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Decomposition of *cis*- and *trans*-*α*-Phenylcinnamoyl Peroxide and *t*-Butyl *cis*- and *trans*-*α*-Phenylperoxycinnamate. Stereochemistry of 1,2-Diphenylvinyl Radical[1]

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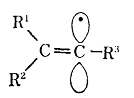
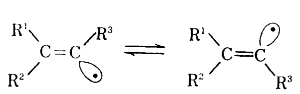
Decomposition of *trans*- and *cis*-α-phenylcinnamoyl peroxide and *t*-butyl *trans*- and *cis*-α-phenylperoxycinnamate were carried out in solution and the products were determined. *t*-Butyl *trans*- and *cis*-α-phenylperoxycinnamate, on decomposition in carbon tetrachloride, gave mixtures of *cis*- and *trans*-α-chlorostilbene in the same *cis* to *trans* ratio at 110°C, but in different ratios at 80°C, the higher ratio being obtained from *t*-butyl *trans*-α-phenylperoxycinnamate. In the decomposition of *trans*- and *cis*-α-phenylcinnamoyl peroxide in various solvents at 60°C, the α-halostilbenes formed in carbon tetrachloride and bromotrichloromethane and the stilbenes produced in cumene, chloroform and triethylsilane were shown to be richer in the isomer of the same configuration as the peroxide decomposed. The stereochemical course of the reaction of the 1,2-diphenylvinyl radical generated from these peroxy-esters and peroxides is discussed.

The stereochemistry of vinyl radicals has recently been investigated by several groups of workers.[2–8] Unsubstituted vinyl[2,3] and 1-methylvinyl radicals[2] have been shown by electron spin resonance measurements to exist not in an *sp*-hybridized linear form but in two sp^2-hybridized bent forms which are interconvertible. However, from the viewpoint of organic reaction mechanisms, the stereochemical behaviour of various vinyl radicals can not be regarded as completely clarified.[4–8]



Linear form

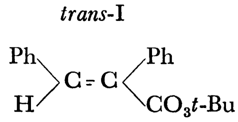


Bent forms

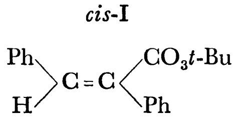
In a previous paper,[6] we showed that styryl radicals exist in two bent forms from the finding that *trans*- or *cis*-cinnamoyl peroxide, on decomposition in carbon tetrachloride at 77°C, gave mixtures of *trans*- and *cis*-*β*-chlorostyrene in the same ratio, whereas in bromotrichloromethane at 77°C, *trans*- and *cis*-*β*-bromostyrene were produced in different ratios. Singer and Kong have also presented evidence that 1-bromo-2-phenylvinyl radicals have *cis*- and *trans*-forms.[4d] Sargent and Browne have shown that *cis*- or *trans*-3-chloro-3-hexene, on treatment with sodium naphthalenide in tetrahydrofuran or dimethoxyethane, gave mixtures of *trans*- and *cis*-3-hexene in different *cis* to *trans* ratios which suggest that the 1-ethyl-1-butenyl radicals intermediately formed are in two bent forms.[7]

It seemed of interest to investigate the stereochemistry of the 1,2-diphenylvinyl radical. It is possible that it might exist in linear form, since this form could be stabilized by a possible conjugation between the unpaired electron in a *p*-orbital on the *sp*-hybridized α-carbon atom and the π-electron system on the adjacent α-phenyl group. Singer and Kong considered these radicals, which they generated by decomposition of *t*-butyl *trans*- and *cis*-α-phenylperoxycinnamate in solution at 110°C, to exist in two bent forms in equilibrium[4b] by analogy with the structure of simpler vinylic radicals.[2,3] Kopchik and Kampmeier have recently concluded that the 1,2-diphenylvinyl radical is *sp*-hybridized at the radical centre, from the analysis of experimental data and of molecular orbital calculations with the 1-vinylvinyl radical as a model.[5d]

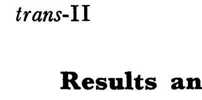
In the present investigation, *trans*- and *cis*-α-phenylcinnamoyl peroxide (I) and *t*-butyl *trans*- and *cis*-α-phenylperoxycinnamate (II) were allowed to decompose in solution in order to generate 1,2-diphenylvinyl radicals and the products were examined.



trans-I



cis-I



trans-II

cis-II

Results and Discussion

Preparation and Properties of α-Phenylcinnamoyl Peroxides. *trans*-α-phenylcinnamoyl peroxide was prepared by treatment of *trans*-α-phenylcinnamoyl chloride with sodium peroxide. It showed characteristic absorption

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[1] Most of the contents of this article was presented at the 20th (April, 1967, Tokyo) and the 21st (April, 1968, Osaka) Annual Meetings of the Chemical Society of Japan.

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[4] a) L. A. Singer and N. P. Kong, *Tetrahedron Lett.*, **1966**, 2089. b) L. A. Singer and N. P. Kong, *J. Amer. Chem. Soc.*, **88**, 5213 (1966). c) L. A. Singer and N. P. Kong, *ibid.*, **89**, 5251 (1967). d) L.A. Singer and N.P. Kong, *Tetrahedron Lett.*, **1967**, 643.

