Table IV

aliquot	time, min	chloride/C_{13} ratio	naphthalene/C_{13} ratio
1	10	1.27	0.76
2	20	1.04	1.11
3	30	1.04	1.16
4	55	1.04	1.16
5	80	0.709	1.12
6	109	0.643	1.43
7	175	0.592	
8	199	0.386	1.73

Table V

aliquot	time, min	chloride	Nap-H_2	Nap	chloride/(Nap + Nap-H_2)
1	8	4290	44 790	67 990	0.0380
2	23	2537	64 260	83 430	0.0172
3	35	721	39 630	63 670	0.00698

deuterated hydrocarbon from column D at 100 °C. The NMR indicated at least 97% D incorporation, with the syn/anti ratio being at least 50:1.

Least-squares fitting of a plot of ln (chloride/C_{13}) vs. time gave a pseudo rate constant of $5.4 \pm 0.7 \times 10^{-3}$ min^{-1}. If the halide were reacting exclusively with the dianion, the second-order rate constant at −78 °C would be $k_{N\text{-}2} = 6.8 \pm 2.0 \times 10^{-2}$ M^{-1} min^{-1}. The data given above indicates the concentration of the radical anion as determined by the relative proportion of naphthalene to internal standard upon hydrolysis increased by a factor of 2.3 from 10 min into the reaction to 200 min. If the halide were reacting exclusively with the radical anion, the plot of ln (chloride/C_{13}) vs. time should curve downward. While the plot does not appear to be curved, the extensive scatter in the data does not allow for definite conclusions to be made. Since the concentration of the radical anion was determined to be 4.7×10^{-4} M before the addition of the halide, it is likely that the concentration is ca. 1.2×10^{-3} M at point no. 8. If one (conservatively) used this to determine the second-order rate constant, assuming reaction with the radical anion rather than with the dianion, the value of 4.5 M^{-1} min^{-1} would be obtained. This is ca. 5 times as large as the actual rate constant determined for the radical anion below. Thus it would seem that most of the halide does in fact react with the dianion.

Kinetics of the Reaction of *anti*-3-Chloro-*exo*-tricyclo[3.2.1.$0^{2,4}$]octane with Lithium Naphthalene. This study was carried out exactly as in the case of the dianion, except that only 50 mg of Li was used, VPC separations were done isothermally at 150 °C, and the sum of the naphthalene (Nap) and dihydronaphthalene (Nap-H_2) signals was used as the VPC internal standard. The data from this study are shown in Table V. Taking the average value for the three aliquots of 2Nap-H_2/(Nap-H_2 + Nap) to be the fraction of the naphthalene converted to the radical anion, we arrive at a concentration of 0.063 M for the radical anion. Least-squares fitting of ln [RCl/(Nap-H_2 + Nap) ratio] vs. time gives a pseudo-first-order rate constant of 6.24×10^{-2} min^{-1} and thus a second-order rate constant of 1.0 M^{-1} min^{-1}, indicating that this reaction is about 15 times faster than the dianion reaction.

Stability Study of *syn*-3-Lithio-*exo*-tricyclo[3.2.1.$0^{2,4}$]octane. After the above kinetic analysis was complete, the reaction mixture was allowed to warm from −78 to 0 °C over a period of 6 h, before being quenched with D_2O. The deuterium incorporation was only 82%, and the syn/anti ratio could not be determined directly from the integration of the NMR signals. As in previous cases, an analysis of the intensities of the splitting of the *syn*-C_3 hydrogen signal was required. The corrected syn/anti ratio is at least 30:1.

Registry No. 1, 3635-95-8; 2, 74007-34-4; 3, 74035-80-6; 4, 29119-63-9; 6, 52882-74-3; 7, 52882-75-4; 8, 6518-27-0; 9, 29119-61-7; 16, 15598-75-1; lithium naphthalene dianion, 29589-67-1; naphthalene, 91-20-3; naphthalene radical anion Li, 7308-67-0; *syn*-3-lithio-*exo*-tricyclo[3.2.1.$0^{2,4}$]octane, 74035-81-7.

