Formylation and acetylation of 2-ethoxynaphthalene with 1,3,5-triazines in polyphosphoric acid

A. V. Aksenov,* I. V. Aksenova, I. V. Borovlev, and A. A. Zamorkin

Stavropol' State University, 1a ul. Pushkina, 355009 Stavropol', Russian Federation. Fax: +7 (865) 235 4033. E-mail: k-biochem-org@stavsu.ru

Heating of 2-ethoxynaphthalene with 1,3,5-triazine or 2,4,6-trimethyl-1,3,5-triazine in polyphosphoric acid leads to the corresponding products of mono- or diacylation: 2-ethoxynaphthalene-1-carbaldehyde, 1-acetyl-2-ethoxynaphthalene, 2-ethoxynaphthalene-1,8-dicarbaldehyde, and 1,8-diacetyl-2-ethoxynaphthalene in $\sim 60-80\%$ yield.

Key words: 2-ethoxynaphthalene-1-carbaldehyde, 1-acetyl-2-ethoxynaphthalene, 2-ethoxynaphthalene-1,8-dicarbaldehyde, 1,8-diacetyl-2-ethoxynaphthalene, 1,3,5-triazines, polyphosphoric acid.

Earlier, we have shown that 1,3,5-triazines and 2,4,6trimethyl-1,3,5-triazines in polyphosphoric acid (PPA) serve as efficient acylating reagents of some naphthalene derivatives, for example, 1*H*-perimidine¹ and 1,8-diaminonaphthalene.² In the present work, we report on the reaction of 2-ethoxynaphthalene (1) with 1,3,5-triazines **2a,b** in PPA.* We showed that monoformylation (acetylation) of compound 1 in this system proceeds already at room temperature and comes to a completion at 40– 45 °C in case of triazine **2a** and at 55–60 °C in case of **2b** for 2 h. The yields of the products of monoacylation **3a** and **3b** under these conditions were 81 and 85%, respectively.

Further heating at 55–60 °C in case of 1,3,5-triazine and at 100–110 °C in case of 2,4,6-trimethyl-1,3,5-triazine for 3 h leads to the diformylation (diacetylation) products. After hydrolysis of the reaction mixture, 1,8-diformyl- and 1,8-diacetyl-2-ethoxynaphthalenes (**4a,b**) were isolated in 63 and 79% yield, respectively (Scheme 1).



Scheme 2



R = H (a), Me (b)

* PPA with 86% content of P_2O_5 , obtained by known procedure,³ was used.

Published in Russian in Izvestiya Akademii Nauk. Seriya Khimicheskaya, No. 1, pp. 207–208, January, 2008.

1066-5285/08/5701-0215 © 2008 Springer Science+Business Media, Inc.

The first step includes the reaction of the protonated triazines with ether 1 to form dihydrotriazines 5, the hydrolysis of which leads to compounds 3a,b. The ring opening in compounds 5 upon treatment with acid leads to cations 6, the intramolecular electrophilic substitution in which results in the formation of azaphenalenes 7. The hydrolysis of the latter afforded compounds 4 (Scheme 2).

In conclusion, the method allows one to accomplish monoacylation and regioselective diacetylation (diformylation) in positions 1 and 8 of the naphthalene ring.

Experimental

¹H NMR spectra were recorded on a Bruker WP-200 spectrometer with the use of SiMe₄ as the internal standard. Melting points were determined in the sealed capillary tubes on a PTP device and were not corrected. 1,3,5-Triazine is a commercial reagent (Aldrich). 2,4,6-Trimethyl-1,3,5-triazine⁴ and 2-ethoxy-naphthalene⁵ were obtained by known procedures.

Acylnaphthalenes 3 and 4 (general procedure). A mixture of 2-ethoxynaphthalene (1) (0.172 g, 1 mmol), the corresponding triazine (1.5 mmol), and PPA (3-4 g) was vigorously stirred under the following conditions: 2 h at 40-45 °C (for the synthesis of compound 3a); 2 h at 55-60 °C (3b); 3 h at 55-60 °C (4a); 3 h at 100-110 °C (4b). The reaction mixture was cooled, poured in cold water (30 mL) under stirring, extracted with ethyl acetate (3×50 mL). The solvent was evaporated for isolation of compounds 4, the reaction mixture was made basic by addition of aqueous ammonia. Ethanol (products 3a,b) or octane (products 4a,b) were used for the recrystallization.

