

ethanol to give 83 g. (92%) of (XIX) as white crystals; m. p. 208°.

Anal. Calcd. for $C_{12}H_{16}N_2O_3S_2$: C, 47.98; H, 5.37. Found: C, 48.20, 48.24; H, 5.48, 5.51.

N-Sulfanyliothiomorpholine (XX).—A mixture of (XIX) (75 g., 0.25 mole) and 4 *N* hydrochloric acid (300 ml., 1.2 mole) was heated on a steam-bath for four hours. The cooled mixture was made alkaline with solid sodium carbonate and the precipitate which separated, filtered and washed with water. The crude product which weighed 61 g. (94%), when recrystallized from 50% ethanol gave pure (XX) as white plates; m. p. 181°.

Anal. Calcd. for $C_{10}H_{14}N_2O_2S_2$: C, 46.49; H, 5.46. Found: C, 46.59, 46.38; H, 5.36, 5.30.

N-(*p*-Arsonobenzenesulfonyl)-thiomorpholine (XIV).—A solution of (XX) (28 g., 0.109 mole), absolute ethanol (260 ml.) concd. sulfuric acid (10.2 g., 0.222 equiv. wt.) and arsenic trichloride (29 g., 0.166 mole) was diazotized at 0° with a saturated aqueous solution of sodium nitrite (7.5 g., 0.109 mole). After adding cuprous bromide (1 g.) and heating at 60° until all the nitrogen was evolved, the solution was steam distilled. The residue was filtered off, suspended in water (300 ml.), treated with sodium bicarbonate (30 g.) and filtered. The two filtrates were united and made acid to congo red paper with hydrochloric acid. The precipitate which formed was filtered off, dissolved in dilute alkali and precipitated with dilute hydrochloric acid; yield, 23.5 g. (59%). By repeatedly dissolving the crude product in dilute alkali and precipitating with dilute acetic acid analytically pure (XIV) resulted, which did not melt below 250°.

Anal. Calcd. for $C_{10}H_{14}AsNO_6S_2$: As, 20.40. Found: As, 20.50, 20.50.

Summary

1. A number of new arsonoarylaminoheterocycles were prepared by condensing certain halo-heterocycles with aminophenylarsonic acids in aqueous acid media.

2. 2-Chloro-5-arsonopyridine was condensed with several aryl and heterocyclic amines, under the same conditions, to obtain the corresponding 2-heterocyclicamino- and 2-arylamino-5-arsonopyridines.

3. Five of the arsonic acids prepared were converted to the corresponding bis-(carboxymethylthio)-arsino derivatives.

4. Morpholine and thiomorpholine were allowed to react with 3-nitro-4-bromophenylarsonic acid to produce 4-morpholino- and 4-thiomorpholino-3-nitrophenylarsonic acids; the corresponding 3-amino- derivatives were obtained by ferrous hydroxide reduction.

5. N-(*p*-Arsonobenzenesulfonyl)-thiomorpholine was prepared by conventional methods.

LINCOLN, NEBRASKA

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, DUKE UNIVERSITY]

Synthesis of Certain N,N-Dialkylethylenediamines¹

BY MELVIN S. BLOOM, DAVID S. BRESLOW AND CHARLES R. HAUSER

N,N-Dialkylethylenediamines have been prepared by the Gabriel synthesis using ethylene bromide and a secondary amine,² by the amination of a dialkylaminoethyl bromide hydrobromide³ and by the reduction of dialkylaminoacetonitriles.^{4,5} The last method appears to be the

several steps are involved, the reaction is readily carried out and requires only one distillation.

