TABLE I

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

	Yield, %	M.P.	Formula	Sulfur	
				Calcd.	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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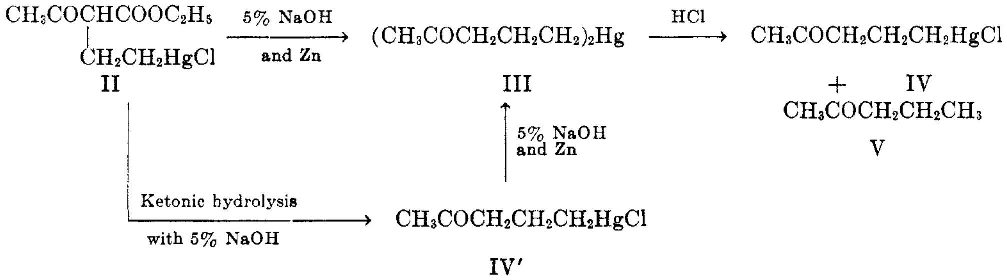
The new reactions which form aralkyl acetates through intermediate mercurials ($ArCH_2CH_2HgZ$)

by the reaction of ethylene–mercuric acetate addition compound with aromatic compounds[1,2] have been extended to the case of ethyl acetoacetate in place of the aromatics.

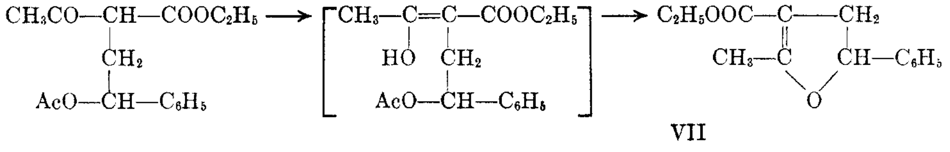
In the presence of boron trifluoride–acetic acid complex, the reaction of ethylene gives ethyl α-(2-acetoxyethyl)acetoacetate (I). This structure was established by the ketonic hydrolysis of the β-ketoester group and by the simultaneous hydrolysis of the other ester group to give 5-hydroxy-2-pentanone. The best yield was obtained by keeping the reaction mixture at a lower temperature for several hours and then at 70–75° for about 1 hr. Prolonged reaction at 70–75° resulted in a lower yield, despite the increased formation of free mercury, because a high-boiling tarry material was formed.

Ethyl α-(2-chloromercuryethyl)acetoacetate (II) was isolated as an intermediate of the reaction, when the reaction product under milder condition was treated with an aqueous sodium chloride solution. The procedure of the structure determination of this new compound is demonstrated by the following reaction scheme (a).

(a)

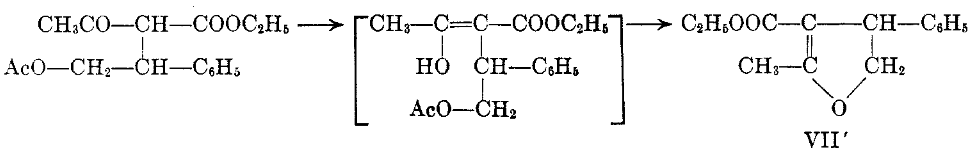


(b)



or

(c)



The results mentioned above are obtained with boron trifluoride as the catalyst. Perchloric acid which has been a successful catalyst in the series of this reaction[1,2] gave the same result in the experiment of the isolation of the intermediate mercurial. This catalyst, however, failed to give the final product I, because I and ethyl acetoacetate were decomposed with perchloric acid at the higher temperature of 90–95° where the free mercury and I are formed from the intermediate mercurial.

The reaction of propylene gives ethyl α-acetyl-β-acetoxymethylbutyrate (VI), whose structure was established by the hydrolysis to 4-methyl-5-hydroxy-2-pentanone. This shows that ethyl acetoacetate reacts with the central carbon of propylene, while the aromatic compounds reacted with the terminal carbon of the same olefin.[2]

The reaction of styrene gives a product which is thought to be ethyl 2-methyl-(4 or 5)-phenyl-4,5-dihydro-3-furoate (VII or VII′). The following two reaction schemes (b and c) appear to be possible, since the reaction of the styrene-mercuric acetate addition compound with anisole gave a mixture of 1-phenyl-2-(*p*-methoxyphenyl)- and 2-phenyl-2-(*p*-methoxyphenyl)ethylmercury salt.[2]

