

oxyphenyl 3-bromopropionate from kinetic runs was allowed to stand until no change in color occurred (1 day). Gas chromatograms showed only peaks with retention times of the acrylate ester, the bromo ester, and 3,4-dinitrophenol. TLC on microscope slides using Silic AR 7FG adsorbent developed with 9:1 pentane:benzene (v/v) showed only the expected spots on fixing with iodine vapor. On evaporation to dryness and dissolution in $\text{Me}_2\text{SO}-d_6$, the NMR spectrum showed absorption maxima at δ 5.87 (q) and 6.19, identical with those from a sample prepared from acryloyl chloride and hydroquinone monomethyl ether. Similar NMR patterns were found for the 3'-nitro ester (δ 5.85 and 6.21), 4'-methyl ester (δ 5.7 and 6.18), and the 4'-bromo ester (δ 5.82 and 6.20). Reaction products from the 3-bromothiolo propionates were more difficult to identify. On evaporation of reaction mixtures, films of obviously polymeric nature were found. Attempted determination of TLC R_f values of phenyl 3-bromothiolo propionates using Silic AR 7GF with pentane/benzene as before gave spots identified as the thiophenol, 3-bromopropionic acid, and the unsaturated thiole ester. Using the same TLC adsorbent with reaction mixtures showed no spots other than the dinitrophenol, thiophenol, 3-bromopropionic acid, and the unsaturated thiole ester. The NMR spectrum showed bromothiolo ester, unsaturated thiole ester, and 3,4-dinitrophenol. The phenyl thioacrylates could not be prepared without substantial polymerization.

Preparation of 4'-Bromophenyl 3-Bromopropionate-2-d. A twofold excess of DBr was allowed to bubble through a solution of 2 g of 4'-bromophenyl acrylate (from 4'-bromophenyl 3-bromopropionate with 3,4-dinitrophenoxide) in cyclohexane at room temperature, and the reaction mixture was stirred for 1 h. The DBr was prepared from D_2O and PBr_3 and purified by passage in a N_2 stream through a U-tube containing PBr_3 , a trap at -30°C to capture PBr_3 , and a trap at -78°C to capture DBr. The DBr was subsequently allowed to flow into the flask containing the 4'-bromophenyl acrylate. The product of DBr addition was extracted into cyclohexane/benzene and washed with D_2O three times, and dried with MgCO_3 , and the solvent was evaporated. Crystallization from benzene/petroleum ether gave the deuterated bromo ester, mp $30\text{--}31^\circ\text{C}$. Assay for deuterium was carried out by using parent peaks at 307, 309, and 311 daltons (ratio 1.00:2.00:1.00) and by NMR peak-area integrations of δ 3.2 and 3.7 maxima (area 1:2).

Kinetics were carried out as previously described. Three runs were made at 35.20°C . k_2 for perhydro compounds, 1.89, 1.82,

1.73, (av 1.81); k_2 for HD compound, 1.07, 1.02, 1.07 (av 1.05). The rate ratio for $\text{H}_2/\text{HD} = 1.69$. Mass spectra were used to determine H/D ratios in the product 4'-bromophenyl acrylate with 226 and 228 dalton peaks for the H_2 and 227 and 229 dalton peaks for the HD compound. The ratio of HD/ H_2 was found to be 1:2.00.

Reaction of 1 g of 4'-chlorophenyl 3-bromothiolo propionate in 20 mL of ether with 10 mL of 0.2 M aqueous KOH gave the ethereal solution of 4'-chlorophenyl thioacrylate. Excess DBr from acetyl bromide and D_2O was passed through the ether solution with N_2 . The ether as evaporated by using a rotary evaporator at room temperature. The residue was evacuated at 0.001 torr for 48 h. A mass spectrum using the m/e 262 and 264 peaks for H compound and m/e 263 and 265 peaks for the D compound at 20-eV ionizing potential gave 37% of one D. After 50% reaction in THF with 3,4-dinitrophenoxide, the mass spectrum showed the same peak ratios to yield 41.8% D. So much polymer and so little bromo thiole ester were formed that it was judged not to be worth further experiments.

Acknowledgment. Support from the Research Committee of the Academic Senate and from the Chancellor's Patent Fund is gratefully acknowledged.

Registry No. 4'-Nitrophenyl 3-bromopropionate, 78939-58-9; 3'-nitrophenyl 3-bromopropionate, 86259-93-0; 4'-acetylphenyl 3-bromopropionate, 86259-94-1; 3'-acetylphenyl 3-bromopropionate, 86259-95-2; 4'-bromophenyl 3-bromopropionate, 86259-96-3; 4'-acetoxypheyl 3-bromopropionate, 86259-97-4; 3'-bromophenyl 3-bromopropionate, 86259-98-5; 4'-chlorophenyl 3-bromopropionate, 86259-99-6; 3'-methoxyphenyl 3-bromopropionate, 86260-00-6; 4'-methoxyphenyl 3-bromopropionate, 6329-88-0; phenyl 3-bromopropionate, 27850-43-7; 3'-methylphenyl 3-bromopropionate, 86260-01-7; 4'-methylphenyl 3-bromopropionate, 86260-02-8; 4'-fluorophenyl 3-bromopropionate, 86260-03-9; 4'-tert-butylphenyl 3-bromopropionate, 86260-04-0; 4'-nitrophenyl 3-bromothiolo propionate, 86260-05-1; 4'-acetylphenyl 3-bromothiolo propionate, 86260-06-2; 3'-acetylphenyl 3-bromothiolo propionate, 86260-07-3; 4'-chlorophenyl 3-bromothiolo propionate, 86260-08-4; 4'-methoxyphenyl 3-bromothiolo propionate, 86260-09-5; phenyl 3-bromothiolo propionate, 31677-04-0; 4'-methylphenyl 3-bromothiolo propionate, 86260-10-8; 4'-bromophenyl 3-bromopropionate-2-d, 86260-11-9; 3,4-dinitrophenoxide sodium salt, 64993-95-9; deuterium, 7782-39-0.

