The ortho isomer melted at 140–141°, the meta isomer at 121–122°. The latter was previously prepared by Michaelis; m.p. 116–117°.[7]

b.—The composition of the reaction mixture was the same as in (a), but the product was worked up by Dye's method.[2a] The aluminum chloride was precipitated with phosphorus oxychloride and the toluenedichlorophosphines were extracted with petroleum ether. Concentration of the solution gave the crude product in 74% yield. This was converted to the phosphonous acids by treatment with ethanol and water.[8]

The product was an uncrystallizing oil, thus immediately suggesting the presence of an isomeric mixture. The crude mixture was oxidized by heating for four hours with a large excess of mercuric chloride in two liters of water. The mixture was treated with hydrogen sulfide to remove the mercury ions and the filtrate was concentrated to approximately 500 ml. The hot solution was treated with excess lead oxide, stirred for two hours and filtered. The solid material, composed of unreacted lead oxide and lead salts of the toluenephosphonic acids, was suspended in two liters of water with stirring and the mixture was saturated with hydrogen sulfide. The filtrate was worked up as outlined under (a). There was obtained 28 g. of pure *p*-toluenephosphonic acid and 17 g. of the benzene-soluble mixture of the ortho and the meta isomers. A five-gram portion of this mixture, which melted at 100–123°, was subjected to fractional crystallization, as outlined under (a). In this way there was isolated 2 g. of the meta isomer and about 0.5 g. of the ortho isomer, thus confirming the findings under (a).

Ethylbenzene.—Only an exploratory trial of this compound was made. The hydrocarbon (0.5 mole) was treated as described under (a) above. There was isolated 52 g. of crude phosphonic acid. Crystallization of this from hot water yielded a total of 35 g. of the *p*-ethylbenzenephosphonic acid, which melted at 174.5–175.0°. Michaelis[7] reported a melting point of 164° for this substance. A similarly higher melting point of the *p*-toluene compound, in comparison with Michaelis' data, was recently reported by Doak and Freedman.[9] The residual material was soluble in benzene. It was repeatedly crystallized from the solvent mixture used in the separation of the toluene derivatives (see above). In this manner there was isolated some four grams of an ethylbenzenephosphonic acid which melted at 116–117°, presumably the more abundant *m*-isomer.

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[CONTRIBUTION FROM THE CANCER RESEARCH LABORATORY, UNIVERSITY OF FLORIDA]

Nitrogen Derivatives of Dibenzoselenophene[1]

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Dibenzoselenophene has been nitrated and the nitro derivatives reduced to the amino compound. The acetyl- and ethylurethan derivatives were then prepared. From a consideration of ultraviolet absorption spectra, it is concluded that nitration has occurred in the 2-position.

Derivatives of dibenzofuran and dibenzothiophene have been shown to be active carcinogens in the rat.[3] In work carried out in this Laboratory on these compounds and other derivatives of dibenzofuran and dibenzothiophene, it was necessary to investigate the chemistry of dibenzoselenophene.

From absorption spectra of dibenzothiophene and dibenzoselenophene, Fig. 1, one might predict that the chemical reactivities of the two molecules will be of the same order. In respect to nitration this was found to be true. Nitration of dibenzothiophene gave dibenzothiophene-5-oxide and 2-nitrodibenzothiophene.[4] The nitration of dibenzoselenophene gave a yellow crystalline nitrodibenzoselenophene. The structure of this compound is based on the spectral curves shown in this paper. Thus, the absorption spectra shown in Fig. 2 for 2-nitrodibenzothiophene and nitrodibenzoselenophene are almost identical. In Fig. 3 are shown the dissimilar curves of 2-carbethoxyaminodibenzothiophene and 3-carbethoxyaminodibenzothiophene.

Comparison of these curves with the absorption spectra of the carbethoxyamino derivative (Fig. 4) derived from nitrodibenzoselenophene points out the remarkable resemblance in the absorption spectra between 2-carbethoxyaminodibenzothiophene and the carbethoxyaminodibenzoselenophene. Substitution of a selenium atom for a sulfur atom in these compounds causes a hypochromic and a bathochromic shift for the large majority of wave length maxima.

On the basis of the evidence presented it is concluded that nitration of dibenzoselenophene gives 2-nitrodibenzoselenophene.

Experimental

Dibenzoselenophene.—Following the procedure of McCullough, *et al.*,[5] colorless crystals of this compound were obtained melting at 76–78° after vacuum distillation and recrystallization from hexane (reported[5] m.p. 73°).

2-Nitrodibenzoselenophene.—To a stirred solution of 3.4 g. of dibenzoselenophene in 20 ml. of acetic acid at approximately 65° was added slowly 1.5 ml. of fuming nitric acid (d. 1.5). After a few minutes standing, the clear dark yellow solution solidified to a yellow mush. After cooling, the mixture was filtered. Recrystallization from ethyl alcohol yielded 1.6 g. (40%) of lustrous yellow needles melting at 180°.

Anal. Calcd. for $C_{12}H_7NO_2Se$: C, 52.20; H, 2.54; N, 5.07. Found: C, 52.26; H, 2.54; N, 5.08.

2-Aminodibenzoselenophene.—To a hot solution of 3.6 g. of 2-nitrodibenzoselenophene in 90 ml. of acetic acid was added a solution of 16.5 g. of hydrated stannous chloride in 90 ml. of concentrated hydrochloric acid. The mixture was refluxed several hours. The clear colorless solution was cooled and then filtered. The crystals were suspended in

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(2) To be submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy, University of Florida.

