Mechanistic Studies in the Photochemical Fries Rearrangement of Enol Esters [1a,b]

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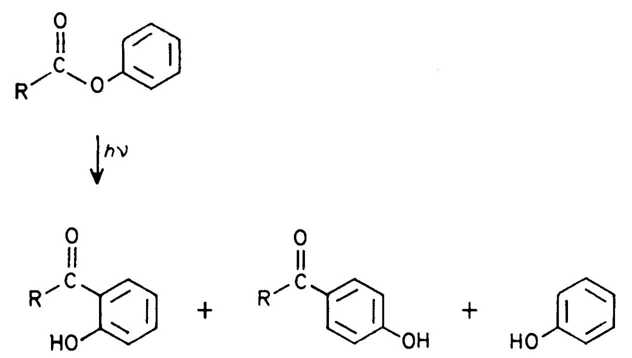
Photolysis of several enol esters produces the corresponding 1,3-Fries products, *i.e.* the keto forms of the β-diketones, as the sole primary photoproducts. The quantum yields of the rearrangements under a variety of conditions were measured. They decrease when the number of fused aromatic rings in the acyl part of the molecules is increased. The photobehaviour of the 2-anthroyl derivative is exceptional, in being affected both by the exciting wavelength and the solvent. Its irradiation at 254 nm results in a photo-Fries rearrangement (p.f.r.) with a yield twice that in ethanol; irradiation at 366 nm causes only inefficient dimerization. Explanations are forwarded for the general photobehaviour of the enol esters and its relation to the 1,3-p.f.r. of aryl esters and to other photoinduced 1,3-shifts.

THE photoinduced Fries rearrangement (p.f.r.) of aryl esters into *ortho*- and *para*-hydroxybenzophenones was first described [2] in 1960 (Scheme 1). Since that time the scope and the mechanism of the p.f.r. of aryloxy compounds have been widely investigated.[3] An analogous intramolecular rearrangement of enol esters, which do not possess the aryloxy functional group, was first reported in 1963.[4] However, few mechanistic studies of this rearrangement have been reported, apart from those based on the photoproducts obtained upon prolonged preparative photolysis.[4-6] The present paper gives a detailed report of the photobehaviour of enol esters under a variety of conditions, and compares the p.f.r. in this class of compounds with that observed with aryloxy compounds.



SCHEME 1

EXPERIMENTAL

Uncorrected m.p.s were measured in capillaries. I.r. spectra were recorded on a Perkin-Elmer Infracord 327 and u.v. spectra on a Cary 14 spectrophotometer. Low temperature measurements were carried out by the copper block technique.[7] Florescence spectra were measured on a home-made recording spectrofluorimeter. N.m.r. spectra were recorded on a Varian A-60 spectrometer, using tetramethylsilane as internal standard.

Compounds.—β-Diketones (IIa—e) were prepared and purified as described.[8] Commercial isopropenyl acetate (Ia) was purified by distillation and preparative g.l.c. (Carbowax 15%, 70% C). Other isopropenyl esters were synthesized *via* the reaction of 2-(chloromercuri)acetone with the corresponding acyl halide which served for the preparation of enol benzoates.[9]

Isopropenyl benzoate (Ib) was twice distilled and the fraction used had b.p. 84—85° at 5 mmHg; $\nu_{max.}$ (CS_2) 1 745, 1 667, 1 282, 1 219, and 1 100 cm^{-1}; $\lambda_{max.}$ (C_6H_{12}) 227 (ε 18 300) and 265 nm (1 520); δ($CDCl_3$) 2.07, 4.85, 7.45, and 8.10. The overall chemical yield was 40%.

Isopropenyl 2-naphthoate (Ic) was purified by preparative g.l.c. (F.F.A.F. 4%; 180°) and had b.p. 119—120° at 0.5 mmHg; $\nu_{max.}$ (CS_2) 1 724, 1 667, and 1 190 cm^{-1}; $\lambda_{max.}$ (C_6H_{12}) 238 (ε 66 200), 260 (4 700), 273 (6 630), 291 (8 160), 292 (7 110), 318 (1 240), and 334 nm (1 860); δ($CDCl_3$) 2.07, 4.90, 7.75, and 8.00 (Found: C, 79.2; H, 5.7. $C_{14}H_{12}O_2$ requires C, 79.0; H, 5.55%). The overall chemical yield was 30%.

