TABLE I

Contaminating impurity	Time of reduction, min.
None	11
Copper sulfate	8
Free sulfur	11
Sodium sulfite	11.5
Sodium hydrosulfite	11
Sodium nitrite	80
Sodium nitrate	12
Sodium arsenite	70
Sodium arsenate	11
Potassium cyanide	33
Sodium sulfate	11
Sodium chloride	11

As a result of other experiments with *p*-nitrophenol, it was found that the rate of reduction was approximately inversely proportional to the weight of catalyst added per molar unit of compound being reduced. Other tests with *p*-nitrophenol indicated that the catalyst could be used repeatedly, but that it gradually fell off in activity. This inactivation of the catalyst was most marked when dealing with a substance which yielded unstable amino derivative, and was probably due to a tarry deposit being formed on the catalyst.

General Procedure for Reducing Nitroarylarsonic Acids.—To a suspension of 0.10 mole of the nitroarylarsonic acid in 100–200 cc. of distilled water was added enough 2 *N* sodium hydroxide to form a solution of the monosodium salt. This solution was placed in the reaction container together with 10 g. of Raney catalyst and the air was swept from the container by a current of hydrogen. The hydrogen pressure was set at 30 lb. and shaking was begun. Within thirty to sixty minutes the pressure gage indicated that the reduction was complete. The colorless solution was filtered from the catalyst and upon cooling the filtrate and making neutral to Congo red paper with 6 *N* hydrochloric acid, the derivative separated as a pure crystalline product. Ordinarily, further purification was unnecessary.

TABLE II

AMINO DERIVATIVES FROM CORRESPONDING NITRO -PHENYLARSONIC ACID

Amino derivatives[a] -phenylarsonic acid	Yield, %
3-Amino-	95
5-Amino-2-chloro-	93
3-Amino-4-hydroxy-	92
3-Amino-4-isoamylamino-	99
3-Amino-4-β-hydroxyethylamino-	96
5-Amino-2-β-hydroxyethylamino-	80
3-Amino-4-β-hydroxy-*n*-propoxy-	52
3-Amino-2-carboxymethylamino-	90

[a] The purity of the products was determined by melting points and/or by arsenic analyses.

Summary

1. A general method for the catalytic reduction of nitroarylarsonic acids to aminoarylarsonic acids was developed and used successfully on several compounds.

2. Experiments were made to determine the effect of various inorganic substances on the activity of the Raney nickel catalyst when used in reducing organic substances.

LINCOLN, NEBRASKA RECEIVED APRIL 27, 1935

[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY OF THE UNIVERSITY OF PENNSYLVANIA]

Reactivities of Groups as Revealed by Hydrogen Bromide Cleavage of Substituted Germanes

BY J. K. SIMONS

The action of hydrogen halides on organotin and lead compounds of the types R_4M and R_3MR' has been studied by a number of investigators.[1] The action of these acids on similar compounds of germanium has been studied only incidentally. Triphenylgermane[2] gives triphenylgermanium halides; tetramethylgermanium[3] in the presence of aluminum bromide gives trimethylgermanium bromide; tetraphenyl- and tetra-*p*-tolylgermanium[4] yield the corresponding triarylgermanium bromide.

The action of hydrogen bromide at room temperature on seven additional compounds of the same types has now been investigated and shown in each case to result in cleavage to substituted germanium bromides and hydrocarbon. Incidental to this work the zinc aryl procedure[4] was applied to the synthesis of the two new unsymmetrical compounds, tri-*m*-tolyl-*p*-tolyl- and tri-*p*-tolyl-*o*-tolylgermanium. Also a new tolyl derivative, tri-*p*-tolylgermanium chloride, was obtained from tri-*p*-tolylgermanium oxide by the action of hydrochloric acid.

The results of the cleavage experiments support the generality of the reaction and serve to place the attached groups in order of decreasing reac-

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[1] F. B. Kipping, *J. Chem. Soc.*, 2365 (1928); Bullard and Holden, THIS JOURNAL, **53**, 3150 (1931); Austin, *ibid.*, **53**, 1548 (1931); Gilman, Towne and Jones, *ibid.*, **55**, 4689 (1933).

