to give 2.05 g of a white solid, mp 41–44°. The perester displayed a characteristic band in the infrared at 1760 cm^{-1} (carbon tetrachloride).

Anal. Calcd for $C_{14}H_{18}O_3$: C, 71.77; H, 7.74. Found: C, 71.59; H, 7.62.

cis-t-**Butyl** α-**Phenylpercinnamate.** *cis,cis*-α-Phenylcinnamic acid anhydride, mp 130–131°, was prepared as described above for the α-methyl system.

To a slurry of 5.6 g of sodium *t*-butyl hydroperoxide (0.050 mole) in 250 ml of anhydrous ether was added a solution of 5.3 g of the acid anhydride (0.013 mole) in 120 ml of dichloromethane at room temperature. The mixture was stirred at room temperature for 16 hr and water was added. The layers were separate and the organic layer was washed twice with 10% sodium carbonate solution and twice with water, dried over anhydrous magnesium sulfate, and concentrated *in vacuo*. The residue was taken up in petroleum ether and washed twice with water to remove traces of *t*-butyl hydroperoxide, dried over anhydrous magnesium sulfate, and concentrated *in vacuo* to 1.3 g of a white solid (35%), mp 79.5–81.5°. Recrystallization from ether-petroleum ether gave mp 80–81°. The perester displayed a characteristic band in the infrared at 1764 cm^{-1} (carbon tetrachloride).

Anal. Calcd for $C_{19}H_{20}O_3$: C, 77.00; H, 6.80. Found: C, 77.15; H, 6.98.

trans,trans-**Bis**-α-**methylcinnamoyl Peroxide.** The diacyl peroxide **9** was prepared according to the procedure of Staab.[10] To a solution of 5.0 g of N,N-carbonyldiimidazole (0.0308 mole) in 25 ml of tetrahydrofuran was added 5.0 g of *trans*-α-methylcinnamic acid (0.0308 mole) over 10 min at room temperature. Vigorous gas evolution occurred after a brief induction period. The solution was stirred for 0.5 hr and then cooled in an ice–water bath. To the cold azolide solution was added 1.6 ml of 30% hydrogen peroxide in 5 ml of tetrahydrofuran. The mixture was stirred in the cold for an additional 2 hr, poured into water, and extracted with dichloromethane. The organic layer was washed three times with salt water, dried over magnesium sulfate, and concentrated *in vacuo* to an oily solid. The oily residue was crystallized from petroleum ether–ether to give 1.7 g of product, mp 71–74° dec. Characteristic bands are observed in the infrared at 5.64 and 5.72 μ (dichloromethane). Recrystallization from petroleum ether–ether gave material with mp 74–75° dec.

Anal. Calcd for $C_{20}H_{18}O_4$: C, 74.52; H, 5.63. Found: C, 74.77, 75.30; H, 6.18, 5.99.

3-Methylcoumarin. A modification of the procedure as described by Perkin[25] was used. A mixture of 12.2 g of salicylaldehyde (0.10 mole), 7.4 g of propionic acid (0.10 mole), 26 g of propionic anhydride (0.20 mole), and 10.1 g of triethylamine (0.10 mole) was heated at 150° for 8 hr. After cooling to room temperature, the mixture was taken up in dichloromethane and washed with 10% dium carbonate and water, dried over anhydrous magnesium sulfate, and concentrated *in vacuo*. The residue was crystallized from dichloromethane–ether to give 5 g of a solid, mp 89.5–91.5° (31%) (lit.[25] mp 90°). A characteristic band is found in the infrared at 5.84 μ (chloroform).

3-Phenylcoumarin. From 12.2 g of salicylaldehyde (0.10 mole), 13.6 g of phenylacetic acid (0.10 mole), 15.3 g of acetic anhydride (0.15 mole), and 10.1 g of triethylamine (0.10 mole) was obtained 11.5 g of 3-phenylcoumarin, mp 141–143°, by the same procedure as described above for 3-methylcoumarin (lit.[26] mp 140–141°). A characteristic band is found in the infrared at 5.80 μ (chloroform).

