Organic and Biological Chemistry

Vinyl Radicals. Stereoselectivity in Hydrogen Atom Transfer to Equilibrated Isomeric Vinyl Radicals[1]

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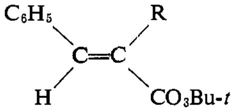
Abstract: Facile equilibration of the isomeric vinyl radicals derived from the *cis*- and *trans-t*-butyl α-methyl- and α-phenylpercinnamates (**1–4**) is observed at 110°. The olefin product mixture is much richer in the *cis* isomer than that expected from the relative stabilities of the *cis* and *trans* olefins, indicating stereoselectivity in the hydrogen atom transfer step. Stereoselectivity increases in going from the α-methyl to the α-phenyl system and also when the effective bulk of the transferring agent is increased in going from toluene or cyclohexene to cumene. The preparation of *trans*-α-methylcinnamoyl peroxide (**9**) is described. Thermal (80–90°) decompositions and low-temperature photodecompositions (1 and −75°) of **9** were carried out in toluene, cyclohexene, and cumene and the *cis*/*trans* propenylbenzene product ratio compared with the thermal data (110°) from the corresponding peresters. Plots of log (*cis*/*trans*) *vs.* $1/T$ for the propenylbenzene products from the perester and diacyl peroxide sources give straight lines for cyclohexene and cumene in the temperature range 110 to −75° and for toluene from 110 to 1°. From the slopes of these lines are calculated the relative stereoselectivities of the three solvents in hydrogen atom transfer to the isomeric 1-methyl-2-phenylvinyl radicals. Some kinetic data and further product studies of the peresters are also included.

Recently, considerable attention has been focused on the question of the configurational stability of vinyl radicals. Studies on free-radical additions to terminal acetylenes indicate that the kinetically determined product is much richer in the *cis* isomer than the equilibrium mixture.[2–4] Skell and Allen[2] observed essentially 100% *cis* product from the addition of hydrogen bromide to propyne at −78° and ascribed this result to a stereospecific *trans* addition of bromine atom to propyne followed by capture of the configurationally stable vinyl radical. Oswald and co-workers[3] found predominantly *cis* product from the addition of mercaptans and thioacetic acid to phenylacetylene. Kampmeier and Chen[4] observed that the kinetic product from the addition of thioacetic acid to 1-hexyne contained 82% *cis* isomer where the position of equilibrium for the *cis* and *trans* products is about 50:50.

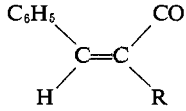
These latter results[3,4] could arise from (i) a nonstereospecific addition of thiyl radical followed by capture of configurationally stable vinyl radicals, or (ii) capture of rapidly equilibrating vinyl radicals where the product ratio is independent of the stereochemistry of the addition step. These studies are further complicated by the facile isomerization of the olefinic products under the reaction conditions.

A less tenuous approach to the problem of the configurational stability of vinyl radicals is to generate isomeric radicals directly from perester sources and determine the *cis*/*trans* olefin product resulting from hydrogen atom transfer to the vinyl radicals. We previously reported our preliminary results utilizing this approach in the *cis*- and *trans-t*-butyl α-methyl- and α-phenylpercinnamates (**1–4**).[1] Equilibration of the isomeric radicals occurs prior to reaction with solvent since the same olefin ratio is obtained from either the *cis* or *trans* perester in any one solvent. These results are in good agreement with those of Kampmeier and Fantazier[5] who observe the same *cis*/*trans* olefin ratio (1.11 ± 0.08) from either *cis*- or *trans-t*-butyl α,β-dimethylpercinnamates.



trans

1, R = CH_3
3, R = C_6H_5



cis

2, R = CH_3
4, R = C_6H_5

Further, high *cis*/*trans* olefin ratios (propenylbenzenes, stilbenes; see Tables II and III) are found in these systems (**1–4**) where the *trans* olefin is clearly favored at equilibrium,[6] suggesting that the product distribution is determined in great part by a *stereoselective hydrogen atom transfer step.* We now wish to report these results in greater detail along with further product and kinetic studies. Also a more quantitative measure of solvent stereoselectivity is available through recent studies on the decomposition of *trans*-α-methylcinnamoyl peroxide.

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[1] For a brief account of this work see L. A. Singer and N. P. Kong, *Tetrahedron Letters*, No. **19**, 2089 (1966).

[2] P. S. Skell and R. G. Allen, *J. Am. Chem. Soc.*, 80, 5997 (1958); **86**, 1559 (1964).

[3] A. A. Oswald, K. Griesbaum, B. E. Hudson, Jr., and J. M. Bregman, *ibid.*, **86**, 2877 (1964).

[4] J. A. Kampmeier and G. Chen, *ibid.*, 87, 2608 (1965).

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

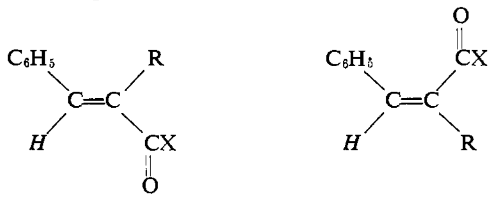
[6] We obtain apparent equilibrium values of *trans*-propenylbenzene of 76.9 and 72.9% starting from the *trans* and *cis* olefins, respectively, from equilibration with a trace of iodine in cumene at 110°. The calculated value of the *trans* olefin at equilibrium at this temperature is 75.8% from the difference in free energy of formation between the isomers of 0.78 kcal/mole: J. E. Kilpatrick, *et al.*, *J. Res. Natl. Bur. Std.*, **42**, 225 (1949). The thermal equilibrium between *cis*- and *trans*-stilbenes has been reported as 93% *trans* at 25°: C. C. Price and M. Meister, *J. Am. Chem. Soc.*, **61**, 1595 (1939).

