

butyl ketone diallyl acetal, bp 90–91 °C (20 Torr), was isomerized to the corresponding di-(*Z*)-propenyl acetal by treatment with KOBu-*t* in Me₂SO, followed by acid-catalyzed cleavage into propionaldehyde and 21, bp 134 °C (760 Torr).

1-(*Z*)-Propenyloxycyclopentene (22) was prepared by acid-catalyzed cleavage of cyclopentanone di-(*Z*)-propenyl acetal⁵ into propionaldehyde and 22, bp 92–95 °C (105 Torr).

(*Z*)- and (*E*)-2-propenyloxy-3-methyl-2-butene (23 and 26, respectively) were prepared by acid-catalyzed cleavage of methyl isopropyl ketone di-(*Z*)-propenyl acetal [bp 84 °C (20 Torr)]. The products 23 and 26 were separated from the isomeric compounds, (*Z*)- and (*E*)-2-propenyloxy-3-methyl-1-butene, by preparative GLC.

α -Isopropenyloxystyrene (28). See preparation of 6 (1-chloro-2-propanol was used instead of 2-chloroethanol), bp 54–56 °C (2 Torr).

(*Z*)- and (*E*)-3-Isopropenyloxy-2-pentene (29 and 30, respectively). See preparation of 7 and 10 (1-chloro-2-propanol was used as the alcohol), bp 111–115 °C (760 Torr).

Methyl Vinyl Ether (31). A commercial product was used.

¹H NMR Spectra. The spectra were taken at 60 MHz in CCl₄ solution with Me₄Si as internal standard. The shifts are given in δ values (ppm) and the coupling constants in hertz. In many cases, the spectra were recorded on mixtures of isomers, and hence all signals could not always be detected. Thus ¹H NMR spectra are not given here for 10, 11, and 30, because of their relatively low concentrations in the synthetic mixtures. 1: 6.36 (H-C _{α}), 4.17 (H-C _{β} , $J_{cis} = 6.4$), 4.48 (H-C _{β} , $J_{trans} = 14.1$). 5: 3.99 and 4.08 (H₂C _{β'} , $J_{gem} = 2.4$), 1.09 (3 Me), 6.28 (H-C _{α}), 4.23 (H-C _{β} , $J_{cis} = 6.0$), 4.57 (H-C _{β} , $J_{trans} = 13.4$). 6: 4.36 and 4.76 (H₂C _{β'} , $J_{gem} = 2.6$), 7.0–7.6 (aromatic protons), 6.44 (H-C _{α}), 4.32 (H-C _{β} , $J_{cis} = 6.2$), 4.70 (H-C _{β} , $J_{trans} = 13.6$). 7: 4.57 (H-C _{β} , $J_{vic} = 6.8$), 1.56 (CH₃-C _{β'}), 2.14 (CH₂), 1.03 (CH₃), 6.20 (H-C _{α}), 4.08 (H-C _{β} , $J_{cis} = 6.1$), 4.43 (H-C _{β} , $J_{trans} = 14.4$). 8: 4.53 (H-C _{β'}), 1.60 (CH₃-C _{β'}), 2.8 (CH), 1.14 (2 Me), 6.23 (H-C _{α}), 4.13 and 4.51 (H₂C _{β'}). 9: 4.81 (H-C _{β'} , $J_{vic} = 3.6$), 1.06 (CH₃, $J_{vic} = 6.9$), 1.6–2.2 (ring protons), 6.30 (H-C _{α}), 4.16 (H-C _{β} , $J_{cis} = 6.1$), 4.51 (H-C _{β} , $J_{trans} = 13.7$). 12: 1.55 and 1.64 (2 CH₃-C _{β'}), 2.18 (CH₂), 0.99 (CH₃), 6.23 (H-C _{α}), 3.94 (H-C _{β} , $J_{cis} = 6.7$), 4.18 (H-C _{β} , $J_{trans} = 13.7$). 13: 1.54 (CH₃), 1.6–2.2 (ring protons), 6.26 (H-C _{α}), 3.96 (H-C _{β} , $J_{cis} = 6.6$), 4.20 (H-C _{β} , $J_{trans} = 14.3$). 20: 3.95 (H₂C _{β'}), 1.86 (CH₃-C _{α'}), 6.11 (H-C _{α}), 4.67 (H-C _{β} , $J_{cis} = J_{vic} = 6.7$), 1.59 (CH₃-C _{β}). 21: 3.93 and 4.02 (H₂C _{β'} , $J_{gem} = 2.4$), 1.13 (3 Me), 6.09 (H-C _{α}), 4.68 (H-C _{β} , $J_{cis} = 6.4$, $J_{vic} = 7.0$), 1.60 (CH₃-C _{β}). 22: 4.55 (H-C _{β'}), 1.8–2.5 (ring protons), 6.20 (H-C _{α}), 4.60 (H-C _{β} , $J_{cis} = 6.4$,

