[CONTRIBUTION FROM STERLING CHEMISTRY LABORATORY, YALE UNIVERSITY]

THE MECHANISM OF THE REACTIONS OF HYDROCARBONS WITH SULFUR[1]

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The reactions of olefins and polyolefins with sulfur at 140° have been discussed recently by Farmer and Shipley (1, 2). These investigators suggested that the sulfur was acting by a free radical mechanism involving either the unsaturation electrons of the hydrocarbons or the active methylene groups.

The main aim of the present research, initiated in September, 1946, has been the elucidation of the mechanism of the high temperature (above 200°) reactions of sulfur with hydrocarbons. In gaining an understanding of the fundamental nature of these processes, a study of the products from alkyl-substituted aromatic compounds has proven of considerable value.

In particular, attention has been centered on the hydrocarbons and heterocyclic compounds formed by the reaction of toluene and sulfur. The reported products (3, 4, 5) whose formation has been confirmed by the writer in an unpublished research are bibenzyl, stilbene, tetraphenylthiophene and a previously uncharacterized compound, $C_{14}H_{10}S$. The following products have also been isolated by the earlier investigators: *o*-bitolyl (5), 1,2,3,4-tetraphenylbutane (6), and a substance, $C_{14}H_{10}S_2$ (3). Renard also reported phenylthiophene ($C_{10}H_8S$) among the products. However, although the reactions of his compound were certainly characteristic of a thiophene derivative, the physical properties differed greatly from those reported for either 2- or 3-phenylthiophene (7, 8). Now, in reviewing the early literature on sulfur heterocyclics, the writer has noted a striking agreement between the melting and boiling points of Renard's "phenylthiophene" and those reported for the so-called "tolallyl sulfide", $C_{14}H_{10}S$ (9, 10). This crystalline material had been previously synthesized by the pyrolysis of benzyl sulfide and disulfide. There seems little doubt now, in the light of the writer's own findings, that Renard did isolate some impure "tolallyl sulfide" from the reaction products from toluene and sulfur.

The attempts of the early workers to determine the structure of this compound were unsuccessful. Actually, since 1903 no mention of it has appeared in the literature. In that year, Fromm and Achert (11) reported a vain attempt to repeat Forst's synthesis of "tolallyl sulfide". They came to the unfortunate conclusion that the material previously isolated was nothing more than a mixture of two other products of the reaction and hence suggested that its name be stricken from the record.

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[1] Taken from the dissertation presented by the author to the faculty of the Graduate School of Yale University in partial fulfillment of the requirements for the degree of Doctor of Philosophy, June, 1948.

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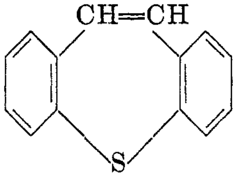
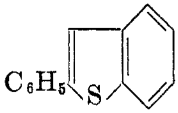
It was obviously essential to any consideration of the mechanism of the reaction to characterize the $C_{14}H_{10}S$ material. The following structures had been suggested by Forst (9):

$C_6H_5C{=}CC_6H_5$, $\backslash S /$

or



However, on the basis of the thiophene-like reactions of the compound reported by Renard (3), the following structure seemed more probable to the writer:



