

affords the theoretically expected mean variance. The ratio of SSQR:SSQP ideally should approach unity but normally will be higher. Presently values of this ratio below 3 were considered acceptable.

Temperature Dependence of Optical Density. The absorption spectra of the triphenyl diene **1** and the 1,1,5,5-tetraphenyl diene **4** were measured at 77°K and at room temperature. The absorbance at low temperature (1.4 for **1** and 1.3 for **4**) is greater than that at room temperature (0.95 for **1** and 1.05 for **4**) presumably due to contraction of the sample, effectively increasing the concentration. The spectra were taken on a Cary 11MS purged with dry nitrogen, first at low temperature and then after allowing the sample to warm to room temperature without moving either the cell or the dewar flask.

Optical Density Dependence of Emission Intensity. The emission spectrum of the triphenyl diene **1** was measured as a function of the optical density in the range 0.9–1.5, under conditions similar to those employed for measuring the magic multipliers (*vide supra*). The emission intensities, expressed in arbitrary units, were: OD = 0.9, 24; OD = 1.2, 16.5; OD = 1.5, 17.

Polarization. A set of Glan prisms was interposed in the excitation and emission beams of the Aminco-Kiers spectrofluorometer. The solutions were made to give an optical density of 1.0 at the wavelength of excitation. The degree of polarization was measured by the method of Azumi and McGlynn.²⁵ For naphthalene (λ_{ex} 312 nm) the degree of polarization increased from zero at room temperature to 0.30 at 77°K. For the triphenyl diene **1** (λ_{ex} 270 nm) the degree of polarization was constant within experi-

mental error: 0.46 at room temperature and 0.31 at 77°K. The degree of polarization at room temperature was 0.28 for the 1,1,3,3-tetraphenyl diene.

Refractive Index Effect on Emission Intensity. A concentrated suspension of fumed silica (Cab-O-Sil Grade M-5, Cabot Corp.) in 4:1 methylcyclohexane–isopentane (45 mg/ml) was prepared as a scatterer. The amount of light scattered at 310 nm was monitored, in arbitrary units, as 6.7 and 6.4, respectively, at room temperature and at low temperature. The magic multiplier of a solution of 9,10-diphenylanthracene (OD = 1.5 at the excitation wavelength, 360 nm) was found to be 1.07 which is not different from unity within experimental error.

The absence of a temperature dependence of emission intensity due to refractive index effects seems to derive from two sources. The usual source of decreased emission intensity assumes perfectly collimated input light reaching the cell while presently the less than perfectly parallel light of the Aminco instrument leads to a counterbalancing increase of light intensity within the cell with increasing glass refractive index. Also, the liquid nitrogen present in the low-temperature runs was found to reduce reflection losses.

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(25) T. Azumi and S. P. McGlynn, *J. Chem. Phys.*, **37**, 2413 (1962).

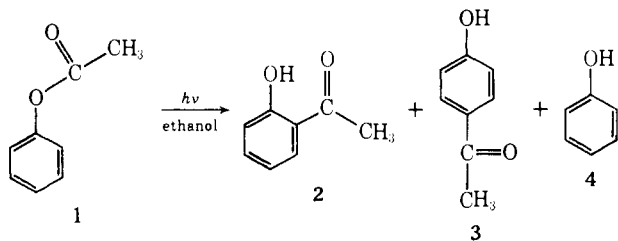
A Mechanistic Study of the Photo-Fries Rearrangement of Phenyl Acetate¹

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Abstract: Evidence is presented for a radical mechanism for the photo-Fries rearrangement of phenyl acetate. Phenoxy radicals were observed in the flash spectra of phenyl acetate in ethanol, hexane, and Freon. An additional transient was identified as a cyclohexadienone, which decayed into *o*-hydroxyacetophenone with a first-order rate constant of $1.25 \pm 0.1 \text{ sec}^{-1}$. An inverse correlation between fluorescence yield of aryl ethers and photochemical yield indicates the photo-Fries reaction proceeds from an excited singlet state. Viscosity effects, coupled with the radicals observed, argue against the "concerted" mechanism. Arguments are presented that the photo-Fries rearrangement is only one example of a general rearrangement of compounds of the type, ArO–X, involving homolytic cleavage to yield radicals ArO· and X· which may recombine or react independently. The role of the solvent cage in these reactions is strongly emphasized.

The photo-Fries rearrangement was first observed by Anderson and Reese in 1960.² A simple example is the rearrangement of phenyl acetate in ethanol to give *o*- and *p*-hydroxyacetophenones and phenol.



(1) (a) Taken in part from the Ph.D. Thesis of C. E. K., M.I.T., Cambridge, Mass., 1971; (b) preliminary results reported: C. E. K. and D. M. H., *Tetrahedron Lett.*, 1575 (1972).

(2) J. C. Anderson and C. B. Reese, *Proc. Chem. Soc., London*, 217 (1960).

Since the initial discovery, a large body of literature has appeared concerning the scope and mechanism of this reaction. The rearrangement has been found to occur for many derivatives of phenol: phenyl esters,^{3–5} aryl alkyl carbonates,^{6,7} phenoxyacetic acids,⁸ and hydroxyphenyl cinnamates.⁹ A recent review of the photo-Fries rearrangement has been published by Bellus.¹⁰

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

(4) J. C. Anderson and C. B. Reese, *Proc. Chem. Soc., London*, 1781 (1963).

(5) R. A. Finnegan and J. J. Mattice, *Tetrahedron*, **21**, 1015 (1965).

(6) C. Pac and S. Tsutsomi, *Bull. Chem. Soc. Jap.*, **37**, 1392 (1964).

(7) E. A. Caross and I. E. Rosenberg, *J. Org. Chem.*, **36**, 769 (1971).

(8) D. P. Kelley and J. T. Pinhey, *Tetrahedron Lett.*, No. 46, 3427 (1964).

(9) H. Obara, H. Takahashi, and H. Hirano, *Bull. Chem. Soc. Jap.*, **42**, 560 (1969).

(10) (a) D. Bellus, *Advan. Photochem.*, **8**, 109 (1971); (b) J. J. Houser and M. C. Chen, *Chem. Commun.*, 1447 (1970).

