Synthesis and Reactions of Cinnamyl Phenyl Sulfide

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Cinnamyl phenyl sulfide was synthesized as part of a study on model compounds for thiolignin. The sulfide was found to be formed from a mixture of cinnamyl alcohol and thiophenol by elimination of water even at room temperature during irradiation with sunlight or ultraviolet light, or alternatively on moderate heating in the presence of aluminium sulfate or sulfuric acid dissolved in glacial acetic acid. The addition of thiophenol to the ethylenic bond also occurred as a side reaction. The ethylenic bond in cinnamyl phenyl sulfide reacted very slowly with, for instance, soda alkaline permanganate solution, bromine, hydrogen peroxide or perbenzoic acid, the two last-named reagents giving mainly cinnamyl phenyl sulfoxide and sulfone. This led to some doubt as to the actual structure of the sulfide. It can however readily be synthesized from cinnamyl bromide and potassium thiophenolate, and its infrared spectrum points to the presence of an ethylenic double bond. Oxidative degradation of the cinnamyl phenyl sulfide with perbenzoic acid or with permanganate solution gave, among other products, sulfuric, benzoic and benzene sulfonic acids. Degradation by hydrogenation with Raney nickel gave benzene and phenyl propane. Thus in fact the cinnamyl phenyl sulfide has a structure corresponding to its name, but its ethylenic bond is peculiarly slow to react.

SYNTHESES

The present work is a continuation of the studies on thiolignin formation with the aid of model compounds by the one of us (E)[1] and later also by Zentner [2] and Lindgren and Mikawa [3]. As it seems probable that thiolignin contains substantial amounts of monosulfidic sulfur [4], it was of special interest to study the formation and properties of lignin model compounds containing such sulfur.

The present paper is an account of the synthesis and reactions of cinnamyl phenyl sulfide. In a later report, corresponding investigations on several other thiolignin models will be described.

Perhaps the most striking observation made during these syntheses was the ease with which sulfides could be formed by splitting off water from cinnamyl or vanillyl alcohol and thiophenol (formula I). The reaction occurred even at room temperature on irradiation with ultraviolet light or sunlight,
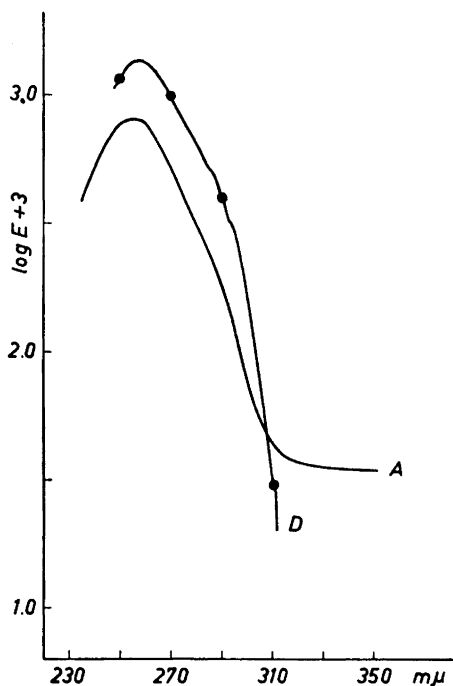
Fig. 1. UV spectrum of cinnamyl phenyl sulfide. D = in dioxan solution. A = in 0.5 N alcoholic sodium hydroxide.
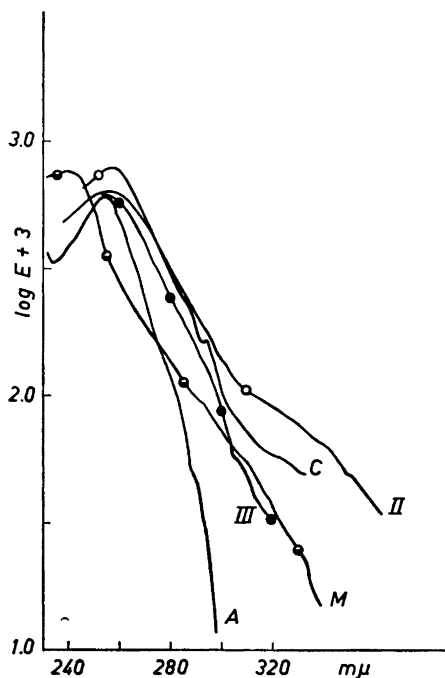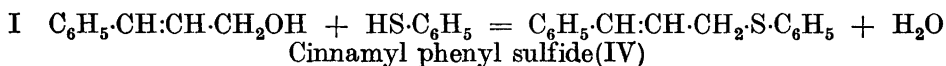
Fig. 2. UV spectra of cinnamyl disulfide (C), of allyl phenyl sulfide (A), of 2-methyl thiocoumarane (M) and of fractions II and III obtained on heating cinnamyl phenyl sulfide.

or alternatively on very moderate heating in the presence of aluminium sulfate or hydrogen ions. Table 1 gives a survey of the syntheses carried out.

