is followed by electron transfer from the phenoxide moiety to 4NM and scission of the N–C bond of 4NM in the rate-determining step. Tetranitromethane is known to readily form charge-transfer complexes,[6] and bond rupture following electron transfer is an established process.[22] The products of the reaction then arise in steps that are kinetically competitive and faster than C–N bond scission. Assuming a steady state in the caged product of the k_e step, the rate of $3NM^-$ production is given by

$$v = K_\pi k_e[XPhO^-][4NM] \qquad (17)$$

so that $K_\pi k_e = k_2$ and the ratio of nitrated phenol to nitrite ion is provided by $k_a:k_b$. The inability to detect free-radical intermediates in water is also accounted for by Scheme I. The change in kinetic order from first to second order in *p*-cresol on going form water to ethanol and the second-order dependence of the rate on *t*-butylphenol in ethanol can be rationalized *via* formation of 2:1 complexes in ethanol and 1:1 complexes in water.

The formation of nitrite ion from tetranitromethane in a reaction in which both trinitromethane anion and a proton are released shows that estimation of the latter two products does not provide a measure of the yield of nitrophenol. Because of absorption by trinitromethane ion the absorbances at the λ_{max} of the nitrophenols also are not good measures of the extent of nitration, unless the trinitromethane anion is removed. These words are provided as a cautionary phrase to those who are employing 4NM in the modification of proteins.

Acknowledgments. This work was supported by grants from the National Science Foundation and the National Institutes of Health.

(22) N. Kornblum, *Trans. N. Y. Acad. Sci.*, **29**, 1 (1966).

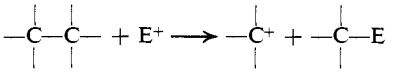
Oxidative Cleavage of Cyclopropanes. IV. Kinetics of the Cleavage of Arylcyclopropanes by Mercuric Acetate[1,2]

Robert J. Ouellette, Richard D. Robins, and Aubrey South, Jr.

Contribution from the Evans Chemical Laboratory, The Ohio State University, Columbus, Ohio 43210. *Received September 1, 1967*

Abstract: The kinetics of cleavage of six arylcyclopropanes by mercuric acetate in acetic acid have been examined. The reaction is over-all second order, first order in each reactant. Activation parameters have been determined from the rates of the reactions at 25, 50, and 75°. Electron-releasing substituents facilitate the reaction. A correlation of the second-order rate constants and σ^+ has been obtained for the substituents *p*-MeO, *p*-Me, *m*-Me, H, *p*-Cl, and *m*-Cl with $\rho = -3.2$ at 50°. Under the reaction conditions the phenylcyclopropane–mercuric acetate adduct is stable. For the slow reactions, with electron-withdrawing substituents on the aryl ring, a side reaction of mercuric acetate leads to some analytical complications. Initial rate studies and the use of excess concentrations of cyclopropanes allow the circumvention of this difficulty. The cleavage reaction is postulated to involve electrophilic attack of mercuric acetate on the cyclopropane ring. There are similarities between the cleavage of cyclopropanes and the oxymercuration of olefins.

The cleavage of a carbon–carbon single bond as the result of a direct bimolecular reaction with an electrophile is fundamentally a simple reaction. Such an attack is designated SE2 in the Hughes–Ingold terminology. In this type of reaction the electrophilic reagent may be thought to displace a carbonium ion. Of the



many possible combinations of electrophiles and leaving groups that can be envisaged as participants in SE2 processes, only electrophilic attack on carbon–metal bonds has been examined in any detail. The only case where carbon–carbon single bonds are cleaved by electrophilic reagents is in compounds containing a cyclopropane ring.

Cyclopropane ring cleavage by reagents, now classified as electrophiles, to yield adducts has been known since the 19th century.[3] The cleavage process can be interpreted in terms of initial electrophilic attack to produce an intermediate of carbonium ion like character followed by addition of a nucleophile. The degree of synchronization of attack by the electrophile and the nucleophile is a subject of some interest. In general the direction of cyclopropane ring cleavage is thought to reflect the stability of the incipient carbonium ion.[4] Most early investigations dealt with the problem of position of ring cleavage as a function of substitution. It has been generalized that Markovnikov's rule can be applied to the reactions of cyclopropanes as well as of olefins. However, the generalization clearly has to be modified to include the effect of other factors, such as ring strain and steric accessibility to the reagent. Of these two factors only ring strain has been examined in detail. In a thorough study of the acid-catalyzed addition of acetic acid to bicyclo[*n*.1.0]alkanes LaLonde[5]

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

(2) This research was supported by Grant GP3873 from the National Science Foundation.

