aminomethylferrocenes that the 1,2 isomer could be distinguished from the 1,3 isomer by the presence of a methylene AB quartet in the nmr spectrum of the 1,2 isomer. This method appears to be solvent dependent, since in the present study the 2-iodo compound gave singlets in both DMSO-$d_6$ and acetonitrile. More importantly each of those 2-haloferrocene derivatives exhibited methylene singlets in $CCl_4$, the solvent utilized in the original study.

**Registry No.**—Ia, 12085-94-8; Ib, 12110-60-0; Ic, 12302-05-5.

**Acknowledgement.**—We would like to thank Professor C. R. Hauser and Professor B. W. Rockett for sending us their procedures for synthesis of the 2-halodimethylaminomethylferrocenes prior to their publication. Acknowledgement is also made of a preprint of an nmr study of diastereotopic protons in 2-substituted dimethylaminomethylferrocenes and derivatives sent by Professor Rockett. Lastly, we would like to thank Professors D. Koster and H. S. Gutowsky for helpful comments. Acknowledgement is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

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# Oxidation of Substituted Styrenes by Thallium Triacetate[1]

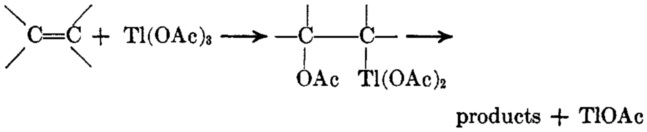
ROBERT J. OUELLETTE, GARY KORDOSKY, CHARLES LEVIN, AND STEVE WILLIAMS

*Evans Chemical Laboratory, The Ohio State University, Columbus, Ohio 43210*

*Received July 7, 1969*

The products and kinetics of the oxidation of six ring-substituted styrenes by thallium triacetate in acetic acid have been determined. Two products, 1-aryl-1,2-ethanediol diacetate and 2-aryl-1,1-ethanediol diacetate, are obtained, with the latter predominating as the electron-donating ability of the ring substituent increases. A correlation of the logarithm of the product ratio with Brown $\sigma^+$ values has been found with $\rho^+ = -1.7$. 1-Deuteriostyrene yields 1-deuterio-1-phenyl-1,2-ethanediol diacetate and 1-deuterio-2-phenyl-1,1-ethanediol diacetate. The rate of oxythallation of styrenes is second order, first order in each reactant. A Hammett-type correlation with Brown $\sigma^+$ values has been established with $\rho^+ = -2.2$. The activation parameters $\Delta H^{\ddagger} =$ 7.9 kcal/mol and $\Delta S^{\ddagger} = -41$ cal/deg for the reaction of *p*-methylstyrene have been evaluated from rate data at 19.7, 50.1, and 75.0°. The activated complex for oxythallation has approximately the same carbonium ion character as for oxymercuration. The effect of styrene structure on product distribution suggests that the decomposition of an oxythallated adduct proceeds *via* a carbonium ion intermediate resulting from loss of thallium(I).

In a limited comparative product study, Kabbe[2] found that the oxidative properties of thallium triacetate toward some styrenes are between those of mercuric acetate and lead tetraacetate. The products of the reaction of styrene with thallium triacetate in acetic acid are 2-phenyl-1,1-ethanediol diacetate (8.5% yield) and 1-phenyl-1,2-ethanediol diacetate (71% yield). Only 2-(*p*-methoxyphenyl)-1,1-ethanediol diacetate was reported for the reaction with *p*-methoxystyrene. The products obtained have been rationalized as being derived from an olefin–metal salt adduct which may then decompose under reaction conditions *via* carbonium ion intermediates. The metal has gained two electrons in the process and is therefore reduced.



$$>C=C< + Tl(OAc)_3 \longrightarrow -\underset{OAc}{\overset{|}{C}}-\underset{Tl(OAc)_2}{\overset{|}{C}}- \longrightarrow \text{products} + TlOAc$$

