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STYRYL RADICALS DERIVED FROM THE THERMAL DECOMPOSITION OF TRANS- AND CIS-CINNAMOYL PEROXIDE

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Recent articles on stereochemical aspects of hydrogen abstraction by vinyl radicals (1) prompt us to submit this report on the study, meanwhile having been under way (2), of the stereochemical behaviour of styryl radicals in abstraction of a halogen atom from carbon tetrachloride or from bromotrichloromethane.

Decomposition of di-trans-cinnamoyl peroxide in boiling carbon tetrachloride under nitrogen gave carbon dioxide (150%) and β-chlorostyrene (50%, trans:cis = 81:19, as determined by gas chromatography (Apiezon Grease L)). Similar experiments carried out in bromotrichloromethane as solvent at the same temperature gave a mixture of trans- and cis-β-bromostyrene in a ratio of 86:14. In the same way di-cis-cinnamoyl peroxide (3) was decomposed and the quantities of chloro- and bromostyrenes formed were determined. The results are summarized in the table.

The homolytic nature of the decomposition of these peroxides is apparent; the point to be considered is the stereo-

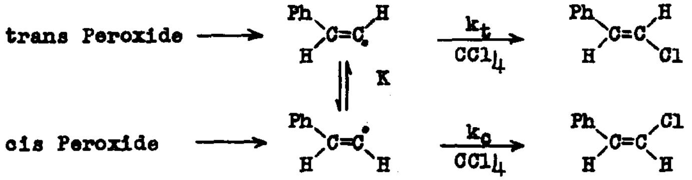
Ratio of trans- to cis-Halogenostyrene formed from Styryl Radicals in Carbon Tetrachloride or in Bromotrichloromethane

Source of radicals	β-Chlorostyrene		β-Bromostyrene	
	trans	cis	trans	cis
Di-trans-cinnamoyl peroxide	81	19	86	14
Di-cis-cinnamoyl peroxide	82	18	73	27

chemistry of styryl radicals thus produced. Separate experiments showed that β-chloro- and β-bromo-styrene do not undergo cis-trans isomerization under the present experimental conditions. Coumarin (21%) was found in the decomposition of di-cis-cinnamoyl peroxide in either of the two solvents used, but not in the experiments with the trans peroxide; further, the cis peroxide gave cis-cinnamic acid, but not trans-cinnamic acid. These findings demonstrate that in the homolysis of the cis and trans peroxide no geometrical isomerization takes place between the original peroxides as well as between the cis- and trans-cinnamoyloxy radical produced from them.

The cis-cinnamoyloxy radical reacts in three ways:
1) decomposition giving styryl radicals and carbon dioxide,
2) formation of coumarin, the benzene nucleus being attacked intramolecularly by the carbonyloxy group situated very close to it, and 3) formation of cis-cinnamic acid by abstraction of a hydrogen atom. The trans-cinnamoyloxy radical reacts similarly except for the formation of coumarin. The styryl radical, whether it is derived from either the cis or the trans peroxide, abstracts a chlorine atom from carbon tetrachloride to give the same mixture of cis- and trans-β-chlorostyrene. This fact indicates that either 1) an equilibrium is quickly established between the cis- and trans-styryl radical, in which

the odd electron occupies an sp^2 hybrid orbital, before they abstract a chlorine atom, or 2) a common intermediate radical of linear configuration alone is involved, in which the hybridization has undergone change from sp^2 to sp at the radical centre of styryl radicals. The latter possibility, however, is ruled out since in bromotrichloromethane the ratio of the cis- and trans-bromostyrene formed is different between the experiments with the cis or trans peroxide. Assuming therefore that the first possibility is the case and using the relevant equilibrium and rate constants shown in the scheme below, the ratio of the trans- to cis-β-chlorostyrene formed is expressed as $K \cdot k_t/k_c = 4.4$. In the absence of any evidence available for assessment of the equilibrium constant K, this value may be assumed to be about unity, since it does not seem that the steric effect caused by the odd electron is significantly different between the two isomeric radicals. Then, k_t/k_c will be about 4.4, i.e., the trans-styryl radical abstracts a chlorine atom about four times as fast as the cis radical does, evidently suggesting that in the cis radical the phenyl group places steric hindrance against the abstraction reaction.



The fact that the ratio (86:14) of the trans- to cis-β-bromostyrene formed from the trans peroxide is larger, whereas the corresponding ratio (73:27) for the cis peroxide, smaller, than the ratio (81:19), in which the isomeric β-chlorostyrenes are invariably formed, indicates that, contrary to the case in carbon tetrachloride the abstraction by the styryl radical of a bromine atom from bromotrichloromethane competes with the rapid cis-trans isomerization between the isomeric styryl radicals, although the latter rate seems to be still much higher. This conclusion is to be expected on account of the weakness of the C-Br bond in comparison with the C-Cl bond and is in keeping with the fact that the homolytic addition of bromotrichloromethane to olefins takes place much more readily than that of carbon tetrachloride and without formation of appreciable quantity of telomeric products (4).

Although the present experimental results eliminate the sole involvement of the linear-type styryl radical as intermediate radicals, without the evidence from electron spin resonance measurements (5) they would not exclude the possibility that the linear radical may also be involved in a rapid equilibrium with the cis- and trans-styryl radicals, these three species abstracting a halogen atom at their respective rates.

References

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(2) The results were presented at the 19th Annual Meeting of the Chemical Society of Japan, Yokohama (April, 1966).

(3) Prepared from cis-cinnamic acid and hydrogen peroxide with N,N'-dicyclohexylcarbodiimide according to Greene and Kazan's method (J. Org. Chem., 28, 2168 (1963)), m.p. 45-46° (Found: C, 73.59; H, 5.00. $C_{18}H_{14}O_4$ requires C, 73.47; H, 4.76%).

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