It has been long established that the photo-Fries rearrangement is intramolecular.^{3,4} The nature of the reactive excited state has been in dispute. The reactive state does not appear to be a triplet since attempts to quench the rearrangement with triplet quenchers such as naphthalene, ferric acetylacetonate,¹¹ and 1,3-cyclohexadiene¹² have been unsuccessful. Attempts at triplet sensitization with acetophenone were also unsuccessful.^{11b,13}

Basically, two mechanisms have been proposed for the photo-Fries rearrangement. The first mechanism was that of a homolytic cleavage of the excited molecule occurring at the ArO-COR bond. The resulting pair of radicals would be restrained by a solvent cage until they combined to form rearrangement products and starting material, or else the radical pair would drift apart and the phenoxyl radical would eventually abstract a hydrogen atom to form phenol.³

A second mechanism views the formation of rearranged products as occurring in a concerted manner. In this mechanism, the excited molecule rearranges while maintaining a bond between the phenyl and acetyl moieties at all times. Formation of phenol and perhaps para-rearranged product could occur as a result of a homolytic cleavage and hydrogen abstraction.¹³ According to this mechanism processes leading to formation of phenol or rearranged products would represent competitive deexcitation pathways.

The work reported here indicates that homolytic cleavage leads both to rearrangement and phenol formation in phenyl acetate. We have observed both the phenoxyl radical (ArO·) and a cyclohexadienone intermediate using flash photolysis. We also present evidence that the reactions of photo-Fries rearrangement occur from only one excited state. Preliminary results of our work have been communicated.^{1b} Humphrey and Roller have reached analogous conclusions from flash studies on bis(4-*tert*-butylphenyl) carbonate.¹⁴

Results

Table I presents uv absorption and fluorescence data for phenyl acetate and some related compounds. Phenyl acetate had identical absorption spectra in ethanol, hexane, and 1,1,2-trichlorotrifluoroethane (Freon). It showed no shoulder at longer wavelengths. Phenyl acetate showed no fluorescence in ethanol or hexane when *carefully purified*. Apparent fluorescence of phenyl acetate is caused by traces of phenol. The absorption maximum of *o*-hydroxyacetophenone (*o*-OHA) is at 325 nm in all solvents. Neither of the other photo-Fries rearrangement products, phenol and *p*-hydroxyacetophenones (*p*-OHA), absorbs significantly at 325 nm.

Photolysis of Phenyl Acetate. Photolysis of either oxygenated or deoxygenated 1–3 × 10⁻³ M solutions of phenyl acetate (PA) in ethanol, hexane, or Freon for less than 5 min resulted in the appearance of only three products as determined by gc-mass spectrometry.

(11) (a) D. A. Plank, *Tetrahedron Lett.*, 4365 (1969); (b) M. R. Sandner, E. Hedaya, and D. J. Trecker, *J. Amer. Chem. Soc.*, **90**, 7249 (1968).

(12) H. J. Hageman, *Tetrahedron*, **25**, 6015 (1969).

(13) M. R. Sandner and D. J. Trecker, *J. Amer. Chem. Soc.*, **89**, 5725 (1967).

(14) J. S. Humphrey and R. S. Roller, *Mol. Photochem.*, **3**, 35 (1971).

Table I. Absorption and Fluorescence Spectra for Phenoxy Derivatives in Hexane

Compd	Uv absorption		Fluorescence	
	λ, nm	Molar absorptivity, ε	λ, nm	Rel quantum yield
Phenol	265	1,970	293 ^a	1.00 ^a
	271			
	278			
Phenyl ether	264	1,900	291	0.41
	271			
	278			
Allyl phenyl ether	264	1,840	290	0.10
	271			
	278			
Phenyl acetate	259	230	None	None
	266			
<i>o</i> -Hydroxyacetophenone	325	3,900	None	None
	249			
<i>p</i> -Hydroxyacetophenone	258	13,500	None	None

^a In Freon phenol also fluoresces at 293 nm; relative quantum yield is 0.1.

These were identified as phenol, *o*-OHA, and *p*-OHA (2, 3, and 4). The uv absorption spectra of solutions after photolysis could be reproduced quantitatively by linear combinations of the spectra of the three products and the starting material.

Separate solutions of each of the three products were prepared in ethanol, hexane, and Freon at concentrations equal to those formed by a 5-min irradiation of a 3 × 10⁻³ M solution of phenyl acetate. All three products in ethanol and hexane were stable when irradiated for as long as 15 min at these concentrations. In Freon, after only a 1 min irradiation, *o*-OHA showed less than 5% decomposition, but both phenol and *p*-OHA were more than 50% decomposed. Longer irradiation times in all solvents produced decomposition.

Since *o*-OHA had an absorption maximum at 325 nm in all three solvents where neither phenyl acetate nor the other two products absorbed, it was possible to monitor formation of *o*-OHA directly by spectrophotometry. Formation of phenol and *p*-OHA also were monitored spectrophotometrically by solution of a set of simultaneous equations. Absorbance values at 298, 266, 254, and 244 nm were used. These values are for ethanol; sufficient ethanol was added to other solvents to validate use of these wavelengths.

From concentration *vs.* photolysis time plots, the estimated slopes at *t* = 0 were used to obtain quantum yields for each species relative to *o*-OHA. These data are summarized in Table II. The absolute quantum yield of *o*-OHA formation in ethanol has been determined by Shizuka.¹⁵ His value of 0.14 mol/einstein was used as reference. Except possibly for the formation of *p*-OHA in hexane, there was no significant effect of oxygen on the quantum yield of any product. Even though the slopes were extrapolated to *t* = 0, the instability of *p*-OHA and phenol in Freon would cause their observed quantum yields of formation to be lower than they actually were. Since their decomposition in 1 min was about 50%, the actual quantum yields in Table II are estimated to be twice the observed values, as indicated in brackets.

(15) H. Shizuka, T. Morita, Y. Mori, and I. Tanaka, *Bull. Chem. Soc. Jap.*, **42**, 1831 (1969).

