Summary

The nine isomeric heptanes have been obtained in considerable quantity and excellent purity and have been identified with certainty. One was isolated from a natural product and the other eight were prepared by two methods, alcohol–olefin–paraffin and modified Würtz. Their boiling points, specific gravities, refractive indices and critical solution temperatures in aniline are presented, with the melting points of five of them.

YONKERS, NEW YORK

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE COLLEGE OF LIBERAL ARTS, NORTHWESTERN UNIVERSITY]

THE REACTION OF ORGANIC MERCURY COMPOUNDS WITH ORGANIC HALIDES. II[1]

BY FRANK C. WHITMORE AND E. N. THURMAN

RECEIVED NOVEMBER 21, 1928 PUBLISHED MAY 6, 1929

The present research was undertaken to study the failure of organic halides to react "metathetically" with organic mercury compounds to give lengthened carbon chains according to the equations

$$R_2Hg + R'X \longrightarrow R{-}R' + RHgX$$
$$RHgX + R'X \longrightarrow R{-}R' + HgX_2$$

The original attempt at such a reaction was partly successful.[2] Mercury diphenyl heated with benzal chloride at 150° without a solvent gave some triphenylmethane. Almost all later attempts to extend this reaction have failed. These attempts have been very scattering and no systematic study of the reaction has been made.[3]

For the present study it was decided to treat a representative variety of organic halides with a single mercury compound under comparable conditions to determine the ease of reaction and the nature of the products formed. It seemed best to use an aromatic mercury compound for the following reasons: (1) aromatic mercury compounds being only slightly volatile are less dangerously poisonous, (2) they are more stable toward heat and (3) they give products more easily identified. The most readily available compound was mercury di-*p*-tolyl.[4] In one case mercury di-*n*-butyl was also used. After the projected study had been completed, work appeared which could be interpreted as indicating mercury diphenyl

---

[1] Presented at the First National Symposium on General Organic Chemistry, Rochester, New York, December, 1925. Whitmore and Thurman, THIS JOURNAL, **45,** 1068 (1923).

[2] Kekulé and Franchimont, *Ber.*, **5,** 907 (1872).

[3] Whitmore, "Organic Compounds of Mercury," The Chemical Catalog Co., Inc., New York, **1921,** pp. 79–83.

[4] Whitmore, Frances Hamilton and Thurman, THIS JOURNAL, **45,** 1066 (1923).

to be much more reactive than mercury ditolyl.[5] Consequently, several of the reactions have been repeated with mercury diphenyl by F. L. Carnahan of this Laboratory. Mercury diphenyl was found to be only slightly more reactive than mercury ditolyl in the cases studied.

The mercury ditolyl proved to be extraordinarily unreactive in about half the cases studied. When reactions took place, the peculiarities of the mercury compound were found to differ only in degree from those of other types of bases in their reactions with organic halides. A thorough search of the literature showed that the types of bases represented by sodium hydroxide, sodium amide, sodium methylate, sodium hydride and sodium methyl, namely, aquo, ammono, alcoholo, hydro and hydrocarbo bases, often fail to give the "metathetical" reactions which would be represented by the equation

$$\mathrm{RX + MB \longrightarrow RB + MX} \qquad \text{(I)}$$

in which R is any organic radical, X is a halogen, M is a metal and B is a "basic" radical such as hydroxyl, amino, methoxyl, negative hydrogen or methyl.

A much more general reaction with all types of bases is the removal of halogen acid to form an ethylenic linkage according to the equation

$$\mathrm{R_2CXCHR_2 + MB \longrightarrow R_2C{=}CR_2 + MX + HB} \qquad \text{(II)}$$

in which the R's represent hydrogen atoms and organic radicals. A special case of the removal of halogen acid is given by the equation

$$\mathrm{2R_2CHX + 2MB \longrightarrow R_2C{=}CR_2 + 2MX + 2HB} \qquad \text{(III)}$$

The "metathetical" reactions illustrated by Equation I probably consist in the union of the two free radicals liberated by the union of M and X to form a salt, MX. Sometimes when hydrocarbo bases are used the *similar* radicals combine according to the equation

$$\mathrm{2RX + 2MR' \longrightarrow R{-}R + R'{-}R' + 2MX} \qquad \text{(IV)}$$

Another possibility with hydrocarbo bases is the disproportionation of the free radicals to form saturated and unsaturated compounds.

$$\mathrm{R_2CHCH_2X + MCH_2CHR_2 \longrightarrow R_2CHCH_3 + R_2C{=}CH_2 + MX} \qquad \text{(V)}$$

Another type of reaction given by hydrocarbo bases but not by aquo, ammono or alcoholo bases is the removal of two halogen atoms from adjacent carbon atoms.

$$\mathrm{R_2CXCXR_2 + MR \longrightarrow R_2C{=}CR_2 + RX + MX} \qquad \text{(VI)}$$

In this case R may also be hydrogen or even halogen.

In certain rare cases the metal takes the place of the halogen, $\mathrm{RX + MB \longrightarrow MR + BX}$. Usually BX is a very reactive substance capable of reacting with another molecule of MB. The net reaction thus becomes

$$\mathrm{RX + 2MB \longrightarrow RM + B{-}B + MX} \qquad \text{(VII)}$$

---

[5] Calvery, This Journal, **48**, 1009 (1926).

The organic mercury compounds studied with various halides were found to give the reactions represented by Equations I, II, III and VI. The surprising fact noted in most of the work was the very slight reactivity of the mercury compounds with halides. In most cases it was necessary to heat the solutions at 110° for about 300 hours to bring about the reactions. Even under such drastic conditions more than half of the halides failed to react and were recovered unchanged.

