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Monothioanthraquinones

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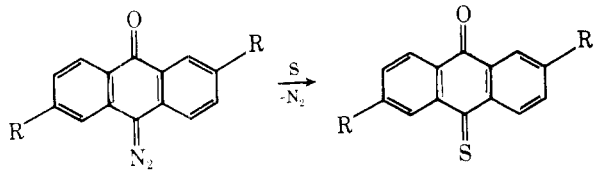
Substances thought to be dithioanthraquinone[2] and 2,5-diamino-1,4-dithiobenzoquinone[3] have been reported, but no monothioquinones appear to have been recorded, though unsuccessful attempts to prepare them have been made[4,5] and they have been postulated as reaction intermediates in the rearrangement of monothiobisphenols.[6,7]

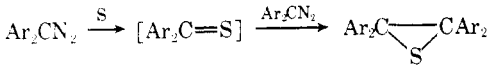
Monothioanthraquinones (**2**) have now been synthesized by the reaction of 10-diazoanthrones (**1**) with sulfur in dimethylformamide at 130–150 °C. The compounds are green with absorption in the visible region at 697 nm for **2a** and 685 nm for **2b** in chloroform.



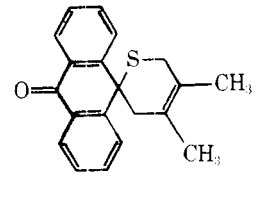
1a, R = H
b, R = CH_3O

2a, R = H
b, R = CH_3O

This is a new method of preparing thiocarbonyl compounds. In previous work, reaction of sulfur with diazo compounds, including 9-diazofluorene, has given thiiranes,[8,9] but thioketones have been postulated as reaction intermediates in this synthesis.



Like other thiocarbonyl compounds,[10] monothioanthraquinone undergoes Diels–Alder reactions. Reactions of **2a** with 2,3-dimethylbutadiene and with cyclopentadiene form **3** and **4**. Crystals of the latter slowly dissociate back to **2a** and cyclopentadiene at 22 °C.



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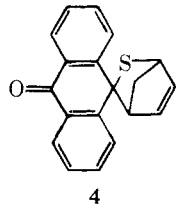
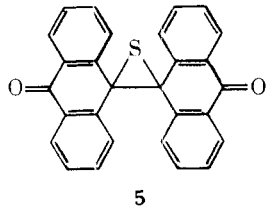


4

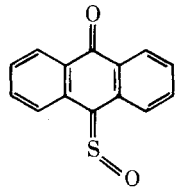
Reaction of monothioanthraquinone with trimethyl phosphite yields the thiirane **5**.

Thiiranes have been proposed as intermediates in the reaction of thiocarbonyl compounds with phosphites,[11–13] but the above case appears to be the first in which the thiirane was isolated. Trimethyl phosphite does not remove sulfur from **5** under the reaction conditions, so the reaction stops at the thiirane stage rather than proceeding to the olefin. The structure of **5** was confirmed by its synthesis by reaction of **1a** with **2a**, which represents a 1,3-dipolar addition to the thiocarbonyl group followed by loss of nitrogen.[14] Compounds **3**, **4**, and **5** are new ring systems.

In common with other thioketones, monothioanthraquinone can be oxidized to a sulfine[15] (**6**).



5



6

Experimental Section

The ^1H NMR spectra were determined on a Varian A-60 instrument using tetramethylsilane as an internal standard. IR spectra were taken on a Perkin-Elmer Model 21 spectrometer. Melting and boiling points are uncorrected.

10-Diazoanthrone (1a). Published directions[16] for preparing *p*-toluenesulfonyl azide were modified to eliminate the isolation of the explosive[17] azide. To 22.5 g (0.118 mol) of *p*-toluenesulfonyl chloride dissolved in 150 mL of ethanol was added 9.3 g (0.143 mol) of sodium azide dissolved in 27 mL of water. The mixture was stirred for 1 h, 150 mL of ethanol was added, and sodium chloride was filtered off. This solution of *p*-toluenesulfonyl azide was used directly in the procedure of Regitz[18] to prepare 10-diazoanthrone. Anthrone (19.4 g, 0.1 mol) was added and then 11.3 mL of piperidine over 30 min. After the mixture had been stirred for 5 h, the 10-diazoanthrone was filtered off and washed with ethanol, 19.6 g (89%). Recrystallization from dioxane left 17.7 g (80%).

Monothioanthraquinone [10-Thioxo-9(10*H*)-anthracenonel (2a)]. 10-Diazoanthrone (17.6 g, 0.08 mol), sulfur (3.07 g, 0.096 mol), and 170 mL of dimethylformamide were heated and stirred in a flask in an oil bath at 150 °C. Heating was continued for 10 min after evolution of nitrogen ceased. The green solution was cooled, and the product was filtered off and washed with acetone. It was then dissolved in dichloromethane, and 0.6 g of an orange substance was filtered off. The solution was evaporated to dryness and the residue sublimed at 0.5 mm and 190 °C. A fluffy residue remained behind. The sublimate was recrystallized from chloroform to give 9.8 g (57%) of green needles in two crops: mp 213–214 °C; IR 3077 (=CH), 1675, 1669 (doublet for conjugated ketone carbonyl), 1600 1580 (aromatic C=C), 1212 (medium band, C=S) cm^{-1}; UV ($CHCl_3$) 697 nm (ϵ 46.5), 334 (14 400), 270 (26 000); UV (CH_3CN) 690 nm (ϵ 48.6), 334 (13 900), 267 (25 800), 224 (24 200).

