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Reaction of Vinylic Radicals with Oxygen[1]

Naoto WADA and Katsumi TOKUMARU[2]

Department of Chemistry, Faculty of Science, The University of Tokyo, Bunkyo-ku, Tokyo, 113

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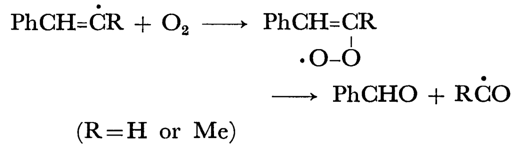
Thermal decomposition of *trans*-α-phenylcinnamoyl peroxide and *t*-butyl *trans*- and *cis*-α-phenylperoxycinnamates and photolyses of 1,1-diphenyl-2-iodoethylene and 1,1,2-triphenyl-2-iodoethylene were carried out in benzene under oxygen and their products were determined. The intermediate vinylic radicals, on reaction with oxygen, undergo oxidative cleavage and dioxygenation of their unsaturated bonds. As an example, 1,2-diphenylvinyl radicals give benzaldehyde together with benzoin.

Much effort has been made to investigate the reaction of alkyl radicals with oxygen and to elucidate the products and reaction mechanism.[3] Aryl radicals have also been shown to react with oxygen giving phenolic products, though a detailed mechanism is not yet fully understood.[4] The reaction of vinylic radicals with oxygen has not been investigated much but one of us showed that *trans*-cinnamoyl peroxide and α-methylcinnamoyl peroxide, on thermal and photochemical decomposition in benzene or carbon tetrachloride under oxygen, gave benzaldehyde together with benzoic acid among the products through the oxidative cleavage of the intermediate styryl or 1-methyl-2-phenylvinyl radicals with oxygen as shown below.[5]



$$\mathrm{PhCH{=}\dot{C}R + O_2 \longrightarrow PhCH{=}\underset{\cdot O-\dot{O}}{CR} \longrightarrow PhCHO + R\dot{C}O}$$

(R=H or Me)

In order to get further insight into the reaction of vinylic radicals with oxygen, the oxidation of 1,2-diphenylvinyl, 2,2-diphenylvinyl, and 1,2,2-triphenylvinyl radicals, generated by the thermal decomposition of suitable diacyl peroxide and peroxyesters or by the photolyses of suitable vinyl iodides, has been undertaken and the results are presented below.

Results and Discussion

Decomposition of *trans*-α-phenylcinnamoyl peroxide (I) in benzene at 60°C in a slow stream of oxygen gave benzoin (24%), benzaldehyde (15%), and benzoic acid (3%) together with products, which resulted irrespective of the atmosphere employed, such as *trans*- and *cis*-stilbene, diphenylacetylene and *trans*-α-phenylcinnamic acid. Decomposition of *t*-butyl *trans*-(II) or

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[2] To whom communications should be addressed.

[3] As general reference for the oxidation of alkyl radicals, see, for example, C. Walling, "Free Radicals in Solution", John Wiley and Sons, New York (1957). Chapter 9; W. A. Pryor, "Free Radicals", McGraw-Hill, New York (1966), p. 287; O. Simamura, T. Migita, N. Inamoto, and K. Tokumaru, "Yuriki Hanno", Tokyo Kagaku Dozin (1969). Chapter 8.

