

## Direct Transformation of Anthrone and Its Derivatives into Monothioanthraquinone *S*-Oxides

V. A. Loskutov

Vorozhtsov Novosibirsk Institute of Organic Chemistry, Siberian Division, Russian Academy of Sciences,  
pr. Akademika Lavrent'eva 9, Novosibirsk, 630090 Russia  
fax: (7383)2344752; e-mail: root@orchem.nsk.su

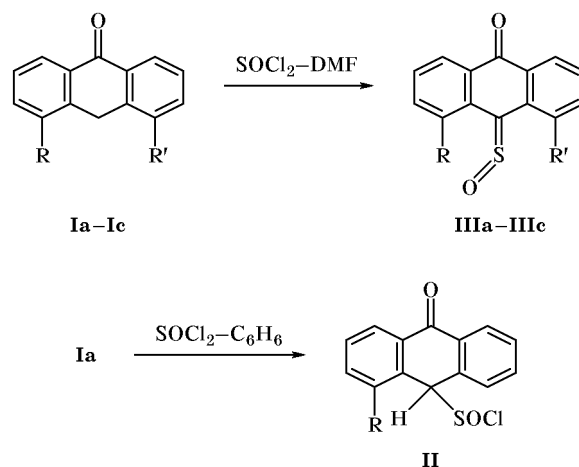
Received April 24, 2000

**Abstract**—The reaction of anthrone with thionyl chloride in benzene yields 10-(chlorosulfinyl)anthrone, while in DMF monothioanthraquinone *S*-oxide is formed; 4-substituted anthrones react with thionyl chloride in DMF in a similar way. The reaction of 4,5-dichloroanthrone with thionyl chloride results in dimerization of the substrate and formation of the corresponding bianthracenedione.

Thioketone *S*-oxides which give rise to sulfur-containing heterocycles via cycloaddition to dienes have been known for about 40 years [1, 2]. However, among quinone derivatives, only one representative of this class of heterocumulenes has been reported, namely unsubstituted monothioanthraquinone *S*-oxide; it was synthesized from anthrone by a three-step procedure and was insufficiently pure [3]. We have developed a new procedure for preparation of monothioanthraquinone *S*-oxides by treatment of anthrones with thionyl chloride. This reaction was used previously to obtain thioketone *S*-oxides from activated methylene ketones [2].

Treatment of anthrone (**Ia**) with thionyl chloride in the absence of a solvent is known to yield unstable 10-(chlorosulfinyl)anthrone (**II**) [4]. We have found that the same product is also formed in nonpolar solvents (such as benzene or chloroform), but the reaction rate is considerably lower. On the other hand, in polar aprotic solvents monothioanthraquinone *S*-oxide (**IIIa**) is formed instead of chlorosulfinyl derivative **II**. The best results were obtained when a twofold molar amount of thionyl chloride was added to a solution of anthrone (**Ia**) in DMF. The reaction takes several minutes, and product **IIIa** can readily be isolated from the reaction mixture in the analytically pure form (yield 70–80%). Compound **IIIa** was also formed on treatment of chlorosulfinyl derivative **II** in benzene with tertiary amines (pyridine or triethylamine), but it was almost impossible to isolate the individual product from the reaction mixture (cf. [3]). There is no need of adding tertiary amine when the

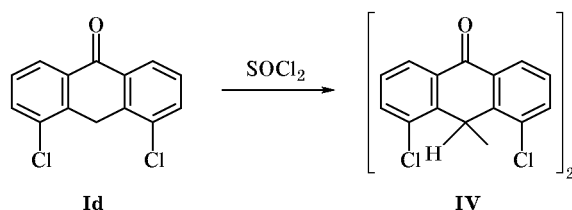
reaction is carried out in DMF, for the presence or absence of pyridine does not affect the process.



R = H (**a-c**); R' = H (**a**), Ph (**b**), Cl (**c**).

In keeping with published data [2], in the first stage thionyl chloride reacts with the enol form of anthrone to give chlorosulfinyl derivative **II**. In nonpolar solvents the concentration of the enol form is insignificant [5], the reaction is slow, and the process stops at the stage of formation of compound **II**. The degree of enolization of anthrone in DMF is considerably greater; therefore, the reaction is faster. Moreover, dimethylformamide itself or basic impurities therein promote elimination of hydrogen chloride, which leads to formation of *S*-oxide **IIIa**.

Product **IIIa** is a yellow crystalline substance which is stable in air only in the dark. On exposure to light or in solution compound **IIIa** is rapidly converted into a mixture of anthraquinone and monothioanthraquinone. With the goal of obtaining more stable *S*-oxides, the reaction was performed with anthrones **Ib–Id** containing substituents in positions 4 and 5. 4-Phenyl- and 4-chloroanthrones **Ib** and **Ic** reacted with  $\text{SOCl}_2$  in DMF in a similar way. The products were *S*-oxides **IIIb** and **IIIc** which turned out to be more resistant to light. However, the reaction of 4,5-dichloroanthrone (**Id**) with thionyl chloride gave bianthracenedione **IV**. These data suggest that the chlorine atoms in **Id** create steric hindrance to attack on the  $\text{C}^{10}$  atom by  $\text{SOCl}_2$  and that the reaction follows the oxidative dimerization pattern typical of anthrone derivatives [6].



