[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE COLLEGE OF LIBERAL ARTS OF NORTHWESTERN UNIVERSITY AND OF THE SCHOOL OF CHEMISTRY AND PHYSICS OF THE PENNSYLVANIA STATE COLLEGE]

The Reaction of Iodine Monochloride with Certain Organic Mercury Compounds

BY FRANK C. WHITMORE AND M. A. THORPE[1]

Although the reaction with iodine is one of the oldest and most widely used reactions of organic mercury compounds,[2] the analogous reaction with iodine monochloride has been neglected. The literature contains only one reference to it, namely, the action of iodine chloride with mercurated camphors to give diiodocamphor.[3]

The present study was undertaken to determine whether iodides or mixtures of iodides and chlorides are formed and to determine the feasibility of using iodine monochloride in place of iodine for the preparation of iodo compounds from organic mercury compounds.[4] The mercury compounds studied correspond to the various parts of Kharasch's table of "relative electronegativity."[5] The mercury compounds selected contained the groups, *p*-anisyl-, β-naphthyl-, *p*-tolyl-, phenyl- and β-phenylethyl-. In all except the last, yields of over 90% of the iodo compounds were obtained. No trace of organic chloro compound was detected. Phenylethylmercuric chloride gave a mixture of phenylethyl iodide and phenylethyl chloride. The latter was probably formed by the action of iodine chloride on the phenylethyl iodide. This is like the action of ethyl iodide with iodine monochloride.[6]

The solvent had a marked effect on the reaction of iodine monochloride with the organic mercury compounds. In general, water was the best medium for the reactions in spite of the extreme insolubility of the mercury compounds in it.

Experimental

Iodine monochloride was prepared directly from the elements.[7]

In studying solvents for use with the iodine monochloride it was observed that widely varying heats of solution were given with different solvents. In experiments under essentially identical conditions the addition of 1 cc. of iodine monochloride to 25 cc. of solvent at 25° gave the following rises in temperature in degrees centigrade: ethylene chloride, 0.2; chlorobenzene, 0.6; distilled water, 2.0; benzene (C. P.), 2.1; acetic acid (glacial), 2.7; hydrochloric acid (C. P.), 3.3; ether (anhydrous), 5.0; ether (U. S. P.), 5.9; ethanol (absolute), 7.5; ethanol (95%), 5.3; chloroform, −1.3; carbon

---

[1] Presented in partial fulfilment of the requirements for the Ph.D. degree at the Pennsylvania State College.

[2] Whitmore, "Organic Compounds of Mercury," Chemical Catalog Co., N. Y., 1921, pp. 67–73.

[3] Marsh, *J. Chem. Soc.*, **97**, 2413 (1910).

[4] *Cf.* Whitmore and Hanson, "Organic Syntheses," 1925, Vol. V, p. 37.

[5] Kharasch and Flenner, THIS JOURNAL, **54**, 674 (1932).

[6] Friedel and Silva, *Bull. soc. chim.*, [2] **17**, 532 (1871).

[7] Jackson and Whitmore, THIS JOURNAL, **37**, 1528 (1915).

tetrachloride, −2.7. Each of these figures is the average of several determinations. The results are given merely as an indication of phenomena which should perhaps be studied with greater refinement.

_p_-Anisylmercury Compounds.—_p_-Bromoanisole, b. p. 215–217°, was prepared in 88% yield from anisole and phosphorus pentabromide. The bromo compound was converted to di-_p_-anisylmercury, m. p. 200–202°, in 48% yield by treatment with 3% sodium amalgam.[8]

Action of Iodine Monochloride with Di-_p_-anisylmercury. (a) In Carbon Tetrachloride.—A solution of 8.3 g. (2 mols) of iodine monochloride in 100 cc. of dry carbon tetrachloride was added with stirring during two hours to a suspension of 10.7 g. (1 mol) of di-_p_-anisylmercury in 250 cc. of the same solvent. The mercuric chloride was filtered off and the solution was shaken with sodium thiosulfate solution to remove a trace of free iodine. The solution was washed with water and the excess solvent removed by distillation. The residue crystallized giving 11.5 g. of _p_-iodoanisole, m. p. 50–51°, a yield of 95%. The melting point of the pure substance is given as 51–52°.

