Mechanisms of Photochemical Reactions in Solution. LXX.[1] Photolysis of Aryl Esters

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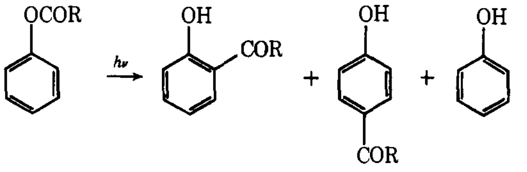
Abstract: Irradiation of phenyl acetate in the vapor phase, in a flow system with nitrogen as carrier gas and isobutane as hydrogen donor, gives products that can be accounted for entirely in terms of a free-radical mechanism. Products identified are: phenol, *o*- and *p*-cresol, *o*- and *p*-hydroxydiphenyl ether, and *p*-benzoquinone. A trace amount of *o*-hydroxyacetophenone was detected in some runs but none of the para isomer was ever observed. Irradiation of various phenyl esters in solution gives rise to *o*- and *p*-hydroxyacetophenone, phenol, and products believed to be derived indirectly from acetyl radicals. We believe that the results are consistent with a common primary mechanism involving fragmentation to give free radicals, which undergo extensive geminate recombination in solution.

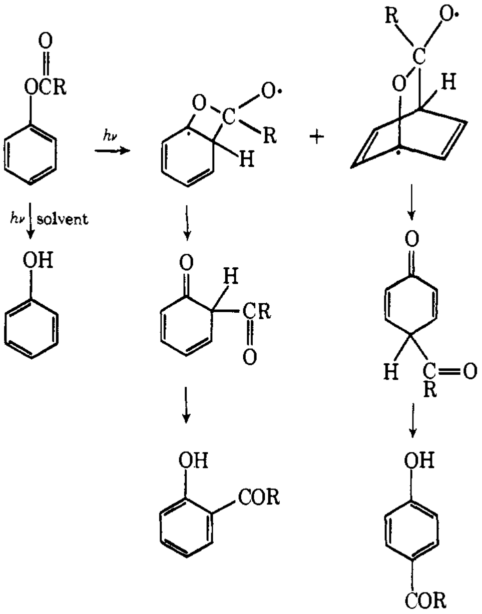
The photo-Fries rearrangement, the photochemical conversion of phenyl esters into hydroxyphenones (Scheme I), has been the subject of considerable study in the last decade.[2-26] Nevertheless, the mechanism of this rearrangement is not well understood, and conflicting interpretations have appeared in the literature.

Scheme I



Basically two alternative mechanistic pathways have been proposed by various investigators to explain the photochemical behavior of phenyl esters in solution. In one (Scheme II), the excited state of the ester molecule reacts in a concerted fashion to give the 2- and 4-acylcyclohexadienones. Throughout the entire course of the rearrangement the acyl and phenoxy portions of the molecule remain bonded to each other in this scheme. Following migration of the acyl group, the 2- and 4-acylcyclohexadienones rapidly enolize in solution giving the observed 2- and 4-hydroxyphenones. It is important to note in this scheme that phenol, which always accompanies the rearrangement products, must be the result of a separate, competing reaction with solvent. Molecular rearrangement mechanisms of this general type have been advanced by many investigators.[4-10] The findings of Sandner, Hedaya, and Trecker from their studies of the viscosity effects on the photoreactions of para substituted phenyl esters in solution provided particularly provocative indications that the rearrangement to the ortho position proceeded by a molecular mechanism.[6,7]

Scheme II



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(1) Part LXIX: M. T. McCall and G. S. Hammond, submitted for publication in *J. Amer. Chem. Soc.*

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(3) H. Kobsa, *J. Org. Chem.*, **27**, 2293 (1962).

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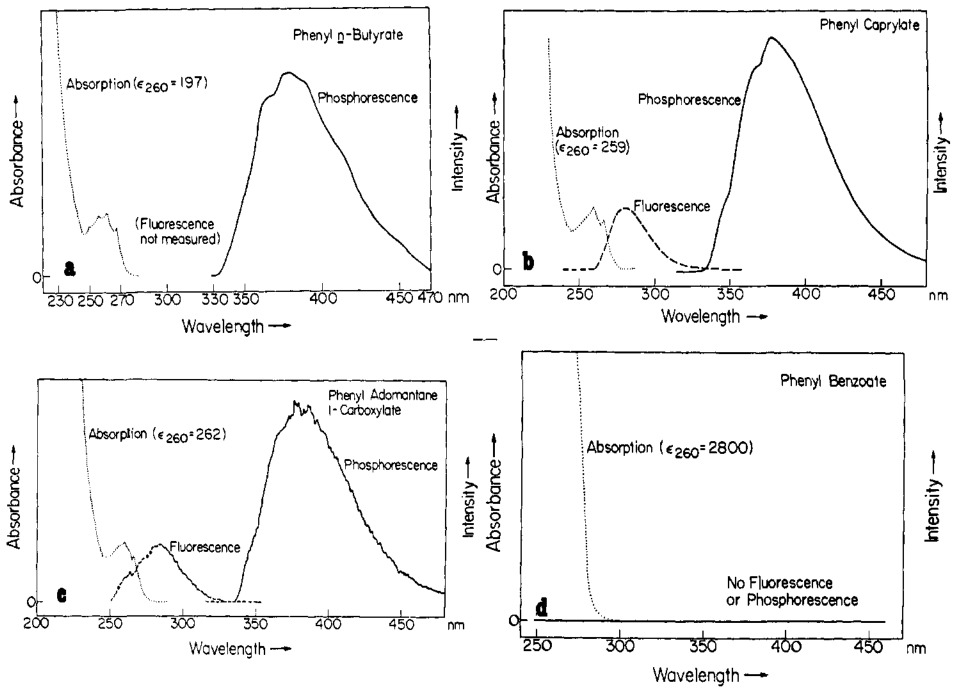
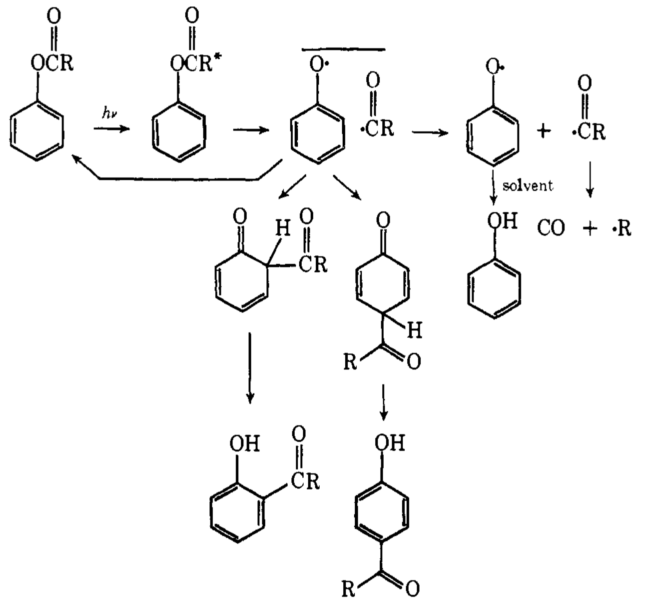


Figure 1. Absorption and emission spectra: a, phenyl *n*-butyrate; b, phenyl caprylate; c, phenyl adamantane-1-carboxylate; d, phenyl benzoate.

