*Anal.* Calcd. for $C_{12}H_8ClN_3O_2$: C, 55.08; H, 3.08. Found: C, 55.28; H, 3.34.

**5-Chloro-2-nitroazobenzene.**—The procedure was as described above. From 1.9 g. (0.01 mole) of 5-chloro-2-nitronitrosobenzene[13] and 1.0 ml. (0.9 g., 0.01 mole) of aniline was obtained after sublimation 2.4 g. (92%) of bright red needles, m.p. 92.6–94.2°. The sublimate was recrystallized from 95% ethanol to give 2.2 g. (84%) of orange needles, m.p. 93.6–94.2° (lit.,[16] m.p. 94°).

**6-Chloro-2-phenylbenzotriazole Oxide.**—A solution prepared by warming 2.6 g. (0.01 mole) of 4-chloro-2-nitroazobenzene in 10 ml. of 95% ethanol was stirred magnetically and a solution of 9.6 g. (0.04 mole) of sodium sulfide nonahydrate in 30 ml. of water was added all at once. After stirring at room temperature for 17 hr. the mixture was cooled in an ice bath and the light tan solid was collected by suction filtration. The crude material was sublimed at 125° (0.05 mm.) to give 2.4 g. (97%) of pale yellow crystals. Two recrystallizations from 95% ethanol (Norit) gave 2.2 g. (90%) of white needles, m.p. 141.6–142.4°. A small sample which had been recrystallized twice more from ethanol melted at 142.2–142.8°.

*Anal.* Calcd. for $C_{12}H_8ClN_3O$: C, 58.67; H, 3.28. Found: C, 58.91; H, 3.15.

**5-Chloro-2-phenylbenzotriazole Oxide.**—The procedure was as described above. From 2.6 g. (0.01 mole) of 5-chloro-2-nitroazobenzene and 9.6 g. (0.04 mole) of sodium sulfide nonahydrate was obtained after sublimation 2.3 g. (94%) of light yellow crystals. Two recrystallizations from 95% ethanol (Norit) gave 2.0 g. (82%) of white needles, m.p. 139.8–140.4° (lit.,[16] m.p. 142.5°).

**Attempted Isomerization of Benzotriazole Oxides.**—Separate 0.1-g. portions of 6-chloro-2-phenylbenzotriazole oxide and 5-chloro-2-phenylbenzotriazole oxide were heated for 2.5 hr. in an oil bath maintained at 145°. The 5-chloro isomer became dark on heating while the 6-chloro compound underwent no visible change. In each case, the infrared spectrum of the sample after heating was identical with that of the pure compound.

---

(16) C. Willgerodt and L. Ellon, *J. prakt. Chem.*, **44**, 67 (1891).

---

## Naphthalene as a Photoquencher

VIRGIL I. STENBERG AND ROBERT J. PERKINS

*Department of Chemistry, University of North Dakota, Grand Forks, North Dakota*

*Received July 3, 1962*

Our interest in a photoadduct between naphthalene and maleic anhydride was intensified by reports of an analogous reaction proceeding with benzene.[1-3] Preliminary evaluation led us to the conclusion the former reaction should proceed in the same manner as the latter and, as a consequence, the reaction would be of lesser significance. However, upon further consideration it was observed that a decision could be made between a 1,2- and a 1,4-addition as the initial reaction of maleic anhydride with naphthlene if the reaction occurred. An analogy could then be made to the benzene photoproduct formation. Two quite different products would be expected depending on the mode of the first addition.

Upon irradiation of naphthalene and excess maleic anhydride in tetrahydrofuran, no photoadduct was found. Naphthalene was recovered quantitatively and the maleic anhydride nearly so with an uncharacterized polymeric material. In an irradiation under identical circumstances without naphthalene, the polymer was obtained exclusively.

On the basis of these results we conclude that naphthalene has a quenching effect on the photoinduced polymerization of maleic anhydride. A similar observation has recently been reported by Moore and Ketchum[4] for the influence of naphthalene on the photoreduction of benzophenone.

### Experimental

The following reaction solutions were irradiated simultaneously in identical quartz vessels with a 140-watt Hanovia high pressure mercury arc lamp.