Product Analysis. Analysis of the hydrocarbon mixtures from samples decomposed in degassed and sealed Pyrex ampoules was by vpc on a 9-ft 30% Carbowax on Chromosorb P column. The olefin, acetylene, and coumarin products were identified by retention time comparison with authentic samples. Commercial samples of *cis*- and *trans*-stilbenes were used. *trans*-Propenylbenzene was prepared by base-catalyzed isomerization of allylbenzene. *cis*-Propenylbenzene was obtained by photoisomerization of the *trans* isomer to a mixture of the *cis* and *trans* isomers followed by preparative vpc. The ultraviolet spectra of the propenylbenzene isomers were identical with those previously reported.[27]

The acid yields were determined by gram scale decompositions of the peresters. The diluted reaction mixtures were washed with aqueous base, and the aqueous layer was acidified and extracted with ether. The ether layer was dried and concentrated and the residue weighed and compared with authentic samples of the acids by infrared spectroscopy.

The photochemical decompositions of the diacyl peroxide (**9**) were carried out by irradiating solutions of **9** in degassed and sealed Pyrex ampoules which were cooled in an ice-water or Dry Ice-ethanol bath maintained in a clear, Pyrex dewar flask. The dewar was held flush against a Pyrex immersion well in which was mounted a 450-w Hanovia lamp.

Kinetic Procedure. The rates of decomposition of peresters **1–4** were obtained by use of the infrared technique described by Bartlett, *et al.*,[28] using a Beckman IR-7 spectrophotometer. Good first-order kinetics were obtained to 80% reaction in all cases.

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[25] W. H. Perkin, *J. Chem. Soc.*, **28**, 11 (1875).

[26] N. Oda, *Yakugaku Zasshi*, **82**, 1185 (1962).

[27] R. Y. Mixer, R. F. Heck, S. Winstein, and W. G. Young, *J. Am. Chem. Soc.*, **75**, 4094 (1953).

[28] P. D. Bartlett, E. D. Benzing, and R. E. Pincock, *J. Am. Chem. Soc.*, **82**, 1762 (1960).

Vinyl Radicals. III.[1] The Thermal Decomposition of *t*-Butyl *cis*- and *trans*-α,β-Dimethylpercinnamates

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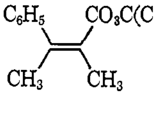
Contribution from the Department of Chemistry, University of Rochester, Rochester, New York 14627. *Received July 21, 1966*

Abstract: Kinetic and scavenger studies confirm a rate-determining oxygen–oxygen homolysis for the thermal decomposition of *t*-butyl *cis*- and *trans*-α,β-dimethylpercinnamates. Activation parameters are essentially identical for the two peresters, ruling out any anchimeric assistance by the aromatic ring in the decomposition of the *cis* perester. Both peresters are similar in behavior to *t*-butyl perbenzoate.

We have previously described[1] the preparation and products of decomposition of the isomeric α,β-unsaturated peresters (I and II) in cumene at 110°. This paper reports kinetic and scavenger studies de-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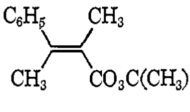
II

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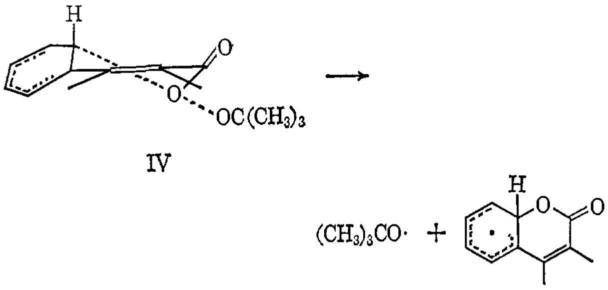
[1] Part II: J. A. Kampmeier and R. M. Fantazier, *J. Am. Chem. Soc.*, **88**, 1959 (1966).

[2] Du Pont Postgraduate Teaching Assistant 1964–1965. National Science Foundation Cooperative Fellow, 1965–1966.

signed to give further insight into the behavior of these compounds. We have studied these peresters in detail as the first examples of a group of useful precursors of vinyl radicals. Similar studies of the decomposition of *cis*- and *trans*-α-phenyl- and -α-methylpercinnamates are reported in this issue by Singer and Kong.[3]

The thorough studies by Bartlett and his co-workers on the thermal decomposition of *t*-butyl peresters have established a correlation between activation parameters, mechanism, and structure.[4] This correlation has been confirmed and applied with success by others.[5] In general, the details of the decomposition are strongly influenced by the nature of the substituent (R) attached to the perester structural unit as in $RCO_3C(CH_3)_3$ (III). Peresters in which R is relatively unstable as a free radical (*e.g.*, R = CH_3, C_6H_9) are characterized by slow rates of decomposition by a simple dissociation of the oxygen–oxygen bond. Substituents which are more stable as free radicals (*e.g.*, $(CH_3)_3C$, $C_6H_9CH_2$, etc.) lead to enhanced rates and two-bond fragmentations in which a radical (R·), carbon dioxide, and a *t*-butoxy radical are formed in the rate-determining step. Variations in the activation parameters have been analyzed in terms of the detailed nature of the transition states. A more complete understanding of the decomposition process for peresters I and II, therefore, should give some preliminary information about the stability of the related vinyl radicals.