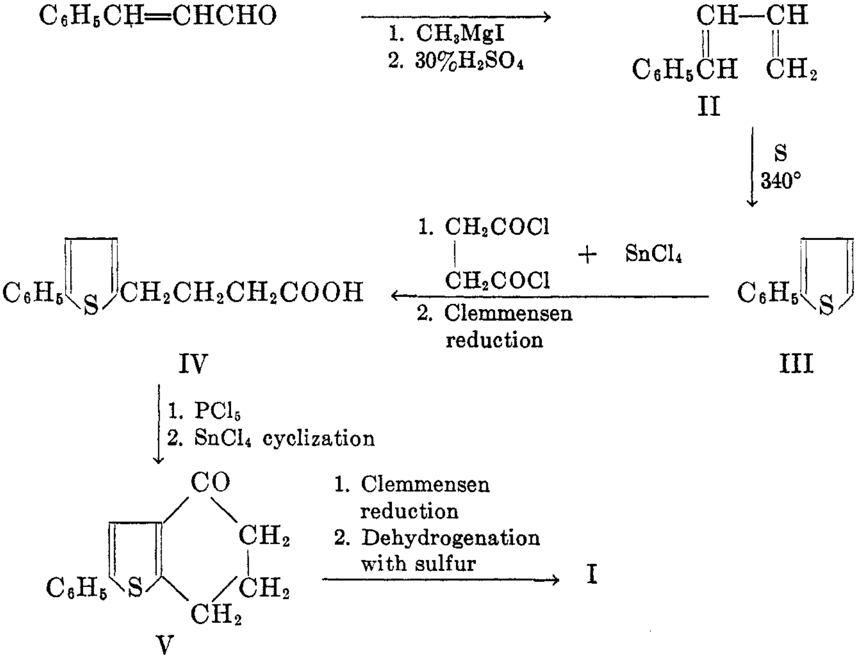
2-phenylthianaphthene

$C_{14}H_{10}S$

I

Since this heterocycle had not been described in the literature as such, its synthesis by standard procedures was undertaken. The following route was employed, the product proving to be identical with the $C_{14}H_{10}S$ product of the reaction of toluene with sulfur:

SYNTHESIS OF 2-PHENYLTHIANAPHTHENE



Having established the molecular structures of the main products formed in the reaction of toluene with sulfur, attention may now be directed to the mechanism involved. In this respect, it has proven particularly illuminating to consider possible relationships between various reactions which form directly one or both of the two heterocyclics, 2-phenylthianaphthene, I, and tetraphenylthiophene, VI.

(a) $C_6H_5CH_3 + S \xrightarrow{250^\circ} I + VI$

(b) $(C_6H_5CH_2)_2S \xrightarrow{200^\circ} I + VI$ (9, 10)

(c) $(C_6H_5CH_2)_2S_2 \xrightarrow{200^\circ} I + VI$ (9, 10)

(d) $(C_6H_5CH_2COO)_2Ba \xrightarrow{S} I + VI$ (12)

(e) $(C_6H_5CHS)_x \xrightarrow{\Delta}$ only VI (10, 13)

(f) $C_6H_5CH_2OH + S \xrightarrow{200^\circ} C_6H_5CHO + VI$ (14)

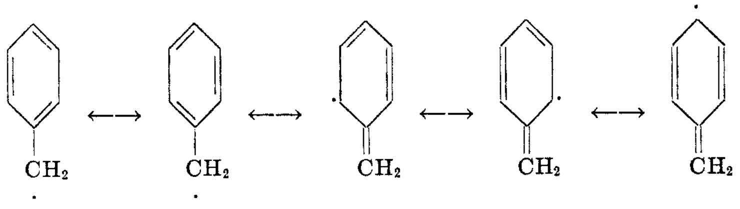
(g) $C_6H_5CH_2CH_2C_6H_5 \xrightarrow{S\text{ at }230^\circ} I + VI$ (6, 14)

(h) $C_6H_5CH{=}CHC_6H_5 \xrightarrow{S\text{ at }230^\circ}$ only VI (6,10)

It is to be noted especially that the thianaphthene derivative, I, was formed only in the reactions of those starting materials which contained the $C_6H_5CH_2$ grouping. Reaction (f) of benzyl alcohol is not necessarily an exception to this rule since its conversion by sulfur probably proceeds by the following steps:

$$C_6H_5CH_2OH + S \rightarrow C_6H_5CHO + H_2S$$
$$C_6H_5CHO + H_2S \rightarrow C_6H_5CHS + H_2O$$
$$C_6H_5CHS \rightarrow \text{VI [see reaction (e)]}$$

The fact that compound I is not formed by reaction (h), even though stilbene has the same carbon structure as I, is strong indication that the benzyl (or 1,2-diphenylethyl) radical is essential for the cyclization to a thianaphthene structure. Since the benzyl radical exists as a resonance hybrid with important contributions from the following structures, the path that is open for the coupling of sulfur in the *ortho* position is quite evident.