The table shows *inter alia* that addition of thiophenol to the ethylenic bond also occurred during the photosynthesis. Attempts to add thiophenol to the ethylenic bond in cinnamyl phenyl sulfide in acetone solution with piperidine as catalyst failed.

I $C_6H_5 \cdot CH{:}CH \cdot CH_2OH$ $+$ $HS \cdot C_6H_5$ $=$ $C_6H_5 \cdot CH{:}CH \cdot CH_2 \cdot S \cdot C_6H_5$ $+$ H_2O
Cinnamyl phenyl sulfide(IV)

THE PROPERTIES OF CINNAMYL PHENYL SULFIDE

Structure. Cinnamyl phenyl sulfoxide has been described in the literature by Barnard[5], who also synthesized cinnamyl phenyl sulfide (private communication), but without publishing anything about it. In June 1956, when the main part of our experimental work was already completed, Briscoe, Challenger and Duckworth [6] published a synthesis of cinnamyl phenyl sulfide and an attempt to determine its structure by reaction with Chloramine T.
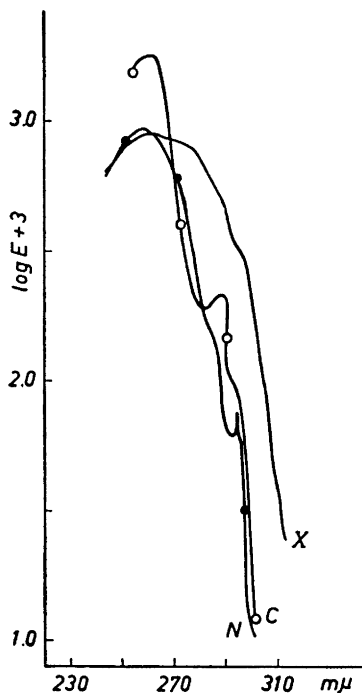
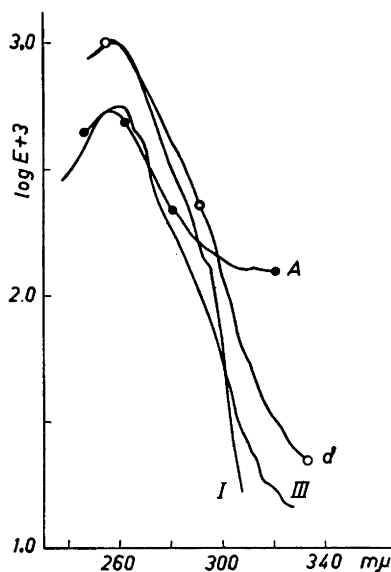Fig. 3. UV spectra in dioxan of cinnamyl phenyl sulfoxide (X) and sulfone (N) and of cinnamyl alcohol (C).

Fig. 4. UV spectra of by-products at syntheses of cinnamyl phenyl sulfide. A = addition product of cinnamyl alcohol and thiophenol (photosyntesis, 1 a). Solvent 0.5 N alcoholic sodium hydroxide. I and III, respectively, first and third chromat.-fraction from synthesis 1 c in dioxan. d = second chromat.fraction from synthesis 1 d in dioxan.

Our work concerning cinnamyl phenyl sulfide started with a photosynthesis of this substance at room temperature from cinnamyl alcohol and thiophenol carried out by Mr Eino Lonkila and one of us (E), in which about 9 mole % of crystalline sulfide was isolated by vacuum sublimation mainly in the fraction 190—230° at 15 mm. Even at this stage it was observed that cinnamyl phenyl sulfide does not react in the usual Baeyer test for unsaturated substances with soda-alkaline permanganate solution at room temperature. This observation led to further investigations concerning the double bond in cinnamyl phenyl sulfide and also raised the question of whether the sulfide possesses the simple structure IV or whether a Claisen rearrangement has occurred during its formation leading ultimately to a thiocoumarane or thiochromane structure (cf Ref.[7,8]).

