double beam infrared spectrophotometer in potassium bromide pellets. Analyses were by Micro-Tech Laboratories, Skokie, Ill. Satisfactory analyses were obtained for all new compounds reported.

General Procedure for Heterogeneous Bromination Using Copper(II) Bromide.—The copper(II) bromide (Matheson Coleman and Bell or Baker and Adamson reagent grades) was routinely ground, without drying, in a mortar and pestle to *ca.* 80 mesh to ensure a large surface area for reaction. Copper(II) bromide (0.050 mole) was placed in an erlenmeyer flask fitted with a reflux condenser, and ethyl acetate (25 ml.) was added and brought to reflux on a magnetic stirrer–hot plate. The compound to be brominated (0.030 mole; it is advisable to use a slight excess to avoid the possibility of dibromination) was dissolved in or diluted with hot chloroform (25 ml.) (or an additional 25 ml. of ethyl acetate if the compound were not soluble in chloroform) and added to the flask. The resulting reaction mixture was refluxed with vigorous stirring to ensure complete exposure of the copper(II) bromide to the reaction medium until the reaction was complete as judged by a color change of the solution from green to amber, disappearance of all black solid, and cessation of hydrogen bromide evolution. With numerous compounds the bromination was estimated, from the composition of the mixed copper bromides recovered, to be 90–95% complete in 30–60 min. even though the deep green color persisted much longer. This color could be removed by decoloration with Norit A after removal of the copper(I) bromide by filtration. An induction period which varied with the starting material was observed in each case. The copper(I) bromide was collected by filtration and washed well with ethyl acetate. Recovery of copper(I) bromide was 96–100% in every case. The solvents were removed from the filtrate under reduced pressure, except when the product had a low boiling point, a property which required fractional distillation.

Bromination of Hydroxyacetophenones.—The above procedure was used, the time required for typical runs being noted in Table

I. The crude products could be recrystallized from benzene except as noted in Table I. Table I also gives physical characteristics of the compounds prepared.

Preparation of the Substituted 1-Benzoylmethylpyridinium Salts.—The pyridinium bromides could be prepared directly from the filtrate containing the crude α-bromo ketone by addition of a slight excess (0.03 mole) of pyridine followed by heating on the steam bath. An alternate procedure was to remove the chloroform–ethyl acetate under reduced pressure and dissolve the crude α-bromo ketone in acetone before addition of the pyridine. The latter method sometimes gave crude products which were less discolored and had higher melting points. Both methods gave good yields. The pyridinium bromides were converted to the corresponding pyridinium iodides or perchlorates by the method of King[3a] (see Table II).

Alkaline Cleavage of the Substituted β-Ketoalkylpyridinium Salts.—About 1 g. of the pyridinium salt was dissolved in water and heated with 1 g. of sodium hydroxide as described by King.[3a] The alkaline solution was treated with Norit A, and the acid fraction was separated and purified by recrystallization from water and/or sublimation (150° at 1.0 mm) (see Table III).

Preparation of Coumaran-3-one.—This compound was prepared from 2-bromo-2'-hydroxyacetophenone by the method of Fries and Pfaffendorf[14] in 48–80% yield. The crude yellow product melted at 94–99°. After sublimation (50° at 1.0 mm), the essentially colorless crystals melted at 101–102° (lit.[15] m.p. 100–101.5°). The infrared spectrum of the sublimed sample corresponded to that reported by Bose and Yates.[15]

(15) A. K. Bose and P. Yates, *J. Am. Chem. Soc.*, **74**, 4703 (1952).

Decompositions of Hydroperoxides in Oxidizing Olefins

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We have examined the reactions at 60° of combinations of styrene, oxygen at a total pressure of 1 atm., and either *t*-butyl or α-tetralyl hydroperoxide. *t*-Butyl hydroperoxide has a half-life of only about 100 min. under these conditions. Several lines of evidence indicate that the hydroperoxide reacts mostly by chain transfer with the peroxy radicals in oxidizing styrene producing styrene polyperoxide with hydroperoxide end groups. Later, some styrene oxide and *t*-butyl alcohol appear. Both chain initiation and peroxide disappearance are initially autocatalytic; the oxidation later becomes slower, but does not stop, as the original free hydroperoxide is exhausted. Formaldehyde forms addition compounds with hydroperoxides and complicates analytical problems and interpretation of the results. So far, these accelerated interactions of unsaturated compounds with hydroperoxide and oxygen have been most marked with styrene. They have not complicated the oxidations of alkenes, where high yields of hydroperoxides have been obtained in oxidations. Butyl methacrylate oxidized too slowly to give a marked effect. Indene gave only a moderate effect, possibly because it produces little or no formaldehyde during its oxidation.

Previous workers have shown that cyclohexyl[1] and *t*-butyl[2,3] hydroperoxide decompose with unexpected rapidity in styrene and thereby initiate polymerization rather rapidly. Farkas and Passaglia[1] showed that cyclohexyl hydroperoxide disappeared and also initiated polymerization at 80° although the decomposition of this peroxide is negligible at this temperature in other solvents. Walling and Chang[3] found similar effects with *t*-butyl hydroperoxide and styrene and detected *t*-butyl alcohol and styrene oxide among the products. This work has been extended recently by Heaton.[4] She reported that the reaction is complex,

and complicated by complexes of hydroperoxide with itself and with styrene; only a small fraction of the decomposing hydroperoxide produces free radicals which initiate polymerization. Brill and Indictor[5] have studied the decomposition of *t*-butyl hydroperoxide in olefins as a means of producing epoxides. Yields were generally poor. For 1-octene the rate was first order in both hydroperoxide and olefin. They suggested that the epoxidation is polar in nature.

From our study of oxidation of mixtures of styrene and tetralin, we eventually found that complicated reactions like those above also occur in the presence of oxygen, and much faster. This paper describes our efforts to determine the nature and scope of hydroperoxide–olefin–oxygen interactions.

