Stereospecificity in Hydrogen Atom Transfer to the Vinyl Radicals Derived from the *cis*- and *trans*-*t*-Butyl α-Chloropercinnamates

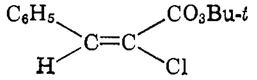
Lawrence A. Singer[1] and Noland P. Kong

Contribution from the Department of Chemistry, University of Chicago,
Chicago, Illinois 60637. *Received May 26, 1967*

Abstract: Partial stereospecificity in hydrogen atom transfer to the isomeric vinyl radicals derived from the *cis*- and *trans*-*t*-butyl α-chloropercinnamates (**1** and **2**) has been observed. Decomposition of the *cis* perester **1** in cumene at 110° leads to β-chlorostyrenes with a *trans*:*cis* composition of 76:24 while the *trans* perester **2** gives a 13:87 mixture. As benzene is added as a diluent, the extent of specificity in the olefin mixture linearly decreases. Plots of the olefin product ratios against donor concentration lead to intercept values of *trans*:*cis* = 66:24 for **1** and 37:63 for **2**. These intercept values reflect hydrogen atom transfer to an equilibrated vinyl radical system and should be the same since the direction of entry into a system that equilibrates is kinetically not important (Scheme I). This inconsistency is ascribed to an acyloxy radical–cumene complex (Scheme II) in the decomposition of **2** which collapses with high stereospecificity to *cis* olefin. A similar result is obtained with the dihydroanthracene (DHA)–benzene scavenging system. Kinetic analyses of the plots of the olefin product ratios against scavenger concentration for **1** indicate that with cumene as hydrogen atom donor, $k_{\mathrm{H\ transfer}}/k_{\mathrm{inversion}} = 0.19\ M^{-1}$ for the *trans* radical and $0.095\ M^{-1}$ for the *cis* radical. With DHA, $k_{\mathrm{H\ transfer}}/k_{\mathrm{inversion}} = 12.1\ M^{-1}$ for the *trans* radical and $4.30\ M^{-1}$ for the *cis* radical. Product studies reveal high acid yields in the decompositions of **1** and **2** which means that they decompose by oxygen–oxygen fission to give acyloxy and *t*-butoxy radicals. Further, the acyloxy radicals must be long-lived enough to escape the "cage" ($>10^{-10}$ sec) before significant decarboxylation takes place. Thus, complexation between the acyloxy radicals and aromatic hydrogen atom donors is possible. Presumably, steric hindrance reduces the importance of such complexation in the acyloxy radicals derived from **1**.

While vinyl radicals with α-alkyl and α-aryl substituents cannot be trapped prior to *cis–trans* equilibration with hydrogen atom transferring agents such as cumene,[2,3] there have been reports of partial stereospecificity in the transfer step with scavengers such as halogenated solvents[4] and radical anions.[5] Recently, we demonstrated that partial stereospecificity can also be obtained in the α-bromo-β-phenylvinyl radical system with hydrocarbon solvents or added dihydroanthracene as scavengers.[6] Unfortunately, we were not able to uniquely explain the cause of the observed specificity in that system. One of our explanations involved postulating an acyloxy radical–solvent complex.

We now wish to report some results on the α-chloro-β-phenylvinyl radical system, generated from the *t*-butyl peresters of *cis*- and *trans*-α-chlorocinnamic acid (**1** and **2**), which shows even higher stereospecificity in the hydrogen atom transfer step and which we believe may offer the first evidence for such complexation.



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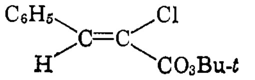

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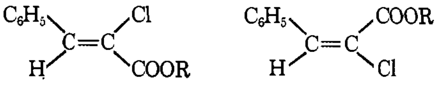
Results

The *cis* perester **1** was prepared by reacting the imidazolide[7] of the *cis* acid with *t*-butyl hydroperoxide while the *trans* perester **2** was obtained by treating the *trans* acid chloride with sodium *t*-butyl hydroperoxide. Good combustion analyses were obtained on both **1** (mp 34–37°) and **2** (oil). All samples of **1** and **2** were chromatographed on Florisil prior to use and were at least 95% isomerically pure as readily determined by nmr analysis (Table I).

Table I. Nmr Data of the *cis*- and *trans*-α-Chlorocinnamic Acids and Their *t*-Butyl Peresters



trans *cis*

R	Isomer	Vinyl H	Aromatic H	H in R
H	*cis*[b]	7.18 s	7.18 s	10.13 s
	trans[b]	7.87 s	7.20 m	10.83 s
O–C(CH$_3$)$_3$	*cis*[c]	7.20 s	7.70 m	
	trans[c]	7.70 s	7.42 s	1.22 s
			7.30 m	1.33 s
			7.70 m	

[a] s = singlet, m = multiplet. [b] Deuteriochloroform. [c] Carbon tetrachloride.

The *cis*- and *trans*-α-chlorocinnamic acids necessary for preparing the peresters were obtained as a mixture by a combined dehydrochlorination–saponification of methyl cinnamate dichloride with potassium hydroxide. The acid mixture, which was mainly the *trans* isomer, was irradiated through a Pyrex filter in benzene solution with benzophenone as a sensitizer to increase the *cis* acid content. The *cis* and *trans* acids were then cleanly separated through their barium salts.[8]

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(1) Author to whom inquiries may be addressed, Department of Chemistry, University of Southern California, Los Angeles, California. 90007.