Ultraviolet and infrared spectra. The ultraviolet absorption spectrum of cinnamyl phenyl sulfide (Fig. 1) shows a single maximum at about 255 mμ,
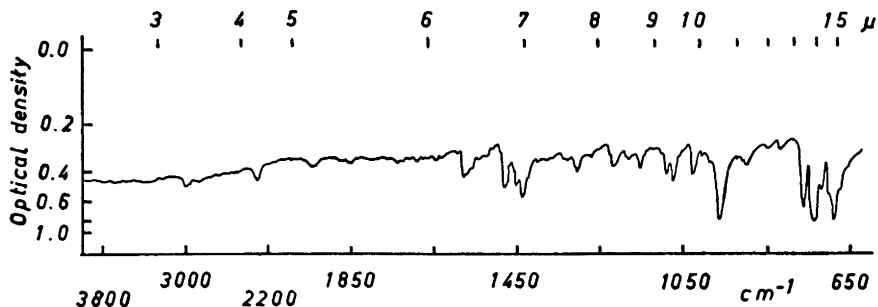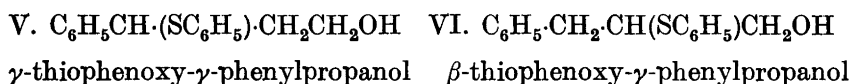
Fig. 5. Infrared spectrum of cinnamyl phenyl sulfide, without solvent.

very much like that of allyl phenyl sulfide and of cinnamyl disulfide, but distinctly different from that of 2-methyl thiocoumarane (Fig. 2). The cinnamyl phenyl sulfoxide and sulfone as well as cinnamyl alcohol have an absorption maximum at a somewhat longer wave length (Fig. 3).

The infrared spectrum of cinnamyl phenyl sulfide (Fig. 5) has an absorption band at 960 cm^{-1}, probably caused by the wagging swings of the :CH·-group. Substances containing a CH$_2$:C-group show absorption[9] at about 890 cm^{-1}. This band is lacking for cinnamyl phenyl sulfide, showing that rearrangement to vinyl groups during the formation of cinnamyl phenyl sulfide is improbable. Moreover, the absorption band of the hydroxyl groups [9] at 3 380 cm^{-1} is lacking, in contrast to the IR-spectrum of the addition product of cinnamyl alcohol and thiophenol (Fig. 6), where the hydroxyl group could also be demonstrated by acetylation, and which thus very probably contains the substances V or VI or both of them.

V. C$_6$H$_5$CH·(SC$_6$H$_5$)·CH$_2$CH$_2$OH   VI. C$_6$H$_5$·CH$_2$·CH(SC$_6$H$_5$)CH$_2$OH

γ-thiophenoxy-γ-phenylpropanol   β-thiophenoxy-γ-phenylpropanol

The ethylenic bond in olefines causes absorption at about 1 660 cm^{-1} also, and cinnamic acid absorbs characteristically at 1 590 cm^{-1} and still more strongly [10] at 1 625 cm^{-1}. This latter absorption also occurs in the spectrum
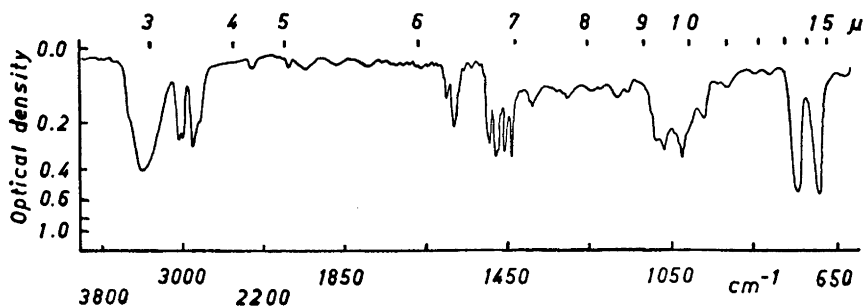

Fig. 6. Infrared spectrum of the addition product of cinnamyl alcohol and thiophenol.

of cinnamyl alcohol and is probably due to the ethylenic bond. In this area of the spectrum of cinnamyl phenyl sulfide, there is an absorption band only at 1 575 cm^{-1}. Probably in this substance, as well as in *trans*-stilbene and indene [11], the absorption band caused in the area in question by the ethylenic bond coincides with the absorption of the double bonds in the benzene nucleus.

OXIDATION REACTIONS

With hydrogen peroxide. Samples of cinnamyl sulfide were oxidized with hydrogen peroxide to the sulfoxide and the sulfone. No glycol derivative, but only the sulfone, could be found among the oxidation products, even after oxidation with 4 moles of 30 % H_2O_2 in acetone solution in UV light for 2 weeks.

The sulfoxide was obtained in 94 mole % yield by using equimolar amounts of hydrogen peroxide and cinnamyl phenyl sulfide at room temperature. The sulfoxide appears in two modifications, one with m.p. 78°, primarily obtained at chromatographic separation on an aluminium oxide column, and another melting at 91.5—92°, formed for instance on recrystallization of the other form from hot petrolether-chloroform solution. The m.p. of Barnards cinnamyl phenyl sulfoxide is recorded as 68°C, but he has privately reported that this figure is a misprint and should be 78°C, and that he likewise has found two modifications of the sulfoxide. A mixed m.p. of our sulfoxide of m.p. 78° and a corresponding sample kindly supplied by Dr Barnard showed that the substances were identical.