Conformational Control of Oxabicyclobutane Fragmentations

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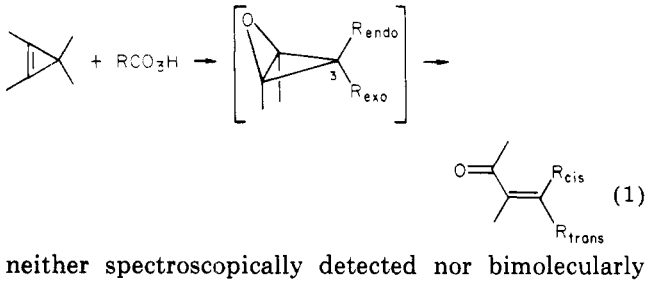
The generation and fragmentation of oxabicyclobutanes **4a–d** are described. These systems yield enones with complete loss of stereochemistry. A stepwise fragmentation is postulated for these and other oxabicyclobutane fragmentations.

Treatment of cyclopropenes with peracids is believed to give oxabicyclobutanes which are unstable and fragment to enones (eq 1). To date oxabicyclobutanes have been



(1)

neither spectroscopically detected nor bimolecularly trapped. The evidence for oxabicyclobutanes is not only that enones are produced[3-7] but also that the kinetics of cyclopropene oxidation are consistent with an epoxidizing transition state.[8-12]

In spite of the inability to isolate oxabicyclobutanes in these reactions, we and others have sought to determine the stereochemistry of oxabicyclobutane fragmentations.

(1) Taken from the Ph.D. thesis of R. A. Leckonby, who did the work on oxabicyclobutane **3b**.
(2) Taken from the Masters thesis of D. M. Stout, who did the work on oxabicyclobutane **3a**.

(3) Ciabattoni, J.; Kocienski, P. J. *J. Am. Chem. Soc.* **1969**, *91*, 6534.
(4) Kocienski, P. J.; Ciabattoni, J. *J. Org. Chem.* **1974**, *39*, 388.
(5) Ciabattoni, J.; Kocienski, P. J. *J. Am. Chem. Soc.* **1971**, *93*, 4902.
(6) Friedrich, L. E.; Cormier, R. A. *J. Org. Chem.* **1970**, *35*, 450.
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(8) Friedrich, L. E.; Fiato, R. A. *J. Am. Chem. Soc.* **1974**, *96*, 5783.
(9) Friedrich, L. E.; Fiato, R. A. *J. Org. Chem.* **1974**, *39*, 2267.
(10) Friedrich, L. E.; Fiato, R. A. *J. Org. Chem.* **1974**, *39*, 416.
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(12) Prinzbach, H.; Fischer, U. *Helv. Chim. Acta* **1967**, *50*, 1669.

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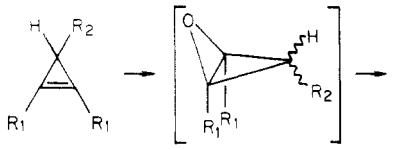
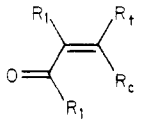
The stereochemical problem is how the endo and exo substituents at C-3 in oxabicyclobutanes correlate with R_{cis} and R_{trans} in the enone product.

The first report by Prinzbach and Fischer[12] was a treatment of cyclopropene **1a** with peracetic acid. They isolated a 30% yield of a 4:1 mixture of the substituted crotonate esters with **2a** predominating (eq 2). It is assumed that a peracid would preferentially transfer oxygen to the least hindered side of the double bond to place R_2 in an exo position. Mechanistically, it is difficult to conclude anything since 70% of the product was missing, and it is unknown if the product stereochemistry was stable to the reaction conditions.



1a, R_1 = Me; R_2 = CO_2Me
1b, R_1 = R_2 = Ph
1c, R_1 = Ph; R_2 = CH_2OH
1d, R_1 = Ph; R_2 = CH_2OMe
1e, R_1 = Et; R_2 = CO_2Et
1f, R_1 = Et; R_2 = CH_2OH
1g, R_1 = Ph; R_2 = CO_2Me
1h, R_1 = Ph; R_2 = Me



(2)

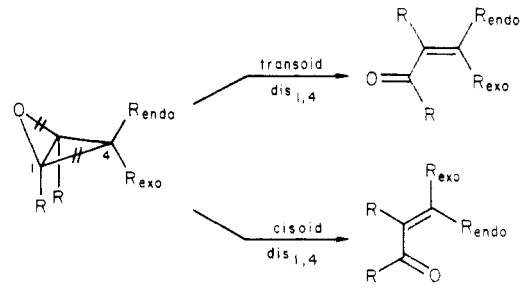
2a, R_t = Me; R_t = CO_2Me; R_c = H
2b, R_t = R_c = Ph; R_t = H
2c, R_t = Ph; R_t = CH_2OH; R_c = H
2d, R_t = Ph; R_c = CH_2OMe; R_t = H
2e, R_t = Et; R_t = CO_2Et; R_c = H
2f, R_t = Et; R_t = CH_2OH; R_c = H
2g, R_t = Ph; R_t = CO_2Me; R_c = H
2h, R_t = Ph; R_c = Me; R_t = H