(2) L. A. Singer and N. P. Kong, *Tetrahedron Letters*, 2089 (1966); *J. Am. Chem. Soc.*, **88**, 5213 (1966).

(3) J. A. Kampmeier and R. M. Fantazier, *ibid.*, **88**, 1959 (1966).

(4) O. Simma, K. Tokumaru, and H. Yui, *Tetrahedron Letters*, 5141 (1966).

(5) G. D. Sargent and M. W. Browne, Abstracts, 153rd National Meeting of the American Chemical Society, Miami Beach, Fla., April 10–14, 1967, p O-54.

(6) L. A. Singer and N. P. Kong, *Tetrahedron Letters*, 643 (1967).

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

(8) J. J. Sudborough and T. C. James, *J. Chem. Soc.*, **89**, 105 (1903).

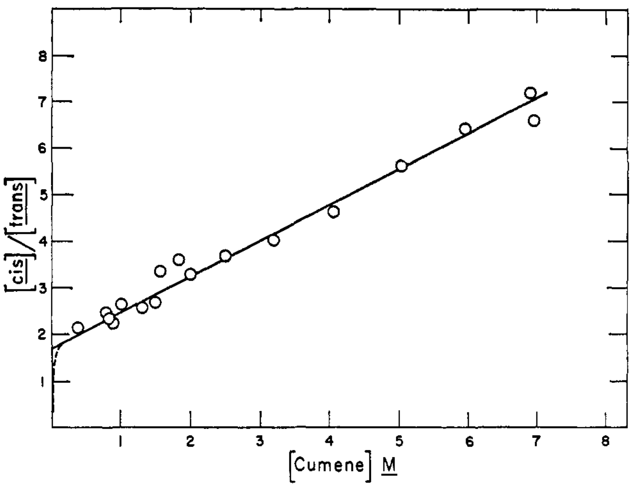


Figure 1. β-Chlorostyrene product ratios from the thermal decompositions of *trans*-*t*-butyl α-chloropercinnamate in cumene–benzene mixtures at 110°.

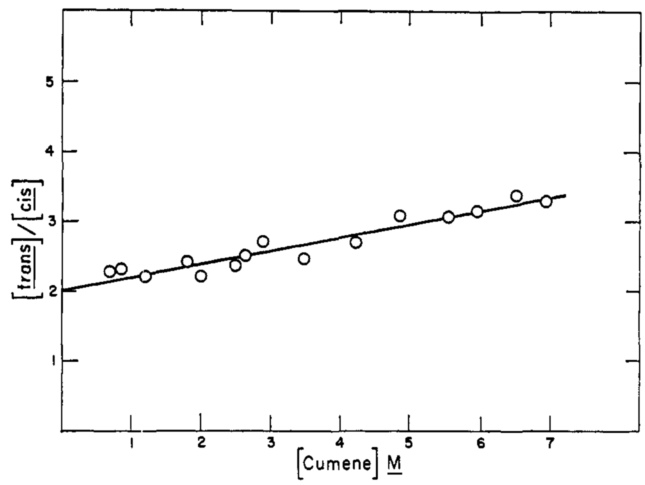
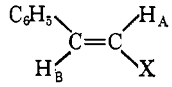


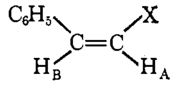
Figure 2. β-Chlorostyrene product ratios from the thermal decompositions of *cis*-*t*-butyl α-chloropercinnamate in cumene–benzene mixtures at 110°.

A mixture of the olefin decomposition products, the *cis*- and *trans*-β-chlorostyrenes, was prepared by decomposition of cinnamic acid dichloride in aqueous sodium carbonate solution at 100°.[9] The isomerically pure olefins were obtained by preparative vpc and identified by nmr analysis by comparison with the data previously reported for the β-bromostyrenes[10] (Table II). These assignments were confirmed by the observed direction of equilibration. Starting from either 100% *trans* olefin or a mixture of 64.8% *cis* and 35.2% *trans* olefin, the position of equilibrium at 110° in cumene was found to be 82% *trans*- and 18% *cis*-β-chlorostyrene.

Table II. Nmr Data of the β-Halostyrenes[a]



trans



cis

X	Isomer	Vinyl H H_A H_B	Aromatic H
Cl	*cis*[b]	6.42 d, 6.80 d J = 8 cps	7.54 m 7.83 m
Cl	*trans*[b]	6.58 d, 6.82 d J = 14 cps	7.28 s
Br[c]	*cis*[b]	6.71 d, 7.23 d J = 9 cps	7.73 m 8.11 m
Br[c]	*trans*[b]	6.63 d, 6.98 d J = 14 cps	7.20 s

[a] s = singlet, d = doublet, m = multiplet. [b] Carbon tetrachloride. [c] Reference 10.