[5] a) J. A. Kampmeier and R. M. Fantazier, *J. Amer. Chem. Soc.*, **88**, 1959 (1966). b) R.M. Fantazier and J.A. Kampmeier, *ibid.*, **88**, 5219 (1966). c) J. A. Kampmeier and G. Chen, *ibid.*, **87**, 2608 (1965). d) R. M. Kopchik and J. A. Kampmeier, *ibid.*, **90**, 6733 (1968).

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[7] G. D. Sargent and M. W. Browne, *J. Amer. Chem. Soc.*, **89**, 2788 (1967).

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bands of diacyl peroxides at 1750 and 1772 cm^{-1} (Nujol). The isomeric *cis*-peroxide was prepared according to Greene and Kazan's procedure[9] from *cis*-α-phenylcinnamic acid and hydrogen peroxide with *N*,*N'*-dicyclohexylcarbodiimide as a condensing agent. Preparation both from *cis*-α-phenylcinnamoyl chloride and sodium peroxide by the conventional procedure[10] and from *cis*-α-phenylcinnamoylimidazole and hydrogen peroxide[11] was unsuccessful. The *cis*-α-phenylcinnamoyl peroxide obtained was a pale yellowish oil at room temperature, and displayed characteristic bands of diacyl peroxides at 1779 and 1795 cm^{-1} (Nujol).

Both peroxides, particularly the *cis*-peroxide, were found unstable in neat state or in solution even at room temperature. The instability of α-phenylcinnamoyl peroxides is attributable to facile conversion into their carboxy-inversion products from the following observations. When the *trans*-peroxide was allowed to stand as Nujol mull at room temperature, its infrared absorption bands due to a diacyl peroxide group at 1750 and 1772 cm^{-1} gradually decreased in intensity and finally disappeared, while new absorption bands at 1810 and 1740 cm^{-1} characteristic of alkyl alkanoyl carbonates[12] appeared and increased in intensity (see Fig. 1); in fact the product from this change was shown to be 1,2-diphenylvinyl *cis*-1,2-diphenylethylenecarbonyl carbonate.[13]

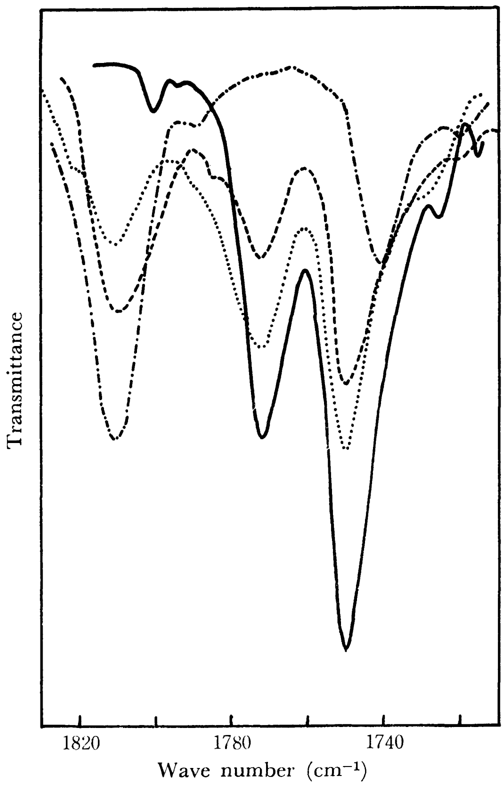

Fig. 1. IR spectra at various times of *trans*-α-phenylcinnamoyl peroxide (Nujol mull) at 24.5°C.
—— immediately after the preparation of the mull; ······ after 55 hr; ---- after 79 hr; —·—· after 258 hr.

The unsuccessful attempt to prepare *cis*-α-phenylcinnamoyl peroxide by treatment of *cis*-α-phenylcinnamoyl chloride with sodium peroxide gave an oily material, which solidified at −78°C, contained no peroxidic oxygen and displayed infrared absorption bands at 1740 and 1803 cm^{-1} characteristic of an alkyl alkanoyl carbonate.[12] On being dissolved in dichloromethane at room temperature, it decomposed spontaneously giving *cis*-α-phenylcinnamic anhydride, while with alkali it afforded *cis*-α-phenylcinnamic acid and diphenylacetylene. This suggests that the reaction of *cis*-α-phenylcinnamoyl chloride with sodium peroxide once gave *cis*-α-phenylcinnamoyl peroxide, which, under the experimental conditions, readily rearranged into the carboxy-inversion product, 1,2-diphenylvinyl *trans*-1,2-diphenylethylenecarbonyl carbonate, and that this carbonate subsequently decomposed, as is generally known to be the case with acyl alkyl carbonates,[12b] to give *cis*-α-phenylcinnamic anhydride and 1,2-diphenylvinyl carbonate, the latter probably giving rise to diphenylacetylene.

Products from Thermal Decomposition. *trans*- and *cis*-α-Phenylcinnamoyl peroxide were allowed to decompose in carbon tetrachloride at 60, 80, and 110°C, and in bromotrichloromethane, chloroform, cumene, and triethylsilane at 60°C, and *t*-butyl *trans*- and *cis*-α-phenylperoxycinnamate were also subjected to decomposition in carbon tetrachloride at 80 and 110°C. The products from these decompositions are listed in Tables 1, 2, and 3.