(1) A. Farkas and E. Passaglia, *J. Am. Chem. Soc.*, **72**, 3333 (1950).
(2) Z. Stannet and R. B. Mesrobian, *ibid.*, **72**, 4126 (1950).
(3) C. Walling and Y. Chang, *ibid.*, **76**, 4878 (1954).
(4) L. Heaton, Ph.D. Thesis, Columbia University, 1964.

(5) W. F. Brill and N. Indictor, *J. Org. Chem.*, **29**, 710 (1964).

TABLE I

OXIDATION OF STYRENE AND OTHER COMPOUNDS WITH DIFFERENT INITIATORS[a]

Monomer	Added materials	Initiator	M	$-d[O_2]/dt$[b]	$-d[ROOH]/dt$[c]	Time, hr.[c]
				Oxygen at 1-Atm. Total Pressure		
Styrene	...	...	...	0.0096	...	...
Styrene	...	ABN	0.010	0.206	−0.0017	1
Styrene	...	THP	0.231	0.115	0.014	5
Styrene	...	THP	0.756	0.298	0.0337	5
Styrene	...	{THP 0.088 / ABN 0.010}		0.173	0.0120	5
Styrene	...	{THP 0.670 / ABN 0.010}		0.259	0.0245	5
Styrene	0.005 M 2,6-di-t-butyl-p-cresol	THP	0.754	0.0[d]	0.157	1.5
Styrene	0.05 M benzaldehyde	{THP 0.077 / ABN 0.010}		0.146	0.0064	5
Styrene	5 wt. % styrene polyperoxide	THP	0.181	0.028	0.014	5
Styrene	...	{ABN 0.010 / Cumyl O₂H 0.0854}		0.228	0.0144	5
Styrene	...	t-BuO₂H	0.0091	0.0265	0.0014	4
Styrene	...	t-BuO₂H	0.0254	0.0409	0.0029	3
Styrene	...	t-BuO₂H	0.085	0.0936	0.0083	5
Styrene	...	t-BuO₂H	0.253	0.194	0.022	5
Styrene	...	t-BuO₂H	0.745	0.663	0.041	4
Styrene	...	{t-BuO₂H 0.085 / ABN 0.010}		0.272	0.017	2
Styrene (2.35 M)	6.57 M C₆H₅Cl	t-BuO₂H	0.290	0.0905	0.0	5
Styrene	Saturated with CH₂O gas	t-BuO₂H	{0.255[e] / 0.044}	0.112	0.004	3
Styrene	0.01 M 2,6-di-t-butyl-p-cresol	t-BuO₂H	0.250	0.0	0	20
Indene	...	t-BuO₂H	0.270	0.143	−0.005	3
Indene	f	ABN	0.01	0.081	...	3
Butyl methacrylate {	...	t-BuO₂H	0.314	0.091	0	...
	...	ABN	0.010	0.145[g]	...	...
				Oxygen Excluded		
		THP	0.217		0.0021	5
Styrene	...	t-BuO₂H	0.22		0.0031	
Styrene	h	THP	0.252		0.0034	5
α-Methylstyrene {	...	{THP 0.252 / ABN 0.010}			0.0031	5
Styrene	91 wt. % C₆H₆	{THP 0.114 / ABN 0.010}			0.0001	5
Tetralin		THP	0.231		0.00025[i]	
Benzene		t-BuO₂H	0.22		3.9×10^{-5j}	

[a] At 60°. [b] Initial rates in mole/l./hr. [c] Average rates in mole/l./hr., during hours shown. [d] Average $-d[O_2]/dt$ for 1.5 hr. = 0.0313 mole/l./hr. [e] t-BuO₂H (0.255 M) was added; only 0.044 M could be titrated. [f] At 50°; see ref. 12. [g] See ref. 13. [h] At 70°; see ref. 4. [i] Extrapolated at 120° from the work of A. Robertson and W. A. Waters [*J. Chem. Soc.*, 1578 (1948)]. [j] At 70°; see ref. 4.

Experimental

Materials.—Styrene was Eastman White Label grade, washed to remove inhibitor, and distilled at reduced pressure prior to use. Indene and butyl methacrylate were treated similarly. t-Butyl hydroperoxide from Lucidol Corp. was purified by vacuum distillation. Our material titrated 99+% of the theoretical using iodometric methods. Tetralin hydroperoxide was prepared by air oxidation of tetralin at 90–100° with stepwise addition of 1,1'-azobis(1-cyanocyclohexane). The products, recrystallized several times from hexane, were 95–98+% pure by iodometric titration. Chlorobenzene and benzene were Baker analytical grade without further purification.

Rate Measurements.—A solution of hydroperoxide (20–40 ml.) in styrene in a long-necked, 100-ml. flask was cooled to 0°, evacuated, and flushed with oxygen three times. The flask was then attached to a wrist-action shaker and immersed in a constant-temperature bath, and the oxygen uptake was followed with a gas buret. The total pressure was about 760 mm. At intervals, samples were syringed out of the solution for analysis.

Analyses.—Hydroperoxides were titrated iodometrically. The Wibaut titration,[6] where hydroperoxide reacts with KI in 80% acetic acid at room temperature in a CO₂ atmosphere, was used for untreated samples of reaction mixtures. Styrene polyperoxide did not give a titer under the conditions specified, nor did the presence of benzaldehyde interfere. The method suffered some loss of precision as the oxidation proceeded, possibly from insolubility of polyperoxide in the aqueous acetic acid medium. With added formaldehyde, titration by the Wibaut method showed only a small fraction of the known amount of hydroperoxide.

In the Hiatt method[7] 0.8 g. of solid NaI and up to 1 mmole of hydroperoxide are added to 15 ml. of a solution of 20% acetic acid–80% isopropyl alcohol and the mixture is refluxed for 10–15 min. Styrene polyperoxide interferes with this method, which was used only on solutions freed from polymer. Formaldehyde, benzaldehyde, and styrene do not interfere. The Hiatt and the Wibaut methods gave identical titers on solutions of pure hydroperoxide in styrene or in benzene.

