

Reactivities of Sterically Hindered Styrenes toward Addition of Free Radicals<sup>1</sup>EARL S. HUYSER AND LEO KIM<sup>2</sup>

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







The relative reactivities of various methylated styrenes toward free-radical additions of bromotrichloromethane and 1-butanethiol have been measured by competition reactions. The reactivities parallel the degree of conjugation of the double bond with the aromatic ring which is dependent, because of steric inhibition, on the extent of substitution on the  $\alpha$  position of the vinyl group and the *ortho* positions of the aromatic ring. Severe steric problems are encountered in  $\alpha,p,o$ -tetramethylstyrene causing anomalous behavior of this compound in free-radical reactions with bromotrichloromethane and 1-butanethiol.

The reactivity of an unsaturated linkage toward addition of a free radical is related to the resonance stabilization of the adduct radical formed in such a reaction. Thus, styrene and 1,3-butadiene, which yield resonance-stabilized benzylic and allylic radicals, respectively, are more reactive than simple terminal alkenes toward addition of trichloromethyl radicals<sup>3</sup> and thiyl radicals.<sup>4</sup> However, when steric factors in a 1,3-diene prevent coplanarity of the double bonds and hence decrease conjugation, as is the case in 2,3-di-*t*-butyl-1,3-butadiene,<sup>5</sup> the reactivity of the double bonds toward radical addition is about that of simple terminal olefins.<sup>6,7</sup> The present work is concerned with the reactivities toward free-radical addition of methylated styrenes in which steric factors are present that diminish the degree of conjugation by preventing coplanarity of the unsaturated linkage with the aromatic ring.

## Results

The substituted styrenes used in this work (Table I) were prepared by dehydration of the appropriate alcohols. The extinction coefficients for the K band of these compounds show that the degree of conjugation of the double bond with the aromatic ring is dependent on the nature and extent of substitution. A single methyl group in the *para* position of both styrene and  $\alpha$ -methylstyrene increases the degree of conjugation relative to the parent compounds. However, a single methyl group in the *ortho* position of styrene does not impart the expected increase in conjugation but appears to cause a decrease in the conjugation as evidenced by the reported extinction coefficients of styrene ( $\lambda_{\max}$  249,  $\epsilon$  15,500, in 95% ethanol) and *o*-methylstyrene ( $\lambda_{\max}$  245,  $\epsilon$  12,600, in 95% ethanol).<sup>8</sup> This decrease in conjugation in *o*-methylstyrene relative to styrene has been attributed to a lack of coplanarity of the conjugated system resulting from steric problems caused by the *ortho* methyl group if the vinyl group is coplanar with the aromatic ring. The lower extinction coefficient of  $\alpha$ -methylstyrene relative to styrene may be due to noncoplanarity of the conjugated system in  $\alpha$ -methyl-

TABLE I  
ULTRAVIOLET ABSORPTION DATA OF  
METHYLATED STYRENES IN CYCLOHEXANE

Name	Structure	$\lambda_{\max}$ , <sup>a</sup> m $\mu$	$\epsilon$
<i>p</i> -Methylstyrene		256	18,000
<i>o,p</i> -Dimethylstyrene		257	14,200
Styrene		256	12,800
$\alpha,p$ -Dimethylstyrene		256	11,600
$\alpha$ -Methylstyrene		254	9,050
<i>o,o,p</i> -Trimethylstyrene		256	4,420
$\alpha,o,p$ -Trimethylstyrene		247	2,090
$\alpha,o,o,p$ -Tetramethylstyrene		253	270

<sup>a</sup> K-band absorption.

styrene resulting from steric problems involving the isopropenyl group and the *ortho* hydrogen.<sup>9</sup> The extinction coefficients we observed for these methylated styrenes in cyclohexane are consistent with these observations in that increasing substitution in the *ortho* position decreases the degree of conjugation and that the effect is more pronounced in the  $\alpha$ -methylstyrenes than in the styrenes.

Free-radical additions of both bromotrichloromethane and 1-butanethiol to styrene occur readily. The light-induced additions of these reagents took place with all of these styrenes<sup>10</sup> (see Experimental Section) with the exception of  $\alpha,o,o,p$ -tetramethylstyrene which did not undergo any addition of 1-butanethiol under conditions that the other styrenes did react. Illumination of a mixture of  $\alpha,o,o,p$ -tetramethylstyrene and

(1) This work was supported in part by Grant GP 5655 from the National Science Foundation.

(2) National Institutes of Health Predoctoral Fellow, 1966-1967.

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














(9) Y. Hirschberg, *J. Am. Chem. Soc.*, **71**, 3241 (1949); H. Suzuki, *Bull. Chem. Soc. Japan*, **33**, 619 (1960).

(10) Attempts to isolate pure samples of the addition products of BrCCl<sub>3</sub> to the more highly substituted styrenes failed because of extensive dehydrohalogenation during distillation of the reaction mixtures. A similar difficulty was encountered by earlier workers.<sup>1</sup>

bromotrichloromethane resulted in consumption of some of the alkene but did not yield any isolable amounts of an addition product. The anomalous behavior of this highly substituted styrene in these addition reactions will be discussed subsequently in this article.

