Mechanistic Studies of the Photo-Fries Reaction[1]

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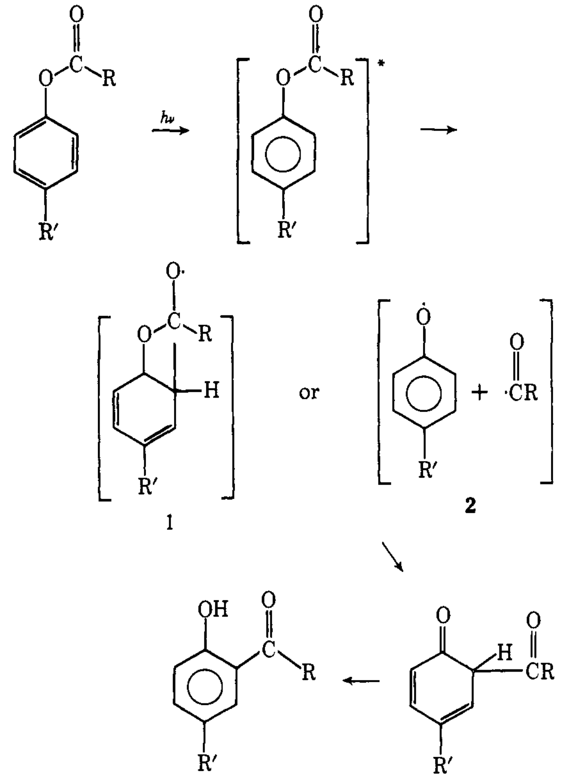
Abstract: Detailed product analyses and quantum yield determinations were carried out on the 2537-Å light-induced reactions of *p*-tolyl acetate, benzoate, and hydrocinnamate. Evidence is presented that the photo-Fries rearrangement originates from an upper singlet state and proceeds to product by a molecular pathway that is independent of its reaction environment. A 1,3-sigmatropic shift is proposed. *p*-Cresol formation, on the other hand, was shown to be highly solvent dependent and appears to arise from reactions of the *p*-methylphenoxy radical. Studies with *p*-tolyl acetate-d_3 showed that alcoholic solvent derived esters, which are formed as coproducts, originate, at least in part, from a ketene intermediate. A comprehensive scheme involving a multiplicity of reaction paths is proposed to account for these results.

Photochemical analogs of the Fries[2,3] and Claisen[4] rearrangements have received considerable attention in recent years, as have photoinduced rearrangements of anilides[3,5,6] and aromatic carbonates.[3,7] These transformations involve a shift of an acyl[2] or alkenyl[4] group (without isomerization) to the *ortho* and *para* positions of the aromatic ring with accompanying formation of a phenolic OH or anilinic NH_2, except in those cases where these positions are substituted.[8–11] Similar rearrangements have been reported for diphenyl ethers and benzyl phenyl ethers.[4,12] In the case of the widely studied photo-Fries reaction, the rearrangement in solution is always accompanied by varying amounts of phenol formation,[12,13] but occurs without side reactions in a polymer matrix.[14–16] Also, the rearrangement is intramolecular; mixed irradiations of combinations of esters gave no mixed Fries products.[12]

Two mechanisms have been proposed for the photo-Fries rearrangement. Anderson and Reese[11] suggested a "molecular" pathway, involving a bridged intermediate of type **1**. A similar intermediate was considered for the *para* rearrangement.

Kobsa[13] and Finnegan and Mattice[17] proposed a "cage radical pair" intermediate **2**, in which C–O homolysis is followed by attack of the resulting acyl radical on the *ortho* or *para* position of the phenoxy radical with subsequent enolization. Out-of-cage reaction of the phenoxy radical with solvent was postulated to account for phenol formation. In support of this, Horspool and Parson[18] have shown that the relative yields of phenol increased markedly when the irradiation of 4-*t*-butylphenol formate was conducted in ethanol rather than in benzene; acetaldehyde was a coproduct.



(1)

The fate of the acyl portion of the ester was investigated in several instances. Finnegan and Knutson detected decarbonylation of the acyl fragment when highly hindered aryl carboxylates were irradiated.[8,9] Barton and coworkers[19] found that irradiation of β-naphthyl fluorene-9-carboxylate gave high yields of carbon monoxide and β-naphthol, apparently *via* decarbonylation of the 9-acylfluorene radical to give the stabilized 9-fluorenyl radical. In a somewhat

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(1) For a preliminary account of this work see M. R. Sandner and D. J. Trecker, *J. Am. Chem. Soc.*, **89**, 5725 (1967).

(2) V. I. Stenberg, "Organic Photochemistry," Vol. 1, O. L. Chapman, Ed., Marcel Dekker, Inc., New York, N. Y., 1967, pp 127–153.

(3) D. Bellus and P. Hrdlovic, *Chem. Rev.*, **67**, 599 (1967).

(4) D. P. Kelly, J. T. Pinkey, and R. D. G. Rigby, *Tetrahedron Letters*, 5953 (1966).

(5) D. Elad, *ibid.*, 873 (1963).

(6) V. E. Stenberg and D. V. Rao, *Proc. N. Dakota Acad. Sci.*, **17**, 37 (1963); D. Elad, D. V. Rao, and V. I. Stenberg, *J. Org. Chem.*, **30**, 3252 (1965).

(7) D. Bellus, P. Hrdlovic, and Z. Manasek, *J. Polymer Sci.*, *Part B*, **4**, 1 (1966).

(8) R. A. Finnegan and D. Knutson, *Chem. Ind.* (London), 1837 (1965).