2-Ethoxy-1-naphthaldehyde (3a). The yield was 0.162 g(81%). Yellow needles with m.p. 111-112 °C (from ethanol) (*cf.* Ref. 6: m.p. 111-112 °C). A mixture with authentic sample did not give a depression of the melting point. Found (%): C, 78.14; H, 5.98. C₁₃H₁₂O₂. Calculated (%): C, 77.98; H, 6.04.

1-Acetyl-2-ethoxynaphthalene (3b). The yield was 0.182 g (85%). Yellow crystals with m.p. 63–65 °C (from ethanol). Found (%): C, 78.61; H, 6.51. $C_{14}H_{14}O_2$. Calculated (%): C, 78.48; H,

6.59. ¹H NMR (CDCl₃), δ : 1.48 (t, 3 H, OCH₂Me, J = 7.0 Hz); 2.57 (s, 3 H, COMe); 4.27 (q, 2 H, OCH₂Me, J = 7.0 Hz); 7.48, 8.00 (both d, 1 H each, H(4), H(3), J = 9.1 Hz); 7.38 (dd, 1 H, H(7), J = 7.3 Hz, J = 8.0 Hz); 7.50 (dd, 1 H, H(6), J = 7.3 Hz, J = 8.0 Hz); 7.65 (d, 1 H, H(5), J = 8.0 Hz); 7.90 (d, 1 H, H(8), J = 8.0 Hz).

2-Ethoxynaphthalene-1,8-dicarbaldehyde (4a). The yield was 0.144 g (63%). Yellow crystals with m.p. 163–164 °C (from octane, subl.). Found (%): C, 73.72; H, 5.18. $C_{14}H_{12}O_3$. Calculated (%): C, 73.67; H, 5.30. ¹H NMR (CDCl₃), δ : 1.52 (t, 3 H, CH₃, *J* = 7.0 Hz); 4.35 (q, 2 H, CH₂, *J* = 7.0 Hz); 7.27, 8.20 (both d, 1 H each, H(3), H(4), *J* = 9.5 Hz); 7.78 (dd, 1 H, H(6), *J* = 7.3 Hz, *J* = 8.4 Hz); 8.11 (d, 1 H, H(5), *J* = 8.4 Hz); 8.47 (d, 1 H, H(7), *J* = 7.3 Hz); 10.84, 12.13 (both s, 1 H each, C(8)CHO, C(1)CHO).

1,8-Diacetyl-2-ethoxynaphthalene (4b). The yield was 0.202 g (79%). Yellow crystals with m.p. 159–161 °C (from octane). Found (%): C, 75.13; H, 6.18. $C_{16}H_{16}O_3$. Calculated (%): C, 74.98; H, 6.29. ¹H NMR (CDCl₃), δ : 1.48 (t, 3 H, OCH₂Me, J=7.0 Hz); 3.07, 3.15 (both s, 3 H each, C(6)COMe, C(1)COMe); 4.14 (q, 2 H, OCH₂Me, J=7.0 Hz); 6.73, 7.71 (both d, 1 H each, H(3), H(4), J=10.0 Hz); 7.64 (dd, 1 H, H(6), J=7.3 Hz, J=8.4 Hz); 7.89 (d, 1 H, H(5), J=8.4 Hz); 8.31 (d, 1 H, H(7), J=7.3 Hz).

References

- A. V. Aksenov, I. V. Borovlev, A. S. Lyakhovnenko, I. V. Aksenova, *Khim. Geterotsikl. Soedin.*, 2007, 629 [*Chem. Heterocycl. Compd.*, 2007, 49 (Engl. Transl.)].
- I. V. Borovlev, A. V. Aksenov, I. V. Aksenova, S. I. Pisareneko, *Izv. Akad. Nauk, Ser. Khim.*, 2007, 2275 [*Russ. Chem. Bull., Int. Ed.*, 2007, 56, 2354.
- 3. F. Uhlig, Angew. Chem., 1954, 66, 435.
- 4. F. C. Schaefer, G. A. Peters, J. Org. Chem., 1961, 26, 2778.
- N. Donaldson, *Khimiya i tekhnologiya soedinenii naftalinovogo ryada* [*Chemistry and Technology of Compounds of Naphthalene Series*], Goskhimizdat, Moscow, 1963, p. 403 (in Russian).
- Organic Syntheses, V. 20, J. Wiley and Sons, New York, 1940, pp. 11.

Received June 27, 2007; in revised form November 6, 2007