With reagents for the ethylenic bond. The sulfide as well as the sulfoxide and the sulfone only very slowly decolorized soda-alkaline permanganate solution at room temperature, after hours of standing, whereas, for instance, cinnamyl alcohol and freshly distilled allyl phenyl sulfide, prepared according to Claisen [12], immediately decolorized the reagent. It was found, however, that cinnamyl phenyl sulfide showed some of the reactions of the ethylenic bond. Thus, when it or the corresponding sulfone are dissolved in pure pyridine, they decolorize potassium permanganate solution.

With tetranitromethane, golden yellow colors were given by cinnamyl phenyl sulfide, the corresponding sulfoxide and sulfone, as well as cinnamyl alcohol, whereas allyl phenyl sulfide gave a red color.

Organic sulfides in general add bromine, and the method of Siggia [13] for determination of sulfidic sulfur makes use of this fact. Cinnamyl phenyl sulfide gave the following bromine numbers: McIlhiney's method [14] (addition only, 3.7 % of the total bromine consumption was found to be due to substitution) 92, Kauffmann's [15] method 89, Siggia's method 117. The theoretical value for cinnamyl phenyl sulfide is 141, supposing that the sulfide sulfur and the ethylenic double bond each of them add two bromine atoms. The actual bromine consumption is thus considerably lower than the theoretical value.

Oxidation with perbenzoic acid.[16] Fig. 7 shows the uptake of oxygen in g.atoms from perbenzoic acid per mole of cinnamyl phenyl sulfide at +3°. It can be seen that 2 atoms of oxygen are added to one molecule of the sulfide within one day, after which the uptake is very slow, in all only 2.72 atoms being consumed after 42 days. According to Stoll and Seebeck [17], in unsatura-
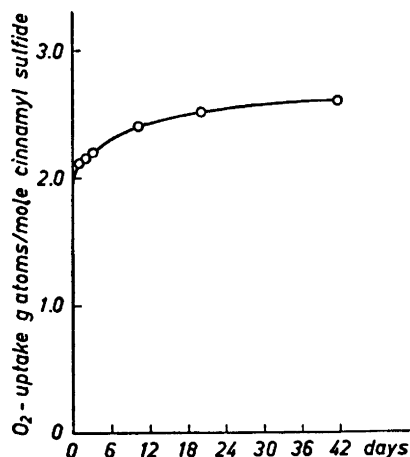
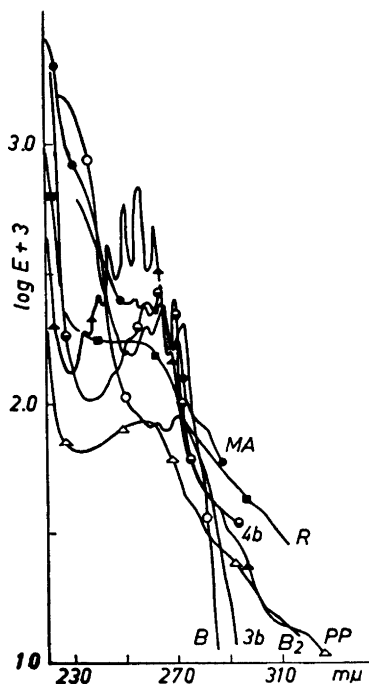Fig. 7. Oxidation of cinnamyl phenyl sulfide with perbenzoic acid.

Fig. 8. UV spectra of degradation products of cinnamyl phenyl sulfide. 3 b = crude benzene sulfonic acid from synthesis 3 b. B = benzoic acid from 4 a. MA = mixture of acids (M.A.) from synthesis 4 b. 4 b = purified benzene sulfonic acid from synthesis 4 b. Bz = benzene from synthesis 5. PP = phenyl propane from synthesis 5. R = residue from synthesis 5.

ted sulfides containing an allyl group the sulfur is oxidized faster than the ethylenic bond by perbenzoic acid.

From the neutral fraction of the reaction products, only cinnamyl phenyl sulfone could be isolated. Thus, the fast uptake of the first two oxygen atoms is obviously due to addition to the sulfur, and the later slow uptake of oxygen to the ethylenic bond.

Oxidative degradation. A sample of cinnamyl phenyl sulfone was oxidized with perbenzoic acid, this time at room temperature. Among the acidic oxidation products benzene sulfonic acid could be detected through mixed m.p. of the S-benzyl thiuronium salt.

