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Mechanism and Products During the Homolytic Addition of CCl_4 and Cl_3CBr to β-Halostyrenes

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During the homolytic reactions of CCl_4 or Cl_3CBr with β-halo[1]-styrenes, β-haloradicals are key intermediates. They are to be stabilized *via* three pathways; β-cleavage, halogen transfer and telomerization. The three reaction paths are *delicately controlled* by the energetics of their formation and stabilization. When the formation of a β-haloradical is accompanied by considerable excess of energy from an exothermic reaction, β-cleavage is often dominant over the halogen transfer. On the other hand, if the radical forms *via* a reversible reaction, two processes become competitive. β-Eliminated bromine atoms from β-bromoradicals generate Br_2 *via* $Cl_3CBr + \cdot Br \leftrightarrows Br_2 + \cdot CCl_3 \cdot Br_2$ may act as a better scavenger than Cl_3CBr for the β-bromoradicals. Different reactivities of chlorine, bromine and trichloromethyl radicals towards olefinic pi–bond are clarified in terms of the heat content of the addition reactions.

Introduction

Perhalomethanes are known to add homolytically to various olefins[2] and are used as free radical scavengers as well[3]. The olefins gave excellent yields of the expected 1:1 addition products. Furthermore many cases are known in which either a shift or a loss of an adjacent halogen takes place. Formation of rearranged products is due to the intermediacy of β-haloradicals undergoing β-cleavage rather than halogen transfer. The β-cleavage constitutes an important process of homolytic reaction and has been a subject of interest until recently[4-9].

We[10] have previously shown that β-halostyrenes react with CCl_4 and Cl_3CBr under homolytic condition and point out the misleading conclusion[11] of other workers[12] on the stereochemical properties of styryl radicals.

We would like to present full result and discuss the subtle difference between the reactions of CCl_4 and Cl_3CBr.

Results

The *trans*-cinnamoyl peroxide 1 was prepared in good

yield according to the method either of Stabb[13] or of Greene[14]. Purified 1 is a white solid showing a characteristic doublet at 1770 cm^{-1} [14] by IR.

A mixture of the *cis*- and *trans*-β-chlorostyrenes was prepared by decomposition of cinnamic acid dichloride in aqueous sodium carbonate solution at 100°C[15]. The mixture was highly in the *trans* form and irradiated by uv to give the mixture containing 53% *cis*-form. *cis*-β-Bromostyrene was prepared by decomposition of cinnamic acid dibromide in anhydrous sodium bicarbonate solution at 90°C in darkness[16].

trans-Trichloromethylstyrene 7 was prepared as follows: A mixture of *cis*- and *trans*-β-bromostyrene was heated in Cl_3CBr with a small amount of benzoyl peroxide in accordance with the reaction condition used by Kharasch[17]. After six half–lives of the peroxide, 7 was separated by vacuum fractional distillation, b.p 92°C[1.75]. 7 was easily hyrolyzed in acidic condition to give *trans*-cinnamic acid.

1,2,2,-Tribromo-1-phenylethane 10 was prepared by the photobromination of a mixture of *cis*- and *trans*-β-bromostyrene with Br_2 in CCl_4 using sun–lamp as the light source. 10 was distilled at 110°C (2.0 mmHg)

NMR and mass spectral data of 7 and 10 are shown in the Tables 1 and 2, respectively.

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TABLE 1: NMR Data[a] of 7 and 10

Compounds	$H_1(\delta)$	$H_2(\delta)$	$J_{1,2}$(cps)
7	6.16,6. 33:d[b]	5.56,5. 73:d[b]	10
10	5.85,5. 93:d[b]	5.23,5. 36:d[b]	8

[a] Samples are neat. [b]d: doublet.