Isopropenyl 2-anthroate (Id) was twice crystallized from a CH_2Cl_2–CH_3OH mixture, m.p. 121°, $\nu_{max.}$ (CS_2) 1 724, 1 667, 1 205, and 1 087 cm^{-1}; $\lambda_{max.}$ (C_6H_{12}) 239 (ε 23 900), 259 (86 800), 270 (79 800), 324 (2 360), 339 (4 060), 356 (4 750), 376 (4 830), and 387 nm (5 190); δ($CDCl_3$) 2.12, 4.90, and 7.4—8.8 (Found: C, 82.25; H, 5.4. $C_{18}H_{14}O_2$ required C, 82.2; H, 5.35%). The overall yield was 10%.

17β-*Acetoxyandrost-2-en-3-yl 2-Naphthoate*.—17β-Acetoxy-5α-androstane-3-one (III) (0.9 g) and 2-naphthoic anhydride (1.7 g) were dissolved in chloroform (8 ml) and a drop of 70% aqueous perchloric acid was added. The solution was warmed to start the reaction, and then stirred at room temperature for *ca*. 15 min. The solid was filtered off and the solution extracted with 5% aqueous $NaHCO_3$ and then with water, dried, and evaporated at room temperature under reduced pressure. Recrystallization of the residue from a CH_2Cl_2–CH_3OH mixture gave *enol ester* (Ie) (0.13 g, 10%), m.p. 191°; $\nu_{max.}$ (KBr) 1 724, 1 639, 1 282, 1 250, and 781 cm^{-1}; $\lambda_{max.}$ (C_6H_{14}) 238 (ε 60 400), 271 (6 710), 280 (7 700), 291 (5 420), 319 (1 140), 326 (1 040), and 334 nm (1 660); δ($CDCl_3$) 0.80, 0.97, 2.05, 4.61, 5.43, and 7.75 (Found: C, 79.0; H, 7.85. $C_{32}H_{38}O_4$ requires C, 78.95; H, 7.8%).

Preparative Photolysis.—Magnetically stirred cyclohexane (spectrograde) solutions of the enol ester in quartz vessels were photolysed by external irradiation, employing low pressure mercury lamps. After several hours of irradiation the solvent was removed under reduced pressure and the residue was chromatographed. The components were identified by comparison with authentic samples.

(a) *Photolysis of isopropenyl 2-naphthoate* (Ic). Compound (Ic) (0.9 g) in cyclohexane (100 ml) were irradiated (Philips 15 W) for 3 h. Preparative t.l.c. (Kieselgel; eluant ethyl acetate–hexane 5 : 95) afforded 2-naphthaldehyde and 2-naphthoic acid. Preparative g.l.c. (F.F.A.P. 4%; 250°) afforded 2-naphthoylacetone (IIc) (0.09 g).