The general procedure was to reflux the halide with an excess of the mercury compound in dry toluene solution for about 300 hours or until reaction had taken place. In a few cases, in which a lower boiling solvent seemed desirable, carbon tetrachloride or chloroform was used.

Of the thirty-two organic halides studied eighteen gave no perceptible reaction even after refluxing for 300–350 hours in dry toluene with an excess of mercury di-*p*-tolyl. In these cases the mercury compounds and the halide were recovered unchanged. The mercury compound was in each case tested qualitatively for halogen to see if any *p*-tolylmercuric halide had been formed, thus indicating some reaction. The mercury ditolyl was free from halogen in each case.

The halides which gave *no reaction* with mercury di-*p*-tolyl on refluxing in toluene for 300–350 hours may be classified as follows: alkyl halides (*sec.*-butyl iodide, lauryl bromide), alicyclic halide (cyclohexyl bromide), unsaturated halide (allyl iodide),[6] halogenated ketone (α-bromo-camphor), halogenated esters, (ethyl dibromo-acetate, methyl α-bromo-*iso*butyrate),[7] acid halide (benzoyl chloride),[8] polyhalogen aliphatic compounds (ethylidene chloride, ethylene dibromide, tetrachloro-ethane, hexachloro-ethane), halogenated ethers (β-bromo-ethyl phenyl ether, γ-bromopropyl phenyl ether), toluene halogenated in the side chain (benzyl iodide, benzal chloride, benzo trichloride) and aromatic halide (*sym.*-trinitrophenyl iodide (picryl iodide)).[9]

[6] Carbon tetrachloride was used as solvent, as the temperature of boiling toluene decomposed the halide. No reaction took place after 120 hours' refluxing in carbon tetrachloride.

[7] No action was noticeable after refluxing in carbon tetrachloride solution for 336 hours. Refluxing for 300 hours in toluene solution appeared to give a slight reaction, as evidenced by the formation of a trace of tolylmercuric bromide.

[8] Benzoyl chloride was also refluxed with mercury diphenyl in dry benzene for 85 hours according to the directions of Calvery (ref. 5) except that an excess of the mercury compound was used. No benzophenone was obtained. The mercury diphenyl was recovered unchanged. The benzoyl chloride was unchanged. It was identified by conversion to the amide. The result of this experiment is in marked contrast to that obtained with an excess of the acid chloride.

[9] The statement appears in the literature, THIS JOURNAL, **43**, 2243 (1921), that 2,4,6-trinitrophenylmercuric chloride reacts with iodine to give a mixture of picryl iodide and "presumably" hexanitrodiphenyl. This might be taken as an indication that picryl iodide reacts with the mercury compound to give hexanitrodiphenyl. An ex-

Six of the halides reacted with mercury ditolyl to give tolylmercuric halides and *tarry products* from which no other known substance could be isolated. These halides were bromonitromethane, which reacted completely on refluxing in carbon tetrachloride for 200 hours (shorter treatments gave no more satisfactory results); acetyl iodide, which reacted vigorously with mercury ditolyl at room temperature; dibenzoylbromomethane, ω-bromo-acetophenone, phenyliodo-acetylene, iodo-acetonitrile. Two of the halides gave indefinite results and should be studied more fully. They were triphenylchloromethane and methyl α-bromo-*iso*butyrate (in toluene).

Ethyl bromomalonate reacted only partly with mercury ditolyl after refluxing in toluene for 336 hours. A considerable amount of tolylmercuric bromide was formed. The other substances found included unchanged ethyl bromomalonate, *ethyl malonate*, *p*-tolyl bromide and a small amount of an unidentified ester boiling at 205–210° (8 mm.). Since these products were hard to explain, the experiment was repeated on a larger scale using 100 g. of the ester and 335 g. of the mercury compound. The same products were obtained. The products separated accounted for 91% of the starting materials.

Five of the halides gave definite reactions. These correspond to four of the general types of reactions given by halides with the various classes of bases.

Reaction I. "Metathesis."—Diphenylbromomethane reacted with mercury di-*p*-tolyl on refluxing in toluene solution for 200 hours to give an 80% yield of diphenyl-*p*-tolylmethane. The same product was obtained when the reaction was repeated using pure *m*-xylene as solvent. This result showed that the solvent did not react with any free radical formed in the reaction. When mercury diphenyl was substituted for the tolyl compound, triphenylmethane was obtained in 90% yield. When mercury di-*n*-butyl was used, the products after refluxing for 340 hours were *n*-butylmercuric bromide, metallic mercury, a trace of mercurous bromide, a little tetraphenylethane and a 35% yield of diphenyl-*n*-butylmethane. The metallic mercury was due to the thermal decomposition of the mercury dibutyl, and the tetraphenylethane resulted from the action of mercury on the original bromide. These reactions were confirmed by side experiments.

The reaction of diphenylbromomethane with organic mercury compounds is as follows

$$(C_6H_5)_2CHBr + R_2Hg \longrightarrow R(C_6H_5)_2CH + RHgBr$$

---

periment showed that these substances do not react with each other. Consequently, the original experiment was repeated. It was found that iodine reacts normally with both 2,4,6-trinitrophenylmercuric chloride and the corresponding mercuri-*bis* compound. In the latter case 66% alcohol had to be used as a solvent instead of water. Picryl iodide was formed in both cases. No hexanitrodiphenyl was found.