A second point of interest concerned the possibility of anchimeric assistance by phenyl in the decomposition of the *cis* perester (I). 3,4-Dimethylcoumarin is formed from I, suggesting the transition state for homolysis shown in IV. Such participation is not possible for the *trans* perester. The studies by Martin and his co-workers[6] have led to the recognition of several anchimerically assited homolyses. Participation by a remotely situated double bond in the rate-determining step for the dissociation of a diacyl peroxide has been observed by Lamb.[7] In general, assisted homolyses are distinguished by enhanced rates when compared to similar unassisted decompositions; accelerations varying from 5- to 25,000-fold[7,8] have been observed, depending on the particular case. Involvement of the aromatic ring of perester I in the rate-determining, rather than product-determining, steps should be apparent in a comparison of the rates and activation parameters for the decompositions of the *cis* (I) and *trans* (II) peresters.


IV

Experimental Section

Materials. *t*-Butyl *cis*- and *trans*-α,β-dimethylpercinnamates were prepared and purified as described previously.[1] Cumene was purified carefully[9] and stored under nitrogen. 2-Thiomesitylene, prepared[10] in 16% yield by $Zn-H_2SO_4$ reduction of 2-mesitylenesulfonyl chloride, was obtained as a colorless liquid, bp 225° (lit.[10] bp 227–229°). Di-*t*-butyl nitroxide, prepared in 10% yield by the method of Hoffmann,[11] had bp 78° (15 mm) (lit.[11] bp 60° (11 mm)); $\lambda_{max}^{cyclohexane}$ 225 mμ (log ϵ 3.32) and 238 mμ (log ϵ 3.34) (lit.[11] λ_{max}^{hexane} 225 mμ (log ϵ 3.30) and 238 mμ (log ϵ 3.33). The infrared spectrum was free of hydroxyl absorption indicating the absence of di-*t*-butylhydroxylamine.

Kinetic Procedure. A solution of perester in purified cumene was transferred to a small reaction vessel fitted with a rubber septum and a nitrogen-filled balloon. The sample was degassed at 0.05 mm for 3 cycles, maintained under nitrogen, and transferred immediately to a thermostated oil bath. Temperature was controlled to ±0.05° and calibrated with an NBS certified thermometer. After a 2-min warm-up, the t_0 sample was removed and quenched at −78°. Subsequent samples were removed at 10-min intervals for 4 half-lives and then at approximately 5, 8, 12, and 18 half-lives. At the end of the run, all samples were warmed to room temperature and the per cent transmittance was determined at the carbonyl maximum in the infrared[12] (*trans* 1761.7 cm^{-1}; *cis* 1752.0 cm^{-1}). Perester solutions in cumene obeyed Beer's law between 17 and 90% transmittance. Each sample was viewed against pure cumene for 3 min; samples were examined in order of increasing perester concentration. Of the samples removed at 8, 12, and 18 half-lives, that having the greatest per cent transmittance was chosen as the infinity value. In general, points beyond 3–4 half-lives showed scatter owing to errors in determining the per cent transmittance of dilute solutions; no curvature of the first-order plot was apparent.

The experimental data were processed with an IBM 1620 digital computer using a least-squares[13] program to give rate constants and Arrhenius parameters. The expression, $\ln(\log T_\infty - \log T_{sample})$ *vs.* time, gave the first-order rate constant. Entropy of activation was calculated[14] from $\Delta S^* = 4.576 \log (A/T) - 49.203$. Results are presented in Tables I and IV.

The accuracy of the infrared rate was checked by following the disappearance of perester by iodometric titration.[15] A solution of *trans* perester II in cumene (0.08 *M*) was decomposed at 109.43°. Aliquots were removed periodically, quenched at −78°, treated with KI–HOAc, and titrated with standard sodium thiosulfate. The rate constant was calculated from the slope of a plot of ln ([perester]$_t$ − [perester]$_\infty$) *vs.* time. The result is shown in Table I and is in good agreement with the infrared determinations.