(9) R. A. Finnegan and D. Knutson, *J. Am. Chem. Soc.*, **89**, 1970 (1967).

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

(11) J. C. Anderson and C. B. Reese, *J. Chem. Soc.*, 1781 (1963).

(12) H. I. Joscheck and S. I. Miller, *J. Am. Chem. Soc.*, **88**, 3269 (1966).

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

(14) S. B. Maerov, *J. Polymer Sci.*, **3**, 487 (1965).

(15) D. Bellus, *et al.*, *Polymer Previews*, **2**, 531 (1966), and references therein.

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

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

(18) W. M. Horspool and P. L. Parson, *J. Chem. Soc.*, 5162 (1965).

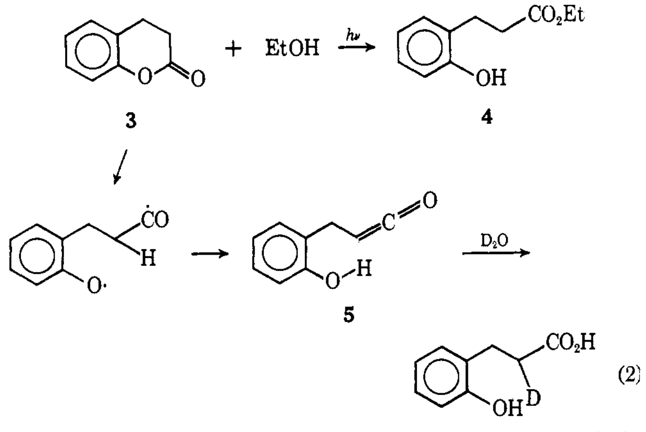
(19) D. H. R. Barton, Y. L. Chow, A. Cox, and G. W. Kirby, *Tetrahedron Letters*, 1055 (1962).

Table I. Quantum Yields[a]

Run	Ester[b]	Solvent (viscosity, cP, 30°)	Reaction time, hr	Φ Ester	Φ Ketone	Φ Cresol
1	*p*-Tolyl acetate	*t*-BuOH (3.00)	46	*c*	0.17	0.08
2			50	0.35	0.18	0.05
3			90	0.35	0.19	0.08
4			136	0.35	0.18	0.07
5		*i*-PrOH (1.73)	90	0.37	0.17	0.09
6		EtOH (1.00)	90	0.62	0.16	0.43
7			136	*c*	0.18	0.48
8		DMSO (1.94)	90	0.32	0.22	0.10
9		Dioxane–H_2O	50	0.32	0.17	0.06
10		*t*-BuOH, O_2	50	0.32	0.17	0.04
11		Carbowax 400 (76)	46	0.32	0.17	0.03
12		Carbowax 600 (109)	46	0.40	0.16	0.02
13	*p*-Tolyl acetate-d_3	*t*-BuOH (3.00)	136	0.34	0.17	0.06
14		EtOH (1.00)	136	*c*	0.16	0.24
15	*p*-Tolyl hydrocinnamate	*t*-BuOH (3.00)	28	0.44	0.34	0.09
16	*p*-Tolyl benzoate		48	0.58	0.38	0.07
17			52	0.58	0.38	0.07
18		*i*-PrOH (1.73)	52	0.62	0.37	0.11
19		EtOH (1.00)	52	0.64	0.29	0.22

[a] At least three points, each analyzed in triplicate, were taken for each quantum yield determination. See Experimental Section. [b] Ester concentration in each run was 0.26 ± 0.01 *M*. [c] Not determined.

different system, Anderson and Reese[11] reported that photolysis of 3,4-dihydrocoumarin (**3**) in ethanol afforded high yields of ethyl *β*-[*o*-hydroxyphenyl]propionate (**4**). Plank,[20] who reinvestigated the reaction in dioxane–D_2O, postulated a ketene intermediate **5** on the basis of finding deuterium in the *α* position of the resulting propionic acid.

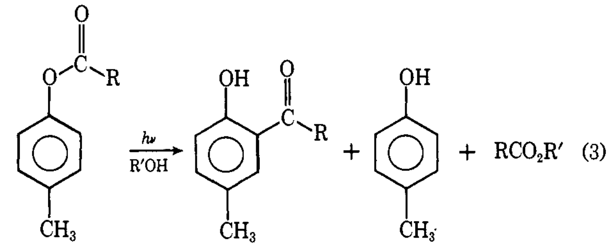


In an attempt to clarify some of the mechanistic aspects of the photo-Fries reaction, we have studied in some detail both the products derived from the photolysis of some *p*-tolyl esters and the quantum yields associated with their formation.

Results

The *p*-tolyl esters of acetic, benzoic, and hydrocinnamic acids (**6**) were irradiated in a nitrogen atmosphere in an all-quartz immersion reactor.[21] In aprotic solvents the expected products, **7** and **8**, were formed, while in alcoholic media, the solvent-derived ester (**9**) was also obtained.

Quantum yields of ester disappearance and of ketone and *p*-cresol formation were determined in a manner previously described (Table I).[21] In each case the reactions followed apparent zero-order kinetics.



