Fisher Hi-Temp oil bath. The resulting melt was diluted with about 100 ml. of water to which 10 ml. of concentrated hydrochloric acid had been added, chilled and filtered. The purified compound was obtained by recrystallizing the crude product twice from absolute ethanol or heptane. Compound I_I was prepared by heating the melt at the above temperature for 21 hr.

Preparation of the phenacyl derivative of I_I. One g. of I_I and 0.5 g. of sodium bicarbonate were mixed in 5 ml. of water. When the reaction had subsided 40 ml. of absolute ethanol and 1 g. of phenacyl bromide were added. The mixture was refluxed for 1 hr. and then poured into about 200 ml. of water containing 10 ml. of concentrated hydrochloric acid. The precipitate was filtered off, dried in air, and recrystallized twice from absolute ethanol, m.p. 229–231°.

Anal. Calcd. for $C_{25}H_{18}O_6$: C, 72.45; H, 4.37. Found: C, 72.64; H, 4.15.

Preparation of compounds of II_{A-G} *series.* One-tenth mole of the pyrone was dissolved in 25 ml. of redistilled trifluoroacetic acid; to this mixture was added, all at once, 0.1 mole of the acyl halide. After thoroughly mixing the reactants the mixture was refluxed for 1 hr., during which time large volumes of hydrogen chloride were evolved.

The reaction product, usually of a brown or purple color, was poured into about 150 ml. of water. The crystallized compound was filtered off, dried in air, and recrystallized several times from absolute ethanol or from boiling heptane.

Bis-malononitrile derivative of II_C. One g. of II_C was mixed with 10 ml. of acetic anhydride along with about 800 mg. of malononitrile, and the resulting solution was refluxed for 1 hr. The brown solution when poured into water precipitated a dark compound which when recrystallized twice from heptane melted at 193–194°.

Anal. Calcd. for $C_{20}H_{12}N_4O$; N, 17.27. Found: N, 17.02.

2,4-Dinitrophenylhydrazone of pyridone of II_C. Six g. of II_C was dissolved in 50 ml. of absolute ethanol and then 10 ml. of concentrated ammonium hydroxide solution was added. The solution was chilled overnight in the refrigerator. A yellow precipitate of the pyridone was obtained, 2 g. of which were reacted with 2 g. of 2,4-dinitrophenylhydrazine in 100 ml. of boiling absolute ethanol. The solution was filtered after 5 min. Cooling the solution permitted an orange precipitate to collect. The compound was recrystallized once from ethanol, m.p. 201–202°.

Anal. Calcd. for $C_{20}H_{17}N_5O_5$: N, 17.20. Found: 17.34.

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New Synthesis of Tetrachlorothiophene

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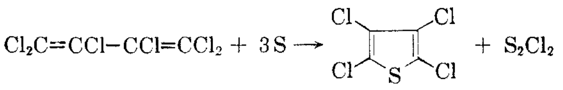
Tetrachlorothiophene has heretofore been prepared by the chlorination of thiophene, by methods involving the dehydrochlorination or dechlorination of one or more chlorine-addition intermediates.[1]

In the synthesis described herein,[2] tetrachlorothiophene is prepared by the interaction of hexachlorobutadiene and elemental sulfur. Formation of the thiophene ring is effected by replacement of two of the terminal chlorine atoms of hexachlorobutadiene by sulfur. The chlorine appears as sulfur monochloride. Both products are produced in essentially quantitative yields as defined by the following stoichiometry.



EXPERIMENTAL

A solution of 11,740 g. (45 moles—200% excess) of hexachlorobutadiene and 1443 g. (45 moles) of sulfur was heated at reflux (205–240°) under a 100 cm. distillation column packed with $^1/_8$ inch glass helices. As sulfur monochloride formed it was removed at the top of the column. During 13 hr. 1946 g. (14.4 moles) of sulfur monochloride was distilled off. The system was then put under 7.8 mm. of vacuum and after the excess hexachlorobutadiene containing some tetrachlorothiophene was removed, 2704 g. (12.2 moles, 81% yield) of tetrachlorothiophene was taken off at 91–94°. The latter portion of this fraction gave the following analysis.