$J_{vic} = 6.9$), 1.59 (CH₃-C _{β}). 23: 1.6 (2 CH₃-C _{β'}), 1.75 (CH₃-C _{α'}), 5.87 (H-C _{α}), 4.37 (H-C _{β} , $J_{cis} = 6.0$, $J_{vic} = 6.8$), 1.6 (CH₃-C _{β}). 26: 1.6 (2 CH₃-C _{β'}), 1.75 (CH₃-C _{α'}), 6.03 (H-C _{α}), 4.70 (H-C _{β}), 1.6 (CH₃-C _{β}). 28: 4.67 and 5.04 (H₂C _{β'} , $J_{gem} = 1.6$), 7.1–7.6 (aromatic protons), 4.20 and 4.13 (H₂C _{β}), 1.91 (CH₃-C _{β}). 29: 4.80 (H-C _{β'} , $J_{vic} = 6.9$), 1.57 (CH₃-C _{β'}), 2.21 (CH₂), 0.97 (CH₃, $J_{vic} = 6.9$), 1.79 (CH₃-C _{α}), 3.77 and 3.91 (H₂C _{β}).

¹³C NMR Spectra. The spectra were taken at 15.03 MHz with CDCl₃ as solvent and Me₄Si as internal standard. Total sample concentration was 20% (v/v). Since many of the spectra were taken on mixtures of isomers, there remained some uncertainty in signal assignment, and thus shift data are not given for all the carbons of the compounds studied. However, the signals of the most important carbon atoms (C- β and C- β') could be assigned with certainty in all cases.

Acknowledgment. The author is grateful to Miss Leena Tuominen, B.S., for some synthetic aid.

Registry No.—Di-2-chloroethyl ether, 111-44-4; methyl *tert*-butyl ketone dimethyl acetal, 62038-48-6; 2-chloroethanol, 107-07-3; 2-(2-chloroethoxy)-3,3-dimethyl-1-butene, 66270-84-6; acetophenone dimethyl acetal, 4316-35-2; 3-methoxy-2-pentene, 41623-41-0; ethyl isopropyl ketone dimethyl acetal, 51945-95-0; 2-bromoethanol, 540-51-2; 1-methoxy-6-methylcyclohexene, 1728-37-6; 1-methoxy-2-methylcyclohexene, 1728-38-7; acetone di-(*Z*)-propenyl acetal, 62322-38-7; methyl *tert*-butyl ketone dialkyl acetal, 66270-85-7; methyl *tert*-butyl ketone di-(*Z*)-propenyl acetal, 66270-86-8; cyclopentanone di-(*Z*)-propenyl acetal, 62322-37-6; methyl isopropyl ketone di-(*Z*)-propenyl acetal, 66270-87-9; 1-chloro-2-propanol, 127-00-4.

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MINDO/3 Calculations on the Stability of Criegee Carbonyl Oxides

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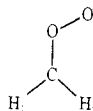
Calculations using MINDO/3 are presented which support the Bailey modification of the Criegee mechanism for ozonolysis. An activation enthalpy for syn-anti interconversion of the planar carbonyl oxides of formaldehyde and acetaldehyde of 25.3 and 24.5 kcal/mol, respectively, is calculated. The cyclization of formaldehyde carbonyl oxide to 1,2-dioxocyclopropane is shown (according to MINDO/3) to proceed with an activation enthalpy of 27.2 kcal/mol. The carbonyl oxide is calculated to be thermodynamically capable of acting as an epoxidizing agent and of giving molecular oxygen on reacting with itself.

The proposal by Criegee¹ of a general mechanism for the reaction of ozone with alkenes involving as an intermediate a carbonyl oxide (R₁R₂C⁺-O-O⁻) has been highly successful in accounting for a considerable body of experimental facts.² The remaining questions center around the apparent stereoselectivity in the cis/trans ratio of the secondary ozonide (1,2,4-trioxolane) products.³ The suggestion that the stereospecificity arises from the preferential formation of syn or anti carbonyl oxides, which then display different reactivities, is partly based on the premise of nonequilibrium of the syn and anti carbonyl oxides.^{4,5} This presumed nonequilibrium is in turn based on the configurational stability of the syn and anti

oximes.⁶ If equilibration of syn and anti carbonyl oxides were rapid compared with reaction to form secondary ozonides then there should be no such stereoselectivity in the 1,2,4-trioxolanes.

