

SHORT
COMMUNICATIONS

Formylation of Anthrone with a Complex Thionyl Chloride–Dimethylformamide

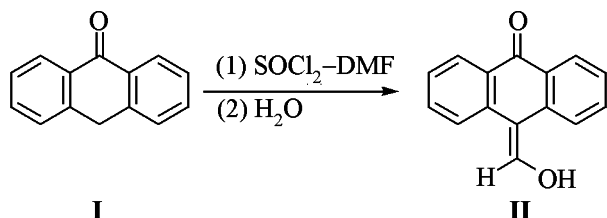
V. A. Loskutov

Vorozhtsov Novosibirsk Institute of Organic Chemistry, Siberian Division,
Russian Academy of Sciences Novosibirsk, 630090 Russia

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At treating with SOCl_2 an anthrone solution in DMF forms S-oxide of monothioanthraquinone [1]. In this report is described the result obtained at the reversed addition order of reagents: charging of anthrone into a solution of SOCl_2 in DMF (reaction conditions of Vilsmeier–Haak). It was shown formerly [2] that the anthrone reacted with a complex POCl_3 –N-methylformanilide to yield 9-chloro-10-formylanthrane.

We established that on addition of anthrone (**I**) to 1.5–2-fold molar excess of the complex SOCl_2 –DMF generated *in situ* in DMF solution followed by treating the reaction mixture with water occurred anthrone formylation. The main reaction product isolated in 40% yield after maintaining the reaction mixture at room temperature for 3 h was (hydroxymethylene)anthrone (**II**) identified by a comparison of its IR spectrum with the spectrum of this compound published in [3].



The ^1H NMR spectrum of compound **II** registered in $\text{DMSO}-d_6$ at 30°C contains in the downfield region (8.50 ppm) a three-proton multiplet that at heating to 53°C transforms into a singlet belonging to the methylene proton attached to the enol carbon and a doublet of $\text{H}^{1,8}$ atoms. This assignment of the singlet is based on the fact that in the ^1H NMR spectra of 1,8-dihydroxy-10-(hydroxymethylene)anthrone [4] and of 10-(methoxymethylene)anthrone (**III**) prepared

by methylation of compound **II** the proton signal from the substituted methylene group appears in the same region (8.47 and 8.04 ppm respectively). In the ^{13}C NMR spectrum of compound **II** are observed signals from ketone and enol carbon atoms (181.1 and 154.9 ppm respectively). Evidently in DMSO solution like in crystalline state (cf. [3]) the tautomeric equilibrium of the product of anthrone (**I**) formylation with the complex SOCl_2 –DMF is shifted to the enol tautomer **II**.

Compound **II** was described several times [3, 5–10]. It was prepared by multistage procedures from anthrone [1, 5–9] or anthraquinone [10]. The reaction of anthrone (**I**) with the complex SOCl_2 –DMF is a new one-stage synthetic method for this compound.

10-(Hydroxymethylene)anthrone (II). To 10 ml of DMF cooled to 0°C was added dropwise at stirring 1 ml of SOCl_2 . The mixture was stirred for 1 h, and 1 g of anthrone (**I**) was added. Ten minutes later the cooling was removed, and the mixture was stirred at room temperature for 3 h more. Then it was poured into ice water, and orange precipitate was separated. Thus was obtained 1.04 g of mixture composed of orange compound **II**, anthrone, and anthraquinone (TLC). Compound **II** decomposes at heating, therefore for purification the mixture has been dissolved at 20 – 15°C in 50 ml of dioxane, 100 ml of benzene was added, and the resulting mixture was kept for 24 h at -18°C . The yield of orange crystalline product **II** 0.45 g (40%), mp 186 – 190°C . Publ.: mp 206 – 208°C [3], 170 – 175°C [5], 230°C [6], 185 – 187°C [7], 200 – 202°C [8], 194 – 195°C [10]. IR spectrum is identical to the spectrum of this compound reported in [3]. ^1H NMR spectrum, δ , ppm: 7.45 t, 7.67 t (4H, $\text{H}^{2,3,6,7}$, J 8.0 Hz), 8.29 d (2H, $\text{H}^{4,5}$, J 8.0 Hz), 8.50 m (3H, $\text{H}^{1,8}$, CH-OH). ^{13}C NMR spectrum, δ ppm: 105.8, 124.7, 125.5, 126.3, 126.6,

128.0, 128.3, 132.4, 137.2, 154.9, 181.1. Mass spectrum at 260°C, m/z (I_{rel} , %): 222 ($[M]^+$, 3.2), 194 (60.7), 193 (100.0), 166 (7.9), 165 (41.2), 164 (9.1), 163 (10.7). Found, %: C 81.22; H 4.60. $C_{15}H_{10}O_2$. Calculated, %: C 81.08; H 4.50.

10-(Methoxymethylene)anthrone (III) was obtained by procedure [3], mp 130–133°C (136°C [3]). IR spectrum, cm^{-1} : 1644 (C=O), 1607 (C=C conjugated with C=O). 1H NMR spectrum, δ ppm: 4.15 s (3H, OCH_3), 7.46 br.t, 7.50 br.t, 7.66 br.t, 7.69 br.t (4H, $H^{2,3,6,7}$, J 8.0 Hz), 8.04 s (1H, $\underline{C}H-OCH_3$), 8.09 br.d, 8.20 d.d, 8.27 d.d, 8.56 br.d (4H, $H^{1,4,5,8}$, J 8.0 and 1.5 Hz). Found: $[M]^+$ 236.08347. $C_{16}H_{12}O_2$. Calculated: M 236.08372.

IR spectra were recorded on spectrometer Vector 22 from KBr pellets. 1H and ^{13}C NMR spectra were registered on spectrometer Bruker AC-200 from solutions in $DMSO-d_6$, as internal reference were used the solvent resonances. Mass spectra were measured on Finnigan MAT-8200 instrument, molecular weight and composition of compound **III** was determined from the precise value of the mass number of the molecular ion. The reaction progress was monitored

and the purity of compounds was checked by TLC on Silufol UV-254 plates, eluent benzene or chloroform.

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