Anal. Calcd. for C_4Cl_4S: Cl, 63.91; S, 14.45. Found: Cl, 63.7; S, 14.4.

The total yield of tetrachlorothiophene as calculated from infrared analysis of all distillation fractions was 99%. The product melted at 29.5–29.7° after crystallization from methanol.

In a second experiment the excess of hexachlorobutadiene was reduced to 10%. The sulfur was added in portions to the hexachlorobutadiene during the reaction in order to avoid the presence of undissolved sulfur. In this case the product was redistilled to remove traces of sulfur chloride. A 94.1% yield of tetrachlorothiophene was obtained, of which 76% was isolated as 99.5–99.7% pure product.

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[1] H. D. Hartough, *Thiophene and its Derivatives*, (The Chemistry of Heterocyclic Compounds series, A. Weissberger, ed.) Interscience Publishers, Inc., New York, 1952, pp. 180, 185.

(2) Further experimental data are included in a pending U. S. patent.

Studies in *p*-Cymene, IV.
Some *N,N'*-Diarylthioureas

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This study is a continuation of the work of LeConte and Chance[2] for the purpose of preparing new *N,N'*-diarylthioureas to be used in the antici-

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(1) (a) Present address: East Carolina College, Greenville, N. C. (b) An abstract of a thesis submitted by William N. Cannon to the Graduate School, University of Georgia, in partial fulfullment of the requirements for the degree of Master of Science. Present address: Eli Lilly & Co., Indianapolis, Ind.

(2) J. N. LeConte and L. P. Chance; *J. Am. Chem. Soc.*, **71**, 2240 (1949).

TABLE I

ARYL 5-HYDROXY-*p*-CYMYLTHIOUREAS AND DERIVED PRODUCTS

	Yield, %	M.P.	Formula	Sulfur Calcd.	Sulfur Found
N,N'-di-(4-hydroxy-5-isopropyl-2-methylphenyl)-thiourea	70	232–233°	$C_{21}H_{28}O_2N_2S$	8.60	8.45
5-Hydroxy-2-*p*-cymyl isothiocyanate	68.5	164–166° 3 mm. (b.p.)	$C_{11}H_{13}ONS$	15.45	15.76
5-Hydroxy-2-*p*-cymyl phenylthiosemicarbazide	84	180–181°	$C_{17}H_{21}ON_3S$	10.15	9.87
o-Tolyl-2-(5-hydroxy-*p*-cymyl)thiourea	51	187–188°	$C_{18}H_{22}ON_2S$	10.19	10.35
m-Tolyl-2-(5-hydroxy-*p*-cymyl)thiourea	71	193°			10.13
p-Tolyl-2-(5-hydroxy-*p*-cymyl)thiourea	35	174–175°			10.15

pated preparation of substituted quinolines by the method of Dziewonski and Moszew.[3]

N,N'-di-(4-hydroxy-5-isopropyl-2-methylphenyl)thiourea was made by standard procedure from 2-amino-5-hydroxy-*p*-cymene and carbon disulfide, then split with acetic anhydride to form 5-hydroxy-2-*p*-cymyl isothiocyanate and 2-acetamino-5-hydroxy-*p*-cymene. There was no evidence of the formation of a guanidine compound. When isolated the isothiocyanate reacted with 2-amino-5-hydroxy-*p*-cymene to reform the original thiourea, proved by the mixed melting point method. The isothiocyanate also was reacted with phenylhydrazine to form 5-hydroxy-2-*p*-cymyl phenylthiosemicarbazide. A sulfur analysis indicated mole to mole reaction in contradiction to the findings of Otterbacher and Whitmore,[4] who found that two moles of isothiocyanates react with one of phenylhydrazine.

