been observed. However, this is in a special highly twisted and strained system which is most conducive to a concerted addition.[10] This system represents the single exception to the above assertion. It must be admitted, however, that the allowed [$\sigma 2_s + \sigma 2_a$] process for the thermal decomposition of cyclobutanes would be nonstereospecific.[11]

(10) K. Kraft and G. Koltzenburg, *Tetrahedron Lett.*, 4357 (1967).

(11) R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Academic Press, New York, N. Y., 1970, p 74.

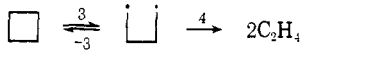
(12) W. H. Richardson and V. Hodge, unpublished results.

(13) S. W. Benson, F. R. Cruickshank, D. M. Golden, G. R. Haugen, H. E. O'Neal, A. S. Rogers, R. Shaw, and R. Walsh, *Chem. Rev.*, **69**, 279 (1969).

(14) H. E. O'Neal and S. W. Benson, *Int. J. Chem. Kinet.*, **1**, 221 (1969).

higher values with the exchange of more than one methylene unit for oxygen atoms. Unfortunately, data are not available for the effect of two adjacent oxygen atoms upon ring strain. Some data are available for sulfur heterocycles. The most reliable values of the strain energy in 1,2-dithiacyclopentane are 4[15] and 6[16] kcal/mol, which may be compared with a value of 1.7 kcal/mol for tetrahydrothiophene.[13] For 1,2-dithiacyclohexane, the strain energy is reported to be 0.5[15] kcal/mol, while there is no strain energy in thiacyclohexane.[13] Thus, the effect of *adjacent* sulfur atoms does not appear to have a profound effect on the strain energy. Presumably this conclusion can be extrapolated to the oxygen heterocycles. We have used a strain energy of 26 kcal/mol for 1,2-dioxetane, the same as that found in oxetane. This may underestimate the strain energy by a small amount and cause the $\Delta H^\circ_{1,-1}$ values to be somewhat high. The implications of this are discussed later. However, it should be noted here that, in terms of the calculations which follow, use of a larger strain energy will predict a more favorable ring opening to the biradical and will therefore tend to support that mechanism as opposed to the concerted process. A minimum estimate of ring strain, then, imposes the most severe restrictions on the biradical mechanism rate constant estimates.

Step 1 of the two-step mechanism (eq 1) is rate determining. In support of this assignment, we examine the relative exothermicities of the competing reactions (eq 2) of the tetramethylene-1,4 biradical (proposed as the intermediate in the cyclobutane decomposition) relative to the exothermicities of the corresponding reactions of the dioxy radicals (II, eq 1). Ring closing exothermicities in the 1,2-dioxetane system



(2)

$\Delta H^\circ_{-3,3} = 56.5$ kcal/mol; $\Delta H^\circ_{4,-4} = 36.6$ kcal/mol
$E_{-3} = 6.7$ kcal/mol; $E_4 = 6.5$ kcal/mol

are appreciably lower ($-\Delta H^\circ_{-1,1} \simeq$ 12–16 kcal/mol) than the above, while decomposition exothermicities are appreciably higher ($-\Delta H^\circ_{2,-2} \simeq$ 68–85 kcal/mol). Thus, reasoning either from the Evans–Polanyi relation[17] or from Hammond's postulate,[18] $E_{-1} > E_{-3}$ and $E_2 < E_4$. Since activation entropies for the competing reactions in the two systems should be very similar, and since $E_{-3} \simeq E_4$, it follows that $k_2 \gg k_{-1}$ and that ring opening (eq 1) should be rate determining in the 1,2-dioxetane decompositions.