This halide reacts similarly with other types of bases. Alcoholic potassium hydroxide gives the ethyl ether of benzhydrol.[10] It also reacts "metathetically" with methyl- and ethylmagnesium bromides, giving the corresponding diphenylalkylmethanes.[11] It reacts with *p*-tolylmagnesium bromide to give good yields of *p*-tolyldiphenylmethane.[12]

Reaction II. Removal of HX.—*Tert.*-butyl bromide reacted almost quantitatively with mercury di-*p*-tolyl in carbon tetrachloride after refluxing for 340 hours. The products were tolylmercuric bromide, toluene and *iso*butylene. Mercury diphenyl gave similar results but seemed to react slightly more rapidly than the tolyl compound.

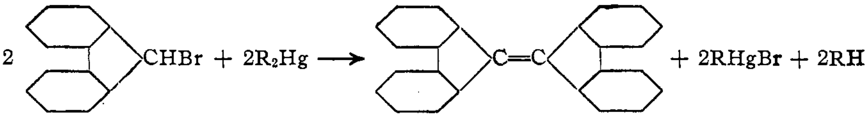
Tert.-amyl iodide gave similar results with mercury ditolyl and mercury diphenyl. When an excess of the iodide was used with mercury ditolyl, the products were mercuric iodide, toluene and trimethylethylene.

The tertiary halides react as follows

$$R_2CXCH_2R + R_2'Hg \longrightarrow R_2C{=}CHR + R'HgX + R'H$$

Tertiary halides react with other types of bases to give olefins.[13] These reactions differ from those with the mercury compounds in giving some of the "metathetical" product as well as the olefin. A similar reaction was obtained with mercury ditolyl and 1-bromo-1,1,2-tricarbethoxyethane, $(C_2H_5O_2C)_2C{=}CHCO_2C_2H_5$, being formed.

Reaction III. Removal of HX through "Methylene Dissociation."—Diphenylenebromomethane (9-bromofluorene), although it differs so slightly from diphenylbromomethane, reacts entirely differently with bases. After refluxing with mercury ditolyl and mercury diphenyl in toluene for 300 hours, the products isolated were the aryl mercuric bromides and *bis*-diphenylene ethylene.



To make sure that the mercury compound was necessary for the formation of the ethylene compound, 9-bromofluorene was refluxed alone in toluene for 120 hours. The halide was recovered unchanged. 9-Bromofluorene gives an entirely similar reaction with alcoholic potassium hydroxide.[14]

Reaction VI. Removal of Bromine.—Stilbene dibromide reacts with

---

[10] Nef, *Ann.*, **298**, 202 (1897).

[11] Späth, *Monatsh.*, **34**, 1965 (1915).

[12] Boudroux, *Bull. soc. chim.*, [4] **17**, 318 (1915); *Ann. chim.*, [9] **5**, 580 (1916).

[13] Aquo and alcohol bases. Lazinsky and Swodkowsky, *Chem. Zentr.*, I, 1119 (1903); Nef, *Ann.*, **309**, 1381 (1899); Kindakow, *J. Russ. Phys.-Chem. Soc.*, **19**, 301 (1887); Beilstein-Präger-Jacobson, 4th ed., Vol. I, p. 138. Hydrocarbo bases: Späth, *Monatsh.*, **34**, 1965 (1913); Markownikoff, *Ber.*, **32**, 1445 (1899); **33**, 1905 (1900); Steinkopf, *Ann.*, **413**, 315 (1916).

[14] Thiele, *ibid.*, **211**, 1 (1896); **376**, 278 (1910).

mercury ditolyl after refluxing in toluene for 340 hours to give the tolylmercuric bromide, tolyl bromide and stilbene.

$$C_6H_5CHBrCHBrC_6H_5 + 2R_2Hg \longrightarrow C_6H_5CH{=}CHC_6H_5 + 2RBr + 2RHgBr$$

The tendency of stilbene dibromide to lose bromine is shown by its reactions with a number of other basic substances. Phenylmagnesium bromide gives stilbene and diphenyl.[15] Sodium malonic ester gives a quantitative yield of stilbene and ethane-tetracarboxylic ester.[16] Potassium sulfhydrate in a sealed tube at 100° gives large quantities of stilbene.[17] Sodium benzene sulfinate and sodium phenylmercaptide give stilbene and diphenylsulfone and diphenyl disulfide, respectively.[18] On the other hand, stilbene dibromide does not react with sodium ethylate, with alcoholic ammonia or with aniline and only slightly with metallic sodium. With alcoholic potassium hydroxide at room temperature it loses a molecule of hydrogen bromide and forms monobromostilbene.[19]

A study of the reactions of mercury di-*p*-tolyl and of mercury diphenyl with organic halides shows that they are far less reactive than the other types of bases. The use of higher temperatures and the omission of solvents would probably speed up the reactions appreciably. Most of the halides used would not withstand such severe conditions, however. When mercury compounds can be made to react with organic halides, the results are reasonably like those obtained with other types of bases, especially those of the hydrocarbo type.

Experimental Part

Only a few typical experiments will be given in detail to indicate the method of procedure.

Reaction of *sec.*-Butyl Iodide with Mercury Di-*p*-tolyl.—A mixture of 3.5 g. (1 mol) of *sec.*-butyl iodide (b. p. 119–122°), 12 g. (2 mols) of mercury ditolyl and 50 cc. of dry carbon tetrachloride (b. p. 76–77°) was refluxed for 380 hours. The condenser was provided with a trap containing bromine to absorb any unsaturated gaseous products. After refluxing, the contents of the trap were entirely soluble in dilute sodium hydroxide. This indicated that no butylene had been formed. The mixture was cooled and filtered. The precipitate of unchanged mercury ditolyl was washed with carbon tetrachloride and dried (wt., 10.4 g.). A sodium fusion test for halogen gave only a slight opalescence, showing that not more than a trace of tolylmercuric iodide was formed.