For runs in the presence of scavenger, the solutions were prepared by diluting a weighed sample of perester with a standard solution of the scavenger in cumene. The kinetic procedure was identical with that previously described. Carboxylic acid was isolated from these experiments by extraction with sodium bicarbonate. Thin layer chromatography showed the acids to be configurationally homogeneous and to correspond to retention of perester stereochemistry. The ratio of *cis*/*trans* 2-phenyl-2-butenes was determined by vpc.[16] Typically, *trans*-2-phenyl-2-butene had a retention time of 13 min; the *cis* isomer was 30 min. The results of the scavenger studies are given in Tables II and III.

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[5] (a) M. M. Martin, *ibid.*, **83**, 2869 (1961); **84**, 1986 (1962); (b) C. Rüchardt and R. Hecht, *Tetrahedron Letters*, 957 (1962).

[6] J. C. Martin and T. W. Koenig, *J. Am. Chem. Soc.*, **86**, 1771 (1964), and previous papers.

[7] R. C. Lamb, F. F. Rogers, Jr., G. D. Dean, Jr., and F. W. Voight, Jr., *ibid.*, **84**, 2635 (1962).

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[11] A. K. Hoffmann, A. M. Feldman, E. Gelblum, and W. G. Hodgson, *ibid.*, **86**, 643 (1965).

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[14] A. Streitweiser, Jr., "Solvolytic Displacement Reactions," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p 8.

[15] L. S. Silbert and D. Swern, *Anal. Chem.*, **30**, 385 (1958).

[16] Wilkens Aerograph A-90-P2, thermal conductivity detector; 15 ft × 0.25 in. Carbowax 20M on 30–60 Chromosorb P at 120°, He flow 100 cc/min.

Table I. Decomposition of *t*-Butyl *cis*- and *trans*-α,β-Dimethyl-percinnamate in Cumene

$[\text{Perester}]_0$, *M*	Temp, °C	$k \times 10^2$ min^{-1}
cis		
0.050	95.00	0.615 ± 0.022^a
0.050	103.22	1.385 ± 0.011
0.050	110.07	3.105 ± 0.10
0.309	110.09	2.904 ± 0.04
trans		
0.050	85.13	0.235 ± 0.006
0.075	95.00	0.710 ± 0.008
0.058	103.15	1.711 ± 0.003
0.052	110.02	3.65 ± 0.02
0.031	110.03	3.59 ± 0.15
0.104	110.03	3.65 ± 0.08
0.308	110.02	3.62 ± 0.03
0.051	110.03	3.79 ± 0.02^b
0.079	109.94	3.5 ± 0.4^c

[a] The rate constant reported is the average of three determinations. The uncertainty is the average deviation of the three rate constants from the mean. The standard deviation of the least-squares line for each determination is less than ±3%. [b] Solvent was cumene plus 10 vol. % of styrene. [c] Titrimetric rate constant.

Table II. Decomposition of *t*-Butyl *trans*-α,β-Dimethylpercinnamate in the Presence of Scavengers[a]

[Scavenger], *M*	$k \times 10^2$ min^{-1}	$t_{1/2}$ min
t-Butylthiol, 0.05	4.76 ± 0.06	14.5
2-Thiomesitylene, 0.05	3.69 ± 0.07	18.7
Di-*t*-butyl nitroxide, 0.05	*b*	*Ca.* 12
None	3.65 ± 0.02	18.9

[a] Solvent cumene; temperature 110°; [perester] = 0.05 *M*. [b] First-order plot not linear.

Table III. Decomposition of *t*-Butyl *cis*- and *trans*-α,β-Dimethylpercinnamate in the Presence of Thiols

		Products	
Per-ester[a]	[Scavenger], *M*	% acid	2-Phenyl-2-butenes, *cis*/*trans*
trans	None[1]	1.9	1.14 ± 0.05
	n-BuSH, 0.34	80.7	Not observed[b]
	t-BuSH, 0.001	5.4	1.07
	t-BuSH, 0.01	10.4	1.12
	t-BuSH, 0.05	16.7	1.78
	t-BuSH, 0.10	42.0	2.8
	MesSH,[c] 0.0005	...	~1.6[d]
	MesSH, 0.01	...	~1.7
	MesSH, 0.05	36.3	~2.7
	MesSH, 0.10	61.4	~2.9
cis	None[1]	1.2	1.18 ± 0.03
	MesSH, 0.0005	...	~1.7
	MesSH, 0.05	...	~1.7

[a] [Perester] = 0.05 – 0.08 *M*. [b] A 5% yield of either 2-phenyl-2-butene was readily detectable. [c] MesSH = 2-thiomesitylene. [d] The estimates of the *cis*/*trans* 2-phenyl-2-butene ratio in the presence of 2-thiomesitylene are complicated by the presence of interfering vpc peaks.