The first step has analogy in the well-known oxymercuration reaction. While the mercuric acetate–olefin adducts can be obtained easily,[3] only two thallium triacetate–olefin adducts have been isolated and characterized.[2,4]

No quantitative information exists on the rates of oxythallation of olefins by $Tl(OAc)_3$ in acetic acid. Therefore, the exact nature of this process and its possible similarity to oxymercuration of olefin by $HgOAc_2$ has yet to be determined. However, the kinetics of oxymercuration[5] by $Hg^{2+}$ and oxythallation[6] by $Tl^{3+}$ have been determined in aqueous perchloric acid.

There are no systematic studies of a series of related olefins which would provide quantitative information about the postulated solvolytic decomposition of oxythallated adducts compared with oxymercurated adducts. The solvolytic stability of carbon–metal bonds decreases in the order Hg > Tl > Pb. The likelihood of isolating oxythallated adducts and being able to determine their reactivity makes these compounds invaluable models for elucidating the parameters controlling lead tetraacetate oxidations.[7,8]

## Results

**Product Studies.**—A series of substituted styrenes was treated with thallium triacetate in anhydrous acetic acid at 75°. Thallium triacetate was prepared and used *in situ* by the addition of thallic oxide to anhydrous acetic acid containing about twice the amount of acetic anhydride needed to remove the water produced in the formation of the thallium triacetate.[9,10] To this solution the styrene was added

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[1] The authors gratefully acknowledge Grant GP 3873 from the National Science Foundation in support of this work.

[2] H. J. Kabbe, *Ann.*, **656**, 204 (1962).

[3] J. Chatt, *Chem. Rev.*, **48**, 7 (1951).

[4] K. C. Pande and S. Winstein, *Tetrahedron Lett.*, 3393 (1964).

[5] J. Halpern and H. B. Tinker, *J. Amer. Chem. Soc.*, **89**, 6427 (1967).

[6] P. M. Henry, *ibid.*, **87**, 4423 (1965).

[7] A. South, Jr., and R. J. Ouellette, *ibid.*, **90**, 7064 (1968).

[8] R. J. Ouellette, D. Miller, A. South, Jr., and R. D. Robins, *ibid.*, **91**, 971 (1968).

[9] A. South, Jr., Ph.D. Thesis, The Ohio State University, 1966.

[10] South[9] has shown that the reaction of phenylcyclopropane with thallium triacetate prepared *in situ* proceeds to give the same product ratio as the reaction with pure thallium triacetate. Therefore, it was assumed that the reaction of styrene with thallium triacetate prepared *in situ* proceeds in a manner identical with the reaction of styrene with pure thallium triacetate which was employed in the kinetic studies.

such that thallic oxide was present in a 50% molar excess. The following series of styrenes was used: styrene, *m*-chlorostyrene, *p*-chlorostyrene, *m*-methylstyrene, *p*-methylstyrene, and *p*-methoxystyrene. The only products observed by vapor phase chromatographic analysis were the 1-aryl-1,2-ethanediol diacetates and the 2-aryl-1,1-ethanediol diacetates. No 1-aryl-1,1-ethanediol diacetates or the related substituted acetophenones were detected. Each product was identified by its vpc retention time compared with that of an authentic sample and by collection from the vpc column and identification by nuclear magnetic resonance spectroscopy. The results obtained are listed in Table I. The products are stable to the analytical conditions.