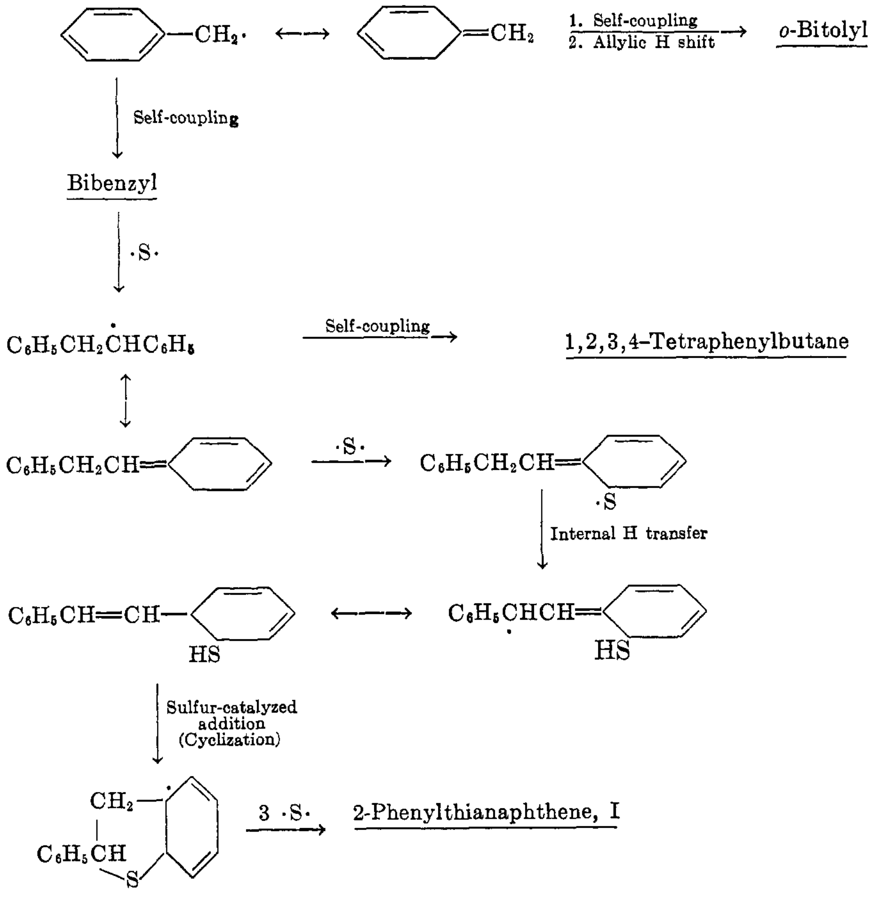
The free radical nature of pyrolytic reactions such as (b) and (c) has long been recognized. Physical evidence to support this hypothesis was recently obtained by Cutforth and Selwood (15), who demonstrated by magnetic measurements that aryl disulfides form free radicals in large amounts by thermal dissociation. Furthermore, it seems quite probable that reaction (d) is closely analogous to the Kolbe electrolytic synthesis of hydrocarbons, a classical example of a coupling best explained by a free radical mechanism (16).

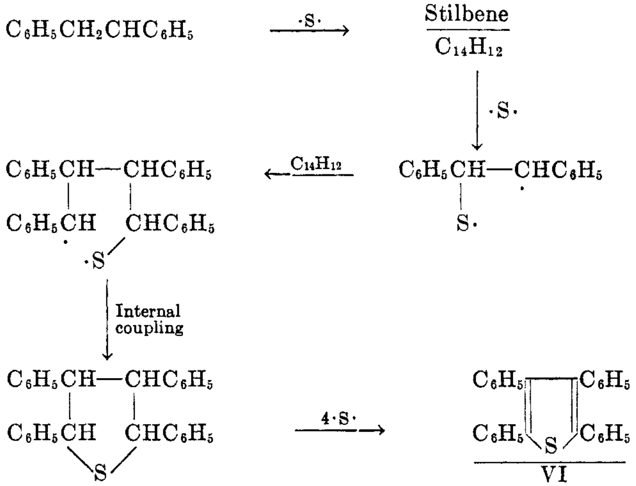
Thus, it is seen that the data not only strongly indicate but seem almost to demand a free radical mechanism for the attack of sulfur on the side chains of aromatic hydrocarbons such as toluene. Utilization of such a theory permits a ready explanation of the formation of all reported products. The sulfur atom or a molecular chain, $\cdot(S_n)\cdot$, where $n = 2$ to 8, is believed to act as a radical in the various dehydrogenation steps. For example,

$$C_6H_5CH_3 + \cdot S\cdot \rightarrow C_6H_5CH_2\cdot + H{:}S\cdot$$

The HS· radicals formed are, of course, equally effective as hydrogen acceptors in subsequent reaction steps.

