

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

Studies on the Polymethylbenzenes. XIII.¹ MercurationBY LEE IRVIN SMITH AND F. LOWELL TAYLOR²

Direct mercuration is a characteristic substitution reaction of aromatic hydrocarbons which has not been studied previously in the series of the polymethylbenzenes. In the study reported in this paper, six polymethylbenzenes, namely, mesitylene, pseudocumene, durene, isodurene, prehnitene, and penta-methylbenzene were mercurated and the acetoxymercuri-, halogenomercuri-, and bis-arylmercury derivatives were prepared and characterized.

Michaelis³ treated bromomesitylene and 5-bromopseudocumene with sodium amalgam in xylene, and obtained the corresponding bis-arylmercury compounds; from the latter he prepared arylmercuric halides by the action of mercuric halides. Whitmore⁴ and his students mercurated mesitylene directly with mercuric acetate, but they did not report the properties of acetoxymercurimesitylene. Jacobsen⁵ obtained bis-(pentamethylphenyl)-mercury when he attempted to prepare pentamethylbenzoic ester from bromopentamethylbenzene, chloroformic ester and sodium amalgam.

The polymethylbenzenes were mercurated by mercuric acetate in methanol solution. Pentamethylbenzene, durene, and mesitylene gave good yields of monoacetoxymercuri derivatives; pseudocumene and prehnitene formed considerable amounts of diacetoxymercuri derivatives. Pseudocumene mercurated first in the 5-position; the position of the second mercury atom in the diacetoxymercuri compound was not determined. Acetoxymercuriisodurene was most conveniently prepared from the fraction of b. p. 79–91° (15 mm.) obtained by direct methylation of xylene. Most of the durene was removed from this fraction by filtration at –10°, and the filtrate then contained about 90% of isodurene.⁶ Since acetoxymercuriisodurene was more soluble than acetoxymercuridurene in alcohol, the two compounds were separated by crystallization. This

procedure avoided the time consuming preparation of pure isodurene. Samples of acetoxymercuriisodurene prepared from the mixture of hydrocarbons and from pure isodurene had the same melting point; the melting point of the substance was depressed by acetoxymercuridurene.

Chloro-, bromo- and iodomercuri derivatives of the hydrocarbons were prepared from the acetoxymercuri compounds by metathesis, since the halides were less soluble than the acetates. Likewise, since the bis-(polymethylphenyl)-mercury compounds were less soluble than the iodomercuri compounds, they were prepared from the iodo compounds by the action of sodium iodide.⁴ Iodomercuripentamethylbenzene could not be prepared from the acetate because even less than one mole of sodium caused the formation of bis-(pentamethylphenyl)-mercury.

The mercury compounds which were previously unknown are listed in the tables, with melting points and analytical data.

Experimental Part

Mercuration.—The hydrocarbons were dissolved in five volumes of methanol, and a mole of mercuric acetate was introduced. Enough acetic acid was added to prevent hydrolysis of the mercury salt^{7,8} and the solutions were refluxed. Mercuration of durene, mesitylene and pentamethylbenzene required five to seven days for completion. Isodurene, prehnitene and pseudocumene were allowed to react for only twenty to forty hours because of the formation of large amounts of diacetoxymercuri derivatives. The procedures for isolation of the products were determined by the solubilities. The following specific conditions were used in the preparation of the individual compounds.

Acetoxymercuripentamethylbenzene was insoluble in the hot reaction mixture; the product was filtered and crystallized from chloroform; m. p. 180°; yield 80%.

Acetoxymercuridurene was soluble in the hot reaction mixture; the solution was filtered from the insoluble diacetoxymercuridurene and cooled. The crude product (m. p. 152–156°, yield 60%) was crystallized from methanol (solubility, 12 g. per 100 cc. at the b. p.; 3 g. per 100 cc. at 0°). The melting point of the pure substance was 158–159°.

Acetoxymercurimesitylene was soluble in the cold reaction mixture. The solution was filtered from diacetoxymercurimesitylene and then diluted with water. The oil⁹

(1) Paper XII, *THIS JOURNAL*, **57**, 1293 (1935).

