[CONTRIBUTION FROM THE COLLEGE OF PHARMACY, UNIVERSITY OF MICHIGAN]

Arsonium Compounds[1]

BY F. F. BLICKE AND E. L. CATALINE[2]

The two general methods available for the preparation of arsonium compounds are the interaction of a tertiary arsine with an alkyl halide and the reaction between a tertiary arsine oxide and a Grignard reagent.[3] The latter procedure is the only one which can be used for the preparation of tetraarylarsonium compounds and it was hoped that a considerable number of new tetraarylarsonium halides might be obtained by means of this process. However, in many instances interaction of a triarylarsine oxide and an arylmagnesium halide yielded only gummy products. The arsonium halides, obtained as glistening, colorless needles, are listed in Table I.

TABLE I

ARSONIUM HALIDES

Compounds 1, 2, 4, 5, 7 and 9 were recrystallized from dilute sodium hydroxide, 3 and 6 from a mixture of ethyl alcohol and ether and 8 from a mixture of methyl alcohol and ether. The arsonium halides are insoluble in ether.

	Arsonium halide	Prepared from
1	Methylcyclohexyldiphenylarsonium iodide	Cyclohexyldiphenylarsine[a] and methyl iodide
2	Methyltriphenylarsonium iodide	Methyldiphenylarsine oxide[a] and phenylmagnesium iodide
3	Methyldiphenyl-α-naphthylarsonium iodide	Diphenyl-α-naphthylarsine[a] and methyl iodide
4	1-Methyl-1-phenyl-*o*,*o*′-diphenylylarsonium iodide	1-Phenyl-*o*,*o*-diphenylylarsine[a] and methyl iodide
5	6-Methyl-6-phenylphenoxarsonium iodide	6-Phenylphenoxarsine oxide[a,c] and methylmagnesium iodide
		6-Methylphenoxarsine oxide[a] and phenylmagnesium iodide
6	6-Methyl-6-α-naphthyl-phenoxarsonium iodide	6-α-Naphthyl-phenoxarsine[a] and methyl iodide
7	Cyclohexyltriphenylarsonium bromide	Cyclohexyldiphenylarsine oxide[a] and phenylmagnesium bromide
8	1,1-Diphenyl-*o*,*o*′-diphenylylarsonium bromide	1-Phenyl-*o*,*o*′-diphenylylarsine[a] oxide and phenylmagnesium bromide
9	6,6-Diphenylphenoxarsonium bromide	6-Phenylphenoxarsine oxide and phenylmagnesium bromide

	% yield	M. p., °C.	Formula	% As Calcd.	% As Found	% Halogen Calcd.	% Halogen Found
1	80	220–221	$C_{19}H_{24}AsI$	16.50	16.49	I 27.95	27.95
2	70	175–176[b]	....	...	...	...	...
3	70	190–191	$C_{23}H_{20}AsI$	15.05	14.98	I 25.48	25.61
4	82	117–118	$C_{19}H_{16}AsI$	16.78	16.58	I 28.42	28.72
5	27	170–171[d]	....	...	...	...	...
	87	.....	....	...	...	...	...
6	50	143–144	$C_{23}H_{18}AsI$	14.63	14.36	I 24.80	24.50
7	40	183–184	$C_{24}H_{26}AsBr$	15.97	16.22	Br 17.04	17.29
8	23	240–241	$C_{24}H_{18}AsBr$	16.25	16.16	Br 17.34	17.44
9	73	229–230	$C_{24}H_{18}AsBr$	15.71	16.15	Br 16.75	16.34

[a] Blicke and Cataline, THIS JOURNAL, **60**, 419 (1938). [b] Prepared by different methods Michaelis [*Ann.*, **321**, 166 (1902)] reported the melting point to be 176° while Blicke and Monroe [THIS JOURNAL, **57**, 722 (1935)] found 173–174°. [c] Aeschlimann, *J. Chem. Soc.*, 415 (1927). [d] Obtained by a different procedure Aeschlimann[c] stated that the melting point is 175°.

It was found that upon thermal decomposition methyltriphenylarsonium iodide is converted into triphenylarsine and methyl iodide, cyclohexyltriphenylarsonium bromide yields triphenylarsine and bromocyclohexane while tetraphenylarsonium bromide decomposes to produce triphenylarsine and bromobenzene.

Tetraphenylarsonium nitrate, sulfate and acetate were obtained by neutralization of aqueous solutions of tetraphenylarsonium hydroxide with the required acid and removal of the solvent. In order to obtain the hydroxide the arsonium chloride[3] was dissolved in a mixture of methyl alcohol and water and shaken with silver oxide.

The bicarbonate was formed when an aqueous

TABLE II

TETRAPHENYLARSONIUM SALTS

	M. p., °C.	Formula		% As Calcd.	% As Found
Nitrate	260–262	$C_{24}H_{20}O_3NAs$		16.83	16.77
Sulfate	257–258[a] (dec.)	$C_{48}H_{40}O_4SAs_2$	(SO_4	11.14	11.25)
Acetate	215–217[a]	$C_{26}H_{23}O_2As$		16.95	17.00
Bicarbonate[b]	173–174 (dec.)	$C_{25}H_{21}O_3As$		16.87	17.14
			(CO_2	9.91	9.85)
Picrate[c]	203–204	$C_{30}H_{22}O_7N_3As$		12.26	12.27

[a] The salt was heated for twelve hours at 120°. [b] Recrystallized from pyridine; soluble in alcohol, insoluble in ether and acetone. [c] Recrystallized from alcohol; soluble in acetone and chloroform, insoluble in benzene.