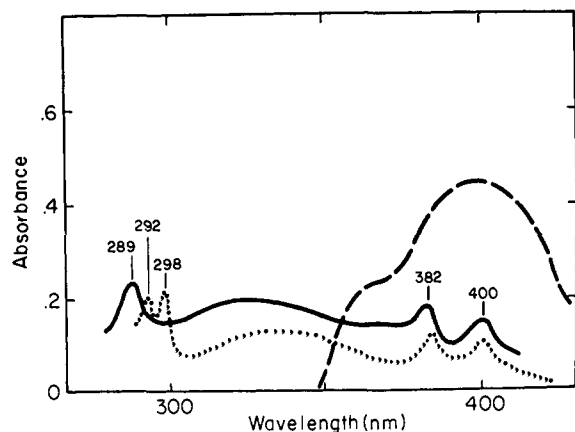


Figure 1. Flash spectra of phenyl acetate and phenol in ethanol, 15 μ sec delay time: phenyl acetate ($1.7 \times 10^{-3} M$) (—) first flash, (---) second flash; phenol ($2 \times 10^{-4} M$) (.....).

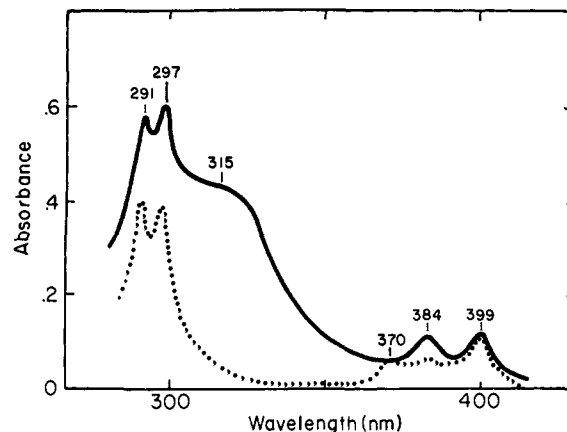


Figure 2. Flash spectra of phenyl acetate and phenol in hexane, 15 μ sec delay time: phenyl acetate ($1.7 \times 10^{-3} M$) (—); phenol ($2.0 \times 10^{-4} M$) (.....).

Table II. Relative Quantum Yields of Formation of Phenyl Acetate Photolysis Products

Conditions	<i>o</i> -OHA	mol/einstein	
		<i>p</i> -OHA	Phenol
Ethanol			
(oxygenated)	0.14 ^a	0.10 ± 0.02	0.09 ± 0.03
(deoxygenated)	0.14 ^a	(0.10 ± 0.02)	(0.09 ± 0.03)
Hexane			
(oxygenated)	0.18 ± 0.02	$(0.02 \pm 0.01)^b$	0.23 ± 0.07
(deoxygenated)	0.18 ± 0.02	$(0.05 \pm 0.01)^b$	0.23 ± 0.07
Freon			
(oxygenated)	0.14 ± 0.02	0.03 ± 0.01	0.09 ± 0.03
(deoxygenated)	0.14 ± 0.02	$[0.06]^c$	$[0.18]^c$

^a Literature reference value.¹⁶ ^b Determined by glpc. ^c Estimated values.

To see if product distribution was dependent on the energy of the exciting radiation, oxygenated solutions of phenyl acetate in ethanol ($3.5 \times 10^{-3} M$) were irradiated at 270, 254, and 232 nm with a bandpass of 10 nm. These wavelengths were chosen to blanket the longest wavelength absorption of phenyl acetate. This long wavelength absorption band is the only phenyl acetate absorption that overlaps with the emission from either a xenon flash lamp or a 253.7-nm mercury arc lamp. The product ratios after irradiation at each wavelength were determined spectrophotometrically. Irradiation times were increased at the shorter wavelengths to make up for a deficiency in the energy output of the lamp and thereby achieve a 0.5% decomposition of phenyl acetate at each wavelength. The product concentration ratios are in Table III. Within the experimental error, no changes in the product ratios were observed.

Flash Photolysis Studies. Transient species in the photolysis of PA in ethanol, hexane, and Freon were

Table III. Irradiation of Phenyl Acetate in Ethanol at Different Wavelengths

Wavelength, nm	Time, hr ^a	(<i>p</i> -OHA)/(<i>o</i> -OHA)	(Phenol)/(<i>o</i> -OHA)
270	1.0	0.54 ± 0.02	0.9 ± 0.2
254	1.2	0.54 ± 0.02	0.8 ± 0.2
232	3.0	0.56 ± 0.02	1.0 ± 0.2

^a Irradiation time increased at shorter wavelengths to achieve 0.5% decomposition of PA.

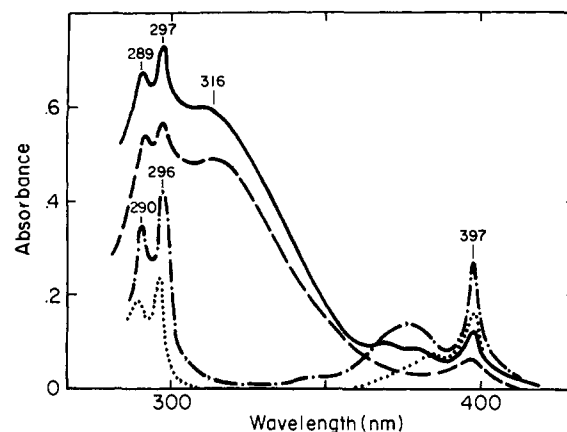


Figure 3. Flash spectra of phenyl acetate and phenol in Freon, 15 μ sec delay time: phenyl acetate ($1.7 \times 10^{-3} M$) (—) deoxygenated, (---) oxygen present; phenol ($2.0 \times 10^{-4} M$) (.....) deoxygenated, (- · - · -) oxygen present.

studied by flash photolysis. The three photolysis products of phenyl acetate, phenol, *o*-OHA, and *p*-OHA, were also investigated for transients by flash spectroscopy. Solutions of phenyl acetate were $1.7 \times 10^{-3} M$ and were deoxygenated by the freeze-pump-thaw method. Solutions of phenol were $2.0 \times 10^{-4} M$ and similarly deoxygenated. Each solution was observed with a spectral flash at a delay time of 15 μ sec measured peak-to-peak from the excitation flash. The transient absorption spectra produced by flash irradiation of separate solutions of phenyl acetate and phenol in ethanol, hexane, and Freon are shown in Figures 1, 2, and 3, respectively. Also in Figure 1 is shown the transient absorption spectrum observed when the solution of phenyl acetate in ethanol was flash photolyzed a second time. In hexane and Freon, second flashes produced transient absorption spectra identical with those produced by the first flash.