Chemical Reactivity and Molecular Structure Relationship of Highly Strained Cage Oxetanes

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The strained cage oxetane 11,12-dimethyl-3,4-diphenyl-5,7-bis(methoxycarbonyl)-2-oxapentacyclo[6.4.0.0^{1,4}.0^{3,7}.0^{5,9}]dodeca-11-ene-6,10-dione (1cI) was shown by single-crystal X-ray analysis not to have an abnormal bond elongation caused by through-bond interaction. However, 1cI underwent rapid decarbonylation at 120°C to give the tricyclic diene 2-oxatricyclo[4.3.2.0^{1,5}]undeca-3,8,10-trien-7-one derivative (4cI), while 1aI isomerized to a 1-oxacyclopenta-3a,8b-dihydrobenzo[b]furan derivative (7aI). The reactivity differences are discussed in terms of a frontier molecular orbital theory based on X-ray data, molecular mechanics calculations, and kinetic data.

During the course of a study of strained cage compounds, we have proposed that two factors influence their reactivity: (1) a through-bond interaction enhanced by inherent strain produces an elongated σ bond, which plays an important role in thermal reactions; (2) a frontier molecular orbital interaction enhances the rate of decarbonylation reactions.

Cage oxetane 1 (Chart I) is of interest in this study because it is a highly strained molecule that contains several functional groups: ether, enone, bridge carbonyl, and vicinal phenyl groups. We here report on studies of 1 that include bond lengths, the conformation of the two phenyl rings, and its reactions under thermal or acidic conditions.

Table I. ¹H NMR Spectral Data^a for Tricyclic Dienes 4 and 6

compd	chemical shift, δ	J, Hz
4ck	3.66, 3.72 (s, 2OCH ₃ , 6 H), 4.32 (s, H ₈ , 1 H), 4.51 (d, H ₉ , 1 H), 5.68 (dd, H ₁₁ , 1 H), 7.74 (d, H ₁₂ , 1 H), 7.20-7.43 (m, Ph H, 10 H)	$J_{9,11} = 2.0$ $J_{11,12} = 11.0$
4cl	1.77, 2.08 (s, 2CH ₃ , 6 H), 3.61, 3.73 (s, 2OCH ₃ , 6 H), 4.18 (s, H ₅ , 1 H), 4.47 (d, H ₆ , 1 H), 6.98-7.58 (m, Ph H, 10 H)	
6ak	1.82 (s, C ₄ -CH ₃ , 3 H), 1.89 (d, C ₁₁ -CH ₃ , 3 H), 2.31-2.71 (m, 2CH ₂ , 4 H), 3.32 (s, H ₅ , 1 H), 3.55 (s, H ₆ , 1 H), 7.10-7.40 (m, Ph H, 10 H)	$J_{6,C_{11}-CH_3} = 1.5$
6ck	2.30-2.70 (m, 2CH ₂ , 4 H), 3.63, 3.73 (s, 2OCH ₃ , 6 H), 3.83 (s, H ₅ , 1 H), 4.13 (s, H ₆ , 1 H), 7.20-7.80 (m, Ph H, 10 H)	

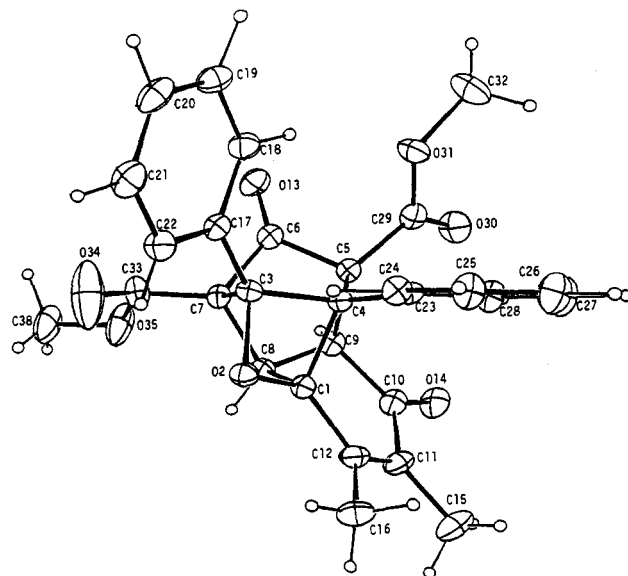
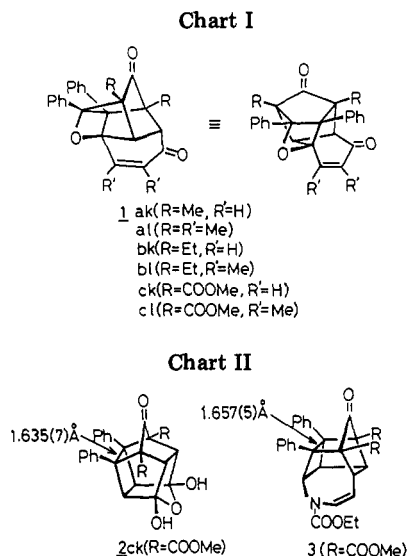
^a CDCl₃.

Figure 1. ORTEP drawing of cage oxetane 1cl.

