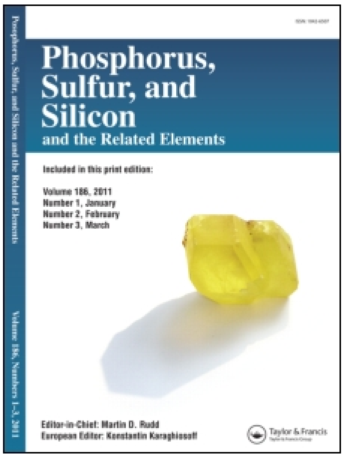


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

THIATION REACTIONS. III. THIATION OF CERTAIN DICARBONYL COMPOUNDS

A. A. El-kateb[a]; I. T. Hennawy[a]; R. Shabana[a]; F. H. Osman[a]
[a] National Research Centre, Dokki-Cairo, Egypt

To cite this Article El-kateb, A. A. , Hennawy, I. T. , Shabana, R. and Osman, F. H.(1984) 'THIATION REACTIONS. III. THIATION OF CERTAIN DICARBONYL COMPOUNDS', Phosphorus, Sulfur, and Silicon and the Related Elements, 20: 3, 329 — 332

To link to this Article: DOI: 10.1080/03086648408077642

URL: http://dx.doi.org/10.1080/03086648408077642

Phosphorus and Sulfur, 1984, Vol. 20, pp. 329–332
0308-664X/84/2003-0329/$18.50/0

THIATION REACTIONS. III. THIATION OF CERTAIN DICARBONYL COMPOUNDS

A. A. EL-KATEB, I. T. HENNAWY, R. SHABANA and F. H. OSMAN

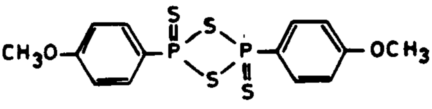
National Research Centre, Dokki-Cairo, Egypt

(*Received February 4, 1984; in final form March 27, 1984*)

1,3,2,4-Dithiadiphosphitane-2,4-bis(4-methoxyphenyl)-2,4-disulfide (**1**) reacts with acenaphthenequinone (**2**) to give acenaphthenenone-2-thione (**3**). Compound **1** also reacts with isatins (**6a, 6b**) to yield isoindigotine (**7a**) and dimethylisoindigotine (**7b**) respectively. Isoindigotine upon reacting with **1** gives [$\Delta^{3,5}$-biindoline]-2,2′-dithione (**8**). Thiation of anthraquinone (**9**) with **1** leads to the formation of 10-monothioanthraquinone (**10**). [$\Delta^{9,9'(10H,10'H)}$-Bianthracene]-10,10′-dithione (**11**) is obtained via thiation of 10-diazoanthraquinone (**12**) or bianthraquinone (**13**) with **1**. Structural assignment are based on analytical, chemical and spectroscopic evidence.

INTRODUCTION

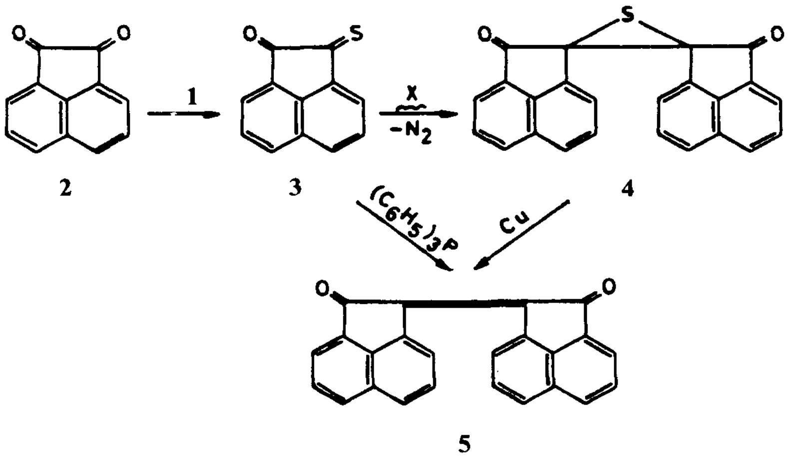
Unsuccessful attempts have been made for the preparation of monothioquinones.[1,2] A literature survey revealed that the first recorded example is monothioanthraquinone, which was prepared via the action of sulfur on 10-diazoanthraquinone.[3] Recently, we have reported on the reaction of 1,3,2,4-dithiadiphosphitane-2,4-bis(4-methoxyphenyl)-2,4-disulfide (**1**) with diazoketones, leading to the formation of thiadiazole or dimeric dithione derivatives.[4] The present investigation was undertaken with the object of examining the action of the effective thiation agent **1**[5–8] on acenaphthenequinone, isatins, anthraquinone and diazoanthraquinone.