The flash spectra of phenol in all three solvents are very similar, and the major peaks correspond to values published for the phenoxyl radical.¹⁶ It is also clear from Figures 2 and 3 that the same transient is produced in the photolysis of PA in hexane and Freon. It is also apparent that there is an additional transient

(16) E. J. Land, G. Porter, and E. Strachan, *Trans. Faraday Soc.*, **57**, 1885 (1961).

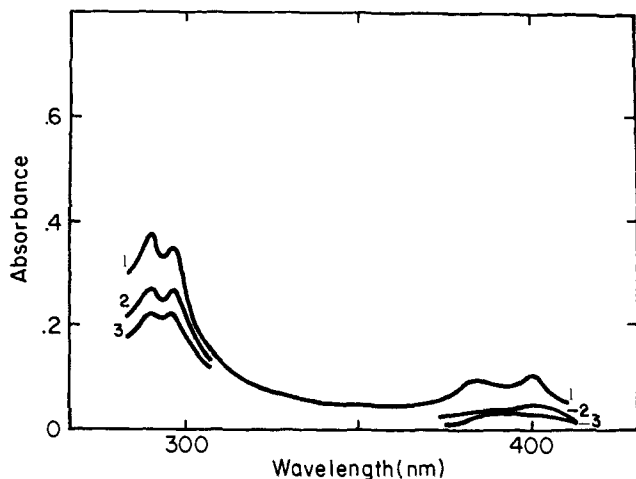


Figure 4. Transient absorption for phenol in hexane at various delay times, concentration $2.0 \times 10^{-4} M$. Delay times: 1, 15, 2, 30, and 3, 60 μsec .

in the spectrum of PA in these solvents, causing the absorption band at *ca.* 315 nm. In ethanol, the *ca.* 290-nm portion of the spectrum from PA does not match well with the phenol transient, but the *ca.* 390-nm section does. From these spectra, it is clear that the band pairs 291–297 and 382–398 nm constitute strong evidence for the phenoxy radical. The presence of oxygen significantly reduced the transient absorption intensity from both PA and phenol.

Figure 4 shows the transient absorption from oxygenated solutions of phenol in hexane at 0.015, 0.030, and 0.060 msec delay after the excitation flash. From Figure 4, the lifetime for the phenoxy radical in oxygen saturated hexane was determined to be 0.1–0.2 msec. When oxygen was removed, the lifetime was increased to 0.2–0.3 msec. Figure 5 shows the transient spectra from an oxygen saturated solution of phenyl acetate in hexane observed at 0.015, 0.13, 2.5, and 7.0 msec after the excitation flash. The phenoxy radical from phenyl acetate had a lifetime similar to that from phenol. However, transient absorption centered at 305 nm persisted long after the phenoxy radical had disappeared.

An oxygenated $3.5 \times 10^{-3} M$ solution of PA in hexane was used to observe the decay of the 305-nm transient and the formation of *o*-OHA. Oxygen was allowed to remain in solution to shorten the lifetime of the phenoxy radical. To reduce mutual interferences, the 305-nm transient was monitored at 295 nm, and *o*-OHA at 335 nm. The flash system was operated in the spectrophotometric mode. A plot of $\ln(A_{295})$ vs. time gave a straight line with a slope of $1.25 \pm 0.05 \text{ sec}^{-1}$, corresponding to the rate constant for decay of the 305 intermediate. A plot of $\ln(A_{325,\infty} - A_{325})$ vs. time gave a straight line with a slope of $1.25 \pm 0.1 \text{ sec}^{-1}$ corresponding to the rate constant for appearance of *o*-OHA must be derived from the 305 intermediate.

The two rearrangement products, *o*-OHA and *p*-OHA, were flash photolyzed to determine if they produced transients which would interfere with the transient absorption spectra from phenyl acetate. A solution of *o*-OHA in hexane produced no transient absorption. Flash photolysis of *p*-OHA in Freon produced a weak transient absorption at 290 nm, while flash photolysis of *p*-OHA in ethanol produced an in-

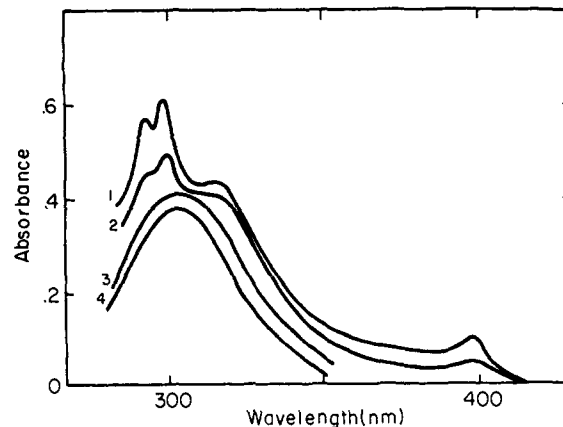


Figure 5. Transient absorption spectra for phenyl acetate in hexane at various delay times, concentration $1.7 \times 10^{-3} M$. Delay times: 1, 15 μsec , 2, 130 μsec , 3, 2.5 msec, and 4, 70 msec.

tense transient absorption centered at 400 nm. When phenyl acetate was flash photolyzed in ethanol, this 400-nm transient was not apparent until the solution was flashed a second time so that the rearranged product from the first flash was being excited. Therefore one may conclude that *o*-OHA and *p*-OHA did not cause any transient absorptions in the first flash absorption spectra from phenyl acetate.

