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 $CDCl_3$ solution on a Bruker WM-250 (250 MHz) FT spectrometer with Me_4Si as internal standard, and the δ 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 Anthraquinone. 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[4] (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.[8] mp 162 °C); mass spectrum, m/e (relative intensity) 270 (M^+, 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^+, 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^+, 7.3), 240 ($M^+ - 82$, 100); NMR 8.44 (d, J = 7.75 Hz, 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 $C_{20}H_{18}S_2$: 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 $C_{14}H_8S_2$: 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

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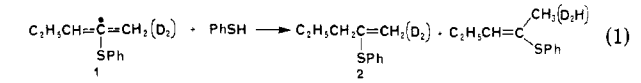
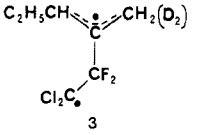
As a part of our detailed mechanistic investigations on radical and diradical intermediate forming reactions of substituted allenes we have measured various H–D isotope effects (IE's).[1,2] In the competitive radical chain addition of benzenethiol to ethylallene an anomously large k_{H2}/k_{D2} of 2.7 ± 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.[1] The IE was



(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.[3] Al-



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

(1) Pasto, D. J.; Warren, S. E. *J. Org. Chem.* **1981**, *46*, 2842.
(2) 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.

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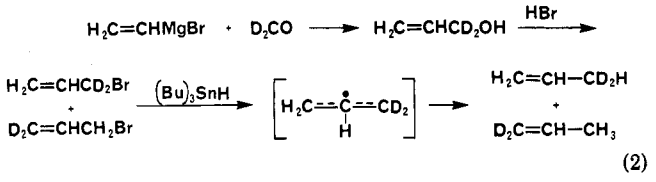
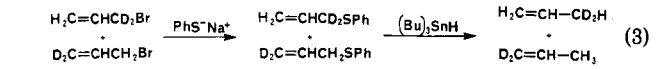
Dideuterioallyl bromide was prepared as shown in eq 2 and was reduced at 50 °C by tributyltin hydride in a radical-chain process. The propene was trapped at low



(2)

temperature in toluene-d_8 and the ratio of 1,1- to 3,3-dideuteriopropene was determined by NMR. Hydrogen atom abstraction is favored at the CH_2 terminus of the 1,1-dideuterioallyl radical by a factor of 1.056 ± 0.002.

Dideuterioallyl phenyl sulfide was prepared from the bromide and was reduced by tributyltin hydride at 78 °C.[4] The deuterium distribution in the resulting propene indicated a preference for hydrogen atom abstraction at the CH_2 terminus of the 1,1-dideuterioallyl radical of 1.080 ± 0.002.



(3)

The secondary H–D isotope effects are much smaller than the apparent isotope effects observed in the reactions of ethylallene and are within a reasonable range for secondary H–D IE's. Even though this reaction involves an *increase* in bonding at the reaction center which might be expected to give rise to an *inverse* secondary effect, the observed value is normal. This suggests that the reaction coordinate involves some motion of the "secondary" hydrogens. Further studies are therefore required in order to derive experimental data which will provide for an understanding of the anomolously high IE's observed in the reactions of ethylallene.

Experimental Section

Preparation of Dideuterioallyl Bromide. An experimental apparatus was constructed as illustrated for the synthesis of 2-(hydroxymethyl)cyclopentanone.[5] Paraformaldehyde-d_2 (1.7 g, 53 mmol) was placed in a two-necked, round-bottomed flask immersed in an oil bath. The outlet side of the flask was attached by glass tubing to an inlet bubbler tube to a two-necked, round-bottomed flask containing a twofold excess of vinylmagnesium bromide in THF (Aldrich Chemical Co.). An argon stream was passed over the paraformaldehyde-d_2 and through the bubbler tube into the vinylmagnesium bromide solution. The flask containing the paraformaldehyde-d_2 was heated to 180–190 °C. After the disappearance of the paraformaldehyde-d_2 the vinylmagnesium bromide solution was refluxed for 1 h. The reaction mixture was cooled and was slowly poured into 25 mL of cold 10% aqueous $MgSO_4$. Aqueous sulfuric acid (30%) was then slowly added. The top organic layer was decanted, and the aqueous layer was extracted twice with 30-mL portions of diethyl ether. The combined organic fractions were dried ($MgSO_4$), and the diethyl ether and THF were carefully removed by fractional distillation, giving 2.5 g (79%) of 1,1-dideuterio-2-propen-1-ol. The NMR spectrum of the product contained only vinyl hydrogen resonances at δ 4.99, 5.11, and 5.85.