The peresters were decomposed in degassed and sealed Pyrex ampoules in cumene–benzene or dihydroanthracene (DHA)–benzene scavenging systems at 110° for a minimum of 10 hr. Infrared analysis revealed no remaining perester after this time. The ampoules were protected from light during and after decomposition to prevent photoisomerization of the β-chlorostyrene products. The total olefin and acid yields are given in Table III. The olefins were identified by vpc retention time comparisons with authentic samples and the yields were measured by use of internal standards. Where only relative olefin yields were desired (Figures 1–4), an internal standard was not added. The acid yields were determined by gravimetric analysis, and the isolated acids showed retained geometry in all cases. A small yield (5.4%) of 3-chlorocoumarin was isolated by Florisil chromatography from the decomposition of the *cis* perester (0.08 *M*) in benzene with DHA (0.35 *M*) as scavenger.[11]

Table III. Product Compositions from the Thermal Decompositions of the *cis*- and *trans*-*t*-Butyl α-Chloropercinnamates at 110°

Perester	[Perester], *M*	Scavenging[a] system	Products, % Total olefin[b]	Acid[c]
cis	0.020	0.10 *M* DHA	...	49
	0.080	0.35 *M* DHA	10.9 ± 0.4	63[d]
	0.12	Cumene, neat	38.1 ± 2.4	...
	0.23	Cumene, neat	15.5 ± 1.4	...
	0.29	Cumene, neat	...	50
	0.14	2.0 *M* cumene	21.0 ± 0.7	...
	0.15	0.86 *M* cumene	11.4 ± 0.2	...
trans	0.019	0.10 *M* DHA	...	49
	0.029	0.10 *M* DHA	10.2 ± 0.4	..
	0.080	0.46 *M* DHA	20.0 ± 0.5	70
	0.13	Cumene, neat	43.6 ± 3.6	...
	0.24	Cumene, neat	24.0 ± 0.4	42
	0.14	2.5 *M* cumene	21.0 ± 0.5	...
	0.13	1.3 *M* cumene	13.4 ± 0.7	...
	0.14	0.84 *M* cumene	8.74 ± 0.01	...

[a] In benzene unless otherwise stated. [b] *cis*- and *trans*-β-chlorostyrenes. Yields determined by vpc analysis on a 12-ft 30% Ucon on Chromsorb P column treated with 2% HMDS (hexamethyldisilane) or a 10-ft 30% Carbowax on Chromosorb P column treated with 2% HMDS. *o*-Dichlorobenzene and bromobenzene were employed as internal standards. [c] Determined by gravimetric analysis. Isolated acids were isomerically pure and of retained geometry. [d] A separate run gave 5.4% of 3-chlorocoumarin by Florisil chromatography.

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(9) H. Biltz, *Ann.*, **296**, 266 (1897).

(10) D. Seyferth and L. G. Vaughan, *J. Organometal. Chem.* (Amsterdam), **1**, 437 (1964).

(11) Low yields of coumarin products were found in the decomposition of the *cis*-*t*-butyl α-methyl- and α-phenylpercinnamates[1] and the *cis*-*t*-butyl α,β-dimethylpercinnmate[3] and presumably arise from cyclization of the intermediate acyloxy radical. Kinetic studies[2,12] revealed no evidence for anchimeric assistance in oxygen–oxygen bond fission in the *cis* peresters.

(12) R. M. Fantazier and J. A. Kampmeier, *J. Am. Chem. Soc.*, **88**, 5219 (1966).

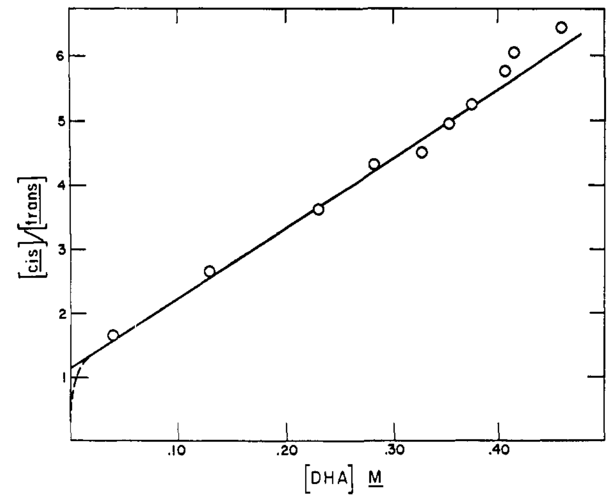
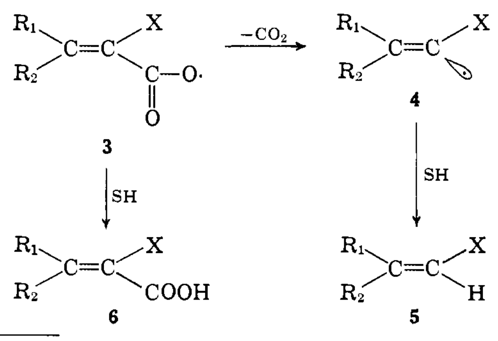


Figure 3. β-Chlorostyrene product ratios from the thermal decompositions of *trans-t*-butyl α-chloropercinnamate in DHA–benzene mixtures at 110°.