The structure of the products was proved by the IR,  $^1\text{H}$  NMR, and mass spectra and elemental analysis. The structure of *S*-oxide **IIIa** was additionally proved by independent synthesis from monothioanthraquinone via oxidation with *m*-chloroperoxybenzoic acid (cf. [3]). It should be noted that the 4-H and 5-H protons in the *peri* position with respect to the  $\text{C}=\text{S}=\text{O}$  group in compound **IIIa** are characterized by different chemical shifts in the  $^1\text{H}$  NMR spectrum,  $\delta$  7.92 and 9.37 ppm, respectively. This is explained by nonlinear structure of the  $\text{C}=\text{S}=\text{O}$  group whose deshielding effect extends over only one part of the molecule [7]. The fragmentation of *S*-oxides **IIIb** and **IIIc** includes elimination of CO and SO fragments from the molecular ion.

## EXPERIMENTAL

The IR spectra were recorded on a Vector 22 spectrometer in KBr. The  $^1\text{H}$  NMR spectra were obtained on Bruker AC-200 and Bruker AM-400 instruments (**IIIa**) in  $\text{CDCl}_3$  using signals from residual protons of the solvent as internal reference. The mass spectra were run on a Finnigan MAT-8200 spectrometer. The molecular weights and elemental composition of compounds **IIIa–IIIc** were determined from the high-resolution mass spectra. Also, the molecular weights

of **IIIa** and **IV** were determined by vapor phase osmometry in chloroform using a Knauer instrument.

**Reaction of substituted anthrones Ia–Ic with thionyl chloride.** *a.* Thionyl chloride, 0.14 ml, was added to a solution of 1 mmol of anthrone **Ia** in 5 ml of dry benzene, and the mixture was kept for 5 days at room temperature. The precipitate was filtered off and washed with benzene. The product was 10-(chloro-sulfinyl)anthrone (**II**). Yield 0.17 g, colorless crystals, mp 258–270°C; published data [4]: decomposition point 260°C. The IR and  $^1\text{H}$  NMR spectra of **IV** were consistent with those reported in [4].

*b.* Thionyl chloride, 0.14 ml, was added to a solution of 1 mmol of anthrone **Ia–Ic** in 3 ml of DMF containing 0.1 ml of pyridine. The mixture was stirred for 10–15 min (compound **Ia**) or 1 h (**Ib** and **Ic**). The yellow precipitate was filtered off, washed with water, and dried. *S*-Oxides **IIIb** and **IIIc** were isolated by pouring the reaction mixture into water and were purified by reprecipitation from chloroform with hexane.

*c.* *m*-Chloroperoxybenzoic acid, 0.1 g, was added to a solution of 0.5 mmol of monothioanthraquinone in 10 ml of methylene chloride. The originally green solution turned yellow. After 20 min, the solvent was distilled off, and the residue was washed with hot water and dried. Yield 0.1 g (85%) of compound **IIIa**. The IR and  $^1\text{H}$  NMR spectra of the product were identical to those of a sample prepared as described above in *b*.

**Monothioanthraquinone S-oxide (IIIa).** Yield 75% (in the absence of pyridine, the yield of **IIIa** was 83%), decomposes above 235°C; published data [3]: decomposition point 209°C. IR spectrum,  $\nu$ ,  $\text{cm}^{-1}$ : 1660 ( $\text{C}=\text{O}$ ); 1129, 1107 ( $\text{C}=\text{S}=\text{O}$ ).  $^1\text{H}$  NMR spectrum,  $\delta$ , ppm: 7.57 t.d, 7.62 t.d, 7.70 t.d, and 7.75 t.d (4H, 2-H, 3-H, 6-H, 7-H,  $J = 8.0, 1.5$  Hz); 7.92 d.d (1H, 4-H,  $J = 8.0, 1.5$  Hz); 8.36 d.d (2H, 1-H, 8-H,  $J = 8.0, 1.5$  Hz); 9.37 d.d (1H, 5-H,  $J = 8.0, 1.5$  Hz). Found, %: C 70.52; H 3.47; S 13.35.  $M$  240.02236 (by mass spectrometry), 237 and 236 (by osmometry).  $\text{C}_{14}\text{H}_8\text{O}_2\text{S}$ . Calculated, %: C 70.00; H 3.33; S 13.33.  $M$  240.02230.