[2] Kraus and Foster, *ibid.*, **49**, 465 (1927).

[3] Dennis and Patnode, *ibid.*, **52**, 2779 (1930).

[4] Simons, Wagner and Müller, *ibid.*, **55**, 3705 (1933).

tivity in the series, *p*-tolyl, *m*-tolyl, phenyl, benzyl.[1,5]

Experimental

General—Germanium Compounds.—Tetra-*m*-tolyl-, tetra-*o*-tolyl- and triphenyl-*m*-tolylgermanium were materials prepared in the course of another investigation.[4] The melting points were, respectively, 149, 175, 137°. Tetrabenzylgermanium, m. p. 109–110°, was prepared in 80–85% yield by the action of the Grignard reagent on germanium tetrachloride.[6] Triphenyl-*p*-tolylgermanium, m. p. 123–124°, was prepared according to Orndorff, Tabern and Dennis.[6a] Tri-*m*-tolylgermanium bromide, m. p. 76–77°, represented an accumulation of material obtained by the action of bromine[4] or of hydrogen bromide on tetra-*m*-tolylgermanium.

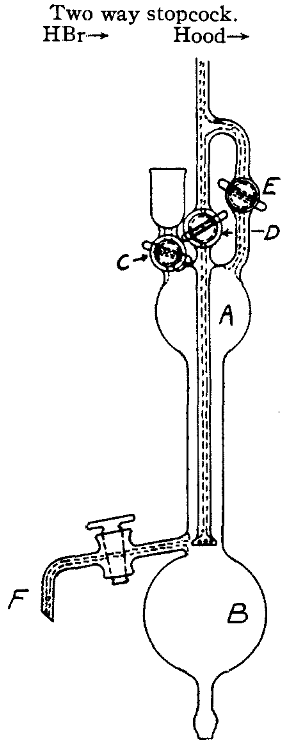

Fig. 1.

Tri-*m*-tolyl-*p*-tolylgermanium.—The Grignard reagent from 50 g. of *p*-bromotoluene and 8 g. of magnesium was treated with 15 g. of anhydrous zinc chloride. Then, by the usual procedure,[4] 9.5 g. of tri-*m*-tolylgermanium bromide was heated with this mixture in xylene solution for twenty-eight hours (sixteen hours on water-bath, twelve hours of refluxing). After decomposing excess zinc and magnesium compounds the xylene solution was dried and distilled. The oily residue after several crystallizations from methyl alcohol yielded 2.2 g. of a white crystalline solid, m. p. 98.5–100.5°. More material (0.6 g.) was obtained from the mother liquors.

Anal. Calcd. for $C_{28}H_{28}Ge$: C, 76.92; H, 6.46. Found: C, 76.7; H, 6.69.

Tri-*p*-tolyl-*o*-tolylgermanium.—The zinc aryl was obtained from 64 g. of *o*-bromotoluene, 12 g. of magnesium, and 19 g. of zinc chloride and was heated in xylene solution with 12 g. of tri-*p*-tolylgermanium bromide for thirty hours. The residue from the xylene solution was steam distilled and then taken up in benzene. The solid material from this solution was subjected to a series of fractional crystallizations from mixtures of alcohol and benzene and yielded finally a small amount of white crystalline material whose melting point was unchanged on further crystallization. It melted at 164–166° and appeared homogeneous under the microscope. Analysis indicated it to be tri-*p*-tolyl-*o*-tolylgermanium.

Anal. Calcd. for $C_{28}H_{28}Ge$: C, 76.92; H, 6.46. Found: C, 76.2; H, 6.72.

Tri-*p*-tolylgermanium Chloride.—Tri-*p*-tolylgermanium oxide was heated on the water-bath with a mixture of alcohol and excess concentrated hydrochloric acid. The white crystalline chloride came out of the alcoholic acid solution on chilling. The crude solid after crystallization from 58–70° ligroin melted sharply at 121°.

Anal. Calcd. for $C_{21}H_{21}GeCl$: C, 66.10; H, 5.55. Found: C, 66.1; H, 5.88.

