This explanation is tentative at this stage. The observation of predominant 1,4 addition is in accord with the electrophilic addition of *t*-butyl hypochlorite to cyclopentadiene, a reaction which also involves a cationic intermediate.[3]

## Experimental Section

*t*-Butyl hydroperoxide (Monomer–Polymer Laboratories) was distilled (helix-packed column), and the fraction, bp 38–39° (20 mm), was used. Gas chromatographic analyses were carried out with a Hewlett–Packard 5750 instrument using a 10-ft 10% Carbowax 20M column at 165°. Gas chromatographic separations were carried out with a Hewlett–Packard 5798A preparative attachment unit. The nmr spectra were run in carbon tetrachloride solution on a Varian HA-100 instrument. Elemental analysis was carried out by Schwarzkopf Microanalytical Laboratories, Woodside, N. Y.

**Reaction of *t*-Butyl Hydroperoxide with Cyclopentadiene.**—A solution of ferrous sulfate ($FeSO_4 \cdot 7H_2O$, 0.25 mol) in 125 ml of distilled water was added dropwise over 90 min to a well-stirred mixture of cupric acetate (monohydrate, 0.25 mol), *t*-butyl hydroperoxide (22.5 g, 0.25 mol), freshly distilled cyclopentadiene (20 g, 0.30 mol), and 275 ml of glacial acetic acid. The temperature of the reaction mixture was kept below 15° during this addition. The reaction mixture was stirred for 30 min with continued ice-bath cooling, then poured into 1 l. of ice water. The product was extracted with methylene chloride, and the extract was washed with sodium bicarbonate and water and dried over anhydrous magnesium sulfate. The product was a clear yellow liquid, 35.3 g. An ir spectrum was consistent with an alcohol and acetate adduct mixture showing O—H str, also acetate C=O str (1742 $cm^{-1}$) and C—O str (1250 $cm^{-1}$), as well as strong ether absorption (1075 $cm^{-1}$).

**Reduction of *t*-Butyl Hydroperoxide Adduct Mixture.**—The crude adduct mixture (30.0 g) was reduced with lithium aluminum hydride (3 g) in diethyl ether. The reaction mixture was hydrolyzed under alkaline conditions[12] giving 21.3 g of product. The crude reduction product (20.1 g) was distilled at reduced pressure (0.7 mm) through an annular Teflon spinning-band column and the following fractions collected: (1) bp 53–64°, 2.2 g; (2) bp 56–66°, 8.1 g; (3) bp 66–66.5°, 5.3 g; (4) bp 48–56° (0.1 mm), 0.3 g; residue 2.4 g. Fractions 1 and 2 had ir spectra consistent with the expected adducts but showed weak carbonyl absorption (C=O str, 1730 $cm^{-1}$) indicating the presence of some unreduced acetate adduct. An ir of fraction 3 was consistent with the expected alcohol adduct (O—H str, 3390 $cm^{-1}$, ether C—O str, 1053 $cm^{-1}$, both very strong). Fraction 4 was identical with 3. Analysis of each fraction was done by gc. Fraction 3 was an isomeric adduct mixture, and this was further verified by elemental analysis.

*Anal.* Calcd for $C_9H_{16}O_2$: C, 69.19; H, 10.32. Found (fraction 3): C, 69.44; H, 10.61.

Pure isomers shown to be *cis*- and *trans*-1,4 adducts Ia and IIa were separated from fraction 3 by preparative gc and these were shown by further analytical gc to be homogeneous and to correspond exactly to the two peaks present in the gc of fraction 3. The structure of each of these adducts was confirmed by nmr as discussed (*vide supra*). The ir spectra of the separated 1,4 adducts Ia and IIa were very similar and consistent with the expected adduct structures. *trans* adduct IIa showed O—H str at 3390 $cm^{-1}$, ether C—O 1053 $cm^{-1}$, =CH str 3067 $cm^{-1}$. Similar bands were present in the spectrum of Ia.

*Anal.* Calcd for $C_9H_{16}O_2$: C, 69.19; H, 10.32. Found (*trans* adduct): C, 69.19; H, 10.49.