(3) A. Baeyer, *Chem. Ber.*, **18**, 2277 (1855); R. Fitlig and F. Roder, *Ann.*, **227**, 13 (1885); G. Gustauson, *J. Prakt. Chem.*, [2] **36**, 300 (1887).

(4) R. A. Raphael, "Chemistry of Carbon Compounds," Vol. II, E. H. Rodd, Ed., Elsevier Publishing Co., New York, N. Y., 1953, p 26; E. E. Royals, "Advanced Organic Chemistry," Prentice-Hall, Inc., Englewood Cliffs, N. J., 1954, Chapter 3.

(5) R. T. LaLonde and L. S. Ferney, *J. Amer. Chem. Soc.*, **86**, 3767

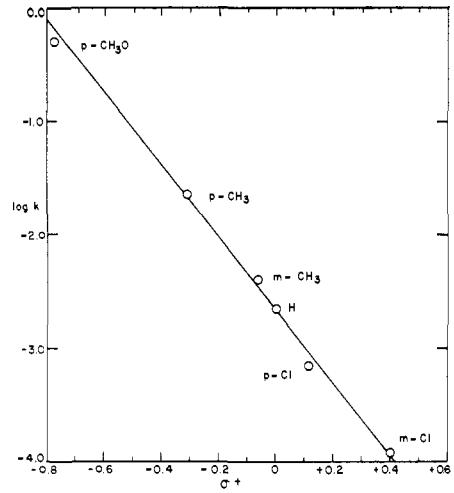
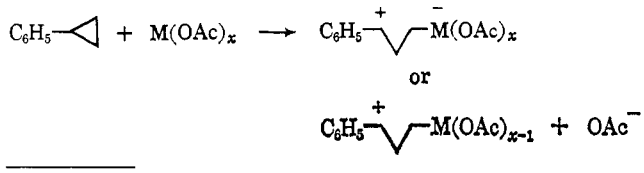


Figure 1. Hammett correlation.

observed that the extent of internal bond cleavage increases with decreasing values of n. In a similar manner the cleavage of the same class of compounds by thallium triacetate and lead tetraacetate has been observed to exhibit the same trends.[1] Levina[6] has cleaved the bicyclo[n.1.0] alkanes with mercuric acetate, but the details of this reaction have not been examined as extensively as with acid, thallium triacetate, and lead tetraacetate.

The stereochemistry of the ring cleavage of cyclopropanes has been examined only recently. LaLonde has shown that addition of the nucleophilic solvent occurs with inversion at the cyclopropane ring carbon. Addition of solvent in the reaction with thallium triacetate and lead tetraacetate also has been shown to occur with inversion. The general question of the stereochemistry of addition of the electrophile is largely an open one. While it appears likely that electrophilic attack will occur with net retention of configuration at the carbon to which the electrophile becomes attached, the postulate has not been experimentally demonstrated in a conclusive manner.

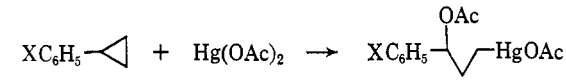
In this study we report an important adjunct to the stereochemical experiments presently available. The nature of the SE2 process can be elucidated by kinetic examination of the effect of substitutents on the rate of reaction. Attachment of aryl groups to the cyclopropane ring simplifies the problem of direction of ring cleavage. Only one of the two different types of bonds in phenylcyclopropane and related compounds is cleaved by thallium triacetate and lead tetraacetate.[7] The reaction potentially involves displacement of a benzyl-type carbonium ion by the electrophilic metal salt.



The degree of deposition of positive charge at the benzyl position can be detected by the response of rates of cleavage as a function of substituents on the aromatic ring.

Kinetic Methods

The kinetics of the cleavage reaction were determined by measuring the thiocyanate equivalence titer of reaction solution aliquots. Excess standardized sodium thiocyanate was added to each aliquot and back-titrated with standardized silver nitrate. Mercuric acetate reacts with 2 equiv of thiocyanate per mole, and the adduct reacts with 1 equiv of thiocyanate per mole. Thus the thiocyanate consumed as determined by back titration with silver ion is equal to $2(A_0 - X) + X = 2A_0 - X$, where A_0 represents the initial molar concentration of mercuric acetate and X is equal to the molar concentration of adduct. Therefore, the order of the reaction can be determined by substitution into the appropriate integrated rate expressions, as the concentration of the cyclopropane is available from the known initial concentration and the stoichiometry of the reaction.



For mathematical convenience equimolar quantities of the cyclopropane and mercuric acetate were utilized in most runs. However, runs involving excess arylcyclopropane also were carried out.