Discussion

Three different types of mechanisms have been proposed for the photo-Fries rearrangement. Briefly, they are: (1) irradiation produces a pair of radicals held together by a solvent cage which ultimately recombine to form rearrangement products or drift apart to form phenol; (2) a concerted mechanism in which the excited molecule rearranges, retaining some form of bonding between fragments at all times; (3) a dual pathway in which the different products are formed from different excited states. Our results indicate that the photo-Fries rearrangement is a general reaction of the phenoxy ($\text{ArO}\cdot$) functional group of ArO-X . Although the nature of the X group can affect the rearrangement, the primary site of the reaction is the phenoxy group. Our observations are consistent with homolytic cleavage at the ArO-X bond, forming two radicals held together by a solvent cage. Recombination of these radicals produces the rearranged products.

Much of the literature published on the photo-Fries rearrangement is of questionable value for mechanistic interpretations. Often irradiation times used ranged from several to hundreds of hours. Photo-Fries products absorb radiation at the same wavelengths as the starting material, usually 10–100 times more strongly. After conversion of a few per cent of starting material to products (which usually takes 1 min or 2), most exciting radiation will be absorbed by products. After hours of irradiation, there is no reason to expect that the product distribution will show any similarity to the distribution initially present. To derive a mechanism on the basis of the products of a reaction, it is the products initially formed that are important. Our results indicate that the products are photoreactive. Therefore, when discussing literature results, only those using short irradiation times are considered.

The concerted mechanism was proposed⁴ because of

insensitivity of ortho rearranged product yield to solvent. Conversely, it has been shown that the formation of phenol depends on solvent viscosity. In a solid polyethylene matrix, phenols were not observed after irradiation of substituted phenyl benzoates.¹⁷ At the other viscosity extreme, the vapor phase, phenol was the major product of irradiation of phenyl acetate and no rearranged products were observed.¹⁸ Photoinduction of other types of rearrangements have been observed in the gas phase.¹⁹ In a study using solvents having different viscosities but similar polarities, the quantum yield of phenol formation decreased from 0.09 mol/einstein in 2-propanol (viscosity = 1.73 cP) to 0.02 mol/einstein in Carbowax 600 (109 cP).¹⁴ These results are consistent with diffusion of the phenoxyl radical out of the solvent cage to produce phenol.

Calculations of the spin density of the phenoxyl radical show the unpaired electron density at the ortho and para positions, not the meta.²⁰ Therefore, if the two radicals are held together in a cage, it is likely that recombination at the ortho and para positions would occur. The observed lack of sensitivity of the ortho product to the solvent viscosity can be accounted for by the "radicals in a cage" mechanism. After cleavage of the parent molecule, the leaving fragment initially would be close to the ortho position, making rapid recombination at the ortho position possible. This would be expected to minimize any effect of solvent viscosity on ortho product formation. Considering these data and arguments, we believe a mechanism other than homolytic cleavage and cage recombination should be postulated only on the basis of strong positive evidence.

The Nature of the Reactive Excited State. The long wavelength absorption bands of phenols, phenyl ethers, and phenyl esters are very similar. The shape of the bands in ethanol consists of a peak with at least one shoulder on either side, showing similar spacings between the peak and the shoulders (see Table I). Molar absorptivities and wavelength maxima for phenols and phenyl ethers are roughly the same. The absorption maxima for phenyl esters are shifted to shorter wavelengths by about 10 nm and the molar absorptivity is reduced by about a factor of 10. These differences can be explained by a σ -inductive effect of the carbonyl and possibly by a steric effect of the carbonyl twisting the lone-pair p electrons of the phenoxy oxygen out of the plane of the ring. However, the lowest energy electronic transitions for phenol and its derivatives are all basically the same transition.

The lowest energy transition for phenols is a $\pi \rightarrow \pi^*$ benzenoid transition with the lone-pair p electrons of the oxygen atom considered as part of the π system.²¹ The net effect of the transition is a displacement of electron density from the oxygen atom into the π system of the ring; *i.e.*, a charge-transfer (CT) state. Porter and coworkers observed that irradiation of phenol results in homolytic bond cleavage to form the neutral phenoxyl radical;¹⁶ the pK_a of phenol changes

(17) G. M. Coppinger and E. R. Bell, *J. Phys. Chem.*, **70**, 3479 (1966).

(18) J. W. Meyer and G. S. Hammond, *J. Amer. Chem. Soc.*, **92**, 2189 (1970).

(19) H. Shizuka, M. Kato, T. Ochai, K. Matsui, and T. Morita, *Bull. Chem. Soc. Jap.*, **43**, 67 (1970).

(20) T. J. Stone and W. A. Waters, *J. Chem. Soc.*, 213 (1964).

(21) H. H. Jaffe and M. Orchin, "Theory and Applications of Ultraviolet Spectroscopy," Wiley, New York, N. Y., 1962, Chapter 12.

from 10.0 in the ground state to 4.0 in the first excited singlet state;²² both are consistent with the CT model.

A mechanism proposed recently views the photo-Fries rearrangement as occurring from two different excited singlet states of the parent molecule.¹⁰ The higher energy excited state would lead to bond dissociation and phenol formation, and the lower excited state would form rearranged products by a concerted, continuously bonded process. If two different electronic excited states are leading to different products, selective excitation by monochromatic radiation should produce mainly those products from the particular state that is being populated. Irradiating PA with varying wavelengths produced no significant variation in product yield, as indicated in Table III. Therefore it seems unlikely that two singlet states of PA are involved.

Phenols and some phenyl ethers are strong fluorescers. However, phenyl acetate was not observed to fluoresce or phosphoresce. The lack of PA fluorescence could be due to quenching by the photochemical reaction or by some involvement of the ester carbonyl. In order to determine the relationship between fluorescence and photochemical activity, we studied a series of phenyl ethers where the carbonyl group could not be involved. The relative fluorescence quantum yields of this series was

phenyl > 2,6-dimethylanisole > phenyl ether >
allyl phenyl ether¹¹ > PA

Conversely, the relative photochemical yields of this series in the photo-Fries rearrangement was

PA > allyl phenyl ether¹¹ > phenyl ether >
2,6-dimethylanisole > phenol

This inverse correlation between fluorescence and photochemical activity clearly indicates that the photo-Fries rearrangement competes as a deexcitation pathway for the excited singlet state of the phenol. The phenols and ethers of the series have integrated intensities for the long wavelength absorption bands that are roughly the same. Therefore, the series of compounds should produce similar intensities of fluorescence. However, their relative quantum yields decreased by a factor of 10 from phenyl to allyl phenyl ether. Coupling this inverse correlation with the inactivity of triplet quenchers^{11,12} and sensitizers,^{11b,13} leads us to conclude that the photo-Fries rearrangement proceeds directly from the lowest excited singlet state of phenyl acetate.