The following series of reactions is presented to illustrate the usefulness of the general concept. Products isolated are underlined.



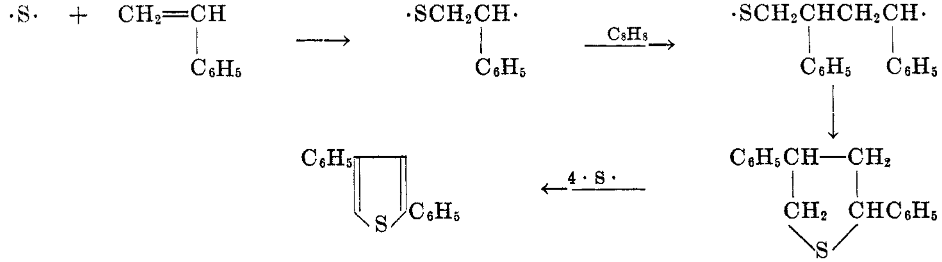


VI

It is evident that it is possible to write several other sequences of such free-radical reactions to explain the formation of the two heterocyclic compounds.

The application of the free radical theory to the mechanism of the reaction of ethylbenzene with sulfur (17) has some interesting aspects. No thianaphthene was obtained by Glass and Reid from the product mixture, 2,4-diphenylthiophene, VII, being the only sulfur-containing organic compound isolated. The same heterocycle and a very small amount of the 2,5-substituted isomer were obtained by Baumann and Fromm (13) by the reaction of styrene with sulfur. The obvious assumption is made that the olefin is the intermediate in the conversion of ethylbenzene to the thiophene derivatives. The phenylethyl radical formed in the initial step would be expected to disproportionate very readily to styrene.

It is now postulated that the further reaction of styrene with sulfur (like that of stilbene and sulfur) proceeds by a mechanism exactly like that generally accepted for the free radical-catalyzed polymerization of such unsaturates (18).

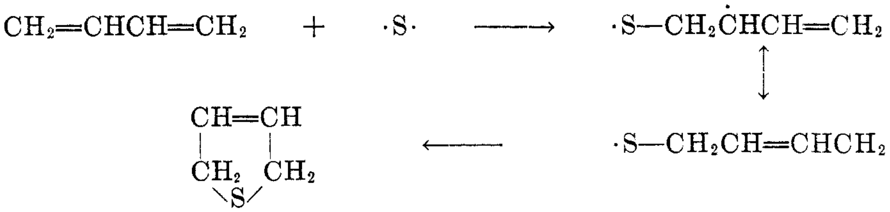


VII

Since the initiating sulfur radical bears two unpaired electrons, the chain reaction is terminated by cyclization as soon as the necessary spatial configuration for stable ring formation obtains. Furthermore, since styrene polymerization proceeds almost exclusively by the "head-to-tail" mechanism pictured, very little

2,5- or 3,4-diphenylthiophene should be formed. This is in accord with the reported results.

The cyclization of conjugated dienes with sulfur (19) probably involves a similar mechanism. The following sequence is suggested:



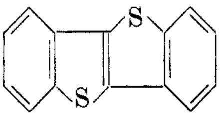
$$CH_2{=}CHCH{=}CH_2 + \cdot S\cdot \longrightarrow \cdot S{-}CH_2\dot{C}HCH{=}CH_2 \longleftrightarrow \cdot S{-}CH_2CH{=}CHCH_2\cdot$$

An alternative explanation which does not differ basically from that above involves the picture of the butadiene molecule described by Pauling (20), who gave evidence that structure B below makes an important contribution (20%) to the resonance hybrid:

$$\underset{A}{CH_2{=}CH{-}CH{=}CH_2} \longleftrightarrow \underset{B}{\cdot CH_2{-}CH{=}CH{-}CH_2\cdot}$$

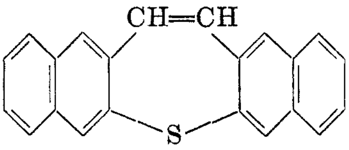
The cyclization with sulfur would then proceed by a 1:4 coupling with structure B, yielding again 2,5-dihydrothiophene, which may be readily dehydrogenated to the fully aromatic heterocycle. The formation of the by-product, thiophene thiol, in the commercial synthesis of thiophene may be nicely explained as a sulfur-catalyzed addition of hydrogen sulfide (21, 22) to this intermediate cyclic olefin, followed by the usual dehydrogenation.