The overall decomposition rate constant is then $k_{\text{decomp}} = k_1 = k_{-1}K_{1,-1}$. The thermodynamics of $K_{1,-1}$ are given in Table I. To calculate decomposition rate constants, the ring closing activation energies (E_{-1}) and activation entropies ($\Delta S^\ddagger_{-1}$) need to be estimated (see eq 3–5). As argued earlier, E_{-1} must

$$E = \Delta H^\circ_{1,-1} + E_{-1} \tag{3}$$

$$\Delta S^\ddagger = \Delta S^\circ_{1,-1} + \Delta S^\ddagger_{-1} + R\ln\left(\frac{\sigma n^\ddagger}{\sigma^\ddagger n}\right) \tag{4}$$[19]

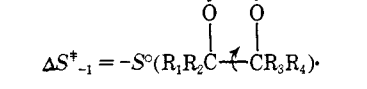
$$A = \frac{ekT}{h}e^{\Delta S^\ddagger/R} \tag{5}$$

be greater than the ring closing activation energies for the corresponding hydrocarbon 1,4 biradical ($E_{-3} \simeq 5.9 + \Delta n$ gauche kcal/mol), but just how much greater has not been calculated *a priori* here. Rather, we have calculated the value of E_{-1} from the experimental data for 3,3,4-trimethyl-1,2-dioxetane (If) and have shown that this value is reasonable in terms of other analogous ring closing reactions of variable exothermicities.

From Table I, $\Delta H^\circ_{1,-1} = 15.2$ kcal/mol for If and with the experimental value[2] of $E = 23.7$ kcal/mol, one calculates $E_{-1} = 8.5$ kcal/mol from eq 3. The value of E_{-1} is indeed larger than E_{-3}, as expected, and satisfies our assumption that $k_2 \gg k_{-1}$. The reasonableness of the E_{-1} value for If can be seen by comparison with the E_{-1} values calculated for various cyclobutane-type decompositions (Table III). There is a general trend to higher E_{-1} values with lower $\Delta H^\circ_{1,-1}$ values. A least-squares fit of the data in Table III, along with that for cyclobutane (eq 2), to the Polanyi relationship, $E_{-1} = \alpha\Delta H^\circ_{1,-1} + C$, gives $\alpha = -0.104$ and $C = 12.2$. The correlation is poor ($r = 0.903$) as would be expected, since large changes in $\Delta H^\circ_{1,-1}$ produce only minor changes in E_{-1}. Nonetheless, the data do suggest that E_{-1} for 1,2-dioxetanes should be larger than the corresponding value for cyclobutanes which is consistent with our calculations and assumption.

From the above Polanyi relationship, E_{-1} is found to be 10.6 kcal/mol for If compared to our calculated value of 8.5 kcal/mol. This difference may result from our assumed ring strain energy of 26 kcal/mol, which, as stated previously, may be somewhat low. A "low" estimate for ring strain will cause a corresponding increase in the calculated ring opening enthalpy ($\Delta H^\circ_{1,-1}$) and this will in turn cause E_{-1} to be low as calculated by eq 3 (using the experimental value of E for If). This difference between E_{-1} predicted by the Polanyi relationship and that calculated on the basis of a 26-kcal/mol strain energy is small, and suggests that our value for the strain energy of the 1,2-dioxetane ring is not unreasonable.

Activation energies for thermal decomposition of 1,2-dioxetanes are calculated from eq 3 using $E_{-1} = 8.5$ kcal/mol and the $\Delta H^\circ_{1,-1}$ values of Table I. The results are given in Table IV. The reaction coordinate for ring closing in 1,4 biradicals is an internal rotation.[8] The activation entropy is then given by

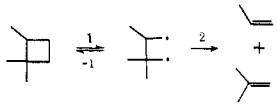
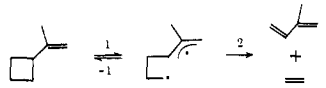
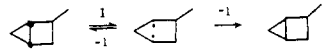
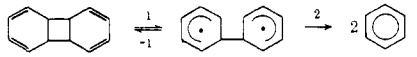