The results of a series of competition reactions of these substituted styrenes and 1-decene toward free-radical addition of bromotrichloromethane and 1-butanethiol are shown in Tables II and III, respectively. Although both of these adding reagents react with styrene to give mainly the 1:1 addition product, the competition reactions were all performed with an excess of the adding reagent in order to minimize the possibility of any telomerization reactions of the styrenes. Table IV shows the reactivities derived from these competition reactions of the styrenes and  $\alpha$ -methylstyrenes, relative to 1-decene, toward addition of these two adding reagents.

TABLE II  
COMPETITION REACTIONS WITH BROMOTRICHLOROMETHANE AT 30°

Reaction	Alkene I	Alkene II	$k_I/k_{II}^a$	No. of runs	Av dev
1			1.21	2	0.08
2			4.06	3	0.44
3			1.31	3	0.06
4			~30	5	~5
5		1-Decene	5.24	3	0.30
6		1-Decene	2.79	2	0.12
7			2.37	3	0.21
8	1-Decene		3.70	3	0.07
9			1.86	2	0.05

<sup>a</sup> Relative reactivity of alkene I with respect to alkene II.

### Discussion

The mechanism of the addition of bromotrichloromethane to an alkene involves the free-radical chain sequence shown in eq 1 and 2. The relative reactivities measured in the competitive addition reactions are therefore those of these compounds toward addition of

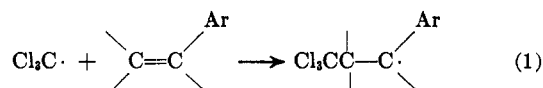















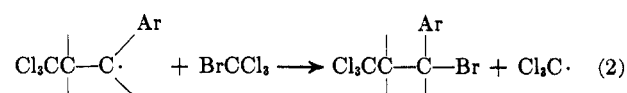


TABLE III

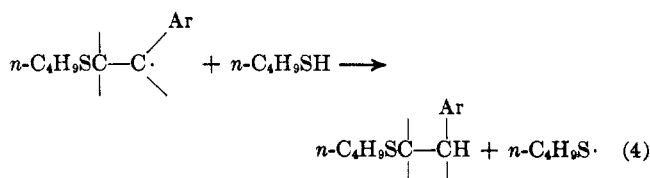
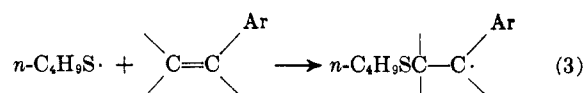
COMPETITION REACTIONS WITH 1-BUTANETHIOL AT 30°

Reaction	Alkene I	Alkene II	$k_I/k_{II}^a$	No. of runs	Av dev
1			0.90	3	0.04
2			5.95	2	0.15
3			1.21	3	0.12
4		1-Decene	7.10	2	0.40
5		1-Decene	2.38	2	0.01
6			2.06	3	0.22
7			~30	3	~5
8	1-Decene		$\infty^b$	2	...
9			1.25	3	0.13

<sup>a</sup> Relative reactivity of alkene I with respect to alkene II.  
<sup>b</sup>  $\alpha,\alpha,\alpha,\beta$ -Tetramethylstyrene undergoes no addition under these conditions.











trichloromethyl radical. Addition of mercaptans to alkenes involves the chain sequence (eq 3 and 4) which



differs from that of the bromotrichloromethane addition in that the addition of the *n*-butyl thiyl free radical to the unsaturated linkage is reversible. The possibility exists, therefore, that competition reactions that measure the relative rates of the alkenes toward over-all addition of the mercaptan may not be a measure of their relative reactivities toward addition of the thiyl radical. However, by employing a high concentration of the mercaptan, such competition reactions can serve as a measure of the reactivities of the alkenes toward addition of thiyl radicals. In similar studies, Walling and Helmreich<sup>4</sup> have shown that the relative reactivi-

TABLE IV  
REACTIVITIES OF METHYLATED STYRENES RELATIVE TO  
1-DECENE TOWARD FREE-RADICAL ADDITION

Styrene	BrCCl <sub>2</sub>	n-C <sub>10</sub> H <sub>17</sub> SH
	26	38
	21	42
	20	31
	5.3	7.1
1-Decene	1.0	1.0
	49	48
	22	23
	2.8	2.4
	(0.27) <sup>a</sup>	(0.0)

<sup>a</sup> This value refers to the amount of  $\alpha,o,o,p$ -tetramethylstyrene that was consumed in both addition and other possible reactions.

ties of several unsaturated compounds toward addition of thiyl radicals are very similar to those reported for trichloromethyl radicals. Our results also indicate a degree of similarity in the reactivity of these two radicals in adding to methylated styrenes.