1

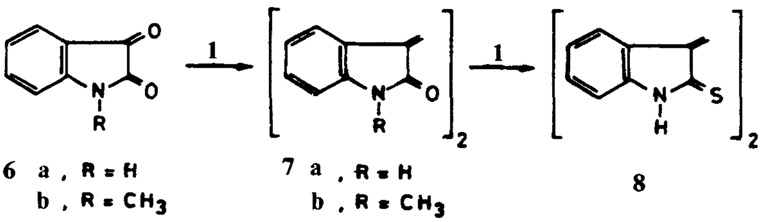
RESULTS AND DISCUSSION

We have found that when compound **1** was allowed to react with acenaphthenequinone (**2**) in refluxing benzene, acenaphthenequinone-2-thione (**3**) was isolated in good yield. The identity of product **3** was established from correct analytical data, IR and mass spectrometric molecular weight determination. The IR spectrum (KBr, expressed in cm^{-1} showed bands at 1780 (C=O), 1220 (C=S) not recorded in the parent compound **2**, 1580 (C=C aromatics). The mass spectrum of **3** gave a prominent ion peak at m/e 198 (60%), loss of a C=S group from the parent ion gave the radical cation at m/e 154 (99%), further loss a C=O group from the latter gave the radical cation at m/e 126 (100%). Compound **3** undergoes some of the reactions of other thio-carbonyl compounds. Thus it reacted with 2-diazoacenaphthenone in refluxing toluene in the presence of copper-bronze to afford [$\Delta^{1,1'}$-biacenaphthene]-2,2′-dione (**5**). Compound **5** was also obtained from the reaction of **3** with triphenylphosphine in the same solvent. The dimeric dione **5** was identical (m.p., mixed m.p. and comparative IR spectra) with an authentic sample.[9] The formation of **5** may occur through ejection of sulfur from the intermediate thiirane (**4**).[10]

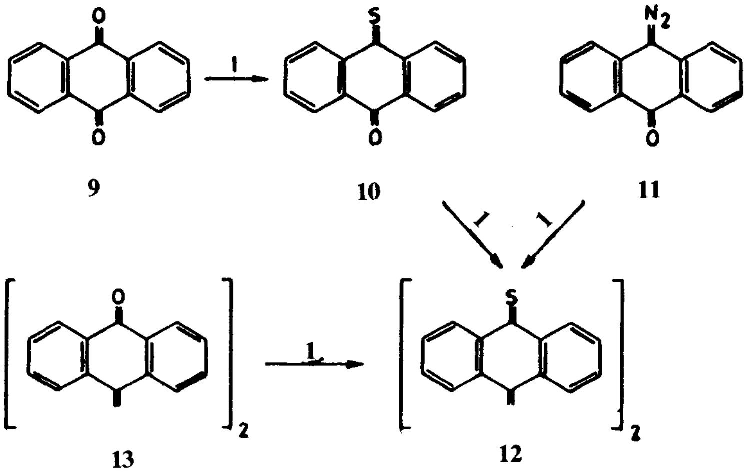


X = 2-diazoacenaphthenone

Treatment of isatin (**6a**) and *N*-methylisatin (**6b**) with reagent **1** in refluxing benzene or toluene leads to the formation of isoindigotin (**7a**) and *N*,*N*′-dimethylisoindigotin (**7b**), respectively (identified from elemental analysis, comparative IR spectra with authentic samples and molecular weight determination).[11,12] Further thiation of isoindigotin with **1** in toluene afforded [$\Delta^{3,3'}$-Biindoline]-2,2′-dithione (**8**). Compound **8** has the same m.p., mixture m.p. and comparative IR spectra with authentic sample prepared via thiation of 3-diazooxindole with **1**.[4]