Preparation of the Cage Oxetanes, 5,7,11,12-Tetra-substituted 3,4-Diphenyl-2-oxapentacyclo-[6.4.0.0^{1,4}.0^{3,7}.0^{5,9}]dodec-11-ene-6,10-diones. The cage oxetanes 1a-k-cl were prepared by the method of Warrenner et al.^{1,2}

Molecular Structure Determination. The cage oxetane 1cl, which bears two methoxycarbonyl groups as does 2ck, was characterized by a single X-ray analysis. The crystal structure was solved by the direct method. Refinement to an *R* factor of 5.3% was obtained by the method of least-squares on 2641 independent reflections.

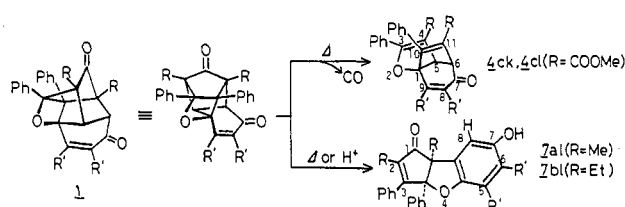
There are many abnormal bond lengths (e.g., 1.58 Å in C(3)-C(7), C(4)-C(5), and C(7)-C(8) and abnormal bond angles which reflect the highly strained nature of the cage oxetane.

The oxetane ring is strongly puckered, oxygen being displaced 0.64 Å out of the plane defined by the three carbons, in contrast to the planar structure of oxetane.³

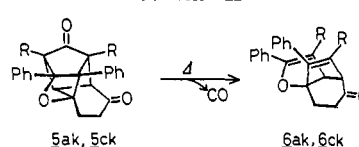
In contrast to 2ck,² the two methoxycarbonyl groups are oriented in a nearly antiparallel disposition, so that the dipoles of the two ester carbonyl functions cancel each other. The two phenyl rings attached to the oxetane ring are not face-to-face but rather are in perpendicular planes.⁴

Obviously, the observed conformation of the two phenyl rings is not favorable for through-bond coupling between the π systems, resulting in the absence of the pronounced bond elongation that has been observed in the oxa-cage

Scheme I



Scheme II



ketone 2ck² and the pentacyclic cage ketone 3⁵ (Chart II, Figure 1).

A molecular mechanics calculation confirmed that the C(3)-C(4) bond length of 1.566 (5) Å is in the range predicted by conventional steric repulsion. This fact indicates that the phenyl orientation has a great influence on bond elongation. The C₃ phenyl ring is located in the shielding area of the bridge carbonyl, which is compatible with the ¹H NMR high-field shift of two aromatic proton signals at 6.5 ppm.²

Chemical Behavior of Cage Oxetane 1. Refluxing of 1ck or 1cl in xylene caused a rapid decarbonylation to give tricyclic dienes 4ck or 4cl, respectively. The IR spectrum of 4ck shows three carbonyl absorption bands at 1725, 1715, and 1690 cm⁻¹ due to the α,β -unsaturated carboxyl

(1) Warrenner, R. N.; Paddon-Row, M. N.; McCay, I. R. *Aust. J. Chem.* 1977, 30, 2189-2194.

(2) Okamoto, Y.; Harano, K.; Yasuda, M.; Osawa, E.; Kanematsu, K. *Chem. Pharm. Bull.*, in press.

(3) Chan, S. I.; Zinn, J.; Gwinn, W. D. *J. Chem. Phys.* 1961, 34, 1319-1329.

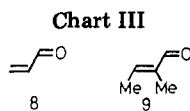
(4) The observed twist angles of ring planes with regard to the C₃-(Ph)-C₄(Ph) bond are 47.5° and -131.2° for the C₃ phenyl ring and 11.7° and -175.1° for the C₄ phenyl ring.

(5) Harano, K.; Ban, T.; Yasuda, M.; Osawa, E.; Kanematsu, K. *J. Am. Chem. Soc.* 1981, 103, 2310-2317.

Table II. Rate Constants for Decarbonylation of 1 and 5

compd	solvent	temp, °C	$10^5 k_1, s^{-1}$	rel rate	E_a , kcal/mol	ΔS^\ddagger , eu
5ak	C ₆ D ₆	129.8	9.34 ^a	1		
5ck	C ₆ D ₆	129.8	105 ^a	11.2		
	sulfolane	120.5	81.8 ^b	8.8		
	sulfolane	129.2	157 ^b	16.8	23.5	-14.9 ^c
	sulfolane	138.3	300 ^b	32.1		
1ck	sulfolane	120.6	14.3 ^b	1.5		
	sulfolane	129.5	31.7 ^b	3.4	27.1	-9.1 ^d
	sulfolane	138.4	66.4 ^b	7.1		

^a Measured by the ampule technique. ^b Measured by UV spectrometry. ^c Calculated from the value obtained at 129.2 °C. ^d Calculated from the value obtained at 129.5 °C.



and carbonyl groups, respectively. The ¹H NMR spectrum of 4ck shows two allylic methine protons at 4.32 and 4.51 ppm. The lack of splitting in the former peak and the presence of long-range coupling in the latter (2.0 Hz) support the structure.⁶ Similarly, the dihydro derivative 5ck underwent decarbonylation to give the analogous product 6ck (see Schemes I and II and Table I).

By contrast, the thermal treatment of cage oxetanes 1al and 1bl, which bear alkyl groups instead of methoxycarbonyl groups, effected isomerization to afford cyclopentenone-annelated benzofuran derivatives 7al and 7bl, which are also obtained from the acid-catalyzed rearrangement of 1al and 1bl under very mild reaction conditions.⁷

The structures given for 7al and 7bl are based on spectral data.