The filtrate was concentrated to about 10 cc., cooled and filtered from more mercury ditolyl. Most of the filtrate distilled at 76–80°. Finally, unchanged butyl iodide distilled at 117–122°. No reaction had occurred.

The experiment was repeated with the same weights of material in boiling toluene for 340 hours. No reaction occurred.

---

[15] Kohler and Johnstin, *Am. Chem. J.*, **33**, 42 (1905).

[16] Bischoff, *Ber.*, **21**, 2071 (1888).

[17] Auwers, *ibid.*, **24**, 1779 (1891).

[18] Otto, *J. prakt. Chem.*, [2] **33**, 3 (1896).

[19] Wislicenus, *Ber.*, **28**, 2699 (1895).

TABLE IA

OTHER HALIDES WHICH GAVE NO REACTION WITH AN EXCESS OF MERCURY DI-*p*-TOLYL

No.	Halide	G.	Hg cpd., g.
1	Lauryl bromide, $CH_3(CH_2)_{10}CH_2Br$, b. p. 185–187° (45 mm.)	8	24
2	Ethylidene chloride, CH_3CHCl_2, b. p. 56–58°	23	22.8
3	Ethylene bromide, CH_2BrCH_2Br, b. p. 130–132°	3	12
4	Tetrachloro-ethane, $CHCl_2CHCl_2$, b. p. 144–146°	4	18
5	Hexachloro-ethane, CCl_3CCl_3, m. p. 185–186°	3	8.7
6	Allyl iodide, $CH_2{=}CHCH_2I$, b. p. 101–103°	3.5	13.8
7	Benzyl iodide,[b] $C_6H_5CH_2I$, m. p. 27–30°	5	17.5
8	Benzal chloride, $C_6H_5CHCl_2$	10	47
9	Benzo trichloride, $C_6H_5CCl_3$, b. p. 212–214°	4	15.6
10	Cyclohexyl bromide, $C_6H_{11}Br$, b. p. 59–60° (10 mm.)	20	94
11	β-Bromo-ethylphenyl ether, b. p. 125–130° (20 mm.)	20	76
12	γ-Bromopropylphenyl ether, b. p. 127° (18 mm.)	20	70
13	Benzoyl chloride, C_6H_5COCl, b. p. 197°	3	16.2
14	Benzoyl chloride, C_6H_5COCl, b. p. 197°	3.5	109.0[a]
15	Ethyl dichloro-acetate, $Cl_2CHCOOC_2H_5$, b. p. 150–154°[c]	4	19.6
16	Methyl α-bromo-*iso*butyrate,[d] $(CH_3)_2CBrCOOCH_3$, b. p. 67° (37 mm.)	15	63
17	α-Bromocamphor, m. p. 75°	10	33
18	*Sym.*-trinitrophenyl iodide, m. p. 159–160°	5.3[e]	3
19	*Sym.*-trinitrophenyl iodide, m. p. 159–160°	5.3	3

[a] Mercury diphenyl was used in this experiment.

[b] The benzyl iodide was prepared by the action of benzyl chloride with sodium iodide in absolute methyl alcohol. The product was freed from alcohol by standing in a vacuum desiccator over solid potassium hydroxide for two weeks. A trace of free iodine was removed by shaking the melted iodide with a little mercury. The product was almost colorless and melted at 27–30°.

[c] No product obtained with a boiling point appreciably higher than those of the solvent and the halide.

[d] When the reaction was carried out in toluene considerable tolylmercuric bromide was formed. The methyl ester of α-methylacrylic acid, which may have been formed, was not detected.

[e] In this experiment the molar ratio of halide to mercury compound was 2:1 instead of the ratio 1:2 used in the other experiments.

TABLE IB

EXPERIMENTAL DATA

No.	Dry toluene, cc.	Refluxing, hours	Hg cpd. recov., g.	Halide recovered, g.	Remarks
1	60	240	23.4	6 b. p. 151–153° (20 mm.)	No dodecylene
2	125[a]	360	20.7	. . .	[b]
3	50	350	11.1	1.1 b. p. 130°	[b,c]
4	70	340	14.8	B. p. 135°	[b,c]
5	50	385	6.8	2 m. p. 176–181°	Trace of metallic Hg
6	50[a]	120	[d]	2.5 b. p. 95–101°	[b,c]
7	100	236	. .	2.4 b. p. 105–107° (20 mm.)	[e]
8	250	336	. .	. . .	[b]
9	60	336	. .	3 b. p. 190–200°	[b]
10	250	335	92.3	. . .	No cyclohexene[b]

TABLE IB (*Concluded*)

No.	Dry toluene, cc.	Refluxing, hours	Hg cpd. recov., g.	Halide recovered, g.	Remarks
11	200	336	74.2	16.7 b. p. 125–127° (24 mm.)	. . .
12	200	336	. .	16 b. p. 135–137° (19 mm.)	. . .
13	85	288	. .	B. p. 146–187°	[b]
14	100	85[f]	7.4	. . .	[b]
15	85	336	. .	B. p. 155–160°	[b]
16	200[a]	430	62	12	. . .
17	125	336	31.3	6.5 b. p. 140–147° (29 mm.) M. p. 74°	Metallic Hg (1.5 g.)[b]
18	100[a]	75	M. p. 235–238°	M. p. 162–164°	No HgI_2 formed
19	100	66	4.5	2	Dark tar, 1 g. No HgI_2

[a] Dry carbon tetrachloride was used as solvent in this experiment.