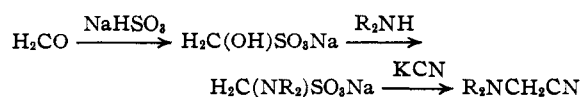
The dialkylaminoacetonitriles were reduced using sodium in ethanol or, preferably, in butanol, to form the corresponding diamines in yields of approximately 50%. The catalytic reduction of

TABLE I

Nitriles, RR'NCH ₂ CN			Yield, ^a		Diamines, RR'NCH ₂ CH ₂ NH ₂			Yield, ^a
R	R'	B. p., °C.	Mm.	%	Solvent	B. p., °C.	Mm.	%
C ₂ H ₅	C ₂ H ₅	60-60.5	14	81	Ethanol	144-145	760	53 ^b
<i>n</i> -C ₄ H ₉	<i>n</i> -C ₄ H ₉	100-102	8	76	Butanol	98-99	13	50 ^c
					Ethanol			46
<i>i</i> -C ₃ H ₇	H	91-93	10	61	Butanol	92-92.5	30	20 ^d
C ₆ H ₅	H	47 (m. p.)		35	Butanol

^a Based on the amine. ^b Picrate, m. p. 207°. ^c α -Naphthylurea, m. p. 102.5-103.5°. ^d Picrate, m. p. 191.5°. Calcd. for $C_{15}H_{21}N_5O_7$: N, 19.5. Found: N, 20.0.

best, since the nitriles are readily prepared in good yields by the following method.⁶ Although



(1) This work was supported in part by a grant from the Duke University Research Council.

(2) Ristenpart, *Ber.*, **29**, 2526 (1896).

(3) Amundsen and Krantz, *THIS JOURNAL*, **63**, 305 (1941).

(4) Winans and Adkins, *ibid.*, **55**, 4167 (1933).

(5) *Chem. Zentr.*, **101**, 11, 3083 (1930).

(6) Knoevenagel, *Ber.*, **37**, 4073 (1904); Knoevenagel and Mercklin, *ibid.*, **37**, 4081 (1904).

N,N-diethylaminoacetonitrile in 37% yield previously has been accomplished.⁴ The reduction of the dibutyl derivative has been reported,⁵ but no details were given. Although other N,N-dialkylethylenediamines could probably be prepared satisfactorily by the method here described, a monoalkylethylenediamine has been obtained in only 20% yield, while the monophenyl derivative failed to be produced in an appreciable yield. The results are summarized in Table I.

Experimental

Reduction of Aminoacetonitriles.—In a 500-ml. three-necked flask equipped with a mercury-sealed Hershberg

stirrer,⁷ reflux condenser and dropping funnel were placed 28 g. (1.2 moles) of sodium and 150 ml. of dry toluene. The sodium was powdered by heating the toluene to refluxing and stirring the solution vigorously. The flask was cooled to room temperature and 0.2 mole of the amino-acetonitrile⁸ dissolved in 100 ml. of *n*-butanol (distilled from sodium) was slowly added with stirring. The solution refluxed during the addition, stirring being continued until all the sodium had reacted and the reaction mixture had cooled to room temperature. Fifty ml. of water was added and the two layers were separated. The toluene-alcohol layer was made acid to congo red with hydrochloric acid, more water was added and the solution was concentrated to remove toluene and alcohol. The solution was then chilled, neutralized with 40% potassium hydroxide

(7) Hershberg, *Ind. Eng. Chem., Anal. Ed.*, **8**, 313 (1936).

solution and the diamine salted out by saturating the solution with anhydrous potassium carbonate. The diamine was extracted with benzene, the benzene solution dried over potassium carbonate, the solvent distilled and the residue distilled through a 15-cm. Vigreux column.

Summary

The reduction of certain *N,N*-dialkylamino-acetonitriles to the corresponding diamines has been effected satisfactorily by means of sodium in butanol or ethanol. The method does not appear to be satisfactory for monoalkyl derivatives.

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[CONTRIBUTION FROM THE RESEARCH LABORATORY OF PHYSICAL CHEMISTRY, POLYTECHNIC INSTITUTE OF BROOKLYN]

The Kinetics of the Thermal Decomposition of Gaseous Tetramethyltin¹

BY CHAS. E. WARING AND WM. S. HORTON^{1a}

The modern theory of reaction mechanism in the gaseous phase would undoubtedly be aided by kinetic studies of the decomposition of a series of molecules in which there is a stepwise gradation of structure and stability. It has been suggested² that the tetra-alkyls of the fourth group of the periodic table might be investigated to advantage because they offer the possibility of varying not only the length of the side chain, but also the size of the central atom. Such a series enables the comparison of the relative effects of various atomic forces.