There have been several semiempirical molecular orbital studies of the primary ozonide (1,2,3-trioxolane) and its breakdown⁷⁻⁹ and two ab initio calculations on the methylene peroxide (CH₂O₂) system.^{10,11} The former studies never address the configurational stability of the carbonyl oxide and the latter studies partially assume a geometry (bond lengths) and therefore do not optimize all geometric parameters and in addition deal only with the static species rather than the

Table I. Formaldehyde Carbonyl Oxide



	ΔH°_f , kcal/mol	Bond length, Å (C-H, C-O, O-O)	Bond angle, deg (H ₁ CO, H ₂ CO, COO)	Dipole moment, D	Ionization potential, eV
This work ^a	+15.8	1.110, 1.252, 1.268	116.1, 129.5, 125.7	3.54	9.67
Ref 10 ^b		1.09, 1.44, 1.48	116, 116, 115	6.08	
Ref 11 ^c	48	1.08, 1.35, 1.37	120, 120, 103	3.03	

^a Bond lengths and angles were optimized. ^b Bond lengths were assumed and bond angles were optimized. ^c All geometry parameters were assumed.

Table II. 1,2-Dioxocyclopropane

	ΔH°_f , kcal/mol	Bond length, Å (C-H, C-O, O-O)	Bond angles, deg (HCO, COO)	Dipole moment, D	Ionization potential, eV
This work	-17.9	1.123, 1.342, 1.456	126.3, 47.17	2.15	11.14
Ref 10 ^a		1.09, 1.44, 1.48	-, 60	3.15	
Ref 11 ^b	7.5 ^{c,d}	1.08, 1.436, 1.45	115.6, 59.7		

^a Bond lengths and angles were optimized. ^b Bond lengths were assumed and bond angles were optimized. ^c All geometry parameters were assumed. ^d Estimated from thermochemical data.

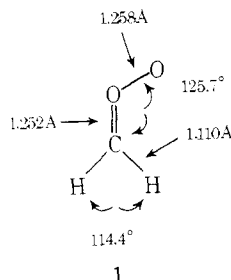
interconversion among the various isomers.

This work uses MINDO/3, a version of the MINDO semi-empirical SCF-MO treatment, developed and extensively tested by Dewar and co-workers to explore the configurational stability of the carbonyl oxide.^{12,13} MINDO/3 has been used by Dewar and co-workers with reasonable success for calculations on ozone, oxygen, and cyclic peroxides,^{12,14} and it seemed reasonable to expect similar success on the carbonyl oxide system. Also the explicit inclusion of electron and nuclear repulsion make the method particularly suitable where there are adjacent heteroatoms with lone pair repulsions and electronegativity effects giving rise to polar bonds.⁹

Results and Discussion

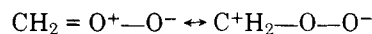
Criegee Formaldehyde Carbonyl Oxide. The calculated properties of the simplest of the Criegee carbonyl oxides, formaldehyde carbonyl oxide, are listed in Table I. For comparison the results of previous calculations are also listed. It was necessary in this work to include configuration interaction (mixing of the lowest doubly excited configuration) since the energy lowering on mixing was significant (22.8 kcal/mol without CI, 15.8 with).¹⁵

The geometry for the formaldehyde carbonyl oxide, 1, as shown below was planar ($\pm 0.1^\circ$) with significant increases in energy on out-of-plane hydrogen movement. The O-O bond



length found is more like ozone (1.278 Å)¹⁶ than that of simple peroxide models (approximately 1.4 Å) as might be expected considering the orbital similarity of ozone and the formaldehyde carbonyl oxide. The C-O bond length is between that of a formal double bond (1.23 Å) and that of a formal single bond (1.43 Å) again reflecting the allyl aspect of the bonding.

The relatively high dipole moment reflects the electron density decrease on carbon and increase on oxygen. All of the above is reasonably consistent with the commonly written structure for the carbonyl oxide as a hybrid of two charge separated structures as shown below.



With the large dipole moment, solvation energy may be important in stabilizing this species relative to other methylene peroxide isomers. Trapping experiments in polar solvents (hydrogen bonding solvents like acetic acid or alcohols) may lead to selecting the chemistry of the carbonyl oxide. Further, the necessary inclusion of configuration interaction in the calculation of the ground state properties of the carbonyl oxide would indicate some singlet "biradicaloid" character.¹⁵ The "biradicaloid" character of the species would also be subject to solvent effects, diminishing in the more polar solvent. Hence solvent effects could be of two sorts: (a) on the stability of the carbonyl oxide and (b) on the reactivity (radical or ionic) of the carbonyl oxide. In the absence of solvents, radical reactivity may predominate giving rise to a different manifold of reactions even though the planar Criegee carbonyl oxide is the principal intermediate. Experiments in the gas phase are most consistent with radical reactivity.¹⁷