[b] No product obtained with a boiling point appreciably higher than those of the solvent and the halide.

[c] Bromine trap used. Contents entirely soluble in dilute sodium hydroxide, indicating that no olefin was formed during the refluxing.

[d] In some of the earlier experiments the recovered mercury ditolyl was not dried and weighed.

[e] The condenser was protected from moisture by a calcium chloride tube.

[f] Dry benzene was used as solvent in this experiment.

The next group of halides to be discussed reacted with mercury ditolyl but gave tarry products which could not be purified.

TABLE II

REAGENTS AND PRODUCTS

Halide	G.	Hg compd., g.	Dry solvent, cc.
Bromonitromethane, $BrCH_2NO_2$, b. p. 146–147°	25	125	250[a]
Acetyl iodide, CH_3COI, b. p. 100–102°	20	90	400[b]
Bromo-acetophenone, $C_6H_5COOCH_2Br$	10	38	150[c]
Bromo-acetophenone, $C_6H_5COOCH_2Br$	10	38	200[a]
Dibenzoylbromomethane, $(C_6H_5CO)_2CHBr$	5	12.3	50[c]
Phenyliodo-acetylene, $C_6H_5C{\equiv}CI$	8[d]	3.5	50[c]
Iodo-acetonitrile, ICH_2CN	20	92	300[c]

[a] Dry carbon tetrachloride. [b] Dry chloroform. [c] Dry toluene. [d] The molar ratio of halide to mercury in this experiment was 1:1 instead of the usual 1:2.

TABLE IIB

TIMES, PRODUCTS AND REMARKS

Refluxing, hours	Products identified	Remarks
200	C_7H_7HgBr	Tarry oil, 26 g. No unchanged $BrCH_2NO_2$
200[a]	C_7H_7HgI, HI and I_2	Black tar, 4 g.
336	C_7H_7HgBr, 1.5 g. of Hg	No odor; 10.5 g. "shellac," 1 g. of substance, m. p. 86–95°
240	Unchanged materials	Odor and lachrymation
70	C_7H_7HgBr	Tar, 7 g. Crystals, 0.2 g., m. p. 120–122°
44	HgI_2, C_7H_7HgI	Red gum. No $C_6H_5{\equiv}CCI$
310	C_7H_7HgI, 6 g. ICH_2CN	Tar

[a] The mixture was allowed to stand at room temperature (about 20°).

Reaction of Ethyl Bromomalonate with Mercury Di-*p*-tolyl.—A mixture of 100 g. (1 mol) of ethyl bromomalonate (b. p. (20 mm.) 130–132°), 335 g. (2 mols) of mercury di-*p*-tolyl (m. p. 235–239°, free from iodide) and 950 cc. of dry toluene was refluxed for 336 hours. The mixture was cooled and filtered from a mixture of unchanged mercury ditolyl and tolylmercuric bromide. This was dried; wt., 300 g. The filtrate was concentrated by distillation to 400 cc. (b. p. of distillate 110–115°). The residual oil gave more of the mixed mercury compound on cooling. This was removed by filtration and dried; wt., 9 g. The filtrate was further concentrated to 150 cc. and filtered from more of the mercury compound; wt., 6 g. This filtrate was distilled at 58–60 mm. Toluene first came over at 44–55°. The temperature then rose rapidly to 125° and then more slowly to 149°. About half of the oil distilled at 140–149° (58–60 mm.). The liquid was water white; wt., 56 g. When the temperature was carried above 150°, considerable mercury ditolyl began to distil. The heating was then stopped. The residual oil solidified to a mush of brown crystals; wt., 42 g.

The oil which distilled at 140–149° (58–60 mm.) was distilled at 38–40 mm. Three fractions were obtained as follows: b. p. 100–116° (mostly 107–116°), wt. 18 g.; b. p. 115–130° (mostly 123–127°), wt. 10.7 g.; b. p. 137–145°, wt. 23 g. About 3 g. of charred residue remained in the flask.

The first fraction was redistilled at atmospheric pressure. It boiled at 180–205° (mostly at 190–195°, b. p. of ethyl malonate 198°). The entire fraction (16 g.) was treated with 40 cc. of concd. ammonium hydroxide. Part of the material was insoluble and this was separated; wt., 4 g. (b. p. 183–185°). It gave a qualitative test for bromine and had the characteristic odor of *p*-bromotoluene. The ammoniacal solution deposited white crystals on evaporation, m. p. 168–169°. A mixture with pure malonamide (m. p. 170–171°) melted at 169–171°.

The third fraction was unchanged ethyl bromomalonate, as shown by its b. p. and by conversion into 1,1,2,2-tetracarbethoxyethylene. Two g. of the oil, 6 g. of anhydrous potassium carbonate and 25 cc. of benzene were refluxed for twenty-four hours. The product melted at 55–57°. The melting point was not lowered by the addition of a known sample of the ester melting at 58°.

The second fraction was not separated into its components. It undoubtedly contained ethyl malonate, ethyl bromomalonate and *p*-bromotoluene.

The 42 g. of residue from the first distillation was too viscous to be filtered. Repeated extractions with alcohol left a residue of impure mercury ditolyl; wt., 20 g. After one crystallization from benzene it melted at 226–238°. The alcohol extracts gave a thick, viscous oil which contained organic mercury compounds. An attempt to distil this at 8-mm. pressure was only partly successful. There was much charring in the flask. About 10 g. of oil distilled at 195–230° (8 mm.), mostly at 205–210°. It contained some mercury ditolyl and tolylmercuric bromide in suspension. The liquid portion was perhaps 1,1,2,2-tetracarbethoxyethylene, b. p. 201° (2 mm.).