TABLE I
PRODUCT RATIOS FOR THE REACTION OF THALLIUM TRIACETATE WITH SUBSTITUTED STYRENES

| Substituent | Registry no. | 1,2-Diacetate, % | 1,1-Diacetate, % | Ratio |
|---|---|---|---|---|
| *p*-$CH_3O$ | 637-69-4 | 35.7 | 64.3 | 1.80 |
| *p*-$CH_3$ | 622-97-9 | 74.6 | 25.4 | 0.34 |
| *m*-$CH_3$ | 100-80-1 | 87.6 | 12.4 | 0.14 |
| H | 100-42-5 | 92.4 | 7.6 | 0.083 |
| *p*-Cl | 1073-67-2 | 94.2 | 5.8 | 0.061 |
| *m*-Cl | 2039-85-2 | 98.0 | 2.0 | 0.020 |

The products do not rearrange under the reaction conditions. *p*-Methylstyrene was treated with thallium triacetate prepared *in situ* and worked up at 33, 48, and 96 hr. The vpc analysis indicated that the relative amounts of the 2-(*p*-methylphenyl)-1,1-ethanediol diacetate and the 1-(*p*-methylphenyl)-1,2-ethanediol diacetate are the same.

Since a 50% excess of thallic oxide was always used, a reaction using a 100% excess of styrene was run in an effort to determine if any unsaturated products such as the $\alpha$- and $\beta$-acetoxystyrene were being produced and then were reacting further. No new products were observed by vpc analysis. The ratio of the 1,2-diacetate to the 1,1-diacetate was 12:1 compared with the ratio 12.2:1 obtained from the reaction using a 50% excess of thallic oxide.

**Kinetic Analysis.**—We have shown that the reaction of thallium triacetate can be followed by quenching the reaction with excess aqueous 5% potassium iodide solution and then back-titrating the triiodide formed with standard sodium thiosulfate.[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.[7] The formation of the

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

double salt causes a rapid decrease in the rate of cleavage of cyclopropanes. In a similar manner, a second-order plot of the reciprocal of the thallium(III) concentration against time for equimolar concentrations of styrene and thallium triacetate demonstrates this decrease (Figure 1). However, there is still reaction occurring after 1 half-life.

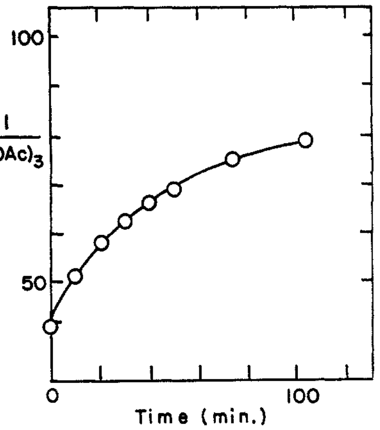


Figure 1.—Kinetic evidence for formation of $Tl_2(OAc)_4$ in the oxidation of styrene at 50.1°.

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 styrenes by *free thallium triacetate*, we have employed the method previously described.[7] For the case in which the concentration of thallium triacetate ($A$) is twice that of styrene, 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 at 50° for the rates of oxidation of the series of substituted styrenes are listed in Table II. The reported values are the average of at least duplicate runs. Individual rate constants deviate from the average values by no more than 2%. A typical run is illustrated in Figure 2. The logarithm of the rate constants at 50.1° correlates well with Brown $\sigma^+$ values. The data is illustrated in Figure 3 with $\rho^+ = -2.2$.

TABLE II
RATES OF REACTION OF THALLIUM TRIACETATE WITH SUBSTITUTED STYRENES

| Substituent | $k$, l./mol min. | Temp, °C |
|---|---|---|
| *p*-$CH_3O$ | 36.4 | 50.1 |
| *p*-$CH_3$ | 0.63 | 19.7 |
| *p*-$CH_3$ | 2.56 | 50.1 |
| *p*-$CH_3$ | 6.4 | 75.1 |
| *m*-$CH_3$ | 0.94 | 50.1 |
| H | 0.68 | 50.1 |
| *p*-Cl | 0.22 | 50.1 |
| *m*-Cl | 0.094 | 50.1 |

For the oxidation of *p*-methylstyrene, the activation parameters were determined from a least-squares analysis of a log $k/T$ *vs.* $1/T$ plot. The enthalpy and entropy of activation are 7.9 kcal/mol and −41 cal/(°K mol). If the precision of the rate constants is ap-