The dependency of the *cis*:*trans* olefin ratio on scavenger concentration is shown in Figures 1–4 for the cumene–benzene and DHA–benzene systems. All the data plotted represent an average of two measurements. The initial perester concentrations were between 0.04 and 0.2 *M* in the cumene system and 0.01 and 0.07 *M* in the DHA–benzene system. At least a fivefold excess of scavenger over initial perester concentration was used in all runs with most runs having a tenfold or higher ratio. The *cis*:*trans* olefin ratio was found to be independent of initial perester concentration although the total olefin yield is clearly inversely related to the initial substrate concentration[2] (Table III). A control experiment showed that *trans*-β-chlorostyrene (0.10 *M*) is essentially configurationally stable in the presence of decomposing *trans-t*-butyl α-bromopercinnamate (0.09 *M*)[13] or with *trans*-α-chlorocinnamic acid (0.08 *M*) at 110° in cumene for 24 hr. Thus, the observed olefin product ratios are kinetically determined.

Discussion

The results in Table III and in Figures 1–4 demonstrate two characteristic features of the *t*-butyl α-halopercinnamate systems: (i) significantly higher acid yields are found relative to the yields observed in the α-methyl and α-phenyl systems,[2] and (ii) partial stereospecificity in the hydrogen atom transfer step (**4** → **5**) is found in contrast to the facile *cis–trans* equilibration of the vinyl radical intermediates in the α-methyl and α-phenyl systems.[2]



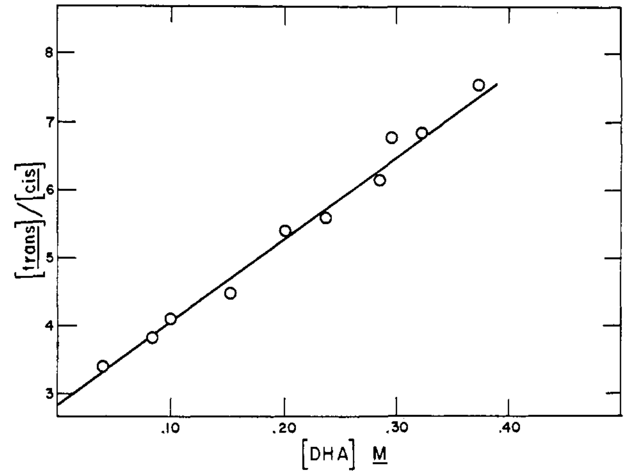
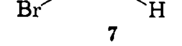


Figure 4. β-Chlorostyrene product ratios from the thermal decompositions of *cis-t*-butyl α-chloropercinnamate in DHA–benzene mixtures at 110°.

Previously,[6] we commented that the high acid yields in the *cis*- and *trans-t*-butyl α-bromopercinnamate system may be due to enhanced stabilization of the acyloxy radical intermediates (**3**) by a direct electronic interaction with bromine. Recent studies on the *cis*- and *trans-t*-butyl β-bromopercinnamates (**7** and **8**)[14] do not



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support this view since decomposition of **7** (which is incapable of such interaction) in cumene leads to a 64% yield of the corresponding acid while **8** gives a 60% acid yield. Rather, we believe that the inductive influence of the α or β halogen substituent is more important. If the ground-state energy of **3** is raised by a strong electron-withdrawing substituent, faster rates of (i) hydrogen atom transfer to give **6** and (ii) decarboxylation to give **4** could result. If, however, the energy of the vinyl radical **4** is also significantly raised by the α-halogen, then only the rate of hydrogen atom transfer (**3** → **6**) may be enhanced, and the rate of decarboxylation (**3** → **4**) may even be retarded.

Further, destabilization of the vinyl radical by α-halogen substituents would lead to a faster rate of hydrogen atom transfer to **4** and would be sufficient to explain the stereospecificity in the olefin products in those systems. A large difference in barriers to inversion between the α-halo and α-methyl and α-phenyl systems is not a necessary conclusion, as will be discussed below.

Kinetic Analysis. Scheme I is the kinetic scheme expected to operate in the α-chloro-β-phenylvinyl radical system. Kinetic analysis using the steady-state approximation gives from the *cis* perester **1** [*trans* olefin]/[*cis* olefin] = $(k_tk_{-1})/(k_1k_c) + \{k_t[\mathrm{SH}]\}/k_1$, and from the *trans* perester **2** [*cis* olefin]/[*trans* olefin] = $(k_ck_1)/(k_{-1}k_t) + \{k_c[\mathrm{SH}]\}/k_{-1}$.

It is immediately seen that if k_1 and k_{-1} are $\gg k_c$ and k_t, the olefin product ratios would be independent of scavenger concentration and they would be the same

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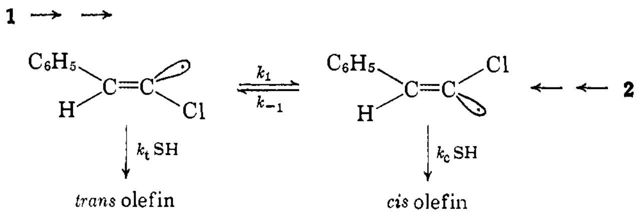
(13) *trans-t*-Butyl α-bromopercinnamate should be a good model for the α-chloropercinnamates because the acyloxy radical is relatively long-lived in that system as in the latter.[6] In addition, isomerization of *trans*-β-chlorostyrene is easier to follow by vpc since the β-bromostyrene products from the decomposing perester have longer retention times.

(14) N. P. Kong, unpublished results.

