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PHOTO-FRIES REARRANGEMENT OF HETEROAROMATIC ACID PHENYL ESTERS[1,2]

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Photolysis of the phenyl esters of pyridine-carboxylic acids **1a**-**b** and furan-2-**4a**, thiophene-2-**4b**, and N-methylpyrrole-2-carboxylic acids **4c** afforded the corresponding *o*- and *p*-hydroxyketones **2**,**3**,**5**,**6**.

The photo-Fries rearrangement has been the subject of considerable study in the last decade.[3-5] However, little attention has been given to the reactions of heterocyclic aryl esters except some examples of pyridine-containing esters[6,7] and *p*-t-butylphenyl furoate[8] with divergent results. In the course of our synthetic photochemical study in the heterocyclic series,[9] we wish to report the photolysis of the phenyl esters of pyridine-carboxylic acids **1a**-**b** and furan-2-**4a**, thiophene-2-**4b** and N-methylpyrrole-2-carboxylic acids **4c**.[10]

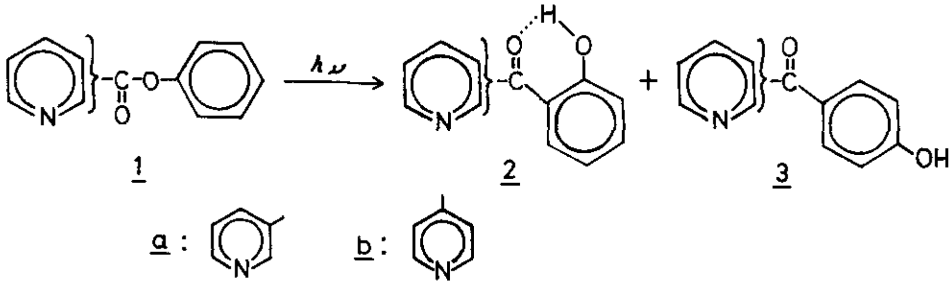
Although it has been generally recognized that both *o*- and *p*-rearranged products are formed from esters of unsubstituted phenol,[3-5] photolysis of aryl nicotinates and isonicotinates was reported to give either the *o*- or the *p*-products.[6] Therefore, the photoreactions of **1a**-**b** were first examined to determine the general photochemical behavior of such typical heteroaromatic esters. The reactions were run in hexane (500 ml; 10 m*M*) using three 10-W low-pressure mercury lamps. As expected, both the *o*-hydroxy- 2a-b and the *p*-hydroxy-ketones 3a-b were obtained (Table). The structural assignment of 2-3 was mainly based on their nmr spectra (comparison of the *p*-, and *o*-disubstituted benzene protons). Further, phenyl esters of five-membered electron-rich heteroaromatic carboxylic acids 4a-c were irradiated in acetonitrile (500 ml; 10 m*M*) with a 500-W high-pressure mercury lamp. The table compiles the results which are again in agreement with the general pattern of the photo-Fries rearrangement. The structures of 5-6 were similarly confirmed by their nmr spectra.

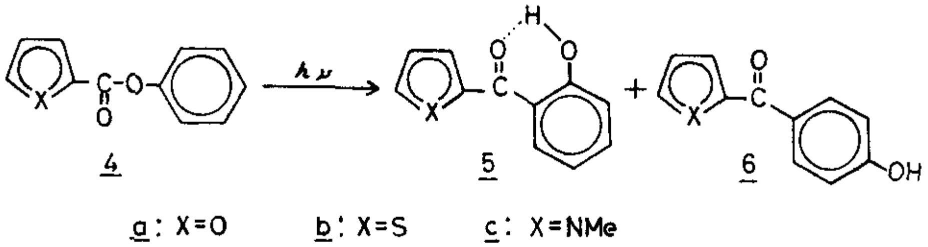
TABLE Photorearrangement of the Heteroaromatic Phenyl Esters

Ester	Reaction time (hr)	Recovered (%)	Hydroxyphenone (% yield)	mp° C (or bp)
1a	48	1a (25)	2a (25)	63-4
			3a (11)	196-6.5$^{a)}$
1b	66	1b (8)	2b (15)	74-5
			3b (6)	257-8.5
4a	1	4a (9)	5a (31)	bp$_3$125-30$^{b)}$
			6a (14)	163-4
4b	2.5	4b (14)	5b (33)	bp$_3$140-5$^{c)}$
			6b (22)	103.5-4.5
4c	1.5	4c (13)	5c (28)	bp$_2$135-40$^{d)}$
			6c (24)	136-6.5

a) lit.[6], mp 192 . Oximes, mp: b) 130-1° c) 128-9° d) 100-1°.

The mechanism of this rearrangement is not yet well understood and conflicting interpretations have been advanced in the literature.[5,11,12] Regardless of the detailed mechanism, however, it is worth noting that phenyl esters of the representative heteroaromatic acids as above undergo such a typical photo-rearrangement. In the conventional acid-catalyzed Fries reaction, the product distribution mostly favors *p*-hydroxyketones[13] and, in addition, very little has been known of examples in heterocyclic systems. Thus by the procedure described in the present work a variety of heterocyclic ketones will be readily accessible as a pair of the *o*- and *p*-hydroxy derivatives under neutral conditions without substantial side reactions. Scope and limitation of these reactions are under investigation.





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10 All new compounds gave satisfactory analyses and their structures were supported by spectral (uv, ir, nmr, mass) data.

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