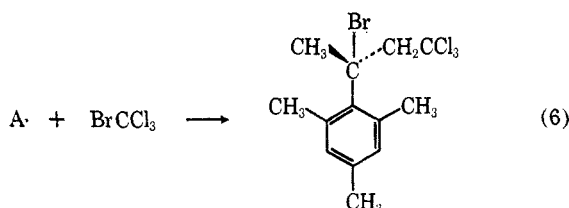
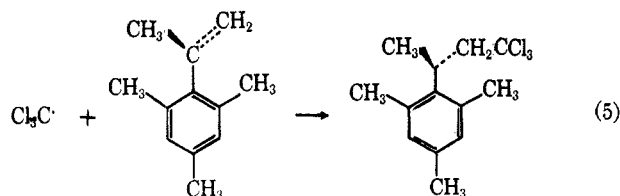
The relative reactivities of the ring methylated styrenes toward free-radical addition parallels the degree of conjugation indicated by the extinction coefficients of their K-band absorptions. The methyl group in the *para* position of *p*-methylstyrene increases both its extinction coefficient and its reactivity relative to styrene. Although the presence of the methyl group in the *ortho* position of *o,p*-dimethylstyrene would be expected to increase both the extinction coefficient and reactivity relative to *p*-methylstyrene, the single *ortho* methyl group prevents the vinyl group from becoming completely coplanar with the aromatic ring due to steric interaction with the *ortho* methyl. Consequently, both the reactivity toward free-radical addition and the extinction coefficient of *o,p*-dimethylstyrene are lower than those of *p*-methylstyrene. Even so, it is interesting that if the vinyl group in *o,p*-dimethylstyrene is not completely coplanar with the aromatic ring, the resonance interactions of the *ortho* and *para* methyl groups with the vinyl group are of such an order that the reactivity toward free-radical addition (particularly toward the thiyl radical) and the extinction coefficient of this compound are greater than those of styrene itself. The two *ortho* methyl groups in *o,o,p*-trimethylstyrene do have a marked effect on both its reactivity

toward free-radical addition and its K-band absorption. In this case, there should be more resonance interaction than in *o,p*-dimethylstyrene but this factor is outweighed by the comparatively high degree of non-coplanarity of the vinyl group with the aromatic ring caused by the steric effect of two *ortho* methyl groups.

The reactivities of the  $\alpha$ -methylstyrenes toward addition of both trichloromethyl radicals and thiyl radicals also parallel the extent of conjugation indicated by the extinction coefficients of the K-band absorptions. The effect of the *ortho* methyl groups is, however, far more pronounced in that one such group, as evident from the reactivity of  $\alpha,o,p$ -trimethylstyrene, decreases the reactivity of the double bond relative to that of the parent compound toward additions to quite a large extent. There are no conformations which will allow the double bond of  $\alpha,o,p$ -trimethylstyrene to be even closely coplanar with the aromatic ring without some steric interference. This is quite apparent from the low extinction coefficient of the K band of this compound. The methyl group in the *para* position of  $\alpha,p$ -dimethylstyrene does increase the reactivity of this compound relative to the parent compound toward free-radical addition and its K-band absorption is also more intense than that of  $\alpha$ -methylstyrene itself.

The most marked effect is noted in  $\alpha,o,o,p$ -tetramethylstyrene. The K-band absorption in this compound is very low, indicating relatively little conjugation of the double bond with the aromatic ring. The reactivity of this compound toward free-radical addition of the trichloromethyl radical as measured by competition reactions is also very low, indeed lower than can be accounted for solely on the basis of a lack of conjugation of the double bond with the aromatic ring since its reactivity could be expected to be about that of 1-decene. It may well be that approach of the trichloromethyl radical to the double bond is sterically hindered by the two *ortho* methyl groups. It would be, however, somewhat surprising to find the steric effect to be this large if the only factor involved in the addition of the free radical to the double bond were formation of a  $\sigma$  bond between the terminal carbon atom and the free radical. What may be indicated by the size of this steric effect is that formation of a  $\pi$  complex between the radical and the unsaturated bond precedes the formation of the  $\sigma$  bond. Such a complex would likely require positioning of the adding radical in a region where steric problems are encountered. The formation of the  $\pi$  complex could be rate determining in such a case, whereas in cases where the  $\pi$  complex is not sterically unfavorable formation of the  $\sigma$  complex would most likely be rate determining. The low reactivity of 2,3-di-*t*-butyl-1,3-butadiene relative to 1-octene toward addition of Cl<sub>3</sub>C·<sup>4</sup> may also be due to the slow rate of formation of a  $\pi$  complex because of steric problems.

It is quite significant that  $\alpha,o,o,p$ -tetramethylstyrene is consumed in these competition reactions with bromotrichloromethane. All attempts to produce isolable amounts of any addition product in the reaction of this material and bromotrichloromethane failed. Quite possibly the major difficulty does not arise in the addition reaction 5, which admittedly is slow, but rather in that the reaction of the adduct radical A· with bromotrichloromethane (eq 6) to yield the addition product may fail to take place. There is evidence that this may



be the case since it was observed that the presence of  $\alpha,o,o,p$ -tetramethylstyrene had a marked retarding effect on the rate of the addition of bromotrichloromethane to 1-decene. Whereas about 60% of the 1-decene in a photochemically induced reaction with bromotrichloromethane at 30° was consumed in the addition reaction after 70 min, it took about 7 hr for 50% of 1-decene to react under the same conditions in the presence of  $\alpha,o,o,p$ -tetramethylstyrene. This observation is consistent with a reaction in which chain carrying trichloromethyl radicals react at an appreciable rate with the substrate but the adduct radical A· formed does not react to propagate the chain reaction.