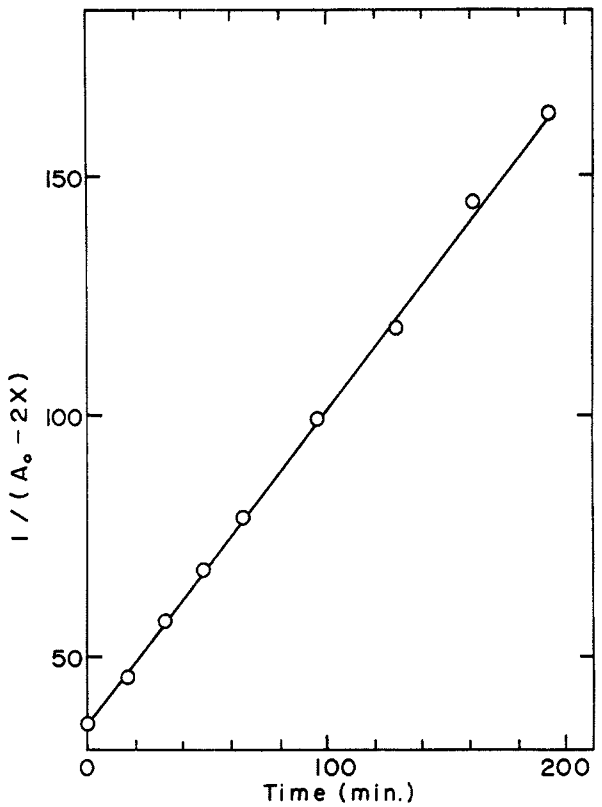
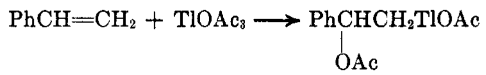


Figure 2.—Typical second-order plot for the oxidation of styrene by thallium triacetate at 50.1°.

proximately 3%, the enthalpy of activation is precise to ±0.2 kcal/mol for the temperature range studied.[11]

## Discussion

The products of oxidation of styrenes by thallium triacetate most likely are derived from an unstable oxythallated adduct which results from Markownikoff ad-



$$PhCH{=}CH_2 + TlOAc_3 \longrightarrow \underset{OAc}{PhCH}CH_2TlOAc$$

dition. Both the negative $\rho^+$ for the reaction and the large negative entropy of activation suggest an ordered transition state in which considerable carbon–thallium bond making has occurred and a substantial positive charge has developed at the benzylic carbon atom.

By comparison, the $\rho^+$ for the cleavage of cyclopropanes by thallium triacetate[7] is more negative (−4.4) and the entropy of activation less negative [−29.2 cal/(°K mol)]. Therefore, it appears that the styrene addition may involve more of a symmetrical $\pi$ complex, whereas the cyclopropane cleavage reaction has more $\sigma$ bonding between carbon and thallium. The more direct $\sigma$ bonding in the case of cyclopropane cleavage creates a higher positive charge at the benzyl carbon atom. In addition, the cleavage of the cyclopropane ring with concomitant thallium triacetate addition would be expected to lead to a somewhat more positive entropy of activation with respect to the styrene addition, in which there is no release of the constraint of atoms of a ring.

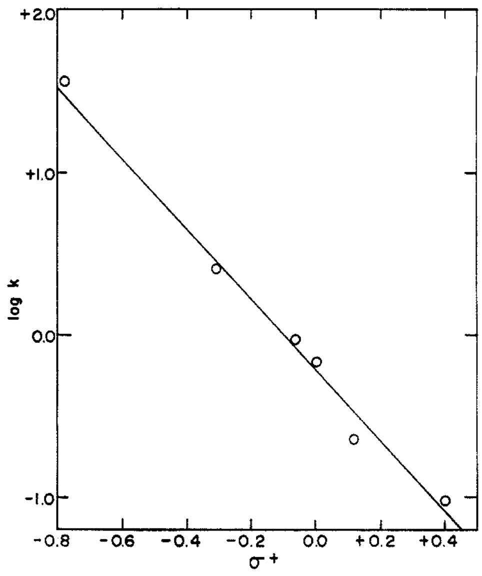


Figure 3.—Hammett plot of the rates of oxidation of styrenes by thallium triacetate.

