

## The Synthesis and Decomposition Kinetics of Some *para*-Substituted *trans*- $\gamma$ -Benzylidenebutyryl Peroxides. The Excess $\alpha,\gamma$ -Bis(biphenylene)- $\beta$ -phenylallyl Method for the Determination of Initiator Kinetics<sup>1</sup>

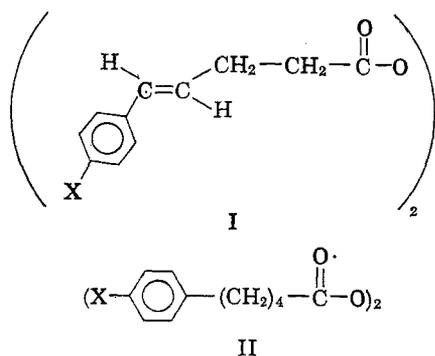
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Syntheses are described for four *trans*-5-(*p*-X-phenyl)-4-pentenoyl peroxides and their precursors, in which the substituents X are Cl, F, CH<sub>3</sub>, and OCH<sub>3</sub>. The decomposition kinetics of these peroxides, as well as the parent peroxide (X = H) were determined in benzene at 50, 60, and 70° by measuring the fading of the stable radical  $\alpha,\gamma$ -bis(biphenylene)- $\beta$ -phenylallyl (BDPA); the free-radical efficiencies of the peroxide decompositions were obtained in the same experiments. The rate constants obtained in this way compare exceedingly well with those obtained by iodometric titration, in experiments carried out in benzene-5% styrene. At 50°, log *k* for the five peroxides gives a linear plot against  $\sigma^+$ , with  $\rho = -1.16$ . Similar decompositions were carried out in propylene carbonate. All of the peroxides decompose more rapidly and form free radicals less efficiently in this highly polar solvent. The kinetics results for decompositions of the *trans*-5-(*p*-X-phenyl)-4-pentenoyl peroxides are interpreted in terms of mechanisms originally proposed by Lamb, *et al.*, for the decomposition of the parent compound (X = H). Results of kinetics experiments on decompositions of 5-phenylpentanoyl, 5-(*p*-methoxyphenyl)pentanoyl, and 4-pentenoyl peroxides are also presented.

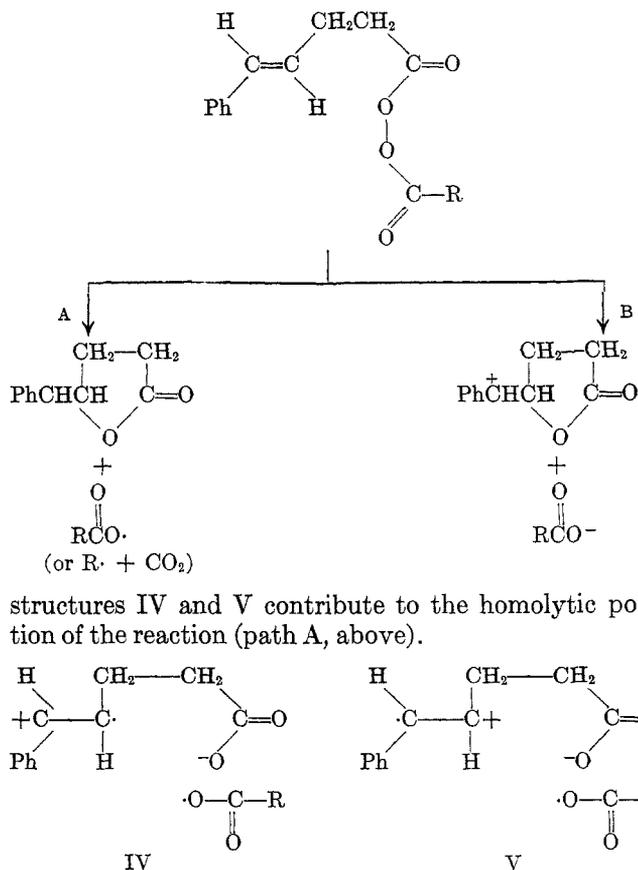
In a previous publication from this laboratory,<sup>4</sup> we have presented data on the kinetics of decomposition of *trans*- $\gamma$ -benzylidenebutyryl peroxide (I, X = H), and  $\delta$ -phenylvaleryl peroxide (II, X = H).<sup>5</sup>



The contrasts in kinetic behavior of the two peroxides were such as to suggest that the two peroxides decompose by substantially different mechanisms. The points of evidence were as follows. (a) Peroxide I (X = H) decomposes five times as rapidly as peroxide II (X = H) in carbon tetrachloride-10% styrene. (b) The rates of decomposition of both peroxides increase with increasing solvent polarity; however, the rate of decomposition of peroxide I (X = H) is more sensitive to solvent polarity than is peroxide II (X = H). Thus, the former decomposes 20 times more rapidly than the latter in propylene carbonate-10% styrene. (c) Peroxide I (X = H) was decomposed in the presence of the stable free radical diphenylpicrylhydrazyl (DPPH); the results showed that not only the specific rate of decomposition of this peroxide (*k<sub>d</sub>*), but also the specific rate of radical production

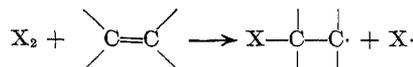
(*2k<sub>d</sub>*) increased in going from carbon tetrachloride to the highly polar solvent, propylene carbonate.

These results were interpreted to mean, firstly, that peroxide I (X = H) undergoes *heterolysis* and *homolysis* via neighboring-group participation of the double bond.<sup>6a,b</sup> In addition, it was proposed that the following



structures IV and V contribute to the homolytic portion of the reaction (path A, above).

(6) This mechanism was based somewhat upon previous evidence which had been reported on intramolecular reactions between olefins and diacyl peroxides: (a) J. C. Martin and E. H. Drew, *ibid.*, **83**, 1232 (1961). (b) F. D. Greene, W. Adam, and J. E. Cantrill, *ibid.*, **83**, 3461 (1961). (c) The literature on reactions of the type



has been summarized recently by M. L. Poutsma, *ibid.*, **87**, 2161 (1965).