With a Perkin-Elmer Model 221 and a matching solvent cell containing styrene, the presence of benzaldehyde, styrene oxide, styrene polyperoxide, and t-butyl hydroperoxide could be detected in reaction mixtures. Quantitative estimation of benzaldehyde was possible, using the band at 5.90 for low amounts

(6) J. P. Wibaut, H. B. van Leeuwen, and B. Van der Wal, *Rec. trav. chim.*, **73**, 1033 (1954).

(7) R. Hiatt and W. M. J. Strachan, *J. Org. Chem.*, **28**, 1894 (1963).

and the 12.10-μ band for higher amounts. t-Butyl hydroperoxide concentrations could be measured from the band at 11.85 μ if the amount of styrene polyperoxide present was not large.

The Wilkens–Anderson instrument with a column of didecyl phthalate on Chromosorb was initially used for the g.l.c. analyses. t-BuO$_2$H was separated from t-BuOH, but partially decomposed, on the column. Injection of a mixture of t-BuO$_2$H and styrene gave peaks identified as benzaldehyde and styrene oxide, apparently produced in the column or the injector. Subsequent use of a glass column packed with didecyl phthalate on Fluoropak and a glass-lined injector cavity eliminated these problems and allowed quantitative determination of the products. The precision obtainable with mixtures of styrene and t-BuO$_2$H was not good but probably better than ±5%.

Precipitation of polymer either by benzene, methanol, or dichloromethane–pentane proved inadequate for the low molecular weight material obtained. Separation of polymer from volatiles was effected by pumping small samples of reaction mixture at high vacuum ($ca.$ 10^{-3} mm.) and room temperature for several hours. Polymer so obtained was shown to be free of styrene and benzaldehyde by both infrared and n.m.r. spectra.

Results and Discussion

Tetralyl Hydroperoxide in Oxidizing Styrene.—A solution of 0.23 M α-tetralyl hydroperoxide (THP) in styrene, well shaken at 60° in 1 atm. of oxygen, initially absorbs oxygen twelve times as fast as styrene alone. Titratable peroxide disappears six to seven times as fast as in a similar tetralin solution in the absence of oxygen. The indicated initial rates increase with time, as shown in Fig. 1. By interpolation, Table I shows that 0.48 M THP has the same initiating properties as 0.01 M 2,2′-azobis(2-methylpropionitrile) (ABN). However, combinations of THP and ABN are less effective than would be expected. Table II shows that the proportion of styrene oxidized directly to benzaldehyde is about the same in ABN- and THP-initiated oxidations but that the latter oxidation also produces styrene oxide.

Table II
Products of Oxidation of Styrene[a]

| [Initiator]₀, mole/l. | Conversion, % | | [BzH], mole/l. | [Styrene oxide], mole/l. | [t-BuOH], mole/l. |
	b	c			
0.010 ABN[d]	6.7	8.6	0.029	0.0016[c]	
0.230 THP		54	0.37	0.15	
0.0291 t-BuO₂H	5.9	7.6	0.090	0.019	0.0025
0.854 t-BuO₂H		50	1.8	0.30	0.29

[a] At 60°; after 20–14 hr. when all hydroperoxide had decomposed or complexed; formaldehyde was present in all products.
[b] Moles of styrene polyperoxide × 100%/mole of initial styrene.
[c] Weight of polymeric material × 100%/total weight of sample.
[d] At 50°, calculated from data of F. R. Mayo [J. Am. Chem. Soc., **80**, 2465 (1958)].

t-Butyl Hydroperoxide in Oxidizing Styrene.—As shown in Tables I and II and Fig. 1, t-butyl hydroperoxide acts much like THP in oxidizing styrene. However, the volatility of the former hydroperoxide makes possible its complete separation from styrene polyperoxide and simplifies analyses. This system has therefore received most of our attention.

Table III and Fig. 2 show results of periodic analyses of a typical t-BuO₂H experiment by vacuum distillation, infrared, and gas–liquid chromatography (g.l.c.) techniques. Although t-butyl hydroperoxide disappears rapidly, nearly as much titratable peroxide (Wibaut[6] method) appears in the residue (only about
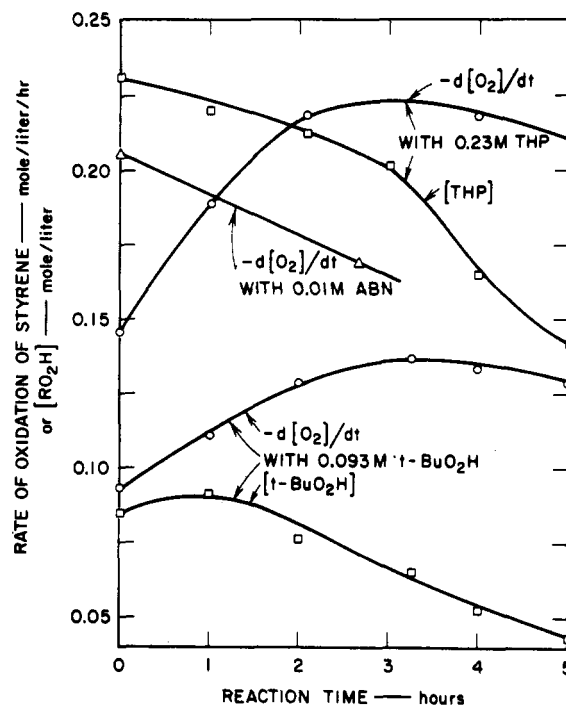

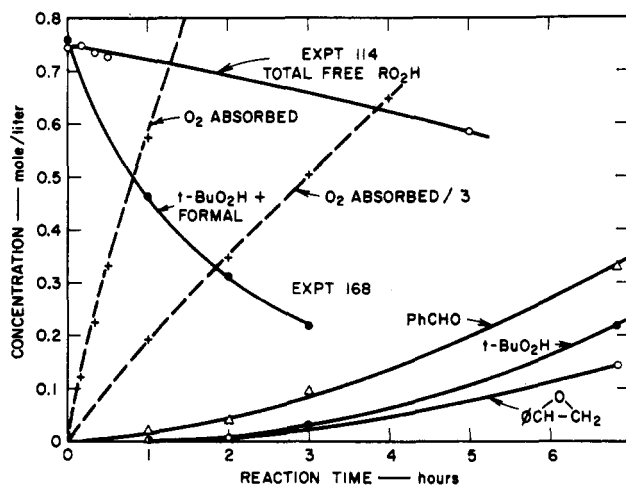Fig. 1.—Autoxidation of styrene with tetralin hydroperoxide or t-butyl hydroperoxide at 60°.