1,2-Dioxocyclopropane. The cyclic 1,2-dioxocyclopropane is calculated to be more stable than the planar carbonyl oxide, 1. The results in this regard are consistent with those of other calculations (see Table II). However, the very negative ΔH°_f of -17.9 kcal is probably too low. MINDO/3 is known to overestimate the stability of ethylene oxide by 13.9 kcal/mol and could be expected in this three-membered oxygen heterocycle to also overestimate stabilities by a like amount.^{18,19} Applying the 13.9 kcal as a correction factor would make the $\Delta H^\circ_f = -4.0$ kcal which is not far different than an estimate based on Benson's group additivity method of +0.9 kcal/mol (see Table III).²⁰ The Benson method assumes a value of +27.6 kcal for a ring strain correction which may be low in this case.

The polarity of species 2 as measured by its dipole moment indicates that it is less polar than the species 1 and hence would be less sensitive to solvent polarity than species 1.

The methylene peroxide system differs from the O₃ system

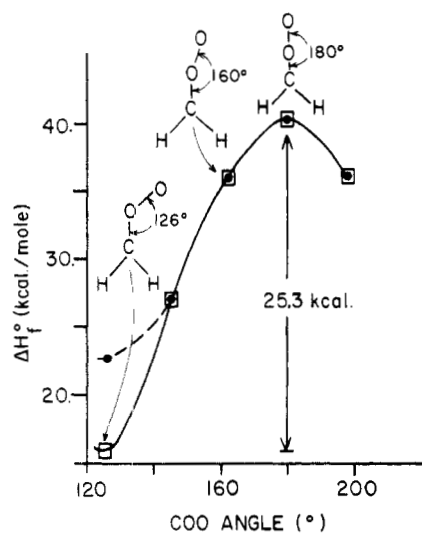


Figure 1. COO angle variation for formaldehyde carbonyl oxide; energy and geometry of the resulting species: (●) without CI, (□) with CI.

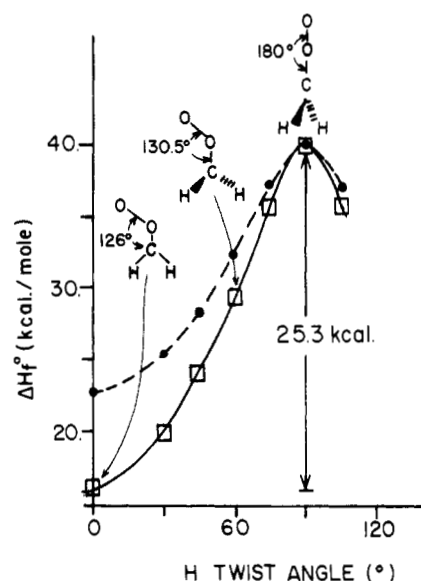


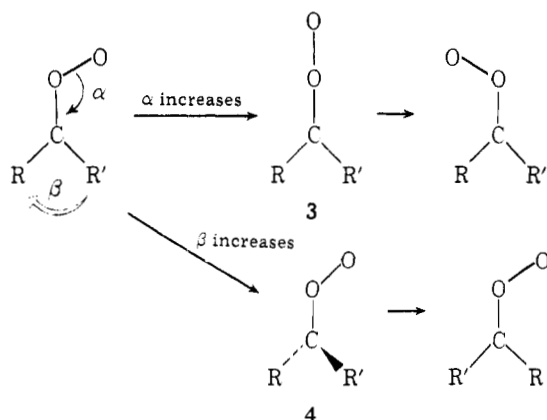
Figure 2. Hydrogen twist angle variation for formaldehyde carbonyl oxide; energy and geometry of the resulting species: (●) without CI, (□) with CI.

Table III. Group Additivity Estimate of ΔH_f° for 1,2-Dioxocyclopropane

	ΔH_f° , kcal/mol
C-(O) ₂ (H) ₂	-17.7
2(O-(O)(C))	-9.0
Ring strain correction	+27.6
ΔH_f°	0.9

in that the cyclic form is more stable than the open or bent form. This is undoubtedly due, as suggested by Goddard and co-workers, primarily to strength of the C-O σ bond vis a vis the O-O σ bond.¹¹

Syn-Anti Isomerization. The configurational integrity of the syn and anti carbonyl oxides can be lost by rapid formation (relative to reaction to give secondary ozonides) of a species in which a plane exists including the COO group that is perpendicular to the plane defined by the RCR' group. This is most easily envisioned as proceeding by either an increase in the COO angle, α , or by an internal rotation of the terminal carbon about the C-O bond, an increase in the angle β ; the two limiting cases are shown below.²¹ In the first case the pseudo-linear species, **3**, is the required symmetrical species. In the second case the species, **4**, a perpendicular form of the carbonyl oxide, is the symmetrical intermediate.