An alternative to the molecular rearrangement mechanism is the solvent cage recombination mechanism (Scheme III) which has likewise enjoyed considerable popularity in the literature.[3,12,15,17,19-22] In this proposal the excited ester molecule severs the C-O bond giving acyl and phenoxy radicals which are held in close proximity to each other by surrounding solvent molecules. Reaction of the radical pairs in this solvent cage should be very fast. Combination of the two fragments by reestablishing the C-O bond would result in the regeneration of the starting ester. However, recombination of the acyl radical at either the 2 or 4 positions of the phenoxy radical would produce acyl cyclohexadienones, tautomers of the hydroxyphenone photoproducts. This mechanism, unlike the concerted mechanism, makes rearrangement and the formation of phenol intimately related processes. Since studies of the efficiency of radical cage recombination reactions indicate that the recombination frequently does not occur with unit probability,[27,28] one would predict that some of the phenoxy radicals should escape recombination by diffusion out of the cage to become kinetically free radicals, abstract hydrogen, and become phenol. In this way the cage recombination mechanism would not only account for formation of the hydroxy ketones but would also provide an attractive, logical explanation of the phenol formation. In like fashion, one might expect the acyl radicals to produce the corresponding aldehyde. However, attempts to isolate aldehydes from the photolyses of phenyl esters in solution have been unsuccessful in every instance except one.[29]

Scheme III



Our experiments have principally been aimed at distinguishing between these two proposed mechanisms and have involved irradiations of phenyl esters in both solutions and the gas phase. The majority of our solution experiments were primarily designed to trap phenoxy and acyl radicals which might escape the solvent cage, while the gas-phase experiments were an attempt to observe the effects on the product distribution of removing the solvent entirely.

Results

Spectra. The absorption and emission spectra of several phenyl esters were taken in ethanol and EPA, respectively. The absorption and emission of phenyl esters of the aliphatic carboxylic acids *n*-butyric, caprylic, and adamantane-1-carboxylic were all very

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(27) H. P. Waits and G. S. Hammond, *J. Amer. Chem. Soc.*, **86**, 1911 (1964).

(28) G. S. Hammond and J. R. Fox, *ibid.*, **86**, 1918 (1964).

(29) Bradshaw, Loveridge, and White[8] report finding a small amount of benzaldehyde from the irradiation of 2-methoxy-4-methylphenyl benzoate in benzene.

similar (Figure 1a–c). In ethanol, these esters revealed an onset for absorption at *ca.* 270 nm increasing to weak absorption maxima ($\epsilon \sim 200$–250) showing some fine structure at *ca.* 250 nm. The spectrum of phenyl benzoate (Figure 1d), the only phenyl ester of an aromatic carboxylic acid we studied, showed only a single strong absorption (λ_{max} 232 nm, ϵ 1.73×10^4) with onset at *ca.* 290 nm.

Phosphorescence and total emission spectra were recorded at 77°K in EPA glasses from the three phenyl esters of aliphatic carboxylic acids studied in this work. Although phenyl benzoate showed no emission at all (even at the most sensitive settings of the spectrophotometer) the other esters all displayed relatively strong phosphorescence bands with a λ_{max} at 380 nm and peak onset at 335 nm which corresponds to a triplet energy of 85 kcal/mol. Phenyl caprylate and phenyl adamantane-1-carboxylate also showed small fluorescent emission peaks (λ_{max} 280 nm) with onset at 260 nm. A similar fluorescent emission was not observed with phenyl *n*-butyrate because of the appearance of a large amount of scattered light from the excitation source in the spectrum. In all cases where emission was observed, excitation spectra were taken and revealed a strong absorption in the region of 265 nm which overlapped the first peak of the absorption spectra of these esters.

Attempts to Observe Short-Lived Intermediates. A number of attempts were made to observe spectroscopically any short-lived intermediates from the solution irradiations of phenyl esters. In particular, it was hoped that direct evidence for the presence of phenoxy and/or acyl radicals could be obtained through the techniques of flash lamp spectroscopy and epr spectrometry. Irradiations of phenyl acetate in the cavity of an epr spectrometer produced a single, weak, structureless peak having a line width of 48 G and a *g* value of 2.0. However, because of the poor quality of the signal, it can only be stated that the signal is not inconsistent with the line widths reported for acetyl and phenoxy radicals.[30,31] Similarly, the results of flash spectroscopic experiments with a number of solutions of phenyl esters were generally inconclusive, and therefore we were unable to obtain reliable data for the presence of phenoxy radicals as intermediates in these irradiations.

Chemical Trapping Experiments. Solutions of 0.1 *M* phenyl *n*-butyrate in cyclohexane, heptane, benzene, and *n*-amyl alcohol were prepared containing large concentrations of compounds which are reactive hydrogen donors. Both *n*-butyl mercaptan in concentrations of 1.0 and 9.5 *M* and triethylsilane in 1.0 *M* concentrations provided a ready source of hydrogen to scavenge any free radicals formed in these experiments.[32] Many irradiations of these solutions in sealed tubes for periods of from 10 to 175 hr, causing from 15 to 95% disappearance of the phenyl *n*-butyrate, produced the expected products *o*-hydroxybutyrophenone, *p*-hydroxybutyrophenone, and phenol. There was a trend in the relative disappearance quantum yields of phenyl *n*-butyrate in these solvents with the least amount of reaction occurring in the hydrocarbon solvents, cyclohexane and *n*-heptane. Reaction was markedly enhanced in benzene, and the highest relative conversions resulted with *n*-amyl alcohol.[33] Analysis of the reaction mixtures by tlc revealed that only the above-mentioned photoproducts were formed in the samples containing hydrocarbon solvents, while the tubes with *n*-amyl alcohol as the solvent gave two additional photoproducts. Although some phenol could be detected from every irradiation in this series, careful analysis by glpc failed to provide a single case in which any *n*-butyraldehyde was found. The analytical technique could detect as little as 0.5% conversion of the phenyl *n*-butyrate into *n*-butyraldehyde.

Based on these results, the photochemical stability of the sought-for compound, *n*-butyraldehyde, was determined by another set of experiments. Samples were prepared containing amounts of phenyl *n*-butyrate and scavenger identical with those used in the previous study plus an additional 0.1 *M* concentration of *n*-butyraldehyde. Again, the samples were exposed to an unfiltered Hanovia 450-W medium-pressure lamp for 54.5 hr and the products were analyzed by glpc. The results, tabulated in Table I, show that *n*-butyraldehyde decomposes under the conditions of the reaction. Although the extent of decomposition, and therefore the rate (with appropriate assumptions), is dependent upon the solvent in all but the cyclohexane solutions, the rate of decomposition of the aldehyde is comparable to, or faster than, the photolysis of phenyl *n*-butyrate. As a result, scavenging experiments designed to trap a butyryl radical as butyraldehyde would be expected to have little probability of success.

Table I. Relative[a] Rates of Decomposition of Phenyl *n*-Butyrate and *n*-Butyraldehyde

Solvent	Ester converted, %	Aldehyde decomposed, %
Cyclohexane	27	17
n-Heptane	24	27
Benzene	99	82
Alcohol	100	100

[a] 54.5 hr on an unfiltered Hanovia 450-W lamp.

During this study, peaks with extremely short retention times were observed in the gas chromatograms of irradiated samples of phenyl *n*-butyrate. Comparison of these with the chromatograms from the *n*-butyraldehyde irradiations suggested that the peaks might be the products of decarbonylation of the acyl fragment of the ester. Once again sample tubes containing 0.1 *M* phenyl *n*-butyrate in the four solvents were prepared and exposed to ultraviolet light. In addition, two sets of control samples were prepared and irradiated, one of which contained only the solvent and scavenger, and another which contained 0.1 *M* *n*-butyraldehyde and solvent. However, gas chromatograms of the samples again showed short retention time peaks which upon further study were identified as hydrocarbon gases dissolved in solution. Table II gives the product distribution from each sample and an approximate

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(30) T. J. Stone and W. A. Waters, *Proc. Chem. Soc. London*, 253 (1962).