Failure of the adduct radical A· to react with bromotrichloromethane may not be surprising since there is ample evidence that species having a tetrahedral carbon bonded to the benzene ring and flanked by two *ortho* methyl groups are reluctant to form. Brown and Grayson reported that reaction of  $\alpha,o,o,p$ -tetramethylstyrene with HCl yielded the carbonium ion-chloride ion pair and not the expected covalent Markovnikov addition product.<sup>11</sup> The normal Fisher esterification of *o,o,p*-trimethylbenzoic acid, a reaction that involves conversion of the carbonyl carbon to an intermediate having an sp<sup>3</sup> configuration,<sup>12</sup> also fails to occur.<sup>13</sup> Indeed, esterification of this acid and hydrolysis of its esters are accomplished best by formation of the acylium ion,<sup>14</sup> a species that experiences no serious steric problems. Although mesitylmagnesium bromide can be prepared with no difficulty, it reacts very slowly with acetone<sup>15</sup> to yield the carbonyl adduct which has an sp<sup>3</sup>-hybridized carbon in the benzylic position. However, *o,o,p*-trimethylbenzoic acid is readily prepared by reaction of mesitylmagnesium bromide with carbon dioxide,<sup>16</sup> but in this case a trigonal and not a tetrahedral carbon is produced. Reactions of *o,o,p*-trimethylacetophenone with the tribromomethyl carbanion and with phenyllithium,<sup>18</sup> reactions which require conversion of the carbonyl carbon to one with a tetrahedral configuration, are also reluctant to occur although the reactions with these reagents occur readily with acetophenone.

(11) H. C. Brown and M. Grayson, *J. Am. Chem. Soc.*, **75**, 20 (1953).

(12) M. L. Bender, *ibid.*, **73**, 1626 (1951).

(13) V. Meyer, *Ber.*, **27**, 510 (1894); V. Meyer and J. J. Sudborough, *ibid.*, **27**, 3146 (1894).

(14) M. S. Newman, *J. Am. Chem. Soc.*, **63**, 2431 (1941).

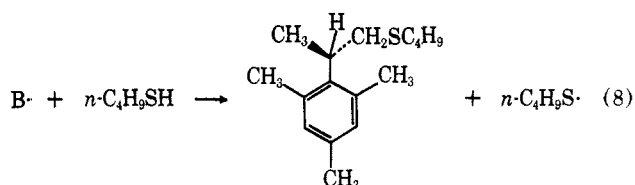
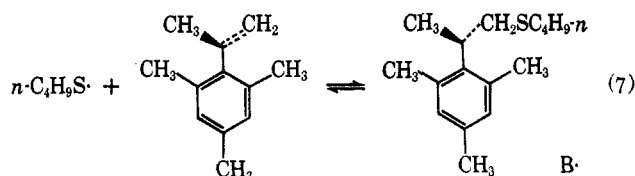
(15) See ref 11 and the Experimental Section.

(16) D. M. Bowen, "Organic Syntheses," Coll. Vol. III, E. C. Horning, Ed., John Wiley and Sons, Inc., New York, N. Y., 1955, p 553.

(17) W. Reeve and E. L. Compere, Jr., *J. Am. Chem. Soc.*, **83**, 2755 (1961).

(18) W. I. O'Sullivan, F. W. Swamer, W. J. Humphlett, and C. R. Hauser, *J. Org. Chem.*, **26**, 2306 (1960).

In view of the reluctance of the adduct radical A· to react with bromotrichloromethane, it is not surprising that  $\alpha,o,o,p$ -tetramethylstyrene does not react with 1-butanethiol to form an addition product by the chain sequence given in eq 7 and 8. The formation of the



adduct radical B· is a reversible process in contrast to the formation A· which is essentially irreversible at these temperatures.<sup>19</sup> Reaction of B· with 1-butanethiol (reaction 8) to form the addition product is most likely a very slow reaction because of the steric problems outlined previously. Consequently, radical B· fragments yielding the styrene and the thiyl radical. In view of this, the presence of  $\alpha,o,o,p$ -tetramethylstyrene should have little effect on the rate of addition of 1-butanethiol to 1-decene. Although thiyl radicals very likely do add to  $\alpha,o,o,p$ -tetramethylstyrene to form B·, no chains would be interrupted if the thiyl radicals are rapidly introduced back into the system in the fragmentation reaction. Rate studies show that 50% of the 1-decene present in a light-induced reaction at 30° with 1-butanethiol is consumed in 50 min and the same extent of reaction of 1-decene is observed in 60 min in a reaction performed under similar conditions with  $\alpha,o,o,p$ -tetramethylstyrene also present in the reaction mixture.

## Experimental Section

**Materials.**—Mesitylene, *p*-methylacetophenone, *o,p*-dimethylacetophenone, *o,o,p*-trimethylacetophenone, and  $\alpha$ -methylstyrene were obtained from Aldrich Chemical Co. and redistilled before using. Chlorobenzene (Fisher Scientific Co.), styrene (Eastman Kodak), 1-butanethiol (Matheson Coleman and Bell), *t*-butylbenzene (Aldrich), and bromotrichloromethane (Dow Chemical Co.) were distilled and gave a single peak on gas chromatographic analysis.