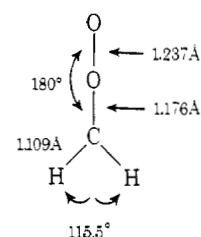


If species **1** is used as a substrate for the above described geometric distortions the reaction is of course a degenerate one, that is, the product is identical with the reactant. The

reaction can, however, serve as a simple model for loss of syn-anti integrity.

In the first case where the COO angle is the reaction coordinate calculations were carried out at several points along the reaction path with optimization of all other bond lengths, bond angles, and twist angles. The H's on the carbon were "free" to twist out of the plane. The results of the calculations are plotted in Figure 1.

Shown are calculations with and without CI. Clearly as the reaction proceeds the biradical character of the species decreases as the transition state is approached. The point of maximum enthalpy of formation along the reaction is the species corresponding to **3** with the COO bond angle at 180°. The C-O bond decreases uniformly reaching 1.176 Å in the linear species. The O-O bond length increases marginally to 1.273 Å. Each of the species along the reaction coordinate is essentially planar with the H's no more than 0.2° out of the plane. The geometry of the species is given below:



The results of the calculations for the syn-anti isomerization via twisting of the CH₂ group about the CO bond axis are shown in Figure 2. Here all other geometric parameters were optimized. There was little difference between a coordinated twist of the CH₂ group about the CO axis and simply twisting a single hydrogen and allowing optimization of the other hydrogen's position. The results for the (single H) twist are shown. Again shown are calculations with and without CI.

As can be seen in the species drawn in Figure 2 the COO angle increases as the twist progresses, reaching the same transition state as in the previous case of forcing the COO angle open. The energy gradient along a path increasing the COO angle is clearly less steep than that decreasing the COO angle otherwise the species on twisting could close to the dioxocyclopropane (vidua infra).

The enthalpy increase to reach the transition state species is 25.3 kcal/mol. With the assumption of the collision factor

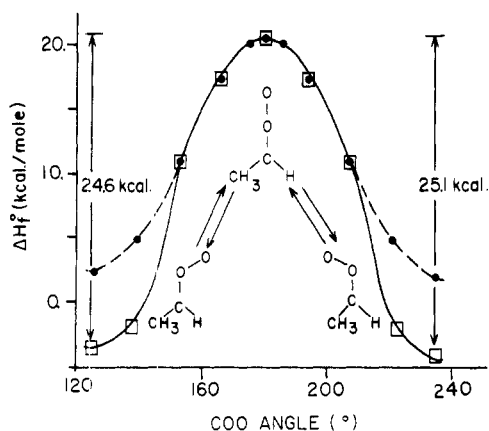
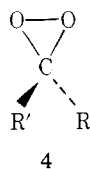


Figure 3. COO angle variation for anti-syn conversion of acetaldehyde carbonyl oxide; energy of the resulting species: (●) without Cl, (□) with Cl.

(A) in the Arrhenius equation of about 5×10^{12} (typical for cis-trans isomerizations) one calculates a first-order rate constant for syn-anti isomerization at 0 °C of $3 \times 10^{-8} \text{ s}^{-1}$.²² Such a rate constant for the syn-anti isomerization is far too slow to compete with other fates for as reactive a species as the carbonyl oxide. Methodological errors in the calculation of the relative energies of the various species may however give rise to a very large difference between the actual and calculated rate constants.

In Figure 3 is shown the results of calculations on the anti-syn transformation for the planar acetaldehyde carbonyl oxide. The process is forced to occur by expansion of the COO bond angle. The transition state is again a pseudo-linear species with a ΔH^\ddagger of 24.6 kcal. The reverse reaction does not differ significantly in rate since the syn form is only 0.5 kcal more stable than the anti. There is therefore little variation in ΔH^\ddagger with simple alkyl substitution. It would not seem unreasonable to suggest that the syn-anti isomerization reaction is not competitive with other reactions.

Cyclization of the Planar Carbonyl Oxide. The permanency, however, of chemically distinguishable initially formed carbonyl oxides depends not only on how rapidly the syn and anti forms interconvert but also on whether some other species intervenes which equates the carbon substituents. The substituted 1,2-dioxocyclopropane, 4, is such a



species. Subsequent reactions of 4 will not account for the dependency of secondary ozonide composition on the cis/trans nature of the starting alkene. It is therefore of some interest to explore the question of how rapidly such a species is likely to form from a planar Criegee carbonyl oxide.

Since 1,2-dioxocyclopropane is also more stable thermodynamically than the Criegee formaldehyde carbonyl oxide it is clearly a possibility that the dioxocyclopropane is a likely fate of all planar carbonyl oxides and as such may well account for some portion of the chemistry observed in ozonolysis reactions.