Dideuterioallyl bromide was prepared with the reported procedure for the preparation of allyl bromide from allyl alcohol.[6] The NMR spectrum of product showed peaks at δ 3.9, 5.1, 5.3, and 6.0. Integration of the resonances indicated the product to be a 3.3:1 mixture of 3,3- and 1,1-dideuterioallyl bromide.

Preparation of Dideuterioallyl Phenyl Sulfide. Dideuterioallyl phenyl sulfide was prepared according to the procedure used for the preparation of crotyl phenyl sulfide[7] by reacting sodium thiophenoxide with the dideuterioallyl bromide in methanol. The NMR of the product showed resonances at δ 3.36, 4.98, 5.07, 5.78, and 7.27. Integration of the NMR spectrum indicated the product to be a 55:45 mixture of 1,1- and 3,3-dideuterioallyl phenyl sulfide.

Reduction of Dideuterioallyl Bromide with Tributyltin Hydride. The reduction of the dideuterioallyl bromide with tributyltin hydride was carried out in a manner similar to that used for the reduction of propargyl bromide.[8] In a 10-mL flask equipped with a condensor were placed 0.18 g (1.45 mmol) of the dideuterioallyl bromide, 0.42 g (1.45 mmol) of tributyltin hydride, and 12 mg of 2,2-azobis(isobutyronitrile) (AIBN). A T-tube was placed in the top of the condensor, one side of which was connected by a short piece of tubing to a long syringe needle which was directed below the surface of toluene-d_8 in an NMR tube maintained at <-40 °C. A slow stream of argon was passed through the T-tube and the syringe needle. The contents of the flask were heated at 50 °C for 3 h. The NMR tube was capped, and the NMR spectrum was recorded and integrated. The ratio of 1,1- to 3,3-dideuteriopropene was calculated from the relative intensities of the CH= and $=CH_2$ resonances, giving a value of 1.057. A second run gave a value of 1.054.

Reduction of Dideuterioallyl Phenyl Sulfide with Tributyltin Hydride. The general procedure for the reduction of dialkyl sulfides with tributyltin hydride[4] was employed. 1,1-Dideuterioallyl phenyl sulfide (0.30 g, 2 mm) was reduced with 0.64 g (2.2 mm) of tributyltin hydride and 5 mol % AIBN in 2 mL of refluxing benzene by using the experimental setup described above. The ratio of 1,1- to 3,3-dideuteriopropene was determined by NMR to be 1.081. The results of a second run gave a value of 1.080.

Acknowledgment. We acknowledge grants from the National Institutes of Health and the University of Notre Dame for the purchase of a Nicolet NB-300 NMR system used in these studies.

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α-Hydroxy Thioamides: Useful Intermediates for the Synthesis of Functionalized Thiazoles

John L. LaMattina* and Christian J. Mularski

Central Research, Pfizer Inc., Groton, Connecticut 06340

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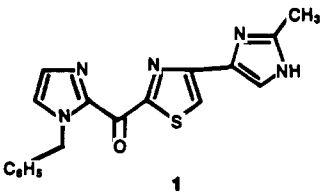
In connection with work designed to discover novel therapeutic agents, a practical synthesis of **1** was sought. A variety of approaches to this compound can be envisioned, and indeed, a number of these were investigated. However, the one that ultimately proved successful hinged on the availability of a key α-hydroxy thioamide. This note describes a novel approach to these compounds which not only allows for the synthesis of **1** but also appears to be quite general.



1

A convergent synthesis of **1** was eventually decided upon in which the α-bromo ketone **2** would be condensed with a properly functionalized thioamide. Surprisingly, at this

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