Operation of a homolytic mechanism in the decomposition of the peroxides and the peroxy-esters is demonstrated by the formation of bicumyl in cumene and of hexachloroethane in carbon tetrachloride, bromotrichloromethane, and chloroform, both arising from dimerization of the radical derived from solvents, and also by the production of α-halostilbenes in carbon tetrachloride and bromotrichloromethane resulting from abstraction of a halogen atom by the 1,2-diphenylvinyl radical; this is further supported by the finding that the presence of 2,2-diphenyl-1-picrylhydrazyl completely suppressed the formation of α-chlorostilbene in the decomposition of the *trans*-peroxide in carbon tetrachloride. The sole production of the α-phenylcinnamic acid of the same geometrical configuration as the starting peroxide or the peroxy-ester shows that neigher the starting materials nor the intermediate α-phenylcinnamoyloxy radicals isomerize to their isomeric forms under the reaction conditions employed. Separate experiments also confirmed that no isomerization of stilbenes or α-halostil-

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[9] F. D. Greene and J. Kazan, *J. Org. Chem.*, **28**, 2168 (1963).

[10] L. F. Fieser and A. E. Oxford, *J. Amer. Chem. Soc.*, **64**, 2060 (1942).

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

[12] a) D. S. Tarbell and N. A. Leister, *J. Org. Chem.*, **23**, 1149 (1958). b) D. S. Tarbell and E. J. Longosz, *ibid.*, **24**, 774 (1959).

[13] Formation of such a carboxy-inversion product is frequently observed with diacyl peroxides such as 4-*t*-butylcyclohexanecarbonyl peroxide,[14] cyclohexanecarbonyl peroxide,[15] α-methylbutyryl peroxide,[16] isobutyryl peroxide[16] and β-phenylisobutyryl peroxide.[17]

[14] F. D. Greene, H. P. Stein, Chin-Chiun Chu, and F. M. Vane, *J. Amer. Chem. Soc.*, **86**, 2080 (1964).

[15] R. C. Lamb, J. G. Pacifici, and P. W. Ayers, *ibid.*, **87**, 3928 (1965).

[16] J. K. Kochi, *ibid.*, **85**, 1958 (1963).

[17] S. Oae, T. Kashiwagi, and S. Kozuka, *Chem. Ind.* (London), **1965**, 1694.

TABLE 1. PRODUCTS FROM DECOMPOSITION OF *trans*- AND *cis*-α-PHENYLCINNAMOYL PEROXIDE IN CARBON TETRACHLORIDE AND YIELDS IN MOL% OF PEROXIDE[a]

Run No.	1	2	3[b]	4	5[c]	6[d]
Temp. °C	80	80	60	60	110	60
Peroxide	*trans*	*cis*	*trans*	*cis*	*trans*	*trans*
Initial concn. (M)	0.0226	0.0090	0.0109	0.0086	0.0083	0.0146
trans-$PhCH{=}CPhCO_2H$	21.8	0	43.2	0	+	8.8
cis-$PhCH{=}CPhCO_2H$	0	35.6	0	35.0	0	0
cis-$PhCH{=}CPhCl$	78.0	0.3	27.6	2.0	54.0	0
trans-$PhCH{=}CPhCl$	1.2	0.1	0.7	2.6	6.8	0
cis-$PhCH{=}CHPh$	1.4	0	1.0	1.0	2.4	0
trans-$PhCH{=}CHPh$	2.8	1.5	8.8	10.4	1.2	0
$PhC{\equiv}CPh$	7.6	0.6	31.4	3.2	48.4	53.8
$PhCH_2COPh$	4.0	0	19.2	13.2	25.6	
$(PhCOCHPh)_2$	0	24.4	0	10.0	0	0
C_2Cl_6	+	+	+	+	+	+
(*cis*-$PhCH{=}CPhCl$) / (*trans*-$PhCH{=}CPhCl$)	99 : 1	75 : 25	97 : 3	43 : 57	89 : 11	

a) A + sign denotes that the product was detected but not determined.
b) Yield of carbon dioxide was determined to be 130 mol% of the peroxide.
c) Carried out in a sealed tube.
d) In the presence of DPPH (six moles per mole of the peroxide).

TABLE 2. PRODUCTS FROM DECOMPOSITION OF *trans*- AND *cis*-α-PHENYLCINNAMOYL PEROXIDE IN CUMENE, CHLOROFORM, BROMOTRICHLOROMETHANE, AND TRIETHYLSILANE AND YIELDS IN MOL% OF PEROXIDE[a]