Results

The *trans-t*-butyl α-methyl- and α-phenylpercinnamates (**1** and **3**) were prepared in good yield by treatment of the corresponding acid chlorides with sodium *t*-butyl hydroperoxide in ether at 0°. The *cis*-α-methyl- and -α-phenylcinnamic acids were obtained by the following general procedure. The *trans*-methyl esters were isomerized by irradiation with a 450-w Hanovia lamp in pentane solution through a Pyrex filter with benzophenone as a sensitizer to a mixture of the *cis* and *trans* esters (α-methyl, 58% *cis*; α-phenyl, 48% *cis*). The *cis*/*trans* ester mixtures are easily measured by vpc techniques. Partial saponification under carefully controlled conditions (see Experimental Section) completely removes the *trans* ester with only minor loss of the *cis* ester. The remaining *cis* ester is separated from the saponified material and then hydrolyzed under more vigorous conditions to the *cis* acid. In this way, the *cis* acids can be prepared in over-all yields of about 25% from the *trans* esters.

All attempts to prepare the *cis* acid chlorides resulted in either isomerization to the *trans* acid chlorides or formation of the *cis* acid anhydrides. It was subsequently found that the *cis* peresters could be prepared in moderate yields from the *cis* anhydrides by treating the latter with sodium *t*-butyl hydroperoxide in ether at room temperature. All four peresters gave satisfactory combustion analyses. Three of the four peresters are solids at room temperature (**2**, mp 40–41°; **3**, mp 108–110°; **4**, mp 80–81°) which minimizes contamination problems. The *trans*-α-methyl perester (**1**) is a liquid at room temperature and was purified by chromatography on Florisil prior to use. Nmr is an aid to structural assignment throughout the whole series since the position of the vinyl hydrogen is consistently found from 0.7 to 1.3 ppm further downfield when it is *cis* to the carbonyl function[7] (*i.e.*, in the *trans* isomer) as shown in Table I.

Table I. Position of the Vinyl Hydrogen in the Nmr as a Guide to Structural Assignments



trans *cis*

		δ			
		R = CH_3		R = C_6H_5	
X	Solvent	*cis*	*trans*	*cis*	*trans*
OH	*a*	6.73	7.80	7.05	7.97
OCH_3	*b*	6.55	7.66	6.75	7.72
OOBu-*t*	*b*	6.68	7.57	7.04	7.80

[a] Deuteriochloroform. [b] Carbon tetrachloride.

Table II. Olefin Compositions from the Thermal Decompositions of *cis*- and *trans-t*-Butyl α-Methylpercinnamates at 110°[a,b]

Perester	Solvent	[Perester], *M*	*cis*-Olefin,[c] %	Olefin yield, %
trans	Cumene	0.048	63.0 ± 1.2	64.6 ± 3.6
		0.10	62.1 ± 0.2	62.9 ± 3.7
		0.20	57.5 ± 0.8	51.1 ± 3.2
		0.30	60.1 ± 0.7	44.4 ± 0.6
		0.47	60.9 ± 0.2	40.6 ± 0.6
cis	Cumene	0.077	61.4 ± 1.1	58.5 ± 0.5
		0.12	60.8 ± 0.6	53.3 ± 2.2
		0.20	61.5 ± 0.4	46.4 ± 0.5
		0.31	60.2 ± 0.2	38.8 ± 0.5
trans	Cyclohexene	0.073	45.8 ± 0.3	50.2 ± 1.5
		0.22	46.4 ± 0.2	52.7 ± 0.7
cis	Cyclohexene	0.18	45.2 ± 3.1	40.2 ± 0.5
trans	Toluene	0.086	47.1 ± 0.5	30.5 ± 0.3
cis	Toluene	0.061	43.3 ± 0.2	36.1 ± 0.6

[a] Analyzed by vpc on 30% Carbowax on Chromosorb P at 140°, flow of 60 cc/min. Retention times: *cis*, 15 min; *trans*, 21 min. [b] Each entry represents two or more determinations. [c] Based on total of olefin yield.

Table III. Olefin Compositions from the Thermal Decompositions of *cis*- and *trans-t*-Butyl α-Phenylpercinnamates at 110°[a,b]

Perester	Solvent	[Perester], *M*	*cis*-Olefin,[c] %	Olefin yield, %
trans	Cumene	0.016	84.2 ± 4.0	71.0 ± 5.0
		0.082	88.5 ± 0.1	59.3 ± 1.2
		0.24	91.8 ± 0.2	51.6 ± 0.5
		0.30	90.6 ± 0.1	43.8 ± 0.6
		0.41	90.6 ± 0.1	37.7 ± 0.5
cis	Cumene	0.038	83.1 ± 1.0	56.1 ± 1.4
		0.064	83.6 ± 1.0	50.9 ± 1.6
		0.16	87.9 ± 0.7	44.6 ± 0.8
		0.40	89.1 ± 0.9	31.2 ± 1.2
trans	Cyclohexene	0.33	78.2 ± 0.2	59.9 ± 2.5
cis	Cyclohexene	0.34	79.8 ± 0.6	40.1 ± 1.0

[a] Analyzed by vpc on 30% Carbowax on Chromosorb P at 230°, flow of 90 cc/min. Retention times: *cis*, 13 min; *trans*, 31.5 min. [b] Each entry represents two or more determinations. [c] Based on total olefin yield.

Degassed solutions of the peresters were decomposed in sealed Pyrex ampoules under the conditions indicated in Tables II and III. The *cis* and *trans* olefins were identified by retention time comparison with authentic samples of the *cis*- and *trans*-propenylbenzenes and *cis*- and *trans*-stilbenes. Hydrocarbon yields were determined by calibration with olefin solutions of known concentration.

Other products from the decomposition in cumene are acetylenes, coumarins, acids, and dicumyl. All of these products, except for the carboxylic acids, were identified by retention time comparison with authentic samples and the yields determined by calibration against solutions of known concentrations. The carboxylic

Table IV. Products from the Thermal Decompositions of the *cis*- and *trans-t*-Butyl α-Methyl- and α-Phenylpercinnamates in Cumene at 110°[a]

	mmole of product/mmole of perester			
Product type	α-Methyl		α-Phenyl	
	cis	*trans*	*cis*	*trans*
Olefin	0.53	0.63	0.44	0.59
Acetylene	0.015[b]	0.025[b]	0.025[c]	0.12[c]
Coumarin	0.079[d]	0.000	0.010[e]	0.000
Acid	0.01	0.01	0.057	0.024
Dicumyl	0.40	0.47	0.30	0.50

[a] *Ca.* 0.1 *M* solutions. [b] Propynylbenzene. [c] Diphenylacetylene. [d] 3-Methylcoumarin. [e] 3-Phenylcoumarin.

