STEREOSPECIFICITY IN HYDROGEN ATOM TRANSFER TO THE ISOMERIC VINYL RADICALS
GENERATED FROM THE CIS- AND TRANS-t-BUTYL α-BROMOPERCINNAMATES.

Lawrence A. Singer and Noland P. Kong

Department of Chemistry, University of Chicago, Chicago, Illinois 60637

Recently, we (1) and Kampmeier and Fantazier (2) reported several examples where equilibration of vinyl radicals ($\underline{1} \rightleftharpoons \underline{2}$) occurs faster than hydrogen atom transfer from hydrocarbon solvents since the same cis/trans olefin product ratio is obtained from both isomeric starting perester sources.
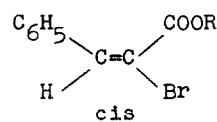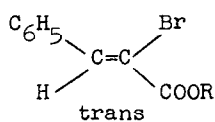
Scheme 1
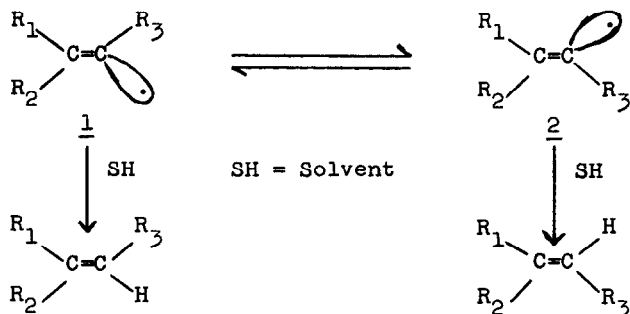
We now wish to present some observations of stereospecificity in the α-bromo-β-phenylvinyl radical system ($R_1=C_6H_5$, $R_2=H$, $R_3=Br$) where the t-butyl peresters of cis- and trans-α-bromocinnamic acid serve as precursors for the vinyl radicals.

The isomerically pure acids were obtained by separating a mixture of cis- and trans-α-bromocinnamic acids (3) through their barium salts (4). trans-t-Butyl α-bromopercinnamate (m.p. 37.5-40.0°) was prepared by treating the trans-acid chloride with sodium t-butylhydroperoxide in benzene solution at 0°. The cis-perester was available by the Staab synthesis (5) which consists of reacting the imidazolide (from the cis-acid and N,N'-carbonyl-diimidazole) with sodium t-butylhydroperoxide in ether solution at room temperature. cis-t-Butyl α-bromopercinnamate is an oil at room temperature and

was chromatographed on Florisil prior to use. Satisfactory combustion analy-

ses were obtained on both peresters. Table 1 contains the n.m.r. data for

the acids and peresters. The perester samples used in this study were at

least 95°/o isomerically pure as readily determined by n.m.r. analysis.

Table 1

N.M.R. Data of the cis- and trans-α-Bromocinnamic Acids

and their t-Butyl Peresters.

$$C_6H_5 \diagdown \quad \diagup Br$$
$$C=C$$
$$H \diagup \quad \diagdown COOR$$
trans

$$C_6H_5 \diagdown \quad \diagup COOR$$
$$C=C$$
$$H \diagup \quad \diagdown Br$$
cis

R	Isomer	Vinyl H	Aromatic H	H in R
			δ^a	
H	cis[b]	7.43 s	7.28 s	10.6 s
	trans[b]	8.35 s	7.50 m 7.90 m	11.5 s
O-C(CH$_3$)$_3$	cis[c]	7.30 s	7.30 s	1.2 s
	trans[c]	8.30 s	7.50 m 7.90 m	1.4 s

[a] s = singlet, m = multiplet. [b] In chloroform -d. [c] In carbontetrachloride.

The peresters were decomposed in degassed and sealed Pyrex ampoules under

the conditions described in Tables 2 and 3. It was necessary to protect the

ampoules from light during and after decomposition because of facile photo-

isomerization of the β-bromostyrenes. The acid yields were determined by

gravimetric analysis while the olefin yields (cis- and trans-β-bromostyrene)

were measured by v.p.c. techniques (6). The cyclohexyl esters were isolated

by chromatography on Florisil and identified by spectral comparison with

authentic samples.

It is observed in Tables 2 and 3 that (i) the major products arise from

direct reactions of the acyloxy radicals (acids and esters) and (ii) the same

olefin product ratio is not obtained from both isomeric starting sources.