The gas chromatographic analyses were performed on an F & M Model 700 instrument and the extinction coefficients determined with a Beckman DU-2 spectrophotometer. The reactions were induced in each case with a 275-w G.E. sunlamp. The elemental analyses were performed by Weiler and Strauss Microanalytical Laboratory, Oxford, England.

**Preparation of Methylated Styrenes.**—The following substituted styrenes were prepared by KHSO<sub>4</sub>-catalyzed dehydrations of the corresponding  $\alpha$ -arylethanols which were obtained by the sodium borohydride reductions of the appropriate acetophenones: *p*-methylstyrene, bp 75° (12 mm), *n*<sub>D</sub><sup>20</sup> 1.5405 (lit.<sup>20</sup> *n*<sub>D</sub><sup>20</sup> 1.5415); *o,p*-dimethylstyrene, bp 70° (10 mm), *n*<sub>D</sub><sup>20</sup> 1.5408 (lit.<sup>20</sup> *n*<sub>D</sub><sup>20</sup> 1.5405); and *o,o,p*-trimethylstyrene, bp 200° (740 mm, *n*<sub>D</sub><sup>20</sup> 1.5304 (lit.<sup>20</sup> *n*<sub>D</sub><sup>20</sup> 1.5305). The following substituted  $\alpha$ -methylstyrenes were prepared by KHSO<sub>4</sub>-catalyzed dehydration of the corresponding aryldimethylcarbinols which were obtained by reaction of methylmagnesium iodide with the appropriate aceto-

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(20) M. M. Koton and T. G. Smloyuk, *Dokl. Akad. Nauk. SSSR*, **102**, 305 (1955).

phenones:  $\alpha,p$ -dimethylstyrene, bp 176° (740 mm),  $n_D^{25}$  1.5228 (lit.<sup>21</sup>  $n_D^{25}$  1.5202); and  $\alpha,o,p$ -trimethylstyrene, bp 200° (740 mm),  $n_D^{25}$  1.5149 (lit.<sup>22</sup>  $n_D^{25}$  1.515).  $\alpha,o,o,p$ -Tetramethylstyrene, bp 215° (740 mm),  $n_D^{25}$  1.5129 (lit.<sup>11</sup>  $n_D^{25}$  1.5108), was prepared by  $\text{KHSO}_4$ -catalyzed dehydration of mesityldimethylcarbinol which was prepared in 11% yield by the reaction of mesitylmagnesium bromide with acetone. The majority of the Grignard reagent was reduced by acetone to mesitylene. The ultraviolet characteristics of the K-band absorptions of these styrenes in cyclohexane are given in Table I.

**Addition of Bromotrichloromethane to  $p$ -Methylstyrene.**—A mixture consisting of  $p$ -methylstyrene (2.36 g, 0.02 mole) and bromotrichloromethane (20 g, 0.20 mole) was illuminated for 3 hr at 30°. Distillation of the reaction mixture yielded 3.7 g (60% of theory) of the crude 1:1 addition product 3-bromo-3-( $p$ -methylphenyl)-1,1,1-trichloropropane, bp 105° (0.08 mm). After recrystallization from methanol, the material melted at 48–49°.

*Anal.* Calcd for  $\text{C}_{10}\text{H}_{10}\text{BrCl}_3$ : C, 37.95; H, 3.19; Br, 25.25; Cl, 33.61. Found: C, 38.07; H, 3.12; Br, 25.65; Cl, 33.80.

**Addition of Bromotrichloromethane to  $o,p$ -Dimethylstyrene.**—A mixture of  $o,p$ -dimethylstyrene (2.6 g, 0.02 mole) and bromotrichloromethane (20 g, 0.20 mole) was illuminated for 3 hr at 30°. Distillation yielded 3.9 g (60% of theory) of the 1:1 addition product, 3-bromo-3-( $o,p$ -dimethylphenyl)-1,1,1-trichloropropane: bp 110–111° (0.15 mm);  $n_D^{20}$  1.5732.

*Anal.* Calcd for  $\text{C}_{11}\text{H}_{12}\text{BrCl}_3$ : C, 39.98; H, 3.66; Br, 24.18; Cl, 32.18. Found: C, 40.02; H, 3.83; Br, 23.80; Cl, 31.85.

**Additions of Bromotrichloromethane to  $o,o,p$ -Trimethylstyrene,  $\alpha,p$ -Dimethylstyrene, and  $\alpha,o,p$ -Trimethylstyrene.**—Addition reactions with these styrenes were performed in the manner described in the previous two reactions. After removal of the unreacted bromotrichloromethane and styrene by distillation, residues remained which amounted to about 40–60% yields of the addition products. Further distillation in each case resulted in extensive dehydrohalogenation. Elemental analyses of the distillates showed the presence of both bromine and chlorine, indicating both dehydrochlorination and dehydrobromination had occurred.