TABLE 2: Mass Spectral Data of 7 and 10

(A) Mass Spectrum of 7

[M–X]$^+$	m/e	Relative intensity (%)	
		Obsvd. (Ratio)	Theoretical ratio
[M–Cl]$^+$	185	36.64(9.37)	9.39
	187	23.62(6.04)	6.13
	189	3.91(1)	1
[M–HCl$_2$]$^+$	149	100 (3.02)	3.07
	151	33.11(1)	1
[M–Cl$_3$]$^+$	115	34.41	
[M–HCl$_3$]$^+$	114	9.82	
[C$_6$H$_5$]$^+$	77	9.23	

(B) Mass Spectrum of 10

[M–X]$^+$	m/e	Relative intensity (%)	
		Obsvd. (Ratio)	Theoretical ratio
[M–Br]$^+$	261	35.8 (1.05)	1.05
	263	72.45(2.12)	2.05
	265	34.10(1)	1
[M–Br$_2$]$^+$	182	55.77(1.07)	1.02
	184	52.21(1)	1
[M–Br$_3$]$^+$	103	100	
[M–HBr$_3$]$^+$	102	56.47	
[C$_6$H$_5$]$^+$	77	68.90	

TABLE 3: Products from the Decomposition of *trans*-Cinnamoyl Peroxide 1

Solvent	β–Halostyrenes[a] Yield(*trans/cis*)	7[b]	10[b]	Telomer[d]
		mmole of product/mmole of 1[c]		
CCl$_4$	0.80(4.40)	0.54	0.00	0.66
Cl$_3$CBr	0.10(5.49)[e]	0.66	0.22	1.02

[a] Analysis by GC with p–dichlorobenzene as an internal standard.
β–Chlorostyrenes on Carbowax 20 M, 35 % on Chromsorb P.
β–Bromostyrenes on Apiezon L, 10 % on Chromosorb P.
[b] Analysis by NMR with toluene as an internal standard. c 100 %
theoretical yield corresponds to ratio of 2.00[18]. [d] Yields of telomers
were calculated by substracting the total yield of β–halostyrenes,
7 and 10 from 2[18]. [e] Accurate *trans/cis* ratio of β–bromostyrene
was difficult to obtain because of very small yield of cis–β–
bromostyrene.

The peroxide 1 was decomposed in degassed and sealed
Pyrex ampoules in CCl$_4$ or Cl$_3$CBr scavenging systems at
76°C for a minimum of 20 hours. IR spectrum analysis
revealed no remaining peroxide (at 1770 cm^{-1} by IR) after
this time. The ampoules were protected from light during and

TABLE 4: Degree of Isomerization and Loss of β–Halostyrenes

β–Halostyrenes[a]	Solvent	Start	Finish	% Loss[b,c]
		(*trans/cis*)		
β–Chlorostyrene[d,f]	CCl$_4$	1.38	1.61	35
β–Chlorostyrene[e,f]	Cl$_3$CBr	1.38	4.26	78
β–Bromostyrene[e,g]	CCl$_4$	0.143	6.35	21
β–Bromostyrene[d,g]	Cl$_3$CBr	0.143	6.50	85

[a] 0.05 M in all cases. [b] Observed loww of added β–halostyrenes.
[c] β–Halostyrenes were reasonably stable under the thermal condi-
tion in the absence of initiators. Isomerization was very minor and
consumption was nil. [d] Initiator: 0.01 M benzoyl peroxide.
[e] Initiator: 0.01 M trans–cinnamoyl peroxide. [f] Equilibration of
β–chlorostyrenes in CCl[d,g] with trace of Br$_2$ at 76°C leads to
trans/cis=4.26±0.29. [g] Equilibration of β–bromostyrenes in
cumene with trace of azo–*bis*–isobutyrylonitrile and p–thiocresol
at 76°C leads to *trans/cis*=6.69±1.03.

after decomposition to prevent photoisomerization of the
β–chloro–and β–bromostyrene products. The β–halo-
styrenes were identified by GC retention time comparisons
with authentic samples and the yields were measured by use
of internal standard. 7 and 10 were identified and the yields
were measured by NMR. The results are shown in the Table 3.