Kreevoy[12] has reported that the rates of deoxymercuration of alkyl-substituted oxymercurated olefin adducts in water are correlated with $\sigma^*$ and exhibit $\rho^* = -2.8$. While both the solvent system and the substrates differ from those reported in this paper, it appears that there are similarities in the addition reaction of thallium triacetate in acetic acid and the deoxymercuration reaction in water. However, the presence of iodide in the deoxymercuration reaction means that, strictly speaking, the two reactions are not reverse of each other.

Halpern[5] reported $\rho^* = -2.77$ for the hydroxymercuration of alkenes in water by $Hg^{2+}$. There is postulated to be "a high degree of positive charge localization (approaching carbonium ion character) in the transition state." However, the carbonium ion is not free or open, as *cis–trans* isomerization was not observed.

Henry[6] observed that the oxythallation of alkenes in water by $Tl^{3+}$ involves an activated complex which has considerably more carbonium ion character than for oxymercuration. Propylene reacts with $Tl^{3+}$ 167 times faster than with ethylene in 0.25 $M$ $HClO_4$ solution. With $Hg^{2+}$ in 0.01 $M$ $HClO_4$, propylene reacts 20 times faster than ethylene. The $\rho^*$ for Henry's data is approximately −4.7.[13] The ordering of $\rho$ values for $Hg^{2+}$ and $Tl^{3+}$ reacting with olefins in aqueous perchloric acid parallels the $\rho^+$ values of −3.2 and −4.3 for the cleavage of cyclopropanes in anhydrous acetic acid by $Hg(OAc)_2$ and $Tl(OAc)_3$, respectively. Therefore, $Tl^{3+}$ is a more selective electrophile than $Hg^{2+}$ under comparable reaction conditions independent of attached ligand or the solvent.

The closest analogous reaction for our system involves the bromination of styrenes in acetic acid.[14] The separated second-order rate constants are correlated with $\sigma^+$ with $\rho^+ = -2.23$. The reaction is postulated to involve a cyclic bromonium ion in contrast to the more open classical carbonium ion in the chlorination of styrenes. The activation parameters, $\Delta H^{\ddagger} = 11.3$ kcal/mol and $\Delta S^{\ddagger} = -27$ cal/°K, also

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(11) J. E. Leffler, *J. Org. Chem.*, **31**, 533 (1966).

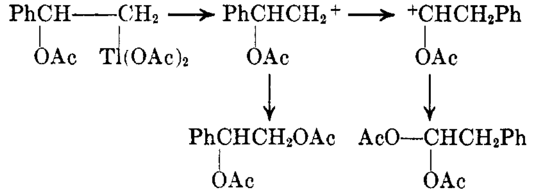
(12) L. L. Schaeleger, M. A. Turner, T. C. Chamberlin, and M. M. Kreevoy, *ibid.*, **27**, 3421 (1962).

(13) The value is calculated by this author.

(14) K. Yates and W. V. Wright, *Tetrahedron Lett.*, 1927 (1965).

resemble those observed in the oxythallation reaction. The similarity of the reaction parameters of oxythallation and bromination support our postulation of a transition state involving a $\pi$ complex which is different in degree from that observed in the oxythallation of cyclopropanes.