The general mechanism herein developed has been of value not only in explaining the formation of all known products of the reactions of hydrocarbons with sulfur, but also in predicting the molecular structures of several heterocyclic compounds with have been isolated but not characterized. Thus, the $C_{14}H_{10}S_2$ compound isolated by Renard (3) from the products from toluene and sulfur probably has the following structure:

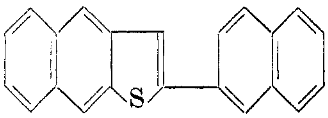


$C_{14}H_8S_2$

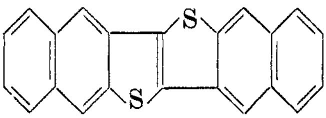
From the reaction of β-methylnaphthalene with sulfur, Friedmann (5) isolated products with the empirical formulas, $C_{22}H_{14}S$ and $C_{22}H_{14}S_2$. For the former he suggested the following structure:



However, it seems to the writer that the five-membered heterocyclic ring system was probably formed as follows:

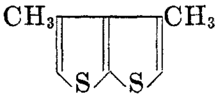


$C_{22}H_{14}S$



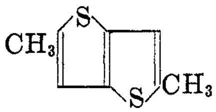
$C_{22}H_{12}S_2$

Friedmann (5) also reported on the reactions of aliphatic hydrocarbons with sulfur under pressure. From *n*-octane he produced a thiophthene derivative to which he assigned the following structure:



$C_8H_8S_2$

Since the formation of this compound would involve a highly improbable isomerization of the hydrocarbon skeleton, it seems much more likely that the product obtained by Friedmann had the structure:



EXPERIMENTAL[3]

1-Phenyl-1,3-butadiene, II. This diolefin was obtained in 69% yield from the reaction of cinnamaldehyde and methyl magnesium iodide by a modification of the method described by Heide (23).

2-Phenylthiophene, III. To a 1-l. flask equipped with a dropping-funnel and a downward condenser for vacuum distillation was added 310 g. (9.7 g. atoms) of sulfur. This was melted and heated to 340°. The pressure was reduced to about 300 mm. and then, while the sulfur was stirred magnetically, 99 g. (0.62 mole) of 1-phenylbutadiene was added dropwise in 30 min. The yellow distillate which formed during the addition was diluted with acetone and filtered to free it from some unreacted sulfur. The solvent was evaporated and the residue fractionated *in vacuo* through a 2-foot Widmer column. Four and five-tenths grams of unreacted diene was recovered as a forerun, followed by 23 g. of phenylthiophene, boiling at 93–95°/3 mm. The product crystallized on cooling, m.p. 34–35°.

Yields obtained by this method were comparable to those from the reaction of sodium β-benzoylpropionate with phosphorus trisulfide (24).

The *mercuriacetate derivative* of the 2-phenylthiophene was prepared in small quantity and recrystallized from absolute alcohol, m.p. 174–175°.

Succinylation of thiophene. This reaction had been successfully accomplished by the use of succinic anhydride and aluminum chloride (25). In the present study, it was found that neither stannic chloride nor iodine would catalyze the substitution. However, β-thenoylpropionic acid was obtained in good yield by the reaction of thiophene with succinyl chloride and stannic chloride in benzene at −5°.

γ-(5-Phenyl-2-thienyl)butyric acid, IV. To a stirred solution of 2 g. (0.0125 mole) of 2-phen-

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[3] All temperatures reported were corrected against NBS–calibrated thermometers.

ylthiophene and 2.0 g. (0.0129 mole) of succinyl chloride in 6 cc. of benzene, held at −10°, was added dropwise a solution of 6 g. (0.0228 mole) of stannic chloride in 8 cc. of benzene. Twenty minutes were required for the addition and the mixture was stirred ten minutes longer as it was allowed to warm to 0°.