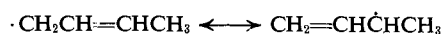
The Primary Photochemical Event. As has been shown in the preceding discussion, the absorption process occurring in the photo-Fries rearrangement is general for the phenoxy (ArO) functional group. The excited molecule would then cleave at the ArO-X bond to form two radicals which may recombine or drift apart. If this view is correct, the "photo-Fries" rearrangement should be general for compounds containing the phenoxy functional group. It would be expected that the order of reactivity of a series of compounds depends on the relative stability of the radical fragment of the X group formed by homolytic cleavage. The more stable the X-radical fragment, the more readily the rearrangement should proceed.

(22) G. G. Guilbault, Ed., "Fluorescence: Theory, Instrumentation and Practice," Marcel Dekker, New York, N. Y., 1967, Chapter 2, p 103.

In the simplest case, phenol, the formation of neutral phenoxy radicals has been shown to be the primary photochemical event.¹⁶ The hydrogen atom and phenoxy radical would recombine to form the starting product.

Rearrangement of simple anisoles has been reported when the X fragment forms a stable radical.^{10a} Also, several alkyl ethers, diphenyl ether, and phenyl benzyl ether photorearrange to yield ortho and para products and phenol.^{23,24} The importance to the photo-Fries rearrangement of this photoinduced Claisen rearrangement of phenyl ethers has not been appreciated.

The photolysis of *trans*-but-2-enyl phenyl ether produced a revealing collection of ortho and para products and phenol.¹¹ Rearrangement to both the ortho and para positions resulted in *cis*-*trans* isomerization of the double bond. Even more important than the *cis*-*trans* isomerization was the addition to the phenyl ring at a secondary carbon of the alkyl chain. By drawing the two resonance structures of the alkyl radical fragment, it is easy to see how the secondary alkyl addition and the *cis*-*trans* isomerization occurred *via* a radical mechanism.



The transient spectra from phenol shown in Figures 1, 2, and 3 are identical with spectra of the phenoxy radical published previously.¹⁶ Phenoxy radical absorption also appears in the transient absorption produced by the flash photolysis of phenyl acetate. The lifetime of the phenoxy radicals produced from phenol was 100–200 μsec while the duration of the exciting flash was 30–50 μsec . If the phenoxy radical leads to phenol product, then a lifetime of 100 μsec for the radical compared to a 50 μsec flash duration would imply that the phenoxy radical observed derived directly from excitation of the phenyl acetate and not from excitation of one of the reaction products.

The observation of phenoxy radicals provides direct evidence for homolytic cleavage. The viscosity effects imply that a cage effect is operative. Therefore the simplest mechanism consistent with all of the data is that of a homolytic cleavage as the primary step, leading both to phenol and the rearrangement products.

Rearrangement of Phenyl Acetate. The quantum yield of *o*-OHA formation was essentially the same in all three solvents. The quantum yield of *p*-OHA formation showed solvent dependence, decreasing from 0.10 mol/einstein in ethanol to 0.02–0.04 mol/einstein in hexane and Freon. Since there is a larger distance involved in para recombination, it would be expected to show a greater need for a strongly caging solvent. Ethanol would produce the strongest solvent cage because of the relatively high degree of molecular association. The nonpolar solvents hexane and Freon would have considerably weaker solvent cages, correlating with the decreased rate of *p*-OHA formation observed: ethanol > hexane \sim Freon.

Formation of phenol was found to increase when *p*-OHA formation decreased. Formation of phenol in-

creased from about 0.09 mol/einstein in ethanol to about 0.23 mol/einstein in hexane. This is consistent with the weaker solvent cage in hexane enhancing escape of phenoxy radicals. Phenoxy radicals, once outside of the cage, abstract hydrogen atoms from solvent molecules.

In Freon, the quantum yield of phenol formation was 0.09 mol/einstein. The sources of hydrogen were probably dissolved water and unreacted ester. Assuming a diffusion controlled abstraction reaction, a phenoxy radical concentration of $10^{-5} M$, and an ester concentration of $10^{-4} M$, less than $10^{-4} M$ of water would account for the observed lifetime of the phenoxy radical. The very weak cage effect expected in Freon should have resulted in a quantum yield of phenol formation comparable to or greater than that observed in hexane. However, a dilute solution of phenol in Freon rapidly decomposed when irradiated. Therefore, a considerable portion of the phenoxy radicals produced by the initial photolysis of phenyl acetate would immediately go to phenol decomposition products. Thus, the quantum yield of formation of phenoxy radicals that escaped from the cage would have been much greater than the quantum yield of phenol formation. The quantum yield of phenoxy radicals observed was *ca.* 0.5 mol/einstein, as opposed to 0.09 mol/einstein for phenol.

The flash spectra of phenyl acetate show a strong absorption band at 305 nm in addition to the phenoxy radical absorption. When oxygenated solutions of phenyl acetate were flashed the phenoxy radical absorption was reduced relative to the 305-nm absorptions as seen in Figure 3. This implies that the species producing the 305-nm absorption was less sensitive to oxygen than the phenoxy radical. It also implies that the mechanism of formation of the species producing the 305-nm absorption was relatively oxygen independent.

In oxygenated hexane the *o*-OHA absorption appeared with a first-order rate constant of $1.25 \pm 0.05 \text{ sec}^{-1}$. Obviously, the species causing the 305-nm absorption was decaying unimolecularly into *o*-OHA. Furthermore, the rates of formation and decay of the transient species producing the 305-nm absorption did not change appreciably in the presence or absence of oxygen.