The methyl groups on the enone residue govern the rate of catalytic rearrangement; 1ak and 1bk required more severe reaction conditions for the rearrangement than 1al and 1bl. This may be attributed to the difference in the proton-accepting ability of the enone system. The CNDO/2 MO calculations on models 8 and 9 show that the n-HOMO of 9 is 0.8 eV higher than that of 8⁸ (Chart III).

Kinetics. (A) Decarbonylation Reaction of Cage Oxetanes. Kinetic data (Table II) were collected by using the ampule technique combined with UV and ¹H NMR spectroscopic analyses. As can be seen in Table II, the rates are very high compared with the reported rates of decarbonylation reactions in other strained molecules, e.g., 3.^{5,9}

Among the substituents examined, methoxycarbonyl is more effective than methyl in increasing the rate. For example, 5ck decarbonylates 11 times faster than 5ak. The rate of reaction is not affected by the nature of the solvent; only a 1.5-fold increase in rate was observed for the decarbonylation in going from C₆D₆ to sulfolane. Furthermore, the activation entropies of the decarbonylation reactions are highly negative. These data indicate a tight transition state with little charge separation in the rate-determining step.

(6) An HGS molecular model of 4 showed H₅ and H₆ in a nearly perpendicular disposition.

(7) This reaction should be compared with that reported for a simple oxetane: Sauers, R. R.; Kelly, K. W. *J. Org. Chem.* 1970, 35, 498-501.

(8) The calculated FMO energy levels by the CNDO/2 MO method for 8 and 9 are as follows: 8, -13.6 (n-HOMO) and 2.47 (LUMO) eV; 9, -12.8 (n-HOMO) and 2.40 (LUMO) eV.

(9) Tezuka, T.; Yamashita, Y.; Mukai, T. *J. Am. Chem. Soc.* 1976, 98, 6051-6052.

Table III. Rate Constants for Acid-Catalyzed Rearrangement of 1bl

solvent	$10^3 \cdot [p\text{-TsOH}], M$	$10^5 k_1, s^{-1}$	$10^5 k_2, s^{-1} M^{-1}$
CHCl ₃ ^a	1.50	1.14	
	2.25	2.02	915
	3.00	2.73	
EtOH ^b	19.8	0.17	~9

^a At 34.1 °C. ^b At 42.4 °C.

(B) Acid-Catalyzed Rearrangement of 1bl. The rearrangement rate was found to be proportional to the concentration of the catalyst, *p*-toluenesulfonic acid (Table III). The ease of rearrangement depends upon the nature of the substituents on C₅ and C₇: 1ck and 1cl, with methoxycarbonyl groups, did not rearrange under these higher conditions. The reaction rate in CHCl₃ is considerably higher than that in EtOH. This may be attributed to the extra desolvation energy necessary to overcome the hydrogen bonding between the enone and the hydroxylic solvent.

These results suggest that both the decarbonylation and the isomerization of cage oxetanes proceed through a highly ordered transition state as depicted in Figure 3.

EFF Calculation.¹⁰ It is known that EFF (empirical force field) calculations provide a diagnostic method for estimating the degree of through-bond coupling.^{5,11} Allinger's MMPI force field calculations of 1cl are summarized in Table IV.

The MMPI calculation roughly reproduced the crystal conformation, although small differences were observed in the twist angles of the Ph-C₃-C₄-Ph system and in the bond lengths of C₇-C₈ and C₅-C₉ (Table IV). This fact indicates that the crystal conformation is energetically stable and that mechanical strain is the dominant factor in determining the molecular conformation and the thermal reactivity of 1. The calculated steric energies and geometries are listed in Table V.

As can be seen in Table V, a larger amount of steric energy is located around the deformed oxetane ring, indicating that the observed high reactivities in the decarbonylation and rearrangement are due to strain release and that bond weakening by through-bond interaction is not operative in this system.

Discussion

The most remarkable feature of cage oxetane 1cl is the bond length of C₃(Ph)-C₄(Ph) and the conformation of the

(10) (a) Wertz, D. H.; Allinger, N. L. *Tetrahedron* 1974, 30, 1579-1586.

(b) Allinger, N. L.; Sprague, J. T. *J. Am. Chem. Soc.* 1973, 95, 3893-3907.

(c) Allinger, N. L.; Sprague, J. T.; Liljefors, T. *Ibid.* 1974, 96, 5100-5104.

(d) Allinger, N. L.; Yuh, H. *QCPE* 1974, 11, 318.

(11) Osawa, E.; Onuki, Y.; Mislow, K. *J. Am. Chem. Soc.* 1981, 103, 7475-7479.

Table IV. MMPI Calculations^a for 1 and 5

compd	steric energy			local strain	
	total	bending	torsion	C ₁ C ₄ C ₃ ^b	C ₅ C ₆ C ₇ ^b
1ak	109.0	59.4	34.0	12.6 (74.1)	2.45 (99.0)
1al	105.5	61.1	31.4	12.6 (74.1)	2.45 (99.0)
1cl	124.0	66.2	23.5	12.9 (73.7)	2.42 (99.1)
5al	108.5	62.1	29.9	12.9 (73.8)	2.38 (99.3)

^a Kilocalories/mole. ^b Interatomic angle in degrees in parentheses.

