THF solution of DNBF or DNBZ (110 mg in 2 mL). The reaction mixtures turned immediately dark orange and were allowed to stand at room temperature for about 1 h. The orange crystals that formed were filtered, ground to a fine powder, washed with copious amounts of ether, and dried in vacuo to eliminate any associated solvent. The two solid adducts darkened at ca. 200-230 °C but failed to melt below 300 °C.

Anal. Calcd for  $2a, H^+$  ( $C_{20}H_{20}N_6O_6$ ): C, 54.54; H, 4.58; N, 19.08. Found: C, 54.20; H, 4.46; N, 18.89. Calcd for  $2b, H^+$  ( $C_{20}H_{20}N_6O_5$ ): C, 56.60; H, 4.75; N, 19.80. Found: C, 56.22; H, 4.67; N, 19.27. The <sup>1</sup>H NMR spectra were recorded at 100 MHz (Varian XL

100) in the CW mode, using Me<sub>4</sub>Si as an internal standard.

Registry No. 1a,H<sup>+</sup>, 97670-24-1; 1b,H<sup>+</sup>, 99808-95-4; 2a,H<sup>+</sup>, 99808-93-2; 2b,H+, 99808-94-3; PS, 20734-58-1; DNBF, 5128-28-9; DNBZ, 70264-71-0; TMB, 621-23-8.

# Thioquinones. Generation of Dithioanthraquinone

M. V. Lakshmikantham,\*1 Matthew Levinson, Mary Menachery, and Michael P. Cava<sup>1</sup>

Department of Chemistry, University of Pennsylvania, Philadelphia, Pennsylvania 19104, and Department of Chemistry, University of Alabama, University, Alabama 35486

#### Received June 5, 1985

In contrast to the extensive literature on quinones, very little is known about the corresponding sulfur analogues. Attempts to prepare thioquinones date back to 1900.<sup>2</sup> Only recently, Bock et al. have succeeded in the pyrolytic generation and spectroscopic characterization of the mono and dithio analogues 1 and 2 of p-benzoquinone, in an argon matrix.<sup>3</sup> It was felt that the annellation of two



benzene rings to the p-dithioquinone system might render the thioquinone system more stable and lead to the synthesis of a stable member of this class. The recent synthesis of monothioanthraquinone 3 by Raasch<sup>4</sup> by the reaction of diazoanthrone and elemental sulfur in refluxing DMF was encouraging, in view of the remarkable stability of the anthraquinone analogue in comparison to the benzoquinone analogue 1.

Although a substance considered to be dithioanthraquinone (4) has been reported once, it was stated that the experiment could not be reproduced.<sup>5</sup> Several pathways to the synthesis of dithioanthraquinone are possible. The simplest of these, in view of the ready availability of substrates, was the direct thionation of anthraquinone. We now report our results on the thionation of anthraquinone.

Anthraquinone underwent ready reaction with the thionating agent. Lawesson's reagent  $(5)^6$  in a variety of solvents like benzene, toluene, etc. However, apart from traces of monothioanthraquinone, and some unreacted anthraquinone, the other products were nondescript powders with variable analyses.<sup>7</sup> However, when boiling solutions of anthraquinone and the thionating reagent were quickly mixed under nitrogen and refluxed, a series of color changes from yellow to green to a red brown was visible, and within an hour a cinnabar-like red microcrystalline material was thrown out of solution. This material after filtration and workup by boiling with ethanol analyzed for an oligomer of the expected dithioanthraquinone containing one half unit of a Lawesson's reagent derived moiety for ten units of the thioquinone.



The intermediacy of the monothioanthraquinone was confirmed by subjecting it to the action of Lawesson's reagent under analogous reaction conditions. Thionation occurred rapidly as expected and the red polymeric material with similar elemental analysis was isolated. These observations clearly indicated that, unlike the monothione 3, the dithioquinone 4 was either unstable or too reactive and polymerized to form a polydisulfide. This conjecture was proved by the sodium borohydride reduction of the red material to a water-soluble dithiolate anion which was readily methylated in 70% yield to give the known 9,10dithiomethylanthracene 6.8 The dithiolate anion could also be readily benzoylated to the dibenzoyl derivative 7. Indeed, this procedure of borohydride reduction of the polymer derived from 4 provides a convenient source of 9,10-dithiosubstituted anthracene derivatives.

An alternate route to dithioanthraquinone was sought. It was shown by Raasch that monothioanthraquinone added readily to 2,3-dimethylbutadiene to give spiroadduct  $8.^4$  It was found that adduct 8 could be readily thionated to a blue crystalline compound 9, which corresponds to the monoadduct derived from dithioanthraquinone and 2.3dimethylbutadiene. After considerable experimentation



it was found that adduct 9 could be subjected to retro-

<sup>(1)</sup> Present address: Department of Chemistry, University of Ala-

<sup>bama, University, Alabama 35486.
(2) Zincke, Th.; Frohneberg, W. Ber. Dtsch. Chem. Ges. 1909, 42, 2727.
(3) Bock, H.; Mohmand, S.; Hirabayashi, T.; Maier, G.; Reiseauer, H.</sup> P. Chem. Ber. 1983, 116, 273

<sup>(4)</sup> Raasch, M. A. J. Org. Chem. 1979, 44, 632.