Run No.	7	8	9	10	11	12	13[b]
Solvent	cumene	cumene	$CHCl_3$	$CHCl_3$	$BrCCl_3$	$BrCCl_3$	Et_3SiH
Temp. °C	60	60	60	60	60	60	60
Peroxide	*trans*	*cis*	*trans*	*cis*	*trans*	*cis*	*trans*
Initial concn. (M)	0.0214	0.0085	0.0201	0.0090	0.0194	0.0157	0.0505
trans-$PhCH{=}CPhCO_2H$	52.0	0	15.4	0	50.0	0	+
cis-$PhCH{=}CPhCO_2H$	0	24.0	0	28.4	0	38.6	0
cis-$PhCH{=}CPhX$			0	1.2[c]	8.8[d]	1.0[d]	
trans-$PhCH{=}CPhX$			0	5.4[c]	1.0[d]	1.0[d]	
cis-$PhCH{=}CHPh$	34.0	0.8	36.0	1.4	0.1	0.1	16.5
trans-$PhCH{=}CHPh$	4.0	3.2	4.8	16.0	0	4.1	5.3
$PhC{\equiv}CPh$	44.0	0.8	15.4	1.4	1.4	0.6	57.4
$PhCH_2COPh$	32.0	+	3.2	0	~50	0	~40
$(PhCOCHPh)_2$	0.8	10.0	0	5.0	0	+	0
C_2Cl_6			+	+	+	+	
$PhCMe_2CMe_2Ph$	+	+					
(*cis*-$PhCH{=}CPhX$) / (*trans*-$PhCH{=}CPhX$)	89 : 11[e]	20 : 80[e]	88 : 12[e]	6 : 94[e]	89 : 11[f]	48 : 52[f]	76 : 24[e]

a) A + sign denotes that the product was detected but not determined.
b) Hexaethyldisilane was detected by vpc.
c) α-Chlorostilbene.
d) α-Bromostilbene.
e) The isomer ratio of *cis*- to *trans*-stilbene.
f) The isomer ratio of *cis*- to *trans*-α-bromostilbene.

TABLE 3. ISOMER RATIO OF α-CHLOROSTILBENE FROM DECOMPOSITION OF *t*-BUTYL *trans*- AND *cis*-α-PHENYLPEROXYCINNAMATE IN CARBON TETRACHLORIDE[a]

Temp. °C	100	110	80	80
Peroxy-ester	*trans*-II	*cis*-II	*trans*-II	*cis*-II
(*cis*-$PhCH{=}CPhCl$) / (*trans*-$PhCH{=}CPhCl$)	73 : 27[b]	76 : 24[b]	84 : 16[c]	77 : 23[c]

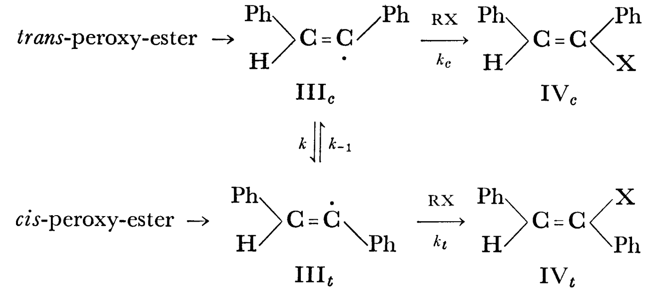
a) Initial concentrations of peroxy-ester were between 0.06 and 0.1 M. Decompositions were carried out in sealed tubes. The yields of α-chlorostilbenes were between 30 and 40%.
b) Mean of triplicate runs.
c) Mean of duplicate runs.

benes took place under the reaction conditions used or in the work-up process. These observations enable us to discuss the stereochemical behaviour of intermediate 1,2-diphenylvinyl radicals by examining the isomer ratio of α-halostilbenes formed in carbon tetrachloride or bromotrichloromethane.

The *trans*- and *cis*-peroxide were found to give more complex mixtures of products than the peroxy-esters. Moreover, the *cis*-peroxide, compared with the *trans*-peroxide, afforded much lower yields of those products which could arise from the reaction of 1,2-diphenylvinyl radicals with solvents. *cis*- and *trans*-Stilbene were produced from the peroxides, not only in solvents carrying a transferable hydrogen atom such as chloroform, cumene, and triethylsilane, but also, though in smaller yields, in solvents containing no hydrogen atom such as carbon tetrachloride and bromotrichloromethane, indicating that the stilbene was not exclusively formed by abstraction of a hydrogen atom by 1,2-diphenylvinyl radicals from solvents. Diphenylacetylene and deoxybenzoin were also shown to arise from both *cis*- and *trans*-peroxides in various solvents. *dl*-1,2-Dibenzoyl-1,2-diphenylethane resulted from the *cis*-peroxide. Some of these compounds might have been formed as cage reaction products or the products from the decomposition of 1,2-diphenylvinyl 1,2-diphenylethylenecarbonyl carbonate.

Decomposition of *cis*- and *trans*-peroxy-ester in carbon tetrachloride, on the other hand, gave neither stilbene nor 1,2-dibenzoyl-1,2-diphenylethane, although diphenylacetylene was formed in lower yield than in the case with the peroxides, showing that the peroxy-esters decompose with less complexity than the peroxides.