(31) J. R. Morton and W. E. Falconer, *Nature (London)*, 197, 1103 (1963).

(32) J. A. Kerr and A. F. Trotman-Dickenson, *J. Chem. Soc.*, 3322 (1957); J. A. Kerr, D. H. Slater, and J. C. Young, *ibid.*, *A*, 134 (1967).

(33) The effect of solvent on the rearrangement has been extensively studied and well documented in the literature. See ref 8, 9, 16, and 24.

Table II. Production of Gaseous Products by Irradiation of Solutions of Phenyl *n*-Butyrate or *n*-Butyraldehyde

Sample	Total gaseous product (arbitrary units)	Rel distribution			
		Ethane	Ethylene	Propane	Propylene
0.1 *M* phenyl *n*-butyrate in cyclohexane	28.5	1	0.34	4.9	
0.1 *M* phenyl *n*-butyrate in *n*-heptane	17.8	1	0.62	8.6	
0.1 *M* phenyl *n*-butyrate in benzene	15.8	1	1.84	6.54	0.15
0.1 *M* phenyl *n*-butyrate in *n*-amyl alcohol	71.5	1	11.3	19.2	4.2
0.1 *M* *n*-butyraldehyde in cyclohexane	126.1	1		6.3	
0.1 *M* *n*-butyraldehyde in benzene	169.1	1	39	32	
1 *M* Et_3SiH in benzene	11.2	1	Trace	Trace	

indication of the total amount of hydrocarbon gas dissolved in solution. Since liquid samples were withdrawn by syringe and injected onto the chromatograph to obtain these data, the total amount of gas in each is subject to variations due to solubility and sample handling techniques. Therefore, the totals are at best semiquantitative indicators of the extent of decarbonylation accompanying ester photolysis, and probably only reliably indicate that considerably more decarbonylation takes place in *n*-amyl alcohol than in the other solvents. It is clear from the product distribution data that irradiation of phenyl *n*-butyrate in all four solvents favors the formation of propane relative to all other hydrocarbons. In the photolysis of *n*-butyraldehyde, however, both propane and ethylene appear to be major products.

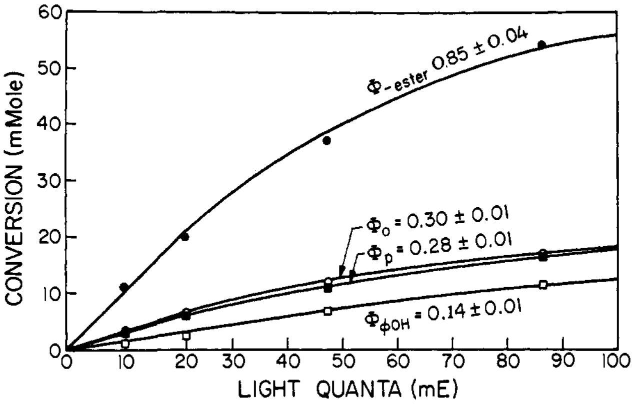

Figure 2. Quantum yields associated with the irradiation of phenyl benzoate.

Quantum Yields. During the course of our studies in solution, we measured the quantum yields for rearrangement of phenyl benzoate in ether. Because of competitive light absorption due to the intense extinction coefficients of the products, determinations were made at low ester conversions. Tubes containing solutions of 0.1 *M* phenyl benzoate in anhydrous ether were irradiated for varying lengths of time on a 254-nm "merry-go-round." Quantitative conversion of phenolic products to their more soluble trimethylsilyl ethers followed by glpc analysis established the product yields. Extrapolation of a plot of these values *vs.* the integrated light intensity produces the quantum yields at 0% conversion (Figure 2, Table III). The quantum yield for ester disappearance was 0.85 ± 0.04. The quantum yields for formation of products were: *o*-hydroxybenzophenone, $\Phi = 0.30 \pm 0.01$; *p*-hydroxybenzophenone, $\Phi = 0.28 \pm 0.01$; and phenol, $\Phi = 0.14 \pm 0.01$. In addition, attempts to measure a quantum yield for benzene, a possible decarbonylation product, indicated that none was formed. Analytical procedures could have easily measured a conversion of 0.1%, or in terms of quantum yields, $\Phi = 1.5 \times 10^{-3}$.

Table III. Irradiation of Phenyl Benzoate

mEinsteins $\times 10^2$	mmol $\times 10^2$			
	Ester[a]	Ortho[b]	Para[b]	PhOH[c]
0	33.9	0	0	0
1.09	31.4	0.33	0.31	0.13
2.16	30.4	0.69	0.63	0.28
4.71	27.8	1.20	1.07	0.76
8.68	26.1	1.70	1.61	1.15
12.7	26.9	1.84	1.77	1.08
17.5	20.7	2.99	2.81	1.84
22.1	22.9	3.15	2.89	1.86

[a] ±5%. [b] ±4%. [c] ±10%.

Irradiation of Phenyl Acetate Vapor. Although a few initial experiments were run in sealed quartz bulbs, a flow system was developed in order to irradiate phenyl acetate in quantities sufficient to permit identification of the photoproducts and reduce the problems of secondary photoreactions. The key component of the system consisted of a large diameter, heated quartz tube surrounded by a battery of 254-nm mercury lamps. Through this tube was passed a mixture of vaporized phenyl acetate (99.9% pure; 0.15 Torr), isobutane (*ca.* 25 Torr), and nitrogen (735 Torr). A total flow rate of 1030 cm³/min was chosen to give a residence time of 56 sec for the irradiation. With flow rates adjusted in this manner about 1.5 g of phenyl acetate was vaporized and irradiated in about 24 hr. The mixture of photoproducts and unreacted starting material was trapped at −70° and then extracted with ether. Glpc analysis showed that the mixture contained six major photoproducts and unreacted phenyl acetate; conversions were typically 3–4%. Although there were a few other small peaks, the six major products accounted for greater than 95% of the total photoproduct yield, with the remaining few per cent distributed among about six other very small peaks. Irradiation of considerable quantities of phenyl acetate, coupled with extensive preparative glpc, permitted successful isolation of all the major photoproducts. Identification was by comparison with authentic samples either purchased or synthesized by other routes. The following compounds were identified as the major products resulting from photolysis of purified phenyl acetate in the gas phase (numbers in parentheses indicate approximate fractions of the total product mixture): phenol (65%), *o*-cresol (7.5%), *p*-cresol (6.0%), *p*-benzoquinone (7.0%), *o*-hydroxydiphenyl ether (4.0%), and *p*-hydroxydiphenyl ether (9.0%). In addition, carbon monoxide was measured in the product flow in concentrations between 0.0025 and 0.004% during the irradiation. This value corresponds to about 2% conversion of ester to carbon monoxide. During the course of the irradiation and product isolation, a seventh compound (whose yield was less than 1% when purified phenyl acetate is irradiated) was recovered in impure form and tentatively identified as *o*-hydroxyacetophenone, one of the two rearrangement products common to solution irradiations of phenyl acetate.

Additional glpc studies were carried out during this study to determine the possible presence of anisole, toluene, benzene, *tert*-butylphenols, and a number of other compounds in the photoproduct mixture. Although the chromatograms had very small peaks with retention times which were close to those for anisole, toluene, benzene, and *p-tert*-butylphenol, the amounts of each of these peaks were well below 1% of the total product mixture and therefore judged not significant to this study.