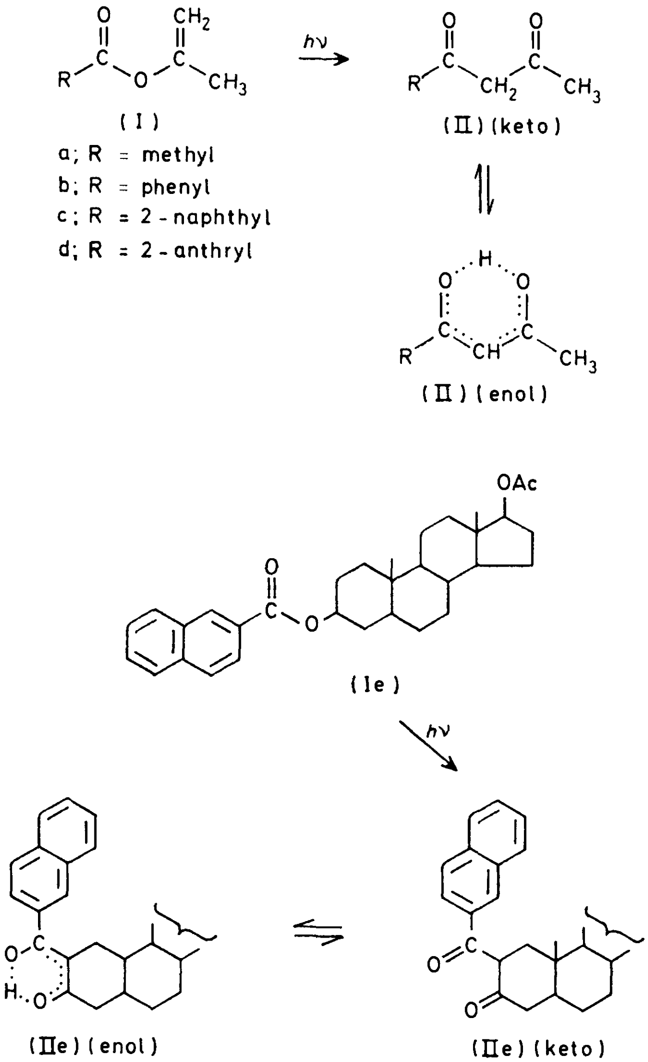
(b) *Photolysis of enol ester* (Ie). Compound (Ie) (0.4 g) in cyclohexane (600 ml) were irradiated (Philips; 15 W) for 2 h. Chromatography of the photolysis mixture over silica gel (30 g) afforded five fractions. Elution with ethyl acetate–hexane (5 : 95) gave 2-naphthaldehyde (15 mg), the starting material (Ie) (30 mg), and the β-diketone (IIe) (250 mg). Elution with ethyl acetate–hexane (10 : 90) yielded the saturated ketone (III) (30 mg) and the unsaturated ketone (IV) (25 mg).

(c) *Photolysis of isopropenyl 2-anthroate* (Id). Compound (Id) (200 mg) in cyclohexane (200 ml) were irradiated in a Rayonet reactor at λ 254 nm for 12 h. Chromatography of the photolysis mixture on a silica gel column (30 g; eluant ethyl acetate–hexane 5 : 95) gave 2-anthroylacetone (IId) (30 mg).

Analytical Photolysis employing Spectrophotometric Techniques. Measurement of Quantum Yields.—U.v. irradiations *in situ* and spectrophotometry were carried out in a Cary 14 recording spectrophotometer. Analysis was based on the changes in the u.v. absorption spectrum. Light sources used for monochromatic irradiation were: at 245 nm a low pressure mercury arc combined with a chlorine filter (30 mm light path, at 1 atm) and a Co–Ni filter [$CoSO_4,7H_2O$ (145 g) + $NiSO_4,6H_2O$ (450 g) in H_2O (1 l), placed in a 30 mm quartz cell]; an Osram HBO-200 high pressure mercury arc, combined with a Schott interference filter for 313 nm, or with a Glass filter combination for 366 nm. Irradiations were carried out in regular 10 mm square cells in the Cary 14 cell compartment; cells of 1, 50, or 100 mm light path were occasionally employed for experiments at various concentrations. The optical density at the wavelength used for irradiation never exceeded 0.6. In determinations of quantum yields the extent of the photoconversion was kept below 15%, and the solution was mixed during and after irradiation. The light flux was determined by ferrioxalate actinomety. Representative values were 4.4×10^{-8}, 5.0×10^{-9}, and 10^{-6} einstein min^{-1} at 254, 313, and 366 nm, respectively. Relative light intensities were determined by means of the fluorescence from a similar cell filled with a solution of Rhodamine B in propylene glycol, serving as quantum converter. Solvents (spectroscopic or AnalaR quality) were dried before use. Dissolved oxygen was removed by bubbling argon (<5 p.p.m. oxygen) through the solution for 15 min.

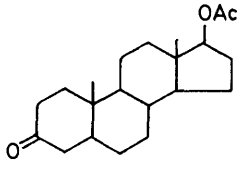
RESULTS AND DISCUSSION

Preparative 254 nm *Photolysis*.—The observations described in the Experimental section indicate that 254 nm irradiation results in the formation of the Fries products at rather low chemical yields [(IIa) (25%),[5a] (IIb) (8%),[4a,c] (IIc) (10%), (IId) (15%) and (IIe) (62%) (present investigation)], together with considerable amounts of byproducts [(Ic) ⟶ (IIc) + 2-naphthaldehyde + 2-naphthoic acid; (Ie) ⟶ (IIe) + (III) + (IV) + 2-naphthaldehyde]. The latter could result from a primary photoreaction (acyl–O homolysis) of the enol esters,[5] but might also be produced as secondary photoproducts *via* the corresponding β-diketones which are photoreactive[8] and absorb light at 254 nm much more strongly than the starting compounds.