The rate of the transformation shown below then becomes an important question. Such a process can be accomplished by simultaneously (although not necessarily synchronously) reducing the COO bond angle and twisting the hydrogens out of the plane of the COO group. It is necessary to use both degrees of freedom to cause cyclization since as already men-

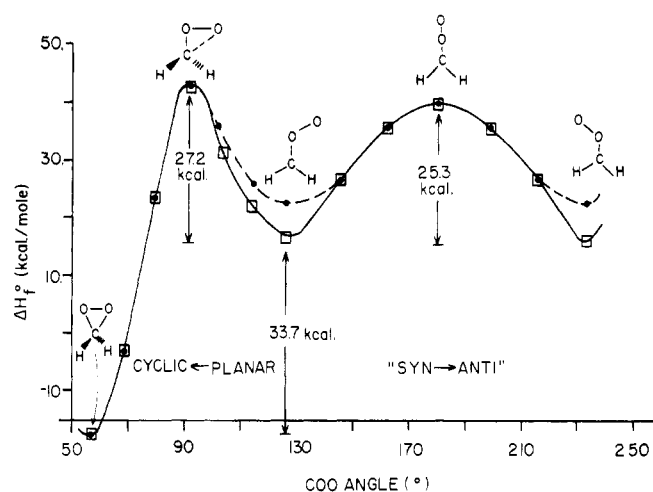
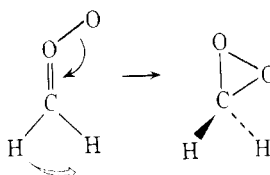
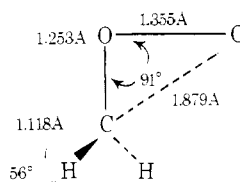


Figure 4. ΔH_f° vs. COO angle for formaldehyde carbonyl oxide "syn-anti" conversion and closure to 1,2-dioxocyclopropane: (●) without Cl, (□) with Cl.



tioned a simple CH_2 twisting opens up the COO angle. A compression of the COO angle will cause the cyclization but the CH_2 group does not twist until late in the reaction and gives a somewhat high ΔH^\ddagger . A smoother transition occurs with a forced synchronous motion coupling CH_2 out-of-plane rotation to COO bond angle compression with optimization of all other geometric parameters. The transition state enthalpy proved relatively insensitive to the CH_2 twist angle, so that the ΔH^\ddagger derived by the synchronous motion for ring closure should be close to the minimum ΔH^\ddagger . The left-hand portion of Figure 4 shows the results of the calculations on the cyclization reaction. The transition state occurs at a COO bond angle of about 91° and ΔH_f° of 42.9 kcal. This gives ΔH^\ddagger of 27.2 kcal/mol for the formation of 1,2-dioxocyclopropane from the planar Criegee carbonyl oxide. This value for the ΔH^\ddagger may be low since, as mentioned, MINDO/3 underestimates strain. The 27.2 kcal/mol may therefore be regarded as a minimum estimate for ΔH^\ddagger .



Such a large activation enthalpy is inconsistent with the notion of the cyclic species being important in the solution phase. In the gas phase where collisional deactivation is slower than in solution a vibrationally hot planar carbonyl oxide may more readily be transformed into the cyclic form.¹⁷

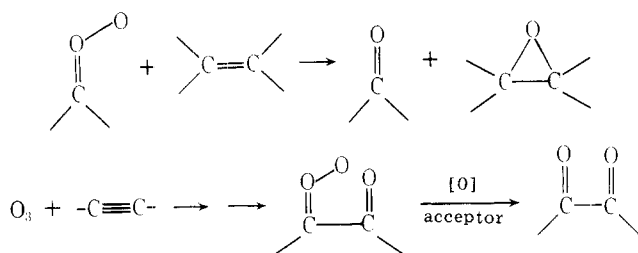
Figure 4 also summarizes the transformations discussed for the planar formaldehyde carbonyl oxide. With the barriers to configuration loss as indicated the simple planar carbonyl oxides, once formed in a particular configuration, are likely to remain in that configuration till they react to form more stable products. The syn-anti isomerization or the cyclization of the carbonyl oxide may be of some importance in the chemistry of the more hindered carbonyl oxides (like that for acetone) which do not give secondary ozonides.²

Table IV. MINDO/3 Calculations of ΔH°_f For Criegee Carbonyl Oxides

Molecule	Registry no.	ΔH°_f , kcal/mol
		+15.8
	65339-04-0	-3.8
	65339-03-9	-4.3
	65339-02-8	-17.3

