

COMPLICATIONS DURING STEREOCHEMICAL STUDIES ON THE STYRYL RADICAL IN
PERHALOMETHANE SOLVENTS

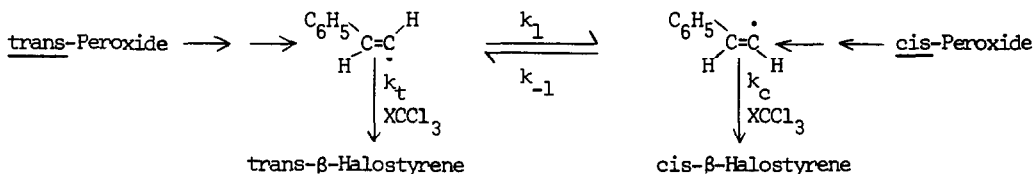
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Several years ago, Sinamura and co-workers (1) reported that styryl radicals derived from cis- and trans-cinnamoyl peroxide (Scheme 1) were partially stereospecifically scavenged by bromotrichloromethane (k_1 , $k_{-1} \approx k_t$, k_c) while with carbon tetrachloride, equilibration of the isomeric bent styryl radicals presumably is faster than the scavenging steps since the same cis/trans olefin ratio was observed from either starting peroxide.

SCHEME 1



We were surprised that the styryl radical could be scavenged before equilibration in bromotrichloromethane since epr data on the simple vinyl radical (2) indicate an inversion barrier of ≤ 2 kcal/mole. Semi-empirical calculations by Kopchik and Kampmeier (extended Huckel) (3) and by us (CNDO) (4) similarly predict low inversion barriers for the vinyl radical, 2.8 and < 1 kcal/mole, respectively. If we assume the inversion barrier in the styryl radical is also small (~ 2 -3 kcal/mole), the reported (1) partial stereospecific scavenging by bromotrichloromethane would need to be at, or very close to, the diffusion limit. We re-examined the scavenging of the styryl radical in bromotrichloromethane and carbon tetrachloride with special attention to some important control experiments. Our results follow.

Thermal decomposition of trans-cinnamoyl peroxide, m.p. 132-3°, lit., 127-30° (5), at 76° in bromotrichloromethane and carbon tetrachloride led to the product mixtures shown in Table I. The olefin product ratios are within experimental error of those ratios obtained under equilibrating conditions. Further, an additional major product from the reaction in both solvents is trans- β -trichloromethylstyrene which was not mentioned by Sinamura and co-workers, while in

bromotrichloromethane, 1,2,2-tribromo-1-phenylethane is also isolated. The structures of both products were determined by nmr and high resolution mass spectroscopic analyses which will be detailed in a later paper. The apparent equilibration of the olefin products under the reaction conditions and the appearance of these new products prompted us to carry out several additional experiments.

TABLE 1. PRODUCTS FROM THE DECOMPOSITION OF TRANS-CINNAMOYLPEROXIDE.

Solvent	β -Halostyrenes ^a		<u>trans</u> - β -Trichloro- ^b methylstyrene	1,2,2-Tribromo-1-phenyl- ^b ethane
	<u>trans/cis</u>	Yield		
	_____mmole of product/mmole of diacylperoxide ^c _____			
BrCCl ₃	5.49 \pm 0.10 ^d	0.10	0.66	0.22
CCl ₄	4.40 \pm 0.15 ^e	0.80	0.54	0.00

^aAnalysis by vpc with internal standard. β -Chlorostyrenes on Carbowax 20 M, 35% on Chromsorb P. β -Bromostyrenes on Apiezon L, 10% on Chromsorb P. ^bAnalysis by nmr with internal standard. ^c100% theoretical yield corresponds to ratio of 2.00. ^dEquilibration of β -bromostyrenes in cumene with trace of azo-isobutyrylnitrile and *p*-thiocresol at 76° leads to trans/cis = 6.69 \pm 1.03. ^eEquilibration of β -chlorostyrenes in carbon tetrachloride with trace of bromine at 76° leads to trans/cis = 4.26 \pm 0.29.

Tables 2 and 3 reveal the fate of the β -halostyrenes sent through the reaction conditions in the presence and absence of decomposing trans-cinnamoyl peroxide. Note, we add β -bromostyrene to the carbon tetrachloride run (where β -chlorostyrene is being formed) (Table 2) so that we can follow accurately any isomerization of the added halostyrene without interference from halostyrene forming from styryl radical scavenging. The experiments in Table 3 were similarly designed. These two sets of experiments clearly show that the β -halostyrenes are isomerized and consumed under the reaction conditions of Table 1 so that conclusions on the stereochemical capabilities of the styryl radical based on such data are inappropriate.