After several hours irradiation of phenyl acetate, build-up of a brown polymeric deposit became noticeable on the quartz irradiation tube and in the first segment of the trap. By the end of 30 hr of exposure, darkening of the polymer became appreciable. However, a check showed that the total build-up of polymer (which proved to be soluble in 10% aqueous potassium hydroxide) in the quartz tube accounted for less than 10 mg of material.

Another rather interesting observation was made during these photolyses. Inspection of the trap contents at −70° after about 30 hr of irradiation revealed that the trapped material had a bright red color. As the trap and its contents were warmed to room temperature the color rapidly disappeared and only a yellow liquid remained. Such behavior could be characteristic of a reactive species which is stable at −70° but decomposes at room temperature.

The stability of *o*-hydroxyacetophenone was checked under the conditions of the flow system irradiations of phenyl acetate. A 0.70-g sample of purified *o*-hydroxyacetophenone was passed through the system over a period of 18.3 hr. Relative to the phenyl acetate runs, the quartz tube remained considerably cleaner in this irradiation. Extraction of the trapped material with ether, followed by glpc analysis, established that none of the major photoproducts observed in the irradiations of purified phenyl acetate were formed by photoreactions of *o*-hydroxyacetophenone.

Discussion

Although direct attempts to observe acyl radicals by flash spectroscopic and epr techniques from the solution irradiations of various phenyl esters gave inconclusive results in our hands, important evidence was obtained from the chemical trapping experiments. Our original efforts were aimed at capture of butyryl radicals with the reactive hydrogen donors *n*-butyl mercaptan and triethylsilane. However, the photoreactivity of *n*-butyraldehyde, the expected product under the conditions of irradiation, forced us to turn our attention to the decarbonylation products. Nevertheless, it is clear from the analysis of the hydrocarbon gases resulting from the irradiations of phenyl *n*-butyrate solutions that decarbonylation of butyryl radicals accompanies the usual photoreactions of rearrangement and phenol formation. Although the data were collected from gases dissolved in solution and are therefore only an approximate indication of relative distribution of the hydrocarbons resulting from decarbonylation, an interesting trend should be noted. The ratio of propane to ethylene resulting from the irradiations of phenyl *n*-butyrate in each of the solvents appears markedly higher than those ratios obtained from the irradiation of *n*-butyraldehyde under these conditions. It has been well established that *n*-butyraldehyde displays two modes of decomposition in solution; a type I process which leads to the formation of propyl radicals and a type II process leading to the formation of ethylene.[34] In contrast, the major mode of decarbonylation of butyryl radical results mainly in the formation of propyl radicals.[35] In the presence of high concentrations of reactive hydrogen donors, the propyl radicals would be expected to be converted efficiently to propane. Based on the above results, the higher relative yields of propane from solutions of phenyl *n*-butyrate in contrast to those from *n*-butyraldehyde *may* mean that the majority of butyryl radicals which are formed from the photolysis of the ester decarbonylate faster than they abstract hydrogen to form the aldehyde. In any case, the finding of hydrocarbon gases which can be unambiguously linked to the irradiation of the phenyl ester constitutes strong evidence for the existence of acyl radicals in the solution photochemistry of phenyl esters. Others have observed similar decarbonylation products which implicate the formation of acyl radicals in the solution photochemistry of other phenyl esters.[7,14,15,17,19]

The results of our studies of the gas-phase irradiations of phenyl acetate are of particular significance since they clearly indicate a different photoproduct composition than that obtained in solution. Most noteworthy is the fact that phenol makes up 65% of all the photoproducts. This suggests that C–O bond cleavage is the major reaction of phenyl acetate in the gas phase. Furthermore, the virtual absence of either *o*- or *p*-hydroxyacetophenone from the gas-phase product mixture, despite their proven stability under the reaction conditions, also suggests the photochemical pathways of phenyl acetate in solution and vapor are substantially different. The following scheme (Scheme IV) is proposed to explain formation of five of the six major photoproducts isolated in this study.

In the first step (1), absorption of a photon results in promotion of a phenyl acetate molecule to an ex-

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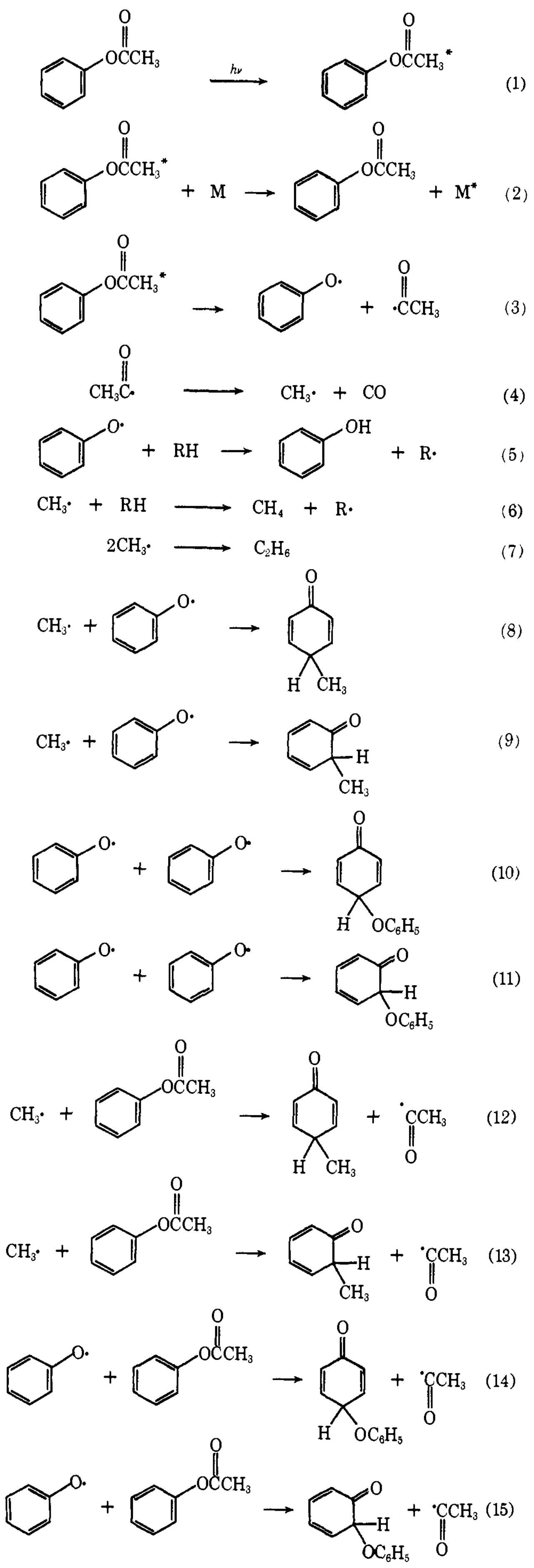
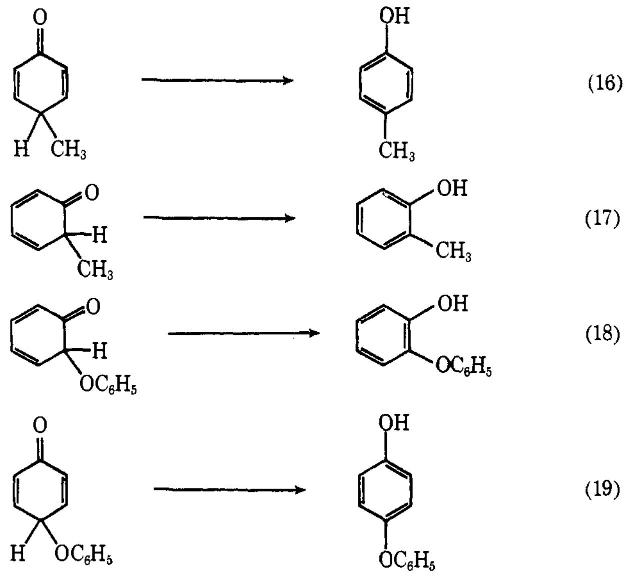
[34] J. G. Calvert and J. N. Pitts, Jr., "Photochemistry," Wiley, New York, N. Y., 1966, p 372.