These values are calculated from the analogous hydrocarbons where the oxy radical is replaced with a methyl group.[8] The overall entropies of activation ($\Delta S^\ddagger$) and log A values are calculated from eq 4 and 5 using $\Delta S^\circ_{1,-1}$ values from Table I and the $\Delta S^\ddagger_{-1}$ values given in Table IV. The results are given in Table IV along with calculated rate coefficients at 60°. It is seen that the estimated log A value for If (12.4) is in excellent agreement with the observed value of 12.2.[2]

(15) S. Sunner, *Nature* (*London*), **176**, 217 (1955).
(16) J. A. Barltrop, P. M. Hayes, and M. Calvin, *J. Amer. Chem. Soc.*, **76**, 4348 (1954).
(17) M. G. Evans and M. Polanyi, *Trans. Faraday Soc.*, **34**, 11 (1938).
(18) G. S. Hammond, *J. Amer. Chem. Soc.*, 77, 334 (1955).

(19) σ, n and $\sigma^\ddagger$, $n^\ddagger$ are the symmetry number and number of optical isomers of the reactant and transition state, respectively. The ratio ($\sigma n^\ddagger/\sigma^\ddagger n$) is the reaction path degeneracy.

Table III. Thermochemistry and Activation Energies of Some Cyclobutane-Type Reactions[a]

Reaction	E_{obsd}	$\Delta H°_{1,-1}{}^{298}$	$\Delta H°_{1,-1}(T_m)$	E_{-1}	Lit.
	62.4	55.4	56.5	5.9	*a, b, f*
	51.0	41.4	42.5	8.5	*b, g*
	49.5	40.7	42.1	7.4	*h*
	39.2	29.4	29.4	9.8	*i*
	36.0	27.8	27.9	8.1	*c, j*
	26.9	15.2	15.2	11.7	*c, d, k*
	(24.6)	12.6	14.7	9.9	*e*

[a] This is a hypothetical reaction based on the cyclobutane results. The compound has the same methyl substituents as If and therefore gives the most analogous E_{-1} comparison. [b] The back reaction is competitive with decomposition, $k_{-1} \simeq k_2$. [c] Reaction 2 is much faster than ring closing (−1). [d] The resonance and strain energy of the reactant are not known. However, the former is probably close to that of an allyl radical (~12.6 kcal/mol), and the latter should be close to the sum of the cyclopropane and cyclobutene ring strains (~57 kcal/mol). The reaction is sterically constrained to be biradical rather than concerted. [e] Arrhenius parameters have not been measured; however, from $A_{est} = 10^{12.9}$ sec^{-1} and the reported half-life of 210 min at 40° in carbon tetrachloride (G. Schroeder, W. Martin, and H. Röttele, Orbital Symmetry Correlations in Organic Reactions Conference, Cambridge, Jan 7–9, 1969), one can calculate the activation energy. Also E_{-1} and $\Delta H°_{1,-1}$ have been obtained by assuming a cyclohexadienyl resonance energy of 20 ± 2 kcal/mol. [f] Reference 8. [g] R. J. Ellis and H. M. Frey, *Trans. Faraday Soc.*, **59**, 2076 (1963). [h] W. von E. Doering, unpublished results; see also W. von E. Doering and W. R. Dolbier, *J. Amer. Chem. Soc.*, **89**, 4534 (1967), for results with 1,2-bis(dideuteriomethylene)cyclobutane. [i] J. D. Chesick, *ibid.*, **84**, 3250 (1962). [j] C. Steel, R. Zand, P. Hurwitz, and S. G. Cohen, *ibid.*, **86**, 679 (1964). [k] J. I. Brouman and D. M. Golden, *ibid.*, **90**, 1920 (1968).

