4-Amino-5-aminomethyl-2-methylpyrimidin (**15**). 3,4 g (25 mmol) **8a** werden in 300 ml Methanol in Gegenwart von 9 g flüssigem Ammoniak und 1 g *Raney*-Kobalt bei 100–110° und 60 atü im Autoklav während 13 Std. hydriert. Die nach Filtration erhaltene teebraune Lösung wird im RV. zur Trockene eingedampft, der ölige Rückstand durch Zugabe von alkoholischer Salzsäure in das Hydrochlorid übergeführt und durch Addition von Äthylacetat zur Kristallisation gebracht. Zweimalige Umkristallisation aus Methanol/Äthylacetat. Ausbeute: 2,2 g (50%). Smp. 248–250° (Zers., Subl.). In allen Eigenschaften identisch mit einem auf anderem Weg [10] hergestellten Präparat.

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134. Effect of Substituents and of Wavelength of Irradiation on the Photo-*Fries*-Rearrangement of Enol-Esters

Preliminary Communication

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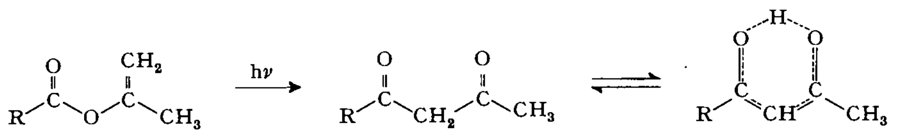
Summary. Enol-esters **1a–1e** undergo clean Photo-*Fries*-rearrangements withouth side reactions. With anthroyl derivatives the reaction is observed only at 254 nm, not at 366 nm.

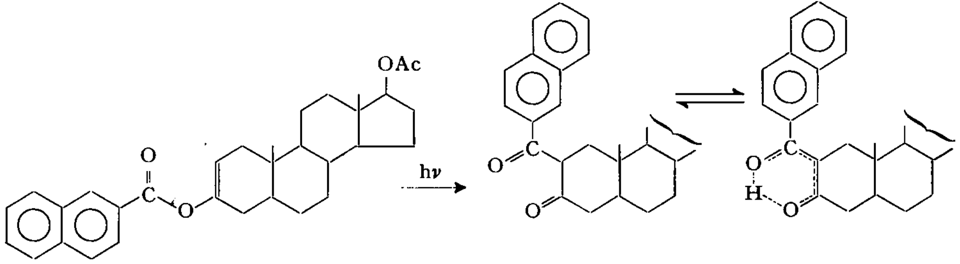
The Photo-*Fries*-rearrangement (PFR.), has in recent years attracted intensive attention [1]. While its mechanism is still under discussion, the general view [2–7] seems to be that the PFR. starts from an excited electronic level assigned to the aryloxy group which characterizes compounds of the type Aryl-OX, where X is hydrogen, methyl, allyl, phenyl, or acyl [4] [5].

We wish to report that UV. irradiation of enol-esters **1a–1e** at 254 nm, and **1c** and **1e** also at 313 nm, causes a clean PFR., without side reactions, with a quantum yield of about 0.1 (*i.e.* similar to that reported for the arylesters [3]) which is practically



1a–d **2a–d** (keto) **2a–d** (enol)

1a: R = methyl; **1b**: R = phenyl;
1c: R = 2-naphthyl; **1d**: R = 2-anthryl



1e **2e** (keto) **2e** (enol)

independent of the concentration and light intensity. There is no significant difference between the behaviour of solutions in hexane and in ethanol. The anthroyl derivative **1d** undergoes PFR. only at 254 nm, not at 366 nm. For preparation and isolation purposes, 1% solutions of **1a**–**1e** in cyclohexane were irradiated at 254 nm for several hours. The solvent was then evaporated and the 1,3-diketone products **2a**–**2e** isolated chromatographically and characterized.