Scheme I



regardless of the direction of entry into the system (**1** or **2**). This situation was observed in the α-methyl and α-phenyl systems.[2]

The stereochemical results from the α-chloro-β-phenylvinyl radical system indicate that equilibration does not precede hydrogen atom transfer. From the slope and intercept values of Figures 1–4, the k_t/k_1 and k_c/k_{-1} ratios can be independently calculated from the data obtained from **1** and **2**, and they are shown in Table IV. The values of these rate constant ratios which are derived from **1** and **2** are not the same.

Table IV. Calculated Rate Constant Ratios (M^{-1}) for Hydrogen Atom Transfer *vs.* Inversion in the α-Chloro-β-phenylvinyl Radical System

	Transferring agent			
	Cumene		DHA	
Source of data	k_c/k_{-1}	k_t/k_1	k_c/k_{-1}	k_t/k_1
cis perester	0.095	0.19	4.30	12.1
trans perester	0.79	0.46	11.1	10.5

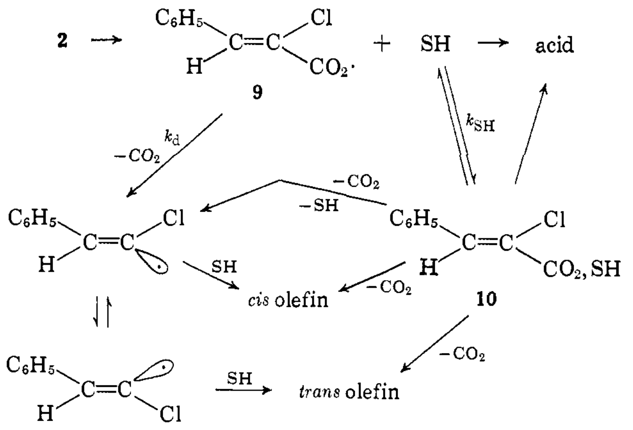
Further analysis of the results suggests that the source of the inconsistency may be the data from the *trans* perester. As shown above, the intercept value $(k_tk_{-1})/(k_ck_1)$ is the *trans*:*cis* olefin ratio obtained from a vinyl radical system that has equilibrated prior to scavenging. With the *cis* perester as precursor, these values are 66:34 in cumene–benzene and 74:26 in DHA–benzene while from the *trans* perester, the *trans*:*cis* olefin ratios are 37:63 in cumene–benzene and 44:56 in DHA–benzene. If the α-methyl-β-phenylvinyl radical system[2] is used as a model for the extent of stereoselectivity (*i.e.*, retardation of k_t relative to k_c because of steric factors in the transfer step) expected in the hydrogen atom transfer step,[15] the values obtained from the *cis* perester appear more reasonable than those from the *trans* perester.

Utilizing the data from the *cis* perester and assuming $k_{-1}/k_1 \approx 3$ gives $k_c/k_t \cong 1.5$ for cumene and 1.1 for DHA. These values are consistent with the previous observation[2] that stereoselectivity increases as the effective bulk of the transferring agent increases.

Acyloxy Radical–Solvent Complexation. The high acid yields in the α-halovinyl radical systems indicate that the acyloxy radical intermediates (**3**) are long-lived enough ($>10^{-10}$ sec) to become significantly involved in nongeminate bimolecular reactions. It should be further noted that the anomalous stereochemical results obtained with the *trans* perester are in the direction of enhanced stereospecificity in the olefin products.

An explanation consistent with both of these observations is an acyloxy radical–hydrogen atom donor complex **10** as shown in Scheme II. The complex could (i) go to acid upon hydrogen atom transfer from the complexing donor molecule, (ii) collapse with high stereospecificity to *cis* olefin by hydrogen atom transfer after decarboxylation, or (iii) enter the "usual" vinyl radical scheme if the donor molecule diffuses away without transferring hydrogen atom following decarboxylation.

Scheme II



The intercept in the plot of *cis* olefin/*trans* olefin against scavenger concentration with such a scheme should still be $(k_ck_1)/(k_{-1}k_t)$. Extrapolation of the plots in Figures 1 and 3 gives different intercept ratios than were obtained from the *cis* perester in Figures 2 and 4. It is possible that there is a curved region (dashed lines in Figures 1 and 3) at lower concentrations (*ca.* 10^{-3} *M* scavenger) which is presently beyond the limits of our analytical method. Such effective complexation would require that k_{SH} (the bimolecular rate constant for complex formation) $\gg k_d$ (the unimolecular rate constant for decarboxylation of **9**).

There are excellent analogies for Scheme II in the work of Walling and co-workers on alkoxy radicals[16a,b] which appear to complex with olefins and aromatic hydrocarbons and in Martin, Taylor, and Drew's study on the decomposition of acetyl peroxide[16c] which suggests that acetoxy radicals rapidly form a π complex with cyclohexene. Russell's work[17] suggesting a chlorine atom–aromatic hydrocarbon complex also falls within this category.

In regard to an acyloxy radical–solvent complex in the *cis* perester system, all that can be said is that there is no evidence that requires one to be postulated. The greater steric congestion around the carboxyl group when it is *cis* to the phenyl may decrease the importance of such complexation relative to the *trans* system.