Next, the reaction of anthraquinone (**9**) with reagent **1** was carried out in toluene to give monothioanthraquinone (**10**). Structure **10** was verified by m.p., mixture m.p. and comparative IR spectra with an authentic sample.[3] Thiation of **10** with **1** gave [$\Delta^{9,9'(10H,10H)}$-bianthracene]-10,10′-dithione (**12**). The dimeric dithione **12** was also isolated with the same m.p., mixture m.p. and comparative IR spectra upon reacting



10-diazoanthraquinone (**11**) with **1** in refluxing benzene or bianthraquinone (**13**) with **1** in refluxing xylene. Additional evidence for structure (**12**) was also gained from analytical data, IR and molecular weight determinations (cf. Experimental).

The results of the present investigation may allow certain conclusions to be stated. Whereas the reaction of compound **1** with acenaphthenequinone and anthraquinone gives stable monothioacenaphthenone and monothioanthraquinone, respectively, its reaction with isatins leads to the formation of isoindigotins. Thus, the isolated products depend on the stability of the thione derivatives under the experimental conditions. If the thione is stable, it can be isolated and characterized, whereas the unstable products eject sulfur to produce the corresponding dimeric dione, through the formation of the respective carbene or thiirane intermediates. On the other hand, the dimeric dithione could be directly obtained via thiation of the respective diazoketones or the corresponding dimeric dione with **1**, but not from the respective dicarbonyl compounds, even when **1** is used in excess.

EXPERIMENTAL

All melting points are uncorrected. Pet. ether solvent was used (b.r. 40–60°). All solvents must be dried. The IR spectra were taken in KBr with a Carl Zeiss Infracord Spectrometer Model UR 10. The mass spectra were run at 70 eV on Varian MAT 112 Spectrometer. The reagent **1** was freshly prepared.[7]

Reaction of Acenaphthenequinone (**2**) *with Reagent* **1**. A mixture of acenaphthenequinone[13] (**2**) (1.82 g, 0.01 mole) and reagent **1**[7] (2.0 g, 0.005 mole) in dry benzene (80 ml) was refluxed for 30 hr. The volatile material was evaporated under vacuum. The residue left was eluted with a mixture of benzene–alcohol (50 : 50) on a column of silica gel. The solvent was evaporated *in vacuo*, the precipitate that formed was crystallized from benzene–ethanol to give monothioacenaphthenone (**3**) as dark yellow crystalline product m.p. 280 in *ca.* 70% yield. Calcd. for $C_{12}H_6SO$: C, 72.72; H, 3.03; S, 16.16 Found: C, 72.69; H, 3.04; S, 16.13%.

Reaction of **3** *with* 2-*Diazoacenaphthenone*. A mixture of compound **3** (0.39 g, 0.002 mole), 2-diazoacenaphthenone[14] (0.38, 0.002 mole) and Cu-bronze (0.4 g) in toluene (25 ml) was refluxed for 20 hr. The mixture was cooled, and filtered while hot. On cooling, the dimeric product **4** precipitated, crystallized from toluene to give m.p. 290°C in 60% yield, and on admixing with authentic sample showed no depression in the m.p. Copper sulfide was detected in the filtrate by t.l.c.

Similarly, the dimeric compound **4** was also obtained (m.p., mixture m.p. and comparative IR spectra) in 55% yield from the reaction of **3** with triphenylphosphine in refluxing toluene for 24 hr. Triphenylphosphine sulfide was detected by t.l.c. in the filtrate.