<sup>(5)</sup> Heilbron, I. M., Heaton, J. S. J. Chem. Soc. 1923, 123, 1735.

<sup>(6)</sup> Pedersen, B. S.; Scheibye, S.; Nilsson, N. H.; Lawesson, S. O. Bull. Soc. Chim. Belg., 1978, 87, 223

<sup>(7)</sup> After the completion of our work, a report by El-Kateb et al. (El-Kateb, A. A.; Hennawy, I. T.; Shabana, R.; Osman, F. H. Phosphorus Sulfur 1984, 20, 329) described the thionation of anthraquinone with Lawesson's reagent in refluxing toluene. We have been unable to reproduce the results claimed in this publication. We thank a referee for drawing our attention to this work.

<sup>(8)</sup> Zweig, A.; Mauer, A. H.; Roberts, B. G. J. Org. Chem. 1967, 32, 1322

Diels-Alder reaction by slow heating on a steam bath in dimethylformamide solution. The resulting red insoluble material analyzed for the expected composition of dithioanthraquinone, but it was polymeric in nature like the direct thionation product. This result clearly demonstrated that the dithioquinone 4 is inherently reactive in contrast to the monothioquinone 3 and tends to polymerize to the polydisulfide 10.

### **Experimental Section**

Melting points are uncorrected. Elemental analyses were carried out by Galbraith Laboratories and Atlantic Microlab, Inc. Proton NMR spectra were determined in CDCl<sub>3</sub> solution on a Bruker WM-250 (250 MHz) FT spectrometer with Me<sub>4</sub>Si as internal standard, and the  $\delta$  values are reported in ppm downfield from it. Mass spectra were recorded on either a Hitachi-Perkin-Elmer RMH2 or a V.G mass spectrometer.

Thionation of Anthraguinone. To a boiling solution of anthraquinone (5 g) in chlorobenzene (200 mL) under nitrogen was added a boiling solution of Lawesson's reagent (10 g) in chlorobenzene (100 mL). A bright green color developed quickly and soon changed to brown and then red in the course of 15 min. The red solution was refluxed for 3 h, and the resulting red precipitate (5 g) was washed several times successively with hot chlorobenzene and methylene chloride. It was then boiled with absolute ethanol (100 mL) for 2 h, filtered, and washed twice more with ethanol. The bright red microcrystalline material (4.6 g; 79.7%) was dried, and it had mp >228 °C dec. Anal. Calcd for  $C_{147}H_{88}O_3PS_{21}$ : C, 67.72; H, 3.41; S, 25.84; P, 1.19. Found: C, 67.54; H, 3.74; S, 26.05; P, 1.24.

Thionation of Monothioanthraquinone. To a solution of monothioanthraquinone<sup>4</sup> (0.45 g) in boiling chlorobenzene (10 mL) under nitrogen was added a boiling solution of Lawesson's reagent (0.50 g) in chlorobenzene (15 mL). Reaction was instantaneous, and within minutes the red precipitate formed. Refluxing was continued for 3 h. The precipitate was then filtered and washed with hot chlorobenzene and methylene chloride successively to give the polysulfide, (0.33 g; 68.5%), mp >220 °C dec. Anal. Calcd for  $C_{147}H_{88}OPS_{23}$ : C, 66.90; H, 3.36; S, 27.96; P, 1.17. Found: C, 66.73; H, 3.41; S, 28.1; P, 1.43.

Reductive Methylation of Anthracene Polydisulfide. A stirred suspension of the foregoing red polymeric disulfide (0.20 g) in a mixture of THF (10 mL) and aqueous NaOH (10%; 10 mL) under nitrogen was treated dropwise with an aqueous alkaline solution of sodium borohydride (0.2 g in 3 mL of 10% NaOH aqueous). The mixture was stirred overnight at room temperature (20 h). The resulting clear yellowish orange solution was treated with methyl iodide (0.5 mL). The color lightened at once. After being stirred 1/2 h, the product was extracted into methylene chloride. Standard workup followed by flash chromatography on alumina afforded 9,10-bis(methylthio)anthracene (6). Crystallization from aqueous methanol afforded the pure product (0.16 g; 71%) as yellow crystals; mp 158 °C (lit.<sup>8</sup> mp 162 °C); mass spectrum, m/e (relative intensity) 270 (M<sup>+</sup>, 75); NMR 9.07 (m, Ar, 4 H), 7.44 (m, Ar, 4 H), 2.44 (s, SMe, 6 H).

9,10-Bis(benzoylthio)anthracene (7). After reduction of the polydisulfide (1.0 g) as described above, the resulting bisthiolate was treated with benzoyl chloride (2.0 mL). After being stirred 1 h, the product was filtered, washed with water, and dried to give the crude product (1.3 g; 69.3%). A sample was crystallized from excess chlorobenzene, and it formed shiny yellow plates: mp >260 °C dec; mass spectrum, m/e (relative intensity) 450 (M<sup>+</sup> 22); NMR 8.72 (m, Ar, 4 H), 8.25 (m, Ar 4 H), 7.61 (m, Ar 10 H). Anal. Calcd for  $C_{28}H_{18}O_2S_2$ : C, 74.64; H, 4.03; S, 14.23. Found: C, 74.01; H, 4.13; S, 14.07.