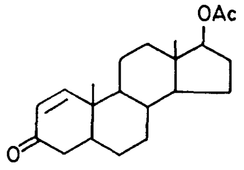


SCHEME 2

'Analytical' Photolysis.—In order to avoid the misinterpretation of the product distribution resulting from the above, the photoconversion was re-examined, using monochromatic irradiation at 254 or 313 nm, relatively low extents of photoconversion, and dilute solutions [10^{-3}—10^{-6}M; compounds (Ia—e)]. The reaction was followed by way of the disappearance of the absorption bands of the esters (Ib—d), and the appearance of absorption bands characterizing the enolic form of the β-diketones (IIa—d) at longer wavelengths. Irradiation of the enol esters (Ib—d) at 0 °C in hexane solution resulted in peaks corresponding to the keto form of (IIb—d), the logical products of p.f.r. (Figure 1). When



(III)



(IV)

the temperature was raised, the 'keto' absorption spectra disappeared, and those of the corresponding enols were formed instead. At room temperature this thermal enolization of the 2-acetyl ketones took a few minutes in ethanol but *ca.* 2 h in hexane or cyclohexane. The hexane solution of (IIe) even retained the keto absorption spectrum indefinitely at room temperature. If the absorption spectra were taken only after completion of the thermal enolization following each irradiation, the spectra represent the absorption of stoicheiometric mixtures of the enol ester and the enolic forms of the corresponding diketones [compounds (Ia—d)]. In (Ie), the sole product is the actual diketone, which does not enolize. In both hexane and ethanol the p.f.r. proceeded smoothly and yielded β-diketones as the only apparent photoproduct, even after 70—90% of the esters (Ib—e) had reacted (Figures 2 and 3a).

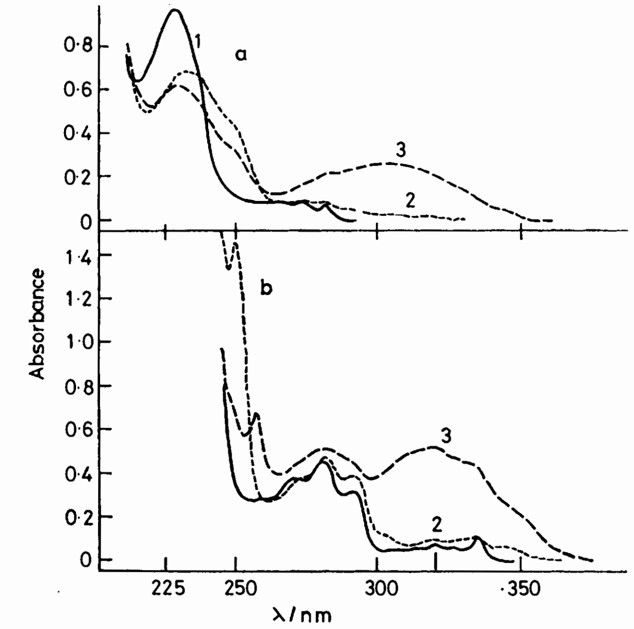


FIGURE 1 Absorption spectra before (curves 1) and after (curves 2) u.v. irradiation at 0°, and after keeping the irradiated solutions at 25° until no further spontaneous changes occurred (curves 3). (a) Isopropenyl benzoate (Ib) in hexane, 4.6×10^{-5}M, irradiation at 254 nm; (b) isopropenyl 2-naphthoate (Ic) in hexane, 4.5×10^{-5}M, irradiation at 313 nm

In this respect, the photorearrangement of the enol esters differs from that of the aryl esters, whose Fries products are always accompanied by phenols which are also primary photoproducts.[3] However, the quantum yields for the formation of the phenol and for 1,5-Fries products were shown [10,11] to be highly solvent-dependent, whereas the quantum yield for the formation of the 1,3-Fries products was insensitive to the reaction environment.[10,11]