The reactions were run in sealed ampoules at 75° and, for the longer runs, at 50°. In those cases where evaporation of solvent was not a problem, a single flask containing the reaction solution was used, and samples were withdrawn periodically by means of a pipet. The reaction was quenched by plunging the sealed tubes into an acetone–Dry Ice mixture. Samples withdrawn by pipet were delivered into flasks cooled to 0°.

A representative kinetic run is shown in Figure 1 for equimolar concentrations (0.033 M) of mercuric acetate and p-methylphenylcyclopropane at 50.1°.

For the reaction of p-methoxyphenylcyclopropane and for some of the runs with p-methylphenylcyclopropane it was necessary to use a partitioned flask. Solutions of mercuric acetate and the cyclopropane in acetic acid were placed in separate compartments and allowed to equilibrate prior to mixing the solutions. The flask was shaken to mix the two solutions. In order to quench such reactions the thiocyanate was delivered directly into the reaction flask.

Stability of Mercuric Acetate

Mercuric acetate reacts in acetic acid to reduce its effective thiocyanate titer by a factor of one-half. While this side reaction does not interfere with the cleavage of activated phenylcyclopropanes, it is a major competing reaction with the deactivated compounds. The nature of the reaction of mercuric acetate in acetic acid has not been examined in detail as it is not our first interest. Using the effective titer change of one-half for infinite reaction the function

$$[SCN^-] = X + 2(A_0 - X)$$

was evaluated where X represents the molar concentration of the mercury species which requires 1 equiv of thiocyanate in the titration and $A_0 - X$ is the concentra-

(1963); R. T. LaLonde and M. A. Tobias, *J. Amer. Chem. Soc.*, **85**, 3771 (1963); R. T. LaLonde and M. A. Tobias, *ibid.*, **86**, 4068 (1964).

(6) R. Ya. Levina, B. N. Kostin, and T. K. Ustynyuk, *Zh. Obshch. Khim.*, **30**, 359 (1960).

(7) We initially reported a small amount of cleavage of the alternate bond on the basis of nmr. However, we have since effected separation by vpc of the possible isomers and there are only products derived from cleavage of one bond.

tion of mercuric acetate. The apparent order of the reaction is quite low. Adequate straight-line fits are obtained for either 0.33- or 0.25-order reactions for two to three half-lives in the concentration range studied. The apparent rate constants at 50 and 75° are given in Table I for an assumed 0.33-order reaction. These

Table I. Decomposition of Mercuric Acetate

$(HgOAc_2)_0$	Temp, °C	k, $mol^{2/3}/l.^{2/3}$ sec
0.0199	50.0	2.0×10^{-7}
0.0215	75.0	4.0×10^{-6}
0.0417	75.0	3.1×10^{-6}

limited values provide sufficient information to allow a determination of the experimental limitations in a study of the cleavage reaction.

Stability of Phenylcyclopropane

In order to ascertain whether the reaction being studied was in fact a mercuric acetate induced cleavage of cyclopropanes and not a more complex sequence of reactions, the stability of phenylcyclopropane was examined. Although an acetic acid catalyzed isomerization to olefinic compounds followed by oxymercuration was regarded as unlikely, this possibility was checked. A solution of phenylcyclopropane in acetic acid was sealed in an nmr tube and maintained at 75° for 8 days. During this time period the sample showed no evidence of appreciable deterioration. The regions of the nmr spectrum where olefinic protons resonate remained blank. In addition there was no evidence of any acetic acid catalyzed cleavage products such as 1-phenylpropyl acetate.

Stability of Phenylcyclopropane–Mercuric Acetate Adduct

The stability of the phenylcyclopropane–mercuric acetate adduct is a necessity for the kinetic analytical scheme used to be valid. At 100° the adduct in acetic acid undergoes no noticeable change in the thiocyanate titer after 5 days. Therefore the decomposition of the adduct cannot complicate the kinetic analysis. Decomposition to yield mercury and cinnamyl acetate does occur slowly at 135° with $k = 8.6 \times 10^{-7}$ sec^{-1}.

For comparative purposes, the stability of 3-phenylpropylmercuric acetate in acetic acid was examined under the same conditions as those used for the adduct. The rate of reaction is approximately 20 times slower. Therefore it is likely that the 3-acetoxyl group in the adduct assists in the decomposition. Such 1,3-acetoxyl participation serves as a rationale for the decomposition product.[8]

Ichikawa[9] reported mercuric acetate increases the decomposition rate of benzylmercuric acetate in acetic acid–water–perchloric acid solvent systems. Therefore it was considered a possibility that mercuric acetate might react with the adduct formed in the cleavage step. The adduct of mercuric acetate and phenylcyclopropane was heated in the presence of mercuric acetate at 75° in acetic acid. The thiocyanate titer decreases with time from 3 to 2 equiv. However the rate of this change corresponds exactly to the decomposition reaction of mercuric acetate in acetic acid. By subtracting the titer equivalent of the adduct from the total titer, only a titer change corresponding to the mercuric acetate decomposition is indicated. Therefore a second-order decomposition of the adduct by mercuric acetate in a manner analogous to the reaction observed by Ichikawa with benzylmercuric acetate does not occur under the experimental conditions.