Barriers to Inversion in the α-Substituted Vinyl Radicals. The k_c/k_{-1} and k_t/k_1 values in Table IV represent the first quantitative measure of inversion barriers in α-substituted vinyl radicals.[18] Unfortu-

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[15] With cumene as donor, decomposition of either *cis*- or *trans*-*t*-butyl α-methylpercinnamate gave an olefin distribution of *trans*:*cis* = 60:40. The equilibrium position of these olefin products at 110° in cumene is *trans*:*cis* = 75:25. It is assumed that the *trans*:*cis* vinyl radical equilibrium distributions (k_{-1}/k_1) for the two systems are similarly related to the observed olefin equilibrium distributions.

[16] (a) C. Walling and A. Padwa, *J. Am. Chem. Soc.*, **85**, 1593 (1963); (b) P. Wagner and C. Walling, *ibid.*, **87**, 5179 (1965); (c) J. C. Martin, J. W. Taylor, and E. H. Drew, *ibid.*, **89**, 129 (1967).

[17] G. A. Russell, *ibid.*, **80**, 4987 (1958).

[18] Esr studies indicate that the barrier to inversion in the simple vinyl radical is around 2 kcal/mole[19,20] and that it is somewhat higher in the 1-methylvinyl radical.[20]

[19] R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.*, **39**, 2147 (1963).

[20] E. I. Cochran, F. J. Adrian, and V. A. Bowers, *ibid.*, **40**, 213 (1964).

nately, until more reliable absolute rate data on hydrogen atom transfer reactions become available, the absolute values of k_1 and k_{-1} can only be estimated.

In our previous study on the α-methyl- and α-phenyl-β-phenylvinyl radical systems,[2] we estimated the inversion rates to be considerably greater than $\sim$10 sec^{-1} [21] and possibly greater than 10^4–10^5 sec^{-1}. The latter value comes from stereochemical studies on additions of mercaptans to terminal acetylenes where mercaptans (which are about 10^4 times more efficient as hydrogen atom transferring agents than hydrocarbons) transfer hydrogen atom to intermediate vinyl radicals.[22,23]

Since it is a rate constant ratio ($k_{\text{H transfer}}/k_{\text{inversion}}$) that determines the extent of stereospecificity, the specificity observed in the α-halo systems could be due to (i) an enhanced $k_{\text{H transfer}}$, (ii) a smaller $k_{\text{inversion}}$, or (iii) a combination of i and ii. If we assume that the inversion rates do not differ significantly in the α-methyl and α-chloro systems, then the ratio of the rate constants for H transfer from cumene ($k_{\alpha\text{-Cl}}/k_{\alpha\text{-CH}_3}$) need only be $\geq 10^2$ to accommodate the results. This number is based on the estimate that a ratio of $k_{\text{H transfer}}/k_{\text{inversion}} \leq 10^{-3}$ would lead to equilibration of the vinyl radical intermediates prior to hydrogen atom transfer. Thus, the observed stereospecificity in the olefin products from the α-halovinyl systems does not necessarily require that there be significantly greater barriers to inversion than in the α-methylvinyl radical system.

Experimental Section[24]

Materials. Cumene, Matheson Coleman and Bell, was shaken with concentrated sulfuric acid until no further coloration occurred. It was then washed with water and aqueous sodium bicarbonate, dried over anhydrous magnesium sulfate, and distilled through a 2-ft glass column packed with glass beads. A center cut was taken and stored under argon away from sunlight. Benzene, Baker and Adamson, reagent, and dihydroanthracene, Aldrich, 99%, were used without purification.

***cis*- and *trans*-α-Chlorocinnamic Acids.** Into a stirred solution of 50 g of methyl cinnamate (0.31 mole) in 150 ml of chloroform, cooled in an ice bath, was dispersed chlorine gas until the yellow color of chlorine persisted. The solvent was removed *in vacuo* to give a white solid, methyl cinnamate dichloride. The dichloride (70 g, 0.30 mole) was taken up in 100 ml of 95% ethanol and slowly added to a stirred solution of 60 g of potassium hydroxide (1.70 moles) in 350 ml of water and 200 ml of 95% ethanol at ice–water temperature. The mixture was stirred at room temperature for 18 hr and then poured into water. Concentrated hydrochloric acid was added and the resulting white solid collected, taken up in ether, dried, and concentrated *in vacuo* to give 50 g (0.27 mole) of mixed α-chlorocinnamic acids. Nmr analysis revealed the mixture to be *ca.* 95% *trans* and 5% *cis* acids.

Photoisomerization of *trans*-α-Chlorocinnamic to *cis*-α-Chlorocinnamic Acid and Their Separation. A solution of 20 g of the mixed acids from above in 750 ml of benzene containing 3 g of benzophenone was irradiated in a Hanovia photochemical assembly with a 450-w Hanovia lamp maintained in a Pyrex immersion well. After 3 hr, nmr analysis indicated no further increase in the *cis* acid content (*ca.* 25%) and the benzene solution was extracted with an aqueous potassium hydroxide solution. The aqueous phase was acidified with concentrated hydrochloric acid, and the precipitated acids were filtered off. The acid mixture was taken up in ether, washed with water, dried over magnesium sulfate, and redeposited by removal of the solvent *in vacuo.* Some 16 g of material (80%) was obtained after this procedure.