The large yield of carboxyl containing product indicates that the

acyloxy radical is long enough lived ($>10^{-10}$ sec) to become significantly

Table 2

Product Compositions from the Thermal Decompositions
of cis- and trans-t-Butyl α-bromopercinnamates at 110°.

Perester	Solvent	[Perester]	Olefin[a] Yield	Acid[b] Yield	Ester[c] Yield	cis-[d] Olefin
		M		°/o[e]		
trans	Cumene	0.041	40.3	-	-	59.4
		0.12	38.9	-	-	25.2
		0.32	25.5	68.6	-	21.1
cis	Cumene	0.048	14.8	-	-	32.1
		0.12	11.2	-	-	30.3
		0.30	8.4	64.0	-	27.4
trans	Cyclohexene	0.19	8.9	-	-	94.5
		0.23	10.3	-	-	95.3
		0.32	5.8	54.2	24.3	92.0
cis	Cyclohexene	0.15	5.2	-	-	8.0
		0.19	4.4	-	-	16.0
		0.32	7.4	45.9	19.8	20.0

[a]Determined by v.p.c. analysis on a 30°/o carbowax on Chromsorb P column at 170°, gas flow of 60 cc/min. Ret. times: cis, 23.5 min., trans, 27.5 min.
b By gravimetric analysis. Acids were isomerically pure of expected geometry.
c Isolated by Florisil chromatography. Cyclohexyl esters were of expected geometry. d Based on total olefin yield. e Olefin yields are accurate to ca ± 3°/o and acid and ester yields to ca ± 5°/o.

Table 3

Product Compositions from the Thermal Decompositions
of cis- and trans-t-Butyl α-bromopercinnamates in
Benzene at 110° with added Dihydroanthracene (DHA).

Perester	[Perester]	[DHA]	Olefin[a] Yield	Acid[b] Yield	cis-[c] Olefin
	M	M		°/o[d]	
trans	0.078	0.38	19.1	-	71.2
	0.14	0.45	21.5	76.0	68.2
cis	0.075	0.38	4.0	-	7.5
	0.11	0.38	4.7	54.5	15.5
	0.14	0.38	5.6	-	11.9

[a]Determined by v.p.c. analysis on a 30°/o Ucon on Chromsorb P column at 180°, gas flow 90 cc/min. Ret. times: cis, 19.5 min.; trans, 22.5 min.
bBy gravimetric analysis. Acid yields were of expected geometry. cBased on total olefin yield. dOlefin yields are accurate to ± 3°/o and acid yields to ± 5°/o.

involved in nongeminate bimolecular reactions. Previous studies (1,2) with vinyl peresters revealed little acid product indicating that decarboxylation in those systems (containing α-methyl and α-phenyl groups) was somewhat faster than hydrogen atom transfer to the acyloxy radical. The slower rate of decarboxylation of the α-bromo-β-phenylvinyl radical may be due to extra stabilization of the acyloxy radical through 1-4 electronic interaction with the bromine and/or to an increase in the energy of the transition state for decarboxylation by the inductive effect of the bromine.

The vinyl radicals that result from decarboxylation of the acyloxy radicals clearly do not equilibrate prior to hydrogen atom transfer from the faster scavengers (cyclohexene and DHA). In view of our previous studies showing the importance of stereoselectivity in determining the cis/trans olefin product distributions in the α-methyl- and α-phenyl-β-phenylvinyl radical systems (1), an equilibrated vinyl radical system in the α-bromo case should lead to an olefin distribution of cis/trans $\cong$ 1 in cyclohexene and in benzene with DHA, and cis/trans $\cong$ 1.5 in cumene. The observed product distributions in the former two scavenging systems reveal various degrees of stereospecificity in the hydrogen atom transfer step.

In cumene some stereospecificity may occur upon entry into the vinyl radical system from the cis-perester side at low substrate concentration. However, there seems to be a trend towards equilibrium in the olefin product at higher perester concentration (10). We do not have an adequate explanation for this apparent subsequent isomerization of the β-bromostyrenes under the reaction conditions. No isomerization of cis-β-bromostyrene is observed in cumene at 110° in the presence of .11 M trans-α-bromocinnamic acid or at 140° in the presence of decomposing di-t-butylperoxide (.05 M). Also, cis-β-bromostyrene is isomerized only 17°/₀ to the trans-olefin when in solution with decomposing trans-t-butyl α-methylpercinnamate (.24 M in cumene) (1) at 110°.