There was insufficient *cis* adduct for C, H analysis. Further gc analysis of a weighed mixture of Ia and IIa showed that the area per cent calculated by the peak height width at half-height method agreed with the weight per cent as expected for similar isomers.

**Registry No.**—*t*-Butyl hydroperoxide, 75-91-2; 1,3-cyclopentadiene, 542-92-7; Ia, 25594-22-3; IIa, 25594-23-4.

**Acknowledgment.**—The authors would like to thank Professor L. M. Jackman of Pennsylvania State University for his constructive suggestions. A portion of the work was done under a City University Doctoral Faculty Research Grant (H. H.).

(12) L. F. Fieser and M. Fieser, "Reagents for Organic Synthesis," Wiley, New York, N. Y., 1967, p 584.

# Oxidative Cleavage of Cyclopropanes. VII. Kinetics of the Cleavage of Some Bicyclo[*n*.1.0]alkanes and Spiro[*n*.2]alkanes by Thallium Triacetate[1,2]

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The rates of cyclopropane ring cleavage of spiro[5.2]octane, spiro[4.2]heptane, and fluorene-9-spirocyclopropane by thallium triacetate in acetic acid at 17.95° have been determined. Bicyclo[5.1.0]octane, bicyclo[4.1.0]heptane, and bicyclo[3.1.0]hexane cyclopropane ring cleavages were studied at 29.30 and 50.05°. The kinetics of the cleavage reactions were overall second order, first order in each reactant. Stability of the incipient carbonium ion is the rate-controlling feature in the case of the spiroalkanes. However, steric features of each molecule are noted in the spiroalkanes and the steric factor becomes preeminent in the case of the bicycloalkanes.

The rates of cyclopropane ring cleavage by mercury(II) acetate,[3] thallium(III) acetate,[4] and lead(IV) acetate[5] have been determined in acetic acid using arylcyclopropanes as reference substrates. In addition to establishing an order of reactivity of $Tl(OAc)_3 > Hg(OAc)_2 > Pb(OAc)_4$ these studies have yielded information concerning the selectivity of the metal acetates as reflected by the magnitude of $\rho^+$. The $\rho^+$ values for $Tl(OAc)_3$, $Hg(OAc)_2$, and $Pb(OAc)_4$ are $-4.3$, $-3.2$, and $-1.7$, respectively. Therefore not only is $Tl(OAc)_3$ the most reactive of the metal acetates studied, it also is the most selective. While the mechanistic interpretation of these data has only been partially successful it is clear that from an experimental viewpoint $Tl(OAc)_3$ is a reagent that should be studied further in a variety of oxidation reactions of organic molecules.

Our kinetic studies of the oxidative cleavage of cyclo-

(1) Paper VI: A. South, Jr., and R. J. Ouellette, *J. Amer. Chem. Soc.*, **90**, 7064 (1968).

(2) This research was supported by Grant GP6778 from the National Science Foundation.

(3) R. J. Ouellette, R. D. Robins, and A. South, Jr., *ibid.*, **90**, 1619 (1968).

(4) Paper VI.[1]

(5) R. J. Ouellette, D. Miller, A. South, Jr., and R. D. Robins, *ibid.*, **91**, 971 (1969).

propanes have dealt exclusively with arylcyclopropanes in which only one of the two nonequivalent bonds is cleaved. This selective cleavage controlled by the stability of the incipient cationic center generated in the electrophilic attack of the metal was a convenient first approach. However, there are other cyclopropanes in which the relative rates of attack of the electrophile at two possible sites may be more comparable. Under such conditions it should be possible to evaluate the effect of other structural features such as ring strain of the cyclopropane and steric accessibility to the electrophile on the rate of reaction. Two classes of compounds were chosen as likely candidates with which to study rate-controlling features other than that which results in stability of a cationic center. These classes are the spiro[*n*.2]alkanes and the bicyclo[*n*.1.0]alkanes represented by general structures **1** and **2**, respectively.