(2) Abstracted from the thesis of F. Lowell Taylor, presented to the Graduate School of the University of Minnesota, in partial fulfillment of the requirements for the Ph.D. degree, March, 1935.

(3) Michaelis, *Ber.*, **23**, 588 (1895).

(4) Whitmore and Sobatzki, *THIS JOURNAL*, **55**, 1128 (1933); Whitmore and Beattie, *ibid.*, p. 1567.

(5) Jacobsen, *Ber.*, **22**, 1220 (1889).

(6) Smith and Cass, *THIS JOURNAL*, **54**, 1611 (1932).

(7) Maynard, *ibid.*, **46**, 1510 (1924); **54**, 2118 (1932).

(8) Mercuric oxide (1 mole) and acetic acid (2 moles) were often substituted for the mercuric acetate.

(9) The oil was a strong vesicant.

TABLE I
 ACETOXYMERCURI-POLYMETHYLBENZENES, $RHgOCOCH_3$

Parent hydrocarbon ^a	M. p., °C.	Formula	Analyses, %					
			Carbon		Hydrogen		Mercury	
			Calcd.	Found	Calcd.	Found	Calcd.	Found
Pentamethylbenzene	180	$C_{13}H_{18}O_2Hg$	38.35	37.9	4.46	4.49		
Durene (1, 2, 4, 5)	158-159	$C_{12}H_{16}O_2Hg$	36.67	36.5	4.11	4.57	51.1	50.6
Isodurene (1, 2, 3, 5)	108	$C_{12}H_{16}O_2Hg$	36.67	35.6	4.11	4.4	51.1	51.2
Prehnitene (1, 2, 3, 4)	147	$C_{12}H_{16}O_2Hg$	36.67	36.2	4.11	4.4		
Mesitylene (1, 3, 5)	102-103	$C_{11}H_{14}O_2Hg$					53.0	52.0
Pseudocumene ^b (1, 2, 4)	145-147	$C_{11}H_{14}O_2Hg$					53.0	53.2

^a The figures denote the positions of the methyl groups. ^b Acetoxymercuri group in the 5-position.

 TABLE II
 HALOGENOMERCURI-POLYMETHYLBENZENES

Parent hydrocarbon	X	Solvent	M. p., °C.	Formula	Analyses, %			
					Carbon		Hydrogen	
					Calcd.	Found	Calcd.	Found
Pentamethylbenzene	Cl	$CHCl_3$	205	$C_{11}H_{15}HgCl$	34.45	34.2	3.96	4.12
	Br	$CHCl_3$	195-196	$C_{11}H_{15}HgBr$	30.87	30.4	3.54	3.6
Durene	Cl	$CHCl_3$	188-189	$C_{10}H_{13}HgCl$	32.51	32.3	3.55	3.93
	Br	$CHCl_3-MeOH$	174	$C_{10}H_{13}HgBr$	29.01	28.8	3.17	3.39
Isodurene	I	$CHCl_3-MeOH$	161-162	$C_{10}H_{13}HgI$	26.05	26.2	2.84	3.37
	Cl	$CHCl_3-MeOH$	174	$C_{10}H_{13}HgCl$	32.51	32.2	3.55	3.84
Prehnitene	Br	$CHCl_3-MeOH$	160	$C_{10}H_{13}HgBr$	29.01	28.7	3.17	3.54
	I	$CHCl_3-MeOH$	163-164	$C_{10}H_{13}HgI$	26.05	25.8	2.84	3.12
	Cl	$CHCl_3$	216-217	$C_{10}H_{13}HgCl$	32.51	32.2	3.55	3.88
	Br	$CHCl_3$	213-214	$C_{10}H_{13}HgBr$	29.01	28.6	3.11	3.3
	I	$CHCl_3$	200	$C_{10}H_{13}HgI$	26.05	25.7	2.84	3.29