Cinnamyl phenyl sulfide was oxidized in benzene suspension with soda-alkaline potassium permanganate in aqueous solution for 59 h at room temperature. The reaction products contained cinnamyl phenyl sulfoxide and sulfone, benzoic acid in a yield of 53 mole %, and further benzene sulfonic acid (mixed m.p. of S-benzyl thiuronium derivative) and sulfuric acid.
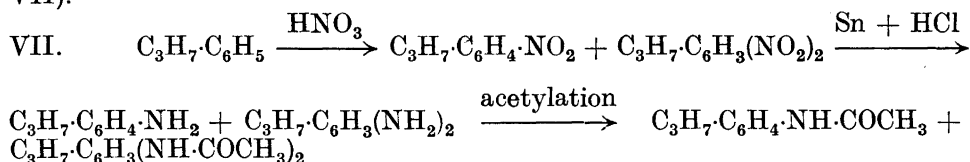
Table 1. Syntheses of cinnamyl phenyl sulfide.

| Reagents | Method [1] | Reaction | | Yield, mole % |
		time	product	
Cinnamyl alcohol (II) + thiophenol (III)	Photosynthesis (1 a)	14 days	Cinnamyl phenyl sulfide (IV) + V or VI	9 13
II + III	Press.heating with Al-sulfate (1 b) [2]	16 h	IV	25
II + III	Boiling in acet. acid + H_2SO_4 (1 c)	16 h	IV	85
Cinnamyl bromide + C_6H_5SK	Boiling in acetone (1 d)	8 h	IV	83
»	Boiling in benzene (1 e)	4 h	IV	72

[1] The numbers in parentheses mean paragraphs in the experiment. part.
[2] In a sealed glass tube.

DEGRADATION BY HYDROGENATING TREATMENT WITH RANEY NICKEL

It is well known that treatment with Raney nickel [18] allows the sulfur in thioethers to be replaced by hydrogen. Cinnamyl phenyl sulfide was boiled with a great excess of Raney nickel in alcoholic suspension. Benzene (demonstrated with UV spectrum and from nitration and mixed m.p. determination m-dinitrobenzene so formed) and phenylpropane were formed (identified as 2-mono- and 2,4-diacetamino phenylpropane, obtained according to scheme VII).

$$\text{VII.} \qquad C_3H_7 \cdot C_6H_5 \xrightarrow{HNO_3} C_3H_7 \cdot C_6H_4 \cdot NO_2 + C_3H_7 \cdot C_6H_3(NO_2)_2 \xrightarrow{Sn + HCl}$$

$$C_3H_7 \cdot C_6H_4 \cdot NH_2 + C_3H_7 \cdot C_6H_3(NH_2)_2 \xrightarrow{acetylation} C_3H_7 \cdot C_6H_4 \cdot NH \cdot COCH_3 + C_3H_7 \cdot C_6H_3(NH \cdot COCH_3)_2$$

Thus, the hydrogenation with Raney nickel has followed the simple scheme VIII.

$$\text{VIII.} \quad C_6H_5CH = CH \cdot CH_2 \cdot S \cdot C_6H_5 + 6H \rightarrow C_6H_5CH_2CH_2CH_3 + H_2S + C_6H_6$$
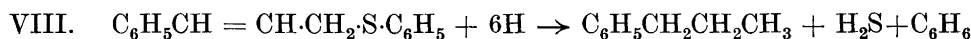
All these facts thus prove that the cinnamyl phenyl sulfide in fact has the structure IV but that the ethylenic bond reacts very slowly with the usual oxidizing reagents. The same low reactivity seems also to characterize the corresponding sulfoxide and sulfone.

Attempt at obtaining a Claisen rearrangement of cinnamyl phenyl sulfide. As no Claisen rearrangement to *o*-cinnamyl thiophenol or further to a thiocoumarane or thiochromane could be observed during the syntheses of cinnamyl phenyl sulfide, this substance was heated in an atmosphere of nitrogen in order to promote rearrangement or destructive splitting. The sulfide decomposed somewhat below 260°C. From the reaction products

57 % of unchanged starting material could be isolated and further a small amount of thiophenol, which after autoxidation gave phenyl disulfide, proven by mixed m.p. with an authentic sample. Among the neutral products two liquid chromatographic fractions (II and III) showed sulfur contents only a little lower than the starting material and UV spectra not dissimilar to that of 2-methyl thiocoumarane (Fig. 2). The high recovery of starting material indicates, however, that the cinnamyl phenyl sulfide is not easily rearranged or split up.