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(3) (a) This work was taken for the most part from the dissertation of Leonard P. Spadafino, presented in partial fulfillment of the Ph.D. degree in Aug. 1963. (b) National Defense Education Act Fellow, 1962-1965.

(4) R. C. Lamb, F. F. Rogers, Jr., G. C. Dean, Jr., and F. W. Voigt, Jr., *J. Am. Chem. Soc.*, **84**, 2635 (1962).

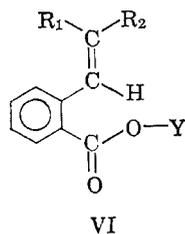
(5) (a) D. F. DeTar and R. C. Lamb, *ibid.*, **81**, 122 (1959); (b) D. F. DeTar and C. Weis, *ibid.*, **79**, 3041 (1957); **78**, 4296 (1956).

TABLE I  
THE RATES AND EFFICIENCIES OF THE DECOMPOSITIONS OF SOME  $\gamma$ -BENZYLIDENE BUTYRYL (I) AND  $\delta$ -PHENYLVALERYL PEROXIDES (II) IN BENZENE<sup>a, b</sup>

Run no.	Peroxide	$10^3(Z)_0$	$(Z)_0/(P)_0$	$10^3(k_d \pm \text{std. dev.}),$ sec. <sup>-1</sup>	$t_{1/2},$ min.	$f$	Temp., °C.
116-8	I, X = H	4.15	1.40	2.372 ± 0.030	487.2	0.385	50
116-9	I, X = H	4.15	1.40	2.442 ± 0.030	473.2	0.389	50
116-4	I, X = H	4.15	1.40	6.811 ± 0.043	169.7	0.398	60
116-5	I, X = H	4.15	1.40	6.801 ± 0.055	169.6	0.400	60
116-7	I, X = H	4.15	1.40	18.45 ± 0.242	62.3	0.408	70
130-8	I, X = Cl	3.96	1.37	2.099 ± 0.010	550.7	0.439	50
130-9	I, X = Cl	3.96	1.37	2.110 ± 0.003	547.6	0.420	50
130-4	I, X = Cl	3.96	1.37	6.538 ± 0.092	176.8	0.453	60
130-5	I, X = Cl	3.96	1.37	6.590 ± 0.062	175.4	0.449	60
130-6	I, X = Cl	3.96	1.37	16.85 ± 0.072	68.6	0.465	70
130-7	I, X = Cl	3.96	1.37	18.10 ± 0.150	63.8	0.420	70
140-6	I, X = F	3.93	1.34	2.669 ± 0.035	432.8	0.491	50
140-9	I, X = F	5.14	2.01	2.764 ± 0.027	418.0	0.497	50
140-4	I, X = F	3.93	1.34	8.437 ± 0.032	137.0	0.503	60
140-7	I, X = F	5.14	2.01	8.828 ± 0.150	130.9	0.503	60
140-5	I, X = F	3.93	1.34	21.19 ± 0.07	52.6	0.514	70
140-8	I, X = F	5.14	2.01	22.42 ± 0.030	51.5	0.521	70
154-5	I, X = CH <sub>3</sub>	3.71	1.24	6.341 ± 0.002	182.2	0.444	50
154-8	I, X = CH <sub>3</sub>	3.71	1.77	6.585 ± 0.008	175.5	0.427	50
154-7	I, X = CH <sub>3</sub>	3.71	1.77	18.15 ± 0.23	63.7	0.439	60
154-6	I, X = CH <sub>3</sub>	3.71	1.24	49.68 ± 0.48	23.3	0.473	70
154-9	I, X = CH <sub>3</sub>	3.71	1.77	47.29 ± 0.48	24.4	0.484	70
170-2	I, X = OCH <sub>3</sub>	3.70	1.30	20.51 ± 0.67	56.4	0.317	50
170-3	I, X = OCH <sub>3</sub>	3.70	1.30	19.97 ± 0.85	57.9	0.317	50
87-3	II, X = H	3.70	1.25	10.544 ± 0.123	109.6	0.496	77
100-2	II, X = H	3.92	1.27	11.389 ± 0.028	101.4	0.483	77

<sup>a</sup> Excess BDPA was used in all experiments, in the sense that some BDPA remained after all the peroxide had decomposed. The rates were measured by following the decrease in absorbance of BDPA at 490 m $\mu$ . <sup>b</sup> Abbreviations used:  $(Z)_0 = (\text{BDPA})_0$ ;  $(P)_0 =$  initial molar concentration of peroxide. The free-radical efficiency,  $f$ , is so defined that  $2f =$  yield of free radicals in moles per mole of peroxide.

More recently, Koenig and Martin<sup>7</sup> have investigated a rather extensive series of peroxides and peresters of formula VI in which R<sub>1</sub> and R<sub>2</sub> were aryl or hydrogen, and the Y groups were *t*-butoxy or aryloxy.



Koenig and Martin showed that in decompositions of compounds of type VI in chlorobenzene, substitution of electron-withdrawing groups on phenyl groups at R<sub>2</sub> retard the rate of decomposition ( $\rho$ , obtained from  $\sigma^+$  plot, = -1.8); substituents on benzyloxy groups at Y have the opposite effect ( $\rho$ , obtained from a  $\sigma$  plot, = +0.7). There was a great deal of variation in the free-radical efficiencies in these decompositions, which presumably reflect variations in the competition between *heterolysis* (similar to path B) and *homolysis* (similar to path A). Koenig and Martin demonstrated that the homolytic portion of the reaction was sensitive to the electronic nature of the substituents. The authors suggested that structures similar to those given in mechanisms A and B above, as well as structures similar to IV and V above, contribute to

the stabilization of the transition states in the homolytic portions of the decompositions. In general, the results presented here tend to corroborate evidence which has been published previously on the intermolecular<sup>6a, b</sup> and intramolecular<sup>4, 7</sup> reactions between peroxide linkages and double bonds.