A modification of the procedure described by Sudborough and James[8] was used for the separation of the *cis* and *trans* acids. A solution of 90 g of barium chloride hydrate in 300 ml of water was added to 67 g (0.37 mole) of the mixed acids dissolved in 2500 ml of 30% ammonium hydroxide. The barium salt of the *trans* acid immediately precipitated and was filtered off. Both the precipitate and the filtrate were acidified with concentrated hydrochloric acid, and the resulting free acids were filtered, washed with water, and dried. Recrystallization from ether–petroleum ether (bp 30–60°) gave *trans*-α-chlorocinnamic acid, 37 g, mp 137.5–140.5° (lit.[8] mp 137°), and *cis*-α-chlorocinnamic acid, 13 g, mp 109–112° (lit.[8] 110°). The nmr data of the pure acids are given in Table I.

***trans*-*t*-Butyl α-Chloropercinnamate.** To a slurry of 12 g of sodium *t*-butyl hydroperoxide (0.11 mole) in 300 ml of petroleum ether, cooled in an ice bath, was slowly added 12 g (0.055 mole) of the *trans* acid chloride (prepared by conventional methods from *trans*-α-chlorocinnamic acid) in 50 ml of benzene. The mixture was then stirred at room temperature for 16 hr. The reaction was quenched with cold water and pentane was added, and the aqueous and organic layers were separated. The organic layer was washed with water twice, dried over anhydrous magnesium sulfate, and concentrated *in vacuo.* The yellow oily residue was chromatographed on Florisil and the *trans* perester (5 g, 0.020 mole) was recovered as an almost colorless oil from fractions eluted with 5% ether in petroleum ether. Characteristic infrared bands showed: (carbon tetrachloride solution) carbonyl at 5.70 μ, strong; double bond at 6.20 μ, strong.

Anal. Calcd for $C_{13}H_{15}O_3Cl$: C, 61.3; H, 5.94; Cl, 13.92. Found: C, 61.38; H, 5.87; Cl, 14.17.

***cis*-*t*-Butyl α-Chloropercinnamate.** To a stirred solution of 4.4 g of 1,1′-carbonyldiimidazole[7] (0.027 mole) in 40 ml of dry tetrahydrofuran at room temperature was added quickly 5 g (0.027 mole) of *cis*-α-chlorocinnamic acid as a solid. Immediate gas evolution occurred. The reaction was stirred for 1 hr, then cooled in an ice bath, and a solution of 5.4 g of *t*-butyl hydroperoxide (purified, 0.060 mole) in 50 ml of petroleum ether was added dropwise. After 4 hr, water and pentane were added, and the layers separated. The organic layer was washed twice with cold water, dried over anhydrous magnesium sulfate, and concentrated *in vacuo* to a yellow oil. The product was chromatographed on Florisil, and 3 g of *cis*-α-chloropercinnamate (0.012 mole) was recovered as a white solid, mp 34–37°, from the fractions eluted with 5% ether in petroleum ether. Characteristic infrared bands showed: (carbon tetrachloride solution) carbonyl at 5.65 μ, strong; double bond at 6.20 μ, weak.

Anal. Calcd for $C_{13}H_{15}O_3Cl$: C, 61.30; H, 5.94; Cl, 13.92. Found: C, 61.3; H, 5.89; Cl, 14.28.

Acid Yield Determinations. The acid yields were determined by gram-scale decompositions of the peresters in degassed sealed Pyrex ampoules in the scavenging systems described in Table III. The samples were checked for complete reaction by infrared analysis, and the free acids were isolated by conventional extraction methods. Infrared comparison of the isolated acids with authentic samples revealed that in all cases the recovered acids were of retained geometry relative to the starting peresters.

Isolation of 3-Chlorocoumarin. A 50-ml benzene solution, containing 0.974 g (3.83 mmoles) of *cis*-*t*-butyl α-chloropercinnamate and 3.24 g (0.0191 mole) of dihydroanthracene, was distributed among several Pyrex ampoules which were degassed, sealed, and allowed to react at 110° for 17 hr. The recombined solution was concentrated and the residue taken up in ether–petroleum ether (some insoluble dihydroanthracene was discarded). The solvent was removed *in vacuo*, and the oil residue was chromatographed on Florisil. The 3-chlorocoumarin (0.035 g, 0.19 mmole, 5.4%) was recovered from fractions eluted with 20–25% ether in petroleum ether, mp 119–123° (lit.[25] mp 122–123°). The nmr of the isolated material was very similar to the nmr spectrum of the previously prepared 3-bromocoumarin;[6] 3-chlorocoumarin (deuteriochloroform): aromatic H, broad multiplet centered at δ 7.67; vinyl H, sharp singlet at δ 8.16; 3-bromocoumarin (deuteriochloroform): aromatic H, broad multiplet centered at δ 7.91; vinyl H, sharp singlet at δ 8.61.

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(21) The estimate was based on the observed equilibration of the intermediate vinyl radicals in the presence of transferring agents such as cumene. The absolute rate constant for hydrogen atom transfer from cumene to the vinyl radicals was crudely calculated from chain transfer constants and absolute rate data on styrene polymerization available in C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, pp 94, 152. It was assumed that chain transfer to the vinyl radical is faster than chain transfer to the more stable styryl radical.