Table V. Calculated Geometries of 1 and 5 by MMPI Method^a

compd	dihedral angles, deg				distances, Å		
	C ₃ C ₄ C ₂₃ C ₂₄	C ₃ C ₄ C ₂₃ C ₂₈	C ₄ C ₃ C ₁₇ C ₁₈	C ₄ C ₃ C ₁₇ C ₂₂	C ₁₇ C ₃ C ₄ C ₂₃	C ₃ -C ₄	C ₁ -C ₄
1ak	73.4	-104.6	-95.5	84.5	28.0	1.566	1.547
1al	66.7	-115.2	-97.2	82.7	26.9	1.566	1.547
1cl	-1.0 (11.7)	176.0 (-175.1)	28.4 (47.5)	-145.9 (-131.2)	52.4 (41.3)	1.555 (1.566)	1.556 (1.571)
5al	-0.2	-179.2	-26.8	152.3	49.1	1.559	1.563

^a Values in parentheses are data from X-ray crystallography.

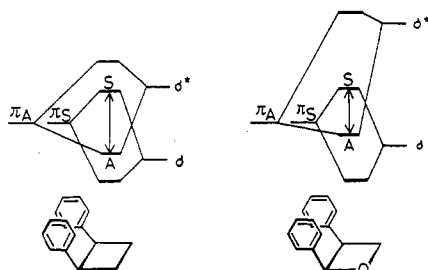


Figure 2. Interaction diagram in through-bond interaction of phenyl π orbitals with cyclobutane and oxetane σ orbitals.

two phenyl groups. As we have pointed out,⁵ inherent strain generally enhances through-bond coupling, and this stabilization is large enough to fix the phenyl groups in a parallel disposition. The absence of an abnormal bond elongation of C₃-C₄ in 1cl clearly shows that through-bond interaction does not occur in this compound. The molecular structure observed in 1cl was unexpected at the outset of the work. However, in the meantime, a frontier molecular orbital analysis of the oxetane has led to a general understanding of the factors that control bond lengthening.

Figure 2 shows the σ_{CC} , σ^*_{CC} , π , and π^* fragments, derived from Fukui's dissection method,¹² of the reactant localized into π and π^* fragments, assuming that substituent effects on σ orbital energies are similar to their effects on π orbital energies.¹³ The effective through-bond coupling depends upon the relative energies of the interacting orbitals, in which the donations of both $\sigma \rightarrow \pi^*$ and $\pi \rightarrow \sigma^*$ play an important role in bond lengthening (weakening).¹⁴

Recently, Mislow and co-workers studied substituent effects on through-bond coupling in *p,p'*-dibenzene and showed that $\pi \rightarrow \sigma^*$ donation is dominant compared to $\sigma \rightarrow \pi^*$ interactions.¹⁵

This fact may rationalize the absence of through-bond interaction in cage oxetanes: oxygen substitution generally raises the energy of the substituted C-C bond and this

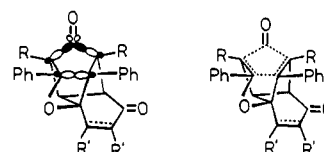


Figure 3. Possible transition state for the decarbonylation reaction.

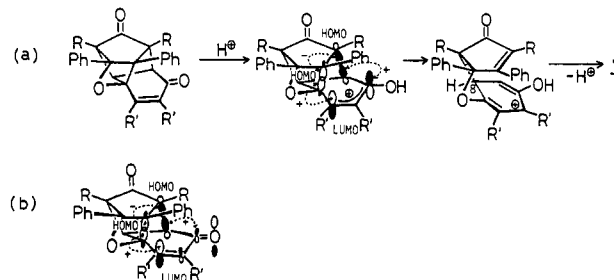


Figure 4. Possible transition state for the rearrangement reaction: (a) catalytic reaction; (b) thermal reaction.

effect may turn off through-bond interaction.

The assumption that the C-O σ bond reduces through-bond coupling is supported by the lack of elongation of the C₁-C₄ bond [1.571 (5) Å], where the C₄ phenyl and the C₁₁-C₁₂ double bond are oriented virtually face-to-face. For the mechanism of decarbonylation and rearrangement, controlling factors other than bond weakening by through-bond coupling should be considered. The kinetic results for decarbonylation (Table II) can be explained by a concerted pathway involving a three-system interaction¹⁶ among the heightened HOMO of the C-O σ bond and the low-lying LUMO's of the bridge C-C σ bonds (Figure 3). In this case, through-bond interaction is not operative, and relief of strain¹⁷ is an important factor affecting the rate. A similar explanation may be also possible for the rearrangement reaction. For the acid-catalyzed rearrangement, a cyclic three-system interaction among the lowered LUMO of the allyl cation moiety, caused by protonation of the enone group, and the heightened HOMO's of the two strained σ bonds (C₁-C₄ and C₅-C₉), which are also affected by electron-donating substituents such as alkyl

(12) Fukui, K. *Acc. Chem. Res.* 1971, 4, 57-69 and references cited therein.

(13) Houk, K. N. "Pericyclic Reactions II"; Academic Press: New York, 1977; pp 181-271.

(14) Dougherty, D. A.; Hounshell, W. D.; Schlegel, H. B.; Bell, R. A.; Mislow, K. *Tetrahedron Lett.* 1976, 3479-3482.

(15) Dougherty, D. A.; Schlegel, H. B.; Mislow, K. *Tetrahedron* 1978, 34, 1441-1447.

(16) Inagaki, S.; Fujimoto, H.; Fukui, K. *J. Am. Chem. Soc.* 1976, 98, 4693-4701.

(17) The calculated strain energy is 107 kcal/mol for 1cl by the MMPI EFF method.

groups, may stabilize the transition state to give the thermodynamically stable compound **7** by liberation of the C₈ proton (Figure 4a).