**1** **2**

In the case of the spiro[*n*.2]alkanes a single bond would be expected to cleave as a reflection of the great difference in stability between a primary and a tertiary cation. In short a strong tendency toward Markovnikov addition should result. Any difference in the rate of cleavage of the ring bond will reflect in part the relative stability of the tertiary cationic center on a ring of variable size. Other features such as ring strain and steric accessibility of the bonds should be evident once the cationic stability factor has been corrected for on the basis of appropriate reference reactions. In the case of the bicyclo[*n*.1.0]alkanes the product studies indicate that both of the possible ring bonds are cleaved.[6] Furthermore, the ratio of the products resulting from cleavage of each bond is a function of ring size. From the product studies previously reported it is possible to calculate rates for individual cleavages of the two bonds from the observed rate constants. Thus structural features controlling the rates of external and internal bond cleavage can be evaluated.

## Results

We have shown that the oxidation reactions of thallium triacetate can be followed by quenching in excess aqueous 5% potassium iodide solution and then back-titrating the triiodide formed with standard sodium thiosulfate.[4,7] When the excess potassium iodide solution is added to the reaction mixture, a yellow heterogeneous mixture is obtained which turns dark upon addition of the starch indicator. This mixture is then titrated with standardized sodium thiosulfate to a pure yellow heterogeneous mixture of thallous iodide.

Thallium triacetate forms a double salt with thallous acetate which arises from the decomposition of the organothallium intermediate.[4] The formation of the double salt causes a rapid decrease in the rate of cleavage of cyclopropanes.

$$Tl(OAc)_3 + TlOAc \rightleftharpoons Tl_2(OAc)_4$$

(6) R. J. Ouellette, A. South, Jr., and D. L. Shaw, *J. Amer. Chem. Soc.*, **87**, 2602 (1965).

(7) R. J. Ouellette, G. Kordosky, C. Levin, and S. Williams, *J. Org. Chem.*, **34**, 4104 (1969).

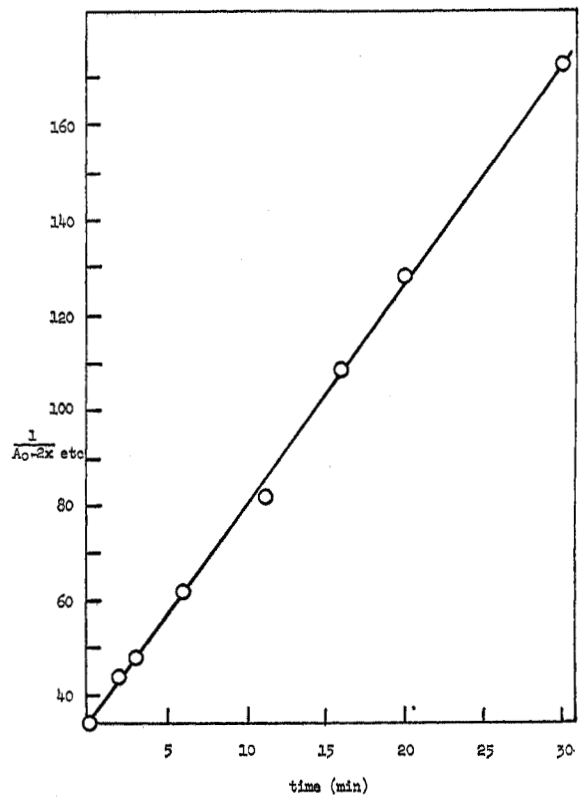



Figure 1.—Graph of typical kinetic run.

The titrimetric analytical method gives directly only the total concentration of thallium(III) species present. This does not correspond to the concentration of thallium triacetate in solution. Therefore, in order to facilitate analysis of the rate of cleavage of cyclopropanes by *free thallium triacetate*, we have employed the method previously described.[4] For the case in which the concentration of thallium triacetate ($A$) is twice that of cyclopropane, the rate of cleavage and formation of products ($X$) is equal to the change in oxidative titer of the solution as indicated by the following rate law and integrated expression.

$$dx/dt = k[A_0 - 2X][A_0/2 - X]$$

$$\frac{1}{A_0 - 2X} = kt + 1/A_0$$

The observed rate constants for the rates of oxidation of the series of cyclopropanes studied are listed in Table I. The reported values are the average of at least duplicate runs. Individual rate constants deviate from the average values by no more than 2%. The typical run illustrated in Figure 1 for spiro[5.2]octane at 29.3° has a correlation coefficient of 0.9996.