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β-Chlorostyrenes. The β-chlorostyrenes were prepared by a decarboxylation–dehydrochlorination of cinnamic acid dichloride with aqueous sodium carbonate at 100°. Pure samples of the *cis* and *trans* olefins were obtained by preparative vpc on a 10-ft × $^{3}/_{8}$-in. 30% Ucon on Chromsorb P column coated with 2% HMDS; column temperature, 165°; flow rate, 54 cc/min; retention times: *cis*, 35 min; *trans*, 53 min. The nmr data used for identification of the olefins is given in Table II.

Equilibration Studies on the β-Chlorostyrenes. No equilibration of the olefins was observed using a trace of iodine in cumene at 110° for 24 hr. Equilibration was accomplished with the *p*-anisylthiyl radical as follows. Degassed and sealed Pyrex ampoules containing the starting olefins and trace amounts of azoisobutyrylnitrile and *p*-thiocresol in cumene were allowed to react at 110° for times up to 24 hr. The *cis* olefin content was monitored by infrared measurement of a band at 1350 cm^{-1} found only in the *cis* isomer and with reference to a calibration curve derived from standard solutions. The analyses were carried out on a Beckman IR-7 spectrometer. In this way, an apparent equilibrium position of 82% *trans*- and 18% *cis*-β-chlorostyrene at 110° in cumene was found starting from either 100% *trans* or a mixture of 35.2% *trans* and 64.8% *cis* olefins.

Control Experiments. Degassed and sealed Pyrex ampoules containing 0.10 *M* β-chlorostyrene (>99.5% *trans* by vpc analysis) and 0.09 *M* *trans*-*t*-butyl α-bromopercinnamate[6] in cumene were held at 110° for 24 hr. The cooled reaction mixture was analyzed directly by vpc and found to contain a β-chlorostyrene composition of 96% *trans* and 4% *cis* olefin. In a similar experiment, a cumene solution of 0.10 *M* β-chlorostyrene and 0.08 *M* *trans*-α-chlorocinnamic acid was held at 110° for 24 hr. Vpc analysis indicated no isomerization of the *trans* olefin.

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Heterocyclic Radical Ions. I. Anion Radicals Isoelectronic with Phthalic Anhydride Anion

Stephen F. Nelsen

Contribution from the Department of Chemistry, University of Wisconsin, Madison, Wisconsin 53706. *Received February 6, 1967*

Abstract: The esr spectra of nine radical anions isoelectronic with phthalic anhydride ion are reported; the anhydride oxygen is replaced by S, NR, and CR$^-$. Hückel and McLachlan calculations predict that the nature of the atom varied should not affect the phenyl ring splittings; this is experimentally verified for CH$^-$ and NR substitution, but greater variations are observed if the atom changed formally bears two electron pairs. The *h* and *k* parameters necessary to fit the observed spectra and spin density at the group varied are discussed. Large spin density variation at this position is observed, and the CCH$_3$$^-$ anion has the spin density at this position six times that at one ring position, and over half that at the other, even though $\rho_X = 0$ by symmetry considerations in the Hückel approximation.

Although quinone[1] and more recently nonaromatic 1,2-dione[2] radical anions have been extensively studied by electron spin resonance (esr), unsaturated anhydride, imide, and 1,4-diketone anions, which should also be relatively stable, have been virtually ignored. We have found that many such anions are stable enough to be conveniently produced by electrolytic reduction and studied at room temperature. Thus electrolytic reduction of maleimide in DMSO gives a transient spectrum consisting of nine main lines, which shows splittings for one nitrogen (a_N = 2.29 gauss) and two hydrogens (a_N = 6.31 gauss). Each line was an ill-unresolved doublet; we did not obtain good enough resolution to measure this NH splitting. We here report esr studies on several radical anions having the phthalic anhydride skeleton, with various substitution at the O ring position (general structure I, Table I). These anions are mostly conveniently stable for esr measurements, and have the advantage for theoretical interpretation of having two phenyl ring proton splitting constants. Better spectra were obtained in DMSO than in CH$_2$Cl$_2$, DMF, acetonitrile, or hexamethylphosphoramide. DMSO with 0.1 *M* tetrabutylammonium perchlorate as supporting electrolyte was used for the measurements reported here. The esr spectra of these compounds are of interest not only because they extend the range of structures studied, but also because of the electronic nature of the odd-electron MO. Since a node passes through the X group in the odd-electron MO, simple HMO theory predicts zero spin density at X, and unless different Coulomb and resonance integrals are employed for the carbonyls with different X groups, spin distribution independent of X. Positions with low or zero spin density by HMO theory are well known to actually have negative spin densities.[3] For such compounds the now well-known simple configuration interaction calculation of McLachlan[3] leads to much more realistic spin distributions. Study of these compounds should help to define the limitations of HMO and McLachlan calculations for interpretation of esr spectra and lead to values for the resonance and Coulomb integrals for heteroatoms necessary to correlate MO calculations with splitting constants.

Experimental Section

Phthalic anhydride, phthalimide, potassium phthalimide, and 2,3-indandione were suitably purified commercial samples. N-Dimethylaminophthalimide was prepared by the method of Drew

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