In 1970, we reported [6] that triphenylcyclopropene (**1b**) gives a 82:18 ratio of isomeric enones, with **2b** predominating. In these studies, the enones were stable to the reaction conditions and were isolated in quantitative yield. It is perhaps significant that enone **2b** is the more thermodynamically stable isomer (~65% at equilibrium).

In 1971, we attempted to determine if the fragmentation stereochemistry was governed by MO correlations between reactant and product. The key cyclopropene **1c** has an allylic CH_2OH group which in cyclohexane solvent might complex with a peracid so that oxygen would be delivered cis to the substituent, R_2.[13] As a control, cyclopropene **1d** was also epoxidized[14] in cyclohexane. Since cyclopropenes **1c** and **1d** give different enone stereochemistries, primarily **2c** and **2d**, we concluded that there was a memory effect in the fragmentation which produced a preferred correlation of R_{exo} into R_{cis} and R_{endo} into R_{trans}.[7] The memory effect, however, is not large since substantial amounts of the minor enone isomers were observed in both cases (28–32%).

In 1978, Crandall[15] reported that cyclopropenes **1e** and **1f** gave mainly enones **2e** and **2f**. Furthermore, the ratios of isomeric enones were rather insensitive to whether the solvent was methylene chloride, methanol, or cyclohexane. In an important conclusion, Crandall suggested that enone product ratios from all the previously studied cyclopropenes are probably determined by subtle substituent interactions that do not lead to very stereoselective reactions.

Scheme I

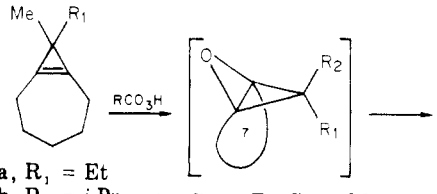


As a final literature comparison that shows the perplexing state of affairs, cyclopropene **1g** gave predominantly enone **2g**,[16] whereas **1h** was reported to give mainly **2h**.[17]

We have felt for some time that a mechanistic interpretation of these results has been hampered by two aspects. First, the stereochemistry of the intermediate oxabicyclobutanes can only be inferred from general steric-effect arguments. Second, as we pointed out in 1970, fragmentation to an enone can occur in two different conformational modes, with each mode capable of giving both enones.

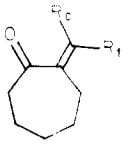
For example, as shown in Scheme I, suppose that fragmentation of $C_{1,4}$ occurs in a disrotatory fashion. As shown, both isomeric enones would be formed if both conformational modes were operating. If a conrotatory $C_{1,4}$ fragmentation occurred, then the two conformational modes would give the opposite enones.

In order to make an attempt at limiting the degrees of freedom which an oxabicyclobutane has for fragmentation, we have synthesized two cyclopropenes, **3a,b**,[11] which can only give cisoid enones (eq 3). In a previous paper[11] we investigated the epoxidation kinetics of **3a,b** in order to discover the diasteriomeric ratio (**4a**/**4b** and **4c**/**4d**) of the oxabicyclobutanes that are produced during the epoxidation. In this paper, we describe our stereochemical results for the fragmentation of oxabicyclobutanes **4a–d** to enones **5a–d**.



3a, R_1 = Et
3b, R_1 = *i*-Pr

4a, R_1 = Et; R_2 = Me
4b, R_1 = Me; R_2 = Et
4c, R_1 = *i*-Pr; R_2 = Me
4d, R_1 = Me; R_2 = *i*-Pr



(3)

5a, R_c = Et; R_t = Me
5b, R_c = Me; R_t = Et
5c, R_c = *i*-Pr; R_t = Me
5d, R_c = Me; R_t = *i*-Pr

(13) Darby, A. C.; Henbest, H. B.; McClenagham, I. *Chem. Ind. (London)* **1962**, 462.
(14) Henbest, H. B.; Wilson, R. A. L. *J. Chem. Soc.* **1957**, 1958.
(15) Crandall, J. K.; Conover W. W., II. *J. Org. Chem.* **1978**, *43*, 1323.
(16) Brown-Wensley, K. A.; Mattes, S. L.; Farid, S. *J. Am. Chem. Soc.* **1978**, *100*, 4162.
(17) In our original publication,[9] we reported a 75% yield of **2h**. A recent reevaluation of the NMR spectrum of the mixture shows that the yield of **2h** is closer to ~85%.