This compound showed negative tests for carbonyl group and positive tests for double bond and was analyzed correctly for VII or VII′. Alkaline hydrolysis gave an acid which is thought to be 2-methyl-(4 or 5)phenyl-4,5-dihydro-3-furoic acid and was analyzed correctly for it. Alkaline oxidation of VII (or VII′) with potassium permanganate gave benzoic acid only. Several attempts to determine the position of the phenyl group 4 or 5 were unsuccessful. However, the fact that no dihydrofuran derivatives are formed in the cases of ethylene and propylene suggests strongly that the phenyl is attached to the position of 5, because 5-phenyldihydrofuran formation is expected to be much easier than that of 4-phenyl derivative.

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(1) K. Ichikawa, S. Fukushima, H. Ouchi and M. Tsuchida, *J. Am. Chem. Soc.*, **80**, 6005 (1958).

(2) K. Ichikawa, S. Fukushima, H. Ouchi and M Tsuchida, *J. Am. Chem. Soc.* **81**, 3401 (1959).

EXPERIMENTAL

Ethyl α-(2-acetoxyethyl)acetoacetate (I). At 18–20°, ethylene was introduced into the mixture of mercuric acetate (96 g.) and acetic acid (90 ml.) with good stirring until the mercuric ion could no longer be detected by sodium hydroxide solution. To this solution, ethyl acetoacetate (78 g.) and then boron trifluoride–acetic acid complex (51 g.) were added under continued stirring. The reaction mixture was kept at 30–32° for 5 hr. and then at 70–75° for 1 hr. After separating the metallic mercury (38 g., 63% of theor.) formed, the reaction mixture was diluted with water (500 ml.) and then extracted with benzene (400 ml.). The benzene extract was washed with saturated salt solution and then dried over anhydrous sodium sulfate. Distillation gave a crude I (24 g., yield, 37%, b.p. 120–130°/5 mm.). After a redistillation, I (22 g., b.p. 115–116°/2.5 mm., n_{D}^{20} 1.4403, d_{D}^{20} 1.0924) was obtained.

Anal. Calcd. for $C_{10}H_{16}O_5$: C, 55.54; H, 7.46. Found: C, 55.61; H, 7.43.

When the reaction mixture of the same composition as in the case above was kept at 70–75° for 1.5 hr. from the beginning of the reaction, a lower yield of I (21%) was obtained, despite the increased formation of free mercury (75% of theor.).

Hydrolysis of I *to 5-hydroxy-2-pentanone.* At 30–32°, I (18.3 g.) was dissolved in 5% aqueous sodium hydroxide solution (90 ml.) under good stirring for 4 hr. About 5 g. of I remained insoluble and was extracted off with ether. The water layer was allowed to stand at room temperature (30–32°) for 8 days and then was acidified with dilute hydrochloric acid. From this water solution, a crude 2,4-dinitrophenylhydrazone of 5-hydroxy-2-pentanone (15.3 g., m.p. 140–142°) was obtained. After a recrystallization from ethanal, the m.p. was 148–149° (reported[3] 150°).

Anal. Calcd. for $C_{11}H_{14}N_4O_5$: C, 46.81; H, 5.00; N, 19.85. Found: C, 46.85; H, 5.04; N, 20.00.

Ethyl α-(2-chloromercuryethyl)acetoacetate (II). To the acetic acid solution of ethylene–mercuric acetate addition compound which was prepared from acetic acid (90 ml.), mercuric acetate (96 g.) and ethylene, ethyl acetoacetate (195 g.), and then boron trifluoride–acetic acid complex (51 g.) were added under good stirring at below 20°. After a period of 4 hr. at 20°, the reaction mixture was poured into water (600 ml.). To this solution, 10% salt solution (200 ml.) was added under stirring. The resulting heavy oil was separated from the water layer. The water layer was extracted with benzene. This benzene extract was combined with the heavy oil mentioned above, washed with saturated salt solution, and then dried over anhydrous sodium sulfate. After the recovery of benzene and ethyl acetoacetate under reduced pressure, a heavy viscous oil (II) (106 g.) was obtained as a residue.