The choice of  $\alpha, \gamma$ -bis(biphenylene)- $\beta$ -phenylallyl (BDPA)<sup>8</sup> as the scavenger in the kinetics-efficiency experiments appears to have been a wise one. The results presented here, and in previous papers,<sup>9</sup> show that this stable free radical behaves in a nearly ideal fashion in experiments of this type in nonpolar solvents at low temperatures. The scavenger was used in excess in all the experiments, in the sense that some BDPA remained after all the peroxide had been destroyed [*i.e.*,  $(\text{BDPA})_0 = (Z)_0 > 2f(P)_0$ ]. The procedures used in these experiments have been described in detail in previous publications.<sup>9a, b</sup>

This paper reports the results of a number of kinetics experiments on peroxides of type I (X = H, Cl, F, CH<sub>3</sub>, and OCH<sub>3</sub>) in benzene and propylene carbonate, using the excess stable radical technique. The kinetics experiments on the decomposition of peroxide II (X = H) in benzene employed the same technique. In addition, results of iodometric kinetics runs on

(8) (a) C. F. Koelsch, *J. Am. Chem. Soc.*, **79**, 4439 (1957); **54**, 4744 (1932); (b) S. L. Solar and R. M. Lindquist, *ibid.*, **82**, 4285 (1960); (c) S. L. Solar, *J. Org. Chem.*, **28**, 2911 (1963); (d) R. Kuhn and F. A. Neugebauer, *Monatsh.*, **95**, 3 (1964).

(9) (a) R. C. Lamb and J. G. Pacifici, *J. Am. Chem. Soc.*, **86**, 914 (1964); (b) R. C. Lamb, J. G. Pacifici, and P. W. Ayers, *ibid.*, **87**, 3928 (1965); (c) R. C. Lamb, J. G. Pacifici, and L. P. Spadafino, *J. Org. Chem.*, **30**, 3102 (1965).

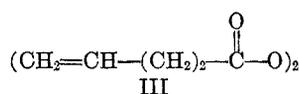
(7) T. W. Koenig and J. C. Martin, *J. Org. Chem.*, **29**, 1520 (1963).

TABLE II  
THE RATES AND EFFICIENCIES OF THE DECOMPOSITIONS OF SOME  $\gamma$ -BENZYLIDENE BUTYRYL PEROXIDES (I)  
IN PROPYLENE CARBONATE\*

Run no.	Peroxide	$10^5(Z)_0$	$(Z)_0/(P)_0$	$10^5(k_d \pm \text{std. dev.}),$ sec. <sup>-1</sup>	$t_{1/2},$ min.	$f$	Temp., °C.
160-5	I, X = H	4.07	1.214	7.23 $\pm$ 0.02	159.7	0.250	40
160-3	I, X = H	4.07	1.214	20.93 $\pm$ 0.13	55.2	0.265	50
160-1	I, X = H	4.07	1.214	51.17 $\pm$ 0.61	22.6	0.265	60
166-11	I, X = Cl	4.07	1.323	5.33 $\pm$ 0.18	216.5	0.293	40
166-9	I, X = Cl	4.07	1.323	14.48 $\pm$ 0.35	79.8	0.313	50
166-7	I, X = Cl	4.07	1.323	27.91 $\pm$ 0.38	41.4	0.310	60
172-3	I, X = F	4.15	1.116	6.53 $\pm$ 0.12	176.7	0.253	40
172-1	I, X = F	4.15	1.116	16.85 $\pm$ 0.87	68.6	0.258	50
172-5	I, X = F	4.15	1.116	45.40 $\pm$ 1.05	25.4	0.264	60

\* See footnotes in Table I.

peroxides of type I (X = H, Cl, F, and CH<sub>3</sub>), type II (X = OCH<sub>3</sub>), and III are presented and discussed.



### Results

Each set of spectrophotometric runs at a given temperature was conducted with three reaction vials constructed of 1-cm. square Pyrex tubing which also served as cuvettes for the spectrophotometer. Two of these vials contained solutions of excess BDPA and peroxide. The other was a control sample which contained a solution of BDPA only. For most of the runs in benzene, two reaction vials contained identical stock solution. However, in some cases, two different stock solutions were used so that the ratios  $(Z)_0/(P)_0$  could be varied.

Ideally, there should be no fading of the scavenger in the control sample in the time required to destroy all the peroxide in the reaction vials. In general, this was found to be essentially the case for decompositions in benzene and propylene carbonate. Usually the initial absorbance reading ( $D_0$ ) fell between 0.9 and 1.3, and the final absorbance readings in the reaction vials fell between 0.20 and 0.75. For example, in the decomposition of peroxide I (X = H) in benzene, the initial absorbances were all 1.09. The final absorbance was between 0.48 and 0.51 for all samples. The readings for the control samples used in this run all fell between 1.11 and 1.10 during the entire course of the experiment. In none of the runs in benzene did the control sample fade more than 0.01 absorbance units during the run. For the decompositions in propylene carbonate, control sample fading was only slightly more serious. In no case, however, did the control sample fading exceed 0.02 units.

The results of the spectrophotometric kinetics runs are recorded in Tables I (benzene) and II (propylene carbonate). The behavior of the systems in benzene (Table I) was very nearly ideal, from the standpoint of precision within a given experiment, reproducibility between experiments, and lack of fading in control samples. Thus, the precision with which values of  $\log(D - D_\infty)$  plotted linearly vs. time (see the kinetic equation given in Experimental Section) through 85% reaction or so was most impressive.<sup>10</sup> In no case did either the rates or efficiencies at a given temperature for a given peroxide differ from each other by more

than 10% relative; and in most cases, reproducibility between experiments was much better than this.