 TABLE III
 BIS-(POLYMETHYLPHENYL)-MERCURY COMPOUNDS, R_2Hg

Derivative of	M. p., °C.	Formula	Analyses, %					
			Carbon		Hydrogen		Mercury	
			Calcd.	Found	Calcd.	Found	Calcd.	Found
Pentamethylbenzene	278 ^a	$C_{22}H_{30}Hg$	53.35	53.1	6.11	6.29		
Durene	242-243	$C_{20}H_{26}Hg$	51.41	50.5	5.61	5.9	43.0	42.5
Isodurene	217-218	$C_{20}H_{26}Hg$	51.41	49.6	5.61	5.8	43.0	42.4
Prehnitene	200	$C_{20}H_{26}Hg$	51.41	50.3	5.61	5.7	43.0	41.4

^a Jacobsen, *loc. cit.* reported the m. p. as 266°.

which separated did not crystallize until unchanged mesitylene had been removed by steam distillation. Crystallization from methanol gave the pure substance; m. p. 102-103°; yield 30%.

Acetoxymercuriisodurene also separated as an oil⁹ when the reaction mixture was diluted with water, but the substance solidified after it was washed by decantation and cooled. It was crystallized from 75% alcohol (warmed only to 60°). The yield of the product, m. p. 108°, was 30%, when prepared from either pure isodurene or the mixture of tetramethylbenzenes ("durene filtrate").

Acetoxymercuriprehnitene was soluble in the hot reaction mixture. The solution was filtered from insoluble diacetoxymercuriprehnitene, cooled, and diluted with water. The substance crystallized from methanol in radial needles, m. p. 147°; yield 15%.

5-Acetoxymercuripseudocumene was isolated in the same manner as the prehnitene derivative; the substance was crystallized from 95% ethanol; m. p. 145-147°; yield 30%.

Crude acetoxymercuri derivatives were recovered by dilution of the alcoholic filtrates with water. The filtrates were then treated with salt or hydrochloric acid to remove the remainder of the organomercury compounds by pre-

cipitation as chloromercuri derivatives. The final filtrates from the reaction mixtures were treated with sulfide to recover mercury.

Halogenmercuri Compounds.—The halides were prepared as follows: the acetoxymercuri compounds were dissolved in chloroform, alcohol or a mixture of the two solvents. Hydrochloric acid, sodium bromide or sodium iodide, respectively, was dissolved in aqueous alcohol and added to the solutions of the mercury compounds. The precipitates were filtered, washed and crystallized. The solvents which were used for the individual substances are listed in Table II.

It was necessary to use less than one equivalent of sodium iodide in the preparation of iodomercuripolymethylbenzenes in order to prevent formation of bis-arylmethylmercury compounds. Despite that precaution, the product from acetoxymercuripentamethylbenzene was a mixture of iodomercuripentamethylbenzene and bis-(pentamethylphenyl)-mercury. Separation of the two substances by crystallization was impossible. Mercuric iodide was formed, which indicated that the iodomercuri compound in solution was converted to the bis-aryl compound by heat alone.

Bis-arylmercury Compounds.—The iodomercuri derivatives were precipitated from alcoholic solutions of the acetates and, without purification, were digested for several hours in alcohol with four moles of sodium iodide.¹⁰ The substances were crystallized from chloroform. Diduryl mercury was prepared also by reduction of the acetate with sodium stannite.^{7,11} The method was unsatisfactory because separation of the product from finely divided mercury was difficult.

Analyses.—Furter¹² demonstrated that mercury causes low analytical values for carbon. However, satisfactory carbon and hydrogen analyses of most of the mercury compounds were obtained by the semi-micro method with a Pregl universal filling in the combustion tube when precautions were taken. The substances were covered with cupric oxide and burned in an oxygen stream which had half the usual velocity. Silver foil was used in the tip of

(10) Steinkopf and Baumeister, *Ann.*, **403**, 50 (1914); Whitmore, *et al.*, *loc. cit.*; Johns and Hixon, *J. Phys. Chem.*, **34**, 2218 (1930); *THIS JOURNAL*, **52**, 2820 (1930); **56**, 1333 (1934).