In Table 1 we present quantum yields for the p.f.r. of the enol esters (Ia—e) under various conditions. The quantum yields for (Ia—d) are seen to be independent of light intensity and wavelength, presence of oxygen, and concentration of the ester. Moreover, they were not affected by wide variations in the hydrogen-donating ability, the polarity, or the viscosity of the solvent. The yields are rather similar to those reported for the 1,3-p.f.r. of the analogous aryl esters (phenyl acetate 0.18,[12] 0.14—0.17,[13] 0.14—0.18; [11] phenyl benzoate 0.19 [14]).

The quantum efficiencies summarized in Table 1 are seen to decrease markedly when the number of fused aromatic rings in the acyl part of the molecule is increased. The anthroyl derivative (Id) which gave the least efficient p.f.r. in this series proved to be exceptional. Its behaviour was affected both by the wavelength and by the solvent though not by oxygen. Irradiation of (Id) at 254 nm resulted in a p.f.r. (Figure 3a) but the yield in hexane was twice that in ethanol. Irradiation at 366 nm caused only inefficient dimerization, as usual in anthracene derivatives,[15] with a quantum yield similar to that of ethyl 2-anthroate (Figure 3b, Table 2).

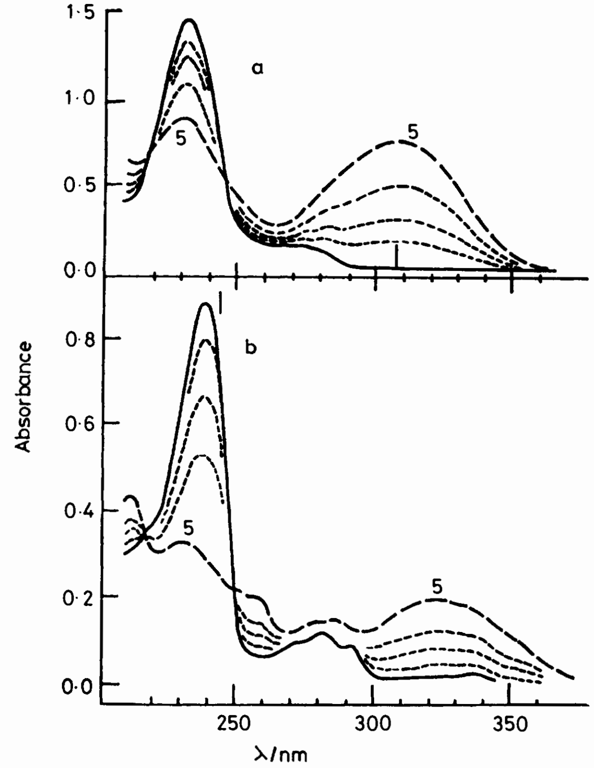


FIGURE 2 Photoinduced changes in the absorption spectra of solutions in ethanol. Each of the spectra following irradiation was taken after all spontaneous changes went to completion (see text). (a) Isopropenyl benzoate (Ib) 8×10^{-5}M, irradiation at 254 mm. Curve 1, before irradiation; curves 2—5; following irradiation for 0.5, 1, 2, and 5 min, respectively. (b) Isopropenyl 2-naphthoate (Ic), 1.3×10^{-5}M, irradiation at 313 nm. Curve 1, before irradiation; curves 2—5, following irradiation for 5 15, 30, and 60 min, respectively

The absorption and emission spectra of the enol 2-anthroate (Id) were similar to those of ethyl 2-anthroate. The fluorescence spectra of both show the same solvent dependence [16] (Figure 4).