**Irradiation of Naphthalene and Maleic Anhydride.**—A solution of 5.6 g. (0.057 mole) of maleic anhydride and 1.44 g. (0.011 mole) of naphthalene in 30 cc. of purified tetrahydrofuran was irradiated for 8 hr. Distillation of the reaction mixture provided 4.88 g. (87%) of maleic anhydride. Chromatography of the residue on alumina produced 1.40 g. (97%) of naphthalene. On further elution a gum appeared which was not completely eluted until ether was passed over the column.

**Irradiation of Maleic Anhydride.**—The above procedure was duplicated omitting the naphthalene. Distillation provided no maleic anhydride and alumina chromatography failed to yield material other than an amorphous gum.

**Acknowledgment.**—The financial support received from the Research Corporation which made this research possible is gratefully acknowledged.

---

(1) E. Grovenstein, Jr., D. V. Rao, and J. W. Taylor, *J. Am. Chem. Soc.*, **83**, 1705 (1961).

(2) G. O. Schenkt and R. Steinmetz, *Tetrahedron Letters*, **21**, 1 (1961).

(3) H. J. F. Angus and D. Bryce-Smith, *J. Chem. Soc.*, 4791 (1960).

(4) W. M. Moore and M. Ketchum, *J. Am. Chem. Soc.*, **84**, 1368 (1962).

---

## Formation of Dibenzothiophene by a Disulfide Ring Closure[1]

E. CAMPAIGNE, L. ERGENER, AND B. G. HEATON

*Chemistry Laboratories of Indiana University, Bloomington, Indiana*

*Received July 6, 1962*

Disulfides, derived by oxidation of β-aryl-α-mercaptoacrylic acids, have been shown in earlier reports[2,3] to undergo cyclization in the presence of a Lewis acid to give the corresponding condensed

---

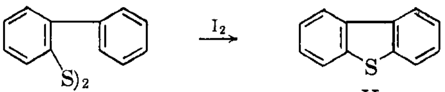
(1) This research was supported in part by the U. S. Army Research Office (Durham) under contract No. DA-33-008-ORD-1916.

(2) E. Campaigne and R. E. Cline, *J. Org. Chem.*, **21**, 39 (1956).

(3) E. Campaigne and W. E. Kreighbaum, *J. Org. Chem.*, **26**, 1326 (1961).

thiophene-2-carboxylic acids. More recently,[4] condensed 2,3-dihydrothiophenes have been obtained from bis(β-arylethyl) disulfides using iodine or aluminum bromide as the catalyst.

During the course of further work on the scope of the disulfide ring-closure reaction, we have found that bis(2-biphenylyl) disulfide (I) will cyclize in good yield in the presence of iodine to give dibenzothiophene (II).



I II

A combination of catalyst and conditions was sought which might be even more favorable for ring closure, and therefore the reaction was repeated, using catalysts other than iodine and varying the solvent and temperature. The results are summarized in Table I.

TABLE I

CYCLIZATION OF BIS(2-BIPHENYLYL) DISULFIDE

| Catalyst | Moles catalyst/ mole disulfide | Conditions, °C. | Dibenzothiophene, % yield |
|---|---|---|---|
| $I_2$ | 1.1 | 198°, 1 hr.[a] | 64 |
| $I_2$ | Excess | 101°, 24 hr.[b] | 0 |
| $I_2$ | 2.0 | Reflux, 12 hr.[c] | 50 |
| $I_2 + Me_2SO_4$ | 0.6, 1.2, resp. | Reflux, 5 hr.[b] | 0 |
| $I_2 + SnCl_4$ | 0.6, 2.1, resp. | Reflux, 2.5 hr.[d] | 0 |
| $AlBr_3$ | 1.0 | 80°, 3 hr.[d] | 38 |
| $AlCl_3$ | 2.0 | 65°, 3 hr.[d] | 35 |
| $BF_3$ | Excess | Reflux, 3 hr.[d] | 0 |
| $Br_2$ | 1.0 | 78°, 37 hr.[e] | 16 |
| Poly-$H_3PO_4$ | Excess | 200°, 24 hr. | 0 |
| Conc. $H_2SO_4$ | Excess | 25° | 0 |

Solvents: [a] Ethylene glycol. [b] Dioxane. [c] Toluene. [d] Benzene. [e] Carbon tetrachloride.