Results and Discussion

The decomposition of peresters I and II in cumene[1] gives small amounts (1–2%) of the related carboxylic acids. In addition, *cis* perester gives a 13% yield of a product retaining the acyloxy function, 3,4-dimethylcoumarin. These products suggest that the peresters decompose by a nonconcerted oxygen–oxygen homolysis. Apparently, the resulting acyloxy radicals may occasionally abstract hydrogen from cumene or cyclize (*cis*-acyloxy radical only). In Table III we report the results of decompositions of peresters I and II in the presence of thiols. The yields of carboxylic acids are clearly a direct function of the concentration of the hydrogen donor. 2-Thiomesitylene is the most well-behaved donor. The data in Table II show that the rate of decomposition of *trans* perester is unaffected by the presence of 2-thiomesitylene. The increased yields of carboxylic acid, therefore, cannot be attributed to a direct reaction between perester and thiomesitylene. Rather, fragmentation of the perester occurs in the normal manner to give acyloxy radicals which are scavenged by thiol. These results clearly demonstrate that peresters I and II dissociate by a one-bond mechanism. Similar scavenging behavior was observed for *n*-butyl- and *t*-butylthiols, although the rate of perester disappearance is slightly accelerated by the presence of *t*-butylthiol.

It was also of interest to examine the ratio of isomeric 2-phenyl-2-butenes in the presence of thiols. The data in Table III show that the vinyl radicals equilibrate rapidly with respect to hydrogen abstraction at low thiol concentration. At higher concentrations of thiol, the butenes are equilibrated ($[cis/trans]_{\text{eq}} \cong 4$ at 100° in glacial acetic acid).[17] In the presence of very large amounts of *n*-butylthiol, essentially all acyloxy radicals are trapped before decarboxylation; detectable amounts of the butenes are not formed.

Rate constants for the decomposition of peresters I and II under a variety of conditions are recorded in Tables I and II in the Experimental Section. The rate of decomposition of *trans* perester is essentially unchanged (1) by a tenfold change in perester concentration, (2) by the presence of 10 vol. % styrene, or (3) by the presence of an equimolar amount of 2-thiomesitylene. No change in rate is observed for *cis* perester with a 6-fold change in initial concentration. Induced decomposition, therefore, is not important for these peresters in cumene. Activation parameters for peresters I and II and reference compounds are given in Table IV.

Intuitively, one might expect phenyl and vinyl radicals to be similar species. This suspicion is supported by the present results. Both peresters fragment by a nonconcerted one-bond cleavage. The rates are also roughly comparable. Thus, there is no special stability associated with these vinyl radicals which can make its presence known in the transition state for perester decomposition. Bartlett and Hiatt[4] have noted that the benzoyloxy radical seems to possess some degree of resonance stabilization with respect to acetyloxy. Such resonance stabilization of benzoyloxy could account for the decreased enthalpy and entropy of activation for dissociation for *t*-butyl benzoate with respect to *t*-butyl peracatate. The exact nature of this stabilization is not clear at the present time.[8] Whatever the mechanism of stabilization, the same effect seems to be operative for the percinnamates. If this stabilization requires restriction of the rotation about the phenyl–carbonyl bond in *t*-butyl perbenzoate as proposed,[4] the same effect is noted for peresters I and II. Interposition of the double bond between phenyl

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[17] D. J. Cram and M. R. V. Sahyun, *J. Am. Chem. Soc.*, **85**, 1257 (1963).

Table IV. Rates and Activation Parameters for Decomposition of Peresters

t-Butyl perester	$t_{1/2}^{60°}$, min	ΔH^*, kcal	ΔS^*, cal/deg	Solvent
Peracetate[4]	5×10^5	38	17	Chlorobenzene
Perbenzoate[a]	3×10^4	33.5	7.8	p-Chlorotoluene
I	7300	28.4 ± 0.9	0.1 ± 2.3	Cumene
II	7160	29.3 ± 0.2	2.9 ± 0.6	Cumene

[a] A. T. Blomquist and A. F. Ferris, *J. Am. Chem. Soc.*, **73**, 3408 (1951).

and carbonyl in the percinnamates now requires restriction about two bonds in the transition state. This should lead to lower entropies of activation for the percinnamates, as observed.