---

(1) This paper represents part of a dissertation submitted to the Horace H. Rackham School of Graduate Studies by E. L. Cataline in partial fulfilment of the requirements for the degree of Doctor of Philosophy in the University of Michigan.

(2) Parke, Davis and Company Fellow.

(3) Blicke and Monroe, THIS JOURNAL, **57**, 720 (1935).

solution of the chloride was shaken with silver carbonate.

The yellow picrate precipitated when picric acid, dissolved in alcohol, was added to an aqueous solution of the chloride.

All of the arsonium salts mentioned above are soluble in water with the exception of the picrate.

Experimental Part

General Procedures. (a) **Arsines and Methyl Iodide.**—The arsine was dissolved in the least possible amount of methyl iodide and the mixture refluxed. The precipitated product[4] was filtered, washed with ether and recrystallized.

For the preparation of compound 1 (Table I) the mixture of arsine and iodide was heated for one hour, for compound 3, twenty-four hours, and for compounds 4 and 6, seventy hours.

(b) **Arsine Oxides and Grignard Reagents.**—One-tenth mole of the arsine oxide, dissolved in warm, dry benzene,[5] was added, slowly, with agitation to 0.3 mole of the Grignard reagent and the mixture refluxed for two hours. The solvents were decanted, the residue treated with 40 cc. of water followed by 15 cc. of constant boiling hydrobromic acid. The arsonium bromide separated in crystalline form when the mixture was cooled.

Thermal Decompositions.—A very slow stream of dry nitrogen was passed through a distillation flask which contained 4.6 g. of tetraphenylarsonium bromide and which was heated in a metal bath at 315–335° for fifteen minutes. The distillate, bromobenzene, weighed 1.4 g. and was identified by conversion into phenylmagnesium bromide. Upon addition of benzophenone to the latter triphenylcarbinol was obtained. The residue of triphenylarsine in the distillation flask was dissolved in absolute ether and treated with mercuric chloride, dissolved in the same solvent. There was obtained 4.5 g. of $(C_6H_5)_3As{\cdot}HgCl_2$; m. p. 245–246°[6] after recrystallization from acetic acid.

When 4.5 g. of methyltriphenylarsonium iodide was heated at 175–200° there was obtained 1.2 g. of methyl iodide and 5.2 g. of $(C_6H_5)_3As{\cdot}HgCl_2$. In order to identify the methyl iodide it was dissolved in 10 cc. of absolute alcohol and heated for one hour with 5.5 g. of the silver salt of 2-methyl-3,5-dinitrobenzoic acid. After removal of the solvent and extraction of the residue with 25 cc. of benzene there was obtained 1.0 g. of methyl 2-methyl-3,5-dinitrobenzoate; mixed m. p. 73–74°[7] after recrystallization from acetic acid.

From 4.5 g. of cyclohexyltriphenylarsonium bromide, heated at 185–270° over a fifteen-minute period, there was produced 1.3 g. of bromocyclohexane and 4.5 g. of $(C_6H_5)_3As{\cdot}HgCl_2$. The refractive index of the bromide obtained was $n^{27.5}$ 1.4937; the index of a known specimen was $n^{27.5}$ 1.4939.

Summary

A number of new arsonium halides have been prepared from a tertiary arsine and methyl iodide and by interaction of a tertiary arsine oxide with a Grignard reagent. In addition tetraphenylarsonium nitrate, sulfate, acetate, bicarbonate and picrate have been described.

---

[4] In some instances it was necessary to remove partially the methyl iodide.

[5] Anisole was used for the preparation of compound 9.

[6] Blicke and Smith, THIS JOURNAL, **51**, 1561 (1929).

[7] Racine, *Ann.*, **239**, 77 (1887).

ANN ARBOR, MICHIGAN RECEIVED SEPTEMBER 20, 1937

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF TEMPLE UNIVERSITY]

A Further Study of the Bromination of the Nitrodiphenyls

BY FRANCIS H. CASE

It was stated by Guglialmelli and Franco[1] that as a result of the bromination of 4-nitrodiphenyl, in addition to large amounts of 4-bromo-4′-nitrodiphenyl, a compound A was obtained, m. p. 102°, which they believed to be 2-bromo-4′-nitrodiphenyl. On reduction A yielded an amine, B, m. p. 120,° which was converted to an acetyl derivative, C, m. p. 155–156°. B when subjected to the Sandmeyer reaction yielded a dibromide, D, m. p. 109°. All these derivatives, they believed to belong to the 2,4′-system.

Finzi and Bellavita[2] pointed out that the true 2-bromo-4′-nitrodiphenyl, m. p. 82.5°, had already been synthesized by Scarborough and Waters[3] by the nitration of 2-acetaminodiphenyl, followed by hydrolysis and replacement of amino by bromine. Since Guglialmelli and Franco's compound A could not be 2-bromo-4′-nitrodiphenyl, and since it yielded on oxidation 4-nitrobenzoic acid, Finzi and Bellavita reasoned that compound A was probably 3-bromo-4′-nitrodiphenyl and that the corresponding derivatives, B, C, and D belonged to the 3,4′-system.

In order to settle this question definitely, the synthesis of 3-bromo-4′-nitrodiphenyl was effected in this Laboratory in the following manner

---

[1] Guglialmelli and Franco, *Anal. asoc. quim. argentina*, **20**, 8 (1932).

[2] Finzi and Bellavita, *Gazz. chim. ital.*, **64**, 335 (1934).

[3] Scarborough and Waters, *J. Chem. Soc.*, 96 (1927).