**Reaction of Bromotrichloromethane with  $\alpha,o,o,p$ -Tetramethylstyrene.**—A reaction mixture consisting of  $\alpha,o,o,p$ -tetramethylstyrene (2.5 g, 0.017 mole) and bromotrichloromethane (30 g, 0.15 mole) was illuminated for 9 hr at 35°. Distillation of the resulting mixture gave unreacted  $\alpha,o,o,p$ -tetramethylstyrene and approximately 0.8 g of a material boiling at 105–118° (1.5 mm). Elemental analysis indicated the presence of both bromine and chlorine but did not correspond to the addition product or any simple dehydrohalogenated product that could have been formed from the simple addition product. In another reaction, illumination of a mixture of  $\alpha,o,o,p$ -tetramethylstyrene and bromotrichloromethane showed, by gas chromatographic analysis, that after 49 hr approximately 20% of the styrene had reacted. Chloroform was also observed as a reaction product indicating hydrogen abstraction by the trichloromethyl radicals was also occurring. After 98 hr of illumination, about 45% of the styrene had reacted.

**Addition of 1-Butanethiol to Styrene.**—A mixture consisting of styrene (2.1 g, 0.02 mole) and 1-butanethiol (18 g, 0.20 mole) was illuminated for 12 hr at 30°. Distillation of the reaction mixture gave 2.7 g (70% of theory) of 2-phenylethyl  $n$ -butyl sulfide: bp 104 (1.2 mm);  $n_D^{20}$  1.5239.

*Anal.* Calcd for  $\text{C}_{12}\text{H}_{18}\text{S}$ : C, 74.17; H, 9.33; S, 16.50. Found: C, 73.92; H, 9.55; S, 16.19.

**Addition of 1-Butanethiol to  $\alpha$ -Methylstyrene.**—A mixture of  $\alpha$ -methylstyrene (2.36 g, 0.02 mole) and 1-butanethiol was illuminated for 12 hr at 30°. The addition product, 2-phenylpropyl  $n$ -butyl sulfide (2.7 g, 65% of theory) distilled at 109° (1.0 mm),  $n_D^{20}$  1.5208.

*Anal.* Calcd for  $\text{C}_{13}\text{H}_{20}\text{S}$ : C, 74.94; H, 9.67; S, 15.39. Found: C, 75.21; H, 9.66; S, 15.39.

**Addition of 1-Butanethiol to  $p$ -Methylstyrene.**—A mixture consisting of 2.36 g (0.02 mole) of  $p$ -methylstyrene and 18 g (0.20 mole) of 1-butanethiol was illuminated for 12 hr at 30°. The addition product, 2-( $p$ -methylphenyl)ethyl  $n$ -butyl sulfide (2.9 g, 70% of theory) distilled at 90–91° (0.2 mm),  $n_D^{20}$  1.5242.

*Anal.* Calcd for  $\text{C}_{13}\text{H}_{20}\text{S}$ : C, 74.94; H, 9.67; S, 15.39. Found: C, 75.02; H, 9.71; S, 15.48.

**Addition of 1-Butanethiol to  $o,p$ -Dimethylstyrene.**—A mixture of  $o,p$ -dimethylstyrene (2.6 g, 0.02 mole) and 1-butanethiol (18 g, 0.20 mole) was illuminated at 30° for 12 hr. Distillation of the reaction mixture yielded 3.3 g (75% of theory) of the 1:1 addition product, 2-( $o,p$ -dimethylphenyl)ethyl  $n$ -butyl sulfide: bp 102–103° (1.10 mm);  $n_D^{20}$  1.5264.

*Anal.* Calcd for  $\text{C}_{14}\text{H}_{22}\text{S}$ : C, 75.61; H, 9.97; S, 14.42. Found: C, 75.66; H, 9.83; S, 14.69.

**Addition of 1-Butanethiol to  $o,o,p$ -Trimethylstyrene.**—A mixture of  $o,o,p$ -trimethylstyrene (2.9 g, 0.02 mole) and 1-butanethiol (18 g, 0.20 mole) was illuminated for 12 hr at 30°. Distillation of the reaction mixture gave 3.8 g (80% of theory) of 2-( $o,o,p$ -trimethylphenyl)ethyl  $n$ -butyl sulfide: bp 164–165° (3 mm);  $n_D^{20}$  1.5285.

*Anal.* Calcd for  $\text{C}_{15}\text{H}_{24}\text{S}$ : C, 76.21; H, 10.23; S, 13.56. Found: C, 76.33; H, 9.97; S, 13.61.

**Addition of 1-Butanethiol to  $\alpha,p$ -Dimethylstyrene.**—A mixture of  $\alpha,p$ -dimethylstyrene (2.6 g, 0.02 mole) and 1-butanethiol (18 g, 0.20 mole) was illuminated for 12 hr at 30°. The addition product, 2-( $p$ -methylphenyl)propyl  $n$ -butyl sulfide (3.8 g, 85% of theory) distilled at 87–89° (0.05 mm),  $n_D^{20}$  1.5204.

*Anal.* Calcd for  $\text{C}_{14}\text{H}_{22}\text{S}$ : C, 75.61; H, 9.97; S, 14.42. Found: C, 75.69; H, 9.78; S, 14.38.