[35] C. H. Nichol and J. G. Calvert, *J. Amer. Chem. Soc.*, **89**, 1790 (1967).

Scheme IV





cited state. Discussion of the nature of this excited state will be temporarily deferred, and it suffices to say that PhOAc* contains enough energy to break the C–O bond. This excited molecule may lose its energy through collision with another gas molecule and revert to an unexcited state (2). Alternatively a significant number of the activated phenyl acetate molecules must undergo C–O bond homolysis (3), rather than collisional deactivation. The phenoxy radicals may abstract hydrogen from a suitable hydrogen donor such as isobutane and form phenol (5), or be involved in one of the numerous successive steps in the scheme which result in the other five minor photoproducts. The fact that phenol composed 65% of all the photoproducts formed indicates that the majority of the phenoxy radicals are consumed in step 5.

The results of studies on photochemistry of aliphatic aldehydes and ketones indicate that the major pathway for the acetyl radicals formed in step 3 is decarbonylation (4) under these conditions to give methyl radicals.[35,36] This hypothesis is supported by the detection of considerable quantities of carbon monoxide from the phenyl acetate irradiations. Attempts to detect either ethane or methane, the expected products from hydrogen abstraction and coupling of methyl radicals (6, 7), were not made.

Four of the five minor photoproducts result from the reactions of methyl and phenoxy radicals. *o*- and *p*-cresols and *o*- and *p*-hydroxydiphenyl ethers result in Scheme IV either from radical–radical coupling reactions of methyl or phenoxy radical and another phenoxy radical (8–11) or by means of radical attack on a phenyl acetate molecule (12–15). These reactions result in the formation of substituted cyclohexadienones which would be expected to enolize rapidly under the conditions of the experiments to give the substituted phenols (16–19). Formation of hydroxydiphenyl ethers by phenoxy radical attack on phenyl acetate is an unlikely step based on the energetics of the reaction, but is included in this scheme since we cannot rigorously exclude this possibility with our experimental data.

Irradiation of purified phenyl acetate in the gas phase failed to produce significant quantities of *o*- or *p*-hy-

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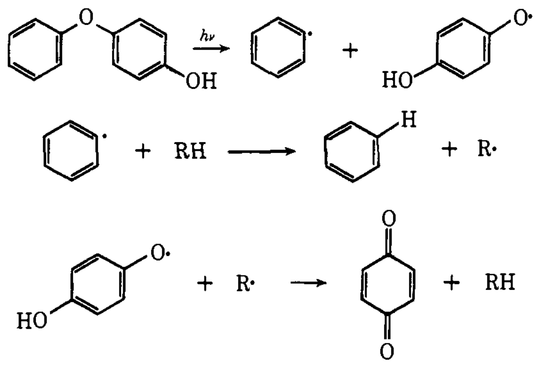
[36] J. A. Kerr and J. G. Calvert, *J. Phys. Chem.*, **69**, 1022 (1965).

droxyacetophenone, which would be expected if acetyl radicals lived long enough to couple with phenoxy radicals. A small amount of *o*-hydroxyacetophenone has been isolated; however, it was found in an experiment carried out with an impure sample of phenyl acetate. In those runs in which freshly purified ester, which had not been exposed to scattered uv light for long periods, was irradiated, the yields of *o*-hydroxyacetophenone were essentially nil. Although a step similar to 6 involving acetyl instead of methyl radicals or a concerted rearrangement cannot be rigorously ruled out as a source of trace amounts of the product, there is an alternative plausible explanation. Small amounts of *o*-hydroxyacetophenone could be produced by the irradiation of liquid phenyl acetate in the vaporizer of the flow system.

The last of the products to be isolated from the vapor phase irradiations of phenyl acetate was *p*-benzoquinone, in 7% yield. This compound, in contrast to all the other identified products, is not believed to be a primary photoproduct. The only attractive scheme that has occurred to us is the one in which *p*-hydroxydiphenyl ether undergoes photolysis of the ether–phenyl bond to give a phenyl radical and a semiquinone radical. The alternative homolytic bond fission would yield two phenoxy radicals. Excellent evidence from the literature on the aqueous solution photochemistry of *p*-hydroxydiphenyl ether suggests the former method of cleavage to give the semiquinone radical is preferred.[37] The semiquinone radical, in the presence of other radicals, would be expected to act as an intensely reactive source of hydrogen. Disproportionation with another radical (probably phenoxy) would produce *p*-benzoquinone (Scheme V). Several observations from the phenyl acetate vapor photolysis support this scheme. First, fluctuations in the yields of *p*-hydroxydiphenyl ether and *p*-benzoquinone over a wide range of conditions appear to generally offset each other. In other words, higher yields of quinone are accompanied by generally lower yields of the diphenyl ether and vice versa. Glpc analysis of the product shows a peak which has a retention time equal to that of benzene, although it is present in relatively small yield. However, as noted earlier, isolation of volatile components with this equipment is subject to question and perhaps more benzene was formed but escaped the trap. Finally, the brown deposit built up on the walls of the quartz tube could be the result of radical reactions resulting from secondary photolysis of *p*-hydroxydiphenyl ether which condensed on the walls following its formation in the vapor.

Scheme V

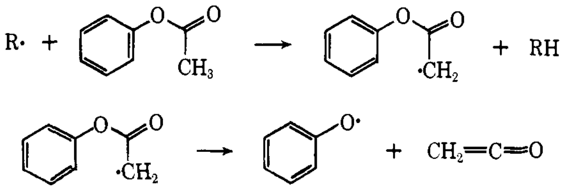


This study of the vapor-phase photolysis of phenyl acetate is, to our knowledge, the only detailed investigation of the gas-phase photoreactions of phenyl esters. However, several studies of the photoanilide rearrangement are relevant to this work.[38-42] Shizuka, *et al.*, have extensively studied the photochemistry of acetanilide[39-42] which closely parallels the photochemistry of phenyl acetate. One of their publications reports that the vapor-phase irradiation of acetanilide fails to give the rearrangement products formed in solution; in their place, ethane and carbon monoxide were detected in the gas sample.[40] Shizuka's interpretation of the vapor-phase photochemistry of acetanilide is very similar to ours for phenyl acetate since the mechanism he proposes includes steps for homolysis of excited acetanilide into anilino and acetyl radicals, decarbonylation of the acetyl radical, and methyl radical coupling and hydrogen abstraction reactions. Our results have been explained with a mechanistic scheme involving similar steps. The close analogy between the results of the gas-phase photochemistries of phenyl acetate and acetanilide provides additional evidence in support of our proposal that the photochemical mechanisms of the two compounds are identical.