6a, R = CH_3
b, R = C_6H_5
c, R = $CH_2CHC_6H_5$
d, R = CD_3

7

8

Several features become apparent upon examination of these data. (1) The quantum yield of photo-Fries product from any given ester does not vary with solvent or added oxygen. (2) The quantum yields in *t*-butyl alcohol and, hence, rates of ester disappearance increase as one goes from acetate to hydrocinnamate to benzoate. The quantum yields in *t*-butyl alcohol for ketone formation correspondingly increase. (3) The quantum yield of *p*-cresol increases in each case as one passes to solvents of decreasing viscosity. (4) The quantum yield of *p*-cresol formation is anomalously high in reactions conducted in ethanol (runs 6, 7, and 19).

p-Tolyl acetate-d_3, prepared from *p*-cresol and acetyl-d_3 chloride, was similarly irradiated. Table I (compare runs 2, 13 and 7, 14) shows that there is a significant isotope effect for *p*-cresol formation in ethanol but not in *t*-butyl alcohol. Furthermore, synthesis runs conducted in ethanol showed that >60% of the *p*-cresol formed was monodeuterated. Appropriate control experiments demonstrated that deuterium exchange under neutral conditions between either the ester **6d** or the photoketone **7d** and ethanol and between *p*-cresol and ethanol could account for only a few per cent of the observed *p*-cresol-d_1.

A complete product analysis was conducted in the irradiations of *p*-tolyl acetate in ethanol and isopropyl

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(20) E. D. A. Plank, Ph.D. Thesis, Purdue University, 1966.

(21) D. J. Trecker, R. S. Foote, J. P. Henry, and J. E. McKeon, *J. Am. Chem. Soc.*, **88**, 3021 (1966).

Table II. Complete Product Analysis

Run	Ester	Solvent	Reaction time, hr	Ester consumed, mmol	Products (mmol)
5	*p*-Tolyl acetate	*i*-PrOH	90	3.18	2-Hydroxy-5-methylacetophenone (1.49), *p*-cresol (0.77), isopropyl acetate (0.06), acetone (0.19), methane, CO, CO_2
6	*p*-Tolyl acetate	EtOH	90	5.16	2-Hydroxy-5-methylacetophenone (1.33), *p*-cresol (3.57), ethyl acetate (3.09), methane, CO, CO_2
18	*p*-Tolyl benzoate	*i*-PrOH	52	2.57	2-Hydroxy-5-methylbenzophenone (1.53), *p*-cresol (0.46), isopropyl benzoate (0.08), acetate (0.19)[a]

[a] Gases were not determined.

alcohol and of *p*-tolyl benzoate in isopropyl alcohol (Table II). Material balances ranged from 71 to 95%, indicating that some undetected products, perhaps polymeric, were formed. In spite of the fact that small amounts of carbon dioxide were produced, none of the corresponding decarboxylation product, *p*-xylene, was detected.[22]

To establish the multiplicity (singlet or triplet) of the photo-Fries reaction, quenching and sensitization experiments were carried out. Identical *p*-tolyl acetate–*t*-butyl alcohol solutions containing naphthalene (3.5×10^{-2} *M*), a triplet quencher,[23] ($E_T = 61$ kcal/mol[23]), ferric acetylacetonate (1.5×10^{-3} *M*), a paramagnetic quencher,[24] and acetophenone (2.8 *M*), a triplet sensitizer ($E_T = 74$ kcal/mol[23]), were irradiated. Neither the rate of ester disappearance (Figure 1) nor of product formation was affected by quenchers, each of which was present in concentrations known to diminish markedly the rates of established triplet processes.[24,25] Moreover, under conditions where acetophenone absorbed 95% of the incident light (3130 Å), no reaction whatever was detected.[26]

Discussion

The quenching and sensitization experiments clearly suggest that the over-all transformations occurred from an upper singlet manifold or from a very short-lived triplet state. The exact mechanistic paths of these transformations are less clear.

One striking result pertinent to the question of mechanism is that of the quantum yield of photoketone formation. As indicated by Table I, the quantum yield of photo-Fries rearrangement for each ester is essentially constant in spite of wide variations in solvent reactivity (ease of H abstraction), solvent polarity (stabilization of polar intermediates), and solvent viscosity (enhancement of cage processes). Moreover, the presence of added oxygen does not affect the rearrangement process. These results constitute compelling evidence that the photo-Fries reaction involves a *tightly bound intermediate* which proceeds to product unaffected by its reaction environment.[27a]

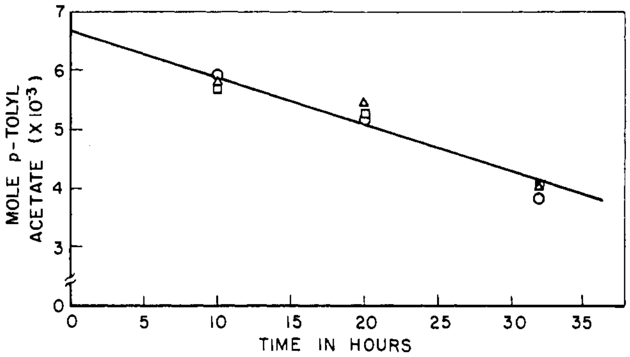

Figure 1. Rate of *p*-tolyl acetate disappearance (○) alone, 0.33 *M* in *t*-butyl alcohol, with 3.4×10^{-3} *M* added naphthalene (□), and with 1.5×10^{-3} *M* added ferric acetylacetonate (△). Irradiation was with mercury resonance lamps (2537 Å) in a Rayonet reactor.

It is instructive to consider the question of a concerted rearrangement pathway for the photo-Fries reactions in terms of the theoretical model recently proposed by Woodward and Hoffmann.[28] The photo-Fries reaction is then represented as a sigmatropic migration of the acyl ligand to the *ortho* or *para* positions. More specifically, the migration involves the interaction between the σ orbital of the acyl group with the aromatic π system in a plane perpendicular to that of the benzene ring (**10**). It is conceivable that the primary interaction could involve the 2p–π orbitals of the carbonyl group. However, this appears to be sterically less favorable.

