Monatshefte für Chemie 116, 353—356 (1985)

Monatshefte für Chemie
Chemical Monthly

Photo-*Fries* Rearrangement: Rearrangement of Benzoyloxy Compounds

Pavan K. Sharma and **Rajinder N. Khanna***

Department of Chemistry, University of Delhi, Delhi-110007, India

(Received 29 February 1984. Accepted 27 March 1984)

Photo-*Fries* migration of the benzoyl group in 1-benzoyloxy-5-methoxy naphthalene, 1,4-dibenzoyloxy-2-methyl naphthalene, 1,4-dibenzoyloxy naphthalene, 1,5-dibenzoyloxy naphthalene, 8-benzoyloxy quinoline, 1,2-dibenzoyloxy benzene, 1,3-dibenzoyloxy benzene, and 1,4-dibenzoyloxy benzene afforded the corresponding mono and di-C-benzoyl products.

(Keywords: Naphthyl benzoate derivatives; 8-Benzoyloxy quinoline; Phenyl dibenzoates)

Photo-Fries-Umlagerung: Umlagerung von Benzoyloxy-Verbindungen

Die Photo-*Fries*-Wanderung der Benzoylgruppe in 1-Benzoyloxy-5-methoxynaphthalin, 1,4-Dibenzoyloxy-2-methylnaphthalin, 1,4-Dibenzoyloxynaphthalin, 1,5-Dibenzoyloxynaphthalin, 8-Benzoyloxychinolin, 1,2-Dibenzoyloxybenzol, 1,3-Dibenzoyloxybenzol und 1,4-Dibenzoyloxybenzol ergab die entsprechenden Mono- und Di-C-Benzoyl-Produkte.

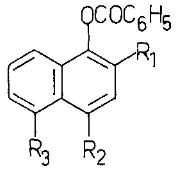
Introduction

Photo-*Fries* migrations[1-12] have drawn considerable attention in recent years. Whereas the migration of acetyl group has been studied extensively, only very few papers have been published on photo-*Fries* migration of the benzoyl group: e.g. phenyl benzoate[3,11] on photo-*Fries* migration gave a mixture of *ortho* and *para* benzophenones.

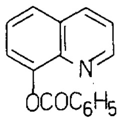
In order to explore the scope of light catalysed rearrangements, photo migrations of the benzoyl group in 1-benzoyloxy-5-methoxy naphthalene (**1**), 1,4-dibenzoyloxy-2-methyl naphthalene (**2**), 1,4-dibenzoyloxy naphthalene (**3**), 1,5-dibenzoyloxy naphthalene (**4**), 8-benzoyloxy quinoline (**5**), 1,2-dibenzoyloxy benzene (**6**), 1,3-dibenzoyloxy benzene (**7**) and 1,4-dibenzoyloxy benzene (**8**) have been studied.

Results and Discussion

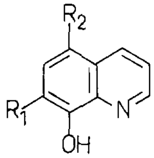
Photo-*Fries* migration of **1** and **2** afforded one product each: 2-benzoyl-5-methoxy-1-naphthol (**9**), and 2-benzoyl-4-benzoyloxy-3-methyl-1-naphthol (**10**), respectively. Photo-*Fries* migration of **3** furnished 2-benzoyl-4-benzoyloxy-1-naphthol (**11 a**) and 2,3-dibenzoyl-1,4-dihydroxynaphthalene (**11 b**). **4** furnished two products: 2-benzoyl-5-benzoyloxy-1-naphthol (**12 a**) and 2,6-dibenzoyl-1,5-dihydroxy naphthalene (**12 b**). **5** afforded 5-benzoyl-8-hydroxy quinoline (**13 a**) and 7-benzoyl-8-hydroxy quinoline (**13 b**). **6** furnished 2-benzoyl-6-benzoyloxy phenol (**14 a**) and 3,4-dibenzoylbenzene-1,2-diol (**14 b**). **7** afforded three products: 2-benzoyl-5-benzoyloxy phenol (**15 a**) 4,6-dibenzoylbenzene-1,3-diol (**15 b**) and 2,4-dibenzoyl benzene-1,3-diol (**15 c**). Finally, **8** afforded 2-benzoyl-4-benzoyloxy phenol (**16 a**) and 2,5-



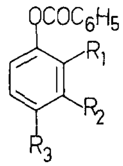
1: $R_1 = R_2 = H$, $R_3 = OCH_3$
2: $R_1 = CH_3$, $R_2 = OCOC_6H_5$, $R_3 = H$
3: $R_1 = R_3 = H$, $R_2 = OCOC_6H_5$
4: $R_1 = R_2 = H$, $R_3 = OCOC_6H_5$



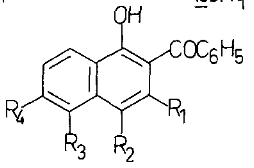
5:



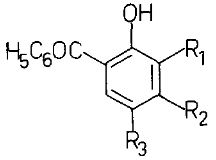
13a: $R_1 = H$, $R_2 = COC_6H_5$
13b: $R_1 = COC_6H_5$, $R_2 = H$