Data obtained on decompositions of peroxides of type I in propylene carbonate (Table II) are not as precise and are probably not as accurate as those obtained in the decompositions in benzene. For one thing, the control samples of BDPA in propylene carbonate faded somewhat more than did control samples in benzene; this error is doubtless compounded further by the fact these experiments should have been carried out at somewhat lower  $(Z)_0/(P)_0$  ratios.<sup>11</sup>

Kinetic procedures are available which allow one to correct for control fading<sup>9c</sup>; however, it was found that the corrections for  $f$  and  $k_d$  for the runs in propylene carbonate were not significant enough to require the more elaborate data treatment.

Similar spectrophotometric runs were also performed with peroxide II (X = H) in benzene at 77°, and the results are entered at the bottom of Table I. A difficulty was encountered in doing experiments on this peroxide with excess BDPA which was not encountered in experiments with peroxides of type I (which decompose more rapidly and at lower temperatures). Rather than becoming constant after "infinity time" as it should, the absorbance due to BDPA dropped to a minimum value at long times, then began to increase very slowly.<sup>12</sup> For the two experiments reported in Table I (87-3 and 100-2), the minimum value of the absorbance was used for  $D_\infty$ . The rates obtained in these experiments (in benzene) are close to those obtained previously for the decomposition of peroxide II (X = H) in toluene at 77°. The same problem was even more severe in attempted spectrophotometric kinetics experiments on decompositions of peroxide II (X = OCH<sub>3</sub>); the consequence is that only iodometric kinetics experiments are reported for this peroxide.

The results of iodometric kinetics runs on peroxides of type I (X = H, Cl, F, and CH<sub>3</sub>) and of peroxide

(10) In some cases, one of the reaction vials was not sealed properly upon degassing so that the BDPA faded out completely within a very short time. This is the reason why there is only one kinetics run reported for peroxide I (X = H) at 70° and for peroxide I (X = CH<sub>3</sub>) at 60°.

(11) The most ideal  $(Z)_0/(P)_0$  ratio used in experiments such as these depends upon the efficiency of radical production of the peroxide. Too high a ratio of  $(Z)_0/(P)_0$  (too little peroxide) leads to a small displacement,  $D_0 - D_\infty$ , and hence to large per cent errors in calculation of  $f$ ,  $f = [(Z)_0 - (Z)_\infty]/2(P)_0$ , and  $k_d$ , which is obtained by statistical adjustment of  $\log(D - D_\infty)$  vs. time (rate equation given in Experimental Section). Additional data, obtained at still higher  $(Z)_0/(P)_0$  ratios, while not seriously different from those given in Table II, are not reported here because of this problem.

(12) Apparently, a material whose visible absorption interferes with that of BDPA is formed very slowly at high temperatures.

TABLE III  
 RATES OBTAINED BY SPECTROPHOTOMETRIC AND IODOMETRIC METHODS

Peroxide	Solvent	Iodometric rate <sup>a</sup>		Spectrophotometric rate	Temp., °C.
		10 <sup>6</sup> (k <sub>d</sub> ± std. dev.), sec. <sup>-1</sup>	t <sub>1/2</sub> , min.	t <sub>1/2</sub> , min.	
I, X = H	Benzene or benzene-5% styrene	6.86 ± 0.07	168.6	169.6	60
I, X = H	Propylene carbonate		54.0 <sup>b</sup>	55.2	50
I, X = H	Propylene carbonate		157.0 <sup>b</sup>	159.7	40
I, X = Cl	Benzene or benzene-5% styrene	6.51 ± 0.05	177.5	176.8	60
I, X = F	Benzene or benzene-5% styrene	8.44 ± 0.04	136.9	137.0	60
I, X = CH <sub>3</sub>	Benzene-5% styrene	17.59 ± 0.61	65.7	63.7	60
I, X = CH <sub>3</sub>	Propylene carbonate	5.00 ± 0.03	230.8		35
I, X = CH <sub>3</sub>	Propylene carbonate	21.44 ± 0.32	53.9		50
II, X = OCH <sub>3</sub>	Benzene-5% styrene	4.61 ± 0.17	250.6		70
II, X = OCH <sub>3</sub>	Benzene-5% styrene	11.95 ± 0.28	96.7		77
II, X = OCH <sub>3</sub>	Benzene-5% styrene	35.80 ± 0.45	32.3		85
III	Benzene-10% MMA	1.044 ± 0.004	1107.0		60.1
III	Benzene-10% MMA	4.06 ± 0.04	284.5		70
III	Benzene-10% MMA	10.33 ± 0.05	111.9		77

<sup>a</sup> In the iodometric runs, initial peroxide concentrations were all between 0.05 and 0.065 M. <sup>b</sup> Taken from ref. 4.

 TABLE IV  
 ACTIVATION PARAMETERS FOR DECOMPOSITIONS OF PEROXIDES OF TYPE I AND II<sup>a</sup>

Peroxide	Solvent	ΔH*, kcal.		ΔS*, e.u.	
		Spectrophotometric	Iodometric	Spectrophotometric	Iodometric
I, X = H	B	21.8		-12.4	
I, X = H	B-5% S				
I, X = H	PrC	19.6	20.5	-14.8	-12.2
I, X = Cl	B	22.7		-9.8	
I, X = Cl	PrC				
I, X = F	B	22.5		-9.9	
I, X = F	PrC				
I, X = CH <sub>3</sub>	B	21.6		-10.9	
I, X = CH <sub>3</sub>	B-5% S				
II, X = OCH <sub>3</sub>	B-5% S		30.5		10.3

<sup>a</sup> B = benzene, B-5% S = benzene-5% styrene, PrC = propylene carbonate.