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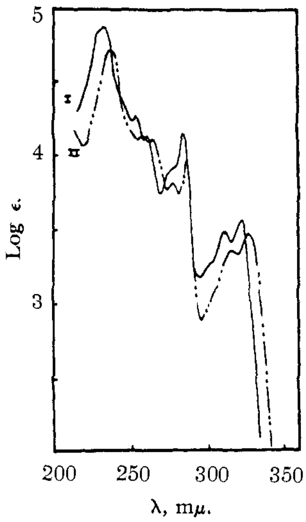

Fig. 1.—Ultraviolet absorption spectra in 95% ethyl alcohol: I, dibenzothiophene; II, dibenzoselenophene.

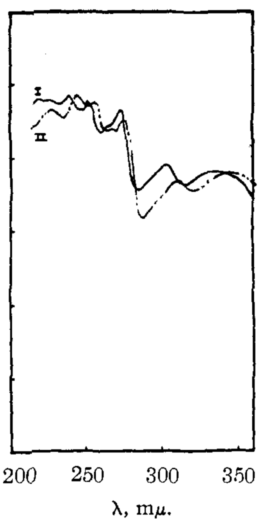

Fig. 2.—I, 2-nitrodibenzothiophene; II, 2-nitrodibenzoselenophene.

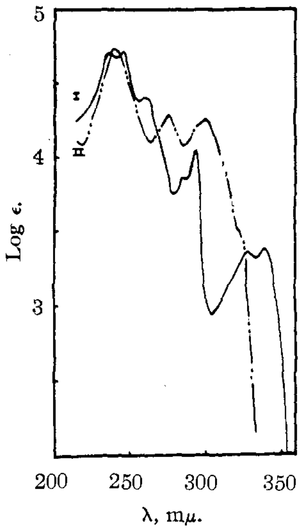

Fig. 3.—I, 2-carbethoxyaminodibenzothiophene; II, 3-carbethoxyaminodibenzothiophene.

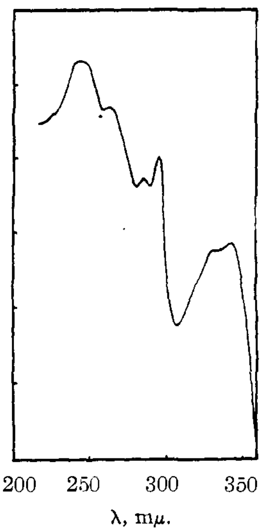

Fig. 4.—2-Carbethoxyaminodibenzoselenophene.

cold water. While this suspension was stirred, ammonium hydroxide was added until the mixture was definitely alkaline. Filtration and crystallization from hexane gave 2.5 g. (78%) of colorless crystals melting at 99°.

Anal. Calcd. for $C_{12}H_8NSe$: N, 5.69. Found: N, 5.77.

2-Acetylaminodibenzoselenophene.—To a hot solution of 0.50 g. of 2-aminodibenzoselenophene in 10 ml. of benzene was added 0.2 ml. of acetic anhydride. In a few minutes the solution solidified. After several hours standing, the mixture was filtered. Glistening colorless needles melting at 181–182° were obtained. Addition of hexane to the mother liquid gave more product. A total yield of 0.54 g. (92%) of compound was obtained. Recrystallization from heptane–benzene gave colorless needles melting at 182°.

Anal. Calcd. for $C_{14}H_{11}NOSe$: N, 4.86; Se, 27.4. Found: N, 4.82; Se, 27.4.

2-Carbethoxyaminodibenzoselenophene.—To a cold solution of 2.0 g. of 2-aminodibenzoselenophene in 40 ml. of pyridine was added 1.2 ml. of ethyl chlorocarbonate. After one hour at 0–10°, excess cold dilute hydrochloric acid was added. This mixture was allowed to stand for several hours at room temperature so as to allow the oil to solidify. After filtration, the residue was recrystallized from hexane. A practically quantitative yield of colorless matted needles was obtained, m.p. 141°.

Anal. Calcd. for $C_{15}H_{13}NO_2Se$: N, 4.40; Se, 24.8. Found: N, 4.49; Se, 24.6.

Dibenzothiophene.—This was prepared from biphenyl by the method of Gilman and Jacoby.[6] The product had a m.p. of 99° and was obtained in 70% yield.

2-Nitrodibenzothiophene.—The product had a m.p. of 188–189° and was obtained in a crude yield of 36% by a modification of the method of Gilman and Nobis.[4]

2-Carbethoxyaminodibenzothiophene.—This compound was prepared in 66% yield from the known 2-aminodibenzothiophene.[7] The preparation was similar to that used for 2-carbethoxyaminodibenzoselenophene. The compound melted at 139–140° after crystallization from hexane.

Anal. Calcd. for $C_{15}H_{13}NO_2S$: N, 5.17. Found: N, 5.13.

3-Carbethoxyaminodibenzothiophene. — This derivative was prepared in 80% yield from the known 3-aminodibenzothiophene[8] (preparation as above). The compound melted at 124–125° after crystallization from heptane

Anal. Calcd. for $C_{15}H_{13}NO_2S$: N, 5.17. Found: N, 5.02.

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