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SOLVENT STEREOSELECTIVITIES IN HYDROGEN ATOM TRANSFER TO THE α-PHENYL-β-METHYLVINYL RADICAL

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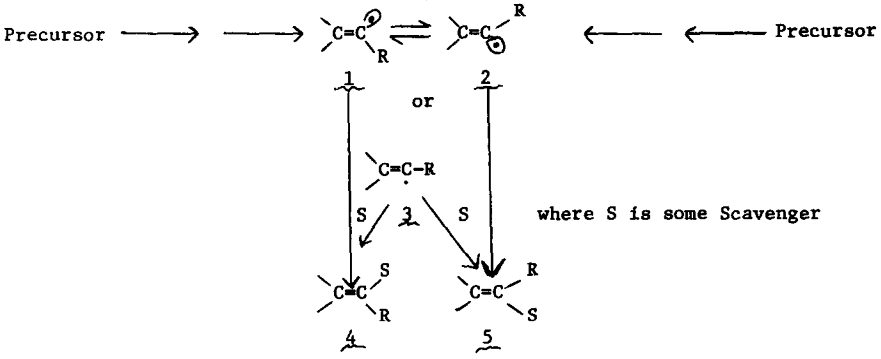
Recently there has been considerable interest in the stereochemical capabilities of vinyl radicals (1-10). One approach to this subject is the stereospecific formation of vinyl radicals from isomeric precursors followed by an analysis of the product mixture (4 and 5) which results from scavenging of the isomeric, bent, radical intermediates (1 and 2) or single, linear, radical intermediate (3). We (1,2) and Kampmeier and co-workers (3) successfully have used peresters as the vinyl radical precursors.



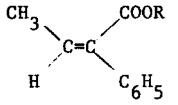
where S is some Scavenger

Results to date suggest that α-alkylvinyl radicals are sp^2 hybridized (bent), at least in the systems studied, but that inversion (1⇌2) is fast relative to scavenging by hydrogen atom transfer from hydrocarbon donors (1,3). However, scavenging by electron transfer (5) and hydrogen atom transfer from tin hydrides (6) apparently can compete with inversion in these systems. Some of our earlier results indicate that α-halovinyl radicals are bent and that the inversion processes have comparable rates to scavenging by hydrogen atom transfer from hydrocarbon solvents (2) while α-arylvinyl radicals involve either (i) fast inversion between bent intermediates or (ii) a single linear intermediate (1).

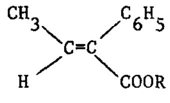
We now wish to report our results on the α-phenyl-β-methylvinyl radical which we believe strongly indicate a single, linear, radical in this system.

The cis- and trans-t-butyl α-phenylpercrotonates were prepared from the corresponding acids by the Staab method (11) using N,N'-carbonyldiimidazole. The nmr data of the peresters and their corresponding acids are given in Table 1. The data for the cis- and trans-acids (m.p.96-8° and 136-8°, respectively) are in excellent agreement with those in the literature (12). Satisfactory combustion analyses were obtained on the cis-perester (liquid) after chromatography on Florisil (Calcd. for $C_{14}H_{18}O_3$: C, 71.77; H, 7.74. Found: C, 71.34; H, 7.47.) The trans-perester could be obtained only in low yields by a variety of perester syntheses and we prepared it only in sufficient quantity to verify that it gave the same olefin product ratios as the cis-perester (13).

Table 1. Nuclear Magnetic Resonance Data for the cis- and trans-α-Phenylcrotonic Acids and their t-Butyl Peresters.



cis



trans

R	Isomer	Vinyl H	Aryl H[a]	CH_3	$C(CH_3)_3$
		δ			
H	cis[b]	6.42 q	7.30 s	2.15 d	-
	trans[b]	7.3 m[c]		1.77 d	-
$OC(CH_3)_3$	cis[d]	6.20 q	7.25 s	1.95 d	1.23 s
	trans[d]	7.3 m[c]		1.75 d	1.17 s

[a] s = singlet, d = doublet, q = quartet, m = multiplet. [b] In chloroform-d. [c] Unresolved. [d] In carbon tetrachloride.

The cis-perester was decomposed in degassed and sealed Pyrex ampoules and the products were analyzed as described in Table 2. Besides the propenylbenzenes and phenylpropyne, low yields of the carboxylic acids were observed. The latter, together with the less than quantitative carbon dioxide yields, suggest that the percrotonates decompose by the one-bond homolysis mechanism (14). However, significant decarboxylation of the intermediate acyloxy radical occurs since substantial yields of the olefins are obtained. Thus, the peresters are suitable precursors for the α-phenyl-β-methylvinyl radical system.