The second-order rate constants for the cleavage of the six arylcyclopropanes studied are listed in Table II.

Table II. Rate of Cleavage of Substituted Phenylcyclopropanes

Substituent	k, l./mol sec		
	25.0	50.1	75.6
p-CH_3O	5.7×10^{-2}	5.0×10^{-1}	
p-CH_3	2.2×10^{-3}	2.2×10^{-2}	1.7×10^{-1}
m-CH_3	3.3×10^{-4}	4.0×10^{-3}	3.7×10^{-2}
H	1.6×10^{-4}	2.2×10^{-3}	2.1×10^{-2}
p-Cl	4.7×10^{-5}	7.0×10^{-4}	7.5×10^{-3}
m-Cl	6.7×10^{-6}	1.2×10^{-4}	1.6×10^{-3}

Each rate constant reported is the average of two or more runs. Individual rate constants were reproducible to the extent of 2 to 3%. Equimolar quantities of mercuric acetate and cyclopropane were used for the p-MeO, p-Me, m-Me, and H compounds. However, it was necessary to use excess cyclopropane for the p-Cl and m-Cl compounds to allow the rate of cleavage to exceed the rate of decomposition of mercuric acetate.

The activation parameters, $\Delta H^{\pm}$ and $\Delta S^{\pm}$, for the compounds studied are listed in Table III. The enthalpies of activation were calculated from a plot of ln k/T *vs.* $1/T$ by the method of least squares. While the precision of the rates is approximately 2%, their accuracy is unknown. However, for an accuracy of 5% the reported enthalpies of activation are accurate to ±0.4 kcal/mol over the 50° range studied. The free energy of activation was calculated from the 50° data and used with the enthalpy of activation to obtain the entropy of activation for each compound.

Table III. Activation Parameters for the Cleavage of Arylcyclopropanes

Substituent	$\Delta H^{\pm}$, kcal/mol	$\Delta S^{\pm}$, cal/deg mol
p-CH_3O	16.0	−10.6
p-CH_3	17.0	−13.6
m-CH_3	18.5	−12.4
H	19.1	−11.7
p-Cl	19.9	−11.4
m-Cl	21.6	−9.8

A Hammett-type plot for the rate constants at 50° *vs.* σ^+ is shown in Figure 2. The calculated response is $\rho = -3.2$ with a correlation coefficient of $r = 0.98$. Although the correlation is not exceedingly good, the correlation with the alternate parameter σ is poorer. Clearly the magnitude of the response of rate to the substituent dictates the use of σ^+. The rate for p-methoxyphenylcyclopropane deviates to the largest extent from the correlation line. It may be that the p-methoxyl group is not as effective an electron-donating group in the reaction medium. One possibility that was con-

(8) R. J. Ouellette and R. D. Robins, *Tetrahedron Letters*, 397 (1968).
(9) K. Ichikawa and H. Ouchi, *J. Amer. Chem. Soc.*, **82**, 3876 (1960).

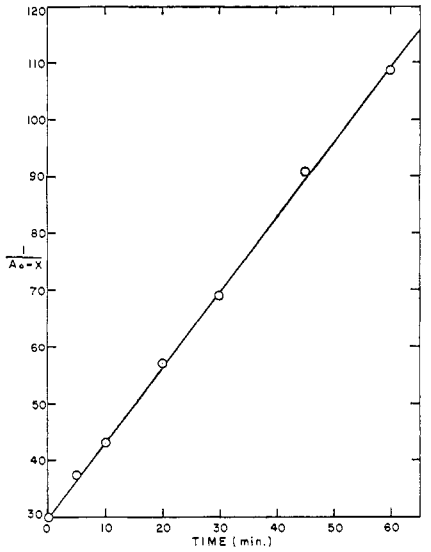


Figure 2.

sidered to explain the relative slowing of the *p*-MeO compound was a complex formed between mercuric acetate and the methoxyl group. Such complex formation should hinder the cleavage reaction. Introduction of anisole into the reaction of *p*-methylphenylcyclopropane and mercuric acetate at 50° does not alter the rate of cleavage. It appears that any decrease in the electron-donating ability of the methoxyl group is the result of the solvent itself. Acetic acid may retard partially the methoxyl group from donating electrons by a specific solvent–solute interaction at the methoxyl group.