(b) **In Water.**—Iodine monochloride (8.3 g., 2 mols) was added with stirring during three hours to a suspension of 10.7 g. (1 mol) of the mercury compound in 100 cc. of water boiling under a reflux condenser. The mixture was cooled to 60° and treated with 50 cc. of carbon tetrachloride, separated and washed with several 20-cc. portions of the solvent. The carbon tetrachloride solution was worked up as before to give 12.1 g. of crude _p_-iodoanisole. Crystallization from 100 cc. of 95% alcohol gave 11.5 g. of the pure substance, m. p. 50–51°.

Action of Iodine Monochloride with _p_-Anisylmercuric Chloride.—The mercury compound was made from mercuric chloride and the mercury-bis compound in boiling alcohol in the usual way (Ref. 2, p. 65).

A solution of 1.3 g. (1 mol) of iodine monochloride in 50 cc. of carbon tetrachloride was added slowly with stirring to a suspension of 2.6 g. (1 mol) of _p_-anisylmercuric chloride in 50 cc. of the solvent. The product was 1.7 g. of _p_-iodoanisole, m. p. 50–51°, a yield of 95%.

β-Naphthylmercuric Chloride.—The mercury compound, m. p. 237–238°, was made from β-naphthylamine in 60% yield.[9] A solution of 5.6 g. (1 mol) of iodine monochloride in 50 cc. of 95% alcohol was added during three hours with stirring to a refluxing suspension of 12 g. (1 mol) of β-naphthylmercuric chloride in 100 cc. of the same solvent. The clear solution was evaporated to half its volume under reduced pressure and then was allowed to evaporate spontaneously. The residue was slightly yellow and contained a few very small red crystals. It was washed with 150 cc. of water to remove mercuric chloride. The pale yellow residue was dried in a desiccator and crystallized twice from 50 cc. of absolute ethyl alcohol. The resulting β-iodonaphthalene, m. p. 53–54°, weighed 8.0 g., a yield of 95%. The pure substance melts at 54.5°.

_p_-Tolylmercuric Chloride.—The mercury compound, m. p. 230–232°, was prepared from _p_-toluene sulfonyl chloride.[10] The experiments with this substance are summarized in Table I. In each case the iodine monochloride or its solution was added to the mercury compound with efficient stirring.

Diphenylmercury.—This was prepared from bromobenzene and 3% sodium amalgam.[11] (a) In carbon tetrachloride. A solution of 32.4 g. (2 mols) of iodine monochloride in 100 cc. of carbon tetrachloride was added during four hours with stirring to a suspension of 35.4 g. (1 mol) of diphenylmercury in 200 cc. of the same solvent at room temperature. The mixture was worked up in the usual way, the product being dried

---

[8] _Cf._ Michaelis and Rabinerson, _Ber._, **23**, 2343 (1890).

[9] Nesmajanow, "Organic Syntheses," 1932, Vol. XII, p. 54.

[10] Whitmore, Hamilton and Thurman, _ibid._, 1923, Vol. III, p. 99.

[11] Calvery, _ibid._, 1929, Vol. IX, p. 54.

TABLE I

ACTION OF *p*-TOLYLMERCURIC CHLORIDE WITH IODINE MONOCHLORIDE

Hg cpd., g.	Solvent	Cc.	ICl, g.	Solvent	Cc.	Temp., ° C.	Time	*p*-Iodotoluene, g.	M. p., ° C.	Yield, %
32.6	CCl_4	200	16.2	CCl_4	100	Boiling	2 days	13.5	33–35	50[a]
163	H_2O	400	81	None		Boiling	5 hrs.	90.5	33–34	87[b]
81.5	H_2O	200	39.6	Water (14.59 NaCl)	200	Boiling	5 hrs.	49	33.5–34.5	92
8	H_2O	100	4.0	Water (1.5 g. NaCl)	100	Boiling	4 hrs.	4.5	33–33.8	88
8	H_2O	100	4.0	Water (1.5 g. NaCl)	100	20	18 hrs.	2.4	30–32	50
16	H_2O	100	8.1	Concd. HCl	25	Boiling	4 hrs.	7.3	33–34	67
16	H_2O	100	8.1	Concd. HCl	15	Boiling	4 hrs.	7.3	33–34	67
16	H_2O	100	8.1	Water (15 g. NaI)	50	Boiling	4 hrs.	8.3	33–34	76
16	H_2O	100	8.1	Water (11 g. $CaCl_2$)	50	Boiling	4 hrs.	5.8	32–33	53
16	H_2O	100	8.1	Water (18 g. KI)	50	Boiling	1 hr.	9.5	34–35	87
8	Dry ether	100	4	Dry ether	50	20	2 hrs.	1.1		21
8	95% Alc.	100	4	Alcohol	50	20	2 hrs.	1.2		27
16	Glac. HOAc	150	8.1	Glacial acetic acid	50	Boiling	4 hrs.	6.3		58
16.3	H_2O	250	12.7 g. I	Water (12.7 g. KI)	50	Boiling	5 hrs.	10.1	34–35	92