Fig. 2.—Oxidation of styrene at 60° with 0.75 M initial t-butyl hydroperoxide. t-Butyl hydroperoxide + formal represent total volatile peroxide determined by Hiatt titration.

0.5% of the oxygen absorbed is titratable in the ABN-initiated oxidation of styrene). Benzaldehyde, a typical primary oxidation product of styrene, appears at an increasing rate (accompanied by formaldehyde, not determined quantitatively). t-Butyl alcohol and styrene oxide (not found in appreciable quantity at this pressure in ABN-initiated oxidations) appear after some delay rather than while the t-BuO₂H is disappearing most rapidly. From the absence of t-butyl residues elsewhere and from the weight and analysis of the polyperoxide formed, we infer that the t-butyl residues are incorporated in the polyperoxide as butylperoxy rather than butoxy groups. A 1.7797-g. sample of 0.760 M t-BuO₂H in styrene, oxidized at 60° for 60 min. and then brought to constant weight under high vacuum at room temperature, gave 0.3026 g. of polyperoxide. The t-butyl groups found in the polymer by n.m.r. checked closely with the t-BuO₂H disappeared.

TABLE III

OXIDATION OF STYRENE[a]

Time, min.	$-d[O_2]/dt$, mole/l./hr.	Total [ROOH], mole/l.	$[t\text{-BuO}_2\text{H}]$, mole/l.	Conversion, %[b]	Polymer, % Found[c]	Polymer, % Calcd.[c]
0	0.663	0.745	0.745	0	0	0
10	0.642	0.749		1.46		
20		0.735		2.71		
30		0.726		3.99		
60	0.524		0.439	6.90	11.04	8.8
120	0.456		0.305	12.50	18.8	15.7
180	0.415			18.09	25.2	21.4
240	0.380	0.583	0.145	23.23	35.5	28.3

[a] At 60°; $[C_8H_8]_0 = 8.35\ M$; $[t\text{-BuO}_2\text{H}]_0 = 0.745\ M$. [b] Moles of O_2 taken up $\times$ 100%/initial moles of styrene. [c] Weight of nonvolatiles $\times$ 100%/weight of sample; calcd. value based on weight of $(C_8H_8O_2)_n$ from O_2 absorbed without any $t\text{-BuO}_2\text{H}$ residues.
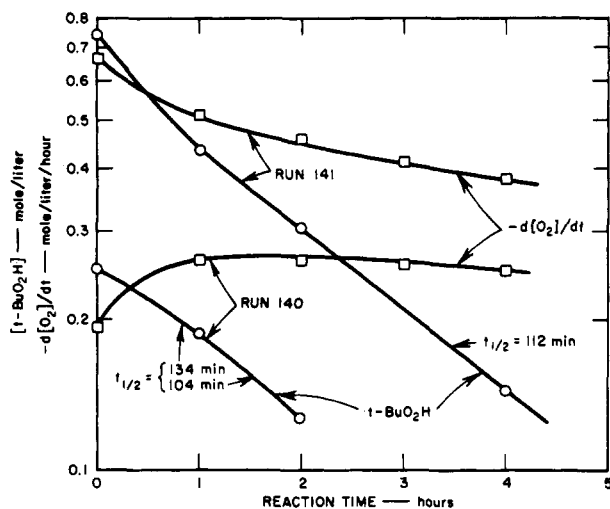
Fig. 3.—Reaction of t-butyl hydroperoxide, styrene, and oxygen at 60°.

Anal. Calcd. for $t\text{-BuO}_2(\text{CH}_2\text{—CHPh—O}_2)_{1.904}\text{H}$: C, 66.12; H, 7.28; 0.145 mmole/g. of HO_2^-, 0.3041-g. total weight for O_2 absorbed. Found: C, 66.43; H, 7.44; 0.153 mmole/g. of HO_2^-, 0.3026-g. total weight.

This agreement excludes incorporation of more than 10% of t-butoxy groups. A similar experiment for 2 hr. with 0.279 M $t\text{-BuO}_2\text{H}$ gave a product (by end-group determinations) averaging 4.0 styreneperoxy units per molecule.

To account for the delayed and then increasing rate of formation of benzaldehyde and t-butyl alcohol in the ratio of about 2:1, we propose that benzaldehyde and t-butoxy radicals arise from the formaldehyde-induced decomposition of accumulated $t\text{-BuO}_2(\text{CH}_2\text{—CHPh—O}_2)_n\text{H}$, where $n \sim 2$. The origin of the styrene oxide is not clear.