The reaction product was hydrolyzed with 5 cc. of ice-water. The benzene solvent and some unreacted phenylthiophene were steam-distilled.

The residue was washed with copious quantities of water and then dissolved in 20 cc. of 5% aqueous sodium carbonate. The alkaline solution was washed twice with ether. Acidification with conc'd hydrochloric acid precipitated the keto acid as a pink solid, weighing 1.5 g. (Yield, 46%). Recrystallization from acetone (decolorization with Norit) gave an almost colorless crystalline product, m.p. 204–205°.

Anal. Calc'd for $C_{14}H_{12}O_3S$: S, 12.3. Found: S, 12.6.

Neut. equiv. Calc'd: 260. Found: 260.

The keto acid was reduced to the butyric acid derivative, IV, by the Clemmensen method. Fifteen grams of mossy zinc was amalgamated by shaking for five minutes with a solution of 1.5 g. of mercuric chloride and 1.5 cc. of conc'd hydrochloric acid in 23 cc. of water. The aqueous solution was then decanted and the zinc amalgam covered with 45 cc. of glacial acetic acid, 27 cc. of conc'd hydrochloric acid and 3.50 g. (0.0135 mole) of β-(5-phenyl-2-thenoyl)propionic acid. The mixture was allowed to stand for 65 hours with occasional shaking and warming, during which time an additional 25 cc. of conc'd hydrochloric acid was added in small portions. Finally, 15 cc. of toluene was added and the mixture was shaken and refluxed for 30 min. After cooling, the layers were separated. The aqueous layer was extracted twice with toluene. The combined toluene solutions were filtered to remove a suspended solid (0.55 g. of unreacted keto acid). The solvent was then evaporated and the residue dissolved in dil. sodium hydroxide. After filtration, the solution was acidified, the desired acid, IV, precipitating; weight 2.75 g. (yield, 84%). After recrystallization from 95% ethanol, it melted at 100–102°.

Anal. Calc'd for $C_{14}H_{14}O_2S$: S, 13.0. Found: S, 13.1.

Neut. equiv. Calc'd: 246. Found: 248.

2-Phenyl-4,5,6,7-tetrahydrothianaphthen-4-one, V. To a solution of 1.0 g. (0.0041 mole) of the acid, IV, in 5 cc. of dry benzene in a 50-cc. Erlenmeyer flask was added 1.0 g. (0.0048 mole) of powdered phosphorus pentachloride, with swirling and external cooling. After standing at room temperature for an hour, the mixture was warmed on the steam-bath for five minutes, and then chilled until the benzene began to solidify. A cooled solution of 1.0 cc. (0.0086 mole) of anhydrous stannic chloride in 1 cc. of benzene was added rapidly with swirling. After standing for fifteen minutes in ice-water, the mixture was hydrolyzed with ice, followed by 5 cc. of conc'd hydrochloric acid. One-half cubic centimeter of ether was added to hasten the hydrolysis and the mixture was shaken until all the solid tin complex was dissolved. The organic layer was separated, washed with several portions of 5% hydrochloric acid, water, 5% sodium hydroxide, and finally again with water. After drying over sodium sulfate, the solvent was evaporated and the residue sublimed *in vacuo* at a bath temperature of 80–90°/0.01 mm. The sublimate was then recrystallized from methanol. The desired cyclic ketone, V, thus obtained weighed 0.64 g. (yield, 69%); m.p. 108.5–109°.

Anal. Calc'd for $C_{14}H_{12}OS$: S, 14.0. Found: S, 14.2.