The effect of added lithium acetate on the reaction is unimportant. The observed rate constant for *p*-methylphenylcyclopropane and mercuric acetate is given in Table IV and compared with the rate constants observed in the presence of lithium acetate and anisole.

Table IV. Effect of Addends on Rate at 50°

Mercuric acetate, *M*	*p*-Methylphenylcyclopropane, *M*	Lithium acetate, *M*	Anisole, *M*	*k*, l./mol sec
0.0334	0.0334	0.0	0.0	2.20×10^{-2}
0.0398	0.0398	0.0	0.0398	2.26×10^{-2}
0.0352	0.0352	0.141	0.0	2.20×10^{-2}

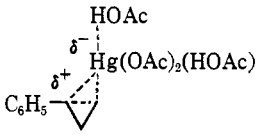
Conclusions

The observed kinetic order for the cleavage of cyclopropanes by mercuric acetate and the known electrophilic nature of mercuric acetate suggest that an Se2 reaction is involved. In addition the magnitude of ρ indicates the deposition of a large positive charge at the benzylic carbon atom in the transition state. The ρ for the cleavage reaction approaches the ρ for the solvolysis of aryldimethylcarbinyl chlorides which Brown[10] used to establish the σ^+ scale.

The electrophilic reagent must be mercuric acetate itself or some related ion pair. If $^+$HgOAc were the attacking reagent then a mass law effect should have been observed with added acetate ion. Another interesting possibility which seems to be precluded on the basis of the same experiments is the formation of $Hg(OAc)_4^{2-}$. Mercury(II) forms tetrahedral complexes readily in aqueous solution. Such complex formation in acetic acid would lead to a dianion which is isoelectronic with the well-known oxidizing agent lead tetraacetate. On the basis of orbital availability of the covalent mercury(II) salts as compared to Pb(IV) compounds it would be expected that mercury(II) acetate would be a more effective electrophile than lead(IV) acetate. Formation of $Hg(OAc)_4^{2-}$ should decrease the rate of cleavage of the cyclopropane ring as the electrophilicity of the mercury(II) has been decreased. The formation of $Hg(OAc)_3^-$ in acetic acid would be anticipated to be more favorable than $Hg(OAc)_4^{2-}$ on the basis of the poor ion-solvating character of the medium. However, the formation of $Hg(OAc)_3^-$ appears unlikely as it is unreasonable to expect $Hg(OAc)_2$ and $Hg(OAc)_3^-$ to be of identical electrophilicity. Since the rate of cleavage is not affected by added acetate ion the species $Hg(OAc)_4^{2-}$ and $Hg(OAc)_3^-$ probably are not formed in acetic acid at the concentrations investigated. The above arguments are largely speculative but will have to be considered when comparisons are made with salts of Tl(III) and Pb(IV).

Two solvent molecules per molecule of mercuric acetate could be attached to mercury forming a four-coordinate mercury(II) electrophile. If this is the case, the mercury species could serve as an electrophile only if it releases one ligand in the transition state. Displacement of solvent would be expected to be more facile than displacement of acetate ion.

The transition state for cleavage of phenylcyclopropane by mercuric acetate is postulated to resemble structure I. The magnitude of ρ dictates the deposition of



I

considerable positive charge at the benzylic position. This in turn indicates that the carbon–mercury bond is significantly formed in the transition state and that the mercury atom is not symmetrically situated with respect to the edge of the cyclopropane ring. Replacement of the ligand acetic acid in the transition state is more palatable than acetate ion although this choice is speculative and the magnitude of the selectivity of such a competitive process cannot be shown. Bimolecular processes often are associated with large negative entropy of activation. In the case of cleavage of arylcyclopropanes, the entropy of activation is not very high and it is possible to rationalize this fact by postulating that a ligand becomes effectively dissociated from mercury in the cleavage step. This postulate is in agreement with the degree of positive charge generated at the benzylic carbon and the extent of carbon–mercury bond formation.

There are similarities between the cleavage of cyclopropanes by mercuric acetate, which may be termed an oxymercuration, and the deoxymercuration reaction investigated by Kreevoy.[11] Oxymercurated adducts of olefins have been deoxymercurated in water. The

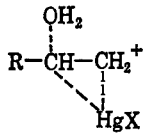
(10) H. C. Brown and Y. Okamoto, *J. Amer. Chem. Soc.*, 79, 1913 (1957).

(11) L. L. Schaeleger, M. A. Turner, T. C. Chamberlin, and M. M. Kreevoy, *J. Org. Chem.*, 27, 3421 (1962).