$^1\text{H}$  NMR spectrum of a sample of **IIIa** prepared as a film between glass plates and exposed to light for 20 days,  $\delta$ , ppm: 7.60–7.83 m (2-H, 3-H, 6-H, and 7-H in anthraquinone and monothioanthraquinone), 8.24–8.34 (1-H and 8-H in anthraquinone and monothioanthraquinone), 8.52 br.d (4-H and 5-H in monothioanthraquinone,  $J = 7.5$  Hz); anthraquinone-to-monothioanthraquinone ratio  $\sim 4:1$ .

**4-Phenylmonothioanthraquinone S-oxide (IIIb).**

Yield 75%. mp 165–167°C. IR spectrum,  $\nu$ ,  $\text{cm}^{-1}$ : 1658 (C=O); 1121, 1096 (C=S=O).  $^1\text{H}$  NMR spectrum,  $\delta$ , ppm: 7.25–7.45 m (5H,  $\text{C}_6\text{H}_5$ ), 7.47–7.73 m (4H, 2-H, 3-H, 6-H, 7-H), 8.37 m (2H, 1-H, 8-H), 8.74 m (1H, 5-H). Found, %: C 76.18; H 3.95; S 10.00.  $M$  316.05588 (by mass spectrometry).  $\text{C}_{20}\text{H}_{12}\text{O}_2\text{S}$ . Calculated, %: C 75.94; H 3.79; S 10.12.  $M$  316.05580.

**4-Chloromonothioanthraquinone S-oxide (IIIc).**

Yield 52%. Decomposes at 135–145°C. IR spectrum,  $\nu$ ,  $\text{cm}^{-1}$ : 1667 (C=O); 1117, 1101 (C=S=O).  $^1\text{H}$  NMR spectrum,  $\delta$ , ppm: 7.47 t (1H, 2-H,  $J = 7.9$  Hz), 7.60–7.82 m (3H, 3-H, 6-H, 7-H), 8.29 m (2H, 1-H, 8-H), 8.81 d.d (1H, 5-H,  $J = 7.9, 1.2$  Hz). Found, %: S 11.00.  $M$  273.98518 (by mass spectrometry).  $\text{C}_{14}\text{H}_7\text{ClO}_2\text{S}$ . Calculated, %: S 11.65.  $M$  273.98553.

**Reaction of 4,5-dichloroanthrone (Id) with  $\text{SOCl}_2$ .**

*a.* A solution of 1 mmol of anthrone **Id** in 2 ml of  $\text{SOCl}_2$  was kept for 50 h at room temperature. The precipitate was filtered off and washed with dry benzene to obtain 0.08 g (30%) of 1,1',8,8'-tetrachloro-9,9'-bianthracene-10,10'-dione (**IV**) as colorless crystals, mp 331–332.5°C. IR spectrum,  $\nu$ ,  $\text{cm}^{-1}$ : 1676 (C=O).  $^1\text{H}$  NMR spectrum,  $\delta$ , ppm: 5.97 s (2H), 7.35 m (8H), 7.64 m (4H). Found, %: C 64.49; H 2.64; Cl 27.20.  $M$  522 and 519.  $\text{C}_{28}\text{H}_{14}\text{Cl}_4\text{O}_2$ . Calculated, %: C 64.12; H 2.67; Cl 27.09.  $M$  524.

*b.* Pyridine, 0.1 ml, and thionyl chloride, 0.14 ml, were added to a solution of 1 mmol of anthrone **Id** in 6 ml of DMF. The mixture was kept for 20 h at room temperature and poured into water, and the yellow precipitate was filtered off and recrystallized from  $\text{CHCl}_3\text{--CCl}_4$  (1:4) to isolate 0.11 g of unreacted anthrone **Id** with mp 194–199°C. The filtrate was evaporated approximately by half, and 0.11 g (40%) of bianthracenedione **IV** was separated, mp 325–327°C. The IR spectrum of the product was identical to that of a sample prepared as described in *a*.

## REFERENCES

1. Zwanenburg, B., *Recl. Trav. Chim. Pays-Bas*, 1982, vol. 101, no. 1, pp. 1–27.
2. Zwanenburg, B., *Phosphorus, Sulfur, Silicon*, 1989, vol. 43, nos. 1–2, pp. 1–24.
3. Raasch, M.S., *J. Org. Chem.*, 1979, vol. 44, no. 4, pp. 632–633.
4. Oka, K. and Hara, S., *J. Org. Chem.*, 1978, vol. 43, no. 23, pp. 4533–4535.
5. Mills, S.G. and Beak, P., *J. Org. Chem.*, 1985, vol. 50, no. 8, pp. 1216–1224.
6. *Methoden der organischen Chemie (Houben-Weyl)*, Stuttgart: Georg Thieme, 1979, vol. 7, part 3c, pp. 298–299.
7. Zwanenburg, B., Thijs, L., and Tangerman, A., *Tetrahedron*, 1971, vol. 27, no. 9, pp. 1731–1735.