Recently, Shizuka has reported results of a study of the solution photochemistry of *N*-acetylcarbazole.[43] In a footnote in this paper it is stated that the vapor-phase irradiation of phenyl acetate gave no rearrangement products. This finding is, of course, in agreement with our results which indicate substantial differences in the composition of the photoproduct mixtures resulting from solution and gas-phase irradiations of this compound.

It is noteworthy that the gas-phase pyrolysis of phenyl acetate at 625° yields phenol and ketene as the major products of reaction.[44] The investigators proposed the following radical chain reaction to explain these results (Scheme VI).

Scheme VI



Comparison of Hurd's results with those obtained in this work suggests that the mode of excitation is important in determining the chemistry leading to products. Although it would be difficult to obtain, we have found no evidence in our studies that would cause us to postulate existence of ketene as an intermediate. Therefore, we suggest that the photolysis and pyrolysis of phenyl acetate proceed by separate

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(37) H.-I. Joschek and S. I. Miller, *J. Amer. Chem. Soc.*, **88**, 3269 (1966).

(38) D. Elad, D. V. Rao, and V. I. Stenberg, *J. Org. Chem.*, 30, 3252 (1965).

(39) H. Shizuka, *Bull. Chem. Soc. Jap.*, 42, 57 (1969).

(40) H. Shizuka and I. Tanaka, *ibid.*, 42, 909 (1969).

(41) H. Shizuka and I. Tanaka, *ibid.*, 41, 2343 (1968).

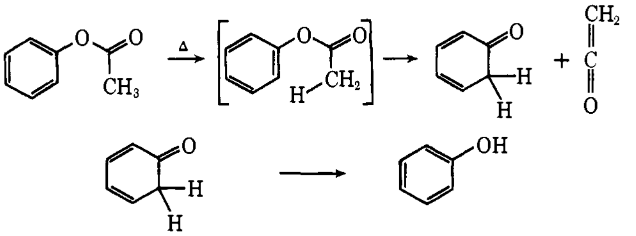
(42) H. Shizuka, *ibid.*, 42, 52 (1969).

(43) H. Shizuka, M. Kato, T. Ochiai, K. Matsui, and T. Morita, *ibid.*, **43**, 67 (1970).

(44) C. D. Hurd and F. H. Blunck, *J. Amer. Chem. Soc.*, **60**, 2419 (1938).

pathways with the likelihood that the pyrolysis products result from the following rearrangement (Scheme VII).

Scheme VII



The emission spectra and quantum yields of several different phenyl esters have provided information useful in relating the excited states to the photochemistry of these compounds. The high-disappearance quantum yields and absence of emission from phenyl benzoate and other phenyl esters of aromatic carboxylic acids[3,5,7] is consistent with fast reaction from the singlet state. Furthermore, to our knowledge, there has yet been no report of definitive success[10] in attempts to sensitize or quench a triplet reaction of these compounds. Reaction from a singlet excited state is also compatible with the observed fluorescence and phosphorescence from phenyl esters of aliphatic carboxylic acids. The lower quantum yield for reaction of these compounds,[7,21] relative to the benzoate esters,[3,7] suggests a lower value for the rate constant for reaction from the singlet excited state, thus allowing a fraction of the excited molecules to fluoresce or undergo intersystem crossing and phosphoresce.

The reaction itself is viewed as internal conversion of electronic excitation to an exaggerated anharmonic vibration of the C–O bond, which ultimately ends in bond homolysis. In this sense, the reaction may be considered as a form of radiationless decay from the singlet excited state. Whether this form of decay involves intersystem crossing to a dissociative triplet σ^* state,[21] or crossing to a dissociative singlet state, is not an easily soluble problem, since both paths are conceived as providing the same end result, dissociation into acyl and phenoxy radicals.

The results from the vapor phase show no requirement for postulation of a concerted rearrangement, because the ultimate products expected from such a process are not formed. Since the hydroxy ketones are produced in substantial quantum yield in solution, some mechanistic feature must change on going from gaseous to condensed phase. It seems to us that the simplest assumption involves maintaining the same basic mechanism for homolysis and then invoking the recombination of geminate radical pairs within the solvent cage. However, we must recognize that the results may also be attributed to a change in the mechanism of decay of the electronically excited state. Since our gas-phase experiments were carried out with rather high pressures of carrier gases, it seems doubtful that special chemistry arises from vibrationally excited forms of the upper electronic state.[45,46] Perturbation of the decay path from the vibrationally relaxed, lowest excited singlet state by a solvent would be a surprising phenomenon, but one that cannot be ruled out rigorously.

The most significant evidence in favor of the concerted mechanism in solution comes from the work of Trecker, *et al.*[6,7] They found that increases in the viscosity of the solvent did not lead to increased quantum yields for the ortho rearrangement of several para-substituted phenyl esters. It is possible that the test is not very sensitive, merely because in all of the solvents geminate radical recombination is extensive, if one takes into account the degenerate reaction to regenerate the parent compound. For example, Shizuka[21] has estimated that the total recombination efficiency in photolysis of phenyl acetate in cyclohexane may be as high as 0.9. If only a few radicals leak out of the cage in any case, even a large increase in viscosity would not be expected to give a dramatic increase in the efficiency of recombination of radicals. We prefer to regard the very large change in product distribution accompanying total removal of the solvent as being a more surely definitive result.

Experimental Section

Materials. *n*-**Amyl alcohol** (J. T. Baker) was stirred over calcium sulfate for several days and distilled from a small amount of sodium (sodium pentoxide). The fraction with bp 137° was collected.

Cyclohexane (Matheson Coleman and Bell (MCB), spectroquality) was passed through an alumina column and then refluxed for 24 hr over granular phosphorus pentoxide. The fraction with bp 79.5–79.7° was used.

n-**Pentane** (Phillips Petroleum Co., 99%) was stirred over concentrated sulfuric acid for several weeks, during which time the discolored acid was replaced several times. Following separation, the pentane was washed several times with aqueous sodium bicarbonate and then with water. The pentane was then dried and passed through an alumina column. The distilled material (bp 36°) had a uv cutoff (OD = 1.0) at 213 nm.

n-**Heptane** (Phillips, 99%) was purified as described above. After the washing and drying procedure, it was refluxed for 24 hr over granular phosphorus pentoxide and then distilled. The fraction with bp 97.5–97.7° was collected and stored under nitrogen.

o-**Hydroxybenzophenone** (Aldrich) was purified by recrystallization from pentane (mp 37–38°).

p-**Hydroxybenzophenone** (Aldrich) was recrystallized from ether–pentane, and then sublimed (mp 133–134°).

Phenyl acetate was purchased from the Aldrich Chemical Co. or prepared by the method of Chattaway.[47]

The product and the commercial material were purified by chromatography on silica gel (40 g/g of ester) with benzene as eluent, followed by distillation at 92–94° (28 Torr). This procedure reduced the phenol impurity to <0.1%.

Phenyl *n*-Butyrate. Phosphorus trichloride (40 g, 0.29 mol) was added to *n*-butyric acid (60 g, 0.68 mol); the mixture was stirred and heated for 1 hr and cooled, and the organic layer was decanted. Distillation gave the acid chloride (bp 99–102°). To this was added a solution of phenol (96 g, 1.02 mol) in dry pyridine (70 ml); the mixture was refluxed for 1 hr and stirred overnight. The organic material was dissolved in ether and extracted several times, first with 10% aqueous hydrochloric acid and then with 10% aqueous sodium hydroxide. The ethereal solution was dried over anhydrous sodium carbonate and the ether was evaporated (crude yield *ca.* 94 g (64%)). The fraction of the distillate with bp 220–225° was freed from the last traces of phenol by elution from a silica gel column (40 g/g of ester) with benzene.