Iodine was found to be the most effective of the catalysts employed, as the reaction can be run at higher temperatures without significant desulfurization occurring, and it has a further advantage over reagents such as aluminum chloride in that it has the ability to oxidize the thiol[4] (formed as the by-product on cleavage of the disulfide) to starting material. However, even with iodine present, no dibenzothiophene could be isolated when stannic chloride was employed.

With bromine, ring closure was expected to proceed in good yield *via* the formation of the sulfenium bromide. In fact a surprisingly low yield of dibenzothiophene was obtained and 70% of the disulfide was recovered. In contrast, bis(2-biphenylyl) diselenide affords an essentially quantitative yield of dibenzoselenophene under the same conditions.[5]

In addition to dibenzothiophene, a very small amount of a compound, m.p. 163–165°, was isolated when iodine and ethylene glycol were employed as the catalyst and solvent respectively. Its analysis was consistent with $C_{14}H_{12}S$ and it seems probable that the two additional carbon atoms are acquired by reaction with either a solvent molecule or a product of the interaction of solvent and iodine. The infrared spectrum indicated the presence of both aromatic and aliphatic carbon–hydrogen bonds. Furthermore, absorption suggesting aromatic monosubstitution together with 1,2,3-trisubstitution and the absence of C-methyl absorption provide reason for the tentative formulation of the by-product, m.p. 163°, as 2,3-dihydro-7-phenylbenzo[*b*]thiophene, which to our knowledge has not yet been reported in the literature.

## Experimental[6]

**Bis(2-biphenylyl) Disulfide (I).**—The disulfide I was prepared as previously reported by Campaigne and Osborn[7] from 2-aminobiphenyl and melted at 117–118°.

**Dibenzothiophene (II).**—The following details exemplify the general work-up procedure for the majority of experiments in Table I and also describe the isolation of the by-product, m.p. 163°.

A solution of I (3.70 g., 0.01 mole), and iodine (2.70 g., 0.011 mole) in freshly redistilled ethylene glycol (300 ml.) was heated under reflux for 1 hr., cooled, and poured slowly into water (1 l.). The small excess of iodine was bleached by the addition of dilute sodium bisulfite solution, and, after cooling overnight, the white solid was collected, washed well with water, and dried under reduced pressure. The solid (3.53 g., m.p. 92–96°) was dissolved in a large volume of boiling ethanol. On cooling the solution, plates (0.1 g.) were obtained which crystallized from benzene–ethanol as fine white needles, m.p. 163–165°. Infrared spectrum: $\nu_{max}^{KBr}$ 3049 cm.$^{-1}$ (aromatic C—H); 2920 and 2841 cm.$^{-1}$ (aliphatic C—H); 702(s) and 744 cm.$^{-1}$ (s) (aromatic monosubstitution); and 697(m) and 769 cm.$^{-1}$ (s) (aromatic 1,2,3-trisubstitution).

*Anal.* Calcd. for $C_{14}H_{12}S$: C, 79.19; H, 5.70; S, 15.10. Found: C, 78.42; H, 5.73; S, 15.35.

The filtrate was partially evaporated and on cooling gave needles, m.p. 97–99° (2.34 g., 64%). Recrystallization afforded white needles m.p. 97.5–99.5°.[8] No melting point depression was observed on admixture with dibenzothiophene prepared by an independent route.

*Anal.* Calcd. for $C_{12}H_8S$: C, 78.22; H, 4.38; S, 17.40. Found: C, 78.17; H, 4.45; S, 17.27.

---

(4) E. Campaigne and B. G. Heaton, *Chem. Ind.* (London), 96 (1962).

(5) J. D. McCullough, T. W. Campbell, and E. S. Gould, *J. Am. Chem. Soc.*, **72**, 5753 (1950).

(6) All melting points are corrected.

(7) E. Campaigne and S. W. Osborn, *J. Org. Chem.*, **22**, 561 (1957).

(8) H. Gilman and A. Jacoby, *ibid.*, **3**, 108 (1938), report the melting point of dibenzothiophene to be 99°.

---

# On the Color Reaction of Khellin with Alkali

MAHMOUD MOHAMED SIDKY
AND MOHAMED REFAT MAHRAN

*Laboratory of Synthetic Chemotherapy,*
*National Research Center, Cairo, Egypt*

*Received July 9, 1962*

Khellin (Ia), the main active principle of the fruits of *Ammi visnaga* (L.), has attracted interest,