## Discussion

Both spiro[5.2]octane and spiro[4.2]heptane react much faster than any of the bicyclo[*n*.1.0]alkanes studied. This large difference must reflect the stability of the tertiary cationic center developed in the case of the spiro[*n*.2]alkanes compared with the secondary cationic center developed in the bicyclo[*n*.1.0]alkanes. On the basis of the earlier studies with arylcyclopropanes in which $\rho^+ = -4.3$ was determined the results reported herein for the differences between the two classes of bicycloalkanes were expected.

TABLE I

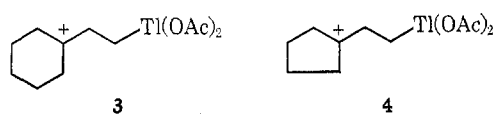
SECOND-ORDER RATE CONSTANTS AND ACTIVATION PARAMETERS

| Compd | $k_{17.95°}$ (l./mol min) | $k_{29.80°}$ (l./mol min) | $k_{50.05°}$ (l./mol min) | $\Delta H^{\ddagger}$ (kcal/mol) | $\Delta S^{\ddagger}$ (cal/deg) |
|---|---|---|---|---|---|
| Spiro[5.2]octane (a)[a] | 1.57 | 4.45 | | 15.5 | −4.5 |
| Spiro[4.2]heptane (b) | $3.62 \times 10^{1}$ | | | | |
| Fluorene-9-spirocyclopropane (c) | $1.65 \times 10^{-1}$ | | | | |
| Bicyclo[5.1.0]octane (d) | | $5.26 \times 10^{-4}$ | $7.09 \times 10^{-3}$ | 23.7 | 4.9 |
| Bicyclo[4.1.0]heptane (e) | | $5.39 \times 10^{-2}$ | $2.68 \times 10^{-1}$ | 14.4 | −16.8 |
| Bicyclo[3.1.0]hexane (f) | | $2.15 \times 10^{-2}$ | $1.16 \times 10^{-1}$ | 15.2 | −16.1 |

[a] Identification for registry number.

The spiro[4.2]heptane reacts faster than the spiro[5.2]octane by a factor of 23.1. However this value must be corrected for differences in the symmetry of the molecules. In spiro[4.2]heptane two cyclopropane bonds are equivalent with respect to the five-membered ring which must be planar or very nearly so. Even if the five-membered ring were nonplanar the difference in the steric environment of the two cyclopropane bonds attached to the ring cannot be large. Furthermore, rapid interconversion by pseudorotation will result in the equivalence of the two bonds on a time average basis. By contrast the two cyclopropane bonds attached to the six-membered ring in spiro[5.2]octane are nonequivalent. One of the bonds is in a pseudoaxial position in which case the axial protons should hinder the approach of the thallium triacetate. The pseudoequatorial bond is much more open to electrophilic attack. While the six-membered ring undergoes chair–chair interconversion rapidly and the two cyclopropane ring bonds become equivalent on a time average basis, there is still only one pseudoequatorial bond accessible at a time. The ratio of the attack at the pseudoequatorial to pseudoaxial bond cannot be calculated from the system studied to date but could be derived from related decalin derivatives. However the maximum rate constant for pseudoequatorial bond attack can be no greater than the observed rate constant and would not be expected to be less than one-half of the observed rate constant. By using a statistical factor of two to obtain the relative rate of attack of an individual bond of spiro[4.2]heptane relative to a pseudoequatorial bond of spiro[5.2]octane the rate factor should be 23.1/2 or 11.5.

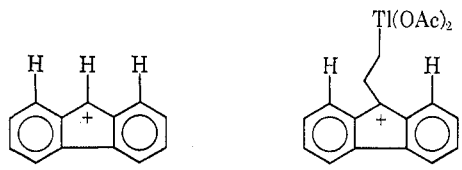
The relative stability of the cyclohexyl cation intermediate **3** compared with the cyclopentyl cation **4** should




**3** **4**

be reflected in solvolysis reaction rates. While data on the appropriate 1-ethylcycloalkyl derivatives are not available, the unsubstituted cyclohexyl and cyclopentyl data are available for the tosylates in acetic acid.[8] Cyclopentyl tosylate solvolyzes 16 times as fast as cyclohexyl tosylate, a value consistent with the rate factor observed in the ring cleavage reaction. Therefore, carbonium ion stability is the dominant rate-controlling feature in these two compounds.

