Photochemistry of Selenol Esters[1]

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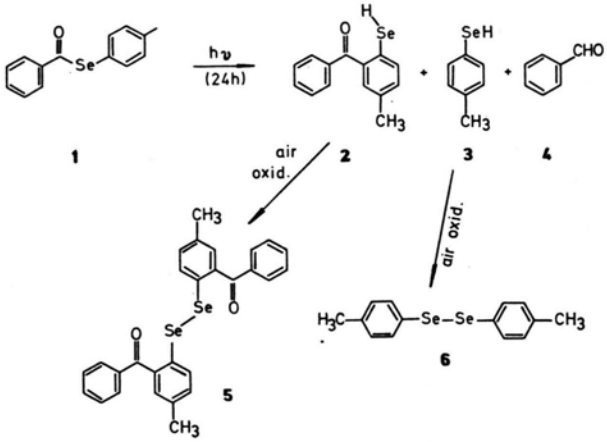
Selenium Compounds, Aromatic Photosubstitution, Seleno-photo-Fries Reaction, Photocyclizations

Depending upon the structure of the starting compounds, seleno-photo-Fries products or cyclization products (phenenthrenequinone or selenoxanthone) are obtained in novel photoreactions from areneselenol esters of aromatic carboxylic acids.

This is the first report on photoreactions of some Se-aryl carboselenoates. The photoproducts are compared with those of aryl carboxylates and S-aryl thiocarboxylates. Hitherto, there is only little published information available on photoreactions of organic selenium compounds[2].

Se-*p*-tolyl selenobenzoate (**1**)[3,4] is irradiated with UV light to give the seleno-photo-Fries product (**2**), *p*-selenocresol (**3**), and benzaldehyde (**4**) in 12% isolated yield. Immediate separation of the reaction products by column and thin-layer chromatography yields the sensitive selenols **2** and **3**, which form the isolatable diselenides **5** and **6**[5] in isolated 33% and 46% yield, resp., on oxidation with air.



The primary formation of **2** and **3** as intermediates in the conversion of **1** → **5** and **6** is proven by their ^{1}H NMR spectra in CCl_4 with peaks at δ 2.2 and 1.3 ppm, resp., using TMS as standard[6], after photolysis of **1** in this solvent in a Pyrex NMR tube while purged with argon.

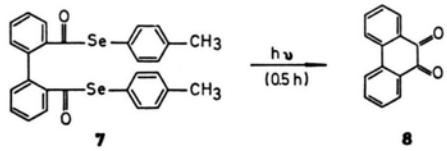
The photoreaction of **1** to give 2-(hydroseleno)-5-methylbenzophenone (**2**) is the first published example of a seleno-photo-Fries reaction.

The structure of the yellow diselenide **5** (m.p. 60–62 °C) is based on the following spectroscopic data: IR (CCl_4) $\nu_{C=O}$ 1640 cm^{-1}; ^{1}H NMR (CCl_4, δ-scale, TMS standard): Ar–H m 6.77–8.13 and Ar–CH_3 s 2.3 ppm, proton ratio 8:3; mass spectrum[7] (Varian MAT 711, evaporation temperature 170 °C): *m/e* 550 (8%, M$^+$), 470 (3%, M$^+$–Se), 390 (<1%, M$^+$–2 Se), 275 (100%, M$^+$/2), and 195 (4%, M$^+$/2–Se), high resolution of the molecular peak: calcd. 549.9950 amu, found 549.9974 amu (based on ^{80}Se).

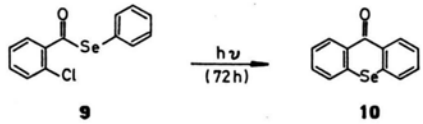
Suprisingly, the selenol ester **1** exhibits a photochemical behavior somewhere between that of the isoelectronic oxygen ester (photo-Fries reaction furnishes hydroxybenzophenones and phenols, but usually no aldehyde[8]) and the corresponding thiol ester (aldehyde formation, no photo-Fries reaction[9]).

The available results on photochemical investigations on di-S esters of 2,2′-dithiodiphenic acid[10,11], yielding phenanthrenequinone (**8**) in ≤33% yield, encouraged us to synthesize and irradiate di-Se-*p*-tolyl 2,2′-diselenodiphenate (**7**)[12].

The diselenol ester **7** furnishes in a suprisingly neat photoreaction[13] both **8** and the diselenide **6** in 89% yield.



Of interest seemed the question if the photochemical behavior of *ortho* acceptor-substituted selenol esters, such as **9**, resembles that of analogous thiol esters, which yield thioxanthones on UV-irradiation[14–16]. Irradiation[4] of Se-phenyl 2-chloroselenobenzoate[17] (**9**) with UV light and subsequent column chromatographic separation gives 19% selenoxanthone[18] (**10**).



Parallelism is observed in the photochemical behavior of the selenol esters **1**, **7**, and **9** and compounds containing the structural element –CO–X– (X = NR-aryl[8], O-aryl[8], or S-aryl[9,14–16]). In all cases the acyl-X bond is cleaved by UV light.

The investigations are continued with respect to both preparative and mechanistic aspects.

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