The products that result from the decomposition of the oxythallated adduct can be rationalized as being derived from a carbonium ion like species. Solvolysis of the carbon–thallium bond leads to the formation of a carbonium ion which may undergo a 1,2-aryl shift. The amount of rearranged product, 2-aryl-1,1-ethanediol diacetate, compared with the amount of unrearranged product, 1-aryl-1,2-ethanediol diacetate, is a function of the ease of migration of the aryl group.



$$\underset{OAc}{PhCH}-\underset{Tl(OAc)_2}{CH_2} \longrightarrow \underset{OAc}{PhCHCH_2^+} \longrightarrow \underset{OAc}{^+CHCH_2Ph}$$

$$\underset{OAc}{PhCHCH_2OAc} \qquad AcO-\underset{OAc}{CHCH_2Ph}$$

The 1- deuterio-1-phenyl-1,2- ethanediol diacetate and 1-deuterio-2-phenyl-1,1-ethanediol diacetate obtained from the oxidation of 1-deuteriostyrene are the products expected from Markownikoff addition followed by solvolytic decomposition of the organothallium intermediate.

The logarithm of the ratio of the amount of 1,1-diacetate to 1,2-diacetate is linearly related to $\sigma^+$ with $\rho^+ = -1.7$ (Figure 4). This indicates quite clearly the resonance interaction of the positive center(s) in the decomposition step with the aromatic ring.

Henry observed a similar trend of products which were postulated to arise from decomposition of the oxythallated adducts. Both glycols and carbonyl compounds were obtained for the six alkenes studied. While the trend of product ratios is qualitatively the same as ours, the data of Henry has not been quantitatively related to any $\sigma$ function.

## Experimental Section

**Purification of Styrenes.**—Styrene, *m*-methylstyrene, *p*-methylstyrene, *m*-chlorostyrene, and *p*-methoxystyrene were purchased from Columbia Chemicals and were purified by means of a vacuum transfer prior to reaction.

**Product Studies.**—In a typical experiment, 0.2368 g (0.002 mol) of *m*-methylstyrene was weighed into a 50-ml round-bottom flask containing 20 ml of glacial acetic anhydride and 0.831 g (0.008 mol) of distilled acetic anhydride. To the resulting solution, 1.3703 g (0.003 mol) of thallic oxide was added and the reaction vessel was stoppered, swirled, and immersed in a 75° constant-temperature bath. After a 60-hr period, the reaction solution was light yellow in color. The reaction mixture was then transferred into a 125-ml separatory funnel and 30 ml of distilled water was added. The resulting solution was a cloudy light yellow and it was extracted with three 15-ml portions of ether. The ether extracts were combined and washed with four 10-ml portions of distilled water, two 10-ml portions of saturated sodium bicarbonate, and again with 10 ml of distilled water. The ethereal layer was dried over a minimum of anhydrous magnesium sulfate for 15 min, filtered, and concentrated on a rotary evaporator. The components of the light yellow oil which remained were identified by comparing vpc retention times with authentic samples using a 2-ft 20% Carbowax 20 M on a 60/80 Chromosorb P column at 165°. In addition, the reaction products were collected from the vpc column and identified by their nmr spectra.

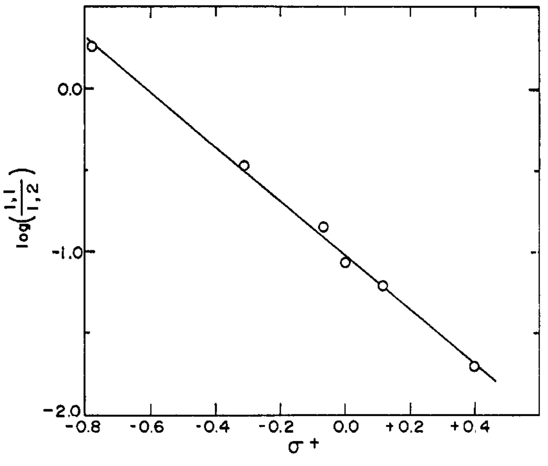


Figure 4.—Correlation of product ratios with $\sigma^+$.