Accurate *trans/cis* ratio of β–bromostyrenes was difficult
to obtain because of very small yield of *cis*– β–bromostyrene.
In order to find out and compare the change of *trans/cis*
ratios of the β–halostyrenes during reactions, following
experiments were designed.

β–Halostyrenes were heated with small amount of initiators
in degassed and sealed Pyrex ampoules in CCl$_4$ or Cl$_3$CBr
as solvents at 76°C for a minimum of 6 half–lives of the
initiators[19]. All the work–up were done in darkness to prevent
photoisomerization by sun–light. The reaction mixtures were
analyzed by GC technique to check the consumption and
degree of isomerization (change of *trans/cis* ratio) of the
starting β–halostyrenes. The result is shown in the Table 4.

Discussion

Homolysis of 1 generates styryl radicals 2 or 2a which are
scavenged by CCl$_4$ or Cl$_3$CBr to give 3, 4 and trichloromethyl
radical. The trichloromethyl radical, in turn, adds to the
olefinic bonds of β–halostyrenes and the chain reactions
begin to take place. We propose Schemes 1 and 2 as the
explanation of the results of the Tables 3 and 4.

Trichloromethyl radical irreversibly[20] adds to 3 or 4 to give
the intermediate radical 5 during this process C–C$_{sigma}$ and
C–C$_{pi}$ bond forms and dissolves, respectively, leaving the
resulting 5 internally energized. The internal energy partitions
to vibration and rotation of the bonds of 5 and may be
favorably utilized to cleave the carbon–halogen bonds (for-
mation of 7) instead of the formation of 1:1 addition product
6. We assume 7 to be in the *trans* form only considering the
free energy difference between the *trans* and *cis* forms[21]. The
β–eliminated chlorine radical from eq. (6) irreversibly adds
olefinic bond while the addition is reversible with bromine
radical. This will be clarified in a later part when we discuss
the isomerization.

trans-Cinnamoyl peroxide $\longrightarrow$

$$\text{C}_6\text{H}_5 \diagdown \text{C} = \text{C} \diagup \text{H} + 2\text{CO}_2 \qquad (1)$$

1   **2**

$$\text{C}_6\text{H}_5 \diagup \text{C}=\text{C} \diagdown \text{H} \cdot + \text{XCCl}_3 \longrightarrow \text{C}_6\text{H}_5 \diagdown \text{C}=\text{C} \diagup \text{H} + \cdot\text{CCl}_3 \qquad (2)$$

2   **3**

$$\text{C}_6\text{H}_5 \diagdown \text{C}=\text{C} \cdot + \text{XCCl}_3 \longrightarrow \text{C}_6\text{H}_5 \diagup \text{C}=\text{C} \diagdown \text{H} + \cdot\text{CCl}_3 \qquad (3)$$

2a   **4**

$$\text{C}_6\text{H}_5\text{CH}=\text{CHX} + \cdot\text{CCl}_3 \longrightarrow \text{C}_6\text{H}_5\dot{\text{C}}\text{H}-\text{CH(X)CCl}_3 \qquad (4)$$

3 or 4   **5**

$$\text{C}_6\text{H}_5\dot{\text{C}}\text{H-CH(X)CCl}_3$$

    XCCl₃
    ───//───→ C₆H₅CH(X)-CH(X)CCl₃ + ·CCl₃   (5)
                              6
    β-Cleavage
    ──────────→ trans-C₆H₅CH=CHCCl₃ + X·   (6)
                              7
    ──────────→ Telomers   (7)

5

(X = Cl or Br)

Scheme 1.