Phenyl Benzoate. Phenol (10.4 g, 0.11 mol) was dissolved in pyridine (*ca.* 100 ml) and benzoyl chloride (14.1 g, 0.10 mol) was added dropwise. After refluxing the mixture for 1 hr, it was cooled, taken up in ether, and washed several times each with dilute hydrochloric acid, dilute sodium hydroxide, and water. The ether solution was dried over magnesium sulfate and then concentrated. Distillation yielded needles, 15.7 g (79%). The phenyl benzoate was purified by sublimation and recrystallization from ether (mp 67–69°).

Phenyl caprylate was synthesized by treating the acid chloride with phenol in pyridine. The chloride was prepared by refluxing

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(45) C. S. Parmenter, *J. Chem. Phys.*, 41, 658 (1964).
(46) R. Srinivasan, *J. Amer. Chem. Soc.*, 84, 3982 (1962).
(47) F. D. Chattaway, *J. Chem. Soc.*, 2495 (1931).

caprylic acid (72.1 g, 0.50 mol) with thionyl chloride (243 g, 2.1 mol) for 30 min. The excess thionyl chloride was removed as its benzene azeotrope and the remaining capryloyl chloride was dissolved in benzene. This solution was added dropwise with stirring to phenol (52.3 g, 0.50 mol) in pyridine (400 ml). After the addition was complete the solution was refluxed for 1 hr, cooled, and then extracted in the usual way with dilute acid, base, and water. The purified ester distilled at 115° (1.3 Torr); yield 88.5 g (80%). Infrared and nmr spectra were consistent with the structure of phenyl caprylate.

Phenyl adamantane-1-carboxylate was prepared from the acid chloride. Adamantane-1-carboxylic acid (15 g, 0.083 mol) was refluxed with thionyl chloride (49.6 g, 0.4 mol) for 30 min. Excess thionyl chloride was removed as an azeotrope with benzene. The resulting material was dissolved in benzene and added dropwise to a pyridine solution of phenol (5.9 g, 0.063 mol). The mixture was stirred at reflux temperature overnight and the ester was extracted from solution and washed in the usual manner. The material was dried over magnesium sulfate and the ether was evaporated; yield, 19.9 g (93.5%). Recrystallization from ether followed by sublimation produced white crystals melting at 45.5–47.0°. The infrared spectrum (CCl_4) showed the following absorptions: 2950 (s), 2905, 2847, 1755 (s), 1745, 1595, 1490, 1478 (s), 1450, 1215, 1190, 1180 (s), 1160, 1050, and 685 cm^{-1}. The nmr ($CDCl_3$–TMS) showed the following signals: δ 1.77 (6 H, s (broad)), 2.06 (9 H, s (broad)), 7.23 ppm (5 H, complex multiplet).

Anal. Calcd for $C_{17}H_{20}O_2$: C, 79.65; H, 7.86. Found: C, 79.63; H, 7.77.

o-Hydroxydiphenyl ether was prepared by the method of Norris, *et al.*[48] Sublimation followed by recrystallization gave white needles, mp 104.5–105° (lit.[48] 105–106°).

Phenol used in calibration for quantum yields was purified by sublimation.

Bis(trimethylsilyl)acetamide (Pierce Chemical Co.) was purified by distillation. The middle fraction (bp 69–70° (40 Torr)) was retained and stored under nitrogen.

1-Butanethiol (MCB), *o*- and *p*-hydroxyacetophenones and *o*- and *p*-hydroxybutyrophenones (Aldrich), *p*-hydroxydiphenyl ether (Eastman), and triethylsilane (PCR, Inc.) were used as received from the suppliers.

Irradiations. Irradiations of solutions were made following one of two general procedures depending upon the nature of the experiment. Most of the general work and quantum yields were done *via* a degassed sealed tube technique. When large amounts of photoproducts were required, a reactor was employed. The techniques employed for the gas-phase irradiations in this work utilized either a gas bulb or a flow system.

Vapor Phase Flow System. The flow system (Figure 3) consists of three major subunits: a vaporizer–mixer, an irradiation chamber, and a trap. The vaporizer portion was a tubular vessel which held *ca.* 15 ml of the substrate through which nitrogen was passed by means of a glass frit on the end of an immersion tube. The nitrogen flow was carefully controlled and the rate was monitored by means of a flow meter. The vaporizer tube was kept at a constant elevated temperature by means of an oil bath. The vaporized substrate was carried out of the tube by the nitrogen flow into the first mixing bulb where isobutane and the major nitrogen carrier flow, which controlled the residence time in the irradiation tube, were added. All gas flows were controlled and monitored by flow meters. The mixture of gases and substrate vapor was passed through two more mixing bulbs before entering the irradiation tube. The entire mixing bulb assembly and connecting tube from the vaporizer were wrapped with Chromel-A wire and heated to a temperature of *ca.* 90°. The gas mixture upon leaving the last mixing bulb entered one end of the 51 cm × 5.0 cm diameter cylindrical quartz irradiation tube of 960 cm^3 volume which was surrounded by a battery of three Ultraviolet Products PCQ-XI 254-nm lamp units.[49] This quartz tube was similarly wound with Chromel-A wire and heated to about 80°. After a specified residence time in the irradiation chamber, the gas mixture emerged at the opposite end and entered the trap. The trap consisted of a length of 14-mm diameter Pyrex tube bent in a "zig-zag" shape and was packed with glass helices. The input end had a female ground glass joint and the first 10 cm was heated by means of a Chromel-A wire winding to about 80°; the output end was fitted with a male ground glass joint and connected to a drying tube. The entire zig-zag section of the trap was half-buried in powdered Dry Ice, with the upper loops of the zig-zag exposed to room temperature air. A styrofoam "beer cooler" with an added baffle was found to make an ideal container for the trap and Dry Ice. Such a configuration required the vapors to be alternately exposed to warm and cold sections as they proceeded through the trap, thereby minimizing aerosol formation. In practice, most of the material was trapped in the first cold loop and essentially no material passed beyond the second one. At the completion of the irradiation, the trap was removed, warmed to room temperature, and, finally, the drying tube was removed and exchanged for a 100-ml round-bottomed flask containing anhydrous ether. The trap was clamped in a vertical position and a reflux condenser with a drying tube was placed in the upper female joint. The trap contents were extracted by refluxing ether through the trap. A few hours of refluxing were sufficient for quantitative removal of the trapped compounds.

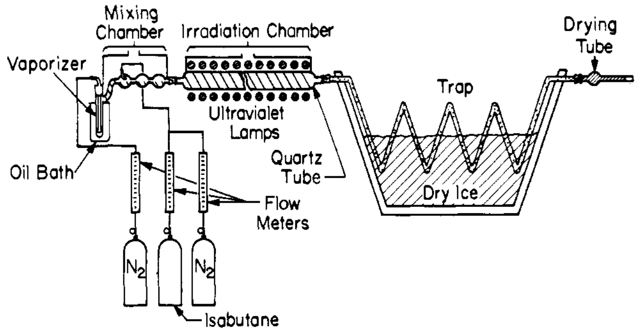

Figure 3. The gas-phase flow system.