**Addition of 1-Butanethiol to  $\alpha,o,p$ -Trimethylstyrene.**—A mixture of  $\alpha,o,p$ -trimethylstyrene (2.9 g, 0.02 mole) and 1-butanethiol (18 g, 0.20 mole) was illuminated for 12 hr at 30°. Distillation of the reaction mixture yielded 3.6 g (75% of theory) of 2-( $o,p$ -dimethylphenyl)propyl  $n$ -butyl sulfide: bp 108–110° (0.2 mm);  $n_D^{20}$  1.5230.

*Anal.* Calcd for  $\text{C}_{15}\text{H}_{24}\text{S}$ : C, 76.21; H, 10.23; S, 13.56. Found: C, 76.36; H, 10.30; S, 13.70.

**Attempted Addition of 1-Butanethiol to  $\alpha,o,o,p$ -Tetramethylstyrene.**—A mixture of  $\alpha,o,o,p$ -tetramethylstyrene (3.2 g, 0.02 mole) and 1-butanethiol was illuminated for 48 hr at 30°. Gas chromatographic analysis of the reaction mixture indicated that no detectable amount of the styrene had reacted. Distillation of the reaction mixture gave only unreacted mercaptan and styrene and no higher boiling fractions.

**Competition Reactions with Bromotrichloromethane and 1-Butanethiol.**—Reaction mixtures consisting of about equivalent quantities of the two unsaturated compounds, chlorobenzene and an excess of the adding reagent (eightfold excess in the case of bromotrichloromethane and fourfold for 1-butanethiol), were chromatographed on an 8 ft  $\times$  0.25 in. gas chromatographic column packed with 10% SE-30 on Chromosorb W using helium as a carrier gas. The reaction mixture was placed in a Pyrex tube fitted with a rubber septum, placed in a water bath at 30°, and illuminated with a 275-w G.E. sunlamp. At 30-min intervals, portions of the mixture were chromatographed under the same conditions. Chlorobenzene, which does not react under these conditions, served as an internal standard for the gas chromatographic analysis. The amount of each styrene remaining was determined by comparison of its peak area after reaction with its peak area before reaction. The relative reactivity ratio,  $k_1/k_2$ , was determined from the data obtained using eq 9. A and B refer to the two unsaturated compounds and the

$$\frac{k_1}{k_2} = \log \frac{(A)_i}{(A)_f} / \log \frac{(B)_i}{(B)_f} \quad (9)$$

subscripts "i" and "f" refer to initial and final amounts of the two reactants. The relative reactivity ratio determined in this manner for additions of bromotrichloromethane and 1-butanethiol are given in Tables II and III, respectively.

**Inhibitory Effect of  $\alpha,o,o,p$ -Tetramethylstyrene.**—A mixture of 1-decene (0.20 g, 0.0014 mole) and bromotrichloromethane (0.74 g, 0.0037 mole) was illuminated at 30°. Samples were removed at the indicated times and the amount of 1-decene remaining was determined by gas chromatographic analysis: 25 min, 70%; 40 min, 60%; 70 min, 40%. A similar reaction mixture containing  $\alpha,o,o,p$ -tetramethylstyrene (0.12 g, 0.007 mole) was illuminated in the same manner and the amounts of alkene remaining at the indicated times were as follows: 120 min, 95%; 270 min, 60%; 420 min, 50%.

A mixture of 1-decene (0.20 g, 0.0014 mole) and 1-butanethiol (0.39 g, 0.0043 mole) was illuminated at 30°. The amounts of 1-decene remaining, determined by gas chromatographic analysis, at the times indicated, were as follows: 50 min, 50%; 130 min,

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20%; 180 min, ca. 5%. Analysis of a similar reaction mixture containing 0.12 g (0.0075 mole) of  $\alpha,o,o,p$ -tetramethylstyrene in the same manner showed the following amounts of 1-decene remaining at the indicated times: 30 min, 70%; 60 min, 50%; 120 min, 10%.

**Registry No.**—*p*-Methylstyrene, 622-97-9; *o,p*-dimethylstyrene, 2234-20-0; styrene, 100-42-5;  $\alpha,p$ -dimethylstyrene, 1195-32-0;  $\alpha$ -methylstyrene, 98-83-9; *o,o,p*-trimethylstyrene, 769-25-5;  $\alpha,o,p$ -trimethylstyrene, 14679-12-0;  $\alpha,o,o,p$ -tetramethylstyrene, 14679-

13-1; bromotrichloromethane, 75-62-7; 1-butanethiol, 109-79-5; 3-bromo-3-(*p*-methylphenyl)-1,1,1-trichloropropane, 14679-14-2; 3-bromo-3-(*o,p*-dimethylphenyl)-1,1,1-trichloropropane, 14679-15-3; 2-phenylethyl *n*-butyl sulfide, 14679-16-4; 2-phenylpropyl *n*-butyl sulfide, 14679-17-5; 2-(*p*-methylphenyl)ethyl *n*-butyl sulfide, 14723-35-4; 2-(*o,p*-dimethylphenyl)ethyl *n*-butyl sulfide, 14679-18-6; 2-(*o,o,p*-trimethylphenyl)ethyl *n*-butyl sulfide, 14746-02-2; 2-(*p*-methylphenyl)propyl *n*-butyl sulfide, 14679-19-7; 2-(*o,p*-dimethylphenyl)propyl *n*-butyl sulfide, 14679-20-0.