Table I. Solvent Shifts[a] of Enone Substituents

compd, group	δ_{CCl_4}	$\delta_{C_6H_6}$	Δ
5a, vinyl Me	1.71	1.47	0.24
CH_2CH_3	1.00	1.07	−0.07
5b, vinyl Me	1.79	1.93	−0.14
CH_2CH_3	1.02	0.82	0.20
5c, vinyl Me	1.57	1.37	0.20
$CHMe_2$	0.93	0.94	−0.01
$CHMe_2$	2.83	3.14	−0.31
5d, vinyl Me	1.61	1.74	−0.13
$CHMe_2$	1.00	0.83	0.17
$CHMe_2$	2.78	2.57	0.21

[a] Shifts are parts per million downfield from internal Me_4Si.

Table II. Products from Epoxidation[a] of Cyclopropenes 3a and 3b

system	ratio[b]
oxabicyclobutanes 4a/4b	78:22[c]
enones 5a/5b (kinetic)	47:53
oxabicyclobutanes 4c/4d	99:1[c]
enones 5c/5d (kinetic)	56:44
enones 5c/5d (thermodynamic)	55:45

[a] Using *m*-chloroperbenzoic acid in CCl_4 as solvent at 0 °C. [b] ±2%. [c] Reference 11.

Results

The synthesis of cyclopropenes **3a** and **3b** were described previously.[11] The enones **5a,b** and **5c,d** were also described, but evidence for their stereochemistry was not given.

Timmons[18] has shown that the solvent shift, Δ, of the β-substituents (eq 4) for cisoid enones is dependent on

$$\Delta = \delta_{CCl_4} - \delta_{C_6H_6} \quad (4)$$

stereochemistry. Substituents cis to the carbonyl show negative Δ's whereas trans substituents show large positive Δ's. The data in Table I are internally consistent and allow an unambiguous assignment of stereochemistry.

The oxidation of cyclopropenes **3a,b** gave quantitative yields of the enones. VPC of the reaction mixtures throughout the oxidations showed that the ratios of enones **5a/5b** and **5c/5d** were constant (±2%). Also, control experiments showed that the enones were stereochemically stable to the reaction conditions. The data is given in Table II.

Also shown in Table II are the previously determined[11] kinetic ratios of oxabicyclobutanes **4a/4b** and **4c/4d** as well as the thermodynamic ratios of the product enones **5c** and **5d** (see Experimental Section). The thermodynamic ratio of enones **5a** and **5b** was not determined but is probably near 50:50.

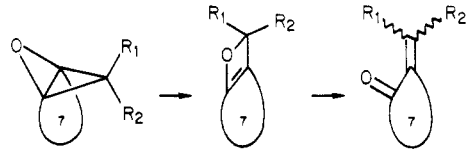
Discussion

The most important result in Table II is that even though only one oxabicyclobutane, **4c**, is produced in the epoxidation of cyclopropene **3b** and even though only one conformational mode of fragmentation is possible, both enones **5c** and **5d** are formed in about equal amounts. This result for cyclopropene **3b** effectively rules out mechanisms of fragmentation which retain any stereochemical correlation of reactant and product, especially since in this system there is no thermochemical bias for formation of either enone.

It is possible that the cisoid fragmentation of **4c** follows two stereochemically different paths. For example, perhaps oxabicyclobutane **4c** fragments both by concerted $dis_{1,4}$ and $con_{1,4}$ modes (see Scheme I as discussed above) which would give both enone products. Such a competitive fragmentation, however, would most likely have different energy transition states due to different orbital interactions. It would seem, therefore, that if two competing concerted mechanisms were operating, an ~50:50 mixture of enones would not be observed. Yet this is what was observed.

It is most reasonable that there is a fundamental feature of the fragmentation mechanism which naturally causes the enone kinetic ratio to equal the thermodynamic ratio. The simplest mechanism is the production of a single intermediate whose transition-state structure for enone formation resembles the enone product.