In Cl₃CBr only

$$\text{C}_6\text{H}_5\text{CH}=\text{CHBr} + \text{Br}\cdot \underset{(8b)}{\overset{(8a)}{\rightleftharpoons}} \text{C}_6\text{H}_5\dot{\text{C}}\text{H-CHBr}_2 \qquad (8)$$

6

$$\text{Cl}_3\text{CBr} + \text{Br}\cdot \underset{(9b)}{\overset{(9a)}{\rightleftharpoons}} \text{Br}_2 + \cdot\text{CCl}_3 \qquad (9)$$

$$\text{C}_6\text{H}_5\dot{\text{C}}\text{H-CHBr}_2$$

    Br₂(Cl₃CBr)
    ──────────→ C₆H₅CH(Br)CHBr₂ + Br· (·CCl₃) (10)
                              10
    ──────────→ Telomers   (11)

9

Scheme 2.

Another sink for the neutralization of **5** which did not undergo β-cleavage would be the formation of telomers.

There are several aspects in the reaction of Cl₃CBr, which would not be properly accounted for by the eqs. (1) through (7). They are as follows: lower yield of β-bromostyrene, formation of **10** and higher yield of telomers. Normally more telomers should have formed with CCl₄ than with Cl₃CBr. (Table 3) ; higher consumption and extensive isomerization of β-halostyrenes (Table 4). These observations lead us to propose additional mechanism (8) through (11).

Unlike the formation of **5**, the radical **9** forms *via* the reversible eq. (8) and does not possess the extra energy available to undergo predominantly β-cleavage [eq. (8b), isomerization] over the bromine transfer [eq. (10), formation of **10**] thus the two processes becoming comparable.

As for the bromine transfer to **9**, we propose Br₂ generated from eq. (9) is a better transferring agent than Cl₃CBr. Alkyl readicals are normally scavenged by Br₂ at the diffusion control limit[24] and the reversibility of eq. (9) has been well established[25].

The isomerization and the consumption of the starting β-halostyrenes (Table 4), would be clarified if we take into consideration of the reversibility of the addition reaction of chlorine and bromine atoms to olefinc bonds, which are expelled from **5**. The halogen atoms may also react with Cl₃CBr to give eq.(9) or Cl· + Cl₃CBr ⇌ Cl-Br + ·CCl₃ ⇌ Cl· + Br· + ·CCl₃.

The β-chlorostyrene in CCl₄ was consumed moderatly and the *trans/cis* ratio changed very little. We interprete this minor change as an evidence of thermal irreversible addition of chlorine atom to olefinic bond, which is consistent with the study of Dainton's *et al.*[27] The β-bromostyrene in CCl₄ was extensively isomerized with moderate consumption. The *trans/cis* ratio of isomerized β-bromostyrene is close to that obtained by thermal equilibration using thiyl radical. Bromine atoms expelled from eq. (6) would be responsible for the isomerization.

In both cases, the consumptions were moderate, which would be *partly* due to the absence of reactions (9) and the like. Even rough calculation of the heat contents of the reaction indicates the improbability of the following reactions, ·Cl + CCl₄ ⇌ Cl₂ + ·CCl₃ and Br· + CCl₄ ⇌ Cl-Br + ·CCl₃.

The different properties of bromine, chlorine and trichloromethyl radicals towards olefinic bond may well be understood in terms of the heat content. In the following type of reaction in which X is trichloromethyl or chlorine

$$\diagdown \text{C}=\text{C} \diagup + \text{X}\cdot \underset{(12b)}{\overset{(12a)}{\rightleftharpoons}} \cdot\overset{|}{\underset{|}{\text{C}}}-\overset{|}{\underset{|}{\text{C}}}-\text{X} \qquad (12)$$

radicals, ΔH for (12a) is -18 or -15 kcal/mole, while in case of bromine or thiyl radicals, it is only $-(2-3)$ kcal/mole[28]. This indicates the rate of (12b) will be much slower with trichloromethyl and chlorine radicals. The reversibility of bromine and thiyl radicals have been established[29].

Conclusion

β-Haloradicals would be normally neutralized by three reaction paths : halogen transfer, β-cleavage and telomerization. If the radicals are internally energized, halogen transfer step may become nil.