The fluorene-9-spirocyclopropane[9] reacts much slower than either of the other two related compounds. From the available solvolysis data on cyclopentyl-[10] and 9-fluorenylmercuric perchlorates[11] in acetic acid it is known that the rates stand in the order of 1 to 0.65 respectively. Therefore, while ring cleavage rate of the spiro[4.2]heptane would be expected to be larger than that of fluorene-9-spirocyclopropane the observed ordering of 1 to 0.005 is clearly indicative of structural features other than carbonium ion stability. There are significant differences between the cation **5** generated in solvolysis of the mercury compound and that from cyclopropane cleavage, **6**. The larger steric bulk of the




**5** **6**

methylene group attached to the 9 position in intermediate **6** should decrease its stability, raise the energy of the transition state, and slow the rate of the reaction. It should be recalled that $\rho^{+} = -4.3$ was observed in the cleavage of arylcyclopropanes and therefore the transition state is located far along the reaction coordinate and strongly reflects product stabilities.

In the bicyclo[*n*.1.0]alkanes the rates of reaction reflect many factors for the cleavage can occur at either an internal or external bond. In both cases the incipient cation is secondary. Since there are two external bonds and one internal bond a statistical factor of two should favor external bond cleavage. It has been established that 91% of the reaction of bicyclo[4.1.0]heptane occurs *via* attack of an external bond whereas 46.5% external bond cleavage occurs in bicyclo[3.1.0]hexane.[6] The deviations from the statistically expected 66.7% in both compounds indicates the importance of structural differences.

Each of the observed rate constants must be separated into specific rate constants for internal and external bond cleavage.

$$k_{obsd} = k_{int} + k_{ext}$$

The ratio of the internal to external rate constants must be equal to the ratio of the amounts of the products derived from the two paths after taking into account the statistical correction. The calculated $k_{int}$ and $k_{ext}$ for bicyclo[4.1.0]heptane are $0.25 \times 10^{-1}$ and $1.21 \times 10^{-1}$ l./mol min at 50°, respectively, and the $k_{int}$ and $k_{ext}$ for bicyclo[3.1.0]hexane are $0.65 \times 10^{-1}$ and $0.27 \times 10^{-1}$ l./mol min at 50°, respectively.

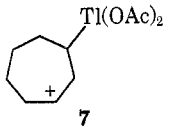
(8) A. Streitwieser, Jr., "Solvolytic Displacement Reactions," McGraw-Hill Book Co., New York, N. Y., 1962, p 95.

(9) The authors gratefully acknowledge the generosity of Professor G. Fraenkel in providing us with this compound.

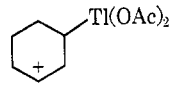
(10) R. J. Ouellette, Ph. D. Thesis, University of California, 1962.

(11) B. G. van Leuwen and R. J. Ouellette, *J. Amer. Chem. Soc.*, **90**, 7056 (1968).

The ratio of the specific rates for internal bond cleavage of bicyclo[4.1.0]heptane to that of bicyclo[3.1.0]-hexane is 0.38. Since a cycloheptyl cation (**7**) results from the former compound and a cyclohexyl cation (**8**)



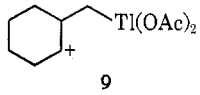

**7**



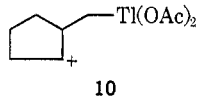

**8**

results from the latter compound this rate ratio does not reflect carbonium ion stabilities. An opposite order of reactivities is observed in cycloalkyl tosylate solvolysis with the cycloheptyl derivative solvolyzing 31 times as fast as the cyclohexyl derivative.[8] Therefore some structural feature must give rise to a rate factor difference of 82 to produce the order observed. In bicyclo[3.1.0]hexane the five-membered ring contains eclipsed hydrogens which are moved to staggered orientations in intermediate **8**. In the bicyclo[4.1.0]heptane the change in the hydrogen–hydrogen interaction in proceeding to intermediate **7** is much smaller. The energy difference which must be involved in reversing the expected rates based on carbonium ion stabilities is only 2.6 kcal/mol, a value well within that possible for removing the eclipsing interactions in the five-membered ring.