Compounds used to establish identity by mixed melting point test were authentic specimens prepared by methods given in the literature. Unless otherwise designated all melting points are corrected. In all cleavage experiments yields are based on one equivalent of reacting hydrogen bromide.

Analyses for bromine were carried out by an adaptation of the saponification procedure of Mulliken,[7] in which alcoholic sodium hydroxide was consumed by the halogen of the germanium compound and excess alkali titrated with 0.1 *N* acid.

Other Reagents.—The chloroform used was a fraction of 0.2° boiling range obtained from dried (over sodium sulfate or calcium chloride) material previously washed with concd. sulfuric acid, dilute alkali and water.

Hydrogen bromide was prepared by dropping bromine into a pseudocumene solution of naphthalene.[8] The liberated gas was purified by passage through an all glass system consisting of a bubbler containing red phosphorus suspended in a fuming aqueous solution of hydrogen bromide, towers filled with red phosphorus to remove bromine and towers filled with fused calcium bromide to remove water. It was then collected over mercury in a graduated buret and used soon afterward according to the procedure outlined below.

Action of Hydrogen Bromide on Substituted Germanes

General Procedure.—The germanium compound in chloroform solution was treated at room temperature with a measured volume of gaseous hydrogen bromide in a gas washing device of special design (Fig. 1). The lower part, B, of the reaction vessel was filled with mercury and connected to a leveling bulb. The space above the mercury (116 cc.) was filled completely with the solution by means of C (E open to hood). Hydrogen bromide was then forced into A through D (E and C closed) by means of a mercury leveler attached to the graduated buret and the leveler attached to B. Gas not absorbed by the solution forced liquid from A to B and was returned intermittently to the buret through E (D closed). In this way a measured volume could be absorbed.

After standing in the closed apparatus at room temperature for twenty to twenty-four hours the solution was run out of F into the bulb of an all glass 8-ball Snyder fractionating column and distilled under high reflux to a residue of about 10–15 cc. Some unreacted hydrogen bromide was always observed. The residue was poured into a side-arm flask (25 cc.) and the rest of the sol-

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[5] Kharasch and Flenner, This Journal, **54**, 674 (1932).

[6] (a) Orndorff, Tabern and Dennis, *ibid.*, **49**, 2512 (1927); (b) Bauer and Burschkies, *Ber.*, **67**, 1041 (1934).

[7] Mulliken, "Identification of Pure Organic Compounds," John Wiley & Sons, New York, Vol. I, 1904, p. 111.

[8] *Cf.* Kastle and Bullock, *Am. Chem. J.*, **18**, 107 (1896); Kochs, *Chemist-Analyst*, **20**, No. 4, p. 11 (1931).

TABLE I

CLEAVAGE OF SUBSTITUTED GERMANES BY HYDROGEN BROMIDE

Substance used			HBr	Substances identified in products					
No.	Name	G.	equiv.	Name	G.	%, yield	M. p., °C.	B. p., °C.	Mm.
1	Tetra-*m*-tolylgermanium (A)	3.0	1.44	(B)	2.45	83.9	77.3[b]	220–224	1–2
				Toluene	0.28	43.8	70.1[c]		
				(A)	.15	..	150.1		
2	Tri-*m*-tolylgermanium bromide (B)	3.0	1.28	Di-*m*-tolylgermanium bromide	1.1	37.7	......	189–190	4
				Toluene	0.47	72.9	70.7[c,b]		
				(B)	.4	..	74.8–75.8[b]		
3	Tetra-*o*-tolylgermanium	3.0	1.63	Tri-*o*-tolylgermanium bromide	.9	30.8	......	203	1
				Toluene	.35	55.5	69.0–69.5[c]		
4	Tetrabenzylgermanium (C)[a]	3.0	1.42	Tribenzylgermanium bromide	.3	10.3	146.5–146.7[b]		
				Toluene	.12	18.6	70.7–71.7[c]		
				(C)	..	..	......		
5	Triphenyl-*p*-tolylgermanium	2.0	1.24	Triphenylgermanium bromide	.7	36.0	136.6–138.1[b]		
				Toluene	.18	38.3	70.8–71.5[c,b]		
6	Triphenyl-*m*-tolylgermanium	1.3	2.60	Triphenylgermanium bromide	.2	15.8	134.3–136.8[b]		
				Benzene	..	..	84.1[d,b]		
7	Tri-*m*-tolyl-*p*-tolylgermanium	3.0	1.49	(B)	.8	27.4	74.8[b]		
				Toluene	.46	72.2	69.6–70.6[c,b]		
				Ditolylgermanium dibromide[e]	.5	..	......	195	2