When carbon radicals are scavenged by Cl₃CBr, no other bromine sources than Cl₃CBr have yet been reported. We now report Br₂ generated under the present reaction conditions acts as another efficient radical scavenger.

Experimental

General. IR spectra were recorded either on a Perkin-Elmer infrared spectrophotometer 137 or 337 using 6.24 band of a polystyrene film as calibration peak. The IR cells are 0.15 mm in path length unless otherwise indicated.

All the NMR spectra were taken on either a Varian Associates A-60 or a T-60 spectrometer with tetramethylsilane (TMS) as an internal standard. Chemical shifts are reported in parts per million downfield from TMS.

Melting point determinations were made with an Electrothermal melting point apparatus and were uncorrected.

All the solvents were fractionally distilled and only center cuts were collected and stored under nitrogen in darkness.

trans-Cinnamoyl Peroxide, **1**. Compound **1** was prepared according to the methods of either Staab's[13] or Greens's[14].

The m.p of **1** is 130–132°C (reported : 127–130°C)[30] ; the carbonyl IR stretching appears at 1770 cm^{-1} as a doublet. ^{1}H NMR (δ, CCl$_4$) : 6.32–6.58 (*d*, 1H), 7.70–7.79(*d*, 1H), Anal. Cald. for C$_{18}$H$_{14}$O$_4$: C, 73.47 ; H, 4.76; Found : C, 73.62; H, 4.60.

β-Chlorostyrene (A Mixture of cis- and trans-Isomers). The cinnamic acid dichloride[15] (22 g) was refluxed in the solution of 16 g Na$_2$CO$_3$ in 300 *ml* H$_2$O at 100°C for 8 hours. The product was then extracted with ether 3 times, washed with water 2 times, dried over MgSO$_4$ and concentrated in a rotary evaporator to give 22.6 g of a mixture of *cis-* and *trans-β*-chlorostyrene, which was purified by a vacuum fractional distillation to yield a colorless liquid. The NMR data of *cis-*and *trans-β*-chlorostyrenes were identical with that of authentic samples. Refer to reference (15) for the NMR data of *cis-* and *trans-β*-chlorostyrenes.

cis-Enriched β-Chlorostyrene. A solution of 5.1 g of *trans*-enriched *β*-chlorostyrene and 0.7 g of benzophenone (photosensitizer) in 250 *ml* of benzene was irradiated by low pressure Hanovia lamp using a Pyrex filter at room temperature for 5.5 hours to give a product having 53.0% *cis*-content. The benzene was evaporated and the residue was vacuum distilled to give 2.8g of *cis*-enriched *β*-chlorostyrene.

β-Bromostyrene. Matheson Coleman & Bell reagent grade was purified by a vacuum fractional distillation, the center cut was collected and kept under nitrogen in darkness.

cis-β-Bromostyrene[16]. Cinnamic acid dibromide (30 g) was refluxed in the solution of 25 g NaHCO$_3$ in 500 *ml* acetone at 90°C for 8 hours under darkness.

The acetone was evaporated and water was added to the residue. The organic material was then extracted with ether 3 times. The ether layer was washed with cold water, dried over MgSO$_4$ and concentrated to give 11.5 g of light yellow liquid which was purified by a vacuum fractional distillation. An assay by vpc analysis shows the product to be more than 88% in the *cis* form[31].

Cinnamic Acid Dibromide[16]. A solution of 28 g of bromine in 50*ml* CHCl$_3$ was irradiated under a sun-lamp for 3 hours.

The reaction mixture was cooled and filtered to give 48 g of white solid. The yield of product having a melting point of 203–208°C was 92%.

trans-β-Trichloromethyl Styrene **7**. A solution of 15 g of *β*-bromostyrene and 1.0 g of benzoyl peroxide in 35 *ml* of of CCl$_3$Br was thermolyzed for 2.5 hours at 100°C; and additional 1.0 g of the peroxide was added and the thermolysis continued for another 4.5 hours.