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[7] L. M. Jackman, "Application of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press, The Macmillan Co., New York, N. Y., 1959, p 122.

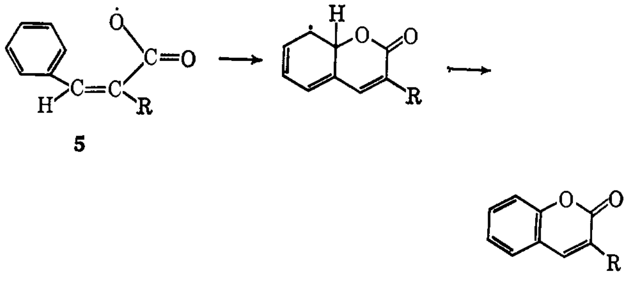
Table V, Variation in Olefin Ratio with Solvent and Temperature in the α-Methyl-α-phenylvinyl Radical System

Source	Solvent	Method	Temp, °C	*cis*/*trans*[a]	Total olefin[b] yield, %
Perester	Toluene	Thermal	109.8	0.758 ± 0.033[c]	...
DAP	Toluene	Thermal	90.0	0.678 ± 0.003	31.5 ± 0.5
DAP	Toluene	Thermal	79.0	0.654 ± 0.006	33.0 ± 0.7
DAP	Toluene	Photo[d]	1.0	0.504 ± 0.014	26.4 ± 0.5
Perester	Cyclohexene	Thermal	109.8	0.844 ± 0.015[e]	...
DAP	Cyclohexene	Thermal	80.0	0.767 ± 0.013	34.9 ± 1.3
DAP	Cyclohexene	Photo[d]	1.0	0.587 ± 0.004	22.1 ± 2.1
DAP	Cyclohexene	Photo[d]	−75.0	0.382 ± 0.007	15.6 ± 1.9
Perester	Cumene	Thermal	109.8	1.55 ± 0.07[f]	...
DAP	Cumene	Thermal	79.0	1.44 ± 0.05	37.9 ± 0.3
DAP	Cumene	Photo[d]	1.0	1.34 ± 0.01	29.9 ± 0.2
DAP	Cumene	Photo[d]	−75.0	1.22 ± 0.03	10.3 ± 0.4

[a] Propenylbenzenes. [b] For solutions *ca.* 0.07 *M* in substrate. [c] Using the value from *cis* perester in Table II which is an average of four determinations. [d] Degassed Pyrex ampoules were irradiated with a 450-w Hanovia lamp for 4.5–5.0 hr while cooled in a clear Pyrex dewar flask. [e] Using the value of *trans* perester at 0.073 *M* in Table I. [f] Average of all nine values in Table II.

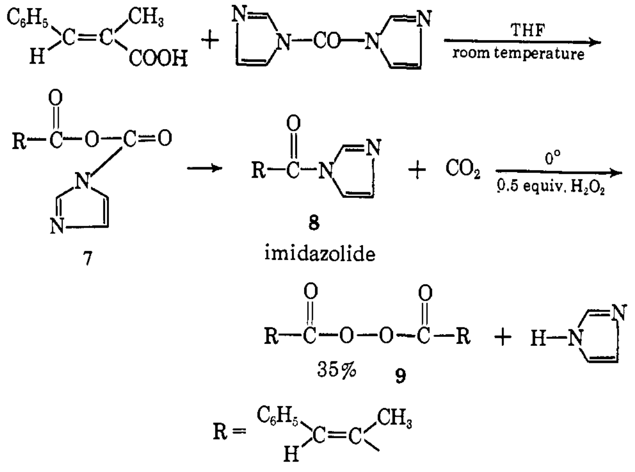
acid yields were determined by gravimetric techniques. These results are summarized in Table IV.

Coumarin products (**6**) were also reported by Kampmeier and Fantazier[5] in their studies and presumably arise from cyclization of the intermediate cinnamoyloxy radical (**5**) in the *cis*-perester systems. The cinnamoyloxy radical can also react with solvent by hydrogen atom transfer to give carboxylic acid so that both the coumarin and acid products are indicative of the one bond cleavage mechanism for the percinnamates.[8] Substantial decarboxylation of the acyloxy radical to the vinyl radical occurs as evidenced by the high olefin yields.



The acetylene products very likely are cage products from the disproportionation of *t*-butoxy radicals with cinnamoyloxy and/or vinyl radicals. Because of the great uncertainty involved in estimating the rate of decarboxylation of the cinnamoyloxy radical, no conclusion can be reached as to the extent of decarboxylation within the lifetime of the cage effect (*ca.* 10^{-10} sec).[9]

Another good source of the 1-methyl-2-phenylvinyl radical is the α-methylcinnamoyl peroxide. The *trans*-diacyl peroxide **9** can be prepared by the method of Staab[10] where the corresponding carboxylic acid is treated with N,N-carbonyldiimidazole in tetrahydrofuran at room temperature. The reaction proceeds through a mixed anhydride (**7**) which rapidly decarboxylates to give an imidazolide (**8**). Addition of 0.5 equiv of hydrogen peroxide (as a 30% aqueous solution) at 0° gives a 35% yield of *trans*-α-methylcinnamoyl peroxide (**9**) (mp 72–74° dec). The position of the vinyl hydrogen in the nmr in carbon tetrachloride solution is at δ 7.47, which is in good agreement with the other compounds in this series (Table I).