The virtual identity of the rates and activation parameters for the *cis* and *trans* peresters clearly shows that there is no important anchimeric assistance (IV) to the dissociation of *cis* perester. 3,4-Dimethylcoumarin is formed in a product-determining step.

Several *trans*-perester decompositions were run in the presence of the stable radical, di-*t*-butyl nitroxide.[11,18] It was hoped that this would provide a measure of the yield of radicals from the perester, as well as an independent measure of the rate of decomposition.[7] Solutions of perester and di-*t*-butyl nitroxide in cumene were heated under nitrogen in sealed, degassed tubes in the cavity of an esr spectrometer.[19] The cavity was thermostated at 110 ± 2°. The disappearance of the stable radical was measured by scanning the spectrum at 2-min intervals. The change in the area under the first derivative curve was taken as a measure of the change in concentration of nitroxide. Plots of $(Z_0 - Z)$ *vs.* time were not linear, indicating other than a zero-order dependence of the rate on nitroxide concentration (Z_0 = area at time zero; Z = area at time t).

In the presence of nitroxide, the infrared rate for perester decomposition was accelerated; first-order plots were not linear. The total consumption of nitroxide was quite low as compared with the yield of radicals expected from the perester.

These observations suggest a direct reaction between the perester and nitroxide. Further, the low consumption of nitroxide indicates that it is a poor scavenger for the radicals formed from *trans* perester in cumene and/or that the scavenging products are unstable at 110° and regenerate nitroxide.

Acknowledgment. This work was supported by National Science Foundation Grant No. NSF GP 2024.

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(18) S. F. Nelson and P. D. Bartlett, *J. Am. Chem. Soc.*, **88**, 143 (1966).

(19) Japan Electron Optics Laboratory Co., Ltd., Model JES 3BS-X electron spin resonance instrument. We are indebted to Dr. R. W. Kreilick for assistance with the esr measurements.

Homolytic Aromatic Cyclohexylation

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Contribution from the Department of Chemistry, Case Institute of Technology, Cleveland, Ohio 44106. *Received July 27, 1966*

Abstract: Cyclohexyl radicals, generated by decomposition of di-*t*-butyl peroxide in the presence of cyclohexane, readily react with aromatic compounds to give substitution products. Yields of such products exceed 50% when an electron-attracting aromatic substituent is present. From the orientation and relative reactivity data resulting from attack of cyclohexyl radicals on a variety of monosubstituted benzenes, it is concluded that the nucleophilicity and selectivity increase for the radical species: phenyl < methyl < cyclohexyl. Partial rate factors for the *meta* and *para* positions have been correlated with Hammett σ parameters to give a ρ value of +1.1 for the reaction. When benzonitrile was employed as substrate, an imine was also formed from addition of cyclohexyl radicals to the cyano group and subsequent acquisition of hydrogen.

The area of homolytic aromatic arylation has been extensively investigated,[1] but among the analogous alkylation reactions only methylation has received much attention.[2,3] However, 2 decades ago it was reported[4] that p-cyclohexylbenzoic acid was among the products formed from the decomposition of benzoyl peroxide in cyclohexane. More recently Walling and Gibian[5] have shown that cyclohexyl radicals, derived from cyclohexane *via* hydrogen abstraction by triplet states of ketones, can attack benzene to ultimately yield cyclohexylbenzene. Apparently other secondary alkyl radicals are capable of this type of reaction, for lead tetraacetate decarboxylation of 2-methylbutyric acid in benzene produced unrearranged *sec*-butylbenzene among other products.[6]

Concurrently, in the course of a study involving the reactions of hydrocarbons with *t*-butoxy radicals, we observed that photolysis of di-*t*-butyl peroxide in cyclohexane gave cyclohexylbenzene along with the ex-

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(2) B. Cowley, R. Norman, and W. Waters, *J. Chem. Soc.*, 1799 (1959).

(3) G. Corbett and G. Williams, *ibid.*, 3437 (1964).

(4) P. Hermans and J. Van Eyk, *J. Polymer Sci.*, **1**, 407 (1946).

(5) C. Walling and M. Gibian, *J. Am. Chem. Soc.*, **87**, 3361 (1965).

(6) J. Kochi, *ibid.*, **87**, 3609 (1965).