II (X = OCH<sub>3</sub>) in benzene-5% styrene and in propylene carbonate, and of iodometric experiments on peroxide III in benzene-10% methyl methacrylate are presented in Table III.<sup>13</sup> Also included in Table III for comparison are the half-lives determined spectrophotometrically for the decompositions of some of the same peroxides at the same temperatures. In general, the agreement between the rates determined by the two methods is excellent, although the initial concentration of peroxide in most of the iodometric experiments was 1000 times greater than in the spectrophotometric experiments. Only in one instance in which the rate was determined by both methods was there serious disagreement between two rates—the decomposition of peroxide I (X = CH<sub>3</sub>) in propylene carbonate. The spectrophotometric experiments on this peroxide in this solvent failed, probably because the ratio (Z)<sub>0</sub>/(P)<sub>0</sub> was too large (the value of D<sub>0</sub> - D<sub>∞</sub> was too small); also, the fading of the control sample was rather serious (0.02 absorbance units). Since the rates determined by the two methods agree so well in other instances, we felt justified in omitting the results of the obviously suspect spectrophotometric experiments on the decompositions of peroxide I (X = CH<sub>3</sub>) in propylene carbonate.

(13) Vinyl monomers were used in the iodometric experiments in order to suppress radical-induced decomposition.

Activation parameters are given in Table IV. These parameters were calculated from average values of rate constants (at the extreme temperatures) in those cases where plots of the average values of log k<sub>d</sub>/T vs. 1/T were reasonably linear.

### Discussion

The following points should be made about the data presented in the Results, and from the table of relative rates (Table V).

(1) Whereas the rates of decomposition of peroxide III and peroxides of type II (X = H and OCH<sub>3</sub>) are rather similar, the rates of decomposition of peroxides of type I are significantly greater. This indicates that both the double bond and the phenyl ring are necessary in order to obtain the rate enhancement.

(2) Whereas there is little, if any, ring-substituent effect on the decomposition rates of peroxides of type II (X = H and OCH<sub>3</sub>), there is a significant ring-substituent effect on the rates of decomposition of peroxides of type I (X = Cl, H, F, CH<sub>3</sub>, and OCH<sub>3</sub>). At 50° (in benzene), at which temperature the rates of decomposition of all five peroxides of type I were determined, the values of log k<sub>d</sub> give a reasonably linear plot vs. σ<sup>+</sup>; ρ = -1.16. At 60 and 70° (in benzene), at which k<sub>d</sub> was determined for four peroxides of type

TABLE V  
RELATIVE RATES OF DECOMPOSITION OF PEROXIDES OF  
TYPES I, II, AND III AT 60°<sup>a,b</sup>

Peroxide	$k_x/k_{III}$ (benzene)	$k_x/k_{III}$ (propylene carbonate)
III	1 (iod.)	
II, X = H	1 <sup>c</sup>	
II, X = OCH <sub>3</sub>	1.1 <sup>d</sup> (iod.)	
I, X = H	6.5	49
I, X = Cl	6.3	27
I, X = F	8.3	44
I, X = CH <sub>3</sub>	17.5	50 <sup>e</sup> (iod.)
I, X = OCH <sub>3</sub>	60.5 <sup>f</sup>	

<sup>a</sup> The abbreviation iod. indicates that the rate was obtained iodometrically; all other relative rates came from spectrophotometric runs. <sup>b</sup> All data were obtained from Tables I, II, and III. <sup>c</sup> Rate compared with that of III at 77°. <sup>d</sup> Rate compared with that of III at 70°. <sup>e</sup> Rate compared with that of I (X = H) in propylene carbonate at 50°. <sup>f</sup> Rate compared with that of I (X = H) in benzene at 50°.

I (X = Cl, H, F, and CH<sub>3</sub>), values of log  $k_d$  for I (X = H, F, and CH<sub>3</sub>) describe lines, when plotted vs.  $\sigma^+$ , with  $\rho$  values near -1.4. [The rates of decomposition of peroxide I (X = Cl) are greater than the values predicted by the  $\sigma^+$  plots at 60 and 70°.]

The ring-substituent effect upon the rates of decomposition of peroxides of type I ( $\rho = -1.2$ ) is intermediate between the substituent effect reported by Koenig and Martin<sup>7</sup> for compounds of type VI (R<sub>1</sub> = H; R<sub>2</sub> = H, *m*- and *p*-nitrophenyl; Y = benzoyloxy) in chlorobenzene at 70° ( $\rho = -1.8$ ), and that observed by Greene, Adam, and Cantrill<sup>6b</sup> for the intermolecular reaction between substituted *trans*-stilbenes and benzoyl peroxide ( $\rho = -1.0$ ).

Although the substituent effect is not large, it is an effect, for the most part, upon the rate of homolysis of peroxides of type I. Since the free-radical efficiencies ( $f$  values) do not vary too greatly for type-I peroxides (all lie between 0.32 and 0.52), the logarithms of the rate constants for radical production (log  $2k_d f$ ) give a somewhat poorer  $\sigma^+$  plot, with  $\rho = -0.95$ .

(3) There is a pronounced solvent effect upon the rates of decomposition ( $k_d$ ) of peroxides of type I in going from benzene to propylene carbonate; this was not unexpected, since similar behavior for the decomposition of peroxide I (X = H) had been reported previously.<sup>4</sup> The effect of solvent on the rates of radical production ( $2k_d f$ ) is not quite so pronounced as is the solvent effect of  $k_d$ , inasmuch as all  $f$  values are lower in propylene carbonate. Nevertheless, values of  $2k_d f$  are significantly greater in propylene carbonate than in benzene for all peroxides of type I. Finally, we call attention, without explanation, to the fact that the substituent effect on peroxides of type I is essentially lost in the more polar solvent, propylene carbonate.

The kinetics data presented here require that there be a greater difference in polarity between the transition states and ground states for decompositions of peroxides of type I than for peroxides of type II and III. They further indicate that electron density is displaced from the double bond to the peroxide linkage in the transition state for homolytic decompositions of peroxides of type I. We feel that the best picture of these transition states is in terms of such resonance structures as IV and V (and following Koenig and

Martin<sup>7</sup>), the closed-ring structures which are presented as *intermediates* in mechanisms A and B.