The diacyl peroxide has one major advantage over the perester as a source of vinyl radicals. It can be decomposed photochemically by irradiation with a 450-w Hanovia lamp through a Pyrex filter in solutions of *ca.* 0.07 *M* in about 4.5 hr. The peresters require about 30 hr for complete photodecomposition, and significant isomerization of the olefin products occurs during this longer period. There is negligible *cis–trans* isomerizations of the propenylbenzenes during the shorter period under the above conditions. The diacyl peroxide (DAP) thermally decomposes at a comfortable rate at about 80°. The *cis*/*trans* propenylbenzene product ratio from both thermal and photodecompositions of **9** at various temperatures is shown in Table V along with the appropriate data from the perester source.

Rate constants for the thermal decompositions of peresters **1–4** in cumene are given in Table VI. Degassed and sealed Pyrex ampoules were periodically

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[8] P. D. Bartlett and R. R. Hiatt, *J. Am. Chem. Soc.*, **80**, 1398 (1958). Authors report 16% carboxylic acid from the decomposition of *t*-butyl percinnamate.

[9] C. D. Cooke and C. B. Depatie, *J. Org. Chem.*, **24**, 1144 (1959), estimate an activation energy of 18–23 kcal/mole for decarboxylation of the benzoyloxy radical. Clearly, such an activation energy for the cinnamoyloxy radical would indicate no decarboxylation within the lifetime of the cage effect.

[10] (a) H. A. Staab, *Angew. Chem. Intern. Ed. Engl.*, **1**, 351 (1962); (b) H. A. Staab, W. Rohr, and F. Graf, *Ber.*, **98**, 1122, 1128 (1965).

Table VI. Rate Constants for the Thermal Decompositions of the *cis*- and *trans*-α-Methyl- and -α-Phenylpercinnamates in Cumene[a]

Perester	Temp, °C	Concn, *M*	$k \times 10^4$ sec^{-1}
α-Methyl *cis*	99.6	0.0107	1.24 ± 0.02
		0.0627	1.26 ± 0.01
		0.0633	1.29 ± 0.03
		0.0748	1.30 ± 0.02
	109.8	0.0140	3.73 ± 0.03
		0.0478	3.80 ± 0.13
		0.0766	3.87 ± 0.05
trans	99.6	0.0127	0.360 ± 0.009
		0.0617	0.404 ± 0.021
		0.0840	0.419 ± 0.043
	109.8	0.0123	1.10 ± 0.02
		0.0523	1.21 ± 0.01
		0.0662	1.30 ± 0.01
		0.0807	1.33 ± 0.01
		0.104	1.41 ± 0.02
α-Phenyl *cis*	90.8	0.0135	1.60 ± 0.01
		0.0512	1.89 ± 0.01
		0.0802	2.05 ± 0.02
	99.6	0.0109	4.49 ± 0.07
		0.0584	4.83 ± 0.05
		0.0713	4.93 ± 0.10
trans	99.6	0.0127	0.860 ± 0.006
		0.0517	0.931 ± 0.004
		0.0815	1.03 ± 0.01
	109.8	0.0121	2.68 ± 0.03
		0.0533	2.76 ± 0.03
		0.0612	3.06 ± 0.03
		0.0807	3.21 ± 0.03

[a] Determined by following the disappearance of the carbonyl band in the infrared using a Beckman IR-7 spectrophotometer.

Table VII. Extrapolated Rate Constants for the Thermal Decompositions of the *t*-Butyl α-Methyl- and α-Phenylpercinnamates in Cumene

Perester	Temp, °C	10^4K sec^{-1}	Rel *k* at 99.6°	ΔH^*, kcal/mole	ΔS^*, eu
α-Methyl					
trans	99.6	0.350 ± 0.010	1.0	30.0 ± 0.6	0.99 ± 1.40
	109.8	1.03 ± 0.02			
cis	99.6	1.23 ± 0.02	3.5	30.6 ± 0.3	5.06 ± 0.71
	109.8	3.70 ± 0.02			
α-Phenyl					
trans	99.6	0.820 ± 0.10	2.3	32.0 ± 0.3	7.99 ± 0.76
	109.8	2.59 ± 0.03			
cis	90.8	1.52 ± 0.02		32.7 ± 0.2	13.3 ± 0.6
	99.6	4.41 ± 0.01	12.3		

withdrawn from a constant temperature bath and analyzed for the disappearance of the perester carbonyl band (**1**, 1749 cm^{-1}; **2**, 1760 cm^{-1}; **3**, 1752 cm^{-1}; **4**, 1764 cm^{-1}) in the infrared on a Beckman IR-7 spectrophotometer. As the initial concentration of the perester is increased from about 0.01 to 0.08 *M*, the rate constants for disappearance of perester show the typical increase due to contributions from induced decomposition pathways.[11]

A plot of these rate constants against perester concentration gives a smooth curve which when extrapolated to infinite dilution gives the rate constant for the unimolecular decomposition (k_1) with no contribution from the bimolecular induced decomposition (k_2) since

$$-\mathrm{d(P)}/\mathrm{d}t = [k_1 + k_2(\mathrm{R})](\mathrm{P})$$

where P = perester and R = radicals involved in induced decompositions.

As the substrate concentration is decreased, the steady-state concentration of radicals is less since

$$(\mathrm{R}) = (k_1/k_t)^{1/2}(\mathrm{P})^{1/2}$$

where k_t is the rate constant for 2R → R–R and the contribution from the bimolecular induced decomposition to the over-all rate constant is less. Activation parameters which should be representative of the unimolecular process (k_1) were calculated from these extrapolated rate constants and are tabulated in Table VII.

Discussion

The results in Tables II and III clearly indicate equilibration of the isomeric vinyl radicals at 110° before reaction with solvent by hydrogen atom transfer. Further, it is observed that the *cis*/*trans* olefin ratio is richer in the *cis* olefin than the equilibrium mixture[6] and that this trend is more pronounced in the α-phenyl system and also in cumene as solvent as opposed to cyclohexene or toluene. These results are most easily explained by stereoselectivity in the hydrogen atom transfer step, *i.e.*, approach by the transferring agent to give *cis* product is less sterically hindered than approach to give *trans* product (see Figure 1, $k_c > k_t$).[12]

As the effective bulk of the R group or of the solvent (SH) is increased, stereoselectivity becomes more operative. A similar effect was noted in studies on the 9-decalyl radical system[13] where a change from cyclohexane to cumene leads to an increase in *cis*-decalin in the product mixture.