Table IV. Calculated Activation Parameters and Rate Coefficients for the Thermal Decomposition of 1,2-Dioxetanes

Reactant	E_1[a]	$\Delta S^{\ddagger}_{-1}$[b,e]	$\Delta S^{=}_{1}$[b]	Log A_1[c]	Log k,[c] 60°
Ia	21.5	−5.6	−1.6	13.1	−1.00
Ib	21.7	−5.6	−2.9	12.7	−1.55
Ic	22.9	−5.4	−2.3	12.9	−2.14
Id	22.7	−5.8	−3.5	12.6	−2.30
Ie	21.7	−5.8	−4.7	12.4	−1.85
If	(23.7)[d]	−5.8	−4.4	12.4	−3.15
Ig	24.7	−5.8	−5.1	12.3	−3.92

[a] Kcal/mol, with $E_{-1} = 8.5$ kcal/mol. [b] Entropy units. [c] Sec^{-1}. [d] Experimental value.[2] [e] For calculational methods see ref 8.

Table V. Calculated Available Energies from the Decomposition of 1,2-Dioxetanes

Reactant	$\Delta H_r°$[a,b]	$(E_1 - \Delta H_r°)$[a]
Ia	−55.4	76.1
Ib	−67.4	89.1
Ic	−79.4	102.3
Id	−79.4	102.1
Ie	−79.4	101.1
If	−91.4	115.1
Ig	−103.4	128.1

[a] Kcal/mol. [b] $\Delta H_r° = \Delta H_f°$ (1,2-dioxetane) − $\Delta H_f°$ (carbonyl products).

The rate constants for decomposition show an interesting trend with substitution. Increased methyl substitution increases the stability of the 1,2-dioxetanes. Thus, the lifetime of Ia at 60° is only 10 sec, while Ig has a lifetime of 2.3 hr at the same temperature.

Since light emission accompanies the decomposition of 1,2-dioxetanes,[1c,1e,12] it is of interest to determine whether or not the calculated thermodynamic values are consistent with this observation. Light emission is most readily explained by generation of an excited singlet state carbonyl molecule (*cf.*, eq 1) which subsequently decays to the ground state with emission of a photon.[1c] Such fluorescence requires that the transition state energy for decomposition of the 1,2-dioxetanes be sufficiently high so that crossing into the excited singlet state energy manifolds of the carbonyl molecules is possible. In other words, the sum of the heat of reaction for 1,2-dioxetanes giving carbonyl products ($-\Delta H_r°$) and E_1 must be equal to or greater than $E_{0,1}$, the energy difference between the 0,0 vibrational levels in the first excited state and the ground state for one of the carbonyl products. The values of $E_{0,1}$ for formaldehyde, acetaldehyde, and acetone are not known exactly. However, reasonable estimates of 83–87[20] and 81[21] kcal/mol have been given for acetone and formaldehyde, respectively. Thus, the quantity $(E_1 - \Delta H_r°)$ must equal or exceed 81–87 kcal/mol for emission by monomer carbonyl species. From Table V it is apparent that only the decomposition of Ia fails to satisfy this condition for emission. Although emission from Ia has not been tested experimentally, emission may still occur from a formaldehyde eximer which may be expected to have a lower excited singlet state energy than the monomer.[22] The eximer postulate seems quite reasonable, since the two carbonyl product

(20) R. F. Borkman and D. R. Kearns, *J. Chem. Phys.*, **44**, 945 (1966).
(21) J. C. D. Brand, *J. Chem. Soc.*, 858 (1956).
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molecules are produced in close proximity (*i.e.*, the same solvent cage in solution) in the 1,2-dioxetane decompositions.

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Cyclopropyl Participation in the Solvolysis of 2-Cyclopropylethyl Brosylates[1]