The observed stereospecificity in hydrogen atom transfer to the α-bromo-β-phenylvinyl radicals may be due to (i) a rate of inversion which is competitive with hydrogen atom transfer for a mechanism as in Scheme 1, or (ii) a mechanism involving complexation of the acyloxy radical with the potential

hydrogen atom donor followed by decarboxylation and an enhanced rate of hydro-
gen atom transfer as shown in Scheme 2.

Scheme 2
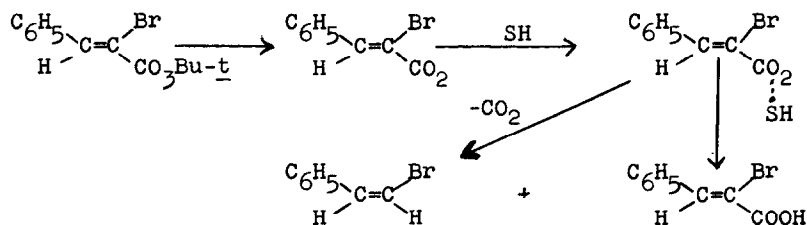
The first alternative requires that the rate constant for inversion of

the α-bromo-β-phenylvinyl radical be $\leq$ 10 sec^{-1} (11). Recently, we argued

that the rate constant for inversion of the α-methyl-β-phenylvinyl radical

must be $>$ 10^3 sec^{-1} (1). A slower inversion rate for the α-bromo system is

not unreasonable considering the difference in mass between methyl and bro-

mine.

There is an excellent analogy for Scheme 2 in the work of Walling and

co-workers on alkoxy radicals (12) which appear to complex with olefins and

aromatic hydrocarbons. If Scheme 2 obtains, the inversion rate in the α-

bromo-β-phenylvinyl radical is not necessarily slower than in the α-methyl

system. Rather, an enhanced rate of hydrogen atom transfer from the complex

stage could accommodate the results.

Studies are in progress which hopefully will distinguish between the two

possibilities.

<div align="center">References</div>

1. L. A. Singer and N. P. Kong, Tet. Letters, No. 19, 2089 (1966); J. Am.
    Chem. Soc., 88, 5213 (1966).

2. J. A. Kampmeier and R. M. Fantazier, J. Am. Chem. Soc., 88, 1959 (1966).

3. A mixture of cis- and trans-α-bromocinnamic acids was prepared by dehydro-
    bromination of methyl cinnamate dibromide in cold, aqueous-alcoholic
    potassium hydroxide solution.

4. T. C. Jones and J. J. Sudborough, J. Chem. Soc., 95, 1538 (1909).

5. H. A. Staab, W. Rohr, and F. Graf, Ber., 98, 1122 (1965).

6. Commercial (Eastman Organic Chemicals) trans-β-bromostyrene was purified
    by preparative v.p.c. The cis-isomer was prepared as previously described
    (7) and purified by preparative v.p.c. The infrared (8) and n.m.r. (9)
    spectra of these olefins were identical with those previously reported.

7. S. J. Cristol and W. P. Norris, J. Am. Chem. Soc., 75, 2645 (1953).

8. E. Grovenstein, Jr., and D. E. Lee, ibid., 75, 2639 (1953).

9. D. Seyferth and L. G. Vaughan, J. Organometallic Chem., 1, 437 (1964).

10. Equilibrations in cyclohexane at 110° with small amounts of azo-iso-
    butyrylnitrile and p-thiocresol give apparent equilibrium mixtures of
    79.0°/₀ and 81.0°/₀ trans-β-bromostyrene from the cis- and trans-olefins,
    respectively.

11. Estimated from chain transfer constants and absolute rate data on styrene
    polymerization in C. Walling, "Free Radicals in Solution", J. Wiley and
    Sons, Inc., New York, New York, 1957, pp 94, 152. It is assumed that chain
    transfer to the vinyl radical is faster than chain transfer to the more
    stable styryl radical.

12. C. Walling and A. Padwa, J. Am. Chem. Soc., 85, 1593 (1963); P. Wagner
    and C. Walling, ibid., 87, 5197 (1965).