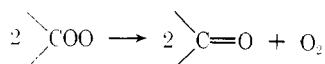
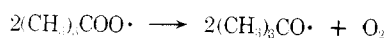
Thermochemical Calculations. It has been suggested by Fliszar and Renard that the cleavage of the initial five-membered ozone addition product is influenced by the relative stabilities of the two fragments, the carbocation stabilizing ability of the substituents being important.²³ Utilizing the results of the calculations on variously substituted Criegee carbonyl oxides (summarized in Table IV) the thermochemical data shown in Table V were compiled for that initial cleavage reaction as well as several other types of reactions possible for the carbonyl oxide. The thermochemical data for species other than the carbonyl oxide were taken from standard sources.²⁴ Thermodynamically the favored cleavage pathway is to yield the more highly alkyl substituted carbonyl oxide, in line with results of Fliszar and Renard.

The Criegee carbonyl oxide is potentially an oxygen atom transfer reagent. It has been suggested by Keay and Hamilton that a cyclic form of the carbonyl oxide generated in the ozonolysis of acetylenes at low temperature is responsible for the epoxidation of subsequently added alkenes.²⁵ Also the observation of epoxides as by-products in the ozonolysis reaction of alkenes and α -diketones as by-products in the ozonolysis of alkynes may be due to the oxygen atom transfer ability of the carbonyl oxide.^{2,26} The type of reaction envisioned is illustrated below. The results indicate the reactions are possible thermodynamically proceeding with large negative enthalpies.



The cyclic species is somewhat less exothermic as an epoxidizing agent due to its greater stability. As one would expect the exothermicity for epoxidation clearly decreases as the stability of the carbonyl oxide increases.

Carbonyl oxides have also proved to be elusive species, none having ever been unambiguously identified spectroscopically. They are transient species which may display unexpected reactivities. If the species does indeed possess considerable diradical character as suggested by the calculations, the reaction illustrated below may be possible in analogy with the corresponding reaction of peroxy radicals.²⁷

**Table V. Thermochemical Calculations**

	ΔH° , kcal/mol
(a) Primary ozonide cleavage	
$\text{H}_2\text{C}=\text{CH}_2 + \text{O}_3 \longrightarrow \text{HCHO} + \text{HCHO}$	-61
$\text{H}_2\text{C}=\text{CHCH}_3 + \text{O}_3 \longrightarrow \text{HCHO} + \text{CH}_3\text{CHO}$	-69
$\text{H}_2\text{C}=\text{C}(\text{CH}_3)_2 + \text{O}_3 \longrightarrow \text{HCHO} + \text{CH}_3\text{C}(\text{O})\text{CH}_3$	-66
$\text{H}_2\text{C}=\text{C}(\text{CH}_3)_2 + \text{O}_3 \longrightarrow \text{HCHO} + \text{CH}_3\text{C}(\text{O})\text{CH}_3$	-78
$\text{H}_2\text{C}=\text{C}(\text{CH}_3)_2 + \text{O}_3 \longrightarrow \text{HCHO} + \text{CH}_3\text{C}(\text{O})\text{CH}_3$	-72
(b) Epoxidation reactions	
$\begin{array}{c} \text{O} \\ \diagup \quad \diagdown \\ \text{C} \\ \diagdown \quad \diagup \\ \text{O} \end{array} + \text{H}_2\text{C}=\text{CH}_2 \longrightarrow \text{HCHO} + \text{H}_2\text{C}(\text{O})\text{CH}_2$	-52
$\begin{array}{c} \text{O} \\ \diagup \quad \diagdown \\ \text{C} \\ \diagdown \quad \diagup \\ \text{O} \end{array} + \text{H}_2\text{C}=\text{CH}_2 \longrightarrow \text{H}_2\text{C}(\text{O})\text{CH}_2 + \text{HCHO}$	-67
$\begin{array}{c} \text{O} \\ \diagup \quad \diagdown \\ \text{C} \\ \diagdown \quad \diagup \\ \text{O} \end{array} + \text{H}_2\text{C}=\text{CH}_2 \longrightarrow \text{H}_2\text{C}(\text{O})\text{CH}_2 + \text{CH}_3\text{CHO}$	-61
$\begin{array}{c} \text{O} \\ \diagup \quad \diagdown \\ \text{C} \\ \diagdown \quad \diagup \\ \text{O} \end{array} + \text{H}_2\text{C}=\text{CH}_2 \longrightarrow \text{H}_2\text{C}(\text{O})\text{CH}_2 + \text{CH}_3\text{C}(\text{O})\text{CH}_3$	-52
(c) O₂ production	
$2\text{HCHO} \longrightarrow 2\text{HCHO} + \text{O}_2(^3\Sigma)$	-83
$2\text{HCHO} \longrightarrow \text{HCHO} + \text{HCHO} + \text{O}_2(^1\Sigma)$	-11 ^b
$2\text{HCHO} \longrightarrow 2\text{HCHO} + \text{O}_2(^1\Delta)$	-61
$2\text{HCHO} \longrightarrow 2\text{HCHO} + \text{O}_2(^1\Sigma)$	-45
$2\text{CH}_3\text{CHO} \longrightarrow 2\text{CH}_3\text{CHO} + \text{O}_2(^1\Sigma)$	-72
$2\text{CH}_3\text{C}(\text{O})\text{CH}_3 \longrightarrow 2\text{CH}_3\text{C}(\text{O})\text{CH}_3 + \text{O}_2(^1\Sigma)$	-69