The originally clear solution became dark brown in color. It was concentrated at 50°C to darker brown colored mixture. Compound **7** was fractionally distilled at 92°C$^{1.75}$ from the mixture.

1,2,2,–Tribromo–1–Phenyl Ethane **10**. A solution of 3.1 g of bromine in 5 *ml* of CCl$_4$ was slowly added to 3.2 g of *β*-bromostyrene in 5 *ml* CCl$_4$. The mixture was irradiated

under a sun-lamp for 2.5 hours at room temperature and concentrated to give 6.4 g of the tribromide, which was purified by a vacuum fractional distillation, b.p 110°C$^{2.0}$.

Thermolyses of trans-Cinnamoyl Peroxide **1** *in CCl$_4$ or Cl$_3$CBr.* 0.0100 *M* solution of **1** in CCl$_4$ and in Cl$_3$CBr, respectively, were thermolyzed at 76°C in sealed, degassed Pyrex ampoules.

After complete decomposition of **1**[32], the reaction mixtures were analyzed by vpc techniques and yields were calculated using *p*-dichlorobenzene as internal standard.

Homolytic Reactions of β-Halostyrenes with CCl$_4$ or Cl$_3$CBr. Solutions of 0.05 *M* of *β*-halostyrenes in CCl$_4$ and in Cl$_3$CBr, respectively, were heated with 0.01 *M* of a radical initiator in sealed, degassed Pyrex ampoules.

After complete decomposition of the peroxide, the remaining *β*-halostyrenes were analyzed by vpc with respect to the consumption and isomerization. The amount of consumption was calculated using *p*-dichlolobenzene as the internal standard in GC analysis.

As the blank reaction of the previous ones, 0.0500 *M* of both *β*-halostyrenes in CCl$_4$ and in CCl$_3$CBr respectively, were heated alone for over 15 hours in sealed degassed Pyrex ampoules.

Thermal Equilibration of β-Halostyrene. The thermal equilibrium values of *trans-β*-bromostyrene is 87.0±2.0% starting from the *cis-* and *trans*-enriched olefins (0.0714 *M*) *via* equilibration with small mounts of 2,2′-azobisisobutyronitrile (AIBN) (0.0096 *M*) and *p*-thiocresol (0.0245 *M*) in cumene at 76°C.

The thermal equilibrium value of *trans-β*-chlorostyrene is 81.0±1.0% starting from the *cis-*and *trans*-enriched olefins (0.0500 *M*) *via* equilibration with small amounts of bromine (0.0100 *M*) in CCl$_4$ at 76°C.

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(31) The β–bromostryrene does not appear to be extremely photosensitive but the *cis*–isomer was observed to isomerize easily to the *trans*–isomer under certain condition. The solution containing the *cis*–isomer was kept in darkness and it must not be left in contact with foreign materials for a long time.

(32) The decomposition of the peroxide was traced by the disappearance of the carbonyl band at 1770 cm⁻¹ by IR.

Complexes of Polyvalent Metal Ions (VI). Complexes of Nickel and Cadmium with Dibasic Organic Acids in Aqueous, Ethanol-Water and Acetone-Water Solutions*

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Solutions of Ni^{2+} and Cd^{2+} were mixed with the solutions of various dibasic organic acids in the presence of cation exchange resin at room temperature. The distribution ratios of the metal ions between resin and solution were measured, using radio-active metal ions as tracer. From the observed variation of the distribution ratios with acid anion concentrations, it was con-cluded that Ni^{2+} and Cd^{2+} formed one-to-one complexes with succinate, malonate, *o*-phthalate and tartarate ions in aqueous, 20% ethanol-water and 20 % acetone-water solutions. The results of the present study indicated that the rela-tive stabilities of the complexes in solution increased generally in the order : $Ni^{2+} < Cd^{2+}$ complexes. Succinate < malonate < *o*-phthalate < tartarate complexes. Aqueous < mixed solvent systems.