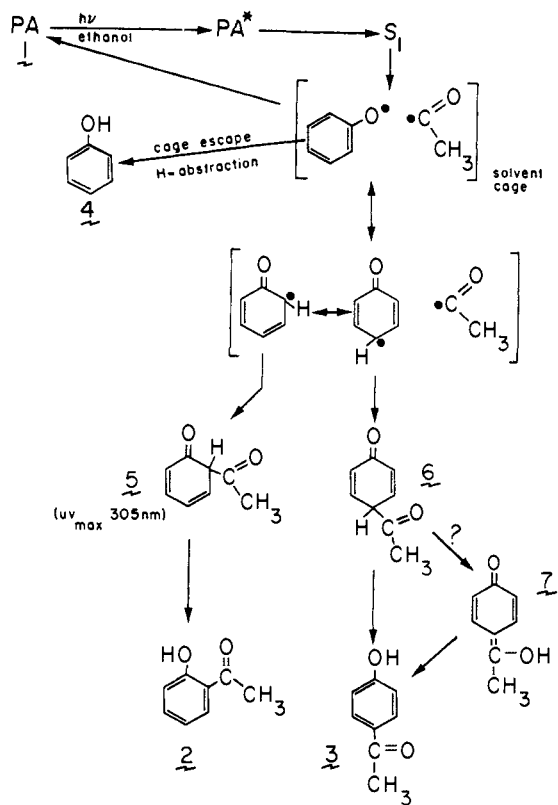
Recombination of the phenoxy and acetyl radicals at the ortho position would produce the cyclohexadienone **5** shown in Scheme I as the logical precursor to *o*-OHA. Using Woodward's rules for conjugated systems, the calculated uv absorption maximum for **5** in hexane is 313 nm. This is close to the observed transient absorption at 305 nm and provides support for the structure of the intermediate. The relative insensitivity to oxygen correlates with the effect of oxygen on the quantum yield of *o*-OHA.

The corresponding intermediate in the formation of *p*-OHA would be **6** in Scheme I. The calculated uv absorption maximum for **6** is 240 nm and the lifetime of **6** would be expected to be longer than **5**. However, due to the strong absorption of phenyl acetate from 240 to 280 nm, it was not possible to observe spectra below 280 nm and the presence or absence of **6** could not be detected. If **6** were being formed, it might tautomerize to **7** before resulting in *p*-OHA. The cal-

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Scheme I. Mechanism of the Rearrangement of Phenyl Acetate



culated absorption maximum for 7 is about 350 nm. No transient absorption was observed in that region which means that 7 was not formed or else decayed immediately into 3.

Scheme I summarizes the mechanism of the rearrangement of phenyl acetate. We feel that this mechanism is general for the rearrangement of phenol derivatives. The mechanism begins with the absorption by the aryloxy (ArO-) portion of the general molecule ArOX. The first excited singlet state cleaves to form two radicals. Some of the radicals drift apart and phenol is formed, while the remainder of the radicals are kept in proximity long enough to recombine. The electron distribution of the phenoxy radical allows recombination at one of three sites either leading back to starting material or to ortho and para rearranged products.

According to this mechanism, any molecule of the ArOX type could rearrange to form ortho and para substituted products. It would be interesting to see if materials such as ortho-deuterated phenol and anisole did rearrange. It is also possible that the rearrangement could occur with complex X groups and also ring type X groups in which the X group is bonded to other portions of the aryl ring.

Experimental Section

Materials. Phenyl acetate (Aldrich) was vacuum distilled and purified by preparative glpc using a $\frac{3}{8}$ in. \times 36 ft Carbowax 600 on Fluoropak column; helium was the carrier gas; collection at 77°K. The collected material was bulb-to-bulb distilled under vacuum and stored in a freezer. Ultraviolet absorption showed the resulting phenyl acetate to be free of phenol.

o-Hydroxyacetophenone (Aldrich) was distilled on a 9-in. Vigreux column under nitrogen. A pale yellow liquid was collected (bp 216° (lit. bp 218°)).

p-Hydroxyacetophenone (Aldrich) was vacuum distilled and then recrystallized twice from phenyl acetate and three times from trichloroethylene. The resulting colorless needles were dried under vacuum (mp 108.2–109.2° (lit. 109°)).

Instrumentation. Ultraviolet absorption spectra were recorded on either a Cary 15 spectrophotometer or a Bausch and Lomb Spectronic 505. Proton magnetic resonance spectra were recorded on a Varian HA-100. Fluorescence spectra were recorded on a Turner Spectro 210. Flash photolysis spectral plates were read using a modified Jarrell-Ash JA-2300 recording microphotometer. The modification, described elsewhere,²⁵ allowed the trace to be recorded with a Moseley 7035B XY recorder. Analytical glpc was done with an Aerograph 1520 using a $\frac{1}{8}$ in. diameter \times 6 ft column of 5% SE-30 on Chromosorb W.

The flash photolysis apparatus is described in detail elsewhere.²⁵ Briefly, it consisted of an excitation flash produced by a Xenon Corp. Model A power supply and a pair of FP-5-100A Xenon Corp. xenon flash lamps. The analyzing flash was produced by a Xenon Corp. Model B power supply driven by a Model D time delay unit and a Suntron 6A xenon flash lamp. The spectrograph was a Hilger-Engis monochromator-spectrograph using a 600 lines/mm grating blazed at 300 nm. The sample was held in a quartz cell. The time delay between the excitation and analyzing flashes was monitored by photodiodes and a Tektronix 564 oscilloscope. The apparatus incorporated several baffles and right angles in order to eliminate stray light. The excitation flash lamps were operated at 10. kV and 5 μ F to give a total electrical energy of 500 J per flash with a pulse having a 1/e width of 25 μ sec and a base-width of 40 μ sec. Uranyl oxalate actinometry was used to establish that the photon flux from 230 to 450 nm entering the cell was 3×10^{18} photons per flash. This is flux rate of about 10^{23} photons per second. The analyzing flash was operated at 5 kV and 4 μ F to give an electrical energy of 100 J per flash. This pulse had a 1/e width of 15 μ sec and a base-width of 5 μ sec. A continuous light source used for kinetic measurements was a PEK X-76 xenon arc lamp operated by six 12-V batteries in series.