EXPERIMENTAL PART

1. Syntheses of cinnamyl phenyl sulfide

a) *Photosynthesis.* 1.250 g (0.009 moles) cinnamyl alcohol and 1.000 g (0.009 moles) of thiophenol were allowed to stand 2 weeks in a quartz tube sealed with a rubber stopper 15 cm from a mercury (quartz) lamp. The reaction product was dissolved in ether, washed with 2 N sodium hydroxide and water, dried, and isolated by evaporation of the solvent. The dryings in the present work were generally carried out with sodium sulfate. The residue was recrystallized several times from 99 % ethanol (preparation P) m. p. 78°, undepressed on admixture with a preparation of cinnamyl phenyl sulfide kindly supplied by Dr. Barnard. (Found: C 79.54; H 6.27; S. 14.06 [1]; mol. wt. (Cryosc. Beckmann) 221. Calc. for $C_{15}H_{14}S$: C 79.60; H 6.23; S 14.17, mol.wt. 226). UV-spectrum Fig. 1, IR-spectrum Fig. 5. Yield of crude product with m. p. 74—75° 0.191 g (9 mole %).

By-products: The mother liquor from the crystallization of the cinnamyl phenyl sulfide was evaporated. The residue was washed with cold methanol in order to remove cinnamyl alcohol, and dried in vacuum. The yield was 0.310 g of yellow oil. It was dissolved in 20 ml carbon tetrachloride-petrolether 1:1 and chromatographed in a column containing 20 g of aluminium oxide (Brockmann). By elution with a total of 15 ml of carbon tetrachloride a small first fraction was obtained, which was dark violet in UV light and showed a m.p. 59—60°, undepressed on admixture of *diphenyl disulfide.*

By further elution with ether and alcohol containing carbon tetrachloride a liquid second fraction was obtained, which was lemon yellow in UV light. Yield 0.299 g. It was chromatographed anew with the same solvents. The Baeyer test was positive and the oil gave a red color in tetranitromethane. UV-spectrum Fig. 4. IR spectrum Fig. 6. (Found: C 73.11; H 6.60; S 13.23; mol. wt. (Beckm. cryosc.) 241. Calc. for $C_{15}H_{16}SO$: C 73.73; H 6.59; S 13.12; mol. wt. 244.)

Acetylation: 0.318 g of substance from another, quite similar experiment was heated 4 h on a water bath with 0.76 ml of acetic anhydride and 0.63 ml of pyridine, using a calcium chloride tube to exclude moisture. The reaction product was poured into 10 ml H_2O, was extracted with ether, washed with sodium hydrogen carbonate solution, dried, and, after evaporation, further dried in vacuum over phosphorus pentoxide. (Found: S 11.31; CH_3CO (according to Ref.[20]) 14.61. Calc. for. $C_{17}H_{18}SO_2$: S 11.20; CH_3CO 15.03.) The product is obviously V or VI.

b) *With aluminium sulfate.* 5.954 g (0.044 mole) of cinnamyl alcohol, 4.706 g (0.043 mole) of thiophenol and 0.359 g anhydrous aluminium sulfate were heated in a sealed glass tube 16 h at 127°. Here, as well as in the following syntheses c—e, the neutral reaction product was isolated in the same way as the cinnamyl phenyl sulfide at the photosynthesis. Yield 2.418 g of m.p. 75—76°. Repeated re-crystallization raised the m.p. to 78°, undepressed on admixture of cinnamyl phenyl sulfide from the photosynthesis.

c) *In acetic and sulfuric acid:* 15.342 g (0.114 mole) of cinnamyl alcohol and 12.669 g (0.115 mole) of thiophenol were refluxed 16 h in 100 ml acetic acid containing 10 ml 2 N H_2SO_4. The cinnamyl phenyl sulfide was isolated in the same way as at the photosynthesis. Yield 21.811 g with m.p. 74—76°, undepressed on admixture of sulfide from the photosynthesis. From the mother liquors liquid fractions were obtained by chromatography on aluminium oxide in about the same way as in the photosynthesis, giving the following data: yield 0.115 g, S 3.69, mol. wt. (Childs [21]) 361; 0.098 g, S 5.97; 0.044 g, S 9.65, mol.wt. (Childs) 344; UV spectra Fig. 4.

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[1] All sulfur determinations were made titrimetrically according to Grote-Krekeler [19].

d) *From cinnamyl bromide in acetone:* 2.200 g (0.020 mole) thiophenol, 3.940 g (0.020 mole) of cinnamyl bromide, 2.800 g anhydrous potassium carbonate and 6 g acetone were refluxed 6 h. Yield 3.739 g cinnamyl phenyl sulfide of m.p. 74 — 75°, undepressed on admixture of sulfide from synthesis 1 a. The substance from the mother liquors (0.317 g of yellow oil) was chromatographed on aluminium oxide in carbon tetrachloride-toluene 1:1 and eluted with toluene containing amounts of ethyl ether rising successively from 10 to 50 %. The first fraction was small and showed a m.p. of 61°, undepressed on admixture of diphenyl disulfide. The second fraction was a yellow oil; yield 0.229 g, S 13.22. UV spectrum, Fig. 4, d.

e) *From cinnamyl bromide in benzene.* 7.615 g of cinnamyl bromide (0.0386 mole) and 4.275 g (0.0388 mole) of thiophenol were refluxed 4 h in 16 g benzene containing 5.41 g of anhydrous potassium carbonate. Yield of cinnamyl phenyl sulfide 6.329 g of m.p. 74 — 76°, after further recrystallization from ethanol 78°, undepressed on admixture of sulfide from 1 a.