In the Woodward-Hoffmann formulation[28] the migration termini are predicted on the basis of the symmetry of the highest occupied molecular orbital (HOMO) of the phenoxy radical for a thermal rearrangement and the lowest unoccupied molecular orbitals for photochemical rearrangements. The signs

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(22) Decarboxylation is a frequent photochemical pathway of certain types of substituted aryl carboxylates: R. A. Finnegan and D. Knutson, *Tetrahedron*, 30, 3429 (1968).

(23) W. M. Moore and M. R. Ketchum, *J. Am. Chem. Soc.*, **84**, 1368 (1962); N. J. Turro, "Molecular Photochemistry," W. A. Benjamin, Inc., New York, N. Y., 1967, p 117.

(24) A. J. Fry, R. S. H. Liu, and G. S. Hammond, *J. Am. Chem. Soc.*, **88**, 4781 (1966).

(25) V. I. Stenberg and R. J. Perkins, *J. Org. Chem.*, 27, 4111 (1962).

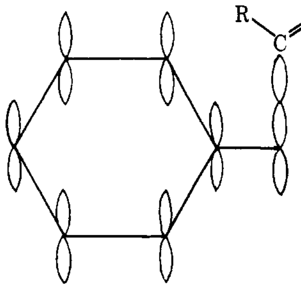
(26) The choice of acetophenone and naphthalene as sensitizer and quencher, respectively, presupposes a *p*-tolyl acetate triplet energy of between 61 and 74 kcal/mol. While it may be argued that a triplet level of 74 kcal/mol is insufficiently high to permit an exothermic transfer to a nonpolynuclear aromatic, a level of 61 kcal/mol is clearly low enough to induce efficient quenching.[23]

(27) (a) An invariant quantum yield indicates that all rate constants which constitute the derived expression for quantum yield are medium independent or, less likely, that compensating variations of two or more rate constants occur. See following discussion and ref 27b. (b) The quantum yield expression for **7a** formation contains only one solvent-dependent term. It is apparent that k_{15} is not significant under our

$$\Phi_{7a} = \frac{\phi k_5}{k_4 + k_5 + k_6 + k_{15}(\mathrm{R'OH})}$$

reaction conditions. A similar derivation of Φ_{7a} based on the scheme proposed by Kobsa with **7a** being formed *via* reaction **7b** leads to the conclusion that Φ_{7a} should be medium dependent.

(28) R. B. Woodward and R. Hoffmann, *Accounts Chem. Res.*, **1**, 17 (1968).



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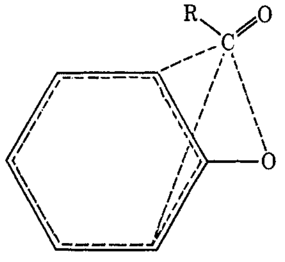
or



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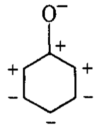
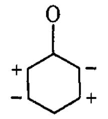
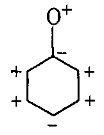
of the π atomic orbital coefficients for the HOMO and the three lowest unoccupied molecular orbitals of the phenoxy radical are given in the diagrams below in order of increasing energy from left to right.[29] These are labeled according to their symmetries with respect to the plane and the C_2 axis, respectively. The designation SA thus signifies that the molecular orbital is symmetric with respect to the plane and asymmetric with respect to the C_2 axis.



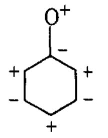
SA



AS



ISA



2SA

Consideration of the symmetry properties of the various MO's represented above leads to the following conclusions. Sigmatropic, suprafacial migration is allowed to both *ortho* and *meta* positions in the first excited state, since the AS molecular orbital has a node along the C_2 axis. However, we can exclude rearrangement to the *meta* position since it would result in an unstable biradical product. Furthermore, antarafacial rearrangement obviously is sterically excluded. The symmetry of ISA, which corresponds to the HOMO of the second excited state, also allows suprafacial migration to *ortho* and *meta* positions, and the latter is again excluded. Rearrangement to both *ortho* and *para* positions is allowed for the third excited state involving the 2SA molecular orbital.

One clear value of this formulation is that it forms the basis for further predictions. First, the *ortho/para* ratio should be wavelength dependent. Second, the rearrangement should occur generally for phenols and simple phenyl ethers. Indeed, a variety of diphenyl ethers,[4,10] allyl phenyl and benzyl phenyl ethers,[4] and aryloxyacetones[30a] undergo analogous light-induced rearrangements. However, anisole apparently does not.[30b]

We propose on this basis that the photo-Fries rearrangement occurs by a concerted, symmetry-allowed process. This differs from Kobsa's formulation of the mechanism (which we believe is experimentally untenable, since his mechanism implies that *both* phenol and ketone formation would be medium dependent) in that in our proposed model each fragment of the radical cage pair retains a memory for symmetry. That is, bond formation and cleavage occur synchronously.

The major differences between our formulation and that of Anderson and Reese (which is experimentally tenable) involves the consideration of symmetry as well as the nature of the primary interactions. The latter proposed that the rearrangement intermediate involves the carbonyl π system as in **1** for both *ortho* and *para* migration. However, we favor the categorization of the rearrangement as a simple sigmatropic shift of the ligand on oxygen because of the stringent steric requirements imposed by the Anderson and Reese model and because the latter interpretation does not encompass the phenyl ethers.