The thermal rearrangement of **1al** and **1bl** in refluxing xylene at 180 °C in the absence of solvent yielded the same products (**7**) in high yield. This rearrangement can be explained as depicted in Figure 4b by taking into account the enone part as an acrolein LUMO.¹⁸

Experimental Section

The melting points were measured with a Yanagimoto micro melting point apparatus and are uncorrected. The ¹H NMR spectra were taken with a JEOL PS-100 and a Hitachi R-600 spectrometer with Me₄Si as an internal standard; chemical shifts are expressed in δ values. The ¹³C NMR spectra were determined with a JEOL FX-100 and refer to solutions in deuteriochloroform as a concomitant standard, downfield chemical shifts being computed relative to Me₄Si. The IR spectra were taken with a JASCO IRA-1 infrared spectrometer. Mass spectra were determined with a JEOL-01SG double-focusing spectrometer operating at an ionization potential of 75 eV. The solid samples were ionized by electron bombardment after sublimation directly into the electron beam at 150–200 °C. All new products gave correct elemental analyses. A Hitachi EPS-3T spectrophotometer was used to measure the rates of rearrangement of decarbonylation. Preparative thin-layer chromatography was performed by using E. M. Merck silica gel 60 PF-254, and column chromatography was done by using E. M. Merck Kiesgel 60 (70–200 mesh) as the stationary phase. Calculations were performed on the FACOM M-200 computer in the computer center of Kyushu University.

Cage Oxetanes 1 (5,7,11,12-Tetrasubstituted 3,4-Diphenyl-2-oxapentacyclo[6.4.0.0^{1,4}.0^{3,7}.0^{5,8}]dodec-11-ene-6,10-diones). Cage oxetanes **1ak–cl** were prepared by the general method of ref 1 and 2.

Catalytic Hydrogenation of Cage Oxetanes 1ak and 1ck [Syntheses of 5,7-Disubstituted 3,4-Diphenyl-2-oxapentacyclo[6.4.0.0^{1,4}.0^{3,7}.0^{5,8}]dodecane-6,10-diones (5ak and 5ck)]. Into a 200-mL autoclave were placed 10 mg of 5% Pd on charcoal, 100 mL of solvent (EtOH–ethyl acetate, 1:1), and 300 mg of the cage oxetane **1**. The suspension was stirred under 5–7 atm of hydrogen at room temperature for 6 h. The reaction mixture was filtered, and the filtrate was evaporated in vacuo. The solid residue was recrystallized from EtOH or benzene to give the dihydro derivative **5**.

5ak: yield 166 mg (55%); mp 199–200 °C; IR (Nujol) 1700, 1755 cm⁻¹; ¹H NMR (CDCl₃) δ 1.01, 1.13 (s, 2CH₃, 6 H), 2.13–2.48 (m, 2CH₂, 4 H), 2.89 (d, H₈, J_{8,9} = 2.0 Hz), 2.99 (d, H₉, 1 H), 6.68–7.32 (m, Ph H, 10 H), ¹³C NMR 8.1 (q), 9.1 (q), 20.9 (t), 36.7 (t), 55.5 (d), 55.7 (s), 59.0 (s), 60.8 (d) ppm; mass spectrum, *m/e* 370 (M⁺), 342 (M⁺ – CO).

5ck: yield 168 mg (56%); mp 158–159 °C; IR (Nujol) 1713, 1735, 1795 cm⁻¹; ¹H NMR (CDCl₃) δ 2.12–2.67 (m, 2CH₂, 4 H), 3.58, 3.64 (s, 2CH₃, 6 H), 3.55 (d, H₈, J_{8,9} = 3.0 Hz, 1 H), 3.76 (d, H₉, 1 H), 6.88–7.30 (m, Ph H, 10 H); mass spectrum, *m/e* 458 (M⁺), 430 (M⁺ – CO).

Thermal Decarbonylation of Cage Oxetanes 1ck and 1cl and Dihydro Derivatives 5ak and 5ck. A xylene solution of the cage oxetane (150 mg) was refluxed for 2 h. After removal of the solvent under reduced pressure, the residue was chromatographed on preparative thin-layer silica gel plates, eluting with chloroform to give the 2-oxatricyclo[4.3.2.0^{1,5}]undecanes **4ck**, **4cl**, **6ak**, and **6ck**. The ¹H NMR spectral data are shown in Table I.

4ck: yield 62%; mp 189–193 °C; IR (Nujol) 1690, 1715, 1725 cm⁻¹; ¹³C NMR 51.4 (q), 52.0 (q), 62.3 (d), 68.9 (d), 94.5 (s), 106.2 (s), 146.7 (d), 195.6 (s) ppm.

4cl: yield 65%; mp 178–183 °C; IR (Nujol) 1685, 1708, 1730 cm⁻¹.

6ak: yield 15%; mp 125–127 °C; IR (Nujol) 1715 cm⁻¹.

6ck: yield 62%; mp 170–172 °C; IR (Nujol) 1718, 1735 cm⁻¹.

Kinetics of Decarbonylation of Cage Oxetanes. Thermolysis rate studies of **1ck** and **5ck** were conducted at about 2.5 mmol/L in anhydrous sulfolane in sealed tubes that were thermostated at constant temperature. Tubes were withdrawn at various times for analysis. The rates were determined spectrometrically by following the increase in the absorption at 330 nm due to the styrene chromophore. Rates of the dihydro derivatives **5ak** and **5ck** were determined in C₆D₆ (30 mg/mL) in sealed NMR sample tubes in the same manner. The rates were determined spectrometrically by following the decrease of methyl (for **5ak**) or methoxyl (for **5ck**) proton signals using tetrabromoethane as an internal standard. The results are summarized in Table II.