**Preparation of 2-Aryl-1,1-ethanediol Diacetates.**—The appropriate styrene was converted into the oxide by means of *m*-chloroperbenzoic acid in methylene chloride. The oxide was isomerized to the arylacetaldehyde by boron trifluoride etherate in anhydrous ether. Conversion of the acetaldehyde into the diacetate was accomplished by the use of acetic anhydride with boron trifluoride etherate catalyst. Proper elemental analytical data was obtained for all compounds except the *m*-methyl and *p*-methoxy derivatives, which were identified by their characteristic nmr spectrum. All compounds exhibited a six-proton singlet near $\tau$ 8, a two-proton doublet at $\tau$ 7 with $J$ = 5.5 Hz, and a one-proton triplet at $\tau$ 3 with $J$ = 5.5 Hz, in addition to the aromatic protons multiplets and ring substituent resonances. Individual descriptions of experimental details are given in thesis form.[15]

**Preparation of 2-Aryl-1,2-ethanediol Diacetates.**—The appropriate styrene was dihydroxylated by means of 88% formic acid and 30% hydrogen peroxide. The diols were acetylated with acetyl chloride in ether containing pyridine. The *p*-chloro and *p*-methoxy derivatives were identified by the nmr of material collected from the vpc column used to analyze the product mixtures. Each compound exhibited two three-proton singlets near $\tau$ 8, a two-proton multiplet at $\tau$ 5.8, and a one-proton quartet (two doublets, $J$ = 7.0 and 5.0 Hz) at $\tau$ 4, in addition to the aromatic and ring substituent resonances.

**Reaction of 1-Deuteriostyrene.**—The reaction of 1-deuteriostyrene was carried out by doubling the proportions described under Product Studies. Analysis of the nmr spectrum of the mixture of two diacetates revealed the complete absence of the $\tau$ 3 signal of 2-phenyl-1,1-ethanediol diacetate and the $\tau$ 4 signal of 2-phenyl-1,2-ethanediol diacetate. Further confirmation of the structure of 1-deuterio-2-phenyl-1,1-ethanediol diacetate is provided by the signal at $\tau$ 7, which appears as a broadened singlet. Similarly, the signal at $\tau$ 5.8 for 1-deuterio-1-phenyl-1,2-ethanediol diacetate is a broadened singlet.

**Preparation of 1-Deuteriostyrene.**—Acetophenone was reduced with lithium aluminum deuteride and the resultant alcohol was acetylated with acetyl chloride in ether–pyridine solution. The acetate was pyrolyzed at 400° by dropping the neat liquid on a column containing glass beads. The resultant product was swept from the system by a stream of nitrogen into a trap immersed in a bath of Dry Ice–acetone.

**Purification of Acetic Acid.**—The acetic acid which was used for the kinetics and reaction of styrenes with thallic acetate was purified by refluxing a solution of 1.5 l. of glacial acetic acid containing 25 ml of acetic anhydride and about 1 g of *p*-toluenesulfonic acid for 12 hr. The acetic acid was distilled through a 60-cm glass-helix packed column. The fraction with bp 116.5–117° was retained.

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

The methods of sampling were dependent upon the rate of the reaction. For slow reactions, in which evaporation could occur,

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(15) G. Kordosky, M.S. Thesis, The Ohio State University, 1966.

2-ml aliquots were sealed in test tubes. For reactions with a moderate rate, where evaporation was not a problem, aliquots were pipeted directly from the reaction flask. For fast reactions, aliquots of each reactant were pipeted 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–iodine 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.