It will be noted that while the quantum yield of ketone formation from each ester does not vary with solvent, the quantum yield of *p*-cresol formation varies strikingly. As indicated by Table I, there is an increase in *p*-cresol formation (from *p*-tolyl acetate) of several fold in passing from viscous polyether solvents to the fluid alcohols. Similar behavior is found with the benzoates. Consequently, the photoreactions of phenolic esters must proceed by a multiplicity of reactions, and those which we believe are most pertinent are summarized in detail in Scheme I.

While the photo-Fries process itself apparently does not involve true "free" radical intermediates, the concomitant process leading to phenol formation almost certainly does.[18] Chemical evidence for the reaction of phenoxy radical with solvent was the formation of nearly stoichiometric amounts of *p*-cresol and acetone from the irradiation of *p*-tolyl benzoate in isopropyl alcohol (Table II, run 18). The fate of the accompanying benzoyl radical from this reaction was not determined. No attempt was made, for example, to analyze for benzil, a likely coproduct.

Substantial amounts of acetone were also formed in the *p*-tolyl acetate–isopropyl alcohol photolysis (Table II, run 5). Moreover, the identification of methane and carbon monoxide among the gaseous products provides evidence for the existence of the acetyl fragment. This intermediate apparently decarbonylated to give CO and a methyl radical, which in turn abstracted a hydrogen from the solvent.

The extent of hydrogen abstraction by free radicals (Scheme I, eq 9 and 10) should depend on the ease of escape from solvent cage (eq 8). It has been firmly established[31] that geminate cage recombination of radicals is a function of solvent viscosity. Viscous media favor recombination at the expense of cage escape.[31] Consistent with this interpretation, inspection of Table I reveals that, as the medium becomes less viscous, the yield of *p*-cresol correspondingly increases.

While cage escape of the phenoxy radical accounts in part for the behavior of the reaction in various solvents, it does not account for the abnormal *p*-cresol formation from **6a** in ethanol as opposed to isopropyl alcohol (Table I, runs 5 and 6), particularly since the latter is a superior hydrogen atom donor.

However, this is readily explicable in terms of a ketene intermediate (**15**). Such a pathway (eq 11) is favored by the particularly low C–H bond dissociation energy of the acetyl radical (43.5 kcal/mol[32]). Depending on the

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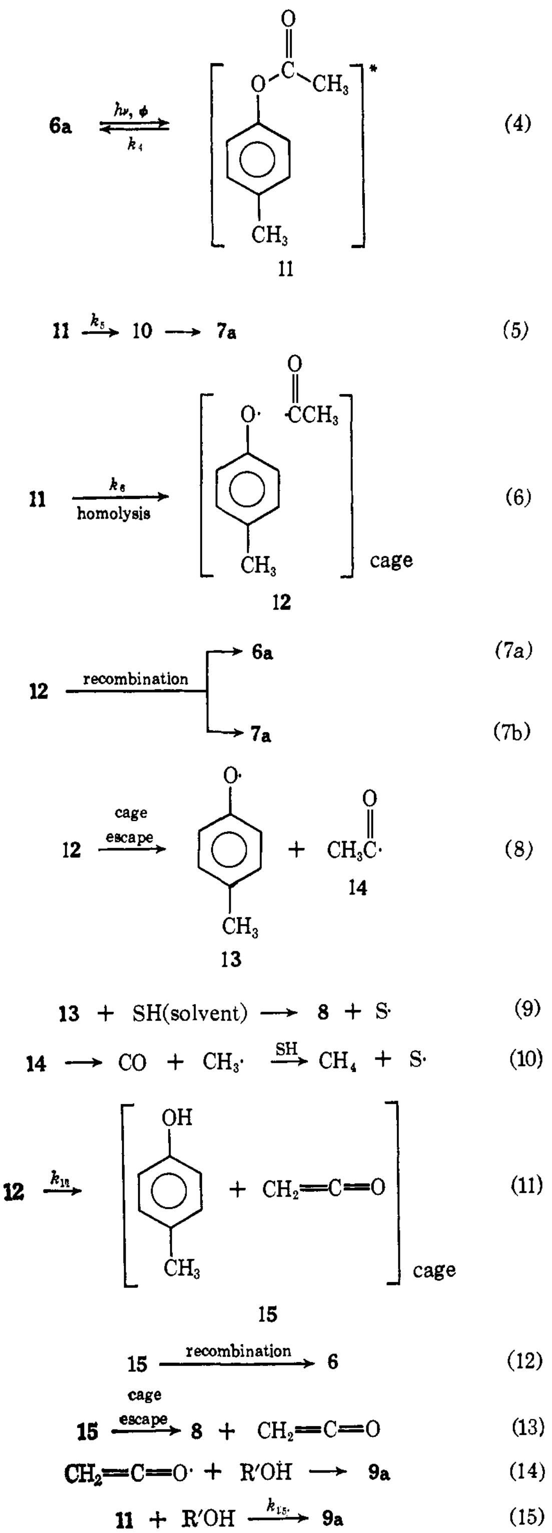
[29] These were ranked according to an extended Hückel calculation.

[30] (a) A. J. Hill, *Chem. Commun.*, 260 (1966); (b) C. L. Osborn, unpublished results.

[31] C. Walling and H. P. Waits, *J. Phys. Chem.*, 71, 2361 (1967); R. Hiatt and T. G. Traylor, *J. Am. Chem. Soc.*, 87, 3766 (1965); W. Braun, L. Rajbenbach, and F. R. Eirich, *J. Phys. Chem.*, 66, 1591 (1962).