The ratio of the external bond cleavage rates for bicyclo[4.1.0]heptane to bicyclo[3.1.0]hexane is 4.4. On the basis of carbonium ion stabilities of the intermediates **9** and **10** a ratio of 0.06 would be expected.[8]




**9**




**10**

In order to account for the difference between the expected ratio and the observed ratio a rate factor of 70 favoring the cleavage of bicyclo[4.1.0]heptane over that of bicyclo[3.1.0]hexane must be accounted for. Examination of models reveals no outstanding differences in the steric accessability of the external bonds of the two compounds. However there are many hydrogen–hydrogen interactions in bicyclo[4.1.0]heptane which contains a nonchair six-membered ring. These interactions are eliminated in intermediate 9 where staggered vicinal hydrogens are present. In bicyclo-[3.1.0]hexane the eclipsed hydrogens in the reactant remain nearly eclipsed in the intermediate **10**. An energy factor of 2.5 kcal/mol does not seem an unreasonable quantity to expect for the change to the chair conformation which occurs in the cleavage of bicyclo[4.1.0]-heptane.

The rate of cleavage of bicyclo[5.1.0]octane is much slower than either of the other two bicyclo[*n*.1.0]alkanes studied. On the basis of carbonium ion stabilities as indicated from solvolysis data this compound should cleave the most rapidly. There appears to be little difference in the steric accessability of the cyclopropane bond as evidenced by inspection of molecular models. However, there is a substantial shielding of the back of the C-1 carbon by the methylene group at C-3. LaLonde[12] observed in the acid cleavage of 2,3-methano-*trans*-decalin that the products are the result of *trans*-diaxial attack. Analogous attack in bicyclo[5.1.0]-octane would be seriously retarded. Solvation of the cationic center from the back side as the electrophile attacks the cyclopropane ring bond may be difficult to achieve and hence slow the rate. The activation parameters for bicyclo[5.1.0]octane are dramatically different from those for the other compounds and may reflect this solvation difference. Other structural features of a more subtle nature may be operative as a result of differences in conformations of the seven-membered ring in the reactant and the transition state.

## Experimental Section

**Purification of Acetic Acid.**—The acetic acid which was used for the kinetics and reaction of cyclopropanes with thallium triacetate was purified by refluxing a solution of 1.5 l. of glacial acetic acid containing 30 ml of acetic anhydride and about 3 g of *p*-toluenesulfonic acid for 18 hr. The acetic acid was distilled through a 60-cm glass-helix-packed column. The fraction with bp 117.5–118° was retained.

**Kinetic Analysis.**—The kinetic solutions were prepared by weighing an amount of the cyclopropane into a volumetrically measured amount of purified acetic acid. From the weight of sample, the desired amount of thallium triacetate was calculated, weighed out, and added to the solution. The concentration of the cyclopropane was ~0.015 *M* and that of thallium triacetate was ~0.030 *M*.

The methods of sampling were dependent upon the rate of the reaction. For slow reactions, in which evaporation could occur, 2-ml aliquots were sealed in test tubes. For reactions with a moderate rate, where evaporation was not a problem, aliquots were pipetted directly from the reaction flask. For fast reactions, aliquots of each reactant were pipetted into opposite sides of a partition flask and allowed to equilibrate at the bath temperature, and the solutions were mixed by shaking so as to allow passage over the partition barrier.

The method of analysis consisted of quenching the aliquot in excess 5% aqueous potassium iodide solution, addition of a starch–iodide indicator to the yellow heterogeneous mixture, and titration of the resulting dark mixture to a pure yellow mixture with standard aqueous sodium thiosulfate.

**Registry No.**—Thallium triacetate, 2570-63-0; Table I—a, 185-65-9; b, 185-49-9; c, 167-02-2; d, 286-43-1; e, 286-08-8; f, 285-58-5.

(12) R. T. LaLonde and M. A. Tobias, *J. Amer. Chem Soc.*, **85**, 3771 (1963).