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VINYL RADICALS. STEREOSELECTIVITY IN HYDROGEN ATOM TRANSFER TO EQUILIBRATED ISOMERIC VINYL RADICALS.

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The question of the facility of cis-trans isomerization in vinyl radical systems has been of interest recently (1-6). Studies on free radical additions to terminal acetylenes indicate that the kinetically determined product is predominantly the cis-isomer and, in all cases, is richer in the cis-isomer than the equilibrium mixture. Some (1) have ascribed this high cis/trans ratio to a stereospecific trans addition followed by capture of the configurationally stable cis-vinyl radical (7). Others (2,3) suggest it may be due to stereoselective capture of the cis-radical from an equilibrated cis-trans radical system.

E.s.r. studies indicate that the barrier to inversion in the simple vinyl radical is around 2 kcal./mole (4,5) and that it is somewhat higher in the 1-methylvinyl radical (4).

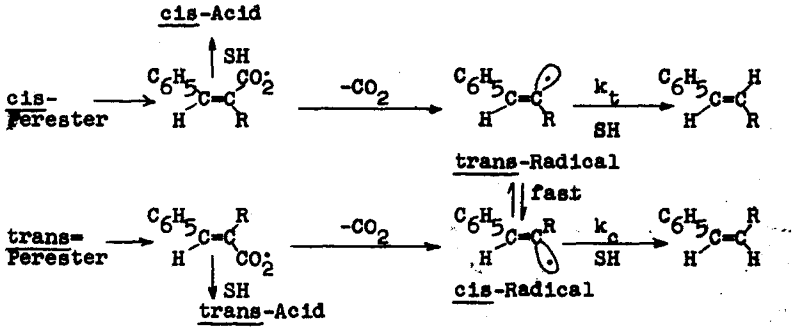
The question of the configurational stability of the vinyl radical can be more easily approached by unambiguously generating the cis- and trans-vinyl radicals from isomeric perester sources and comparing the product compositions. Most recently, Kampmeier and Fantazier (6) reported on their utilization of this approach with the cis- and trans-isomers of t-butyl-α, β-dimethylpercinnamate. They observed the same cis/trans olefin ratio (1.11 ± 0.08) with both isomers after thermal decomposition of the peresters in cumene solution indicating equilibration of the radicals before reaction with solvent.

We wish to now report our results from the thermal decompositions of the cis- and trans-isomers of t-butyl-α-methyl- and α-phenylpercinnamate which confirm the findings of Kampmeier and Fantazier (6) on the facility of isomerization of vinyl radicals at higher temperatures, but also provide an explanation for the observed stereochemical course of hydrogen atom transfer to equilibrated vinyl radicals. High cis/trans product ratios are found in these systems where the trans-olefin is clearly favored at equilibrium (8) suggesting that the product distribution is determined in great part by a stereoselective hydrogen atom transfer step.

The t-butyl-α-methyl- and α-phenyl-trans-percinnamates (referring to a trans-relationship of the phenyl and percarboxylate groups) were prepared in good yield by treatment of the corresponding acid chlorides with sodium t-butylhydroperoxide in ether at 0°. The cis-peresters were obtained by reaction of sodium t-butylhydroperoxide with the cis-acid anhydrides in ether at room temperature. The anhydrides were prepared by dropwise addition of .5 equivalents of thionyl chloride (9) in ether to a mixture of one equivalent each of the cis-acid (10) and pyridine in ether at room temperature. All four peresters gave satisfactory combustion analyses (11). The n.m.r. data also support the assigned structures (α-methyl: cis, m.p. 40-1°, trans, liquid; α-phenyl: cis, 80-1°, trans, m.p. 108-110°).

Degassed solutions of the peresters were decomposed under the conditions indicated in Table 1. 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 (12). Hydrocarbon yields were determined by calibration with authentic olefin solutions of known concentration.

The t-butyl-α-methyl- and α-phenylpercinnamate systems probably decompose by a one bond cleavage since a small amount of the corresponding carboxylic acids can be isolated (14). However, decarboxylation of the acyloxy radical (Figure 1) to the vinyl radical is a major pathway as evidenced by the high olefin yields in Table 1. It is seen that as the concentration of perester is decreased, the olefin yields increase. This may simply be due to a decrease in induced decomposition at lower perester concentrations. If this is the cause, then it should be revealed by a kinetic study. We will report on a complete product study at a later time.



R = CH_3 or C_6H_5
SH = Cumene or Cyclohexene

Figure 1

Table I

Product Compositions from the Thermal Decompositions of t-Butyl-α-methyl- and -α-phenylpercinnamates at 110°[a].