The Primary Photochemical Event.—Formally, the photoinduced intramolecular [5a] rearrangement of the enol esters is closely related to the p.f.r. of the aryl

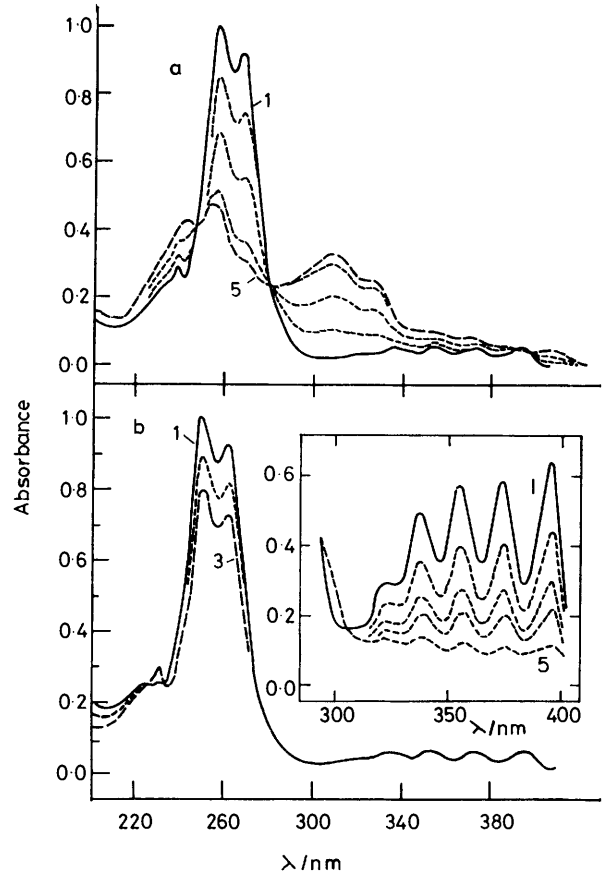


FIGURE 3 Photoinduced changes in the absorption spectrum of isopropenyl 2-anthroate (Id) in cyclohexane, 1.1 × 10^{-4}M, in a 1 mm cell. Full curves, before irradiation. (a) Irradiation at 254 nm. (b) Irradiation at 365 nm. Insert in (b); 10 mm cell, before and after irradiation at 365 nm during 30, 60, 120, and 300 min, respectively. Note gradual disappearance of the characteristic anthracene bands

esters. However, whereas the rearrangement of the aryl esters has been subject to intense scrutiny, few mechanistic photochemical studies of the enol esters have been reported. The comparison of the photobehaviour of these two ester types appears highly desirable, as differences in molecular structure, spectroscopic properties and ground state chemistry might contribute to a better understanding of both rearrangements.

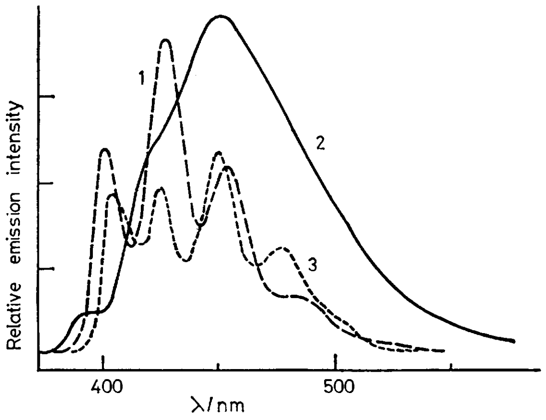


FIGURE 4 Emission spectra at room temperature (uncorrected): curves 1 and 2, isopropenyl 2-anthroate (Id) 2 × 10^{-5}M in hexane and in ethanol, respectively; curve 3, (2-anthroyl)-acetone (IId) in hexane 10^{-5}M

TABLE 1

Quantum yields Q of p.f.r. of various enol esters in several solvents. Wavelength of irradiation are indicated by superscripts: 1, 254; 2, 313; 3, 366 nm. Solvents: H, hexane; E, ethanol, H_2O, water; M, methanol; 2P, propan-2-ol; DD, n-dodecane; TB, t-butyl alcohol. *Denotes degassed solutions. Irradiation intensity refers to the actinometric result obtained with 3 ml of ferrioxalate solution in a cell identical with the ones used for irradiation of the solutions

