Anal. Calcd. for $C_{11}H_{11}N_2Br$: Br, 31.84. Found: Br, 31.96.

It was converted by alkali to the corresponding hydroxide, m. p. 129°, identical with the substance described by Reynolds and Robinson,[6] who reported m. p. 130°. This hydroxide is alkaline to litmus in dilute methyl alcohol.

On addition of concentrated hydrobromic acid to the hydroxide in methyl alcohol, it was reconverted to the original bromide and was isolated by precipitation with absolute ether. A mixed melting point of this bromide and that made by addition of allyl bromide to quinazoline gave no depression.

Summary

1. 3-Allyl-4-quinazolone and 3-allyl-3,4-dihydroquinazoline are both easily reduced catalytically with the absorption of two atoms of hydrogen and the formation of the corresponding propyl derivatives. Vasicine and desoxyvasicine, on the other hand, cannot be reduced under similar conditions.

2. Desoxyvasicine and 3-allyl-3,4-dihydroquinazoline are not identical. Their derivatives also have different properties.

3. Dihydrodesoxyvasicine and 3-allyl-1,2,3,4-tetrahydroquinazoline are not identical. Their derivatives have different properties.

URBANA, ILLINOIS RECEIVED NOVEMBER 13, 1934

NOTES

Selenium and Tellurium as Carriers in Bromination of Benzene

BY A. A. O'KELLY

Recently a series of experiments were conducted in which benzene was brominated in the presence of selenium and tellurium as carriers, bromine being present in excess. The method employed was that of Adams and Johnson ["Laboratory Experiments in Organic Chemistry," p. 203] and a comparison of degree of bromination thus obtained was made with that resulting when iron was used. In each case 70.3 g. of benzene was used together with 2 g. of carrier and 80% excess bromine. The reaction mixture was allowed to stand for twelve hours without heat and then slight heating was conducted over a period of seven additional hours in each case. The yields reported are of that fraction of boiling point 154–156°. The yield was checked in each case by duplicate preparations under the same conditions and is based on a theoretically possible 100% bromination of the benzene, either to mono- or di-bromobenzene. Table I gives the results of these experiments.

TABLE I

COMPARISON OF DEGREE OF BROMINATION OF BENZENE IN PRESENCE OF Fe, Se, Te AND Fe–Te MIXTURE

Carrier	Benzene, g.	Monobromobenzene, g.	Yield, %	Dibromobenzene, g.	Yield, %
Fe	70.3	65.6	46.2	10	4.6
Se	70.3	36.0	25.4	7	3.2
Te	70.3	43.5	30.7	15	6.9
Te–Fe	70.3	65.6	46.2	10	4.6

STATE TEACHERS COLLEGE
MURFREESBORO, TENNESSEE
RECEIVED JULY 3, 1934

The Preparation of Certain Nitrogen-Substituted Sulfon-*o*-toluidides

BY GEORGE H. YOUNG

In a previous communication from this Laboratory[1] the preparation of several N-alkyl *p*-toluene sulfonanilides was described. This paper reports the synthesis of still others, none of which, with the exception of the methyl compound, have been recorded previously in the literature. The methyl sulfon-*o*-toluidide was prepared in another manner by Witt and Uermenyi[2] who reported a melting point of 119–120°. Our compound, recrystallized four times from methanol, melted at 87–87.5°, and additional recrystallizations failed to raise the melting point.

Yields varied from 67–98% of the theoretical. All were purified by successive recrystallization from methanol, from which they deposit as colorless, odorless, prismatic plates and blunt needles. The compounds are insoluble in water, sparingly soluble in ether and methanol, and soluble in ethanol, acetic acid, acetone and the higher carbinols. They are stable in air and melt sharply without decomposition.

TABLE I

p-Toluene sulfon-*o*-toluidide	Formula	M. p., °C.	S, analyses, % Calcd.	Found
N-methyl	$C_{15}H_{17}O_2NS$	87–87.5	11.64	11.31
n-Propyl	$C_{17}H_{21}O_2NS$	72–72.5	10.56	10.69
Isopropyl	$C_{17}H_{21}O_2NS$	92–92.5	10.56	10.61
n-Butyl	$C_{18}H_{23}O_2NS$	82.5–83	10.09	9.82
Isobutyl	$C_{18}H_{23}O_2NS$	106–106.5	10.09	9.95
n-Amyl	$C_{19}H_{25}O_2NS$	80–80.5	9.55	9.49
Isoamyl	$C_{19}H_{25}O_2NS$	95–95.5	9.55	9.70

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[1] Young, THIS JOURNAL, **56**, 2167 (1934).

[2] Witt and Uermenyi, *Ber.*, **46**, 296–308 (1913).