Isomer Ratios of Olefins Resulting from Decomposition. Decomposition of *t*-butyl *cis*- or *trans*-α-phenylperoxycinnamate in carbon tetrachloride at 110°C gave α-chlorostilbenes in an approximately equal ratio of the *cis*- to *trans*-isomer, *viz*., 73:27 from the *trans*- and 76:24 from the cis-peroxy-ester. Decreasing the reaction temperature to 80°C, however, resulted in different *cis* to *trans* ratios of the chloro-olefins: 84:16 from the *trans*- and 77:23 from the *cis*-peroxy-ester. These findings clearly exclude the possibility that the 1,2-diphenylvinyl radical is directly produced in linear form by homolysis of the peroxy-esters, because the linear radical would lead to the same *cis* to *trans* ratio of α-chlorostilbenes, irrespective of the configuration of the peroxy-ester decomposed. Thus, the results are readily explained by assuming that the 1,2-diphenylvinyl radical exists in two bent forms corresponding to *cis* and *trans* configurations in line with the prevalent view on the structure of various vinylic radicals,[2-8,18] and the reaction steps are formulated in the following scheme ($RX=CCl_4$).



Scheme 1.

Both forms of the 1,2-diphenylvinyl radical, at 110°C, rapidly isomerize to each other to attain equilibrium before abstraction of a chlorine atom from carbon tetrachloride, so that the same *cis* to *trans* ratio of the the products is obtained irrespective of the configuration of the starting material. Singer and Kong concluded such a rapid equilibration for this radical on the basis of the finding that the ratio of *cis*- to *trans*-stilbene resulting from decomposition of both *t*-butyl *cis*- and *trans*-α-phenylperoxycinnamate in cumene, cyclohexane or toluene at 110°C were not dependent on the configuration of the peroxy-esters.[4b] However, it is evident that at 80°C, the equilibration of these radicals is sufficiently slow in rate for the abstraction from carbon tetrachloride to compete with it; the *trans* peroxy-ester, therefore, gave a higher *cis* to *trans* ratio of α-chlorostilbenes (84:16) than the *cis* peroxy-ester (77:23), the configuration of the starting peroxy-ester being partly reflected in the isomer ratio.

Decomposition of *cis*-α-phenylcinnamoyl peroxide in carbon tetrachloride gave mixtures of *cis*- and *trans*-α-chlorostilbene in *cis* to *trans* ratios of 43:57 at 60°C and of 75:25 at 80°C, while the *trans*-peroxide gave *cis* to *trans* ratios of 97:3 at 60°C, 99:1 at 80°C, and 89:11 at 110°C; it is apparent that with decreasing temperature these peroxides tend to yield α-chlorostilbene predominantly of the same configuration as the starting peroxide. The same tendency was also observed in the decomposition at 60°C in some other solvents (Table 2), indicating that, at 60°C, the interconversion between *cis*- and *trans*-1,2-diphenylvinyl radicals is not so rapid as to complete the equilibration before abstraction.

In a previous paper,[6] decomposition of *trans*- or *cis*-cinnamoyl peroxide at 77°C was shown to afford mixtures of *trans*- and *cis*-β-chlorostyrene in the same *cis* to *trans* ratio in carbon tetrachloride, but mixtures of *trans*- and *cis*-β-bromostyrene in different *cis* to *trans* ratios in bromotrichloromethane, the *cis*-peroxide giving a higher *cis* to *trans* ratio. These findings led to the conclusion that the isomerization between *cis*- and *trans*-styryl radicals takes place rapidly enough to be complete before the abstraction of a chlorine atom from carbon tetrachloride, but its rate is comparable with that of the abstraction of a bromine atom from bromotrichloromethane. However, in contrast with this, the isomerization between isomeric 1,2-diphenylvinyl radicals at 60°C or 80°C is not so rapid as to complete equilibration before reaction with various solvents. This difference between the styryl and 1,2-diphenylvinyl radical is attributed to the presence, in the latter, of an α-phenyl group, which is heavier than the α-hydrogen in the former, the phenyl group moving less rapidly than the hydrogen in the isomerization step. This result is in line with the observation by Singer and Kong that 1-bromo-2-phenylvinyl radicals do not equilibrate at 110°C, owing to the presence of a heavier α-bromine atom,[4d] and with the fact that, according to the electron spin

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[18] O. Simamura, "Topics in Stereochemistry," Vol. 4, ed. by N. L. Allinger and E. L. Eliel, Wiley-Interscience, New York (1969), p. 21.

resonance spectroscopy, at −172°C, 1-methylvinyl radicals do not isomerize,²⁾ whereas unsubstituted vinyl radicals isomerize.²,³⁾

Notwithstanding the above arguments, the possibility is not ruled out that a linear form of 1,2-diphenylvinyl radical corresponding to a state of energy minimum exists between those two bent forms in which the radicals are initially produced and which also correspond to energy minima. If the linear form exists as well, the *cis* to *trans* product ratio should be the same irrespective of the configuration of the starting material or reflect its difference according to whether the equilibration among the three forms of the radical is rapid or slow.