2. Investigation of cinnamyl phenyl sulfide. Oxidation with hydrogen peroxide

a) *To sulfoxide.* 0.226 g (0.001 mole) cinnamyl phenyl sulfide were dissolved in 20 ml glacial acetic acid and 0.001 mole 30 % hydrogen peroxide were added with stirring. After the mixture had stood 5 days at room temperature, water was added. The precipitated yellow oil was dissolved in chloroform, washed with sodium hydrogen carbonate solution and dried. After evaporation in vacuum the residue crystallized on cooling to 0°. Yield of crude product 0.227 g (94 mole %); m. p. 90 — 91° after recrystallization three times from hot petrolether containing 5 % chloroform. (Found: S 13.18. Calc. for $C_{15}H_{14}SO$: S 13.23). UV spectrum, Fig. 3, X. 70 mg of the crude sulfoxide were not purified by recrystallization, but were chromatographed on aluminium oxide (Brockmann) with carbon tetrachloride as solvent and eluting first with carbon tetrachloride containing 5 — 20 % of ether and then with ether containing 10 — 20 % of ethanol. The main fraction melted at 76 — 78°. When a sample of this sulfoxide was recrystallized from hot petrolether containing 5 % chloroform it was transformed into a substance of m. p. 91.5 — 92°.

b) *To sulfone.* This oxidation was made in the same way as a), but using the double amount (0.002 mole) of 30 % hydrogen peroxide. The reaction product was isolated by the same method as the sulfoxide. Yield 0.236 g (92 mole %); m.p. 111 — 112° after recrystallization from ligroin; UV spectrum, Fig. 3, N. (Found: C 69.89; H 5.47; S 12.32. Calc. for $C_{15}H_{14}SO_2$: C 69.74; H 5.46; S 12.41.)

c) *Oxidation in UV light.* 0.226 g (0.001 mole) cinnamyl phenyl sulfide was dissolved in 10 ml acetone containing 0.004 mole of 30 % hydrogen peroxide, and was irradiated 10 days in a quartz test tube at 10 cm distance from a mercury lamp. The reaction product was isolated as the sulfone under 2b. M. p. 110 — 111°, undepressed on admixture of cinnamyl phenyl sulfone from synthesis 2b.

3. Oxidations with perbenzoic acid

a) *Oxidation of cinnamyl phenyl sulfide.* 0.452 g cinnamyl phenyl sulfide were weighed in an Erlenmeyer flask equipped with a ground glass stopper; 50 ml of 0.1249 M solution of perbenzoic acid in chloroform were added and allowed to stand at +3°, in a refrigerator together with a blank perbenzoic acid solution without sulfide. 5 ml samples of the oxidation mixture and the blank solution were titrated with sodium thiosulfate after addition of a potassium iodide solution acidified with acetic acid (Fig. 7). After 41.6 days the neutral reaction products were isolated from the benzoic acid-CHCl₃ solution after washing with sodium hydrogen carbonate solution and once with water, drying, evaporating and drying again in vacuum over phosphorus pentoxide. Yield 41 mg of an oil which was dissolved in 20 ml carbon tetrachloride and chromatographed in a column containing aluminium oxide (Brockmann). Only one band could be seen in ultraviolet light. Yield 34 mg, m. p. 109 — 111°, undepressed on admixture of cinnamyl phenyl sulfone from 2 b.

b) *Oxidation of cinnamyl phenyl sulfone.* 0.190 g cinnamyl phenyl sulfone were oxidized with 0.1429 M perbenzoic acid in CHCl₃ at room temperature during 42.6 days.

Thereafter the solution was washed with 5 ml cold water. The water layer was allowed to evaporate at 30° in a glass bowl. The residue, a clear, thickish liquid, was washed with 4 ml ether, and dried 5 h in vacuum over phosphorus pentoxide. Yield 119 mg; UV-spectrum, Fig. 8, 3b. The substance was neutralized with 0.2 N sodium hydroxide and a S-benzyl-thiuronium salt prepared in the usual way [22], m. p. after recrystallization three times from 50 % ethanol 143—145°, undepressed on admixture with S-benzyl thiuronium salt of benzenesulfonic acid of m. p. 147°.