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# Stereochemistry of the Radical Addition of Polyhalomethanes to Bicyclo[2.2.1]heptenyl Systems[1]

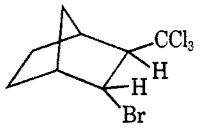
Adriane G. Ludwick[2] and J. C. Martin[3]

*Department of Chemistry and Chemical Engineering, University of Illinois, Urbana, Illinois 61801*

*Received April 7, 1969*

The radical addition of tribromofluoromethane to *endo*-2-substituted bicyclo[2.2.1]hept-5-enyl systems is shown to give both *trans* and *exo,cis* addition products, the relative amounts of each being dependent on the steric nature of the *endo*-2 substituent. The addition of tribromofluoromethane tobicyclo[2.2.1]hept-5-ene-*endo*-2,3-dicarboxylic anhydride (**10**) gives the *trans* adduct, *exo*-5-dibromofluoromethyl-*endo*-6-bromobicyclo[2.2.1]-heptane-*endo*-2,3-dicarboxylic anhydride (**11**), and the *exo,cis* adduct, *exo*-5-dibromofluoromethyl-*evo*-6-bromobicyclo[2.2.1]heptane-*endo*-2,3-dicarboxylic anhydride (**12**), in yields of approximately 40 and 60%, respectively. The temperature-dependent $^{19}$F nmr spectra of **12** reflect the steric hindrance to rotation of the dibromofluoromethyl group of this adduct, with peaks for each of the three conformers of this compound being resolved below −30°. The *trans* adduct gives only one peak in its $^{19}$F spectrum. This difference is used to assign structures in a number of systems. The addition of tribromofluoromethane to bicyclo[2.2.1]hept-2-ene gives the *trans* adduct in greater than 95% yield.

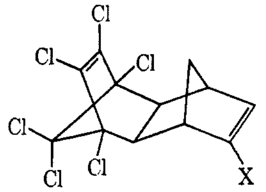
Fawcett[4] suggested that the unreactivity of the bicyclo[2.2.1]hept-2-ene-bromotrichloromethane adduct toward potassium hydroxide, as observed by Kharasch and Friedlander,[5] supported a *trans* stereochemistry for this adduct. He argued that, since in this structure (**1**, *endo*-2-bromo-*exo*-3-trichloromethylbicyclo[2.2.1]-heptane) the hydrogen at carbon 3 would be *cis* to the bromine, the preferred *trans* elimination would be prohibited. Evidence has since accumulated[6–11] to show that in systems with rigid structures *trans* elimination is not necessarily preferred.



**1**

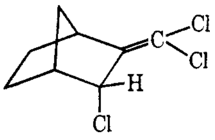
Dipole moment studies[12] of the adducts of chloroform and bromotrichloromethane with bicyclo[2.2.1]hept-2-ene have given some support for the formation of the *cis* adduct in the free-radical additions of these substrates.

The additions of carbon tetrachloride and of bromotrichloromethane to aldrin (**2a**) were found to give, respectively, the same products as the additions of chloroform to 6-chloroaldrin (**2b**) and 6-bromoaldrin (**2c**), respectively.[13] One can conclude from this observation that either *trans* addition is occurring in the carbon tetrachloride and bromotrichloromethane additions to **2a** and *cis* addition in the chloroform additions to **2b** and **2c** or that the reverse stereochemical result is correct.



**2a**, X = H
**b**, X = Cl
**c**, X = Br

Tobler and Foster[14] have presented evidence from nmr that the dehydrohalogenation product of the bicyclo[2.2.1]hept-2-ene–carbon tetrachloride adduct is 2-dichloromethylene-3-*endo*-chlorobicyclo[2.2.1]heptane (**3**). Hence, if one assumes that no rearrangement has occurred in the dehydrohalogenation of the bicyclo-[2.2.1]hept-2-ene–carbon tetrachloride adduct and that the trichloromethyl group is *exo*, then this must be the *trans* adduct.



**3**

During the course of this work, Osborn, VanAuken, and Trecker[15] reported the use of proton nmr spectros-

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[1] Taken in part from the Ph.D. thesis of A. G. L., University of Illinois, 1967.

[2] National Institutes of Health Predoctoral Fellow, 1965–1967.

[3] Fellow of the Alfred P. Sloan Foundation, 1962–1966.

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