The Difference in Reactivity between cis- *and* trans-*1,2-Diphenylvinyl Radicals*; *the Steric Effect.* By reference to Scheme 1 ($RX=CCl_4$) the product isomer ratio and the four reaction rate constants are correlated, so that a quantitative measure of the difference in reactivity between *cis-* and *trans*-1,2-diphenylvinyl radicals may be obtained on the assumption that a linear form of this radical is not involved. The ratio of *cis-* to *trans*-α-chlorostilbene formed from *trans*-peroxy-ester, $(IV_c/IV_t)_{\rm yield}$, which may be denoted by C, is expressed by the use of the steady state approximation as follows:

$$C = (IV_c/IV_t)_{\rm yield} = k_c/k_t\cdot\{k_{-1}+k_t[CCl_4]\}/k \qquad (1)$$

Similarly, the ratio of *trans-* to *cis*-olefin, arising from *cis*-peroxy-ester, $(IV_t/IV_c)_{\rm yield}$, which may be denoted by T, isgiven as follows:

$$T = (IV_t/IV_c)_{\rm yield} = k_t/k_c\cdot\{k+k_c[CCl_4]\}/k_{-1} \qquad (2)$$

Elimination of the concentration of carbon tetrachloride $[CCl_4]$ from Eqs. (1) and (2) leads to

$$(T+1)/(C+1) = k_t/k_c\cdot k/k_{-1} \qquad (3)$$

When the isomeric vinyl radicals III_c and III_t equilibrate, we have $k/k_{-1}=[III_t]/[III_c]=K_{eq}$ where K_{eq} denotes the equilibrium constant of interconversion between these radicals. In the absence of any evidence available for assessment of the equilibrium constant K_{eq}, this value may be assumed to be approximated by the equilibrium constant of isomerisation between *trans-* and *cis*-stilbene, since it does not seem unreasonable that the steric effect caused by an odd electron is not significantly different from that caused by a hydrogen atom. The value for K_{eq} or k/k_{-1} is therefore estimated at 100 and 180 at 110°C and 80°C, respectively, on the basis of the data reported for stilbenes.¹⁹⁾

Substitution of the observed values of C and T and of the estimated values of k/k_{-1} in equation 3 gives $k_t/k_c= 1.2\times10^{-3}$ at 80°C and 3.5×10^{-3} at 110°C. Thus, the *cis* radical III_c abstracts a chlorine atom from carbon tetrachloride several hundred times faster than the *trans* radical III_t; evidently, this difference is attributable to a crowded situation around the radical centre of the *trans* radical, which places steric hindrance to an incoming molecule of carbon tetrachloride.

The above ratios of the rate constants at 80°C and 110°C correspond to the difference in activation free energy of 4.7 and 5.1 kcal/mol, respectively, since $\Delta G_t^{\neq}-\Delta G_c^{\neq}=-2.3\boldsymbol{R}T\cdot\log(k_t/k_c)$. These values are larger than what one would expect on the ground of the presence of a phenyl group at the β-position, since the *cis*-styryl radical reacts with carbon tetrachloride at 77°C with an activation free energy higher by 1.0 kcal/mol than the *trans*-styryl radical, the cause of this being evidently steric retardation exerted by the *cis*-phenyl group.⁸,¹⁶⁾ The higher value of $\Delta G_t^{\neq}-\Delta G_c^{\neq}$ for the 1,2-diphenylvinyl radical is explained by the fact that the disposition of the α-phenyl group is different between III_c and III_t. In III_t the α-phenyl lies in the plane of the double bond, so that its ortho-hydrogen exerts steric hindrance toward an approaching carbon tetrachloride molecule in addition to that exerted by the β-phenyl group, whereas, in III_c, the α-phenyl is twisted away from the plane of the C=C double bond because of the β-phenyl group on the same side of it,²⁰⁾ so that the hindrance due to the ortho-hydrogen is absent.

Experimental

Preparation of trans-*α-Phenylcinnamoyl Peroxide.* *trans*-α-Phenylcinnamic acid, prepared by the usual procedure,²¹⁾ was treated with six molar equivalents of thionyl chloride in dry benzene at room temperature for 52 hr and the resulting *trans*-α-phenylcinnamoyl chloride was recrystallized from petroleum ether (boiling below 40°C), mp 42.5—44°C (lit,²²⁾ mp 47—48°C). This chloride (3.2 g, 0.0132 mol) was added with stirring to a mixture of sodium peroxide (2.4 g, 0.031 mol), ice (15 g), water (15 m*l*), and petroleum ether (40 m*l*) cooled in an ice bath. Stirring was continued for 5 hr, and the precipitate was filtered off by suction, washed repeatedly with cold water, and dried between sheets of filter paper in a vacuum for 2 hr at 8°C to afford 2.0 g (68%) of the required peroxide (purity, 94.0% as determined by iodometric titration). It decomposed at 52—55°C with gas evolution. IR($\nu_{C=O}$): 1750 and 1772 cm⁻¹ (Nujol). NMR: τ 2.1 (singlet, 1H) and 2.8 (multiplet, 10H); *trans*-α-phenylcinnamic acid shows peaks at τ 2.1 (singlet, 1H) and 2.7 (multiplet, 10H).