[a] Reaction time, 42 hours; a duplicate experiment gave no reaction. [b] Gave satisfactory mixed melting point test. [c] M. p. of the dinitro compound (2,4-dinitrotoluene). [d] M. p. of the dinitro compound (*m*-dinitrobenzene). [e] This was an oily substance shown by analysis to be largely ditolylgermanium dibromide. Calcd. for $C_{14}H_{14}GeBr_2$: Br, 38.6. Found: Br, 31.8.

vent distilled off into the bulb of a micro fractionating column (26 cm. high × 8 mm. i. d.) of the Vigreux type. Platinum triangles or glass beads were used in this and the above distillations to prevent bumping. The chloroform was distilled off carefully until the temperature at the head began to rise sharply; distillation was then stopped. The residue (0.7–0.8 cc.) was a mixture of toluene and chloroform whose composition was ascertained by comparing its density with those of known mixtures. All densities were obtained with a micro pycnometer.[9]

The toluene-chloroform mixture was then nitrated according to Mulliken's directions for the identification of toluene as 2,4-dinitrotoluene.[10]

The germanium compounds left as a residue in the 25-cc. flask were worked up by methods best suited to their properties. In reaction No. 3 (see Table I) vacuum distillation sufficed to isolate the tri-*o*-tolylgermanium bromide. In reactions No. 1, 2, 7, vacuum distillation served to make a preliminary separation into fractions of different boiling points. From these, crystallization from methyl alcohol isolated tri-*m*-tolylgermanium bromide and further vacuum distillation separated any recognizable quantity of ditolylgermanium dibromide. Essentially this procedure was employed in isolating tribenzylgermanium bromide (No. 4). In Nos. 5 and 6 fractional crystallizations from ligroin, and alcohol and benzene were resorted to to isolate triphenylgermanium bromide.

Cleavage Experiments.—The data are collected in Table I. The experiment with tri-*m*-tolylgermanium bromide is given in detail below as an example of the isolation procedure and because the product, di-*m*-tolylgermanium dibromide, is new.

Tri-*m*-tolylgermanium Bromide.—This halide treated by the general procedure gave a germanium residue which yielded two fractions on distillation at 1–2 mm.: (1) 1.8 g., b. p. 175–190°; (2) 0.7 g., b. p. 195–210°. Crystallization of (2) from methyl alcohol gave 0.4 g. of the unreacted bromide, m. p. 74.8–75.8°. Mixed with bromide melting at 78.6° the melting point was 75.9–76.3°. The residue from this crystallization was combined with (1) and the mixture distilled at 4–5 mm. The fractions were: (a) 0.5 g., b. p. (5 mm.) 175–185°; (b) 1.1 g., b. p. (4 mm.) 189–190°; (c) 0.2 g., residue. The substance boiling at 189–190° at 4 mm. was a colorless liquid whose analysis for bromine indicated it to be di-*m*-tolylgermanium dibromide.

Anal. Calcd. for $C_{14}H_{14}GeBr_2$: Br, 38.6. Found: Br, 38.5.

Debenzylation of Tetrabenzylgermanium

Action of Hydrogen Bromide.—The low yield of cleavage products and the large quantity of unreacted material in the experiments with tetrabenzylgermanium indicated a resistance to splitting by hydrogen bromide which is in contrast to the ease with which the various tolyl and phenyl compounds were split. Experiments designed to

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(9) Ref. 7, p. 228.

(10) Ref. 7, p. 202.

increase reaction showed the tetrabenzyl compound to be resistant even at higher temperatures and at pressures above atmospheric.