Table V. α-Arylallyl Alcohols

X	Yield, %	Bp, °C (mm)	Calcd C	Calcd H	Calcd Cl	Found C	Found H	Found Cl
p-MeO	64	100–103 (0.35)	73.15	7.37	...	73.27	7.31	...
p-Me	66	72–73 (0.35)	81.04	8.16	...	81.29	8.23	...
m-Me	56	72–75 (0.40)	81.04	8.16	...	81.04	8.10	...
H	60	76–77 (18)	...	...	...	...	...	...
p-Cl	66	80–81 (0.18)	64.11	5.38	21.03	64.03	5.42	20.69
m-Cl	45	82–84 (0.65)	64.11	5.38	21.03	63.93	5.33	20.72

alkyl-substituted adducts exhibit $\rho = -2.8$. Although the solvent systems and structures of the compounds in Kreevoy's and this work are different there are great similarities in the electronic requirements for the two reactions. The transition state suggested by Kreevoy is represented as structure II and our postulated transition state is a homologated version of Kreevoy's.



II

Levina[12] has determined that complexes form between mercuric acetate and cyclopropanes which do not involve bond cleavage. The conclusion is based on conductivity measurement and the calculated equilibrium constant is very low. Under the kinetic conditions employed in this study such a complex would constitute less than 1% of the total species present. However, such complex formation could be accommodated in the kinetic scheme by placing the complex in equilibrium with the starting materials. The complex could be transformed into the activated complex or free starting material could proceed to the transition state *via* an associative process which is different from that involved in complex formation.

Cyclopropane complex formation has been reported in the case of chloroplatinic acid.[13] However, the apparent complex has been shown to have resulted from cleavage of the cyclopropane ring.[14]

It was considered of interest to determine if complex formation with mercuric acetate might be detected. The ultravolet spectrum of phenylcyclopropane and mercuric acetate in methanol is identical with that calculated from the summation of the spectrum of each compound. These observations are illustrated in Figure 3. While these data do not eliminate in a rigorous manner the presence of a complex without ring cleavage, they are suggestive that such a possibility is not an important consideration in the cleavage reaction studied.

Experimental Section

Preparation of α-Arylallyl Alcohols. The general method for the preparation of α-arylallyl alcohols is described for α-phenylallyl alcohol. Phenylmagnesium bromide was prepared by adding 3 ml of a solution of 31.4 g (0.20 mol) of bromobenzene in 25 ml of anhydrous ether to a mixture of 100 ml of ether and 5 g (0.21 g-atom) of freshly polished magnesium turnings. In order to ensure rapid initiation of the reaction, several drops of ethylene bromide were added. The remaining ethereal solution of bromobenzene was added dropwise, and the reaction mixture was continuously stirred. Thirty minutes after completion of the addition of the bromide, a solution of 11.8 g (0.21 mol) of acrolein in 15 ml of anhydrous ether was added dropwise. The resultant product was poured into 100 ml of 15% aqueous ammonium chloride and ice. After suction filtration through a glass wool pad the layers of the

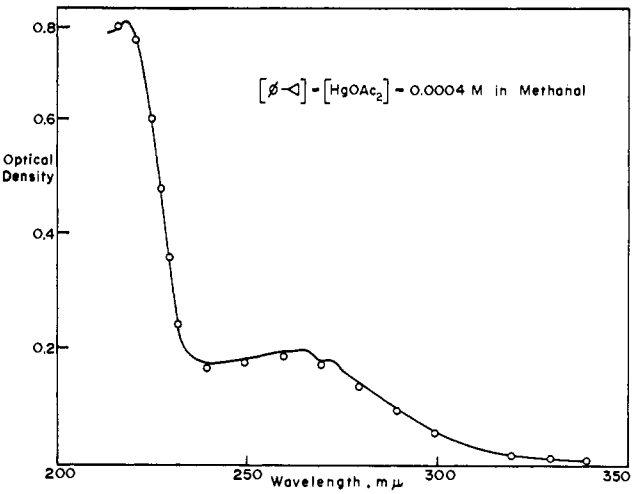


Figure 3.

filtrate were separated, and the aqueous layer was extracted with 50 ml of ether. The combined extracts were dried over magnesium sulfate, filtered, and concentrated under reduced pressure. The concentrate was vacuum distilled through a 15-cm Vigreux column. A 60% yield or 15.7 g of α-phenylallyl alcohol was obtained, bp 76–77° (18 mm) (lit.[15] 53–54° (0.15 mm)). Analysis by nmr of this compound and the analogous compounds listed in Table V showed complex multiplets at τ 3.7–4.3 (1 H) in carbon tetrachloride which are characteristic for these structures.

