and dilute alcohol, yielding as a major component benzoyl-*unsym*-*m*-xylidine (m. p. 185° obs.; mixed m. p. 186°). There was present also a more soluble benzoyl derivative (m. p. 143° after three crystallizations) of another base, formation of which excludes a compound of formula VI whose cleavage by reduction should yield only *unsym*-*m*-xylidine.

The filtrate from the crystalline precipitate referred to first was steam-distilled to remove alcohol, made alkaline with sodium hydroxide, and steam-distilled further. No oily base passed over, but some fine needle crystals appeared in the distillate (about 0.1 g. in 500 cc.), and were identified as Tröger's base (m. p. 135.5°; mixed m. p. 136°), thus shown to be slightly volatile with steam. The residue in the distilling flask was removed, dissolved in 6 *N* hydrochloric acid and Tröger's base recovered as hydrochloride (about 27%).

The foregoing results show clearly that in the conversion of *o*-amino-*m*-xylyl-*p*-toluidine to Tröger's base, 3-*p*-tolyl-6-methyl-1,2,3,4-tetrahydroquinazoline is intermediate.

Preparation of Tröger's Base from Tolylmethyltetrahydroquinazoline.—The results reported by Spielman were duplicated.

Conversion of Methylene-bis-*p*-toluidine to *o*-Amino-*m*-xylyl-*p*-toluidine.[9]—A mixture of 2.3 g. of methylene-bis-*p*-toluidine, 2.3 g. of *p*-toluidine hydrochloride, 5.5 g. of *p*-toluidine and 1 cc. of nitrobenzene was kept at 60° for two hours. The mixture was made alkaline and steam-distilled to remove nitrobenzene and excess *p*-toluidine. From the residue there was obtained *o*-amino-*m*-xylyl-*p*-toluidine, isolated as the benzal compound (m. p. 128°),[8] the conversion being 35%.

Summary

The formation of Tröger's base (V) from *p*-toluidine (I) and formaldehyde in acid solution was shown to involve four steps yielding as successive intermediate compounds methylene-bis-*p*-toluidine (IIa) or methylene-*p*-toluidine (IIb), *o*-amino-*m*-xylyl-*p*-toluidine (III), and 3-*p*-tolyl-6-methyl-1,2,3,4-tetrahydroquinazoline (IV). This was demonstrated by the formation of Tröger's base from each of these compounds under the conditions which yield it from *p*-toluidine, and by effecting separately the conversion of II to III, of III to IV, and of IV to Tröger's base.

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[9] These results were obtained by Dr. J. K. Simons.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF NEBRASKA]

Catalytic Reduction of Nitroarylarsonic Acids

BY MELVIN R. STEVINSON[1] AND CLIFF S. HAMILTON

Several methods have been developed for the reduction of nitroarylarsonic acids to the corresponding amines. The alkaline ferrous hydroxide method[2] is generally applicable, but it involves tedious experimental manipulation. Sodium hydrosulfite may also be used, but, unless the temperature is controlled carefully, the arsono group may be converted into the arseno group. In this investigation a catalytic reduction method was developed.[3]

In view of the fact that nitroarylarsonic acids are sparingly soluble, at room temperature, in water, alcohols and acids, but readily soluble in alkalies, a catalyst which would effect reduction in alkaline solution seemed advisable. Raney nickel[4] prepared by the method of Covert and Adkins[5] was used. The apparatus utilized in the reduction work was essentially that of a standard "set-up" for effecting hydrogenation in the liquid phase with hydrogen gas under moderate pressures.

The method was used successfully on a number of nitroarylarsonic acids, and without exception the arsono group was unaffected. In every case the yields were as near the calculated amounts as individual properties, such as stability, would permit.

A search of the literature has failed to reveal the use of Raney nickel for the catalytic hydrogenation of nitro compounds, and for the hydrogenation of a compound containing a halogen as well.

Experimental

Several experiments were made to determine which of the common contaminating impurities of nitroarylarsonic acids tended to inactivate the nickel catalyst. The data were obtained as follows.

A solution of 1.4 g. (0.01 mole) of pure *p*-nitrophenol (m. p. 114°) in 100 cc. of water and 5 cc. of 2 *N* sodium hydroxide was reduced by hydrogen under 30 lb. pressure in the presence of 2 g. of Raney nickel. The time of reduction was eleven minutes, which was used as a control. Similar experiments were run with all conditions held constant except that 10% by weight (based on *p*-nitrophenol) of various impurities were added.

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[1] Parke, Davis and Company Fellow.

[2] Jacobs, Heidelberger und Rolf, THIS JOURNAL, **40**, 1580 (1918).

[3] Boehringer und Soehne, German Patent 286,547 (1914).

[4] Raney, U. S. Patent 1,628,190 (1927).

[5] Covert and Adkins, THIS JOURNAL, **54**, 4116 (1932).

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.

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[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).