The preparations of *N*-(*o*-, *m*-, and *p*-)tolyl-*N'*-4-hydroxy-5-isopropyl-2-methyl-phenylthioureas were accomplished by the reaction of 2-amino-5-hydroxy-*p*-cymene with the respective *o*-, *m*-, and *p*-tolyl isothiocyanates. Results are found in Table I. The sulfur content of new compounds was determined by the Parr bomb method. All melting points are uncorrected.

EXPERIMENTAL

I. Preparation of N,N'-di-(4-hydroxy-5-isopropyl-2-methylphenyl)thiourea and its derivatives. 2-Amino-5-hydroxy-*p*-cymenē, 200 g. (1.21 moles), was dissolved in 400 ml. of absolute ethanol and the resulting solution added to a mixture of 228 g. (3.0 moles) of carbon disulfide and 5 g. of solid potassium hydroxide in a 2-l. flask equipped with a reflux condenser. The reaction flask was heated on a water bath. A soda-lime trap was attached to the condenser to absorb the hydrogen sulfide liberated in the reaction. The reaction mixture was refluxed for 22 hr. when hydrogen sulfide ceased to be evolved. The solution was concentrated to about half its original volume, and on cooling a heavy separation of white crystals was observed. These were filtered and immediately washed with cold alcohol. Several recrystallizations from ethanol were necessary to obtain a sample for analysis. However, the crude product proved satisfactory in preparing the isothiocyanate.

5-Hydroxy-2-p-cymyl isothiocyanate. A mixture of 130 g (0.35 mole) of the thiourea and 62 g. (0.6 mole) of acetic anhydride were mixed in a 500-ml. flask equipped with a reflux condenser. The solution of the thiourea was complete when warmed. The solution was refluxed for 5 min. and poured into 400 ml. of hot water. A heavy dark oil settled out. The mixture was steam distilled, the distillate extracted with ether, dried overnight over anhydrous sodium sulfate, ether evaporated, and the product distilled under reduced pressure. The main fraction was a pale, straw-colored oil boiling at 164–166°/3 mm. No boiling point could be determined at atmospheric pressure because of decomposition.

5-Hydroxy-2-p-cymyl phenyl thiosemicarbazide. A mixture of 10 g. (0.05 mole) of 5-hydroxy-2-*p*-cymyl isothiocyanate, 5 g. (0.05 mole) phenylhydrazine and 25 ml. absolute ethanol was made in a 50 ml. Erlenmeyer flask. Heat was evolved immediately. After cooling slightly, the reaction mixture was warmed on a water bath for 20 min. The white crystals which separated on cooling were filtered, washed with cold ethanol, and recrystallized from hot ethanol.

II. Preparation of the N,N'-tolyl(hydroxy-p-cymyl)thioureas. The tolylisothiocyanates were prepared in the usual way from their symmetrical thioureas. Mixtures of each were made with 34 g. of the isothiocyanate, 37 g. of 2-amino-5-hydroxy-*p*-cymene (one to one mole ratio) in 200 ml. of absolute ethanol. The resulting solutions were refluxed for 2 hr., concentrated to half their original volumes by distilling off part of the ethanol. As the solutions cooled, the white crystalline products separated, were filtered and recrystallized from ethanol. The *m*-tolylisothiocyanate reacted on contact with the amine and refluxing was unnecessary.

SUMMARY

5-Hydroxy-2-*p*-cymylisothiocyanate was prepared and from it several new *N,N'*-diarylthioureas were made and characterized.

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[3] K. Dziewonski and J. Moszew, *Roczniki Chem.*, **12**, 482, 925 (1932); *Chem. Abstr.*, **27**, 3937 (1933); **28**, 152 (1934).

[4] T. Otterbacher and F. C. Whitmore, *J. Am. Chem. Soc.*, **51**, 1909 (1929).

Reactions of Olefin-Mercuric Acetate Addition Compounds with Ethyl Acetoacetate in the Presence of Alkylating Catalyst

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The new reactions which form aralkyl acetates through intermediate mercurials ($ArCH_2CH_2HgZ$)