Stereoselectivity can be put on a more quantitative basis by the following treatment of the data in Table V. From the scheme shown in Figure 1[14] can be derived

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(11) W. A. Pryor, "Free Radicals," McGraw-Hill Book Co., Inc., New York, N. Y. 1966, pp 92–94. See A. T. Blomquist and A. F. Ferris, *J. Am. Chem. Soc.*, 73, 3408 (1951), for a study of the effect of substrate concentration on the rate of decomposition of *t*-butyl perbenzoate.

(12) It has been pointed out by a referee that the radical in the α-phenyl system may be sp rather than sp^2 hybridized so that a direct comparison with the α-methyl system may not be meaningful. The observed high *cis*/*trans* ratio from a single sp-hybridized intermediate would still be due to stereoselectivity, however.

(13) P. D. Bartlett, R. E. Pincock, J. H. Rolston, W. G. Schindel, and L. A. Singer, *J. Am. Chem. Soc.*, 87, 2590 (1965). The transition state leading to *cis*-decalin has the hydrogen atom transferring agent in a less crowded environment relative to the transition state leading to *trans*-decalin.

(14) This kinetic scheme is a demonstration of the Curtin–Hammett principle. See E. Eliel, "Stereochemistry of Carbon Compounds," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, pp 151, 237–239.

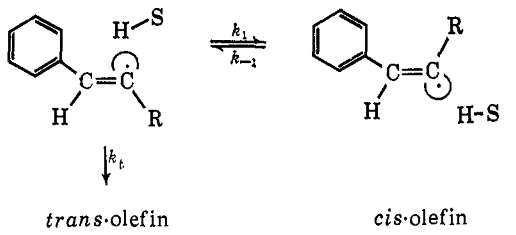

Figure 1.

the following expression by use of the steady-state approximation.

$$(\textit{cis}\ \text{olefin})/(\textit{trans}\ \text{olefin}) = (k_ck_1)/[k_t(k_{-1} + k_c)] \approx (k_ck_1)/(k_tk_{-1})$$

if $k_{-1} \gg k_c$. Let

$$k_{-1}/k_1 = (\textit{trans}\ \text{radical})/(\textit{cis}\ \text{radical}) = K_{eq}$$

Then

$$(\textit{cis}\ \text{olefin})/(\textit{trans}\ \text{olefin}) = (k_c/k_t)(1/K_{eq}) = [\exp(\Delta\Delta F^*{}_{t-c}/RT)][\exp(\Delta F^\circ{}_{t-c}/RT)]$$

and

$$\log[(\textit{cis}\ \text{olefin})/(\textit{trans}\ \text{olefin})] = \Delta\Delta F^*{}_{t-c}/2.3RT + \Delta F^\circ{}_{t-c}/2.3RT = (\Delta\Delta H^*{}_{t-c} + \Delta H^\circ{}_{t-c})/2.3RT - (\Delta\Delta S^*{}_{t-c} + \Delta S^\circ{}_{t-c})/2.3R$$

Thus, a plot of log [(*cis* olefin)/(*trans* olefin)] *vs.* $1/T$ should give a straight line with the slope determined by $(\Delta\Delta H^*{}_{t-c} + \Delta H^\circ{}_{t-c})/2.3R$ and the intercept equal to $-(\Delta\Delta S^*{}_{t-c} + \Delta S^\circ{}_{t-c})/2.3R$. Figure 2 shows the data from Table V plotted in this way.

The differences between the slopes of curves 1, 2, and 3 are due to the differences in the $\Delta\Delta H^*{}_{t-c}$ terms assuming $\Delta H^\circ{}_{t-c}$ is the same in all three solvents. That the slopes are negative in all three cases means that the enthalpy difference between the *cis*- and *trans*-vinyl radicals ($\Delta H^\circ{}_{t-c}$) is greater than the difference in the enthalpy of activations for the two scavenging reactions (k_t and k_c). However, the more positive the slope, the greater the $\Delta\Delta H^*{}_{t-c}$ term. Thus, cumene (most positive slope) is more stereoselective than cyclohexene by 0.43 kcal/mole and than toluene by 0.53 kcal/mole in hydrogen atom transfer to the 1-methyl-2-phenylvinyl radical (Table VIII).

Table VIII. Solvent Stereoselectivities in Hydrogen Atom Transfer to the 1-Methyl-2-phenylvinyl Radical

Solvent	$(\Delta\Delta H^*{}_{t-c} + \Delta H^\circ{}_{t-c})$, kcal/mole	$\Delta\Delta\Delta H^*{}_{t-c}$,[a] kcal/mole
Cumene	−0.21	0.53
Cyclohexene	−0.64	0.10
Toluene	−0.74	. . .

[a] Stereoselectivities relative to toluene.

It follows that facile equilibration of the 1-methyl-2-phenylvinyl radical must also occur at −75° since the data at that temperature correlate well with the rest of the data in two separate solvent systems.

A crude estimate on the absolute rate of hydrogen atom transfer from cumene to the 1-methyl-2-phenylvinyl radical[15] provides a value somewhat greater than 10^{-1} l. mole^{-1} sec^{-1}. Therefore, the competing inversion process in the vinyl radical must have a barrier considerably less than 23 kcal/mole. This estimate can be improved upon by utilizing the information available on additions of mercaptans to terminal acetylenes. The observed high *cis*/*trans* olefin ratios[3,4] can be explained in terms of stereoselectivity in the hydrogen atom transfer step following equilibration of the intermediate vinyl radical. Since mercaptans are about 10^4 times more efficient than hydrocarbon solvents in hydrogen atom transfer[15,16] the upper limit of the inversion process in the 1-methyl-2-phenylvinyl radical can be revised downward to about 17 kcal/mole. Esr studies indicate that the barrier to inversion in the simple vinyl radical is around 2 kcal/mole[17,18] and that it is somewhat higher in the 1-methylvinyl radical.[18]