The data insist that the major portion of the decomposition of peroxides of type I is *homolytic* (mechanism A); they permit, but do not require, minor portions of these decompositions to be *heterolytic* (mechanism B). There are two points of evidence which suggest a certain amount of heterolysis. One is that the slope of the plot of log ( $2k_d f$ ) vs.  $\sigma^+$  is 20% less than is the slope of the plot of log  $k_d$  vs.  $\sigma^+$ . The efficiencies of radical production vary curiously for decompositions of type-I peroxides in benzene. They do not vary in any regular way with the molecular weights of the radicals which are formed in the decompositions. For that portion of the series X = F  $\rightarrow$  CH<sub>3</sub>  $\rightarrow$  OCH<sub>3</sub>, there is a smooth decrease in  $f$  with increasing electron-releasing capacity of the substituents; this fact seems to suggest that an increasing fraction of the decomposition is heterolytic along the series X = F  $\rightarrow$  CH<sub>3</sub>  $\rightarrow$  OCH<sub>3</sub>, but the fact that the trend does not include X = Cl and H casts an element of doubt upon this conclusion. A second point of evidence is that the  $f$  values for all peroxides of type I decrease in going from benzene to the highly polar solvent, propylene carbonate. Again, this could be explained by assuming that there is more heterolysis of type-I peroxides in the polar solvent; but it is reasonable to assume that, since propylene carbonate is more viscous than benzene, there would be more cage reaction of radicals (lower  $f$  values) in the former. Therefore, our evidence for heterolysis (mechanism B) is not without ambiguity.

Finally, we should like to emphasize that the spectrophotometric kinetics method using excess BDPA appears to be a convenient method for determining kinetics and radical efficiencies for free-radical initiators at concentrations near  $10^{-5}$  M.

### Experimental Section<sup>14</sup>

Peroxides of type I (X = Cl, F, and CH<sub>3</sub>) were all synthesized by the reaction sequence shown in Scheme I.

The method of preparation of the  $\alpha$ -*p*-X-phenylallyl alcohol was identical with that used by Burton and Ingold<sup>15</sup> except that aryl bromides (rather than iodides) were used in our work. The  $\alpha$ -(*p*-X-phenyl)allyl alcohols were transformed into *p*-X-cinnamyl bromides by a method which was also devised by Burton and Ingold.

The  $\gamma$ -(*p*-X-benzylidene)butyric acids were prepared from the cinnamyl bromides according to a standard procedure which has been outlined for the preparation of pelargonic acid.<sup>16</sup> The acid chlorides and peroxides were synthesized by procedures which have been described for the parent compounds (X = H).<sup>4</sup> The intermediates and peroxides made by the above reaction sequence which have not been reported previously are as follows:  $\alpha$ -*p*-fluorophenylallyl alcohol; *p*-fluorocinnamyl bromide,  $\gamma$ -(*p*-fluorobenzylidene)butyric acid, and the corresponding peroxide;  $\gamma$ -(*p*-chlorobenzylidene)butyric acid and its corresponding peroxide; and  $\gamma$ -(*p*-methylbenzylidene)butyric acid and its peroxide. Some physical properties, compositional analyses, and neutralization equivalents of acids are listed in Table VI for these and other compounds. In addition, some pertinent infrared absorptions are listed in Table VII.

(14) A line-operated Beckman Model DU spectrophotometer, equipped with a specially built boxlike cover for the cell chamber, was used for measuring stable radical concentrations spectrophotometrically. A Perkin-Elmer Model 421 spectrophotometer was used to record the infrared spectra.

(15) H. Burton and C. K. Ingold, *J. Chem. Soc.*, 904 (1928).

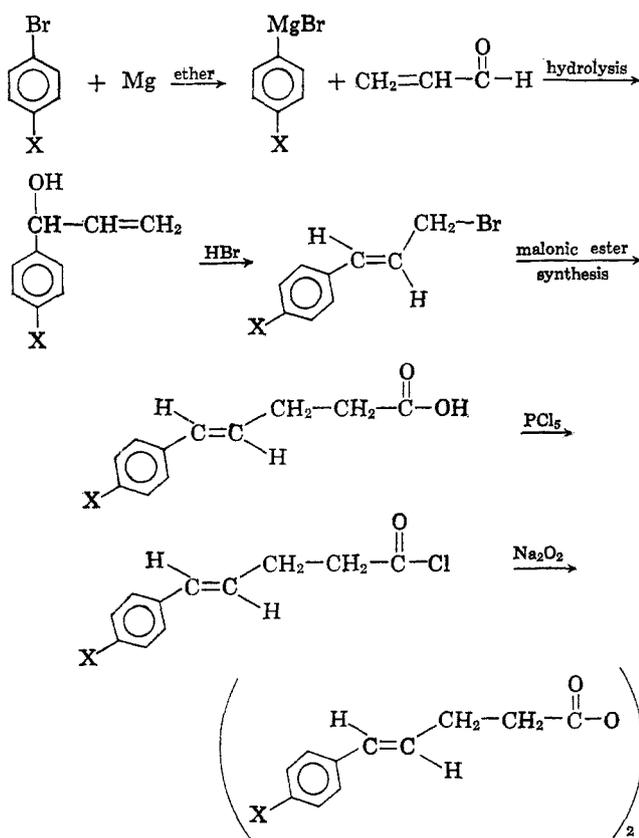
(16) E. E. Reid and J. R. Ruhoff, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 474.