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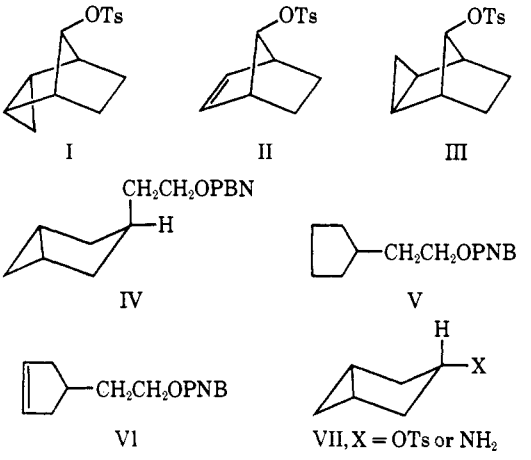
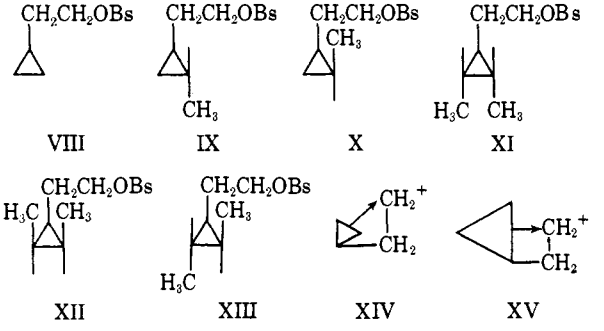
Abstract: Rates of solvolysis are reported for 2-cyclopropylethyl brosylate, and its *cis*- and *trans*-2′-methyl and 2′,3′-dimethyl derivatives, in formic acid containing sodium formate. The results indicate that cyclopropyl can participate, but less efficiently than vinyl.

It has recently been reported[2,3] that the cyclopropane analog (I) of *trans*-7-norbornenyl tosylate (II) solvolyses 10^{14} times faster than the isomer III, and 10^3 times faster than II itself. This was taken as evidence that cyclopropane acts as a more effective neighboring group than a double bond, a claim which has led to widespread interest in the reactions of analogous cyclopropyl derivatives.[4-6] Thus Sargent, *et al.*,[4] found that the rate of solvolysis of IV (PNB = *p*-nitrobenzoyl) is almost the same as that of the cyclopentane analog V, and 87-fold less than that of the cyclopentene analog VI; this observation certainly seems to suggest that cyclopropane is inherently a less effective neighboring group than ethylene and that the exceptional activating effect of cyclopropane in the case of I is due to other factors, *e.g.*, the fact that the geometry of I is ideally suited to participation, and to possible relief of ring strain. There is also the long-standing controversy concerning participation in the solvolytic and deamination reactions of VII.[7]



Here we wish to report some studies of cyclopropyl participation, based on rates of solvolysis of 2-cyclopropylethyl brosylate (VIII) and its *cis*- and *trans*-2′-methyl and 2′,3′-dimethyl derivatives (IX–XIII). If the cyclopropyl group does not participate, all these compounds would be expected to react at similar rates, because the methyl groups are too far away from the reaction center to have any significant field or inductive effects. If, however, the reaction takes place *via* nonclassical π-complex analogs such as XIV, methyl substitution in the 2′ and 3′ positions should enhance the rate. A similar argument has been used very effectively by Schleyer[8] in a study of analogous participation in the solvolysis of cyclopropylcarbinyl derivatives.



(1) This work was supported by the Air Force Office of Scientific Research through Grant No. AF-AFOSR-1050-67. A preliminary account of some of this work has appeared: M. J. S. Dewar and J. M. Harris, *J. Amer. Chem. Soc.*, **90**, 4468 (1968). Full details will be found in a thesis by J. M. Harris, Ph.D. Dissertation, The University of Texas at Austin, 1969.

(2) H. Tanida, T. Tsuji, and T. Irie, *J. Amer. Chem. Soc.*, 89, 1953 (1967).

(3) M. A. Battiste, C. L. Deyrup, R. E. Pincock, and J. Haywood-Farmer, *ibid.*, **89**, 1954 (1967).

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(6) Y. E. Rhodes and T. Takino, *J. Amer. Chem. Soc.*, **90**, 4470 (1968).

(7) See H. Tanida, *Accounts Chem. Res.*, **1**, 239 (1968).

(8) P. von R. Schleyer and G. W. Van Dine, *J. Amer. Chem. Soc.*, **88**, 2322 (1966).