Preparation of cis-*α-Phenylcinnamoyl Peroxide.* This peroxide was prepared according to Greene and Kazan's procedure.⁹⁾ To a cold stirred solution of *N,N′*-dicyclohexylcarbodiimide (2.0 g, 0.01 mol) and anhydrous solution (10 m*l*) of hydrogen peroxide in ether (5M) was added dropwise a solution of *cis*-α-phenylcinnamic acid²³⁾ (2.2 g, 0.01 mol) in dichloromethane (25 m*l*). The mixture was stirred at 0°C for 3 hr and then filtered by suction through a sintered glass funnel, and the *N,N′*-dicyclohexylurea collected in the funnel was slurried three times with 20 m*l* portions of cold dichloromethane and the washings were added to the main filtrate. This filtrate was added with 60 m*l* of cold ether and was

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19) The equilibrium ratio of *trans-* to *cis*-stilbene of 96 : 4 at 200°C (T. W. J. Taylor and A. R. Murray, *J. Chem. Soc.*, **1938**, 2078). corresponds to the difference in free energy of $\Delta G=3.03$ kcal/mol. This value and the difference in heat of hydrogenation between *cis-* and *trans*-stilbene, 5.7 kcal/mol (R. B. Williams, *J. Amer. Chem. Soc.*, **64**, 1395 (1942).), which corresponds to ΔH, give the difference in entropy of 5.7 e.u. These values enable ΔG, and, accordingly, equilibrium constants at given temperatures to be estimated.

20) H. Suzuki, This Bulletin, **33**, 379 (1960).

21) R. E. Buckles and K. Bremer, "Organic Syntheses," Coll. Vol. IV, p. 777 (1963).

22) R. Riemschneider and H. Kampfer, *Monatsh. Chem.*, **90**, 518 (1959).

23) L. F. Fieser, "Experiments in Organic Chemistry," Maruzen, Tokyo (1958), p. 182.

washed in succession with three 25 m*l* portions of cold saturated ammonium sulphate solution, two 25 m*l* portions of cold 10% sodium carbonate solution, and two 25 m*l* portions of cold aqueous saturated sodium chloride solution. The organic layer was dried over anhydrous sodium sulphate and the solvent was completely removed under reduced pressure at 0°C in a rotary film evaporator. The remaining *cis*-α-phenylcinnamoyl peroxide (0.35 g, yield 17%) was pale yellowish oil at room temperature and solidified at -35°C (purity, about 30% as determined by iodometry). It was extremely unstable at room temperature and decomposed with gas evolution, and attempted recrystallization from several solvents was unsuccessful. IR($\nu_{C=O}$): 1779 and 1795 cm^{-1} (Nujol).

Preparation of t-*Butyl* trans-α-*phenylperoxycinnamate.* This compound was prepared according to the procedure of Milas and Surgenor.[24] To a cold stirred mixture of *t*-butyl hydroperoxide (4.5 g, 0.05 mol) and potassium hydroxide (2.8 g, 0.05 mol) in 60 m*l* of water was added dropwise a solution of *trans*-α-phenylcinnamoyl chloride (8.0 g, 0.034 mol) in 60 m*l* of ether in 10 min, and the mixture was stirred for a further 22 hr at room temperature. The reaction mixture was then washed with three 150 m*l* portions of 5% aqueous sodium carbonate and dried over anhydrous sodium sulphate. After removing ether, the remaining white material was recrystallized from ether–petroleum ether to give 5.0 g (50% yield) of the required peroxy-ester, mp 107—108°C (purity, 99% as determined by iodometric titration. Found: C, 76.89; H, 6.80%; Calcd for $C_{19}H_{20}O_3$: C, 77.03; H, 6.76%). Its spectroscopic data (IR and NMR) were in accord with those reported by Singer and Kong.[4b]

Preparation of t-*Butyl* cis-α-*phenylperoxycinnamate.* *cis*-α-phenylcinnamic acid (5.0 g, 0.022 mol) was treated with thionyl chloride (20.0 g, 0.17 mol) in dry benzene at room temperature for 49 hr in the dark. Volatile matter was removed from the resulting mixture in a rotary film evaporator, and the remaining yellowish matter was repeatedly recrystallized from petroleum ether to give *cis*-α-phenylcinnamoyl chloride, mp 66.0—68.0°C (Found: C, 73.74; H, 4.62%; Calcd for $C_{15}H_{11}OCl$: C, 74.08; H, 4.53%). IR($\nu_{C=O}$): 1740 cm^{-1} (Nujol). NMR: τ 2.60 (multiplet, 10H) and 3.16 (singlet, 1H). The required peroxy-ester was prepared from this chloride in a similar way to the preparation of the *trans* isomeride. The *cis*-peroxy-ester, mp 78—80°C (purity, 99%), obtained in 60% yield, showed satisfactory spectroscopic data[4b] (IR and NMR) and elementary analysis (Found: C, 77.05; H, 6.95%; Calcd for $C_{19}H_{20}O_3$: C, 77.03; H, 6.76%).

Authentic Materials and Solvents. The authentic samples, used for comparison with reaction products, of *cis*- and *trans*-α-chlorostilbene, *cis*- and *trans*-α-bromostilbene, *cis*- and *trans*-stilbene, deoxybenzoin, diphenylacetylene, and bicumyl *etc.* were prepared in the usual way. Carbon tetrachloride (Wako, special grade) was used without further purification. Commercial chloroform was shaken with concentrated sulphuric acid, washed with 5% aqueous sodium carbonate and water, dried over calcium chloride and distilled. Cumene was shaken with concentrated sulphuric acid, washed with water and 5% aqueous sodium carbonate, dried over calcium chloride, and distilled over sodium wire. Bromotrichloromethane (Eastman Kodak) was distilled in the dark immediately before use. Triethylsilane was prepared from trichlorosilane and ethylmagnesium bromide.[25]