Table 2. Products from the Decomposition of the *cis*-*t*-Butyl α-Phenylpercrotonate.

		mmole of product/mmole of perester		
Solvent	Temp.	Propenylbenzenes[a]	Phenylpropyne[a]	CO_2[b]
Cumene[c]	106[d]	0.50 ± 0.01	0.11 ± 0.04	0.74 ± 0.04
Cumene[c]	26[e]	0.28 ± 0.01	0.14 ± 0.01	0.68[f]
Cyclohexene[g]	106[d]	0.42 ± 0.02	0.068 ± 0.007	0.64 ± 0.01
Cyclohexene[g]	26[e]	0.39 ± 0.01	0.13 ± 0.01	0.66[f]
Toluene[g]	106[d]	0.23 ± 0.04	0.066 ± 0.007	0.43[f]
Toluene[g]	26[e]	0.16 ± 0.003	0.10 ± 0.007	0.48[f]

[a]Analyzed by vpc on a 30% Carbowax on Chromsorb P column at 130°. [b]Manometric determination. [c]0.099 *M* in perester. [d]Thermal decomposition. [e]Photochemical decomposition with a 450-w Hanovia mercury arc using a Pyrex filter. [f]Single determination. [g]0.095 *M* in perester.

The *cis*/*trans* olefin ratios for the photodecompositions listed in Table 3 are zero time values obtained by extrapolation. This procedure was necessary because the propenylbenzenes slowly isomerize under the photolysis conditions. To obtain the desired kinetic ratios (15), samples were analyzed from several minutes and up to several hours after the start of the photolysis. This time period covers a decomposition range of the perester of several percent up to 10-15%. The remaining perester in each sample was reduced with lithium aluminum hydride (a control experiment showed that the propenylbenzene ratio was unaffected by this workup). The mixture was quenched in water, ether extracted, and the ether layer was analyzed by vpc. Smooth curves of the olefin ratios were obtained which were extrapolated back to zero time. A plot of the log (*cis*-olefin/*trans*-olefin) vs 1/T using the values in Table 3 appears in Figure 1.

For a scheme involving a single intermediate (**3**) partitioning to the olefin products, the slopes of the curves in Figure 1 are defined by $(\Delta H^{\ddagger}_{\underline{trans}} - \Delta H^{\ddagger}_{\underline{cis}})/2.3R$ where $\Delta H^{\ddagger}_{\underline{trans}}$ and $\Delta H^{\ddagger}_{\underline{cis}}$ represent the enthalpies of activation for the olefin forming steps. If the system involves interconverting isomeric vinyl radicals, the slopes of the curves in Figure 1 are defined as $(\Delta\Delta H^{\ddagger}_{\underline{t-c}} + \Delta H^{o}_{\underline{t-c}})/2.3R$ where the additional enthalpy term is the difference between the heats of formation of the *trans*- and *cis*-radicals.

Table 3. Initial Olefin Ratios from the Decomposition of cis-t-Butyl α-Phenylpercrotonate at Various Temperatures.

Solvent	Temp.	Propenylbenzenes cis/trans	Decomposition Method
Cumene	0°	4.55 ± 0.05	Photochemical
	25	3.70 ± 0.10	Photochemical
	50	3.15 ± 0.05	Photochemical
	105	2.45 ± 0.03	Thermal
Cyclohexene	0	2.10 ± 0.03	Photochemical
	22	1.87 ± 0.02	Photochemical
	48	1.77 ± 0.01	Photochemical
	105	1.58 ± 0.01	Thermal
Toluene	0	1.45 ± 0.01	Photochemical
	22	1.43 ± 0.02	Photochemical
	50	1.42 ± 0.01	Photochemical
	105	1.39 ± 0.01	Thermal

In the previously studied α-methyl-β-phenylvinyl radical system (1), negative slope values were obtained in a plot corresponding to Figure 1. The most negative slope was obtained with toluene as the scavenger and the least negative with cumene. We interpreted these results in terms of interconverting vinyl radicals ($\underline{1}\rightleftharpoons\underline{2}$) so that the slopes are determined by the difference between the enthalpies of activation and also the difference between the heats of formation. We believe the negative slopes result because the $\Delta H^{o}_{\underline{t}-\underline{c}}$ term is negative (16) and of greater absolute magnitude than the $\Delta\Delta H^{\ddagger}_{\underline{t}-\underline{c}}$ term which is positive (17). If we assume that the $\Delta H^{o}_{\underline{t}-\underline{c}}$ term is the same in the three solvents, we can calculate the relative solvent stereoselectivities given in Table 4.