Preparation of 1,3-Dibromo-1-arylpropanes. The general method used to prepare the 1,3-dibromo-1-propanes is described for 1,3-dibromo-1-phenylpropane. Hydrogen bromide was bubbled through a solution of 6.50 g (0.04 mol) of α-phenylallyl alcohol in 20 ml of ether at 10° with stirring for 30 min. Subsequently 0.1 g of antimony tribromide was added and the hydrogen bromide addition continued for 2 hr. The mixture was poured over ice and extracted with ether. The ethereal solution was washed with cold water, dried over anhydrous magnesium sulfate, filtered, and concentrated under reduced pressure. The concentrate was vacuum distilled through a 10-cm Vigreux column and a 65% yield of 8.84 g (0.032 mol) of 1,3-dibromo-1-phenylpropane, bp 93–95° (0.75 mm) (lit.[16] bp 142–143° (10 mm)), was obtained. Tables VI and VII give further analyses of 1,3-dibromo-1-arylpropanes.

The time required for complete reaction is a function of the ring substituent with the *p*-methoxy and *p*-methyl compounds reacting rapidly without addition of antimony tribromide. However, the compounds with *p*-methoxy and *p*-methyl substituents were unstable. Therefore, only their nmr spectra were determined prior to closing the cyclopropane ring. All dibromides exhibited a quartet

(12) R. Ya. Levina, *Zh. Obshch. Khim.*, **34**, 2512 (1964).
(13) C. F. H. Tipper, *J. Chem. Soc.*, 2045 (1955).
(14) D. M. Adams, J. Chatt, R. G. Guy, and N. Sheppard, *ibid.*, 738 (1961).
(15) E. A. Braude, E. R. H. Jones, and E. S. Stern, *ibid.*, 401 (1946).
(16) M. Lespieau, *Compt. Rend.*, **190**, 1129 (1930).

Table VI. Yields and Boiling Points of 1,3-Dibromo-1-arylpropanes

Substituent	Yield, %	Bp, °C (mm)
m-CH_3	84	108–110 (0.6)
H	80	94–95 (0.7)
p-Cl	82	102–104 (0.2)
m-Cl	70	105–106 (0.2)

Table VII. Elemental Analysis of 1,3-Dibromo-1-arylpropanes

	Calcd				Found			
Substituent	C	H	Br	Cl	C	H	Br	Cl
m-CH_3	41.13	4.14	54.73	...	41.13	4.32	54.56	...
H	38.89	3.63	57.47	...	38.98	3.51	57.39	...
p-Cl	34.60	2.90	51.15	11.35	34.99	2.98	51.13	10.96
m-Cl	34.60	2.90	51.15	11.35	34.58	2.95	51.25	11.20

(1 H) at τ 4.9 and multiplets (2 H) at τ 7.45 and (2 H) at τ 6.65 in carbon tetrachloride.

Preparation of Arylcyclopropanes (Method I). The preparation of the arylcyclopropanes by the closure of 1,3-dibromide is illustrated using phenylcyclopropane as an example. To a mixture of 14 g (0.21 mol) of granular zinc–copper couple and 700 ml of anhydrous ether was added 33.6 g (0.12 mol) of 1,3-dibromo-1-phenylpropane in one portion. Upon addition of the dibromide the ether immediately began to reflux. The mixture was stirred under reflux for 24 hr and the ethereal solution was decanted from the excess zinc and washed once with saturated ammonium chloride, once with saturated sodium bicarbonate, and finally with water. The ether was dried over anhydrous magnesium sulfate, filtered, and concentrated. The remaining liquid was vacuum distilled through a 15-cm Vigreux column. A 35% yield of 4.9 g (0.042 mol) of phenylcyclopropane was obtained, bp 69–70° (21 mm) (lit.[17] bp 170–175°). Analysis by nmr showed complex multiplets at τ 8.25 (1 H) and τ 9.25 (4 H).

Preparation of *p*-Methoxyphenylcyclopropane (Method II). To a stirred slurry of 9.6 g (0.24 mol) of lithium aluminum hydride in 300 ml of dry glyme, a glyme solution of 48.6 g (0.24 mol) of ethyl *p*-methoxycinnamate was added dropwise. The mixture was stirred under reflux for 16 days. The mixture was cooled to room temperature, 250 ml of ether was added, and the hydride was hydrolyzed with water. The solid was suction filtered and washed with ether. The filtrate was washed several times with water, and the ethereal solution was dried over anhydrous magnesium sulfate, filtered, and concentrated under reduced pressure. The residue was vacuum distilled through a 15-cm Vigreux column. A 50% yield of 18.2 g (0.12 mol) of *p*-methoxyphenylcyclopropane was obtained, bp 77–80° (8 mm).