Thermal Rearrangement of Cage Oxetanes 1ab and 1bl. Compound **1al** (150 mg, 0.38 mmol) was dissolved in 50 mL of xylene that had been allowed to stand over anhydrous K₂CO₃, and the solution was refluxed for 5 h. After evaporation of the solvent, the resulting yellow solid was chromatographed on silica gel by elution with chloroform to give **7al** (7-hydroxy-2,6,7,8b-tetramethyl-3,3a-diphenyl-1-oxacyclopenta-3a,8b-dihydrobenzo-[b]furan) as yellow crystals. A similar workup gave **7bl** from **1bl**. Heating **1al** and **1bl** at 180 °C without solvent gave the same results.

7al: yield 75%; mp 260–263 °C; IR (Nujol) 1700, 3430 cm⁻¹; ¹H NMR (CDCl₃) δ 0.96, 2.00, 2.18, 2.27 (s, 4CH₃, 12 H), 6.14 (br s, OH, exchangeable by D₂O, 1 H), 6.78 (s, H₈, 1 H), 7.14–7.41 (m, Ph H, 10 H); UV (CHCl₃) λ_{max} 283 nm (log ε 4.10), 335 (inflection; 2.97).

7bl: yield 76%; mp 206–209 °C; IR (Nujol) 1700, 3460 cm⁻¹; ¹H NMR (CDCl₃) δ 0.21, 1.04 (t, 2CH₃, 6 H), 1.40, 2.27 (q, 2CH₂, 4 H), 2.21, 2.28 (s, 2CH₃, 6 H), 6.02 (br s, OH, exchangeable by D₂O, 1 H), 6.73 (s, H₈, 1 H), 7.02–7.31 (m, Ph H, 10 H); ¹³C NMR 7.8, 12.0, 12.4, 13.0 (q, 4CH₃), 17.6, 24.1 (t, 2CH₂), 65.0 (s, C_{8b}), 98.1 (s, C_{3a}), 107.2 (d, C₈), 119.8 (s, C_{3a}), 133.5, 136.6 (s, C₅ and C₆), 143.4, 149.0, 149.5 (s, C₂, C_{4a}, and C₇), 165.1 (s, C₃), 207.8 (s, C₁) ppm; UV (CHCl₃) λ_{max} 280 nm (log ε 3.97), 331 (inflection; 2.97).

Acid-Catalyzed Rearrangement of Cage Oxetanes 1al and 1bl. The cage oxetane (**1al** or **1bl**, 300 mg) was dissolved in a chloroform solution (10 mL) of *p*-toluenesulfonic acid (3 × 10⁻³ M), and the solution was refluxed for 1 h. The solvent was removed under reduced pressure. The residue was purified by chromatography on silica gel to give **7al** and **7bl**, respectively.

Kinetics of Acid-Catalyzed Rearrangement of Cage Oxetane 1bl. The rates of the acid-catalyzed rearrangement of **1bl** in CHCl₃ and EtOH were determined in thermostated 1 × 10 mm quartz cells by following the increase in the 330-nm absorption of the cinnamaldehyde moiety. Chloroform was purified by treatment with alumina followed by distillation. The first-order rate constants *k*₁ were calculated by the least-squares method. The second-order rate constants *k*₂ were determined from the least-squares slopes of the lines obtained by plotting *k*₁ vs. the concentration of *p*-toluenesulfonic acid. The results are summarized in Table III.

X-ray Structural Determination. Cubic crystals of **1cl** were grown from benzene-*n*-hexane-ether solution. X-ray intensity data were collected on a Syntex Pī four-circle diffractometer with the θ–2θ scan mode by using a scan speed 24.0–4.0°/min. Data were collected with Mo Kα (0.71069 Å) radiation monochromated by a graphite crystal to a scattering angle of 2θ ≤ 50° for a total of 3068 reflections, from which 2641 independent reflections with *I* > 2σ(*I*) were obtained. Three reflections were monitored after every measurement of 97 reflections. The reflections whose peak-counting rate exceeded 5 × 10⁴ counts/s were remeasured with a lower beam intensity to minimize counting losses. The intensities were corrected for Lorentz and polarization effects, but no correction was applied for absorption. The space group is Pī, with the following cell parameters: *a* = 10.219 (4) Å, *b* = 15.531 (5) Å, *c* = 8.701 (5) Å, α = 97.31 (4)°, β = 110.87 (3)°, γ = 104.03 (3)°, *V* = 1216 (1) Å³, *d*_m (KI/H₂O) = 1.312 g cm⁻³, *d*_c = 1.323 g cm⁻³.

Statistical Wilson analysis of the data indicated a centrosymmetric distribution of intensities. The space group Pī was selected from the number of molecules per unit (*Z* = 2) and was confirmed in the course of the structure refinement.

Observed structure factors were converted into normalized structure factor amplitudes, |*E*| values, by use of the scale factor

(18) Houk, K. N.; Strozier, R. W. *J. Am. Chem. Soc.* 1973, 95, 4094–4096.

and the overall temperature factor obtained from Wilson's statistics. The structure was solved by the direct method, using the MULTAN 78 series of programs.¹⁹ The atomic scattering factors were from the tables of Cromer and Weber.²⁰

An *E* map calculated with 244 signed *E*'s ($|E| \geq 1.74$), which gave a combined figure of merit of 2.4255, revealed the position of all the expected nonhydrogen atoms.

Refinements were carried out by the block-diagonal least-squares method by using isotropic temperature factors for the hydrogen atoms placed in calculated positions and anisotropic temperature factors for the remaining atoms. In the course of the refinement, the O(34) atom was divided into two parts according to the populations estimated by the peak height in a difference Fourier map. The final *R* value was 0.0527 for the observed reflections.