2-Phenyl-4,5,6,7-tetrahydrothianaphthene. A mixture of 12 g. of mossy zinc, 1.5 g. of mercuric chloride, 1.5 cc. of conc'd hydrochloric acid, and 23 cc. of water was shaken for 5 minutes. The aqueous solution was decanted and the zinc amalgam washed with water. It was then covered with 30 cc. of acetic acid and 18 cc. of conc'd hydrochloric acid. The ketone, V, 1.20 g. (0.0053 mole), was added and the mixture allowed to stand for 15 hours with occasional shaking and warming to 50°. To complete the reaction, 8 cc. of toluene was then added and the mixture warmed in a water-bath at 80° for 8 hours. After standing overnight, the layers were separated. The toluene solution was washed with dil. sodium bicarbonate and with water, and then dried over sodium sulfate. After evaporation of the solvent, the product was obtained as a yellow solid, weight 1.07 g. Sublimation at a bath temperature of 60°/0.01 mm., followed by recrystallization from acetone, yielded almost colorless 2-phenyl-4,5,6,7-tetrahydrothianaphthene, melting at 82.5–83.5°.

Anal. Calc'd for $C_{14}H_{14}S$: C, 78.5; H, 6.5.

Found: C, 78.4; H, 7.1.

2-Phenylthianaphthene, I. An intimate mixture of 2.70 g. (0.0126 mole) of the heterocyclic compound described in the previous paragraph, and 0.89 g. (0.0278 g. atom) of sulfur was heated at 235–245° until evolution of hydrogen sulfide ceased (fifteen minutes required). The product was dissolved in 30 cc. of boiling benzene. The solution was cooled and filtered from some unreacted sulfur which crystallized. It was then shaken with two 40-cc. portions of 10% aqueous sodium sulfite to complete removal of elemental sulfur. The solvent was then evaporated and the solid residue sublimed *in vacuo* at a bath temperature of 125–130°/0.1 mm. The colorless sublimate, 2-phenylthianaphthene, weighed 1.12 g. (yield, 42%). After recrystallization from ethanol, the product melted at 175.5–176.0°.

Anal. Calc'd for $C_{14}H_{10}S$: C, 80.00; H, 4.76; S, 15.24.

Found: C, 80.25; H, 4.40; S, 15.47.

Forst (9) reported a melting point of 172–173° for his "tolallyl sulfide" obtained by pyrolysis of benzyl sulfide. The $C_{14}H_{10}S$ compound obtained by the writer from the reaction of toluene with sulfur was purified in the same manner as described above for 2-phenylthianaphthene. It then melted at the same temperature (176°) and a mixture with the product synthesized from 2-phenylthiophene showed no depression of the melting point. Identical blue-green dyes were obtained by the reaction of either material with isatin in conc'd sulfuric acid.

Reaction of bibenzyl with sulfur. It had been reported by Szperl (6) that tetraphenylthiophene was the exclusive product of this reaction. Since the general mechanism of the reaction of sulfur with hydrocarbons developed herein seemed to indicate that 2-phenylthianaphthene should also be formed in this reaction, the following experiment was carried out.

Bibenzyl, 50 g. (0.275 mole), was mixed intimately with 26.4 g. (0.825 mole) sulfur and heated at 260–285° for 5 hours. The product was subjected directly to vacuum distillation. A single cut was taken; boiling range 220–250°/22 mm., weight 10 g. The residue (45 g., probably mostly tetraphenylthiophene) was not investigated further. A small part of the distillate was dissolved in benzene, washed with two 50-cc. portions of 10% aqueous sodium sulfite and with water. The solution was dried over calcium chloride and then the solvent evaporated until crystallization began. The solid was redissolved by warming. It recrystallized on cooling and was filtered and dried, m.p. 173–174.5°. A mixture with pure tetraphenylthiophene had m.p. 145–150°. A mixture with 2-phenylthianaphthene, however, had m.p. 173–175°.

Thus, as would be predicted by the free radical mechanism, both heterocyclic compounds are formed by the reaction of bibenzyl with sulfur.

ACKNOWLEDGMENTS

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SUMMARY

A general free radical mechanism of the reactions of hydrocarbons with sulfur has been developed. It has been applied successfully to the explanation of the formation of all known products of the reactions, as well as to the prediction of molecular structures of several heterocyclic compounds which have been isolated but not characterized.

In particular, it was shown that an important product of the reaction of toluene and sulfur was identical with 2-phenylthianaphthene, synthesized by a standard method of ring addition from 2-phenylthiophene. The thianaphthene derivative was, in all probability, the same as a $C_{14}H_{10}S$ product of the pyrolysis of benzyl sulfide, known as "tolallyl sulfide," described in the German literature of 1875–1900.

NEW HAVEN, CONNECTICUT

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