These considerations show that the following chain reaction is the principal reaction occurring in the early stages of the t-butyl hydroperoxide initiated oxidation of styrene. Since in a solution containing about ten

$$t\text{-BuO}_2\cdot + \text{H}_2\text{C=CHPh} \longrightarrow t\text{-BuO}_2\text{—CH}_2\text{—}\dot{\text{C}}\text{HPh}$$

$$t\text{-BuO}_2\text{—CH}_2\text{—}\dot{\text{C}}\text{HPh} + \text{O}_2 \longrightarrow t\text{-BuO}_2\text{—CH}_2\text{—CHPh—O}_2\cdot$$

$$t\text{-BuO}_2(\text{CH}_2\text{—CHPh—O}_2)_n\cdot + \text{H}_2\text{C=CHPh} \xrightarrow{k_p}$$
$$t\text{-BuO}_2(\text{CH}_2\text{—CHPh—O}_2)_n\text{—CH}_2\text{—}\dot{\text{C}}\text{HPh}$$

$$t\text{-BuO}_2(\text{CH}_2\text{—CHPh—O}_2)_n\text{—CH}_2\text{—CHPh}\cdot + \text{O}_2 \longrightarrow$$
$$t\text{-BuO}_2(\text{CH}_2\text{—CHPh—O}_2)_{n+1}$$

$$t\text{-BuO}_2(\text{CH}_2\text{—CHPh—O}_2)_n\cdot + t\text{-BuOOH} \xrightarrow{k_t}$$
$$t\text{-BuO}_2(\text{CH}_2\text{—CHPh—O}_2)_n\text{H} + t\text{-BuO}_2\cdot$$
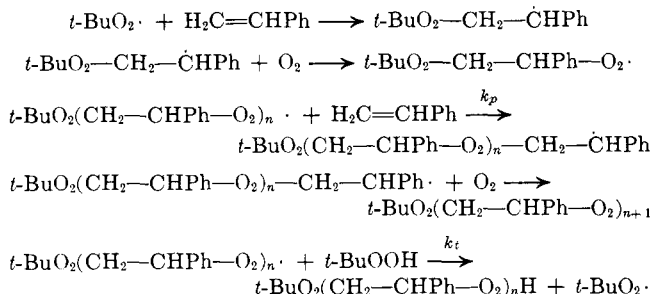
times as many styrene molecules as monomeric hydroperoxide the consumption of styrene is only twice that of $t\text{-BuO}_2\text{H}$, the chain transfer constant, k_t/k_p, is about 5. When the monomer to hydroperoxide ratio is 16, the relative consumption ratio of 4 gives a similar value. The net result of these reactions is a telomerization with $\text{—O}_2\text{—}$ between every organic grouping and conversion of hydroperoxide to a nonvolatile but still titratable form.

These results suggest that Thomas and Tolman[8] were observing the same type of hydrogen transfer between peroxy groups in their tetralin hydroperoxide retarded oxidation of cumene. They calculated that THP is 27 times as reactive as cumene toward cumylperoxy radicals. Other work in our laboratory shows that styrene is about 6 times as reactive as cumene toward peroxy radicals and therefore that THP should be about 27:6 or 4.5 times as reactive as styrene toward peroxy radicals, in excellent agreement with our results with $t\text{-BuO}_2\text{H}$.

Two methods, detailed in the Experimental section, were used to determine hydroperoxides. The Wibaut method, which measures only uncomplexed hydroperoxide and is not affected by polyperoxide groups, was used on whole samples. The Hiatt method, which measures both hydroperoxides and their formaldehyde compounds but reacts with some polyperoxide groups, was used only on the volatile fractions; here it measures both t-butyl hydroperoxide and its formaldehyde addition compound.

Figure 2 shows the results of a representative decomposition. The slow decrease in total free hydroperoxide approximates the amount of formaldehyde formed (assuming this to be equal to the benzaldehyde), but a little of the decrease must be associated with radical production for chain initiation. As pointed out previously, the t-butyl hydroperoxide is initially being converted rapidly to polyperoxide with hydroperoxide end groups, and later partly to formaldehyde addition compound.

Figure 3 shows that the disappearance of $t\text{-BuO}_2\text{H}$ is nearly first order with a half-life of about 2 hr. at 60°. Table I lists two experiments where the oxidation inhibitor, 2,6-di-t-butyl-p-cresol, was added. With 0.01 M inhibitor and 0.25 M hydroperoxide, no oxygen was taken up for at least 20 hr. and no hydroperoxide disappeared during that time. With less inhibitor and more initial hydroperoxide (0.754 M THP), the period of complete inhibition was less than 0.5 hr. and a titra-

(8) J. R. Thomas and C. A. Tolman, *J. Am. Chem. Soc.*, **84**, 2079 (1962).

TABLE IV

RATES OF INITIATION

Temp., °C.	System	k_d, sec.$^{-1}$	$R_i \times 10^{10}$ moles/l./sec.	Ref.
60	0.25 M t-BuO$_2$H in benzene	1.0×10^{-11}	0.05	a
70	0.22 M t-BuO$_2$H in benzene	5.7×10^{-11}	0.25	a
70	0.22 M t-BuO$_2$H in benzene	5×10^{-8}	220	b
60	0.25 M t-BuO$_2$H + styrene + O$_2$		1200	c
60	0.01 M ABN + styrene + O$_2$		1200	d
70	0.22 M t-BuO$_2$H + styrene		270	b
60	Styrene + O$_2$		2.6	e
60	Styrene only		0.84	f
60	Styrene only		1.3	g
60	Styrene + DPPH		110	g
60	Styrene + benzoquinone		79	g

^{a} Extrapolated from work of Hiatt and Strachan[7] at 150–170°, using 0.05 M t-BuO$_2$H. The rate of decomposition with 0.25 M t-BuO$_2$H would probably be two to three times as fast from induced decomposition, but the rate of radical production should not be affected. ^{b} Calculated from work of Heaton.[4] ^{c} This work. ^{d} P. Smith and S. Carbone, $J. Am. Chem. Soc.$, 81, 6174 (1959). ^{e} A. A. Miller and F. R. Mayo, $ibid.$, 78, 1017 (1956). ^{f} F. R. Mayo, $ibid.$, 75, 6136 (1953). ^{g} K. E. Russel and A. V. Tobolsky, $ibid.$, 75, 5052 (1953); DPPH = diphenyl-picrylhydrazyl.

tion after 1.5 hr. showed that more hydroperoxide had disappeared than in the absence of inhibitor. While more experiments would be necessary to account fully for the effect of 2,6-di-t-butyl-p-cresol, under our conditions hydroperoxide probably disappears only by the free-radical chain reaction (detectable by the uptake of oxygen), and any polar decomposition seems to be insignificant. This conclusion differs from those of Heaton[4] and of Brill and Indictor[5] but does not directly contradict their findings since they worked in the absence of oxygen where 2,6-di-t-butyl-p-cresol does not inhibit free-radical chain reactions. It seems unlikely that the presence or absence of oxygen affects the proposed polar decomposition.