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SCHOOL OF CHEMISTRY AND PHYSICS
PENNSYLVANIA STATE COLLEGE
STATE COLLEGE, PENNA.
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The Preparation of Higher Aliphatic Bromides

BY JOHN R. RUHOFF,[1] ROBERT E. BURNETT AND E. EMMET REID

The preparation of higher aliphatic bromides from the alcohol and aqueous hydrobromic acid, or hydrobromic–sulfuric acid mixtures, has not been found by us to be satisfactory; the yields are not high, and the purification of the product is difficult because of the presence of residual alcohol and some charred material—both of which give rise to troublesome emulsions after the usual washing of the crude bromide with concentrated sulfuric acid. However, by the use of anhydrous hydrobromic acid and a new method of washing, these difficulties are largely eliminated. The results are summarized in Table I.

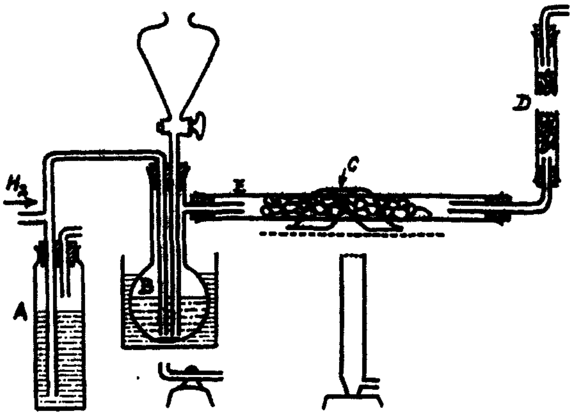

Fig. 1.—A, safety bottle; B, 125-cc. distilling flask, supported in a water-bath; C, one or two small pieces of asbestos paper;[2] D, tube 60 × 1.8 cm. filled with copper turnings to remove any uncombined bromine which may be carried over; E, reaction tube 30 × 1.8 cm., packed with pieces of porous plate about 8 mm. in diameter, and supported on a wire gauze, preferably with an asbestos center.

TABLE I

THE PREPARATION OF HIGHER BROMIDES

Alcohol	Reaction temp., °C.	Concn. MeOH for washing, %	Soly. of bromide in wash MeOH, g. per 100 cc.	Yield of bromide, %
Cyclohexyl	80–100	65	<1.0	73
n-Heptyl	80–100	50	<0.5	88
Dodecyl	100–120	50	< .1	89
Tetradecyl	100–120	50	< .1	89
Octadecyl	100–120	90	< .1	90

Gaseous hydrobromic acid is passed into the alcohol which is kept at about 100° until no more is absorbed. At least one and one-half hours is allowed for saturation. Approximately 1.5 moles of acid per mole of alcohol is required to form the bromide and to saturate the water formed. The crude product, which has a very pale straw color, is washed first with concentrated sulfuric acid, which is run off; phenolphthalein is added, and the bromide is shaken with dilute methyl alcohol containing sufficient ammonia to neutralize any residual acid; it is finally washed with dilute methyl alcohol, dried with calcium chloride, filtered and distilled.

The sulfuric acid converts the residual alcohol present in the crude bromide to the alkyl acid sulfate, which is dissolved out by the dilute methyl alcohol and ammonia, but which is not appreciably soluble in sulfuric acid. The use of methyl alcohol instead of water in washing the crude bromide increases the sharpness and rapidity of the separation since the difference in density is greater and the tendency to form emulsions is less.

The anhydrous hydrobromic acid was obtained by the direct combination of hydrogen and bromine in an all-Pyrex apparatus shown in Fig. 1.[3] The apparatus is thoroughly flushed out with hydrogen, bromine is immediately introduced into the flask B, and the Meker burner beneath C is lighted.[4] After a minute or two a slow stream of hydrogen is turned on. A flickering yellow flame indicates that the reaction is occurring. The temperature of the water-bath is adjusted so that the vapor pressure of bromine is just less than half an atmosphere—about 40°. A length of at least 10 cm. of the combustion tube between the flask B and the flame should be maintained at about room temperature to prevent the flame from striking back. The apparatus will produce up to 300 g. of hydrobromic acid an hour, and may be operated as slowly as desired.

JOHNS HOPKINS UNIVERSITY
BALTIMORE, MARYLAND
RECEIVED OCTOBER 26, 1934

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(1) Kewaunee Manufacturing Company Fellow in Chemistry, 1929–1933.

(2) The paper, which is to prevent the top of the tube from being cooled below the ignition temperature of an equimolar mixture of hydrogen and bromine, should not touch the tube, but should form a shield around it. If it is not placed in the proper position, the combination is incomplete, and free bromine is present in the hydrogen bromide.

(3) This is essentially a simplification of the method of Baxter and Coffin, THIS JOURNAL, **31**, 297 (1909).

(4) A small electric furnace is preferable, but by no means necessary.