Preparation of *p*-Methylphenylcyclopropane (Method II). Using above procedure with 51.8 g (0.27 mol) of ethyl *p*-methylcinnamate and 10.8 g (0.27 mol) of lithium aluminum hydride in 300 ml of dry glyme for 16 days at reflux, 58% yield of 20.6 g (0.16 mol) of *p*-methylphenylcyclopropane was obtained, bp 67–68° (8 mm).

Kinetic Analysis. Solutions of the desired concentrations of arylcyclopropanes and mercuric acetate in acetic acid were prepared gravimetrically. The concentration range employed was 0.004–0.08 *M*. Aliquots of 2 ml were sealed in test tubes for runs at the higher temperatures. When volatility was not a problem, 2-ml aliquots were directly taken from a flask containing the reaction mixture. Samples were cooled in either isopropyl alcohol–Dry Ice or in ice water depending on the rate of the reaction and the temperature being examined. The samples were transferred to a 50-ml flask by adequately washing out the test tubes containing the sample with water. An aliquot of standardized sodium thiocyanate (*ca.* 0.02 *m*) was added to ensure an excess of the reagent. Titration of the excess thiocyanate was carried out at 0° using standardized silver nitrate. The indicator was ferric ammonium sulfate in dilute nitric acid.

Similar procedures as described above were used to determine the stability of mercuric acetate and the phenylcyclopropanemercuric acetate adduct.

Preparation of 3-(*p*-Anisyl)-3-acetoxypropylmercuric Acetate. Into a 100-ml, round-bottomed flask was placed 2.93 g (0.0196 mol) of *p*-methoxyphenylcyclopropane, 5.64 g (0.0177 mol) of mercuric acetate, and 100 ml of glacial acetic acid. The reaction mixture was maintained at 50° for 2 hr at which time a trace of mercury was noted. The solvent was removed under vacuum at room temperature and a white solid was obtained. This white solid was purified by stirring with 50 ml of hexane for 16 hr. The white solid was filtered and 7.75 g of the adduct, mp 70.0–71.5°, was obtained analytically pure. *Anal.* Calcd for $C_{14}H_{18}HgO_5$: C, 36.01; H, 3.89. Found: C, 35.90; H, 3.98. The nmr spectrum of the adduct in pyridine exhibited resonances at τ 4.3 (t, benzyl proton), 6.5 (s, methoxyl protons), 8.0 (s, acetate protons), and 8.1 (s, acetate protons). The remaining protons were complex multiplets in the τ 8–9 region. The Hg^{199} satellites were not determined.

The adduct was demercurated by the method of Brown[18] to produce 1-(*p*-anisyl)propyl acetate which was identified by its nmr spectrum.

3-Phenyl-3-acetoxypropylmercuric Acetate. This adduct was prepared in a manner similar to that described for the *p*-methoxyphenylcyclopropane adduct. It was identified by its nmr spectrum, τ 4.2 (t, benzyl proton), 8.1 (s, acetate protons), and 8.2 (s, acetate protons), and chemical analysis. *Anal.* Calcd for $C_{13}H_{16}HgO_4$: C, 35.65; H, 3.68; Hg, 45.90. Found: C, 35.63; H, 3.57; Hg, 45.65.

Table VIII. Yields and Boiling Points of Substituted Phenylcyclopropanes

X	Yield, %	Bp, °C (mm)	Lit. bp, °C (mm)
p-MeO	16[a]	103–104 (34–36)	223.5–224 (745)[c]
p-Me	22[a]	79–80 (14)	194–194.5 (745)[c]
m-Me	44	100–103 (34–36)	194 (742)[d]
p-Cl	51	107–109 (24–25)	76–77 (7)[e]
m-Cl[b]	49	113–115 (35)	...

[a] Yield was based on the starting phenylallyl alcohol. [b] *Anal.* Calcd for C_9H_9Cl: C, 70.82; H, 5.94; Cl, 23.30. Found: C, 70.76; H, 6.09; Cl, 23.41. [c] R. Ya. Levina, Y. S. Shabarov, K. S. Shanazarov, and E. G. Treschclova, *Vestn. Mosk. Univ., Ser. Mat. Mekh. Astron. Fiz. Khim.*, **12**, 145 (1957). [d] R. Ya. Levina, P. A. Gembitskii, V. N. Kostin, and E. G. Treshchova, *Zh. Obshch. Khim.*, **33**, 359 (1963). [e] R. Ya. Levina, V. K. Potapov, A. M. Osipov, and E. G. Treshchova, *ibid.*, **30**, 3874 (1960).

(17) T. F. Corbin, R. C. Hahn, and H. Shechter, *Org. Syn.*, **44**, 30 (1964).

(18) H. C. Brown and P. Geoghegan, Jr., *J. Amer. Chem. Soc.*, **89** 1522 (1967).