4. Oxidation with permanganate

a) 1.706 g (0.007 mole) of cinnamyl phenyl sulfide were suspended in 60 ml 2 N sodium carbonate solution. 70 ml benzene and thereafter a solution of 4.762 g potassium permanganate in 200 ml water were added with stirring during 59 h. The manganese dioxide precipitate was filtered off and washed first with 2 N soda solution, then with hot water and at last with benzene. The mixed liquids were allowed to separate into a benzene and an alkaline water layer. The benzene layer was dried and evaporated in vacuum, the residue (neutral products) weighing 0.636 g. It was chromatographed on aluminium oxide (Brockmann) as described under 1 a. Three fractions were obtained in yields of 0.101, 0.326 and 0.099 g, m. p. 74—76°, 90—92°, 109—111°, undepressed on admixture of cinnamyl phenyl sulfide, sulfoxide and sulfone, respectively.

The soda alkaline layer was acidified (indicator Congo red) with 2 N sulfuric acid and extracted with ether. Drying and evaporation in vacuum gave a crystalline residue, which was purified by sublimation in vacuum; yield 0.495 g, m. p. 121°, undepressed on admixture of benzoic acid; UV-spectrum, Fig. 8 B.

b) 1.6108 g cinnamyl phenyl sulfide was oxidized with 4.495 g potassium permanganate as under 4 a. The soda-alkaline layer was passed through a cation exchanger Amberlite IR-120, the volume of the liquor so passed being 645 ml and the pH about 1. 150 ml of the solution was evaporated at about 30°, and dried over phosphorus pentoxide. Yield 235 mg; UV-spectrum, Fig. 8 MA. The mixture of acids (MA) thus obtained was chromatographed 16 h at 18° on Whatman paper No. 1 with 50 μg in each spot and n-butanol saturated with ammonium carbonate buffer [23] as mobile phase. The spots were developed with 0.1 N silver nitrate solution, or with phenol and 0.5 N sodium hydroxide according to Löffler [24]. Two spots were obtained corresponding to the R_F-values 0 and 0.30, respectively. Since the solution gave a barium salt insoluble in acidic solution, and the substance in the first spot did not give any characteristic UV-spectrum, and a blank chromatography of dilute sulfuric acid also gave $R_F = 0$, the first spot obviously corresponds to sulfuric acid. Parallel tests with benzoic and benzene sulfonic acid showed that both gave $R_F = 0.30$. Therefore an undeveloped spot with $R_F = 0.30$ from a new chromatogram was extracted twice with 5 ml ice-water, a treatment which dissolves benzene sulfonic acid, but leaves the benzoic acid practically undissolved. The UV-spectrum of the cold water eluate (Fig. 8, 4b) is identical with that of autenthic benzene sulfonic acid purified by paper chromatography. A fresh portion of the mixture of acids (MA) described was extracted with ether to remove benzoic acid. The residue (171 mg from 150 ml of acid solution) was converted to an S-benzyl thiuronium salt, m.p. after recrystallization three times from 50 % ethanol 143—145° undepressed on admixture of the corresponding derivative of authentic benzene sulfonic acid.

5. Degradation by hydrogenation

3.722 g cinnamyl phenyl sulfide dissolved in 400 ml aldehyde-free ethanol were refluxed 7 h with about 30 g Raney nickel. The nickel sulfide formed was filtered off and washed with alcohol and ether. Water was added to the filtrate, which was extracted five times with ether. The ether solution was dried with calcium chloride and distilled at 760 mm by means of a Skärblom-Linder column [25]. After the ether had distilled off, the following fractions were obtained: b.p. 79—80°, 0.765 g, UV-spectrum Fig. 8, Bz; b. p. 159—160°, 1.181 g, UV-spectrum Fig. 8, PP, n_D 1.4918 (18.4°C), and residue 0.061 g, UV-spectrum Fig. 8, R. The fraction of b. p. 79—80° was nitrated according to Ref.[26].

The reaction product after recrystallization from 50 % ethanol had m. p. 90°, undepressed on admixture of *m*-dinitrobenzene. The fraction of b. p. 159—160° was redistilled, 0.5 g of the distillate was nitrated and the nitration product reduced to a mixture of amines. This mixture was separated into monoamine and diamine, of which only the former gives an ether soluble salt with tin chloride in presence of hydrochloric acid. Both amines were acetylated, all according to [27]. The acetylated diamine was purified by chromatography on silica gel with chloroform and sublimation in vacuum, m. p. 207—208°. (Found: C 66.63; H 7.72; N 11.88. Calc. for $C_{13}H_{18}N_2O_2$: C 66.64; H 7.74; N 11.96). The acetylated monoamine was purified in a corresponding way, m. p. 97°. The corresponding authentic derivatives were prepared from phenyl propane obtained from benzyl magnesium chloride and diethyl sulfate according to Ref.[28]. No depression on the m. p. occurred on admixture of the two pairs of preparations.

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