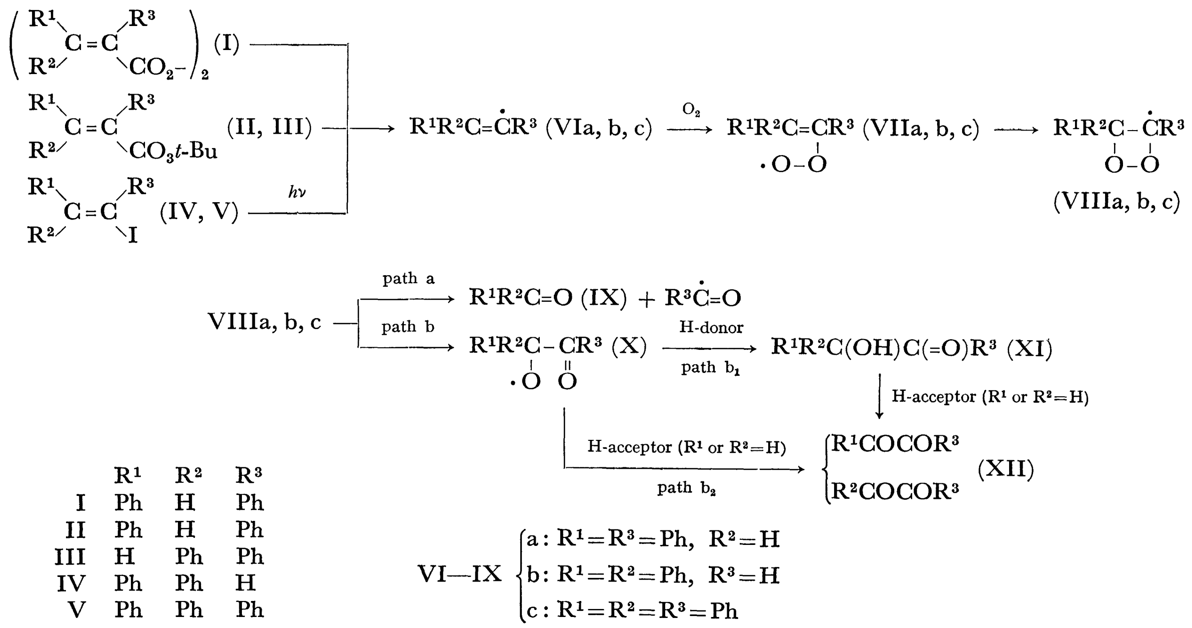
[4] M. Eberhardt and E. L. Eliel, *J. Org. Chem.*, **27**, 2289 (1962); G. A. Russell and R. F. Bridger, *J. Amer. Chem. Soc.*, **85**, 3765 (1963); K. Tokumaru, K. Horie, and O. Simamura, *Tetrahedron*, **21**, 867 (1965).

[5] K. Tokumaru, *Chem. Ind.*, **1969**, 297.

TABLE 1. PRODUCTS FROM DECOMPOSITION OF VINYLIC RADICALS-GENERATORS IN BENZENE UNDER OXYGEN OR NITROGEN

Generators[a,b]	Reaction conditions[c]	Time (hr)	Oxidation products (%)[b]					Other products (%)[b]
			PhCHO	$PhCO_2H$	Ph_2CO	PhCHOHCOPh	PhCOCOPh	
(t-$PhCH{=}CPhCO_2)_2$ (I)	T, 64°, O_2	8	15	3		24		$PhC{\equiv}CPh$, 34 $PhCH_2COPh$, 3 c-$PhCH{=}CHPh$, 2 t-$PhCH{=}CHPh$, trace t-$PhCH{=}CPhCO_2H$, 6
t-$PhCH{=}CPhCO_3t$-Bu (II)	T, 75°, O_2	88	12	n.d.		3	15	$PhC{\equiv}CPh$, 15 t-$PhCH{=}CPhCO_2H$, n. d.
c-$PhCH{=}CPhCO_3t$-Bu (III)	T, 75°, O_2	64	19	n.d.			19	c-$PhCH{=}CPhCO_2H$, n. d.
$Ph_2C{=}CHI$ (IV)	P, 25°, O_2	24			54			I_2, 78
$Ph_2C{=}CHI$ (IV)	P, 25°, N_2	26						I_2, 25 $Ph_2C{=}CHI$ (recovered), 68 $Ph_2C{=}CH_2$, 5 $PhC{\equiv}CPh$, trace $(Ph_2C{=}CH)_2$, 11
$Ph_2C{=}CPhI$ (V)	P, 25°, O_2	24	trace	n.d.	34			I_2, n. d.

a) Initial concentration: 0.03—0.05M. b) t: *trans*; c: *cis*; n.d.: detected but not determined. c) Reaction conditions show method of decomposition, temperature and atmosphere. T: thermal decomposition; P: photolysis with a low pressure (160 W) mercury lamp.



	R^1	R^2	R^3
I	Ph	H	Ph
II	Ph	H	Ph
III	H	Ph	Ph
IV	Ph	Ph	H
V	Ph	Ph	Ph

Scheme 1.

cis-α-phenylperoxycinnamate (III) carried out under oxygen in benzene afforded benzaldehyde (12% or 19% from II or III, respectively) and benzil (15% or 19% from II or III, respectively). Benzoin (3%) and benzoic acid along with diphenylacetylene (15%) were also found among the products from II.

Irradiation of 1,1-diphenyl-2-iodoethylene (IV) or 1,1,2-triphenyl-2-iodoethylene (V) in benzene in a stream of oxygen at room temperature with a low pressure mercury lamp afforded benzophenone (54% and 34% from IV and V, respectively).

The results are summarized in the table. In view of the generation of 1,2-diphenylvinyl radicals from the peroxidic sources, I, II, and III,[6] and the formation of 1-propyl-1-butenyl radicals from the photolysis of 4-iodo-3-heptene,[7] formation of the oxidation products can be attributed to the reaction of the intermediate vinylic radicals with oxygen. This might proceed as in the following scheme.