TABLE VI  
PHYSICAL PROPERTIES AND ANALYSIS DATA FOR SOME INTERMEDIATES IN THE SYNTHESIS OF THE TYPE-I  
AND TYPE-II PEROXIDES

X	B.p. of $\alpha$ -( <i>p</i> -X-phenyl)allyl alcohol, °C. (mm.)	M.p. of <i>p</i> -X-cinnamyl bromide, °C.	M.p. of $\gamma$ -( <i>p</i> -X-benzylidene)-butyric acid, °C.	—Neut. equiv.— of acid		—Calcd. for— acid, %		—Found— for acid, %		M.p. of peroxide, °C.	Peroxide purity, % <sup>a</sup>
				Calcd.	Found	C	H	C	H		
Cl	122–123 (10)	60–61.5	129–130	210.7	210.1 210.7	62.72 <sup>b</sup>	5.26	63.00	5.33	93–95	97.5
F	91–93 (1.5)	43.5–44.5	91–93.5	194.2	194.0 194.4	68.03	5.71	68.04	5.83	59–60	98.5
CH <sub>3</sub>	87–88 (1.7)	64–65	138–140	190.2	188.2 192.3	75.77	7.41	75.83	7.24	93–93.5	95.2
OCH <sub>3</sub>			144–145	206.2	205.0	69.88	6.84	69.78	6.91		94.5
Type-II Peroxides and Intermediates											
OCH <sub>3</sub>			M.p. of $\delta$ -( <i>p</i> -X-phenyl)valeric acid, °C.	208.2	209.2 208.0					61–62.5	97.5

<sup>a</sup> Iodometric titration. <sup>b</sup> Anal. Calcd.: Cl, 16.83. Found: Cl, 16.79. <sup>c</sup> Lit.<sup>18</sup> m.p. 116–118°.

SCHEME I



$\gamma$ -*p*-Anisoylbutyric acid and its ethyl ester were synthesized by methods which have been described by Johnson, Jones, and Schneider.<sup>17</sup>

$\delta$ -(*p*-Methoxyphenyl)valeric acid<sup>18</sup> was prepared by a reduction of  $\gamma$ -*p*-anisoylbutyric acid using a procedure similar to that used by Huang-Minlon<sup>19</sup> for the preparation of  $\gamma$ -(*p*-methoxyphenyl)butyric acid. Pertinent data on  $\delta$ -(*p*-methoxyphenyl)valeric acid and its peroxide are given in Table VI.

$\gamma$ -(*p*-Methoxybenzylidene)butyric acid was synthesized by the sequence shown in Scheme II.

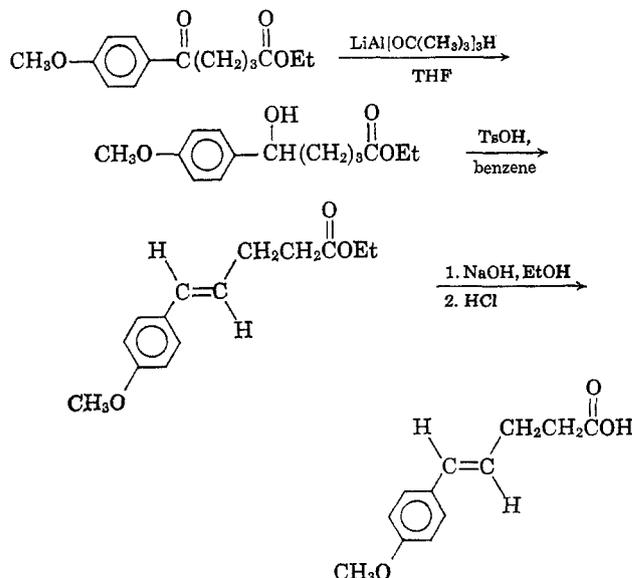
Ethyl  $\gamma$ -*p*-anisoylbutyrate (25 g., 0.1 mole) was dissolved in 150 ml. of tetrahydrofuran (which had been previously distilled from lithium aluminum hydride) in a 500-ml. round-bottom flask.

To this solution was added lithium tri-*t*-butoxyaluminum hydride (50 g., 0.2 mole).<sup>20</sup> The mixture was allowed to stand at room temperature for 22 hr. The solution was then poured into 500 ml. of 5% acetic acid. The resulting mixture was extracted with ether; the ether layer was washed with saturated sodium bicarbonate solution and dried over anhydrous magnesium sulfate. The ether was removed at the aspirator.

The hydroxy ester was not further purified; it was dissolved in 300 ml. of benzene in a 500-ml. round-bottom flask. *p*-Toluenesulfonic acid (1.5 g., 0.009 mole) was added (and dissolution was effected before heating was begun). A Dean-Stark trap and reflux condenser were attached to the flask, and its contents were refluxed overnight. The benzene solution was then washed with water and dried over anhydrous magnesium sulfate; the benzene was then removed at the aspirator. The resulting ethyl ester of  $\gamma$ -(*p*-methoxybenzylidene)butyric acid was not purified (approximately 20 g. was obtained; its melting point was near 15°), but was dissolved directly in 250 ml. of ethyl alcohol. To this solution was added a solution of sodium hydroxide (4 g., 0.1 mole) in 100 ml. of water. The resulting mixture was stirred overnight.

The supernatant liquid was removed from the resulting sodium salt at the aspirator, and the salt was then dissolved in 400 ml. of water. This solution was filtered, cooled in an ice bath, and acidified with excess dilute hydrochloric acid. The carboxylic

SCHEME II



(17) W. S. Johnson, A. R. Jones, and W. P. Schneider, *J. Am. Chem. Soc.*, **72**, 2395 (1950).

(18) D. Papa, E. Schwenk, and H. Hankin, *ibid.*, **69**, 3018 (1947).

(19) Huang-Minlon, *ibid.*, **68**, 2487 (1946).

(20) J. Fajkoš, *Chem. Listy*, **52**, 2134 (1958); cf. *Chem. Abstr.*, **53**, 5344e (1959).