One mechanism would be an "allowed"[19,20] formation of an intermediate oxetene **6**, followed by opening to the enone (eq 5). Another possibility is a stepwise fragmentation to diradical **7** (eq 6), which lives long enough for bond rotation before cleavage to enone. Whether or not



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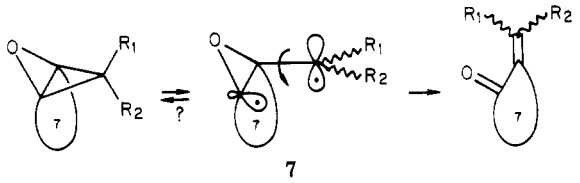
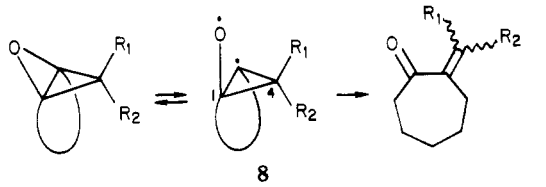


(6)

7

the diradical recloses to a mixture of diasteriomeric oxabicyclobutanes is unknown. Either of these two mechanisms would be expected to produce a cisoid enone mixture that favors the thermodynamic isomer.

A stepwise fragmentation to diradical **8** (eq 7) also seems to be a possibility, but it also suffers from the same mechanistic problem possessed by the two competing concerted fragmentations discussed earlier. Any preference for $dis_{1,4}$ or $con_{1,4}$ cleavage of diradical **8** would produce a kinetic ratio of enones which would not be equal to the observed ~55:45 thermodynamic ratio.



(7)

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In summary, we favor a stepwise fragmentation to the oxetene **6** intermediate and/or the diradical **7**.

Concerning the monocyclic cyclopropenes **1a–h**, the mixtures of enones produced is also suggestive of a stepwise fragmentation process. Crandall's[15] cyclopropenes, **1e,f**, showed complete loss of stereochemistry. Cyclopropene **1b** produced an enone ratio within 0.5 kcal/mol of the thermodynamic ratio. And even though cyclopropenes **1c** and **1d** produced opposite ratios of enones, which does suggest some preservation of stereochemistry,[7] their ratios correspond to a $\Delta\Delta G^*$ of only ~1 kcal/mol.

The most perplexing aspect for the oxidation of cyclopropenes **1a–h** is that the preferred enone stereochemistry

(18) Timmons, C. J. *Chem. Commun.* **1965**, 576.

(19) Wiberg, K. B. *Tetrahedron* **1968**, *24*, 1083.
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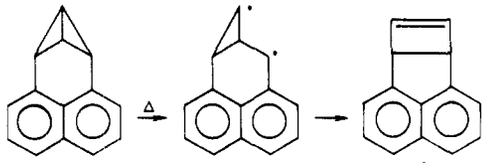
for **2a** and **2e–2g** is opposite that for the other enones. The enones **2a** and **2e–2g** convert what is presumed to be an R_{exo} substituent on the oxabicyclobutane preferentially into an R_{trans} position in the major enone. The other enones, **2b–2d** and **2h**, apparently prefer correlation of R_{exo} with R_{cis}. These differences might be expected from a stepwise mechanism if the thermodynamic enone ratios for **2a** and **2e–2g** were opposite to the thermodynamic ratios for the other enones, **2b–2d** and **2h**. Further experimentation is needed to test this hypothesis. The most critical systems to test are the enones **2g** and **2h** whose thermodynamic ratios are expected to be similar on the basis of their similar structures.

The hypothesis of a stepwise fragmentation mechanism is not without precedent. Dewar[21,22] has suggested, on the basis of MINDO/3 calculations and literature experiments,[23] that bicyclobutanes fragment by a stepwise mechanism that involves an intermediate diradical similar to diradical **7**.

Turro[24] et al. have also proposed that diradicals such as **7** are involved when bicyclobutane **9** thermally cleaves to give cyclobutene **10** (eq 8). A diradical mechanism for the cleavage of oxabicyclobutanes is therefore reasonable.