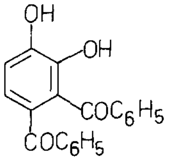
6: $R_1 = OCOC_6H_5$, $R_2 = R_3 = H$
7: $R_1 = R_3 = H$, $R_2 = OCOC_6H_5$
8: $R_1 = R_2 = H$, $R_3 = OCOC_6H_5$



9: $R_1 = R_2 = R_4 = H$, $R_3 = OCH_3$
10: $R_1 = CH_3$, $R_2 = OCOC_6H_5$, $R_3 = R_4 = H$
11a: $R_1 = R_3 = R_4 = H$, $R_2 = OCOC_6H_5$
11b: $R_1 = COC_6H_5$, $R_2 = OH$, $R_3 = R_4 = H$
12a: $R_1 = R_2 = R_4 = H$, $R_3 = OCOC_6H_5$
12b: $R_1 = R_2 = H$, $R_3 = OH$, $R_4 = COC_6H_5$



14a: $R_1 = OCOC_6H_5$, $R_2 = R_3 = H$
15a: $R_1 = R_3 = H$, $R_2 = OCOC_6H_5$
15b: $R_1 = H$, $R_2 = OH$, $R_3 = COC_6H_5$
15c: $R_1 = COC_6H_5$, $R_2 = OH$, $R_3 = H$
16a: $R_1 = R_2 = H$, $R_3 = OCOC_6H_5$
16b: $R_1 = H$, $R_2 = COC_6H_5$, $R_3 = OH$



14b:

dibenzoyl benzene-1,4-diol (**16 b**). Products (**9–16 b**) were characterized by their spectral data and by chemical studies.

It has been observed that the benzoyl group migrates across a double bond to the available *ortho* position in the benzene and naphthalene units. In the naphthalene unit the migration takes place to the *ortho* position while in benzene units *para* products were also obtained in small amounts. In the case of 8-benzoyloxy quinoline the *para* product was the major and *ortho* the minor product.

In the photo-*Fries* migration, the benzoyl migration is comparatively easy and gives better yields than acetyl migration. Under similar conditions in diacetoxy or triacetoxy naphthalenes[13] only one acetyl group migrates while other acetyl groups remain intact. In dibenzoyl naphthalene, however, one and both benzoyl groups migrate depending upon the reaction time.

These results could be exploited to prepare C-benzoyl compounds.

Experimental

General Procedure

Reactant (**1–8**) (20 mmol) was dissolved in benzene (600 ml). The solution was divided into three equal portions and each portion was irradiated under N_2 atmosphere at a low wavelength using a 450 W Ace Hanovia UV lamp (model 6575) for 8 h. The portions were then combined, the solvent evaporated and the residue was chromatographed on a silica gel column to isolate the products. Elution was performed with petroleum ether and then with increasing amounts of benzene. The data are listed below (NMR in $CDCl_3$/*TMS*).

9: From **1** in 45% yield; m.p. 120°; NMR: 14.00 (s, 1 H, −OH chelated), 8.10 (d, 1 H, $J = 9$ Hz, C_3-H), 7.35–7.75 (m, 8 H, $C_{6,8}$-H and COC_6H_5), 6.95 (d, 1 H, $J = 9$ Hz, C_4-H), 3,95 (s, 3 H, OCH_3).

10: From **2** in 30% yield; viscous oil; NMR: 12.60 (s, 1 H, −OH chelated), 7.40–7.65 (m, 4 H, C_{5-8}-H), 7.15–7.35 (m, 5 H, $OCOC_6H_5$), 6.95–7.15 (m, 5 H, COC_6H_5), 3.35 (s, 3 H, CH_3).

11 a: From **3** in 35% yield; m.p. 206–207°; NMR: 12.30 (s, 1 H, −OH chelated), 8.45 (s, 1 H, C_3-H), 7.85 (d, 1 H, $J = 8.5$ Hz, C_8-H), 7.80 (d, 1 H, $J = 8.5$ Hz, C_5-H), 7.40 (d, 1 H, $J = 9$ Hz, C_7-H), 7.36 (d, 1 H, $J = 9$ Hz, C_6-H), 7.10–7.25 (m, 10 H, 2 × COC_6H_5).

11 b: From **3** in 35% yield; m.p. 145° (Methylether 142°); NMR: 12.80 (s, 2 H, 2 × −OH chelated), 8.20 (d, 2 H, $J = 9$ Hz, C_5 and C_8-H), 7.70 (d, 2 H, $J = 9$ Hz, C_{6-7}-H), 7.35–7.50 (m, 10 H, 2 × COC_6H_5).

12 a: From **4** in 25% yield; m.p. 242–243° (Acetate 217–218°); NMR: 13.80 (s, 1 H, OH− chelated), 7.80 (d, 2 H, $J = 9$ Hz, $C_{3,4}$-H), 7.30–7.85 (m, 3 H, C_{6-8}-H), 6.95–7.25 (m, 10 H, 2 × COC_6H_5).