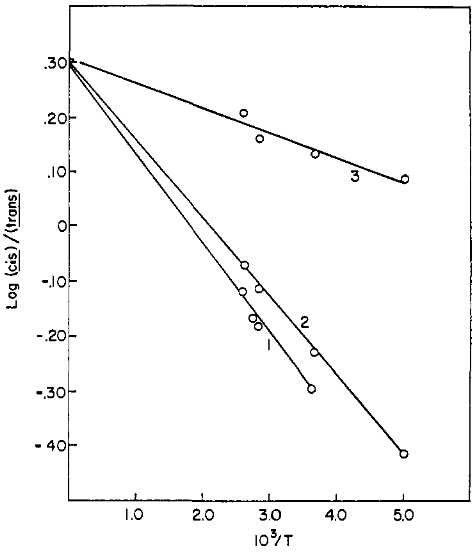

Figure 2. Log (*cis*/*trans*) for propenylbenzenes *vs.* $1/T$: curve 1, toluene; 2, cyclohexane; 3, cumene.

The observed stereospecific addition of hydrogen bromide to terminal acetylenes which suggested a high barrier to inversion in vinyl radicals[2] can be satisfactorily explained by a configuration holding bromine bridge in the vinyl radical[19] for which there is esr evidence.[20]

The relative rate constants for decomposition of peresters **1**–**4** show a spread of only 12.3, as would be expected for the one bond cleavage mechanism.[8] However, it is rather interesting that the rate sequence is determined almost entirely by the entropy terms. In each series the *cis* isomer decomposes faster than the *trans* isomer. This difference resides entirely in the entropy terms and may be related to the more restricted ground states of the *cis* isomers as compared to the

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(15) Estimated from chain-transfer constants and absolute rate data available on styrene polymerization in C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 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.

(16) Attempts to use mercaptans as scavengers in the present work resulted in almost a quantitative recovery of the carboxylic acids.

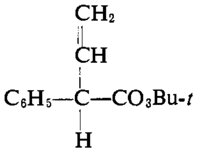
(17) R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.*, **39**, 2147 (1963).

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

(19) This alternative explanation was pointed out by Skell and Allen in footnote 5 in ref 2.

(20) P. I. Abell and L. H. Piette, *J. Am. Chem. Soc.*, **84**, 916 (1962).

trans isomers. This type of effect was previously noted by Bartlett and Hiatt[8] in comparing the activation parameters derived from the rates of decomposition of *t*-butyl 1-phenyl-2-propene-1-percarboxylate (**10**) and *t*-butyl 3-phenyl-2-propene-1-percarboxylate (**11**). While **10** and **11** have similar enthalpy of activation values, the entropy of activation terms are −1.1 and −5.9 eu, respectively, and this difference is attributed to a greater freedom of rotation in the ground state of **11** as compared to **10**.



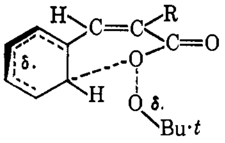
$$\begin{array}{c} CH_2 \\ \| \\ CH \\ | \\ C_6H_5{-}C{-}CO_3Bu\text{-}t \\ | \\ H \end{array}$$

10

$C_6H_5CH{=}CHCH_2CO_3Bu\text{-}t$

11

There does not seem to be any kinetic evidence for any important contribution from anchimeric assistance in the decompositions of the *cis* peresters (**2** and **4**) as shown in **12** and as might be inferred from isolation of the coumarin products.[21] Anchimerically assisted homolyses are revealed by substantial decreases in the enthalpy and entropy of activation terms as compared to nonassisted homolyses.[22] The results in Table VII clearly argue against such an interpretation.



12

Experimental Section[23]

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 collected and stored under argon away from the sunlight.

Toluene, Baker and Adams reagent, was similarly purified.

Cyclohexene, Eastman Organic Chemicals, was purified by fractional distillation.

***trans-t*-Butyl α-Methylpercinnamate.** *trans*-α-Methylcinnamoyl chloride, mp 50–51°, was prepared by conventional methods from thionyl chloride. Sodium *t*-butyl hydroperoxide was prepared by dropwise addition of purified[10] *t*-butyl hydroperoxide in ether to a slurry of sodium hydride in ether (vigorous hydrogen evolution) at room temperature. After stirring for 16 hr, the salt was collected by suction filtration, dried under a rubber dam, and stored in a tightly closed bottle at −10° (the dry salt is very hygroscopic).

To a slurry of 8.0 g of sodium *t*-butyl hydroperoxide (0.071 mole) in 100 ml of petroleum ether, cooled in an ice bath, was added a solution of 6.0 g of the acid chloride (0.033 mole) in 25 ml of benzene followed by 3.2 g of pyridine (0.040 mole) in 25 ml of benzene. The mixture was stirred for 2 hr at ice temperature and 3 hr at room temperature. The organic layer was washed successively with cold water, cold dilute sulfuric acid, cold aqueous sodium carbonate, and water. It was dried over anhydrous magnesium sulfate and concentrated *in vacuo* to a slightly green oil, 4.8 g. The infrared spectrum of this compound displayed only a single carbonyl band at 1749 cm^{-1} (carbon tetrachloride). The product was purified by chromatography on Florisil to give a clear oil which solidified at −10°.

Anal. Calcd for $C_{14}H_{18}O_3$: C, 71.77; H, 7.74. Found: C, 72.04; H, 7.98.

***trans-t*-Butyl α-Phenylpercinnamate.** *trans*-α-Phenylcinnamoyl chloride, mp 44–47°, was prepared by conventional methods from thionyl chloride.

To a slurry of 8.0 g of sodium *t*-butyl hydroperoxide (0.08 mole) in 200 ml of anhydrous ether, cooled in an ice–water bath, was added 8.0 g of *trans*-α-phenylcinnamoyl chloride (0.034 mole) dropwise over 1 hr. The mixture was stirred at ice temperature for 2 hr and then at room temperature for 16 hr. Then, 100 ml of ice–water and 150 ml of pentane were added; the organic layer was separated and washed four times with 10% sodium carbonate solution and five times with water. The organic layer was dried over anhydrous magnesium sulfate and concentrated *in vacuo*. The oily residue was crystallized from ether–petroleum ether to give 2.4 g (24%) of a white solid, mp 108–110°. This material displayed the characteristic perester band in the infrared at 1752 cm^{-1} (carbon tetrachloride).