Compd.	Solvent	Concentration (M)	Irradiation intensity [einstein min^{-1} $(3 ml)^{-1}$]	Q	$\frac{Q\ (solvent)}{Q\ (hexane)}$
(Ia)^1	H	1.3 × 10^{-2}	4.4 × 10^{-8}	0.18	1.0
	E	6.0 × 10^{-2}	,,	0.17	0.96
	E	1.3 × 10^{-2}	,,	,,	,,
	E	,,	5.7 × 10^{-9}	,,	,,
	E *	,,	4.4 × 10^{-8}	,,	,,
	E	,,	,,	,,	,,
	H_2O	1.5 × 10^{-2}	,.	,,	,,
	0.01N-HCl	1.5 × 10^{-2}	,,	0.16	0.91
(Ib)^1	H	5.4 × 10^{-5}	4.4 × 10^{-8}	0.12	1.0
	E	5.4 × 10^{-5}	,,	,,	,,
	E	5.4 × 10^{-4}	,,	,,	,,
	E	1.1 × 10^{-5}	,,	,,	,,
	E *	5.4 × 10^{-5}	,,	,,	,,
	E	5.4 × 10^{-5}	5.7 × 10^{-9}	,,	,,
(Ic)^1	H	8.5 × 10^{-5}	4.4 × 10^{-8}	0.08	1.0
	E	8.5 × 10^{-5}	,,	,,	,,
	E	8.5 × 10^{-4}	,,	,,	,,
	E *	8.5 × 10^{-5}	,,	,,	,,
	E	8.5 × 10^{-5}	5.7 × 10^{-9}	,,	,.
(Ic)^2	H	4.5 × 10^{-5}	5.0 × 10^{-9}	0.06	1.0
	E	4.5 × 10^{-5}	,,	0.07	1.1
	E	4.5 × 10^{-4}	,,	,,	,,
	E	9 × 10^{-6}	,,	,,	,,
	E *	4.5 × 10^{-5}	,,	,,	,,
	E	,,	6.5 × 10^{-10}	,,	,,
	DD	,,	5 × 10^{-9}	0.06	1.0
	TB	,,	,,	0.07	1.1
	2P	,,	,,	0.07	1.1
	M	,,	,,	0.07	1.1
(Ie)^1	H	2.3 × 10^{-5}	4.4 × 10^{-8}	0.06	1.0
	H	,,	5.7 × 10^{-9}	0.06	1.0
(Ie)^2	H	2.3 × 10^{-5}	5 × 10^{-9}	0.06	1.0
	H *	,,	5 × 10^{-9}	0.06	1.0
(Id)^1	H	8.0 × 10^{-5}	4.4 × 10^{-8}	0.02	1.0
	E	8.0 × 10^{-5}	,,	0.01	0.57
	E	8.0 × 10^{-6}	,,	,,	,,
	E	8.0 × 10^{-7}	,,	,,	,,
	E *	8.0 × 10^{-6}	,,	,,	,,
	E	8.0 × 10^{-6}	5.7 × 10^{-9}	,,	,,
(Id)^3	H	2.3 × 10^{-5}	1.3 × 10^{-6}	<0.001	
	E	2.3 × 10^{-5}	1.3 × 10^{-6}	<0.001	

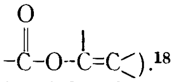
The enol esters were considered by several reviewers [3] to possess an unfavoured electronic configuration (n,π^* lowest singlet state), supposedly resulting in low conversions into the Fries products, and production of a number of α-cleavage products. However, no attempt has been made to identify the primary photoproducts in the photolysis mixture and to measure the quantum yield of their formation.

Our results indicate that aliphatic and aromatic enol esters undergo efficient p.f.r. with similar quantum yields (0.1—0.2) and insensitivity to the environment, as reported for the 1,3-acyl shift of the aryl esters. The enol ester rearrangement proceeds smoothly, up to 90% photoconversion, with a variety of enol esters excited within the absorption region assigned to the acyl group. These conversions are much higher than those observed in aryl esters excited in the absorption band assigned to aryloxy group.[11] Therefore, it seems unjustified to claim that the p.f.r. results only from the excitation of the aryloxy group,[10b,11,12] or that the excitation of the carbonyl group must result in the formation of cleavage products.[17]

TABLE 2

Relative rates of photoinduced disappearance of ethyl 2-anthroate (EA) and isopropenyl 2-anthroate (Id) in hexane at the concentrations indicated. Irradiation at 365 nm

Compound	Concentration (M)	Relative rate
(Id)	1.9×10^{-5}	1.2
EA	1.9×10^{-5}	1.0
(Id)	1.3×10^{-4}	1.1
EA	1.1×10^{-4}	1.0