In two experiments, 3-g. samples of the germane were treated in sealed tubes with 35–40 cc. of pseudocumene which had been partly saturated with hydrogen bromide. One was heated at 107° for one hour, then at 180° for two hours; the other at 170° for three hours. In neither case was there any evidence of tribenzylgermanium bromide formation.

Action of Bromine. 1. In Ethylene Bromide.—The action of bromine on tetrabenzylgermanium is reported by Bauer and Burschkies[6b] to give tribenzylgermanium bromide, m. p. 145°. Their brief directions were carried out in one experiment with 26.2 g. of the germane and 9.7 g. of bromine in a total of 262 cc. of ethylene bromide. Decoloration was rapid at a temperature just below the boiling point of the solvent and some hydrogen bromide formation was observed. When the reaction was complete the solvent was removed by distillation under reduced pressure and the residue crystallized from methyl alcohol. After a primary deposition of oily material the solution finally gave solid. The oily material was separately crystallized from glacial acetic acid, yielding some solid which was combined with the other (total weight, 4.6 g.). Recrystallization of this material from ethyl alcohol yielded 3.0 g. of unreacted tetrabenzylgermanium, m. p. 106–107° obsd. The mother liquors yielded a residue which was vacuum distilled, giving largely a fraction boiling at 235–245° (1 mm.). Its bromine content was 13.3%; calcd. for $(C_7H_7)_3GeBr$: 18.8%.

The material was accordingly treated with more bromine in ethylene bromide solution and the product vacuum distilled. Some material came over below 235° at 1 mm. (m. p. 121–140°) and after crystallization from methyl alcohol and some benzene melted at 143.2–144.2° (0.8 g., 3.2%). A much larger and unidentified fraction of resinous material distilled from 235–50° at 1 mm.; bromine content, 12.6%.

2. In Acetic Anhydride.—Smaller quantities of tetrabenzylgermanium were more successfully brominated in acetic anhydride. The procedure which gave the best results follows. Five grams of the germane in 25 cc. of acetic anhydride was treated with 6 g. of bromine in 10 cc. of the same solvent. The reaction proceeded rapidly at a temperature kept just high enough to dissolve the tetrabenzylgermanium. No hydrogen bromide was liberated, but some bromine reacted with the solvent.[11] When the color of bromine had disappeared the solution was chilled strongly. The separated solid melted at 136.5–140.0°; yield, 0.6 g.; 12.3%. The mother liquors gave more solid of lower melting point yet above that of tetrabenzylgermane. Crystallization from methyl alcohol and benzene gave 0.4 g. (8.2%) of product, m. p. 140.5–142.5°.

The writer sincerely thanks Prof. E. C. Wagner for his advice and suggestions during the course of this work.

Summary

1. The following new compounds have been prepared and characterized: tri-*p*-tolylgermanium chloride, tri-*m*-tolyl-*p*-tolyl- and tri-*p*-tolyl-*o*-tolylgermanium.

2. The action of hydrogen bromide on substituted germanes has been investigated for the symmetrical compounds, tetra-*m*-tolyl-, tetra-*o*-tolyl-, and tetrabenzylgermanium, and for the unsymmetrical derivatives, triphenyl-*p*-tolyl-, triphenyl-*m*-tolyl-, tri-*m*-tolyl-*p*-tolylgermanium and tri-*m*-tolylgermanium bromide, and shown in each case to effect cleavage at room temperature.

3. As major products of reaction substituted germanium bromides and hydrocarbons have been isolated and identified.

4. Tetrabenzylgermanium in experiments with hydrogen bromide and bromine has been shown to be more resistant to cleavage than tetraarylgermanes.

5. The results of cleavage experiments serve to place the groups in order of their decreasing reactivity in the series, *p*-tolyl, *m*-tolyl, phenyl, benzyl.

PHILADELPHIA, PA. RECEIVED APRIL 30, 1935

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[11] Urech, *Ber.*, **13**, 1687 (1880); Orton and Jones, *J. Chem. Soc.*, **101**, 1722 (1912).