[a] No *p*-chlorotoluene could be detected. [b] Allowing for 7.7 g. of unreacted mercury compound. There was also obtained 5 g. of an oil which solidified at 5°. No evidence of *p*-chlorotoluene was obtained.

by the addition of 60 cc. of dry benzene and then distilling. The residue boiling above 100° was carefully fractionated with a 30 × 0.7 cm. adiabatic total condensation variable take-off column[12] using a reflux ratio of 20:1. The properties of the pure substances which might be formed are as follows: chlorobenzene, b. p. 132°, n_{D}^{20} 1.525; iodobenzene, b. p. 188°, n_{D}^{20} 1.621. The distillation gave the following fractions (with b. p. at 735 mm., wts. and n_{D}^{20} as given): No. 1, 100–147°, 1.7 g., 1.502; No. 2, 147–182°, 2.8 g., 1.544; No. 3, 182–184°, 14.6 g., 1.617; No. 4, 184–185°, 17.2 g.; residue 2.1 g. Fractions 3–4 represent a 78% yield of iodobenzene. The above experiment was repeated but the carbon tetrachloride solution was dried and distilled directly. The same yield of iodobenzene, b. p. 181–185° and n_{D}^{20} 1.618 was obtained. (b) In water. This run was like that of di-*p*-anisylmercury. The fractionation of the product gave no material boiling under 175°. The yield of iodobenzene, b. p. 182–185°, was 78%.

In order to test the efficiency of the fractionation, a mixture of 2.92 g. of chlorobenzene and 26.3 g. of iodobenzene was fractionated in the same way. The fractions (including b. p. at 736 mm., wt., and n_{D}^{20}) follow: No. 1, 130–137°, 1.4 g., 1.532; No. 2, 137–144°, 0.63 g., 1.539; No. 3, 144–152°, 0.55 g., 1.5452; No. 4, 152–162°, 0.50 g., 1.556; No. 5, 162–173°, 0.71 g., 1.578; No. 6, 173–183°, 4.3 g., 1.609; No. 7, 183–184°, 19.1 g., 1.620; residue, 1.4 g.; loss 0.59 g. The recovery of iodobenzene, b. p. 173–184°, was 89%.

β-Phenylethylmercuric Chloride.—Phenylethyl chloride, b. p. 81–84° (14 mm.), n_{D}^{20} 1.5294, was prepared in 87% yield by the action of thionyl chloride on the alcohol. The chloride was converted to the Grignard reagent which was then refluxed with mercuric chloride[13] to give an 85% yield of the mercury compound, m. p. 163–166°. When this product was recrystallized from alcohol and analyzed by decomposing with sulfuric acid and hydrogen peroxide and precipitating mercuric sulfide in the usual way, it gave results for mercury one per cent. low.

A solution of 35.6 g. (1 mol) of iodine monochloride in 20 cc. of carbon tetrachloride was added during five hours with stirring to a refluxing suspension of 75 g. (1 mol) of phenylmercuric chloride in 200 cc. of the same solvent. The process was interrupted in the middle and the mixture stood overnight at room temperature. The mixture was worked up as usual and the product was fractionated through the 30 × 0.7 cm. column at 14 mm. using a 15:1 reflux ratio. Six fractions were obtained amounting to 26.5 g. The chief fraction was No. 6, b. p. 107–115° (14 mm.), 15.5 g., n_{D}^{20} 1.597. Fraction 2, b. p. 83–85° (14 mm.), 4.7 g., n_{D}^{20} 1.533, contained 23.2% chlorine and Fraction 6 contained 54.5% iodine, indicating them to be nearly pure phenylethyl chloride and iodide, respectively. The yields of these two substances were about 35 and 30%.