In the α-phenyl-β-methyl system, positive slopes are obtained in all three solvents with their relative magnitudes being cumene>cyclohexene>toluene. We believe that this system involves a single intermediate which partitions to the two olefin products. Therefore, the slopes in Figure 1 are determined only by the $\Delta\Delta H^{\ddagger}_{\underline{t}-\underline{c}}$ term. We observe that the greatest stereoselectivity is found with the bulkiest donor and the least with the donor of least bulk. These values and the relative solvent stereoselectivities are given in Table 4.

Comparison of the results from the two systems reveals more selectivity in the transfer step in the α-phenyl case. This observation is consistent with a single, linear, vinyl radical intermediate in the α-phenyl system and interconverting bent vinyl radicals

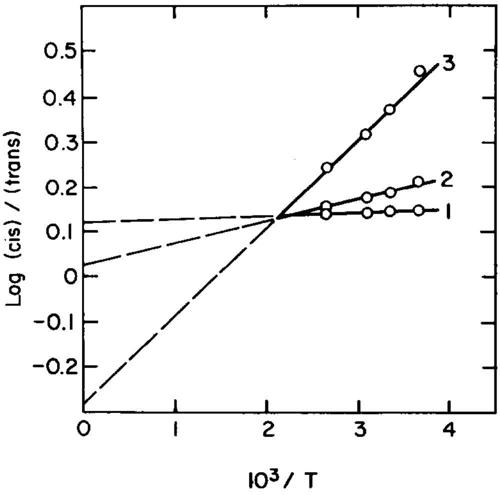
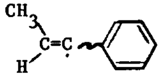
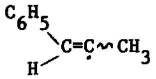


Figure 1. Plots of the Log (cis-Olefin/trans-Olefin) vs 1/T for the α-Phenyl-β-methylvinyl Radical in 1, Toluene, 2, Cyclohexene, 3, Cumene.

Table 4. Solvent Stereoselectivities in Hydrogen Atom Transfer to Vinyl Radicals.

Radical System			
Donor	$\Delta\Delta H^{\ddagger}_{\underline{t-c}}$	$\Delta\Delta\Delta H^{\ddagger\,a}_{\underline{t-c}}$	$\Delta\Delta\Delta H^{\ddagger\,a,b}_{\underline{t-c}}$
		(Kcal/mole)	
Cumene	0.87	0.83	0.53
Cyclohexene	0.22	0.18	0.10
Toluene	0.040	(0.00)	(0.00)

[a] Relative to toluene. [b] Ref. 1

in the α-methyl system. Steric interactions between the incoming donor and the groups on the β-carbon would be expected to be greater in the transition states involving a linear vinyl radical intermediate because the donor approaches the radical site on a line that brings it closer to the groups on the β-carbon when contrasted with the transition states involving bent radicals. Kopchik and Kampmeier have examined these cases in detail (10b).

Further work is directed towards the generation of vinyl radicals in the probe of an epr spectrometer where, hopefully, detailed structural information will become available by analysis of the hydrogen coupling constant.

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(13) The *trans*-perester gave identical results for the olefin ratios as the *cis*-perester in the cases examined as follows: cumene (105°), *cis/trans* = 2.47 ± 0.01; toluene (105°), *cis/trans* = 1.39 + 0.04. Therefore, the α-phenyl-β-methylvinyl radical system involves either (i) isomeric, bent, vinyl radicals that interconvert faster than scavenging by hydrogen atom transfer from hydrocarbons or (ii) a single, linear, vinyl radical intermediate.

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(15) For comparison, the calculated equilibrium distributions based on published thermal data (16) are: *cis/trans* = 0.350 (100°), 0.297 (50°), 0.281 (25°), and 0.242 (0°). Thus, the observed kinetic olefin ratios and the equilibrium distributions are quite different and also show opposite temperature dependencies. The apparent photostationary distributions under our conditions in cumene at 25° are: from *trans*-propenylbenzene, *cis/trans* = 1.85; from *cis*-propenylbenzene, *cis/trans* = 1.94.

(16) In the propenylbenzenes, the difference between the enthalpies of formation is $\Delta H^{o}_{\underline{t}-\underline{c}} = -1.0$ Kcal/mole. "American Petroleum Research Project 44 at the National Bureau of Standards." Selected Values of Properties of Hydrocarbons, Table 13P, Heat of Formation, Entropy, and Free Energy of Formation at 25°. Feb. 29, 1949.

(17) We would expect that approach to the vinyl radical by the donor on the side having the larger group on the β-carbon would have the larger activation energy. Thus, $\Delta\Delta H^{\ddagger}_{\underline{t}-\underline{c}} > 0$ and is a measure of the stereoselectivity in the transfer step.