We propose Scheme 2 as an explanation for the β -halostyrene isomerization and formation of trans-trichloromethylstyrene and 1,2,2-tribromo-1-phenylethane. Eq. 1 is irreversible (6) so that the addition of trichloromethyl radical to β -haloolefin is responsible for the consumption but not the isomerization of the latter. The observed isomerization is caused by reversible addition of X[•] (from eq. 2) to the β -halostyrenes (eq. 3). We assume that the isolated single isomer of β -trichloromethylstyrene has the trans structure. (7) The 1,2,2-tribromo-1-phenylethane could result from trapping of C₆H₅ĊHCHBr₂ according to eq. 4.

TABLE 2. CONSUMPTION AND ISOMERIZATION OF β -BROMOSTYRENE DURING THE THERMOLYSIS OF TRANS-CINNAMOYL PEROXIDE AT 76° IN CCl_4 .

Conditions ^a	β -Bromostyrene ^b		%Loss ^c
	Before Reaction	After Reaction	
	(trans/cis)		
t-CP (0.010 M)	5.94 ± 0.70	6.14 ± 0.10	20.8 ± 0.90
\bar{t} -CP (0.010 M)	0.143 ± 0.006	6.35 ± 1.00	21.5 ± 1.5
t-CP (0.000 M)	5.94 ± 0.70	6.28 ± 0.18	trace
\bar{t} -CP (0.000 M)	0.143 ± 0.006	0.379 ± 0.050	trace

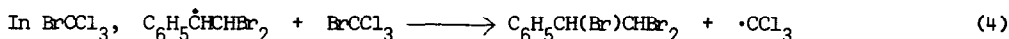
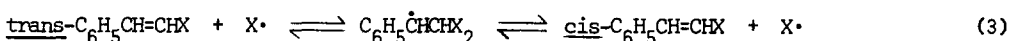
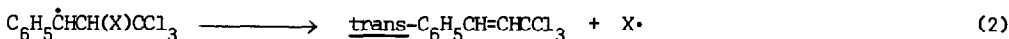
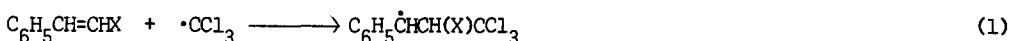
^at-CP is trans-cinnamoyl peroxide. ^bca 0.05 M in all cases. Reaction time 20 hrs. in all cases. ^cObserved loss of β -bromostyrene under conditions.

TABLE 3. CONSUMPTION AND ISOMERIZATION OF β -CHLOROSTYRENE DURING THE THERMOLYSIS OF TRANS-CINNAMOYL PEROXIDE AT 76° IN BrCCl_3 .

Conditions ^a	β -Chlorostyrene ^b		%Loss ^c
	Before Reaction	After Reaction	
	(trans/cis)		
t-CP (0.010 M)	4.68 ± 0.03	4.29 ± 0.90	81.3 ± 1.0
\bar{t} -CP (0.010 M)	1.40 ± 0.04	4.43 ± 0.44	79.6 ± 1.6
t-CP (0.000 M) ^d	4.68 ± 0.03	5.57 ± 0.30	trace
\bar{t} -CP (0.000 M)	1.40 ± 0.04	1.67 ± 0.04	trace

^at-CP is trans-cinnamoyl peroxide. ^b0.05 M in all cases. Reaction time 20 hrs. in all cases. ^cObserved loss of added β -chlorostyrene. ^dCarried out at 100° for 19 hrs.

SCHEME 2



In support of Scheme 2, we find that the propenylbenzenes (starting trans/cis = 0.068) are consumed but not isomerized in the presence of decomposing benzoyl peroxide at 76° in carbon tetrachloride. In this system, X· is not released as it is with the β -halostyrenes (i.e. eq. 1 and 2). Further, the isomerization of β -bromostyrene in the presence of decomposing peroxide in carbon tetrachloride can be retarded by the addition of cumene as a X· trap (Table 4). We assume that at 3.6 M cumene, isomerization via eq. 3 was eliminated for the β -chlorostyrene products as well as for the β -bromostyrene probe. Accordingly, the product ratio

TABLE 4. CONSUMPTION AND ISOMERIZATION OF β -BROMOSTYRENE DURING THE THERMOLYSIS OF TRANS-CINNAMOYL PEROXIDE AT 76° IN CCl_4 IN THE PRESENCE OF ADDED CUMENE.

Cumene (M)	β -Bromostyrene (<u>trans/cis</u>)		% Loss of β -Bromostyrene	β -Chlorostyrene (<u>trans/cis</u>)
	Start	Finish		
0.0	0.053	5.36	34.2	4.40
1.05	0.053	0.43	23.1	3.40
3.62	0.053	0.056	12.2	2.86

trans/cis = 2.86 represents the kinetic product ratio of $(k_t k_{-1})/(k_c k_1)$. (10) Our results are consistent with earlier work on the free radical addition of perhalomethanes to olefins. (11, 12)

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