(11) Dimroth, *Ber.*, **36**, 2032, 2853 (1902); *ibid.*, **54**, 1504 (1921).

(12) Furter, *Mikrochem.*, **9**, 27 (1931); see also Hernler, *ibid.*, *Pregl Festschrift*, 154 (1929); Verdino, *ibid.*, **6**, 5 (1928); Grignard and Abelmann, *Bull. soc. chim.*, [4] **19**, 25 (1916).

the combustion tube to collect free mercury. Silver was not very satisfactory for the purpose, but gold was not available.

Mercury analyses, in the absence of halogens, were made by titration with potassium thiocyanate after the organic material had been destroyed by hot concentrated nitric acid and permanganate.¹³

Summary

1. The mercuriation of six polymethylbenzenes (mesitylene, pseudocumene, durene, isodurene, prehnitene and pentamethylbenzene) has been studied.

2. A number of related mercury derivatives have been prepared from each of the primary products of mercuriation.

3. Twenty new organomercury compounds have been described.

(13) Tabern and Shelberg, *Ind. Eng. Chem., Anal. Ed.*, **4**, 401 (1932).

MINNEAPOLIS, MINN.

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Organic Flocculating Agents in the Quantitative Precipitation of Zinc Sulfide¹

BY JOHN R. CALDWELL AND HARVEY V. MOYER

Comprehensive reviews of proposed methods for the precipitation of zinc sulfide are to be found in the comparatively recent publications of Jeffreys and Swift,² J. N. Frers,³ and Mayr.⁴

Practically all of the efforts made to obtain the precipitate in a suitable physical form are based on three general procedures: (a) precipitation from hot solution; (b) salting-out with a large excess of some neutral salt; (c) maintenance of a low pH value by means of buffers. It is a well-recognized fact that in the early stages of precipitation most sulfides exist as hydrosols, and the formation of an insoluble precipitate depends to a large extent on the rate of transformation from sol to flocculent state. This transformation may be promoted by the presence of finely divided solid matter as demonstrated by Kolthoff⁵ and by Frers.³

Recently we have found that certain organic substances may be used to alter the nature of

analytical precipitates.^{6,7} It seemed quite probable that flocculation of colloidal zinc sulfide could be induced by a somewhat similar procedure. The coagulation of precipitates by means of small concentrations of organic substances has been reported frequently by colloid chemists. Contrary to the ordinary behavior, certain hydrophilic colloids such as agar-agar, gelatin, gum arabic, etc., will not stabilize suspensoid sols if present in minute traces, but will bring about complete and rapid flocculation. This phenomenon, called sensitization, has been known for many years, but apparently never before has been applied to analytical chemistry. A brief review of recent colloid literature furnished ample indication that this field offers attractive possibilities for further investigation.

Rossi and Scandallari⁸ showed that minute quantities of gelatin brought about rapid coagulation of sulfur sols. Chaudhury⁹ reported that sols of ferric hydroxide and arsenic trisulfide were sensitized and flocculated by methyl alcohol,

(1) Presented before the Division of Physical and Inorganic Chemistry at the 89th meeting of the American Chemical Society, New York City, April 22 to 26, 1935.

(2) Jeffreys and Swift, *THIS JOURNAL*, **54**, 3219 (1932).

(3) J. N. Frers, *Z. anal. Chem.*, **95**, 1-36 (1933).

(4) Mayr, *ibid.*, **96**, 273 (1934).

(5) Kolthoff, *J. Phys. Chem.*, **36**, 549 (1932).

(6) Caldwell and Moyer, *Ind. Eng. Chem., Anal. Ed.*, **7**, 38 (1935).

(7) Caldwell, *THIS JOURNAL*, **57**, 96 (1935).

(8) Rossi and Scandallari, *Ann. chim. appl.*, **23**, 67 (1933).

(9) Chaudhury, *J. Phys. Chem.*, **32**, 1481 (1927).