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Photo-*Fries* Rearrangement of 2-Naphthylbenzoate

Short Communication

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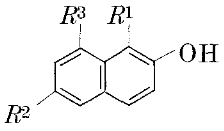
Photo-*Fries* rearrangement of 2-Naphthylbenzoate gives 6-benzoyl-2-naphthol and 8-benzoyl-2-naphthol in addition to the expected product, 1-benzoyl-2-naphthol.

(Keywords: Benzoyl-2-naphthols; Photochemistry)

Photo-Fries-Umlagerung von 2-Naphthylbenzoat (Kurze Mitteilung)

Die Photo-*Fries*-Umlagerung von 2-Naphthylbenzoat gibt zusätzlich zum erwarteten 1-Benzoyl-2-naphthol als weitere Produkte 6-Benzoyl-2-naphthol und 8-Benzoyl-2-naphthol.

The Photo-*Fries* rearrangement of esters of 1-naphthol are reported to give both *ortho* and *para* migrated products[1], while 1-naphthyl acetate exclusively gives 2-acetyl-1-naphthol[2]. In continuation of our earlier work[4], we report in this paper the Photo-*Fries* rearrangement of 2-naphthylbenzoate (**1**) in methanol. **1** was irradiated in nitrogen atmosphere by Ace Hanovia UV lamp for 6 h at 25°. The products were separated by column chromatography using silica gel. In addition to the expected product i.e. 1-benzoyl-2-naphthol (**2**) [m.p. 141°, 22%, (Lit.[5] m.p. 139-140°)], two other products i.e. 6-benzoyl-2-naphthol (**3**) [m.p. 155-157°; 18%; M^+248; NMR, $CDCl_3$ δ: 8.15 (s, H-5), 7.41-7,89 (m, 9H), 7.18 (d, $J = 3$ Hz, H-1)] and 8-benzoyl-2-naphthol (**4**) [m.p. 113°; 12%; M^+ 248; NMR, $CDCl_3$ δ: 8.05-8.23 (m, 2H), 7.12-7.82 (m, 9H)] were formed.



2: $R^1 = COPh$, $R^2 = R^3 = H$
3: $R^2 = COPh$, $R^1 = R^3 = H$
4: $R^3 = COPh$, $R^1 = R^2 = H$

The formation of these products (**2**-**4**) can be explained that the homolytic cleavage of the ester gives benzoyl and 2-naphthyloxy radicals, the latter is resonance stabilised by three different radicals with possible radical positions at C1, C6, and C8. Recombination[6] of these radicals gives the corresponding products.

The Photo-*Fries* rearrangement normally gives *ortho* and/or *para* migrated products[4,6,7] but in the present case migration has been observed in the condensed benzene ring as well; the intermediate radicals for the 6- and 8-benzoyl products allow for a favourable quinoid structure.

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