Anal. Calcd for $C_{14}H_8OS$: C, 74.98; H, 3.60; S, 14.29; M_r 224. Found: C, 75.31; H, 3.70; S, 14.11; M_r 220 (osmometric, C_6H_6, 37 °C), 217 (ebullioscopic, C_6H_6).

2,6-Dimethoxyanthrone. 2,6-Dimethoxyanthraquinone[19] (13.4 g, 0.05 mol) was added to a solution of 12 g (0.3 mol) of sodium hydroxide and 30 g (0.17 mol) of sodium hydrosulfite in 260 mL of water. The mixture was refluxed for 1.5 h and cooled, and the anthrone was filtered off and washed with water. Recrystallization from acetone gave 9.08 g (74%) of the pale yellow anthrone: mp 160–161 °C; NMR ($CDCl_3$) 3.88 (s, CH_3), 3.92 (s, CH_3), 4.24 (s, CH_2), 6.75–8.4 (m, 6 H, aromatic) ppm.

Impure 2,6-dimethoxyanthrone, mp 156 °C, prepared by stannous chloride reduction of the anthraquinone, has been reported.[20]

10-Diazo-2,6-dimethoxyanthrone (1b). This compound was prepared from 2,6-dimethoxyanthrone as described for 10-diazoanthrone and recrystallized from benzene: mp 137–138.5 °C dec (53%); NMR ($CDCl_3$) 3.84, 3.89 ppm (s, s, OCH_3).

Anal. Calcd for $C_{16}H_{12}N_2O_3$: C, 68.56; H, 4.32; N, 9.99. Found: C, 68.88; H, 4.46; N, 9.67.

2,6-Dimethoxymonothioanthraquinone (2b). 10-Diazo-2,6-dimethoxyanthrone (1.4 g, 0.005 mol), 0.19 g (0.006 mol) of sulfur, and 7 mL of dimethylformamide were heated and stirred in a flask in an oil bath at 130 °C. Nitrogen was evolved, and heating was continued for 10 min after evolution ceased. The mixture was cooled, and the thione (0.90 g) was filtered off and rinsed first with dimethylformamide and then with carbon tetrachloride. Recrystallization from chloroform gave 0.64 g (42.5%) of brown crystals of **2b**: mp 207 °C; NMR ($CDCl_3$) 3.97 ppm (OCH_3); UV ($CHCl_3$) 685 nm (ϵ 65.6), 390

0022-3263/79/1944-0632$01.00/0

(15 900), 352 (10 300), 298 (28 000). The compound was green in solution.

Anal. Calcd for $C_{16}H_{12}O_3S$: C, 67.59; H, 4.25; S, 11.28. Found: C, 67.35; H, 4.27; S, 11.01.

Monothioanthraquinone–2,3-Dimethylbutadiene Adduct (3). To 2.24 g (0.01 mol) of monothioanthraquinone dissolved in 50 mL of warm chloroform was added 0.98 g (0.012 mol) of 2,3-dimethylbutadiene. The solution turned from green to yellow. The solution was treated with Darco and allowed to evaporate. The residue (3.01 g, 98%) was recrystallized from carbon tetrachloride to give 2.71 g (89%) of 3',6'-dihydro-4',5'-dimethylspiro[anthracene-9(10*H*),2'-[2*H*]thiopyran]-10-one: mp 143–146 °C; NMR ($CDCl_3$) 1.96 (s, $2CH_3$), 2.75 (s, CH_2), 3.21 (s, CH_2S) ppm.

Anal. Calcd for $C_{20}H_{18}OS$: C, 78.40; H, 5.92; S, 10.46. Found: C, 78.51; H, 5.90; S, 10.22

Monothioanthraquinone–Cyclopentadiene Adduct (4). To 1.12 g (0.005 mol) of monothioanthraquinone partly dissolved in 25 mL of dichloromethane was added cyclopentadiene until the green color was discharged. The solution was treated with Darco and then allowed to evaporate at room temperature. The residue of pale yellow crystals of spiro[anthracene-9(10*H*),3'-[2]thiabicyclo[2.2.1]-5-heptene]-10-one was washed with pentane: yield 1.30 g (90%); NMR ($CDCl_3$) AB pattern (J = 10 Hz) for CH_2 composed of triplets at 1.39 and 1.55 ppm and singlets at 1.98 and 2.14 ppm; 2.83 (m, H-4), 4.32 (m, H-1), 5.18 (q, H-5), 6.41 (q, H-6) ppm. The compound slowly dissociated back to **2a** and cyclopentadiene at 22 °C.