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In final refinements, the following weights were used for the observed reflections: $w = 1.0$ for $F_0 < 30.0$, $w = 900/F_0^2$ for $F_0 \geq 30.0$.

All structure-solving programs were from the computer center of Kyushu University with the Universal Crystallographic Computation Program System (UNICS II).²¹

Registry No. 1ak, 65007-17-2; 1al, 86259-46-3; 1bl, 86259-47-4; 1ck, 86259-44-1; 1cl, 86259-45-2; 4ck, 86259-48-5; 4cl, 86259-49-6; 5ak, 86259-42-9; 5ck, 86259-43-0; 6ak, 86259-50-9; 6ck, 86259-51-0; 7al, 86259-52-1; 7bl, 86259-53-2.

Supplementary Material Available: Tables of final positional and final thermal parameters of nonhydrogen atoms, hydrogen atom parameters, interatomic distances, and interatomic angles for 1cl, MMPI EFF conformation of 1cl, and elemental analysis of 4ck, 4cl, 5ak, 5ck, 6ak, 6ck, 7al, and 7bl (8 pages). Ordering information is given on any current masthead page.

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Flash Vacuum Thermolysis of Functionalized γ -Sultines

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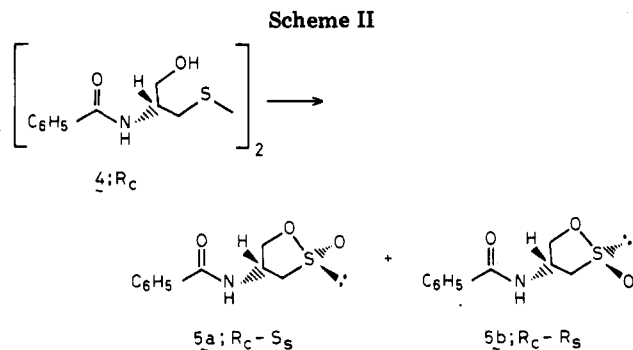
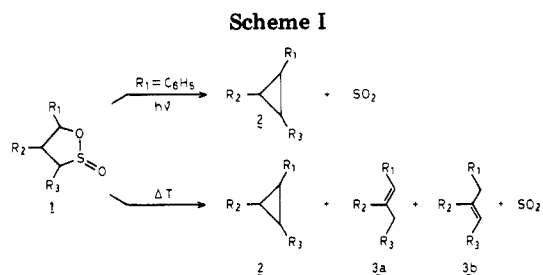
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The flash vacuum thermolysis (FVT) of the 4-benzamido γ -sultines **5a** and **5b** is shown to lead to a mixture of the *N*-allyl amide **6** and enamides **7** and **8**, the allyl amide being the main product. This reaction involves a novel migration of the benzamido group, which is proposed to proceed as depicted in path c of Scheme IV. This proposed mechanism features heterolytic bond fission, accompanied by neighboring group participation. Support for this proposal has been found by flash vacuum thermolysis (FVT) of **5a-d₂** (Scheme IV).

During the last decade several aspects of the chemistry of cyclic sulfinate esters (sultines) received incidental attention, but all those studies^{1,2} concerned sultines containing only phenyl or simple alkyl substituents or sultines condensed with aromatic rings. Recently, we reported³ for the first time an efficient route to functionalized cyclic sulfinate esters, viz., the *N*-protected β -amino γ -sultines, and showed that nucleophilic ring-opening reactions can be performed by selective cleavage of either the S-O or the C-O bond.

Durst et al. have studied the photochemical⁴ and thermolytic⁵ breakdown of nonfunctionalized γ -sultines **1**. Photolysis was only observed with sultines having a γ -phenyl substituent and gave phenylcyclopropanes **2**



(1) Squires, T. G.; Venier, C. G.; Hodgson, B. A.; Chang, L. W.; Davis, F. A.; Panunto, T. W. *J. Org. Chem.* 1981, 46, 2373. Hanson, G.; Kemp, D. S.; *Ibid.* 1981, 46, 5441. Pirkle, W. H.; Hoekstra, M. S. *J. Am. Chem. Soc.* 1976, 98, 1832. Harpp, D. N.; Vines, S. M.; Montillier, J. P.; Chan, T. H. *J. Org. Chem.* 1976, 41, 3987. Sharma, N. K.; De Reinach-Hirtzbach, F.; Durst, T. *Can. J. Chem.* 1976, 54, 3012 and references cited therein. Kroll, J. O.; Wojcicki, A. *J. Organomet. Chem.* 1974, 66, 95. Henrick, K.; Johnson, B. L. *Aust. J. Chem.* 1972, 25, 2263. Thomasson, J. E.; Robinson, P. W.; Ross, D. A.; Wojcicki, A. *Inorg. Chem.* 1971, 10, 2130. Applequist, D. E.; McKenzie, L. F. *J. Org. Chem.* 1977, 42, 1251. King, J. F.; de Mayo, P.; McIntosh, C. L.; Piers, K.; Smith, D. J. H. *Can. J. Chem.* 1970, 48, 3704.

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(4) Durst, T.; Huang, J. C.; Sharma, N. K.; Smith, D. J. H. *Can. J. Chem.* 1978, 56, 512.

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(Scheme I). Thermolysis gave the alkenes **3a** and **3b** beside **2**.⁶ The authors assumed that thermolysis of **1** proceeds via an intermediate diradical by consecutive cleavage of the C-O and C-S bond.⁵ It seemed worthwhile

(6) Photochemical and thermolytic breakdown of γ -lactones, which are carbon counterparts of γ -sultines, yield also **2** and **3**. See: Givens, R. S.; Oettle, W. F. *J. Org. Chem.* 1972, 37, 4325.