Reaction of Diphenylbromomethane and Mercury Di-*p*-tolyl.—Preliminary experiments using carbon tetrachloride, toluene, xylene and tetrachloro-ethane as solvents showed that a reaction took place.

A mixture of 50 g. (1 mol) of diphenylbromomethane (b. p. 180–182° (17 mm.), m. p. 40–42°), 120 g. (2 mols) of mercury di-*p*-tolyl and 250 cc. of dry toluene was refluxed for 170 hours. The mixture was cooled and filtered from 110 g. of mixed mercury compounds. The filtrate was concentrated to 75 cc. by distillation, cooled and filtered from 5 g. of mercury compounds. The filtrate was freed from toluene by distillation. The residual oil (wt., 43 g.) solidified on cooling. It gave no test for bromine (sodium fusion). Recrystallization from alcohol gave white needles, m. p. 64–66°. Part of the material was distilled at atmospheric pressure, b. p. above 360°. The distillate solidified and melted at 70°. The melting point was not lowered by mixing with a known sample of *p*-tolyldiphenylmethane (m. p. 71°) made from benzhydrol and toluene with stannic chloride. The product was further identified by oxidation to form *p*-carboxytriphenylcarbinol, m. p. 196–200°.[20]

Reaction in *m*-Xylene.—A mixture of 47 g. (1 mol) of diphenylbromomethane, 117.5 g. (2 mols) of mercury di-*p*-tolyl and 400 cc. of *m*-xylene (Eastman Kodak Co., b. p. 138–139°) was refluxed for 200 hours. The mixture was treated as in the preceding experiment. The crude *p*-tolyldiphenylmethane boiled at 225–232° (18 mm.). The distillate on recrystallization from a mixture of acetic acid and ether melted at 68–78°. The melting point was not lowered by addition of some of the known compound. No evidence of the formation of *m*-xylyldiphenylmethane was found.

Reaction of Diphenylbromomethane with Mercury Di-*n*-butyl.—A mixture of 20 g. (1 mol) of the halide, 50 g. (2 mols) of mercury di-*n*-butyl (b. p. 225–230°) and 100 cc. of dry toluene was refluxed for 340 hours. The top of the condenser was connected with a flask of concd. nitric and sulfuric acids to destroy any traces of organic mercury compounds which might escape from the condenser. The reaction mixture was separated as usual. The products obtained were 5 g. of metallic mercury, 15 g. of unchanged mercury di-*n*-butyl, 25 g. of *n*-butylmercuric bromide, 2 g. of mercurous bromide, 2 g. of tetraphenylethane and 6 g. of oil boiling at 277–278° (probably diphenyl-*n*-butylmethane).

Reaction of Diphenylbromomethane with Mercury.—Two g. of the halide, 15 g. of metallic mercury and 20 cc. of dry toluene were refluxed for twenty-four hours. The hot solution was filtered from a residue of mercury and mercurous bromide. On cooling it deposited white crystals of *sym.*-tetraphenylethane, m. p. 208–209° corr.; wt., 1 g. The melting point was not lowered by addition of known tetraphenylethane made from diphenylbromomethane and zinc dust.

Reaction of Diphenylbromomethane with Mercury Diphenyl.—A mixture of 10 g. (1 mol) of diphenylbromomethane, 21.72 g. (2 mols) of mercury diphenyl and 50 cc. of dry toluene was refluxed for 170 hours. The mixture was allowed to cool and the precipitated mercury compounds were filtered off and washed with a little toluene and dried; wt., 15 g. The filtrate was concentrated *in vacuo*. The residue solidified on cooling; wt., 15 g. Extraction with petroleum ether (b. p. 30–60°) left 6 g. of mixed mercury compounds. The soluble portion was found to be triphenylmethane. It crystallized from petroleum ether on standing, m. p. 85–90°. Recrystallization from petroleum ether raised the melting point to 88–90°. (Melting point of triphenylmethane, 92°.) The identity of the material was further established through the test given by Mulliken.[21] The material was nitrated by dissolving 0.1 g. in fuming nitric acid without the application of heat. The mixture was diluted with water and the precipitate filtered off. The precipitate was dissolved in 10 cc. of glacial acetic acid and reduced by the successive additions of small quantities of zinc dust to the hot solution until the strong red color that at first appeared was nearly discharged. A portion of the supernatant liquid was decanted and a little lead dioxide added. A very intense fuchsin-red color (pararosaniline) formed at once, indicating that the substance tested was triphenylmethane. The yield of triphenylmethane was about 90%.

Reaction of *tert.*-Butyl Bromide with Mercury Di-*p*-tolyl.—1. A mixture of 10 g. (1 mol) of *tert.*-butyl bromide (b. p. 72–74°), 55 g. (2 mols) of mercury di-*p*-tolyl and 200 cc. of dry carbon tetrachloride was refluxed for 340 hours. The top of the con-

---

[20] Bistrzycki and Gyr, *Ber.*, **37**, 657 (1904).

[21] Mulliken, "Identification of Pure Organic Compounds," John Wiley and Sons, Inc., New York, Vol. I, p. 177.

denser was connected with a trap containing 85% sulfuric acid. After twenty-four hours an oily layer separated above the acid. This was probably tri-*iso*butylene.