Figure 4 shows that the known products of the styrene–t-BuO$_2$H–O$_2$ reaction are not catalysts for the decomposition of t-BuO$_2$H. However, formaldehyde catalyzes the decomposition of THP and this reaction of aliphatic aldehydes with primary and secondary hydroperoxides may be general.[9]

A more striking effect of formaldehyde is its rapid reaction with hydroperoxides, presumably to form the peroxidic addition compound, R—O$_2$—CH$_2$OH.[9,10] Figure 4 shows how addition of some formaldehyde to a benzene solution of t-BuO$_2$H reduced the "Wibaut hydroperoxide" below the "Hiatt hydroperoxide." The figure also shows that the compound was broken down only very slowly in refluxing benzene. Formation of an addition compound was also demonstrated by disappearance of the carbonyl absorption in the infrared when t-BuO$_2$H was added to a solution of formaldehyde in carbon tetrachloride.

Rates of Chain Initiation.—Table IV summarizes rates of chain initiation by various combinations of

(9) L. Durham and H. Mosher, $J. Am. Chem. Soc.$, 84, 2811 (1962), and previous papers.
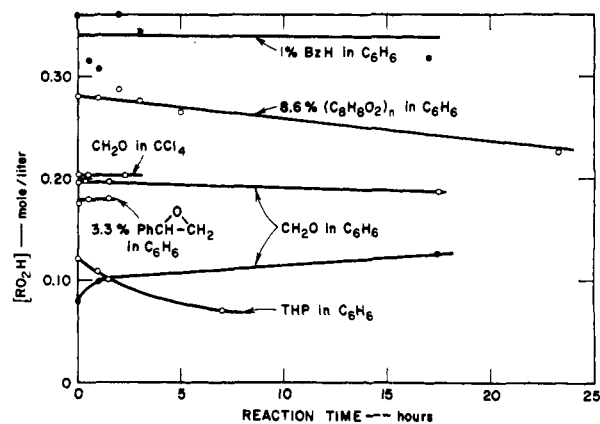(10) F. H. Dickey, F. F. Rust, and W. E. Vaughan, $ibid.$, 71, 1432 (1949).

Fig. 4.—Decompositions of t-butyl hydroperoxide and tetralin hydroperoxide (marked THP) in refluxing benzene (83°) or carbon tetrachloride (80°): ○, Hiatt titrations; ●, Wibaut titrations. CH$_2$O indicates that the solution was saturated with formaldehyde gas before refluxing.
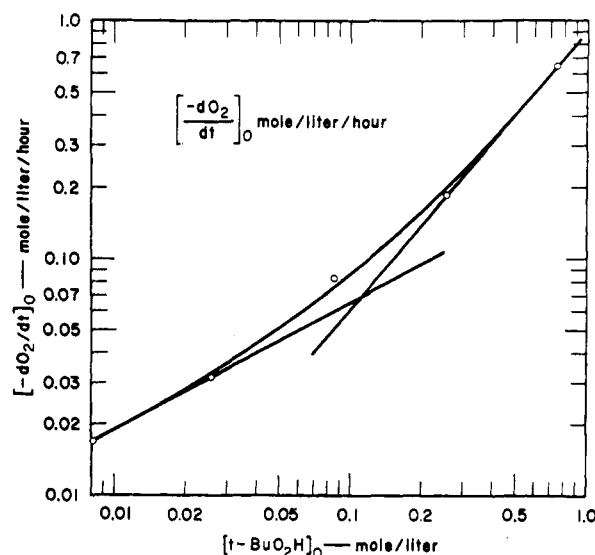

Fig. 5.—Initial rates of the t-butyl hydroperoxide initiated oxidation of styrene at 60°.

styrene, hydroperoxides, and other initiators. The rate of initiation by styrene–t-BuO$_2$H–O$_2$ at 60° far exceeds that possible with any one or two components of the mixture. Although the rate of initiation is impressive, the loss of hydroperoxide at 0.25 M by this route is only about 0.1% hr., a tiny fraction of our measured rates of disappearance.

Figure 5 shows a log–log plot of the rate of oxidation of styrene over a 90-fold range of t-BuO$_2$H concentrations. Determination of the rate of the hydroperoxide-initiated oxidation necessitated a correction for the rate of oxidation in the absence of added hydroperoxide. This correction was made by simple subtraction, since, with ABN–t-BuO$_2$H mixtures, this method gave better results than a more sophisticated one. The limiting slopes in Fig. 5 were not sensitive to the method of correction. The rate of oxidation appears to change from half order in peroxide at the lowest concentrations to first order at the highest concentrations. On the assumption of a second-order chain termination, these relations indicate that chain initiation involves one molecule of hydroperoxide at low concentrations and two at high concentrations, relations
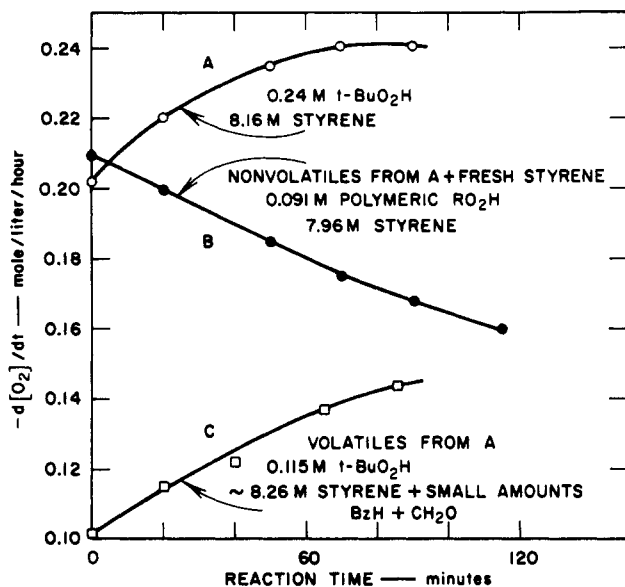
Fig. 6.—Rates of the t-butyl hydroperoxide initiated oxidation of styrene at 60°.