Anal. Calcd for $C_{19}H_{20}O_3$: C, 77.00; H, 6.80. Found: C, 76.90; H, 6.98.

***cis*-α-Methylcinnamic Acid.** A solution of 43 g of *trans*-methyl α-methylcinnamate in 500 ml of pentane containing 5.0 g of benzophenone was irradiated in a Hanovia photochemical assembly with a 450-w Hanovia lamp maintained in a Pyrex immersion well for 16 hr. At the end of this time, vpc analysis on a 30% Carbowax column at 225° indicated a mixture of 58% *cis* and 42% *trans* esters. The solvent was removed *in vacuo* and the ester mixture was taken up in 100 ml of dimethoxyethane and added to a solution of 10 g of potassium hydroxide in 100 ml of water. The aqueous dimethoxyethane mixture was stirred and refluxed for 25 min and quickly quenched in a large volume of water. Ether was added, and the layers were separated. The ether layer was washed with water, dried over magnesium sulfate, and concentrated *in vacuo*. Analysis of the residue by vpc indicated 95% *cis* and 5% *trans* esters. The residue was taken up in 100 ml of dimethoxyethane and added to a solution of 30 g of potassium hydroxide in 100 ml of water. After refluxing for 16 hr, the mixture was poured into water. The neutral material was removed by ether extraction, and the aqueous solution was acidified. The precipitated white solid was taken up in ether. The ether layer was washed twice with water, dried over anhydrous magnesium sulfate, and concentrated *in vacuo* to give 13.2 g of a white solid, mp 78–91°. Upon recrystallization of the material from ether–petroleum ether the melting point was raised to 93–95° (lit.[24] mp 91–92°).

***cis*-α-Phenylcinnamic Acid.** A solution of 30 g of *trans*-methyl α-phenylcinnamate in 500 ml of pentane and 250 ml of methanol containing 3 g of benzophenone was irradiated as described above for 6 hr. At the end of this time, the mixture analyzed for 48% *cis* and 52% *trans* ester on a silicon rubber column at 230°. The solvent was removed *in vacuo* and the residue dissolved in 150 ml of dioxane and added to a solution of 5.6 g of potassium hydroxide preheated to about 50°. The mixture was stirred and heated for 30 min with refluxing occurring during the latter portion of this time. The mixture was quenched in a large volume of water and ether extracted. The ether extract was washed twice with water, dried over anhydrous magnesium sulfate, and concentrated *in vacuo*. The residue, 12 g, analyzed by vpc for 95% *cis* ester. The residue was taken up in 80 ml of dioxane and added to a solution of 14 g of potassium hydroxide in 80 ml of water. The mixture was refluxed for 16 hr and worked up as described above for the *cis*-α-methylcinnamic acid. In this way was obtained 7.9 g of material, mp 138–140° (lit.[24] mp 137–138°).

***cis-t*-Butyl α-Methylpercinnamate.** *cis,cis*-α-Methylcinnamic acid anhydride, mp 77–80°, was prepared by dropwise addition of thionyl chloride (0.5 equiv) to a mixture of *cis*-α-methylcinnamic acid and pyridine (1 equiv each) cooled in an ice bath.

A solution of 5.0 g of the *cis,cis*-anhydride (0.016 mole) in 100 ml of ether was added to a slurry of 5.6 g of sodium *t*-butyl hydroperoxide (0.050 mole) in 150 ml of ether at room temperature. The mixture was stirred at room temperature for 16 hr and then 100 ml of cold water and 100 ml of petroleum ether were added. The organic layer was separated. The aqueous layer was acidified and 2.5 g of *cis* acid was recovered (92% of theoretical). The organic layer was concentrated *in vacuo* and the residue taken up in petroleum ether. The petroleum ether layer was washed successively with water, dilute sodium carbonate solution, and water, dried over anhydrous magnesium sulfate, and concentrated to 2.50 g of an oily residue. The oily residue was crystallized from petroleum ether

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(21) A similar conclusion was reached by Fantazier and Kampmeier in their kinetic study of the *cis*- and *trans-t*-butyl α,β-dimethylpercinnamates: R. M. Fantazier and J. A. Kampmeier, *J. Am. Chem. Soc.*, **88**, 5219 (1966).

(22) T. W. Koenig and J. C. Martin, *J. Org. Chem.*, **29**, 1520 (1964), and references therein.

(23) All melting points are uncorrected. All combustion analyses were performed by Micro-Tech Laboratories, Skokie, Ill.

(24) R. Stoermer and G. Voht, *Ann.*, **409**, 36 (1915).

to give 2.05 g of a white solid, mp 41–44°. The perester displayed a characteristic band in the infrared at 1760 cm^{-1} (carbon tetrachloride).

Anal. Calcd for $C_{14}H_{18}O_3$: C, 71.77; H, 7.74. Found: C, 71.59; H, 7.62.

***cis-t*-Butyl α-Phenylpercinnamate.** *cis,cis*-α-Phenylcinnamic acid anhydride, mp 130–131°, was prepared as described above for the α-methyl system.

To a slurry of 5.6 g of sodium *t*-butyl hydroperoxide (0.050 mole) in 250 ml of anhydrous ether was added a solution of 5.3 g of the acid anhydride (0.013 mole) in 120 ml of dichloromethane at room temperature. The mixture was stirred at room temperature for 16 hr and water was added. The layers were separate and the organic layer was washed twice with 10% sodium carbonate solution and twice with water, dried over anhydrous magnesium sulfate, and concentrated *in vacuo*. The residue was taken up in petroleum ether and washed twice with water to remove traces of *t*-butyl hydroperoxide, dried over anhydrous magnesium sulfate, and concentrated *in vacuo* to 1.3 g of a white solid (35%), mp 79.5–81.5°. Recrystallization from ether–petroleum ether gave mp 80–81°. The perester displayed a characteristic band in the infrared at 1764 cm^{-1} (carbon tetrachloride).