[32] S. W. Benson, *J. Chem. Educ.*, 42, 502 (1965).

Scheme I



solvent, the *p*-cresol and ketene thus formed may recombine to regenerate starting material (eq 12) or alternatively react with a favorable alcoholic solvent to give the corresponding acetate (eq 13 and 14). We propose that this latter route is particularly favored in ethanol and accounts for the increased quantum yield of **6a** disappearance and **8** formation. Consistently, Anderson and Reese[11] observed that **4** was obtained when 3,4-dihydrocoumarin was irradiated in ethanol.

Confirming evidence for this pathway was obtained in the irradiation of *p*-tolyl acetate-d_3 (**6d**). This reaction was carried out in both ethanol and *t*-butyl alcohol. In *t*-butyl alcohol, as predicted, little cage escape of ketene-d_2 and *p*-cresol-d_1 took place (reaction 13) as evidenced by the fact that only traces of *p*-cresol-d_1 and *t*-butyl alcohol-d_1 could be detected in the mass spectrum. Moreover, there was no change in quantum efficiencies for any of the products (compare runs 4 and 13, Table I). In striking contrast, the run in ethanol afforded large quantities of *p*-cresol-d_1, as well as detectable amounts of ethanol-d_1. Since ethanol is a poorer cage solvent and a better nucleophile than *t*-butyl alcohol, these results are altogether consistent with reactions 11–14 and provide striking affirmation for this alternate pathway.

Still a third pathway must be considered. Because small quantities of solvent-derived esters were formed from the irradiation of *p*-tolyl benzoate (**6b**) (Table II, run 18), the possibility of photochemical transesterification (eq 15) cannot be discounted. Since it is apparent that the ketene route is not available to the benzoates, some sort of heterolytic C–O bond-weakening or -breaking process in the excited state must be postulated to account for the formation of ethyl benzoate and isopropyl benzoate. The data (Table I, runs 17–19) are consistent with such an interpretation, the extent of transesterification decreasing as one passes from primary to secondary to tertiary alcohols.[33] A similar process was proposed by Finnegan and Mattice,[17] and has recently been investigated in more detail.[34] It is important to note that this is the only reaction of the excited state whose rate would be expected to be solvent dependent.[27b]

Experimental Section

Preparation of *p*-Tolyl Hydrocinnamate. A solution of *p*-cresol (100 g, 0.93 mol) in pyridine (500 ml) was treated portionwise with hydrocinnamoyl chloride (189 g, 1.12 mol). A conventional work-up afforded a viscous oil, which upon distillation (bp 123–124° (0.4 mm)) gave *p*-tolyl hydrocinnamate (180.3 g, 81.0% yield). The distillate crystallized upon standing and was recrystallized three times from ethanol to give white plates with mp 34.0–34.5°; infrared, $\nu_{\max}^{\mathrm{KBr}}$ 1748 (ester carbonyl), 844 (1,4-substituted benzene), and 749 and 704 cm^{-1} (monosubstituted benzene); ultraviolet, $\lambda_{\max}^{\mathrm{EtOH}}$ 265 μ (ϵ 650) and end absorption; nmr ($CDCl_3$), τ 7.72 (singlet, three methyl protons), 7.21 and 5.99 (A_2B_2 pair, J = cps, four methylene protons), 3.16 and 2.90 (AB pair, J = 9 cps, four *p*-tolyl ring protons), and 2.78 (singlet, five phenyl protons).

Anal. Calcd for $C_{16}H_{16}O_2$: C, 79.97; H, 6.71; parent mass, 240. Found: C, 80.18; H, 6.81; parent mass, 240.

Preparation of 2-Hydroxy-5-methylacetophenone. A mixture of *p*-tolyl acetate (112 g, 0.743 mol) and anhydrous aluminum chloride (121 g, 0.900 mol) was heated at 130° for 30 min, then treated successively with ice, concentrated HCl, and water and extracted with benzene. The benzene extracts were washed with water, 8% sodium carbonate, and water, then dried and evaporated. The residual oil was distilled (bp 60–62° (0.2 mm)) to afford 2-hydroxy-5-methylacetophenone (82.5 g, 73.6% yield), which solidified upon standing. Two recrystallizations from methanol provided light yellow needles with mp 47° (lit.[35] mp 50°); infrared, $\nu_{\max}^{\mathrm{KBr}}$ 3480 (hydroxyl), 1642 and 1617 (conjugated chelated carbonyl), and 828 and 800 cm^{-1} (1,2,4-aromatic substitutions); ultraviolet, $\lambda_{\max}^{\mathrm{EtOH}}$ 340 (3000) and 255 mμ (ϵ 8400); nmr (CCl_4), τ 7.73 (singlet, three tolyl methyl protons), 7.49 (singlet, three acetyl methyl protons), 3.25 and 2.83 (AB pair, J = 8 cps, adjacent aromatic protons), 2.60

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[33] Control experiments demonstrated that, under the neutral reaction conditions, ester interchange in the dark occurred only to a very limited extent.

[34] R. A. Finnegan and D. Knutson, *J. Am. Chem. Soc.*, **90**, 1670 (1968).

[35] K. W. Rosemund and W. Schnurr, *Ann.*, **460**, 56 (1928).

(broadened singlet, one aromatic proton), and −1.6 (singlet, phenolic proton).

Anal. Calcd for $C_9H_{10}O_2$: C, 71.98; H, 6.71; parent mass 150. Found: C, 72.07; H, 6.63; parent mass, 150.