The reaction mixture was cooled and filtered from 53 g. of a mixture of unchanged mercury ditolyl and tolylmercuric bromide. The filtrate was concentrated to 90 cc. by distillation (b. p. 76–77°). The residue was cooled and filtered from 0.5 g. of mercury compounds. It was further concentrated to 15 cc. (b. p. of distillate, 76–80°). Cooling gave 0.5 g. more mercury compounds. The filtrate on distillation gave 10 cc. of product boiling at 80–110°. The temperature then rose rapidly to 155°, at which point charring took place. Less than 1 cc. of high-boiling oil was obtained. Treatment of the main distillate with fuming sulfuric and nitric acids proved the presence of toluene. The melting point of the nitration product was 69–70° (m. p. of 2,4-dinitrotoluene, 70.5°).

2. The experiment was repeated using 66% sulfuric acid in the trap. No oily layer separated. At the end of 200 hours the contents of the trap was neutralized with sodium hydroxide and distilled. The distillate gave the red ring test for *tert.*-butyl alcohol.[22] This proved that *iso*butylene was formed in the reaction.

Reaction of *tert.*-Butyl Bromide with Mercury Diphenyl.—A mixture of 5 g. (1 mol) of *tert.*-butyl bromide, 24.9 g. (2 mols) of mercury diphenyl and 100 cc. of dry carbon tetrachloride was refluxed for 340 hours. A trap containing 70% sulfuric acid was used to catch any unsaturated gases. The reaction mixture was cooled and filtered from 12 g. of mercury compounds. The filtrate was distilled (75–81°), leaving a residue of 15 g. of mercury compounds in the flask. The distillate on treatment with fuming nitric and fuming sulfuric acids gave *m*-dinitrobenzene melting at 88–89°. The sulfuric acid in the trap was diluted with water and neutralized with sodium hydroxide solution. It gave the test for *tert.*-butyl alcohol, indicating that *iso*butylene had been formed.

Reaction of *tert.*-Amyl Iodide with Mercury Di-*p*-tolyl.—A mixture of 6.5 g. (2 mols) of the iodide, 6.3 g. (1 mol) of the mercury compound and 45 cc. of dry carbon tetrachloride was refluxed for seventeen hours. Red crystals of mercuric iodide separated. The cooled mixture was filtered from 7.2 g. of mercuric iodide and tolylmercuric iodide. Distillation of the filtrate gave 3 cc. of a product boiling at 83–113°. This was mainly toluene, as was proved by conversion to dinitrotoluene (m. p. 68–70°). A small amount of unchanged amyl iodide was recovered.

Reaction of *tert.*-Amyl Iodide with Mercury Diphenyl.—A mixture of 6.5 g. (2 mols) of *tert.*-amyl iodide, 5.7 g. (1 mol) of mercury diphenyl and 45 cc. of chloroform was refluxed for seventeen hours. A trap containing 70% sulfuric acid was used to catch any volatile unsaturated compounds. The mixture of unchanged mercury diphenyl and phenylmercuric iodide left weighed 5.4 g. The contents of the trap gave a small amount of *tert.*-amyl alcohol. Benzene was identified as *m*-dinitrobenzene (m. p. 88–89°). A small amount of the amyl iodide was recovered unchanged. No mercuric iodide was formed.

Preparation of 1-Bromo-1,1,2-tricarbethoxyethane (Bromo-ethenyltricarboxylic Ester).—Ethenyltricarboxylic ester was prepared from ethyl chloro-acetate and sodium malonic ester. It boiled at 163–165° (17 mm.). It was brominated without a solvent. The bromo ester boiled at 175–177° (15 mm.); yield, 76%.

Anal. Subs., 0.4092, 0.3565: AgBr, 0.2348, 0.2032. Calcd. for $C_{11}H_{17}O_6Br$: Br, 24.6. Found: Br, 24.3, 24.4.

Reaction of 1-Bromo-1,1,2-tricarbethoxyethane with Mercury Di-*p*-tolyl.—A mixture of 25 g. (1 mol) of the ester, 58.8 g. (2 mols) of the mercury compound and 200 cc. of dry toluene was refluxed for 288 hours. The reaction mixture was dark brown and a small globule of mercury had appeared. The cooled mixture was filtered to

---

[22] Mulliken, ref. 21, Vol. I, p. 171.

separate 48.2 g. of mercury ditolyl and tolylmercuric bromide. The filtrate was concentrated to 25 cc. (b. p. of distillate mostly 110–112°, a little up to 120°). The residue on cooling gave 4.8 g. of mixed mercury compounds. The filtrate freed from solvents weighed 16 g. It was twice distilled at 12-mm. pressure. A small amount was obtained which boiled at 157–159° (12 mm.). This was 1,1,2-tricarbethoxyethylene (ethenetricarboxylic ester).[23]

Reaction of 9-Bromofluorene with Mercury Di-*p*-tolyl.—A mixture of 4 g. (1 mol) of the halide (m. p. 102–103°), 12.4 g. (2 mols) of the mercury compound and 60 cc. of dry toluene was refluxed for 310 hours. The cooled mixture was filtered, leaving 11.1 g. of mercury ditolyl and tolylmercuric bromide. The filtrate was concentrated to 10 cc. (b. p. of distillate 109–112°) and cooled. It was filtered from 1.1 g. of mixed mercury compounds. The filtrate was evaporated to a tarry mass; wt., 3 g. This was dissolved in benzene and treated with a concd. benzene solution of picric acid. On spontaneous evaporation beautiful crystals of the picrate of *bis*-diphenylene-ethylene separated, m. p. 176–177°.

Action of Heat on 9-Bromofluorene.—Three g. of the halide and 25 cc. of dry toluene were refluxed for 120 hours. The original bromide was recovered unchanged. No trace of the orange ethylene compound was noted.