Anal. Calcd for $C_{19}H_{20}O_3$: C, 77.00; H, 6.80. Found: C, 77.15; H, 6.98.

***trans,trans*-Bis-α-methylcinnamoyl Peroxide.** The diacyl peroxide **9** was prepared according to the procedure of Staab.[10] To a solution of 5.0 g of N,N-carbonyldiimidazole (0.0308 mole) in 25 ml of tetrahydrofuran was added 5.0 g of *trans*-α-methylcinnamic acid (0.0308 mole) over 10 min at room temperature. Vigorous gas evolution occurred after a brief induction period. The solution was stirred for 0.5 hr and then cooled in an ice–water bath. To the cold azolide solution was added 1.6 ml of 30% hydrogen peroxide in 5 ml of tetrahydrofuran. The mixture was stirred in the cold for an additional 2 hr, poured into water, and extracted with dichloromethane. The organic layer was washed three times with salt water, dried over magnesium sulfate, and concentrated *in vacuo* to an oily solid. The oily residue was crystallized from petroleum ether–ether to give 1.7 g of product, mp 71–74° dec. Characteristic bands are observed in the infrared at 5.64 and 5.72 μ (dichloromethane). Recrystallization from petroleum ether–ether gave material with mp 74–75° dec.

Anal. Calcd for $C_{20}H_{18}O_4$: C, 74.52; H, 5.63. Found: C, 74.77, 75.30; H, 6.18, 5.99.

3-Methylcoumarin. A modification of the procedure as described by Perkin[25] was used. A mixture of 12.2 g of salicylaldehyde (0.10 mole), 7.4 g of propionic acid (0.10 mole), 26 g of propionic anhydride (0.20 mole), and 10.1 g of triethylamine (0.10 mole) was heated at 150° for 8 hr. After cooling to room temperature, the mixture was taken up in dichloromethane and washed with 10% dium carbonate and water, dried over anhydrous magnesium sulfate, and concentrated *in vacuo*. The residue was crystallized from dichloromethane–ether to give 5 g of a solid, mp 89.5–91.5° (31%) (lit.[25] mp 90°). A characteristic band is found in the infrared at 5.84 μ (chloroform).

3-Phenylcoumarin. From 12.2 g of salicylaldehyde (0.10 mole), 13.6 g of phenylacetic acid (0.10 mole), 15.3 g of acetic anhydride (0.15 mole), and 10.1 g of triethylamine (0.10 mole) was obtained 11.5 g of 3-phenylcoumarin, mp 141–143°, by the same procedure as described above for 3-methylcoumarin (lit.[26] mp 140–141°). A characteristic band is found in the infrared at 5.80 μ (chloroform).

Product Analysis. Analysis of the hydrocarbon mixtures from samples decomposed in degassed and sealed Pyrex ampoules was by vpc on a 9-ft 30% Carbowax on Chromosorb P column. The olefin, acetylene, and coumarin products were identified by retention time comparison with authentic samples. Commercial samples of *cis-* and *trans*-stilbenes were used. *trans*-Propenylbenzene was prepared by base-catalyzed isomerization of allylbenzene. *cis*-Propenylbenzene was obtained by photoisomerization of the *trans* isomer to a mixture of the *cis* and *trans* isomers followed by preparative vpc. The ultraviolet spectra of the propenylbenzene isomers were identical with those previously reported.[27]

The acid yields were determined by gram scale decompositions of the peresters. The diluted reaction mixtures were washed with aqueous base, and the aqueous layer was acidified and extracted with ether. The ether layer was dried and concentrated and the residue weighed and compared with authentic samples of the acids by infrared spectroscopy.

The photochemical decompositions of the diacyl peroxide (**9**) were carried out by irradiating solutions of **9** in degassed and sealed Pyrex ampoules which were cooled in an ice–water or Dry Ice–ethanol bath maintained in a clear, Pyrex dewar flask. The dewar was held flush against a Pyrex immersion well in which was mounted a 450-w Hanovia lamp.

Kinetic Procedure. The rates of decomposition of peresters **1–4** were obtained by use of the infrared technique described by Bartlett, *et al.*,[28] using a Beckman IR-7 spectrophotometer. Good first-order kinetics were obtained to 80% reaction in all cases.

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[25] W. H. Perkin, *J. Chem. Soc.*, **28**, 11 (1875).

[26] N. Oda, *Yakugaku Zasshi*, **82**, 1185 (1962).

[27] R. Y. Mixer, R. F. Heck, S. Winstein, and W. G. Young, *J. Am. Chem. Soc.*, 75, 4094 (1953).

[28] P. D. Bartlett, E. D. Benzing, and R. E. Pincock, *J. Am. Chem. Soc.*, **82**, 1762 (1960).

Vinyl Radicals. III.[1] The Thermal Decomposition of *t*-Butyl *cis-* and *trans*-α,β-Dimethylpercinnamates

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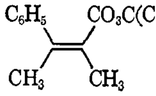
Abstract: Kinetic and scavenger studies confirm a rate-determining oxygen–oxygen homolysis for the thermal decomposition of *t*-butyl *cis-* and *trans*-α,β-dimethylpercinnamates. Activation parameters are essentially identical for the two peresters, ruling out any anchimeric assistance by the aromatic ring in the decomposition of the *cis* perester. Both peresters are similar in behavior to *t*-butyl perbenzoate.

We have previously described[1] the preparation and products of decomposition of the isomeric α,β-unsaturated peresters (I and II) in cumene at 110°. This paper reports kinetic and scavenger studies de-



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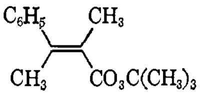

II

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[1] Part II: J. A. Kampmeier and R. M. Fantazier, *J. Am. Chem. Soc.*, **88**, 1959 (1966).

[2] Du Pont Postgraduate Teaching Assistant 1964–1965. National Science Foundation Cooperative Fellow, 1965–1966.