Spectrophotometric and photochemical experiments were carried out in solutions in hexane and in ethanol, in regular spectrophotometric cells. Irradiation was carried out with monochromatic light from a low- or medium-pressure mercury lamp isolated by means of suitable filters. The reaction was followed by way of the disappearance of the absorption band due to the esters **1b**–**1e** and the appearance of the absorption bands of the enolic form of the diketo-esters **2a**–**2e** at longer wavelengths. In both hexane and ethanol, the PFR. proceeded smoothly with similar quantum yields, and without side reactions, even after 70–90% of the ester had reacted. The PFR. is followed by thermal equilibration with the enol form, the rate of which depends on the solvent. Neither the course of the reaction nor the quantum yield Q of the PFR. changed with the ester concentration in the range 10^{-3}–10^{-6} M or with the light intensity (5×10^{-9} to 5×10^{-8} Einstein min^{-1} incident on the cell surface), nor was it affected by the presence of air. The quantum yields summarized in the Table are seen to decrease markedly when the number of fused aromatic rings in the acyl part of the molecules is increased. The behaviour of **1d** was exceptional. Its irradiation at 366 nm caused only inefficient dimerization, as usual in anthracene derivatives [8]. Irradiation at 254 nm resulted in a PFR., but the yield in hexane was twice as that in ethanol. The photobehaviour of **1d** *is* thus affected by the wavelength and the solvent:

$$\text{dimer} \xleftarrow{366\ \text{nm}} \mathbf{1d} \xrightarrow{254\ \text{nm}} \text{PFR. (+ dimer).}$$

On the background of the extensive earlier reports on the PFR., the following conclusions appear plausible: (a) The PFR. proceeds smoothly with a variety of enol-esters R–CO–O–C(CH_3)=CH_2 excited within the absorption region assigned to the acyl group, just as observed in a variety of aryl-esters R–CO–O–Ar excited in the aryloxy group [4]. Therefore it seems unjustified to claim that the PFR. results only from the excitation of the aryloxy group [3] [4] or that excitation of the carbonyl group must result in the formation of cleavage products [5] [6]. (b) The decline in Q (PFR.) with the increase in the number of fused aromatic rings in the acyl part is not accompanied by the appearance of side reaction products, and has therefore to be attributed to competing photophysical processes, such as fluorescence, radiationless transitions $S_1 \rightarrow S_0$, and intersystem crossing $S_n \rightarrow T_n$. The decisive factor regarding the PFR. quantum yield seems to be the energy of the lowest excited singlet state of the enol ester. (Estimated S_1 energies are – in kcal mol^{-1}) – **1a**: 114, **1b**: 97, **1c** and **1e**: 83, **1d**: 70). A possible explanation would be that the PFR. takes place from a specific electronic level S_X. 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 **1a**–**1c** and approaches S_X, energy is increasingly channeled into S_{Ar}, resulting in a lowering of the quantum yield of the PFR. in the order **1a**–**1c**. In **1d**, S_{Ar} is considerably below S_X and direct excitation of the S_{Ar} level (by irradiation at 366 nm) no longer causes a PFR., while excitation to S_2 and higher electronic levels [9], by irradiation at 254 nm, results in an, albeit inefficient, PFR. competing with the usual fast $S_2 \rightarrow S_1$ internal conversion. The fact that such a competition is at all possible, together with the absence of side reactions and of appreciable solvent effects, indicates that the PFR. is fast enough to compete not only with fluorescence but even to some extent with internal conversion. *Ullman's* [9] description of short-lived upper excited states undergoing "dissociative processes ... virtually instantaneously upon excitation" might fit

Table. *Quantum Yields, Q*[a]), *of the PFR. in Various Enol-esters*

Compound	Solvent	Irradiation Wavelength (nm)	Monitoring Wavelength (nm)	Q	$Q_{ethanol}/Q_{hexane}$
1a	ethanol	254	274	0.17	0.96
	hexane	254	270	0.18	
1b	ethanol	254	308,229	0.12	1.00
	hexane	254	306,227	0.12	
1c	ethanol	254	320,238	0.08	
	ethanol	313	320,238	0.07	1.05
1c	hexane	313	318,238	0,06	
1e	hexane	254	238,248	0.06	
	hexane	313	238,248	0,06	
1d	ethanol	254	259,315	0,01	0.57
	hexane	254	259,310	0,02	
1d	ethanol	366	259	< 0.001	
	hexane	366	259	< 0.001	

[a]) Q values are estimated to be correct within 20% of the stated values.

the PFR.'s described here. (According to *Bellus* [1], the overwhelming majority of results in the literature indicate that the PFR. takes place from excited singlet levels); (c) Since we find that the enol-esters **1b–1e** undergo the 1,3-PFR. without any cleavage products [1], we conclude that *if* enol and acyl radicals are formed at all [10], they are kept together by strong interactions between them. The absence of pronounced differences between various solvents does not detract from the essential role played by the solvent, both in accepting excess energy and in serving as a cage.

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Erratum

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