which have well-known analogs in the absence of oxygen. At low concentrations in an inert solvent, t-BuO_2H is known to decompose unimolecularly,[7] but bimolecularly[11] at moderate concentrations in olefinic solvents. Together with the data of Heaton[4] on the association tendencies of t-BuO_2H, our data suggest that both the monomeric and dimeric forms may be involved with styrene and oxygen in radical production. Further speculation will await determination of the order of the initiation with respect to styrene and oxygen, both with and without hydroperoxide.

Rates of Oxidation.—Changes with time in rates of oxidation of styrene–t-BuO_2H–O_2 mixtures vary with the concentration of hydroperoxide. Figures 1 and 3 show that the initial rate of oxidation increases with time when less than 0.3 M hydroperoxide is initially present. These rates eventually decrease. Since Fig. 1 shows a retarding effect from the beginning with 0.01 M ABN, a retarder is apparently being formed in all oxidations. Figures 2 and 3 show that the initial rate decreases steadily with about 0.7 M hydroperoxide. Apparently at these concentrations, the effect of the retarder outweighs the effect of the new catalyst.

The following experiment (Fig. 6) indicates that the new catalyst is the polymeric peroxide–hydroperoxide being formed from t-BuO_2H. Polymeric peroxide (1.5

g.) was prepared by autoxidizing a 0.24 M solution of t-BuO_2H in styrene (curve A) for 100 min. and separating the volatile and nonvolatile products. To the 1.26 g. of polyperoxide, which titrated as 1.6 mmoles of $RO_2H/g.$, was added 18.338 g. of fresh styrene to make the solution 0.091 M in RO_2H at 60°. This solution (curve B) took up 0.210 moles of oxygen/l./hr., more than twice as fast as the 0.090 mole/l./hr. calculated for the initial rate of an oxidation initiated by 0.090 M t-BuO_2H. The polyperoxide-initiated reaction did not show any autocatalysis; the rate gradually declined over 2 hr. to 0.158 mole/l./hr., while the hydroperoxide titer declined to 0.064 M. The volatile fraction, which still contained 0.115 M t-BuO_2H, showed no enhanced rate of oxidation (curve C).

Oxidations of styrene with hydroperoxides ordinarily stopped when titratable peroxide (Wibaut) was exhausted. However, this cessation of reaction was found to be due to accumulation of formaldehyde gas which displaced oxygen. When such a reaction mixture was removed from the bath every 2 hr., degassed, and resupplied with oxygen, absorption of O_2 followed the usual course for the first 6–8 hr., but reaction persisted thereafter at a rate corresponding roughly only to gradual depletion of the styrene, even though the Wibaut peroxide was exhausted. The nonvolatile fraction did not. Apparently the formaldehyde compound with the polymeric peroxide–hydroperoxide remains an effective initiator over long periods.

Other Monomers.—Both indene[12] and butyl methacrylate[13] form polyperoxides. Table I shows that both oxidations can be initiated with t-BuO_2H. Butyl methacrylate gave a low rate of oxidation which decreased with time, but the indene rate compared with that of styrene, with similar autocatalysis. The loss of titratable hydroperoxides in oxidizing indene, which does not produce formaldehyde, is much less rapid than in styrene, but amounts to 50% in 20 hr. There is an initial increase in hydroperoxide concentration which is outside the range of experimental error, and may result from some attack on the allylic hydrogen of indene.

(11) L. Bateman, H. Hughes, and A. L. Morris, *Discussions Faraday Soc.*, **14**, 190 (1953).

(12) G. A. Russell, *J. Am. Chem. Soc.*, **78**, 1035, 1041 (1956).

(13) F. R. Mayo and A. A. Miller, *ibid.*, **80**, 2493 (1958).

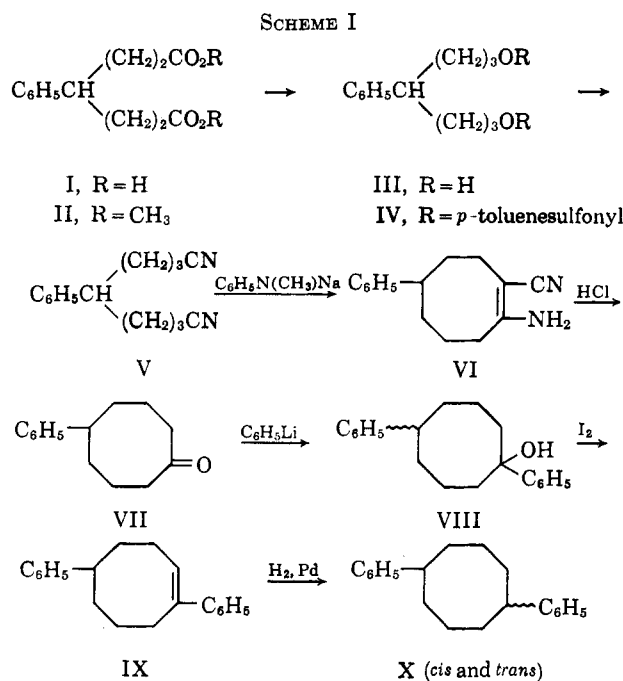# cis- and trans-1,5-Diphenylcyclooctane

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The synthesis of *cis*- and *trans*-1,5-diphenylcyclooctane, used in assigning structures to 1,5-diphenylcyclo-octatetraene, is reported. The *cis* and *trans* isomers were separated but configurations were not assigned to them.

cis- and *trans*-1,2-[2] and -1,3-diphenylcyclooctanes[3,4] have been reported. This paper describes the synthesis of the 1,5-isomers (*cis* and *trans*), needed for comparison with the reduction products of the diphenylcyclooctatetraenes in order to assign structures to the four isomeric forms (1,2-, 1,3-, 1,4-, and 1,5-).[5] The reaction sequence shown in Scheme I was used.