(8)

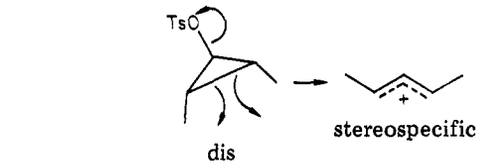
9 **10**

One question is whether the observed rate of oxabicyclobutane rearrangement is consistent with a simple bond cleavage to give a diradical such as **7**. The postulated stepwise fragmentation of bicyclobutanes occurs with a $\Delta H^{\ddagger} \approx 30$–40 kcal/mol and $\Delta S^{\ddagger} \approx 0$ eu.[24,26] Since simple epoxides have the same strain as cyclopropanes,[27] one might expect similar $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ values for oxabicyclobutanes. This is not observed, since oxabicyclobutanes fragment at room temperature.

The simplest explanation for the fast rate of oxabicyclobutane fragmentation would seem to be that the liberated carboxylic acid (from the peracid) is catalyzing the fragmentation by an ionic mechanism.

Various kinetic and product studies have been done,[4] however, to eliminate all but a concerted fragmentation of a protonated oxabicyclobutane.[6] Even this mechanism is unlikely because it is similar to solvolysis of cyclopropyl tosylates which fragment stereospecifically[28,29] (eq 9 and 10).

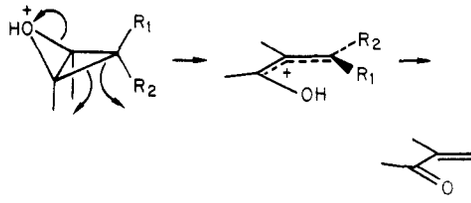
A reasonable explanation for the instability of oxabicyclobutanes is that they possess more strain than bicyclobutanes. As argued earlier,[10] cyclopropenes should epoxidize considerably faster than other cycloalkenes if oxabicyclobutanes possess the same strain energy as bicyclobutanes. Rather, oxabicyclobutanes epoxidize at about the same rate as other cycloalkenes. The cause of the unexpected slower rate of epoxidation for cyclopropenes may be the same as the cause for the fast oxabicyclobutane decomposition, namely, that oxabicyclobutanes are considerably more strained than bicyclobutanes. In terms of orbitals (see I), this could be due to the mixing



(9)

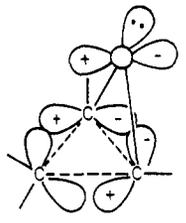
stereospecific

dis



(10)

not exclusively observed



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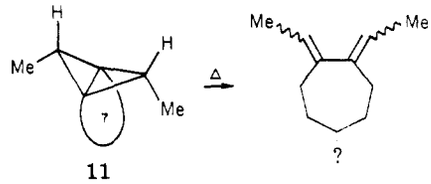
of the higher energy nonbonding orbital on oxygen with the appropriate e′ orbital of cyclopropane[30–33] to produce an oxirene-like $4n$-electron system.[34] A good ab initio MO calculation for oxabicyclobutane is called for to settle this question.

A final suggestion is that even though the configurational stereochemistry of bicyclobutane fragmentations has been worked out,[23] the conformational stereochemistry now needs to be studied. If bicyclobutanes were forced to fragment in a cisoid manner without structurally biasing the configurational stereochemistry, different results may be found. It should be a simple matter to prepare bicyclobutanes such as **11** (eq 11) so that this feature can be studied.



(11)

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Experimental Section

^{1}H NMR spectra were obtained on either a JEOLCO Model C-60HL or Model MH-100 spectrometer.

Preparative VPC was done on a Varian A-90P chromatograph with thermal conductivity detectors: column A, 6 ft × $^1/_4$ in., 20% Carbowax 20-M on 40/60-mesh Chromosorb P, non-acid-washed.

Analytical VPC was done on a Perkin-Elmer Model 900 chromatograph with flame-ionization detectors: column B, 15 ft × $^1/_8$ in., 10% Carbowax 20-M on 45/60-mesh Chromosorb P, non-acid-washed.

Stereochemistry of Enones 5a and 5b. The enones were prepared as described previously[11] and were separately collected by VPC at 110 °C (column A). Enone **5b** had a slightly longer

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retention time. The ^1H NMR spectra were run in CCl_4 and PhH as solvents, and the results are given in Table I.

Stereochemistry of Enones 5c and 5d. The enones were prepared as previously described.[11] Inasmuch as preparative VPC using a 10-ft, 20% Carbowax 20-M on Chromosorb P column would not totally separate the isomers, ^1H NMR spectra were run on two enriched samples of **5c** and **5d**, respectively. Enone **5c** had the earlier retention time. The results are given in Table I.