Thiation of Isatin (**6a**). A mixture of isatin (**6a**) (1.47 g, 0.01 mole) and compound **1** (2 g, 0.005 mole) in benzene or toluene (70 ml) was refluxed for 30 hr. The volatile materials were removed under reduced pressure, elution with a mixture of ethanol–benzene (60–40) on a column of silica gel gave isisondigotin (**7a**) which crystallized from methanol in *ca.* 65% yield with m.p. over 360°C. The IR spectra was identical with an authentic sample.[11]

Similarly, dimethyl isoindigotin (**7b**) was isolated (70% yield) from the reaction of N-methylisatin with **1** in toluene for 24 hr. Elution solvent was ethanol–benzene (60–40) and it was crystallized from ethanol (m.p. and mixed m.p. 288°C).[12]

Formation of Compound **8**. Thiation of isoindigotin with **1** as described above in toluene for 40 hr gave the dimeric dithione (**8**) after elution with chloroform–petroleum ether (30 : 70) in 50% yield as a gray crystalline product (m.p. and mixed m.p. 270–272°C and comparative IR spectra with an authentic sample).[4]

Reaction of Anthraquinone (**9**) *with Reagent* **1**. A mixture of anthraquinone (2.08, 0.01 mole) and compound **1** (2.0 g, 0.005 mole) in toluene (80 ml) was refluxed for 30 hr. Removal of the solvent and elution with methylene chloride–petroleum ether (70 : 30) gave monothioquinone (**10**) as a green product which crystallized from chloroform with m.p. and mixed m.p. 214–215°C in *ca.* 65% yield. Compound **10** has an identical IR spectra with an authentic sample.[3]

Thiation of Monothioanthraquinone (**10**). Thiation of **10** with **1** as described above and elution with benzene–petroleum ether (80 : 20) gave the dimeric dithione (**11**) which was crystallized from benzene as yellow crystalline material, m.p. 190–192°C in 70% yield. Anal. Calcd. for $C_{28}H_{16}S_2$: C, 80.76; H, 3.84; S, 15.40. Mol. Wt., 416, 404. Found: C, 80.66; H, 3.82; S, 15.34. Mol. Wt. (MS), 416. IR spectra (expressed in cm^{-1}), no carbonyl band was recorded, 1210 (C=S), 1620 (C=C conjugated), 1530 (C=C aromatic).

Similarly, compound **11** was obtained from the reaction of 10-diazoanthraquinone in benzene or bianthraquinone (**13**) in xylene with **1** in *ca.* 70% and 65% yields, respectively, with the same m.p., mixed m.p. and comparative IR spectra.

REFERENCES

1. T. Zinke and W. Glahn, *Ber. Dtsch. Chem. Ges.*, **40**, 3039 (1907).
2. H. A. Stevenson and S. Smiles, *J. Chem. Soc.*, 1740 (1930).
3. M. S. Raasch, *J. Org. Chem.*, **44**, 632 (1979).
4. A. A. El-Kateb, R. Shabana and F. H. Osman, Chemistry & Industry, (submitted for publication) (1983).
5. S. Scheibye, B. S. Pedersen and S. O. Lawesson, *Bull. Soc. Chim.*, **87**, 299 (1978).
6. B. S. Pedersen, S. Scheibye, K. Clausen and S. O. Lawesson, *Bull. Soc. Chim. Belg.*, **87**, 293 (1978).
7. B. S. Pedersen, S. Scheibye, N. H. Nilsson and S. O. Lawesson, *Bull. Soc. Chim. Belg.*, **87**, 223 (1978).
8. R. Shabana and A. A. El-Kateb, *Egypt. J. Chem.*, (in press) (1983).
9. W. Mieczyslaw and U. Tadeusz, *Rocz. Chem.*, **43**, 881 (1969).
10. A. Schonberg and S. Nickel, *Ber.*, **64**, 2323 (1931); M. M. Sidky, M. R. Mahran and L. S. Boulos, *J. Prakt. Chemi.*, **312**, 51 (1970).
11. H. Staudinger and J. Goldstein, *Ber. Dtsch. Chem. Ges.*, **49**, 1923 (1916).
12. J. H. Mason and R. F. J. Ingleby, *J. Chem. Soc.*, 4782 (1958).
13. A. Schonberg, R. Moubasher and A. Mostafa, *J. Chem. Soc.*, 966 (1946).