## Highly Strained Bicyclic Systems. XII. Synthesis and Solvolysis of 1,5,5-Trimethylbicyclo[2.1.1]hex-2-yl *p*-Toluenesulfonate<sup>1-3</sup>

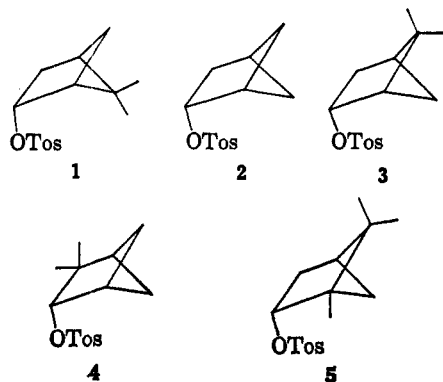
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The synthesis of 1,5,5-trimethylbicyclo[2.1.1]hex-2-yl *p*-toluenesulfonate (5) from *l*-bornyl acetate (6) is described. Acetolysis of 5 results chiefly in the formation of a ring-opened product, 25a. The solvolysis rate shows that significant enhancement results from the presence of the bridgehead methyl group at C<sub>1</sub>, in accord with positive charge delocalization to this position in the transition state.

Earlier in this series an argument has been presented favoring the view that the acetolysis of a 2-substituted bicyclo[2.2.1]hexane (1) showed marked rate enhancement compared with a hypothetical, classical model.<sup>5</sup> Recently, the parent ester, bicyclo[2.1.1]hex-2-yl *p*-toluenesulfonate (2), was prepared and studied in this laboratory.<sup>6,7</sup> Data on the effect of methyl substituents on the rate of solvolysis of this tosylate were also obtained *via* the synthesis and solvolysis of tosylates 3<sup>6,7</sup> and 4.<sup>6,7</sup> It was of interest in this connection to synthesize tosylate 5 in order to study the effect of the introduction of a bridgehead methyl group at C<sub>1</sub> on the solvolysis rate as compared with the rates of those esters already studied.



### Synthesis of 1,5,5-Trimethylbicyclo[2.1.1]hex-2-yl *p*-Toluenesulfonate.—In order to make use of the

(1) The partial support of this research by grants (G-22,541 and GP-4128) from the National Science Foundation, and by Hoffmann-LaRoche, Inc., is acknowledged with pleasure.

(2) For the previous paper in this series, see J. Meinwald and J. K. Crandall, *J. Am. Chem. Soc.*, **88**, 1292 (1966).

(3) Taken in part from the Ph.D. dissertation submitted by J. C. Shelton to Cornell University, Ithaca, N. Y., Sept 1964.

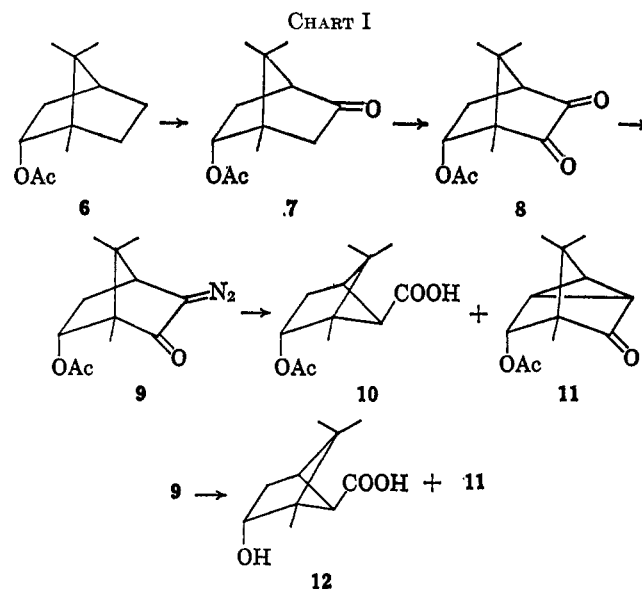
(4) Department of Chemistry, The University, Glasgow, Scotland.

(5) J. Meinwald and P. G. Gassman, *J. Am. Chem. Soc.*, **85**, 57 (1963).

(6) Abstracts, 18th National Organic Chemistry Symposium, Columbus, Ohio, June 16–20, 1963, pp 37–44.

(7) See also ref 2.

valuable Horner and Spietschka<sup>8</sup> bicyclo[2.1.1]hexane synthesis, the acetoxy diazo ketone 9 was required. This compound was prepared and utilized as shown in Chart I.



The direct chromic acid oxidation of bornyl acetate (6) to 5-ketobornyl acetate (7) has been described by Bredt and Goeb.<sup>9</sup> In our hands this oxidation gave modest yields of crystalline 7, mp 78°. The diketone 8, mp 103–105°, was prepared by selenium dioxide oxidation of 7 in acetic anhydride, as described by Asahina and coworkers.<sup>10</sup>

Asahina, *et al.*,<sup>11</sup> have prepared the diazo ketone 9 by oxidation of the monohydrazone of ketone 8 with mercuric oxide. This method was found to be less satisfactory than the base decomposition of the *p*-toluene-

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