Conversion of II *to bis(2-pentanon-5-yl)-mercury* (III). II (93 g.) was dissolved into 5% aqueous sodium hydroxide solution (350 ml.). This solution was warmed up to 95° and then zinc dust (40 g.) was added in several portions during a period of 1.5 hr. under stirring. After the addition of zinc dust, the stirring was continued for 10 min. A resulting heavy oil was separated from the reaction mixture and combined with the ether extract of the water layer. This was washed with saturated salt solution and then dried over anhydrous sodium sulfate. Distillation gave a heavy liquid (III) (25.5 g., b.p. 167–169°/3 mm.) (Hg analysis; Calcd. for $C_{10}H_{18}HgO_2$ 54.09; found, 54.22.).

Conversion of III *to 5-chloromercury-2-pentanone* (IV) *and 2-pentanone* (V). III (5.2 g.) was dissolved into concentrated hydrochloric acid (8 ml.) at room temperature and then was kept at 60–70° for several minutes. By adding water (40 ml.) to this solution white plates (IV) (3.9 g., m.p. 74.5–75°) were obtained. Recrystallization from hot water did not change the melting point. Hg analysis: Calcd. for C_5H_9ClHgO 62.46; found 62.20. The water solution which was separated from IV was distilled under reduced pressure to almost dryness. From the distillate, a crude 2,4-dinitrophenylhydrazone of 2-pentanone (V) (3.5 g., m.p. 139–140°) was obtained. Recrystallization from a mixture of alcohol and ethyl acetate gave the m.p. 144.5–145° (reported[3] 144°).

Anal. Calcd. for $C_{11}H_{14}N_4O_4$: 49.62; H, 5.30; N, 21.04. Found: C, 49.60; H, 5.43; N, 21.24.

Conversion of II *to 5-chloromercury-2-pentanone* (IV′). II (87 g.) was dissolved into 5% aqueous sodium hydroxide solution (450 ml.) and was kept 25–30° under stirring for 4 hr. After being acidified with 18% hydrochloric acid, the reaction mixture was warmed on a steam bath for about 30 min. until the evolution of carbon dioxide was complete. By cooling the reaction mixture in an ice bath, a crude 5-chloromercury-2-pentanone (IV′) (55 g., m.p. 70–73°) was obtained. Recrystallization from hot water gave white plates, m.p. 74.5–75°. Mixed melting point with IV showed no depression.

Conversion of IV′ *to* III. By the same method as in the case of II, IV′ (27 g.) was reduced with zinc dust (12 g.) and 5% aqueous sodium hydroxide solution (100 ml.). Mercury content of the resulted heavy oil (III) (10.2 g., b.p. 162–163°/2.5 mm.) was 53.47% (calcd., 54.09%). Treatment of this product (8.5 g.) with concentrated hydrochloric acid (12 ml.) resulted in the formation of IV (4.5 g., m.p. 74.5–75°). Mixed melting point with IV′ showed no depression.

Ethyl α-acetyl-β-acetoxymethyl butyrate (VI). Under the conditions similar to the case of ethylene, the reaction of propylenemercuric acetate addition compound with ethyl acetoacetate gave VI (18 g., yield, 26%, b.p. 108.5–110.5°/2.5 mm., n_{D}^{20} 1.4425, d_{D}^{20} 1.0648).

Anal. Calcd. for $C_{11}H_{18}O_5$: C, 57.38; H, 7.88. Found: C, 57.39; H, 8.08.

Hydrolysis of VI *to 4-methyl-5-hydroxy-2-pentanone.* VI (2.5 g.) was dissolved into 5% aqueous sodium hydroxide solution (22 ml.) and was kept at room temperature (30–32°) for 8 days. After a small amount of unreacted VI was extracted with ether, the water layer was acidified with dilute hydrochloric acid. From this solution, a crude 2,4-dinitrohydrazone of 4-methyl-5-hydroxy-2-pentanone (2.6 g., m.p. 98–104°) was obtained. The melting point was 104–105.5° after a recrystallization from 80% ethanol (reported[4] 104°).

Anal. Calcd. for $C_{12}H_{16}N_4O_5$: C, 48.64; H, 5.44; N, 18.91. Found: C, 48.61; H, 5.40; N, 19.02.

Ethyl 2-methyl-5-phenyl-4,5-dihydro-3-furoate (VII). Under the same conditions as in the case of ethylene, except that 155 g. of acetoacetate was used and the final reaction temperature was 77–81° for 50 min., the reaction of styrene-mercuric acetate addition compound gave a liquid (24 g.) which is thought to be VII, b.p. 128–130°/3 mm., n_{D}^{20} 1.5285, d_{D}^{20} 1.1008.