TABLE VII  
PERTINENT INFRARED ABSORBANCES USED IN THE IDENTIFICATION OF SOME PREVIOUSLY UNREPORTED COMPOUNDS  
PREPARED FOR THIS INVESTIGATION

Compd.	Wave length region, $\mu$				
	0.0-3.0	5.5-6.0	6.0-7.0	8.0-10.0	10.0-11.0
$\gamma$ -Benzylidenebutyryl peroxide		5.55-5.64 (s) (doublet)		9.38 (s)	10.32 (s)
$\gamma$ -( <i>p</i> -Chlorobenzylidene)butyric acid		6.82 (s)	6.67 (s)		10.33 (s)
$\gamma$ -( <i>p</i> -Chlorobenzylidene)butyryl peroxide		5.50-5.60 (s) (doublet)	6.70 (s)	9.13-9.40 (s) (doublet)	10.32 (s)
$\alpha$ -( <i>p</i> -Fluorophenyl)allyl alcohol	2.30 (m) 3.40 (s)		6.22 (s)	8.13 (s)	10.10 (s)
<i>p</i> -Fluorocinnamyl bromide			6.62 (s)	8.63 (s)	10.75 (s)
			6.22 (s)	8.11 (s)	10.37 (s)
			6.62 (s)	8.31 (s)	
$\gamma$ -( <i>p</i> -Fluorobenzylidene)butyric acid		5.61 (s)	6.20 (m)	8.10 (s)	10.33 (s)
			6.60 (s)	8.60 (s)	
$\gamma$ -( <i>p</i> -Fluorobenzylidene)butyryl peroxide		5.5-5.59 (s) (doublet)	6.22 (m)	8.21 (s)	10.35 (m)
			6.62 (s)	8.62 (m)	
$\gamma$ -( <i>p</i> -Methylbenzylidene)butyric acid		5.86 (s)	7.10 (m)		10.36 (s)
$\gamma$ -( <i>p</i> -Methylbenzylidene)butyryl peroxide		5.51-5.61 (s) (doublet)		9.43 (m)	10.35 (m)
$\gamma$ -( <i>p</i> -Methoxybenzylidene)butyric acid		5.98 (s)	6.28 (m)	8.07 (s)	10.25 (m)
$\delta$ -( <i>p</i> -Methoxyphenyl)valeryl peroxide		5.54-5.61 (s) (doublet)	6.64 (s)	8.04 (s)	
			6.22 (m)	8.56 (m)	
			6.86 (m)	9.67 (m)	

acid separated as a white, creamy solid. It was extracted into ether; the latter was washed with water and dried over magnesium sulfate, and the ether was removed. The resulting solid was recrystallized from toluene. The over-all yield of  $\gamma$ -(*p*-methoxybenzylidene)butyric acid from the ethyl ester of the keto acid was 67%. Some chemical and physical properties of this acid are listed in Table VI; its infrared spectrum is described in Table VII.

BDPA was synthesized by the method of Koelsch<sup>8a</sup> as modified by Solar and Lindquist,<sup>8b</sup> and also by the simpler procedure of Kuhn and Neugebauer.<sup>8d</sup>

**Kinetic Runs.**—The techniques used in the spectrophotometric kinetics runs have been described in previous papers.<sup>9a,b</sup> The same wave length ( $\lambda_{\max}$  490 m $\mu$ ) was used for runs in benzene and in propylene carbonate. The difficulty in obtaining precise

values of the extinction coefficient of BDPA has been discussed.<sup>9b</sup> The values 26,300 and 24,100 were used throughout for benzene and propylene carbonate runs, respectively.

Values of  $f$  were calculated from the formula  $f = (D_0 - D_\infty) / 2\epsilon(\text{In})_0$ , where  $D$  = absorbance,  $\epsilon$  = extinction coefficient, and  $(\text{In})_0 = (P)_0$  = initial molar concentration of peroxide.

Rate constants were obtained by least-squares adjustment of the absorbance-time data to the formula

$$\log 100(D - D_\infty) = - \frac{k_d}{2.303} t + \log 100(D_0 - D_\infty)$$

The standard deviations in  $k_d$  were calculated by standard statistical procedures.

## Nitrobenzenesulfonyl Peroxides as Reagents for Aromatic Substitution<sup>1</sup>

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The three isomeric bis(nitrobenzenesulfonyl) peroxides have been prepared in 22-45% yield and found to be quite stable at room temperature. The thermal decomposition of *m*-nitrobenzenesulfonyl peroxide in benzene, fluorobenzene, chlorobenzene, and toluene produces 1 mole of *m*-nitrobenzenesulfonic acid and a 56-70% yield of the phenolic esters resulting from substitution in the aromatic substrate. The exclusive *ortho-para* substitution leads to the following orientations: fluorobenzene, 11% *ortho*, 89% *para*; chlorobenzene, 22%, 78%; and toluene, 35%, 65%. From the relative yields and orientations of the esters obtained from mixtures of benzene or toluene with chlorobenzene, the following partial rate factors were obtained: benzene, 1; chlorobenzene, *ortho* 0.5, *para* 3.7; and toluene, 17, 65. These data are most consistent with the classification of the reaction as an electrophilic substitution.

The published chemistry of the bis(arylsulfonyl) peroxides is very limited. After the synthesis of bis(benzenesulfonyl) peroxide in 1903,<sup>2</sup> no further work was reported until 1924 when Fichter and Stock<sup>3</sup> described its decomposition in water to form phenol, sulfuric acid, and presumably benzenesulfonic acid. In

1946 Walter<sup>4</sup> patented the use of *p*-toluenesulfonyl peroxide as a polymerization catalyst. Crovatt and McKee<sup>5</sup> recently attempted unsuccessfully to improve the yields of synthesis of benzenesulfonyl peroxide, investigated its use as a catalyst for vinyl polymerization, and found that its thermal decomposition in benzene produced phenyl benzenesulfonate.

(1) Supported by the U. S. Army Research Office (Durham) through Grant No. DA-ARO(D)-31-124-G242.

(2) R. F. Weinland and H. Lewkowitz, *Ber.*, **36**, 2702 (1903).

(3) F. Fichter and E. Stocker, *Helv. Chim. Acta*, **7**, 1071 (1924).

(4) H. A. Walter, U. S. Patent 2,467,280; *Chem. Abstr.* **43**, 6002 (1949).

(5) L. W. Crovatt and R. L. McKee, *J. Org. Chem.*, **24**, 2031 (1959).