The 2,4-dinitrophenylhydrazone was prepared. The orange crystals melted at 268–270°.

Anal. Calcd for $C_{15}H_{14}O_5N_4$: C, 54.54; H, 4.27; N, 16.97. Found: C, 54.39; H, 4.35, N, 17.16.

Preparation of 2-Hydroxy-5-methylbenzophenone. In a similar manner, *p*-tolyl benzoate (15.0 g, 0.071 mol) was allowed to react with aluminum chloride (11.5 g, 0.085 mol) to afford a yellow oil which crystallized on standing (8.3 g, 55% yield). Three recrystallizations from ethanol gave 2-hydroxy-5-methylbenzophenone as yellow prisms with mp 83.5–84.0° (lit.[37] mp 84°); infrared, $\nu_{\max}^{\mathrm{KBr}}$ 3410 (hydroxyl), 1638 and 1608 (conjugated chelated carbonyl), 864 and 830 (1,2,4-aromatic substitution), and 764 and 703 cm^{-1} (monosubstituted benzene); ultraviolet, $\lambda_{\max}^{\mathrm{EtOH}}$ 350 (4400) and 257 mμ (ϵ 14,800); nmr ($CDCl_3$), τ 7.81 (singlet, three methyl protons, 3.10–2.20 (unresolved multiplet, eight aromatic protons), and −1.8 (singlet, phenolic proton).

Anal. Calcd for $C_{14}H_{12}O_2$: C, 79.22; H, 5.70; parent mass, 212. Found: C, 79.02; H, 5.71; parent mass, 212.

The 2,4-dinitrophenylhydrazone was prepared. The orange crystals melted at 240–242°.

Anal. Calcd for $C_{20}H_{16}O_5N_4$: C, 61.22; H, 4.11; N, 14.26. Found: C, 60.90; H, 4.36; N, 14.01.

Preparation of 2-Hydrocinnamoyl-4-methylphenol. In like manner, *p*-tolyl hydrocinnamate (18.0 g, 0.075 mol) was allowed to react with aluminum chloride (11.5 g, 0.085 mol) to give a viscous oil, which upon distillation (bp 154–156° (0.05 mm)) afforded 2-hydrocinnamoyl-4-methylphenol (9.5 g, 52.8% yield). The distillate solidified upon standing and was twice recrystallized from ethanol to give pale yellow plates with mp 39.0–39.5°; infrared, $\nu_{\max}^{\mathrm{KBr}}$ 3420 (hydroxyl), 1639 and 1618 (conjugated chelated carbonyl), 877 and 831 (1,2,4-aromatic substitution), and 756 and 703 cm^{-1} (monosubstituted benzene); ultraviolet, $\lambda_{\max}^{\mathrm{EtOH}}$ 338 (4100) and 255 mμ (ϵ 10,900); nmr ($CDCl_3$), τ 7.78 (three methyl protons), 7.02 and 6.82 (A_2B_2 pair, J = 7 cps, four methylene protons), 3.20 and 2.82 (AB pair, J = 8 cps, adjacent tolyl protons), 2.60 (singlet, one aromatic proton), 2.81 (singlet, five phenyl protons), and −1.8 (singlet, phenolic proton).

Anal. Calcd for $C_{12}H_{16}O_2$: C, 79.97; H, 6.71; parent mass, 240. Found: C, 79.98; H, 6.77; parent mass, 240.

The 2,4-dinitrophenylhydrazone was prepared. Its red crystals melted at 183–185°.

Anal. Calcd for $C_{22}H_{20}O_5N_4$: C, 62.85; H, 4.80; N, 13.33. Found: C, 62.64; H, 4.80; N, 13.18.

Preparation of *p*-Tolyl Acetate-d_3. A solution of *p*-cresol (11.8 g, 0.109 mol), pyridine (21 ml), and benzene (10 ml) was treated with acetyl-d_3 chloride (10.0 g, 0.123 mol), then washed with water and extracted with benzene. The benzene extracts were washed successively with water, dilute hydrochloric acid, water, 5% sodium carbonate, and water. After drying, the benzene solution was evaporated, and the residual oil was distilled (bp 40–41° (0.03 mm)) to afford *p*-tolyl acetate-d_3 (10.3 g, 61.7% yield); >97% isotopic purity by mass spectral analysis and nmr.

Quantum Yield Determinations. The 2537-Å tubular quartz quantum yield apparatus described previously[21] was utilized for this study. Uranyl oxalate actinometry was employed.[36] Quantum outputs decreased from 2.92 × 10^{18} to 2.53 × 10^{18} quanta/sec during the course of the study. Representative of the reaction solutions were the following: (1) *p*-tolyl acetate (8.36 g, 0.556 mol) in *t*-butyl alcohol (144.30 g), (2) *p*-tolyl benzoate (12.10 g, 0.0570 mol) in *t*-butyl alcohol (160.84 g), and (3) *p*-tolyl hydrocinnamate (14.22 g, 0.0592 mol) in *t*-butyl alcohol (148.96 g). In each instance, throughout the course of the reaction, better than 99% of the light was absorbed by the reaction solution. At least five points were taken in each run.