Photolysis of Phenyl Acetate (Vapor). Phenyl acetate (8.8 g) was placed in the vaporizer of the flow system. The heating wire on the system was adjusted to give a temperature of *ca.* 80–90°, and the vaporizer oil bath was set at 40°. The flows were adjusted to give 100 cm^3/min of nitrogen through the vaporizer, 30 cm^3/min of isobutane, and 900 cm^3/min of main carrier nitrogen, giving a total flow rate of 1030 cm^3/min and an irradiation residence time of 56 sec. The bath around the trap was filled with *ca.* 30 lb of Dry Ice and the baffle was inserted. The lamps were turned on, and the irradiation was continued for 48 hr. In that time 3.08 g (7.9×10^{-6} mol/min) was collected in the trap; this value is in agreement with approximate measurements of ester depletion in the vaporizer.

Instruments. Infrared spectra were obtained with either a Perkin-Elmer 257 grating infrared spectrometer or a Beckman IR-7 infrared spectrometer. A Varian A-60-A spectrometer was used to record nmr spectra. Ultraviolet spectra were obtained with a Cary-14 recording spectrophotometer. Melting points were taken on a Thomas-Hoover melting point apparatus or a hot stage microscope and are uncorrected. Emission spectra measurements were made on an Aminco-Bowman spectrophotofluorometer with a phosphorescence accessory.

Flash spectroscopy and double-flash spectroscopy were carried out with an instrument from this laboratory. The apparatus and general technique of making the measurements have been previously described.[50]

The electron paramagnetic resonance spectrum of phenyl *n*-butyrate in benzene was obtained while being irradiated with ultraviolet light with an apparatus from this laboratory.[51]

Mass spectra of some of the products in the mixture resulting from the gas-phase irradiations of phenyl acetate were obtained from a combination gas chromatograph–mass spectrometer. A Hewlett-Packard Model 7620A temperature programming research gas chromatograph, interfaced with an EAI Quad 300 quadrupole mass spectrometer, was employed for the determinations.

Gas Chromatography. Photoproduct formation from liquid phase scavenging experiments, phenyl benzoate quantum yields, and trapped photoproducts from the gas-phase irradiations were analyzed quantitatively by gas chromatography (glpc).

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[48] J. F. Norris, B. G. Macintire, and W. M. Corse, *Amer. Chem. J.*, **29**, 120 (1903).

[49] PCQ-XI lamps are manufactured by Ultraviolet Products, Inc., San Gabriel, Calif.

[50] C. C. Wamser, Ph.D. Thesis, California Institute of Technology, Pasadena, Calif., 1970.

[51] S. A. Weiner and G. S. Hammond, *J. Amer. Chem. Soc.*, **90**, 1659 (1968); **91**, 986 (1969).

Quantum Yields. Samples of phenyl benzoate (0.1 M) in various solvents were irradiated by means of the sealed tube technique with a 254-nm "merry-go-round" apparatus. Light intensities of *ca.* 6.1×10^{-8} einstein/min were monitored throughout the irradiation period with potassium ferrioxalate actinometry.[52] Consumption of ester and conversions to nonphenolic products were measured directly by glpc. Phenolic products resulting from the irradiation were analyzed by first converting them quantitatively to their more volatile trimethylsilyl ethers, by the action of bis(trimethylsilyl)acetamide, which were determined by gas chromatography. Measurement of peak areas from the chromatograms was made by means of either the cutting and weighing technique or by using a Disc integrator. Triplicate data points were taken for each value.

The inclusion of an internal standard in the solutions provided accurate values of the amounts of conversion for measured volumes of solution. Comparison of these values with calibration curves for each compound gave the concentration of photoproducts in each sample. By plotting the millimoles of conversion *vs.* millieinsteins of light, extrapolating the curve to zero at zero time, and measuring the slope, we obtained the quantum yields at low conversion.

Silylation of Phenols with Bis(trimethylsilyl)acetamide (BSA).[53] A 2-ml aliquot of the photolyzed solution (typically 0.1 M in phenyl benzoate) was placed in a 5-ml serum bottle fitted with a serum cap. To this sample 0.5 ml of purified BSA was introduced through the cap by means of a syringe and needle. (An additional 1 ml of BSA was added to those samples which contained acid.) The bottle was agitated a few seconds and allowed to stand for 24 hr. Independent experiments showed that this period was sufficient to assure quantitative conversion of the sample.

Detection of Gases Resulting from Photodecarbonylation. The hydrocarbon gases resulting from photodecarbonylation in phenyl *n*-butyrate solutions were qualitatively analyzed by coincident injection of authentic gas samples with injections of the solutions containing dissolved gases on a silica gel column. Enhanced peak heights without a change in the shape were taken as strong evidence of the identity of the gas.

Measurement of Carbon Monoxide. Measurement of carbon monoxide produced by irradiation of phenyl acetate vapor in the flow system was made by channeling the effluent gas from the drying tube through a three-necked flask. The center neck of the flask contained a punctured serum cap through which a carbon monoxide analyzer tube could be placed. A Bacharach Universal Gas Sampler No. 1907016 with potassium palladosulfite type carbon monoxide sampling tubes No. 19-0195 permitted measurement of concentrations to 10 ppm. The unit is manufactured by the Bacharach Instrument Co., Pittsburgh, Pa.

Identification of Gas-Phase Photoproducts. All photoproducts were isolated by preparative gas chromatography and compared to authentic samples. Identical nmr, ir, and mass spectra for the isolated materials and an authentic sample along with coincident retention times on three different glpc columns constituted positive identification of the photoproducts.

Acknowledgments. This work was supported by the National Science Foundation, the U. S. Army Research Office-Durham, and by a graduate fellowship awarded to J. W. M. by the National Defense Education Act. We are grateful to Professor Norman Davidson for his helpful suggestions concerning the design of the flow reactor.

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The E2C Mechanism in Elimination Reactions. III.[1] Dehydrobromination of *tert*-Butyl Bromide in Acetone

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Canberra, Australia. Received October 13, 1970

Abstract: Rates of E2C-like dehydrobromination of *tert*-butyl bromide by bases in acetone containing 2,6-lutidine have been studied. The reactions are bimolecular, with both base and *tert*-butyl bromide present in the transition state. This is confirmed by solvent and salt effects on rate and by the dependence of rate on the nature and concentration of the base. Rate constants for elimination decrease in the order of bases: $SC_6H_5 > CH_3CO_2 >$ CN, Cl $>$ NO_2, $N_3 > OC_6H_4NO_2\text{-}p > SC_6H_4NO_2\text{-}p >$ Br $>$ I, SCN $> C_5H_5N$, 2,6-lutidine. This order correlates poorly with nucleophilic tendencies toward carbon in a tight transition state, *e.g.*, in the SN2 reactions of *n*-butyl bromide, nor is there a Brønsted correlation between these elimination rates and the basicity toward hydrogen of these bases. There is a good correlation of rates of elimination from *tert*-butyl bromide with rates of bimolecular substitution in cyclohexyl tosylate by these bases. The effects of ion association on rates of E2 and SN2 reactions in acetone are different when tetrabutylammonium, rather than lithium salts, are the source of base. Transition-state anions associate with NBu_4^+ to much the same extent as do reactant anions. However, Li^+ associates much more strongly with many reactant anions than with E2C or SN2 transition-state anions. The initial E2C-like reaction of *tert*-butyl bromide with chloride ion is an endo energetic process.

The pioneering studies of Hughes and Ingold[3] are largely responsible for the interest in the substitution and elimination reactions of *tert*-butyl bromide.[3-11]

This paper describes some bimolecular reactions of *tert*-butyl bromide in the presence of electrolytes in

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(1) Part II: G. Biale, D. Cook, D. J. Lloyd, A. J. Parker, I. D. R. Stevens, J. Takahashi, and S. Winstein, *J. Amer. Chem. Soc.*, 93, 4735 (1971).

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