12 b: From **4** in 30% yield; m.p. 194–195°; NMR: 13.86 (s, 2 H, 2 × −OH chelated), 8.20 (d, 2 H, $J = 8.5$ Hz, $C_{3,7}$-H), 7.60 (m, 10 H, 2 × COC_6H_5), 7.30 (d, 2 H, $J = 8.5$ Hz, $C_{4,8}$-H).

13 a: From **5** in 15% yield; m.p. 73°; NMR: 14.00 (1 H, −OH, chelated), 8.70 (d, 1 H, $J = 4$ Hz, C_2-H), 8.00 (m, 2 H, $C_{3,4}$-H), 7.35 (d, 1 H, $J = 9$ Hz, C_6-H), 7.20–7.35 (m, 5 H, COC_6H_5), 7.10 (d, 1 H, $J = 9$ Hz, C_7-H).

13b: From **5** in 20% yield; m.p. 111–113°; NMR: 8.85 (d, 1 H, J = 3 Hz, C_2-H), 8.70 (d, 1 H, J = 3 Hz, C_4-H), 7.55–7.85 (m, 6 H, C_3-H and COC_6H_5), 7.35 (d, 1 H, J = 8.5 Hz, C_7-H), 6.95 (d, 1 H, J = 8.5 Hz, C_6-H).

14a: From **6** in 15% yield; m.p. 74°; NMR: 12.40 (s, 1 H, −OH chelated), 8.25 (dd, 1 H, C_3-H), 8.05 (d, 2 H, J = 10 Hz, $C_{4,5}$-H), 7.15–7.65 (m, 10 H, 2 × COC_6H_5).

14b: From **6** in 28% yield; m.p. 134–136°; NMR: 12.20 (1 H, −OH chelated), 8.15 (d, 1 H, J = 10 Hz, C_5-H), 7.35 (d, 1 H, J = 10 Hz, C_6-H), 6.80–7.15 (m, 10 H, 2 × COC_6H_5).

15a: From **7** in 35% yield; m.p. 77–80° (methyl ether 116°); NMR: 12.60 (s, 1 H, −OH chelated), 8.18 (d, 1 H, J = 10 Hz, C_3-H), 7.05–7.95 (m, 10 H, 2 × COC_6H_5), 7.15 (d, 1 H, J = 10 Hz, C_4-H), 6.78 (dd, 1 H, C_6-H).

15b: From **7** in 15% yield; oily liquid (methyl ether, oil); NMR: 7.80 (d, 1 H, J = 1 Hz, C_2-H), 7.35–7.65 (m, 10 H, 2 × COC_6H_5), 6.65 (d, 1 H, J = 1 Hz, C_5-H), 3.65 and 3.95 (2 s, 2 × 3 H, 2 × $-OCH_3$).

15c: From **7** in 10% yield; oily liquid (methyl ether, m.p. 159–161°); NMR: 7.75 (d, 1 H, J = 9 Hz, C_5-H), 6.70–7.48 (m, 10 H, 2 × COC_6H_5), 6.55 (d, 1 H, J = 9 Hz, C_4-H), 3.58 and 3.55 (2 s, 2 × 3 H, 2 × OCH_3).

16a: From **8** in 30% yield; m.p. 213–214°; NMR: 11.20 (s, 1 H, −OH chelated), 7.30 (dd, 1 H, C_3-H), 6.90 (d, 1 H, J = 10 Hz, C_5-H), 6.60–6.80 (m, 10 H, $OCOC_6H_5$ and COC_6H_5).

16b: From **8** in 10% yield; m.p. 172–173°; NMR: 11.40 (s, 2 H, 2 × −OH chelated), 7.25 (d, 2 H, J = 1 Hz, $C_{3,5}$-H), 6.90–7.15 (m, 10 H, 2 × COC_6H_5).

References

[1] *Anderson J. C., Reese C. B.,* Proc. Chem. Soc. **1960**, 217.
[2] *Kobsa H.,* J. Org. Chem. **27**, 2293 (1962).
[3] *Anderson J. C., Reese C. B.,* J. Chem. Soc. **1963**, 1781.
[4] *Bradshaw J. S., Loveridge E. L., White L.,* J. Org. Chem. **33**, 4127 (1968).
[5] *Finnegan R. A., Hagen A. W.,* Tetrahedron Lett. **1963**, 365.
[6] *Plank D. A.,* Tetrahedron Lett. **1968**, 5423.
[7] *Hageman H. J.,* Tetrahedron **25**, 6015 (1969).
[8] *Crouse D. J., Hurlbut S. L., Wheeler D. M. S.,* Syn. Comm. **9**, 877 (1979).
[9] *Bellus D., Herdlovic P.,* Chem. Rev. **67**, 599 (1967).
[10] *Meyer J. W., Hammond G. S.,* J. Amer. Chem. Soc. **94**, 2219 (1977).
[11] *Finnegan R. A., Mattice J. J.,* Tetrahedron **21**, 1015 (1965).
[12] *Pathak V. P., Khanna R. N.,* Synthesis **1981**, 882.
[13] *Sharma P. K., Khanna R. N.,* Indian J. Chem., in press.