The decisive factor regarding the efficiency of the p.f.r. of the enol esters seems to be the energy of the reacting excited state. This is demonstrated in our results by the substituent effect on the quantum yield, as well as by the photobehaviour of (Id). Thus, the quantum yield decreases with an increase in the number of fused rings in the acyl part of the molecule, or with the decline of the energy of the lowest excited singlet state of the enol esters. [Estimated S_1 energies are (Ia) 114, (Ib) 97, (Ic and e) 83, (Id) 70 kcal mol^{-1}.] The decline in quantum yield is not accompanied by the appearance of additional reaction products, and has therefore to be attributed to competing photophysical processes, such as fluorescence, radiationless transitions $S_1 \longrightarrow S_0$, and inter-system crossing $S_n \longrightarrow T_n$. Therefore, the p.f.r. of the enol esters seems to take place from a specific electronic level S_x in which a large proportion of the light energy is accumulated in the reaction centre (*i.e.*  $-\overset{\overset{\displaystyle O}{\|}}{C}-O-\overset{|}{C}=C\!<$).[18] As long as the first excited electronic level S_{ar}, due to the aroyl group, is above S_x, the latter is populated either by direct excitation or by internal conversion from higher levels, including S_{ar}. As S_{ar} is lowered in the series (Ia—c) and approaches S_x, less S_{ar} energy is channelled into S_x, resulting in a lowering of the quantum yield of the p.f.r. in the order (Ia—c). In (Id), S_{ar} is considerably below S_x, and direct excitation of the S_{ar} level (by irradiation at 366 nm) no longer causes a p.f.r., while excitation to higher electronic levels,[18] by irradiation at 254 nm, results only in inefficient p.f.r., competing with the usual fast $S_2 \longrightarrow S_1$ internal conversion.

The 1,3-p.f.r. might occur *via* short-lived excited states (vibrationally excited levels of S_1 and S_2) undergoing dissociative processes virtually upon excitation.[18] The 1,3-p.f.r. of the aryl esters and the aryl amides might well fit this description, as they exhibit a similar substituent effect of the acyl moiety on the quantum yield Q of formation of the 1,3-Fries products.[19] (The following Q values have been reported: CH_3-CO-OC_6H_5, 0.27; C_6H_5-CO-OC_6H_5, 0.17; CH_3-CO-NH-C_6H_5, 0.07; C_6H_5-CO-NH-C_6H_5, 0.01).

The Rearrangement.—Basically, two different intramolecular mechanisms have been proposed for the 1,3-p.f.r.[3] A concerted one, in which the acyl and the alkenyloxy (or aryloxy) portions retain some form of bonding throughout the entire course of the rearrangement,[10] or one involving formation of a radical pair held together by the solvent cage and undergoing a subsequent recombination.[2b] The radical-in-cage mechanism implies that reactions such as escape from the solvent cage, epimerization, and physical phenomena such as CIDNP should be observable in 1,3-Fries reactions. The experimental facts are that the enol ester rearrangement is not accompanied by any cleavage products and is independent of its reaction environment; it is also reported [5a] to be sterically controlled for some cyclic enol esters. Hence, a mechanism *via* a concerted intermediate is more plausible. However, a mechanism *via* an ‘ interacting radical pair ’ cannot be ruled out, since CIDNP was observed in 1,3-Fries products upon photolysis of *p*-cresyl *p*-chlorobenzoate.[20] An ‘ interacting radical pair ’ may be best described [3d] as a ‘ ground-state sigmatropic shift transition state ’ which is only slightly more stable, at best, than a radical pair and may collapse into a caged radical pair with rather subtle changes in molecular structure or reaction conditions.

We conclude that the enol ester rearrangement closely resembles the 1,3-p.f.r of aryl esters, as well as the general 1,3-shift in γβ-unsaturated carbonyl compounds.[3d] However, other γβ-unsaturated carbonyl compounds exhibit a complicated photochemistry, in which the 1,3-shifts are always accompanied by one or more parallel primary photoreactions, whereas in the enol esters the only photoreaction is the 1,3-acyl shift. This reaction may therefore serve as the simplest case of a clean photoinduced 1,3-shift in γβ-unsaturated carbonyl compounds.

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