SCHEME I

I, R = H
II, R = CH₃

III, R = H
IV, R = p-toluenesulfonyl

V

VI

VII

VIII

IX

X (*cis* and *trans*)

4-Phenylpimelic acid (I) was prepared in an over-all yield of 67% from the Michael condensation product[6-8] of diethyl malonate and ethyl cinnamate *via* 3-phenylglutaric acid,[8] dimethyl 3-phenylglutarate,[9] 3-phenyl-1,5-pentanediol,[10,11] 3-phenyl-1,5-pentanediol di-*p*-toluenesulfonate, and 4-phenylpimelonitrile.[12] Although the syntheses of 3-phenyl-1,5-pentanediol[10,11] and 4-phenylpimelonitrile[12] have been reported, different synthetic methods were used in this investigation. Dimethyl 3-phenylglutarate was converted to 3-phenyl-1,5-pentanediol in 95% yield by reduction with lithium aluminum hydride. The di-*p*-toluenesulfonate of this glycol, prepared in nearly quantitative yield with *p*-tol-

uenesulfonyl chloride in pyridine, was converted to 4-phenylpimelonitrile in 96% yield by refluxing a solution of the ditosylate and potassium cyanide in 80% ethanol. Although the melting point (45.2–46.2°) of this material was lower than that reported in the literature[12] (50–51°), the elemental analysis and infrared spectrum were consistent with the assigned structure. In addition, hydrolysis with concentrated hydrochloric acid proceeded smoothly to give 4-phenylpimelic acid (I) in 82% yield. Dimethyl 4-phenylpimelate (II), prepared in 85% yield by esterification of the acid with methanol and sulfuric acid, was reduced with lithium aluminum hydride yielding 97% of the theoretical amount of 4-phenyl-1,7-heptanediol (III). Conversion of the glycol to the di-*p*-toluenesulfonate (IV), which was not purified, followed by treatment with potassium cyanide in 80% ethanol led to 5-phenylazelanitrile (V) in 54% yield. The yield of the dinitrile may have been lowered because its melting point (34.0–34.6°) made isolation of the product difficult.

Cyclization of 5-phenylazelanitrile with sodium methylanilide[13,14] using the conditions of Ziegler[15,16] led to a 54% yield of 2-cyano-5-phenylcyclooocten-1-yl-amine (VI) when V was added to the reaction mixture through a simple dilution apparatus.[17] A 33% yield was realized when the dilution apparatus was not used.[13] The product was characterized by analysis and its infrared spectrum, which was similar except for bands due to the phenyl group to the spectrum of 2-cyano-cycloocten-1-ylamine, obtained by a similar cyclization of azelanitrile. Hydrolysis of VI with concentrated hydrochloric acid yielded 80% of 5-phenylcyclooctanone (VII). Hydrolysis of VI with sulfuric acid under conditions that have been used successfully in similar cases[13,14] resulted in resinification and no ketone could be isolated. The 5-phenylcycloooctanone was characterized by its infrared spectrum, analysis, analysis of a crystalline semicarbazone, and by conversion in 68% yield to phenylcyclooctane by the modified Wolff–Kishner method of Huang-Minlon.[18] The phenylcyclooctane was identified by its melting point, mixture melting point with an authentic sample,[19] and comparison of its infrared spectrum with that of an authentic sample.

Reaction of 5-phenylcyclooctanone with an ethereal solution of phenyllithium proceeded smoothly yielding 72% of *cis*- and *trans*-1,5-diphenylcyclooctanol (VIII). Recrystallization gave an analytically pure mixture of isomers melting at 149.8–154.2°. Attempted short-

(1) American Cyanamid Co. Fellow, 1953–1954.
(2) A. C. Cope and D. S. Smith, *J. Am. Chem. Soc.*, **74**, 5136 (1952).
(3) A. C. Cope, F. S. Fawcett, and G. Munn, *ibid.*, **72**, 3399 (1950).
(4) A. C. Cope, M. R. Kinter, and R. T. Keller, *ibid.*, **76**, 2757 (1954).
(5) A. C. Cope and W. R. Moore, *ibid.*, **77**, 4939 (1955).
(6) A. Michael, *Am. Chem. J.*, **9**, 115 (1887).
(7) S. Ruhemann and A. V. Cunnington, *J. Chem. Soc.*, **73**, 1015 (1898).
(8) J. Jackson and J. Kenner, *ibid.*, 577 (1928).
(9) D. Vorlander, *Ann.*, **320**, 84 (1902).
(10) R. H. Manske, *J. Am. Chem. Soc.*, **53**, 1104 (1931).
(11) B. Wojcik and H. Adkins, *ibid.*, **55**, 4939 (1933).
(12) J. v. Braun and K. Weissbach, *Ber.*, **64B**, 1785 (1931).

(13) E. M. Fry and L. F. Fieser, *J. Am. Chem. Soc.*, **62**, 3489 (1940).
(14) H. E. Schroeder, Ph.D. Thesis, Harvard University, 1938.
(15) K. Ziegler, H. Eberle, and H. Ohlinger, *Ann.*, **504**, 94 (1933).
(16) K. Ziegler and R. Aurnhammer, *ibid.*, **513**, 43 (1934).
(17) A. C. Cope and E. C. Herrick, *J. Am. Chem. Soc.*, **72**, 985 (1950).
(18) Huang-Minlon, *ibid.*, **68**, 2487 (1946).
(19) A. C. Cope and A. A. D'Addieco, *ibid.*, **73**, 3419 (1951).