9,10-Dithioanthraquinone-2,3-Dimethylbutadiene Monoadduct 9. The known adduct  $8^4$  (0.7 g) was treated with Lawesson's reagent (0.50 g) in benzene solution (15 mL). The mixture was refluxed for 2 h under nitrogen. The solvent was removed in vacuo, and the residue was chromatographed on silica with benzene-cyclohexane (1:3) as eluent. The blue band which was the second fraction was collected separately, and the product was obtained by evaporation. The blue residue was crystallized from methylene chloride-hexane to give chunky crystals of 9, (0.44 g; 59.7%): mp > 126 °C dec; mass spectrum m/e (relative intensity) 322 (M<sup>+</sup>, 7.3), 240 (M<sup>+</sup> – 82, 100); NMR 8.44 (d, J = 7.75Hz, 2 H), 7.70 (d, J = 7.75 Hz, 2 H), 7.54 (t, J = 7.75 Hz, 2 H), 7.35 (t, J = 7.75 Hz, 2 H), 3.00 (s, 2 H), 2.89 (s, 2 H), 1.88 (s, 3 H), 1.75 (s, 3 H). Anal. Calcd for C<sub>20</sub>H<sub>18</sub>S<sub>2</sub>: C, 74.52; H, 5.68; S, 19.85. Found: C, 74.37; H, 5.56; S, 20.11.

Pyrolysis of Adduct 9. A solution of adduct 9 (0.109 g) in DMF (1.5 mL) was heated on a steam bath overnight. The blue color characteristic of the C=S moiety was destroyed, and a red precipitate was formed. This red material was filtered, washed with more DMF, methylene chloride, and methanol, and dried (0.0475 g, 59.2%). The IR spectrum was essentially the same as the material obtained by direct thionation. It exhibited a mp of >225 °C dec. Anal. Calcd for C<sub>14</sub>H<sub>8</sub>S<sub>2</sub>: C, 70.00; H, 3.36; S, 26.64; Found: C, 70.14; H 4.00; S, 26.26.

Acknowledgment. This investigation was supported by a grant from the National Science Foundation (CHE 83-03897).

Registry No. 3, 68629-85-6; 4, 99838-41-2; 4 (homopolymer), 99838-44-5; 6, 10075-83-9; 7, 99838-42-3; 8, 68629-87-8; 9, 99838-43-4; 9 (homopolymer), 99838-45-6; 10, 70304-09-5; anthraquinone, 84-65-1.

## Measurement of the Secondary H-D Isotope Effect in Atom Transfer Reactions of the 1,1-Dideuterioallyl Radical

### Daniel J. Pasto\* and Nai-Zhong Huang

Department of Chemistry, University of Notre Dame, Notre Dame, Indiana 46556

### Received May 3, 1985

As a part of our detailed mechanistic investigations on radical and diradical intermediate forming reactions of substituted allenes we have measured various H-D isotope effects (IE's).<sup>1,2</sup> In the competitive radical chain addition of benzenethiol to ethylallene an anomously large  $k_{\rm H2}/k_{\rm D2}$ of  $2.7 \pm 0.8$  was observed for the hydrogen atom abstraction from benzenethiol by the intermediate substituted allyl radical 1 to form 2 in which a strong preference is shown for hydrogen atom abstraction at the non-deuterium labeled end of the substituted allyl radical.<sup>1</sup> The IE was

$$C_{2}H_{3}CH = \overset{\bullet}{C} = CH_{2}(D_{2}) + PhSH \longrightarrow C_{2}H_{3}CH_{2}C = CH_{2}(D_{2}) + C_{2}H_{3}CH = C \overset{CH_{3}(D_{2}H)}{\underset{s Ph}{\overset{\circ}{S}}}$$
(1)

calculated on the basis of changes in product distribution and the  $H_2-D_2$  content of 2. A similar unusually large IE has been observed in the preference for ring closure of the diradical intermediate 3 formed in the cycloaddition of ethylallene with 1,1-dichloro-2,2-difluoroethene.<sup>3</sup> Al-



though several IE studies have been devoted to the measurement of secondary H-D IE's in radical additions of  $\pi$  systems, to our knowledge no IE's have been measured for the hydrogen atom transfer step to a  $\pi$ -radical system. We have now measured the product distribution IE for hydrogen atom transfer to the 1,1-dideuterioallyl radical.

Pasto, D. J.; Warren, S. E. J. Org. Chem. 1981, 46, 2842.
 Pasto, D. J.; Warren, S. E. J. Am. Chem. Soc. 1982, 104, 3670.

Pasto, D. J.; Heid, P. F.; Warren, S. E. Ibid. 1982, 104, 3676. (3) Pasto, D. J.; Warren, S. E., unpublished observations.