Some work on these series of tetra-alkyl compounds has already been reported. Silicon tetramethyl,³ tetraethyl² and tetrapropyl,² germanium tetraethyl,⁴ and lead tetraethyl⁵ have been investigated and found to thermally decompose homogeneously in accordance with a first order law.

It was with the view of adding another methyl compound to the existing data, and also of initiating parallel studies in the tin series of tetra-alkyls, that the present investigation was undertaken.

Experimental

Tetramethyltin was prepared by a Grignard method suggested by Dr. George Calingaert of the Ethyl Gasoline Corporation.⁶ Essentially 6 to 8 moles of methylmagnesium iodide was prepared in a suitable amount of ether. One mole of stannic chloride dissolved in 100 ml. of toluene or xylene was slowly added to this with vigorous stirring and then the entire mixture refluxed for about five hours. Each preparation was carefully fractionated and only that product which had a constant boiling point of $76.8 \pm 0.1^\circ$, corrected, was used. This compound had a refractive index of 1.4409 and a specific gravity of 1.2904 =

0.0002. After purification, different preparations gave the same physical constants within the limit of error.

A micro-organic analysis gave the following results—calculated for $\text{Sn}(\text{CH}_3)_4$: C, 26.26; H, 6.15. Found: C, 28.00, 28.25; H, 6.85, 6.75. The difference between the calculated and observed values for the micro analysis are about as accurate as can be expected for this type of compound.

The course of the decompositions was followed in the usual manometric method using a mercury column in a 1.5-mm. capillary tube which had been previously examined and chosen for its uniformity of bore. The vapor reacted in Pyrex bulbs of 150-cc. capacity. Small bore capillary tubing was employed throughout so that the dead space was reduced to less than 2% of the total volume.

In the tests for the homogeneity of the reaction, a packed bulb was used which contained 100 small pieces of 7-mm. Pyrex tubing. The surface-to-volume ratio of the packed bulb was 8.8. That of the unpacked reaction bulb was calculated to be 0.94.

The reaction flask was placed in an electric furnace which was maintained at constant temperature within $\pm 0.05^\circ$ by a thyatron control device previously described.⁷ Temperatures were measured by a platinum-platinum-rhodium thermocouple in conjunction with a type K potentiometer. This latter instrument was checked regularly by a Mueller bridge and a standard platinum resistance thermometer.

Since the normal boiling point of $\text{Sn}(\text{CH}_3)_4$ is well above room temperature, all tubing and taps were heated electrically by means of nichrome resistance wire. The temperature of the taps did not vary more than 2° over a period of several hours. A special high temperature tap grease was employed. The remainder of the apparatus consisted of the usual system for obtaining low pressures and no run was made unless the pressure of the system, as measured by a calibrated McLeod gage, was at least 10^{-6} mm.

The gaseous reaction products were analyzed in a modified Bone and Wheeler apparatus. The higher olefins were separated from ethylene by the method of Hurd and Spence.⁸

Data and Results

1. Nature of the Decomposition.—From photochemical evidence with allied organo-metallic compounds, one might reasonably expect the

(7) Waring and Robison, *Rev. Sci. Instr.*, **14**, 143 (1943).

(8) Hurd and Spence, *This Journal*, **61**, 3353 (1929).

(1) Original manuscript received August 21, 1944.

(1a) Present address: The Ohio State University, Columbus, Ohio.

(2) C. E. Waring, *Trans. Faraday Soc.*, **235**, 1142 (1940).

(3) Heim and Mack, *This Journal*, **59**, 60 (1937).

(4) Geddes and Mack, *ibid.*, **52**, 4372 (1930).

(5) Leermakers, *ibid.*, **55**, 4508 (1933).

(6) Private communication.