Perester	Solvent	Perester M	Olefin Yield (%)	cis-[b] Olefin (%)
α-Methyl-[c]				
trans	Cumene	0.048	64.6 ± 3.6	63.0 ± 1.2
		0.10	62.9 ± 3.7	62.1 ± 0.2
		0.20	51.1 ± 3.2	57.5 ± 0.8
		0.30	44.4 ± 0.6	60.1 ± 0.7
		0.47	40.6 ± 0.6	60.9 ± 0.2
cis	Cumene	0.077	58.5 ± 0.5	61.4 ± 1.1
		0.12	53.3 ± 2.2	60.8 ± 0.6
		0.20	46.4 ± 0.5	61.5 ± 0.4
		0.31	38.8 ± 0.5	60.2 ± 0.2
trans	Cyclohexene	0.22	52.7 ± 0.7	46.4 ± 0.2
cis	Cyclohexene	0.18	40.2 ± 0.5	45.2 ± 3.1
α-Phenyl-[d]				
trans	Cumene	0.016	71.0 ± 5.0	84.2 ± 4.0
		0.060[e]	66.0	84.2
		0.082	59.3 ± 1.2	88.5 ± 0.1
		0.30	43.8 ± 0.6	90.6 ± 0.1
		0.41	37.7 ± 0.5	90.6 ± 0.1
cis	Cumene	0.038	56.1 ± 1.4	83.1 ± 1.0
		0.064	50.9 ± 1.6	83.6 ± 0.8
		0.16	44.6 ± 0.8	87.9 ± 0.7
		0.40	31.2 ± 1.2	89.1 ± 0.9
trans	Cyclohexene	0.33	59.9 ± 2.5	78.2 ± 0.2
cis	Cyclohexene	0.34	40.1 ± 1.0	79.8 ± 0.6

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[a] Each entry represents two or more runs except where indicated.

[b] Based on total olefin yield. [c] Analyzed by v.p.c. on 30% carbowax on Chromsorb P column at 140°, flow of 60 cc/min. Ret. times: trans, 21 min.; cis, 15 min. [d] Analyzed by v.p.c. on 30% carbowax on Chromsorb P at 230°, flow of 90 cc/min. Ret. times: trans, 31.5 min.; cis, 13 min. [e] Single determination.

It is very clear that the same olefin ratio is obtained from either the *cis*- or *trans*-perester in any one solvent indicating equilibration of the radicals before reaction with solvent. The high *cis/trans* ratio is most easily explained by a faster rate of capture of the *cis*-vinyl radical ($k_c > k_t$) because of steric reasons. The trend towards more *cis*-product as the hydrogen atom donor is changed from cyclohexene to the bulkier cumene is in agreement with this scheme. A similar effect was noted in studies on the 9-decalyl system (15) where a change from cyclohexane to cumene as the donor leads to an increase in *cis*-decalin in the product mixture.

Currently, we are investigating the low temperature photodecomposition of the *cis*- and *trans*-*t*-butyl-α-methylpercinnamates.

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7. By the *cis*-radical is meant the one that gives the *cis*-olefin on addition of a hydrogen atom.

8. We obtain apparent equilibrium values of *trans*-propenylbenzene of 76.9°/₀ and 72.9°/₀ 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°/₀ from the difference in free energy of formation between the isomers of .78 kcal./mole. J. E. Kilpatrick *et al.*, *J. Res. Nat. Bur. Stand.*, **42**, 225 (1949). The thermal equilibrium between *cis*- and *trans*-stilbenes has been reported as 93°/₀ *trans* at 25°. C. C. Price and M. Meister, *J. Am. Chem. Soc.*, **61**, 1595 (1939).

9. Attempts to prepare and isolate the *cis*-acid chlorides failed because of facile isomerization to the *trans*-acid chlorides and/or competing anhydride formation.

10. We find that the α-methyl- and α-phenyl-*cis*-cinnamic acids can be prepared in overall 25°/₀ yield from the *trans*-acids by the following general route. The *trans*-acid is converted to the methyl ester which is photoisomerized to a mixture of the *cis*- and *trans*-esters. The mixture is partially saponified under controlled conditions so that only the *cis*-ester remains. (The *cis*-*trans*-ester composition is easily determined by v.p.c. analysis). After separation of the acid and ester components, the *cis*-ester is saponified to the *cis*-acid.

11. Micro-tech Laboratories, Skokie, Illinois.

12. 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. The *cis*- and *trans*-Propenylbenzenes were purified by preparative v.p.c. Their u.v. spectra were identical with those reported in the literature in reference (13).

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