Anal. Calcd for $C_{19}H_{14}OS$: C, 78.58; H, 4.86; S, 11.04. Found: C, 78.34; H, 5.01; S, 10.89.

Reaction of 2a with Trimethyl Phosphite to Form 5. To 2.24 g (0.01 mol) of monothioanthraquinone dissolved in 30 mL of hot chloroform was added 1.24 g (0.01 mol) of trimethyl phosphite. White crystals separated. The mixture was cooled, and 1.34 g (64%) of crystals was filtered off. Recrystallization from dichloromethane gave 1.26 g (60%) of the thiirane **5**, dispiro[anthracene-9(10*H*),2'-thiirane-3',9''(10''*H*)-anthracene]-10,10''-dione: mp 169.5–170.5 °C dec; IR 3086 (=CH), 1686 (C=O), 1605 (aromatic C=C) cm^{-1}; NMR (CD_2Cl_2) 7.20, 7.67 ppm (anthraquinone-type pattern).

Anal. Calcd for $C_{28}H_{16}O_2S$: C, 80.83; H, 3.87; S, 7.70. Found: C, 80.75; H, 3.85; S, 7.95.

Synthesis of 5 from 1a and 2a. Monothioanthraquinone (0.22 g, 0.001 mol) in 15 mL of dichloromethane was added to 0.22 g (0.001 mol) of 10-diazoanthrone in 10 mL of dichloromethane. Nitrogen was evolved. Crystals deposited when the solution was allowed to stand for 16 h. The solution was reduced in volume by boiling and cooled to give 0.22 g (53%) of **5**: mp 170–171 °C dec; mixture melting point with the $(MeO)_3P$ product above, 170–171 °C; IR spectrum was the same as that for the $(MeO)_3P$ product.

Monothioanthraquinone S-Oxide (6). A solution of 2.24 g (0.01 mol) of monothioanthraquinone in 125 mL of chloroform was stirred, and 0.01 mol of 40% peracetic acid was added. The solution turned from green to orange-yellow. Drying agent ($MgSO_4$) was added, the solution was filtered, and the solvent was removed under vacuum. The product can be recrystallized from dichloromethane to give yellow-orange needles but remains contaminated with anthraquinone. The sulfine was further purified chromatographically by two passages over 5-μm silica gel using 2:3 CH_2Cl_2–*n*-BuCl as solvent. The sulfine issued from the column after the anthraquinone. The solvent was quickly removed under vacuum to leave the sulfine in 95% purity by sulfur analysis. It decomposed at 209 °C when placed in a hot bath and had IR bands at 3067 (=CH), 1658 (C=O), 1126, 1105 (C=S=O), and 768 (ortho-substituted aromatic band) cm^{-1}. The compound could not be obtained in higher purity by this method as it changes in solution with time, demonstrated by UV absorption.

Anal. Calcd for $C_{14}H_8O_2S$: C, 69.98; H, 3.36; S, 13.34. Found: C, 70.22; H, 3.41; S, 12.71.

Acknowledgment. The author is indebted to N. E. Schlichter and E. W. Matthews for IR and UV spectral interpretations and to A. J. Mical for chromatographic purification of **6**.

Registry No.—**1a**, 1705-82-4; **1b**, 68629-84-5; **2a**, 68629-85-6; **2b**, 68629-86-7; **3**, 68629-87-8; **4**, 68629-88-9; **5**, 68629-89-0; **6**, 68629-90-3; 2,6-dimethoxyanthrone, 961-57-9; *p*-toluenesulfonyl azide, 941-55-9; 2,6-dimethoxyanthraquinone, 963-96-2; 2,3-dimethylbutadiene, 513-81-5; cyclopentadiene, 542-92-7.

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gem-Dinitroenamines. Synthesis of 2-(Arylamino)-1,1-dinitroethylenes

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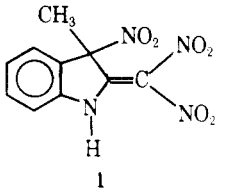
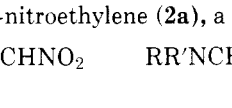
As part of a study of new synthetic routes to *gem*-dinitroolefins, this report describes a synthesis of 2-(arylamino)-1,1-dinitroethylenes. The method involves direct reaction between dinitromethane or its salts, triethyl orthoformate, and aromatic amines. Only one *gem*-dinitroenamine appears to have been reported previously; compound **1** is described as



1

the product of reaction of skatole with tetranitromethane in diethyl ether solvent at room temperature.[2] This structure assignment appears tentative on the basis of the reported data.

Mononitroenamines are known.[3] Severin's reagent, 1-(dimethylamino)-2-nitroethylene (**2a**), a useful reaction in-



2a

2b

X = CN, $CO_2C_2H_5$

R,R' = H, alkyl, aryl

termediate, is prepared by reaction of nitromethane with dimethyl sulfate–dimethylformamide complex and ethanolic sodium ethoxide.[3a,b] In our hands replacement of dinitromethane for nitromethane in Severin's procedure failed to yield a dinitroenamine. The preparation of substituted mononitroenamines **2b** has recently been reported by Wolfbeis.[3d]