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[6] N. Wada, K. Tokumaru, and O. Simamura, This Bulletin, **44**, 1112 (1971).

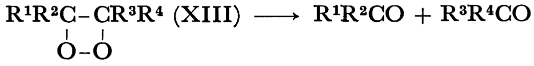
[7] R. C. Neuman, Jr. and G. D. Holmes, *J. Org. Chem.*, **33**, 4317 (1968).

Vinylic radicals (VI) generated from suitable sources react with oxygen to afford vinylperoxy radicals (VII), which subsequently cyclize to give 2,3-dioxetanyl radicals (VIII).[5)] These radicals are either decomposed into carbonyl compound (IX) and acyl radicals (path a), or converted into α-ketoalkoxy radicals (X) (path b), which abstract hydrogen atoms from the reaction medium to give α-ketoalcohol (XI) (path b_1) or lose hydrogen atoms to give α-diketone (XII) (path b_2). Path a proposed previously[5)] is supported by the formation of benzaldehyde, benzoic acid or benzophenone. Path b is proposed herewith on the basis of the production of benzoin and benzil from the decomposition of I, II, and III under oxygen.

Production of benzil at the expense of benzoin from the peroxyesters II and III might be due to the high reactivity of *t*-butoxy radicals to abstract hydrogen atom from benzoin or from the α-ketoalkoxy radical (X). A low yield of deoxybenzoin (3%) from I seems to occur with no participation of oxygen, on taking account of its formation from I decomposed under nitrogen,[6)] although its path is ambiguous at the present time. The absence of α-ketoalcohol among the products from the irradiation is undoubtedly attributable to its further labile photolysis into aroyl and α-hydroxyaralkyl radicals[8)] followed by their reaction with oxygen:

$$ArRC(OH)C(=O)Ar \xrightarrow{h\nu} Ar\dot{C}O + ArR\dot{C}OH$$

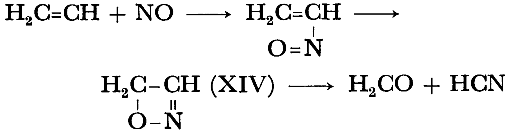
Postulation of 2,3-dioxetanyl radicals as an intermediate undergoing facile cleavage is supported by the recent findings on 1,2-dioxetane (XIII), which was actually prepared and shown to decompose readily into two carbonyl components.[9)]



$$\begin{array}{l} R^1R^2C-CR^3R^4\ (XIII) \longrightarrow R^1R^2CO + R^3R^4CO \\ \qquad\ |\quad\ | \\ \qquad O-O \end{array}$$

$(R^1=R^2=R^3=Me,\ R^4=H;$[9a)] $R^1=R^3=OEt,$
$R^2=R^4=H;$[9b)] $R^1=R^2=R^3=R^4=OMe$[9c)]$)$

1-Oxa-2-azacyclobutene-2 (XIV) was also proposed to be an intermediate during the course of the reaction of unsubstituted vinyl radicals with nitric oxide in gas phase and facilely decompose into formaldehyde and hydrogen cyanide.[10)]



$$\begin{array}{lll} H_2C=\dot{C}H + NO \longrightarrow & H_2C=CH & \longrightarrow \\ & \qquad\ | & \\ & \quad\ O=N & \end{array}$$

$$\begin{array}{l} H_2C-CH\ (XIV) \longrightarrow H_2CO + HCN \\ \ \ |\qquad \| \\ \ \ O-N \end{array}$$

Irradiation of IV in benzene under nitrogen afforded 1,1,4,4-tetraphenyl-1,3-butadiene (11%), 1,1-diphenylethylene (5%) and diphenylacetylene (trace). A large amount of the starting material was recovered. In contrast, in the irradiation of the same iodide in a slow stream of oxygen under the same conditions as above, no starting iodide was recovered and iodine was liberated in 78% yield. The results suggest that the presence of oxygen, by capturing the vinylic radicals, prevents their reactions with iodine atoms or with molecular iodine returning to the starting iodide.

$$Ph_2C=CHI\ (IV) \longrightarrow Ph_2C=\dot{C}H\ (VIb) + I\cdot$$

$$Ph_2C=\dot{C}H + O_2 \longrightarrow Ph_2C=CHOO\cdot \longrightarrow \text{Products}$$

$$Ph_2C=\dot{C}H + I\cdot\ (\text{or } I_2) \longrightarrow Ph_2C=CHI\ (\text{or } +I\cdot)$$

Formation of 1,1,4,4-tetraphenyl-1,3-butadiene might be due to either dimerization of the intermediate vinylic radicals (VIb) or addition of the radical (VIb) to IV followed by elimination of an iodine atom.