Anal. Calcd. for $C_{14}H_{16}O_3$: C, 72.39; H, 6.94. Found: C, 72.10; H, 6.97.

Hydrolysis of VII *to 2-methyl-5-phenyl-4,5-dihydro-3-furoic acid.* VII (10 g.) was dissolved into 20% ethanolic potassium hydroxide solution (50 g.) and was heated on a steam bath under reflux for 7 hr. Ethanol was removed and then a small amount of water was added to the residue. An unreacted VII (about 4 g.) was extracted off with ether. The water layer was acidified with dilute hydrochloric acid. The resulting crystals were recrystallized from 80% ethanol to give white needles (2.3g .), m.p. 172.5° (with decomposition), which are thought to be 2-methyl-5-phenyl-4,5-dihydro-3-furoic acid.

Anal. Calcd. for $C_{12}H_{12}O_3$: C, 70.57; H, 5.92. Found: C, 70.54; H, 6.08.

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(3) R. Paul and S. Tchelitcheff, *Bull. soc. chim. France*, 418 (1953).

(4) J. Colonge and R. Gelin, *Bull. soc. chim. France*, 801 (1954).

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Fluorination of Hexachlorobenzene with Antimony Pentafluoride

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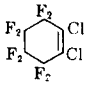
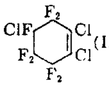
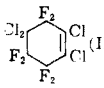
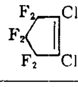
The reaction of hexachlorobenzene with antimonypentafluoride has been described in the literature,[1] but further work has shown some unreported facts. Care must be taken in heating the reaction mixture since at 160° there is a large evolution of heat which will cause loss of product unless cooling is used.

In the original procedure the only product described is I, *cf.* Table I, b.p. 111–113° and the yield is stated to be 44%. In addition to I, three other fluorinated materials have been recovered, their properties are listed below.

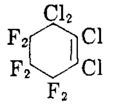
TABLE I

				Analyses		
Compound	B.P.	d_4^{20}	n_D^{30}	Theor.	Found	Yield, %
 (I)	113°	1.729	1.3653	Cl 24.05	24.23	20–30
 (II)	140–1.8°	1.767	1.3995	Cl 34.10 C 23.11	33.71 24.07	20
 (III)	95°/63 mm.	1.793	1.4313	Cl 43.30 C 22.02	42.70 23.18	5
 (IV)	89–90°	1.642	1.3619	Cl 29.0	28.43	<1%

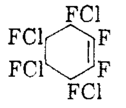
The purity of compounds I–III was checked by gas chromatography and structure determinations were made with the aid of infrared and nuclear magnetic resonance[2] measurements.

The following basis was used for structural assignments. In compounds I–III a single infrared absorption band was found at 6.15 μ and was assigned to the CCl=CCl grouping. Compounds with F atoms attached to the doubly bonded carbon atoms absorb at higher frequencies as has been observed with a number of compounds. The NMR absorption for I shows two different kinds of F atoms in agreement with the formula assigned and oxidation with $KMnO_4$ gives the expected perfluoroadipic acid.[1] The compound II was shown to have four different kinds of F atoms and the boiling point, refractive index, and density show the proper incremental changes.

The highest boiling material (III) was assigned the structure shown since NMR indicates three types of fluorine each containing two F atoms. Other structures for III which are unlikely but cannot be ruled out by NMR are as follows:



A



B

In both of these cases one would expect to find a signal very near the high field reference line from either C=CF or CF_2—CF_2—CF_2 groupings. However, the 6.15μ CCl=CCl band definitely rules out structure B.

Also isolated was a very small amount of IV.[3] Further identification was made by chlorinating this material under the influence of ultraviolet light to give a solid m.p. 138–145°, Cl 43.4%. The reported product of the chlorination is $C_5F_6Cl_4$, m.p. 151°, Cl 44.9%. Comparison of the infrared spectrum of IV with the authentic $C_5F_6Cl_2$ was also in agreement.

It was first assumed that the source of IV was the presence of a cyclopentene impurity in the starting material. An examination was made for impurities in the starting C_6Cl_6 by extraction with

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(1) E. T. McBee, P. A. Wiseman, and G. B. Bachman, *Ind. Eng. Chem.*, **39**, 415 (1947).

(2) Performed by Varian Associates, Palo Alto, Calif.

(3) A. L. Henne and W. J. Zimmerschied, *J. Am. Chem. Soc.*, **67**, 1265 (1945).