Analysis was accomplished by vpc analysis in which a 6 ft × $^1/_3$ in. column containing 10% SE-30 on 80–100 mesh Gas-Chrom S was employed. The products determined, the column temperature used, and the internal standards employed, in parentheses, are listed: (1) *p*-cresol, *p*-tolyl acetate, 2-hydroxy-5-methylacetophenone, 130° (dimethyl phthalate); *p*-tolyl benzoate, 2-hydroxy-5-methylbenzophenone, 170° (4-carbomethoxy-4-methylpentyl isobutyrate); (3) *p*-cresol, 130° (dimethyl phthalate), *p*-tolyl hydrocinnamate, 2-hydroxycinnamoyl-4-methylphenol, 180° (4-carbomethoxy-4-methylpentyl isobutyrate). Analyses were made in triplicate for each point taken.

In the cases of *p*-tolyl acetate and *p*-tolyl benzoate, product absorption presented no problem; conversions were held below 10%. With *p*-tolyl hydrocinnamate, however, the photo-Fries product absorbed much more strongly at 2537 Å (ϵ 9800) than did the starting material (ϵ 470). To correct for the amount of light absorbed by products, the following equation[37] was employed

$$\phi_{\mathrm{calcd}} = \left(\frac{(R_0 - R)}{It}\right) \times \left(\frac{1 + \epsilon_{\mathrm{R}} + \epsilon_{\mathrm{D}}b - \epsilon_{\mathrm{B}}f - \epsilon_{\mathrm{C}}c - \epsilon_{\mathrm{D}}}{R}\right) + \left(\frac{2.3R_0 \log (R_0/R)}{It}\right)\left(\frac{\epsilon_{\mathrm{B}}b + \epsilon_{\mathrm{C}}c + \epsilon_{\mathrm{D}} - \epsilon_{\mathrm{D}}b}{\epsilon_{\mathrm{R}}}\right)$$

where the extinction coefficients were ϵ_{R}, *p*-tolyl hydrocinnamate; ϵ_{B}, 2-hydrocinnamoyl-4-methylphenol; ϵ_{C}, *p*-cresol; ϵ_{D}, unknown components, and where b and c are the concentrations of 2-hydrocinnamoyl-4-methylphenol and *p*-cresol, respectively. Ultraviolet spectroscopic readings were made on a Beckman DU.

The results from all determinations are compiled in Table I.

Product Determinations. Gaseous products (Table II) were identified by mass spectroscopy and confirmed by vpc analysis employing a 16 ft × $^3/_{16}$ in. Porapak Q column (He), at −78° for 10 min, then programming to 250° at 25°/min.

The acetates and benzoates derived from solvent interaction and the solvent oxidation products were identified by comparison of their vpc retention times on three columns (see Quantum Yield Determinations, and above) with those of authentic samples.

The photo-Fries products were, in each instance, isolated from the reaction mixture as their respective 2,4-dinitrophenylhydrazones and compared with authentic samples (melting point, infrared, nmr).

Sensitization and Quenching Studies. Ultraviolet spectral determinations gave the following molar extinction coefficients at 2537 Å for the compounds used in this study: *p*-tolyl acetate (5740), acetophenone (6300), naphthalene (3980), and ferric acetylacetonate (11,300). On the basis of these figures, the concentrations of the following solutions were adjusted so that naphthalene and ferric acetylacetone absorbed 1% of the light and acetophenone absorbed 95% of the 2537-Å light: (1) *p*-tolyl acetate (1.0 g, 6.65 × 10^{-3} mol) in *t*-butyl alcohol (15 g), (2) *p*-tolyl acetate (1.0 g, 6.65 × 10^{-3}) and ferric acetylacetonate (0.010 g, 3 × 10^{-5} mol) in *t*-butyl alcohol (15 g), (3) *p*-tolyl acetate (1.0 g, 6.65 × 10^{-3} mol) and naphthalene (0.090 g, 7 × 10^{-4} mol) in *t*-butyl alcohol (15 g), and (4) *p*-tolyl acetate (1.0 g, 6.65 × 10^{-3} mol) and acetophenone (6.90 g, 5.7 × 10^{-2} mol) in *t*-butyl alcohol (10 g).

The tubes were centrally placed and periodically rotated during irradiation in the Rayonet reactor. Total reaction time was 32 hr. Three points were taken during this time and analyzed by vpc at 235° (He) on a 6-ft column of 5% Carbowax 20M on Chromosorb G. Dibutyl adipate served as an internal standard. Analysis showed that neither the rate of disappearance of *p*-tolyl acetate (Figure 1) nor the rate of formation of 2-hydroxy-5-methylacetophenone was affected by the presence of the additives. It was likewise shown that irradiation in the presence of acetophenone produced no reaction whatsoever. Similarly, irradiation of an acetophenone–ester solution with a broad-spectrum mercury (>3000 Å) arc afforded no products.

Deuterium Studies. Preparative irradiations were carried out in Vycor microtubes containing *p*-tolyl acetate-d_3 (0.831 g) in *t*-butyl alcohol (1.298 g) and *p*-tolyl acetate-d_3 (0.888 g) in ethanol (1.386 g) with 2537-Å light from the Rayonet reactor. The irradiation period was 260 hr. Product analysis was accomplished *via* vpc as described above. Microdistillation afforded a sample for mass spectral analysis. In a control to determine the facility of exchange from the photo-Fries product, a solution of 2-hydroxy-5-methylacetophenone (0.132 g) in methanol-d_1 (2.411 g) was allowed to stand in the dark for 192 hr, and was then analyzed by mass spectroscopy.

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(36) W. G. Leighton and G. S. Forbes, *J. Am. Chem. Soc.*, **52**, 3139 (1930).

(37) H. E. Zimmerman and J. S. Swenton, *ibid.*, **89**, 906 (1967).