$$2Ph_2C=\dot{C}H \longrightarrow Ph_2C=CH-CH=CPh_2$$

$$Ph_2C=\dot{C}H\ (VIb) + Ph_2C=CHI\ (IV) \longrightarrow$$

$$Ph_2C=CH-CHI-\dot{C}Ph_2 \longrightarrow Ph_2C=CH-CH=CPh_2 + I\cdot$$

It should be pointed out that the absence of the products which would result from the substitution of the vinylic radicals on benzene, *viz*., 1,1,2-triphenylethylene from I, II, III, or IV, or 1,1,2,2-tetraphenylethylene from V, indicates a low reactivity of the vinylic radicals towards aromatic substitution, in contrast to aryl radicals, which also belong to sp^2-hybridized σ-radicals and effectively undergo aromatic substitution.[11)]

Experimental

Materials. *trans*-α-Phenylcinnamoyl peroxide (I), *t*-butyl *trans*- (II) and *cis*-α-phenylperoxycinnamate (III) were prepared as described before.[6)] 1,1-Diphenyl-2-iodoethylene (IV) and 1,1,2-triphenyl-2-iodoethylene (V) were prepared according to literature.[12,13)]

Thermal Decomposition of I, II, and III under Oxygen. One to three grammes of I, II, or III in 300 ml of benzene was placed in a 300—500 m*l* three-necked round-bottomed flask fitted with a gas inlet tube, a stopper and a reflux condenser. The mixture was kept in a slow stream of oxygen in a thermostat at a specified temperature for 8—70 hr until the peroxide was completely decomposed.

Photolyses of IV and V under Oxygen or Nitrogen. About 1 g of IV or V was irradiated in 100 m*l* of benzene for 20—24 hr with an immersion-type 160 W low pressure mercury lamp in a slow stream of oxygen or nitrogen.

[8)] P. de Mayo and A. Stoessl, *Can. J. Chem.*, **40**, 57 (1962); P. de Mayo, *Pure Appl. Chem.*, **9**, 597 (1964).

[9)] a) K. R. Kopeckey and C. Mumford, *Can. J. Chem.*, **47**, 709 (1969); E. H. White, J. Wiecko, and D. F. Roswell, *J. Amer. Chem. Soc.*, **91**, 5195 (1969); E. H. White, J. Wiecko, and C. C. Wei, *ibid.*, **92**, 2167 (1970). b) P. D. Bartlett and A. P. Schaap, *J. Amer. Chem. Soc.*, **92**, 3223 (1970). c) S. Mazur and C. S. Foote, *ibid.*, **92** 3226 (1970).

[10)] A. G. Sherwood and H. E. Gunning, *J. Amer. Chem. Soc.*, **85**, 3506 (1963); A. M. Tarr, O. P. Strausz, and H. E. Gunning, *Trans. Faraday Soc.*, **61**, 1946 (1965).

[11)] As general reference for homolytic aromatic substitution, see, for example, D. H. Hey, in G. H. Williams ed., "Advances in Free-radical Chemistry", Vol. II, Logos Press, London (1967), p. 47; G. H. Williams, "Homolytic Aromatic Substitution", Pergamon Press, Oxford (1960); O. Simamura, T. Migita, N. Inamoto, and K. Tokumaru, "Yuriki Hanno", Tokyo Kagaku Dozin, Tokyo (1969). Chapter 11; K. Tokumaru, *Yuki Gosei Kagaku Kyokai Shi* **28**, 773 (1970); K. Tokumaru, *Nippon Kagaku Zasshi* **92**, 886 (1971).

[12)] D. Y. Curtin and E. W. Flynn, *J. Amer. Chem. Soc.*, **81**, 4714 (1959).

[13)] L. L. Miller and D. A. Kaufman, *ibid.*, **90**, 7286 (1968).

Product Analysis. Determination of iodine liberated from the irradiation run was carried out by titration of an aliquot of the reaction mixture with a standard sodium thiosulphate solution.

For determination of the organic products the reaction mixture was shaken with 5% aqueous sodium carbonate. However, the reaction mixture from the photolysis was shaken with 5% aqueous sodium thiosulphate to remove iodine prior to the extraction with the carbonate. The alkaline layer was acidified with 5% hydrochloric acid, shaken with ether to remove acids and the extract was treated with diazomethane and the resulting methyl benzoate or α-phenylcinnamate was determined by vpc using Ucon Oil as a liquid phase. The benzene layer was dried over anhydrous sodium sulphate, and benzene was distilled off. The residue was subjected to chromatography on alumina and vpc using silicon oil or Ucon Oil as a liquid phase.

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