^a ΔH°_f as estimated in Table I was used. ^b Formaldehyde triplet at 72 kcal above ground state: G. W. Robinson, *Can. J. Phys.*, **26**, 1761 (1957). ^c Registry no. 74-85-1. ^d Registry no. 115-07-1. ^e Registry no. 115-11-7.

The thermochemical data support the feasibility of O₂ production from two carbonyl oxides and even allow for the production of excited state products.

Conclusion

Calculations using MINDO/3 support the Bailey modification of the Criegee mechanism for ozonolysis in which the

carbonyl oxide is proposed to exist in syn or anti forms. The barriers to syn-anti interconversion and to cyclization of the carbonyl oxide are shown to be substantial so that the chemistry observed in the ozonolysis reaction in solution is very likely that of the initial mixture of carbonyl oxides generated by cleavage of the primary ozonide. The 1,2-dioxocyclopropane is shown, however, to be more stable than the carbonyl oxide, in agreement with previous studies.

Thermochemical calculations are permissive for various fates of the carbonyl oxide including reduction via epoxidation and oxygen formation.

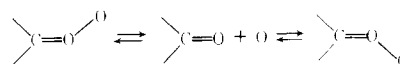
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Registry No.—Formaldehyde carbonyl oxide, 62024-18-4; 1,2-dioxocyclopropane, 157-26-6.

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1,2-Diazetidone Conformation. Double Nitrogen Inversion^{1,2}

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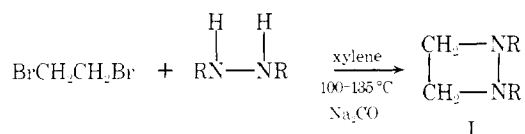
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Several 1,2-dialkyl-1,2-diazetidines have been synthesized and their NMR spectra examined as a function of temperature. The methylene protons exhibited an AA'BB' pattern at temperatures below 0 °C, but as the temperature was raised, the AA'BB' pattern broadened, and then coalesced into a singlet. Line-shape analysis as a function of temperature gave ΔH^* values in the range 14.9–18.9 kcal mol⁻¹ and ΔS^* values in the range +1 to -7 cal deg⁻¹ mol⁻¹. The effect of *N*-alkyl substituents on the rate of double nitrogen inversion and on the 1,2-diazetidone ring conformation is discussed. Mass spectral data of 1,2-diazetidines are presented.

Conformational studies on saturated ring systems containing two adjacent nitrogen atoms have been the subject of a number of reports during the last several years.^{3–19} However, there appears to have been only a few reports on the 1,2-diazetidone ring system.^{8,16–19} We would like to report the synthesis of several 1,2-dialkyl-1,2-diazetidines and the results of a proton magnetic resonance study on these interesting compounds.

The 1,2-dialkyl-1,2-diazetidines used in this study were prepared by direct reaction of 1,2-dibromoethane and the corresponding 1,2-dialkylhydrazine in hot xylene in the presence of anhydrous sodium carbonate.



This procedure was reported by Horwitz²⁰ in a patent. However, we were not able to prepare 1,2-dimethyl-1,2-diazetidone in a useful yield using the procedure in the patent. It was found that the yields could be increased substantially by using a large excess of ethylene bromide (a considerable amount is lost during the reaction by undergoing elimination) and adding it dropwise to the 1,2-dialkylhydrazine and sodium carbonate in a large volume of xylene over a period of several hours. This high dilution technique gave yields as follows (R's, yield): CH₃, 32%; C₂H₅, 28%; (CH₃)₂CH, 60%; (CH₃)₃C, 2.3%.

The 1,2-dimethyl-1,2-diazetidone prepared by the above method was contaminated by an impurity (ca. 10%) which could not be removed, but it did not interfere with the NMR study. The 1,2-di-*tert*-butyl-1,2-diazetidone was prepared only once in 2.3% yield. In spite of several attempts, we were never able to isolate it a second time. Other dibromides can be used. Reaction of 1,2-dibromopropane with 1,2-diethylhydrazine