Epoxidation of Cyclopropenes 3a and 3b. Analysis of Enones 5a-5d. The cyclopropenes were prepared as described previously.[11] An ~0.15 M solution of the cyclopropene in CCl_4 with dodecane as an internal standard was prepared. Less than 1 equiv of *m*-chloroperbenzoic acid was added, and the solution was stirred at 0 °C. Aliquots were analyzed by VPC (column B), and the areas of the enone peaks were measured by a planimeter. The ratio of enones did not change throughout the run from ~10 to 70% reaction. The enones were also independently shown to be stable to the reaction conditions.

Equilibration of Enones 5c and 5d. Two runs were done, one enriched in enone **5c** and the other in **5d**. An ~0.03 M solution of the enone mixture in Spectrograde $CHCl_3$ was refluxed with approximately 0.5 equiv of *p*-toluenesulfonic acid. The solution darkened almost immediately, but only a slow decomposition was detected by VPC. Equilibration of the enones occurred with a half-life of ~5 h with an overall decomposition rate which was ~7 times slower. VPC analysis (column B) showed that in one run, an 81:19 ratio of **5c**/**5d** equilibrated to a 56:44 ratio. In the other run, a 29:71 ratio of **5c**/**5d** equilibrated to a 55:45 ratio.

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Registry No. 3a, 64425-32-7; **3b**, 64425-34-9; **4a**, 73986-28-4; **4b**, 74034-35-8; **4c**, 73986-29-5; **4d**, 74034-36-9; **5a**, 64425-37-2; **5b**, 64425-35-0; **5c**, 64425-43-0; **5d**, 64425-41-8.

Kinetics and Mechanism of the Oxidation of L-Phenylalanine by Hydrogen Peroxide in the Presence of Ferrous Sulfate as a Catalyst

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The kinetics of oxidation of L-phenylalanine by hydrogen peroxide in the presence of Fe(II) ions have been studied. The reaction is first order with respect to both phenylalanine and Fe(II) ions but zero order with respect to hydrogen peroxide. The energy of activation has been calculated to be 11.45 ± 0.01 kcal mol^{-1}. A reaction mechanism has also been proposed.

Hydrogen peroxide is a common oxidizing agent for analytical and synthetic organic chemistry. The chemistry of metal ion catalyzed reactions of hydrogen peroxide commenced at the end of the last century, when Fenton[1] described the reaction of tartaric acid with hydrogen peroxide in the presence of ferrous sulfate. Thereafter, a free-radical mechanism was proposed for this reaction by a few investigators.[2-5] However, a few reports[6-10] described the oxidation of some amino acids by the Fenton reagent. These studies refer mainly to their oxidation products, but no work appears to have been done on the kinetics of the oxidation of amino acids by this reagent. Since the oxidative degradation of amino acids is important in the biological systems, the kinetics of oxidation of phenylalanine by hydrogen peroxide in the presence of Fe(II) ions as catalyst were studied in acidic medium and are reported in this paper.

Experimental Section

General Methods. All the chemicals used were of AnalaR (BDH) grade. The ionic strength of the reaction mixture was maintained by the addition of sodium nitrate solution. The concentration of hydrogen peroxide in kinetic runs was measured colorimetrically.[11]

After the reactants had reached thermostat temperature, the reaction was started by addition of the catalyst. The kinetics were followed by examining 5-mL aliquots of the reaction mixture for hydrogen peroxide content. The aliquots were added to 5 mL of titanium sulfate solution to stop the reaction. Optical density was measured at 420 nm, and the concentration of hydrogen peroxide was read from the calibration graph. All the reactions were studied in an open atmosphere. However, the dependence of the reaction on atmosphere was checked by studying two identical reaction mixtures, one under nitrogen and the other without nitrogen. The rate constants in both cases were almost equal.

Identification of Products. For identification of the products the following reaction mixture was prepared and heated to 70 °C for about 2 h: 20 mL of 0.5 M phenylalanine, 5 mL of 0.01 M ferrous sulfate, 20 mL of 1 M perchloric acid, 15 mL of water mixed with 40 mL of 0.5 M H_2O_2. The gaseous products formed were passed through a freshly prepared lime-water solution, which turned milky and thus confirmed the presence of carbon dioxide. The formation of formic acid in the reaction mixture was tested by its reduction with a known procedure. The formaldehyde thus obtained was confirmed by chromotropic acid, which gave a violet-pink color.[12] Its formation was further confirmed by reaction

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