Procedures. The variable wavelength irradiation was performed with a 3.5×10^{-3} M solution of phenyl acetate in ethanol. A Hanovia 1000-W mercury-xenon lamp and the excitation monochromator from an Aminco fluorometer were used to obtain a bandpass of 10 nm. The samples were irradiated in a 1-cm square quartz cell for a length of time sufficient to produce 0.5% decomposition and then analyzed spectrophotometrically in the same cell to determine the concentrations of products.

Photolyses to determine quantum yields were performed in a Rayonet Reactor with 253.7-nm lamps, an eight cell merry-go-round assembly, and quartz cells. The solutions were prepared to have an absorbance in 1 cm of 0.1–1.0. The solutions were deoxygenated by bubbling with dry, high purity nitrogen for 1 hr in the photolysis cell. Irradiation times were less than 2 min. A solution of phenyl acetate in ethanol was concurrently irradiated with each set of samples and was the reference against which all values were determined. Samples were analyzed spectrophotometrically or by glpc.

Flash photolysis solutions were prepared to have an absorbance in 1 cm of 0.2–0.5. Hexane and Freon were dried over 4 Å molecular sieves. The glassware was dried by heating to 120° and then stored under vacuum. Dry nitrogen was used to fill the glassware to atmospheric pressure. Deoxygenation of solutions was done by the freeze-pump-thaw method. The cycles were continued until opening the frozen cell to the vacuum did not raise the pressure above 2×10^{-6} Torr. The deoxygenating cell was attached to the sample cell by stopcocks and ground glass joints. The sample cell was degassed concurrently with the solution. After degassing, a few hundred millimeters of helium was let into the assembly to prevent boiling of the solution when it was flashed. Oxygenated solutions were made by using dried solvents and no degassing procedure.

The flash photolysis spectra were recorded on 4 in. \times 5 in. Kodak 103a-O spectroscopic plates. A sample solution was usually flashed only once to minimize effects of products on the transient absorption spectra. The transient spectra were compared to reference spectra either before or after the excitation flash. The difference in the two traces was used to calculate the transient absorption. Wavelength calibration was accomplished using characteristic emission spikes from the analyzing xenon flash spectrum.

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To obtain flash photolysis kinetics, the spectrograph was operated as a monochromator with a 1P21 photomultiplier at the exit slit. The photomultiplier signal was fed through a logarithmic amplifier to an oscilloscope in order to record intensity changes in units of absorbance.

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Thermal π -Route Rearrangement of 4-Cycloheptene-1-methyl Acetate

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Abstract: Pyrolysis of 4-cycloheptene-1-methyl acetate under flow conditions gives only rearranged acetates and rearranged hydrocarbons whereas static conditions lead only to a simple elimination product and its Cope rearrangement isomer. The rearranged bicyclic acetates formed under flow conditions are strikingly similar to those of π -route solvolysis of the corresponding brosylate. The reaction rates under flow conditions were sensitive to conditioning of the reactor with allyl bromide.

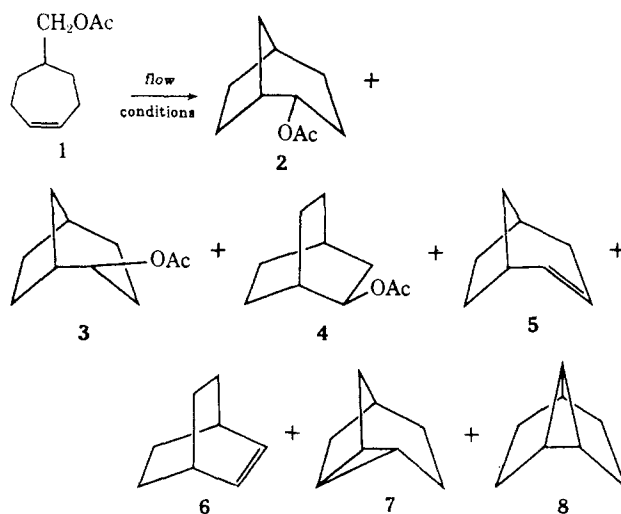
Ester pyrolysis is a well-established method for generating olefins, normally without rearrangement.¹ Considerable data indicate a concerted loss of carboxylic acid through a transition state that is somewhat polar, but less so than in halide pyrolyses.¹ When carried out in well-conditioned reactors, many such eliminations have been shown to be well-behaved homogeneous gas phase reactions. A few cases are known that give carbonium ion like rearrangements.²⁻⁴ Only one of these has been shown to be a homogeneous gas phase reaction.^{2a} The other systems^{3,4} show evidence for surface catalysis.^{1a}

The system studied here, 4-cycloheptene-1-methyl acetate (1), is one that has been studied solvolytically as the brosylate^{5,6} and gives " π -route" entry⁷ to the bicyclo[3.2.1]octyl system. Thus it is a system with a different type of potential carbonium ion like rearrangement than esters pyrolyzed previously.

Results

4-Cycloheptene-1-methanol was prepared by the method outlined previously^{6,8} and then converted to the acetate (1). Pyrolysis of 1 under various flow conditions, including those normally used for preparative ester pyrolysis (slowly dripping 1 through a column of glass beads at 350° under a nitrogen flow), gave only rearranged products. The products that result are three bicyclic acetates 2, 3, and 4, two bicyclic olefins 5

and 6, and two tricyclic hydrocarbons 7 and 8. The



structural assignments of the products were made by spectral and glc retention time comparison with authentic samples.⁹

The reaction was examined in a stirred flow reactor¹⁰ to determine whether surface effects are important and to study to what extent products 5-8 arise from acetates 2-4. The reactor design was tested by measuring values for the cracking of norbornene.¹¹ The rate constants for that system were reproducible, invariant with changes in flow rate over the range used in the acetate study, and gave activation parameters ($E_a = 45.9$ kcal/mol, $\log A = 14.86$) in reasonable agreement with literature values¹¹ ($E_a = 42.8$ kcal/mol, $\log A = 13.78$).

Rate measurements for 1 in the stirred flow reactor were not reproducible although the measured values

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