Decomposition of trans-α-*Phenylcinnamoyl Peroxide at Room Temperature.* The infrared spectrum of this peroxide was examined in five times amount of Nujol at 24.5°C at intervals with a Hitachi EPI-G2 infrared spectrophotometer. The spectrum in the carbonyl region changed during 258 hr as shown in Fig. 1. Another specimen of the same peroxide was set aside at 24.5°C for 258 hr without apparent change, but it displayed the same infrared spectrum as the above sample in Nujol after 258 hr, and was further shown, by iodometric titration, to contain only 2.8% of the active oxygen initially present in the peroxide. This material (0.87 g) was dissolved in 20 m*l* of ether and extracted with three 200 m*l* portions of 5% aqueous sodium carbonate to afford 0.224 g of *trans*-α-phenylcinnamic acid on acidification of the extract. Removal of ether from the organic layer gave 0.665 g of a yellowish solid, and it was recrystallized twice from chloroform–petroleum ether to give 1,2-diphenylvinyl *cis*-1,2-diphenylethylenecarbonyl carbonate, mp 127—135°C (Found: C, 80.88; H, 4.71%; Calcd for $C_{30}H_{22}O_4$: C, 80.72; H, 4.93%); IR($\nu_{C=O}$): 1810 and 1740 cm^{-1} (Nujol).

Decomposition of cis-α-*phenylcinnamoyl Peroxide at Room Temperature.* To a cold solution of *cis*-α-phenylcinnamoyl chloride (2.0 g, 8.2 mmol) in 30 m*l* of tetrahydrofuran were added dropwise 1.0 g (8.7 mmol) of 30% aqueous hydrogen peroxide and 2 m*l* of aqueous sodium hydroxide (0.33 g, 8.3 mmol), and the mixture was stirred at 0°C for 26 hr. Cold dichloromethane (50 m*l*) was added. It was then washed with three 100 m*l* portions of cold water and three 100 m*l* portions of 5% sodium hydrogen carbonate, and dried over anhydrous sodium sulphate. The solvent was removed at 0°C in a rotary film evaporator, the remaining yellowish oil was dissolved in a small amount of dichloromethane, methanol was added to the solution at 10°C and this was cooled to -78°C to deposit a white solid. The mixture was centrifuged at -78°C and the supernatant liquid removed with a pipette; the remaining solid was washed with cold methanol and dried *in vacuo* at -78°C to give 1.5 g of a white solid. This was found to contain only a trace of active oxygen by iodometric titration, and showed absorption bands at 1803 and 1740 cm^{-1} (in carbon tetrachloride) characteristic of the alkyl alkanecarbonyl carbonate. When a portion of this substance was added to dichloromethane at room temperature in an attempt at recrystallization, gas evolved vigorously indicating its decomposition; work-up of the mixture gave *cis*-α-phenylcinnamic anhydride, characterized by mp and mixed mp 149.5—150°C, and comparison of its spectrum with an authentic specimen. Hydrolysis of the above substance by heating with potassium hydroxide (5 g) for an hour in a mixture of 40 m*l* of ethanol and 20 m*l* of water afforded *cis*-α-phenylcinnamic acid and trace of diphenylacetylene.

General Procedure for Thermal Decomposition. In a round-bottomed three-necked flask fitted with a gas inlet, a stopper, and a reflux condenser, to which were connected a trap cooled with dry ice–ethanol, a magnesium perchlorate tube and an Ascarite tube, in the order mentioned, was placed a measured amount of a solvent (60—100 molar excess of the peroxide to be added). This was heated under reflux in a slow stream of nitrogen for an hour and cooled down to room temperature; then a weighed amount of the peroxide was added. The resulting solution was allowed to stand under nitrogen in a thermostat kept at a specified temperature until the peroxide had been completely decomposed (6—10 hr). In the decomposition of *cis*-α-phenylcinnamoyl peroxide which is unstable, reaction solutions were prepared by dissolving in a measured amount of a solvent the *cis*-peroxide immediately after it was obtained by removal of the solvent from the reaction mixture for

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24) N. A. Milas and D. M. Surgenor, *J. Amer. Chem. Soc.*, **68**, 642 (1946).

25) H. Ishii, "Yukikagobutsu Goseiho," Vol. IV, Gihodo, Tokyo (1966), p. 107.

the preparation of this peroxide, and the concentration of the peroxide in the solution was determined by iodometry.

In decompositions conducted at higher temperatures, a solution of the peroxide or peroxy-ester (0.3—0.5 g) in 20 m*l* of a solvent was placed in a small pyrex ampoule which was connected to a vacuum line, degassed by three cycles of the usual procedure consisting of solidification by chilling, evacuation and thawing, and sealed at 3×10^{-3} mmHg. The ampoule was kept in a thermostat until the peroxide had been completely decomposed.

Product Analysis. A reaction mixture, transferred to a separating funnel with ether, was shaken with three 100 m*l* portions of 5% aqueous sodium carbonate to isolate and determine α-phenylcinnamic acid. The organic layer was dried over anhydrous sodium sulphate and ether was distilled off. The residue was subjected to vpc (Perkin-Elmer 154-D with a column of silicone oil) for determination of products; products in some runs were isolated by either column or gas chromatography and identified by comparison with authentic specimens.