Treatment of Phenylethyl Iodide with Mercuric Chloride.—A mixture of 15 g. (1 mol) of phenylethyl iodide and 17.5 g. (1 mol) of mercuric chloride in 100 cc. of carbon tetrachloride was refluxed with stirring for twelve hours. After standing for forty-eight hours a few red crystals were visible in the solid material. The mixture was worked up in the usual way and the product was fractionated to give 10.4 g. of unchanged phenylethyl iodide, b. p. 107–111° (13 mm.), n_{D}^{20} 1.595. The low boiling material was only 0.7 g. Its n_{D}^{20} was 1.555. Thus no phenylethyl chloride (b. p. 80–82.5° (13 mm.), n_{D}^{20} 1.529) had been formed.

Treatment of Phenylethyl Iodide with Iodine Monochloride.—To 9 g. (1 mol) of phenylethyl iodide in a small flask was added dropwise 6.2 g. (1 mol) of iodine monochloride. The reaction was very vigorous. Free iodine separated. The mixture was treated with 50 cc. of a cold 50% potassium iodide solution. The oil layer gave 4.1 g. of phenylethyl chloride, b. p. 82–84° (14 mm.), n_{D}^{20} 1.5295, a yield of 76%.

---

(12) *Cf.* Whitmore and Lux, THIS JOURNAL, **54**, 3451 (1932).

(13) Marvel, Gauerke and Hill, *ibid.*, **47**, 3009 (1925).

Summary

1. The action of iodine monochloride with several organic mercury compounds has been studied.

2. The products obtained are organic iodides except when a secondary reaction with the iodine chloride converts the organic iodide to a chloride.

3. The yields of organic iodides obtained are sufficiently high to justify the use of iodine monochloride in place of iodine in converting organic mercury compounds to organic iodides.

STATE COLLEGE, PENNSYLVANIA

RECEIVED AUGUST 11, 1932
PUBLISHED FEBRUARY 9, 1933

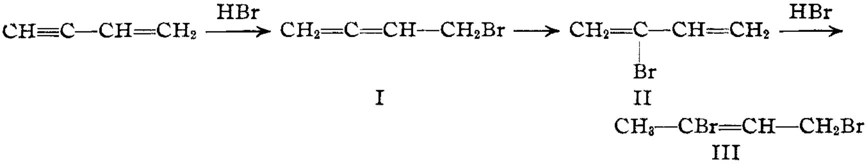
[CONTRIBUTION NO. 106 FROM THE EXPERIMENTAL STATION OF E. I. DU PONT DE NEMOURS & COMPANY]

Acetylene Polymers and their Derivatives. IV. The Addition of Hydrogen Bromide to Vinylacetylene, Bromoprene and Dibromobutene

BY WALLACE H. CAROTHERS, ARNOLD M. COLLINS AND JAMES E. KIRBY

Observations on the combination of vinylacetylene with hydrogen chloride[1] have been extended to the analogous case of hydrogen bromide.

The two reactants are closely similar in their behavior, but hydrogen bromide appears to act somewhat more slowly than hydrogen chloride. Concentrated aqueous hydrobromic acid containing cuprous bromide, when shaken with vinylacetylene at the ordinary temperature, yields the two products, bromo-2-butadiene-1,3 (bromoprene, II) and dibromo-2,4-butene-2 (III). It seems likely, in view of the results already described for the hydrogen chloride reaction[1b] that the primary product of reaction between hydrogen bromide and vinylacetylene is bromo-4-butadiene-1,2 (I), which then rearranges to yield bromoprene, but no decisive direct evidence for the formation of this primary product is yet available. Its presence among the reaction products has not been established—even when no cuprous bromide (catalyst) was used. The structure of the dihydrobromide has not yet been directly established either, but formula III, in view of the results with hydrogen chloride, is not open to serious doubt.



$$CH\equiv C-CH=CH_2 \xrightarrow{HBr} \underset{I}{CH_2=C=CH-CH_2Br} \longrightarrow \underset{II}{CH_2=\underset{\underset{Br}{|}}{C}-CH=CH_2} \xrightarrow{HBr} \underset{III}{CH_3-CBr=CH-CH_2Br}$$

---

(1) (a) Carothers, Williams, Collins and Kirby, THIS JOURNAL, **53**, 4203 (1931); (b) Carothers, Berchet and Collins, *ibid.*, **54**, 4066 (1932).