Reaction of 9-Bromofluorene with Mercury Diphenyl.—A mixture of 4 g. (1 mol) of the halide, 11.2 g. (2 mols) of mercury diphenyl and 60 cc. of dry toluene was refluxed for 238 hours. The mixture turned deep orange. It was cooled and filtered from the mixed mercury compounds. The toluene was distilled and the residue was extracted with petroleum ether (b. p. 30–60°). Evaporation of the solvent left an orange red oil which consisted mainly of *bis*-diphenylene-ethylene.

Reaction of Stilbene Dibromide with Mercury Di-*p*-tolyl.—A mixture of 4 g. (1 mol) of the halide (m. p. 226–229°), 10 g. (2 mols) of the mercury compound and 70 cc. of dry toluene was refluxed for 340 hours. The mixture was cooled and filtered from unchanged mercury ditolyl and tolylmercuric bromide. The toluene was removed by distillation *in vacuo*. The residue was extracted with absolute ethyl alcohol. Evaporation of the extracts gave crystals of m. p. 103–115°; recrystallization from ligroin raised the m. p. to 113–115°. This was impure stilbene. Bromination of a sample gave stilbene dibromide, m. p. 224–225°. A small amount of oil having the odor of *p*-bromotoluene was obtained from the mother liquors of the crude stilbene.

Treatment of Mercuri-*bis*-2,4,6-trinitrophenyl with Picryl Iodide.—One g. (1 mol) of the mercury compound[24] (m. p. 271°), 1.1 g. (2 mols) of picryl iodide and 25 cc. of acetone were refluxed for nineteen hours. The mixture was evaporated spontaneously. Nothing but the original substances could be found in the mixture.

Reaction of 2,4,6-Trinitrophenylmercuric Chloride with Iodine.—One g. (1 mol) of the mercury compound, 0.6 g. (1 mol) of iodine, 4.5 g. of sodium iodide and 25 cc. of water were refluxed for two hours. The mixture was filtered. The residue was completely soluble in ether, m. p. 164°. The melting point was not lowered by addition of picryl iodide. The filtrate contained sodium mercuric iodide, sodium iodide and sodium chloride. No hexanitrodiphenyl was formed.

Reaction of Mercuri-*bis*-2,4,6-trinitrophenyl with Iodine.—A mixture of 0.6 g. (1 mol) of the mercury compound, 0.6 g. (2.2 mols) of iodine and 30 cc. of 66% alcohol was refluxed for eight hours. Practically all of the iodine had reacted. Less than 0.1 g. of unchanged mercury compound was recovered. Evaporation gave needles of picryl iodide melting at 162–163°. A mixture with the known substance melted at 162–164°. The other product was mercuric iodide.

---

[23] Ruhemann and Cunnington, *J. Chem. Soc.*, **73**, 1012 (1898).

[24] Kharasch, This Journal, **43**, 2242 (1921).

Summary

1. Thirty-two organic halides of widely varying types have been treated with mercury di-*p*-tolyl under very vigorous conditions.
2. Some of the halides have also been treated with mercury di-*n*-butyl and mercury diphenyl.
3. In general the mercury compounds are extraordinarily unreactive toward the halides studied.
4. In the cases of the five halides which gave definite reactions the behavior of the mercury compounds was analogous to that of other types of bases with the same halides.
5. It has been shown that 2,4,6-trinitrophenylmercuric compounds react normally with iodine.

EVANSTON, ILLINOIS

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, YALE UNIVERSITY]

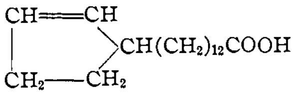
NEW PHENOLIC COMBINATIONS OBTAINED BY COUPLING CHAULMOOGRIC ACID WITH RESORCINOL[1]

BY W. S. HINEGARDNER[2] AND TREAT B. JOHNSON

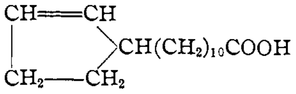
RECEIVED DECEMBER 5, 1928 PUBLISHED MAY 6, 1929

Chaulmoogric (I) and hydnocarpic (II) acids[3] in the form of their salts and esters are extensively used in leprosy therapy.[4] Notwithstanding the fact, however, that many cures have been effected through their application, many objections have been raised to their prolonged therapeutic use, and there is still much to be desired before an ideal germicidal agent is found for the treatment of patients suffering from leprosy. New compounds of high germicidal power and low toxicity are very much desired for clinical work in the study of methods to eradicate this disease. In view of the striking bactericidal properties of alkylresorcinols and the established clinical success of hexylresorcinol[5] it seemed desirable to prepare

I



II



---

[1] Constructed from a dissertation presented by Wilbie S. Hinegardner to the Faculty of the Graduate School of Yale University, June, 1927, in candidacy for the degree of Doctor of Philosophy.

[2] Holder of the Richard Wrenshall Research Prize in 1925–1926.

[3] Barrowcliff and Power, *J. Chem. Soc.*, **91**, 557 (1907); Shriner and Adams, THIS JOURNAL, **47**, 2727 (1925).

[4] Rogers, *Brit. Med. J.*, 4, 550 (1916); **5**, 277 (1917); McDonald and Dean, *J. Am. Med. Assoc.*, **76**, 1470 (1921); Muir, *Indian J. Med. Research*, **11**, 543 (1923).

[5] Johnson and Lane, THIS JOURNAL, **43**, 348 (1921); Dohme, Cox and Miller, *ibid.*, **48**, 1688 (1926); V. Leonard, *Science*, **62**, 408 (1925); Leonard and Feirer, *Surgery Gynecol. Obstet.*, **45**, 603–611 (1927).