

(15 min., slightly exothermic). After standing at room temperature for 18 hr. the deep lilac-colored solution was quenched in 800 ml. of water, allowed to stand for 1 hr., and filtered. The washed and dried crude product crystallized from *n*-hexane in long rods, m.p. 139.4–141.2°; $[\alpha]_D^{25}$ –99.4° (1% in CHCl_3). The yield was 3.18 g.

Anal. Calcd. for $\text{C}_{27}\text{H}_{38}\text{O}_4$: C, 76.02; H, 8.98. Found: C, 76.30; H, 8.75.

17 α -Ethinylandro-5-ene-3 β ,17 β -diol 3,17-di(3-cyclohexylpropionate). A mixture of 3.14 g. (0.01 mole) of 17 α -ethinylandro-5-ene-3 β ,17 β -diol, 8.9 g. (0.03 mole) of cyclohexylpropionic anhydride and 50 ml. of c.p. pyridine was refluxed for 18 hr. After the usual workup, the product was chromatographed on 250 g. of silica gel. The diester was eluted with 5% ether-pentane and recrystallized from alcohol, m.p. 114.0–115.6°; $[\alpha]_D^{25}$ –61.0° (1% in CHCl_3).

Anal. Calcd. for $\text{C}_{39}\text{H}_{58}\text{O}_4$: C, 79.27; H, 9.89. Found: C, 79.47; H, 10.06. The mixed melting point with the 3-monoester was 105–112°.

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Preparation of 2-Nitroisonicotinic Acid Hydrazide and 2-Aminoisonicotinic Acid Hydrazide

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Previous investigators² have shown that the introduction of a substituent in the pyridine ring of isonicotinic acid hydrazide usually causes almost complete loss of *in vitro* antituberculous activity. However, the 3-aminoisonicotinic acid hydrazide did show slight activity. For this reason, it seemed worthwhile to prepare and test the isomeric 2-amino derivative for effectiveness.

Another group, the nitro, which has not previously been tested for its effect on antituberculous activity when in the ring, was also introduced into the 2-position and tested.

EXPERIMENTAL³

Biological assays. The biological activity of the compounds was determined, using the biologic assay method for isonicotinic acid hydrazide.⁴ The inhibitory concentration of 2-nitroisonicotinic acid hydrazide for the standard H37Rv is greater than 10 mcg./ml; that of 2-aminoisonicotinic acid hydrazide is between 2.5 and 5.0 mcg./ml. The standard test organism is inhibited by 0.03 to 0.07 mcg./ml. of isonicotinic acid hydrazide.

2-Amino-4-methylpyridine. Eastman Kodak material recrystallized from hot water was used as the starting material.

(1) Present address: United States Department of Agriculture, Agricultural Research Service, Southern Utilization Research Branch, New Orleans, La.

(2) J. Bernstein and coworkers, *Am. Rev. Tuberc.*, **67**, 354 (1953).

(3) Biological Assays by P. Z. Morse and B. T. Miyahara. All melting points were taken on a Fisher-Johns melting point block. Microanalyses by Galbraith Microanalytical Laboratories and Huffman Microanalytical Laboratories.

(4) Transactions of the Fifteenth Conference on the Chemotherapy of Tuberculosis, 1956, p. 581.

2-Nitro-4-methylpyridine. This was prepared by the method of Wiley and Hartman.⁵ Oxidation of the 2-amino-4-methylpyridine with persulfuric acid gave a 52% yield of 2-nitro-4-methylpyridine, m.p. 65.5–67° (lit.⁵ 61–62°).

2-Nitroisonicotinic acid. This was prepared by the permanganate oxidation of the 2-nitro-4-methylpyridine according to the procedure given by Brown.⁶ The yield which was calculated after subtracting the amount of recovered starting material was 26%, m.p. 172.5–173.5° (lit.⁶ 175°).

Methyl 2-nitroisonicotinate. One ml. of methanol, 0.4 g. of Victor polyphosphoric acid, and 0.168 g. (0.001 mole) of 2-nitroisonicotinic acid were mixed and heated at reflux for 6 hrs. The methanol was removed *in vacuo* and the acid was neutralized with sodium hydroxide solution. Ether was added to extract the ester. The ether was evaporated to obtain needles, 0.124 g. (68%), m.p. 80–81°. The ester was recrystallized from benzene and washed with petroleum ether before analysis.

Anal. Calcd. for $\text{C}_7\text{H}_8\text{N}_2\text{O}_4$: C, 46.16; H, 3.32. Found: C, 46.75; H, 3.27.

2-Nitroisonicotinic acid hydrazide. Methyl 2-nitroisonicotinate (0.036 g., 0.0002 mole) was refluxed with a slight excess of 85% hydrazine hydrate dissolved in 0.6 ml. of ethanol. After 10 min., crystals began to come out of the solution. Heating was continued for 1 hr. The crystals were filtered; yield 0.024 g. (67%), m.p. 181.5–183.5°.

Anal. Calcd. for $\text{C}_6\text{H}_8\text{N}_4\text{O}_3$: C, 39.56; H, 3.32. Found: C, 40.01; H, 3.41.

Methyl 2-aminoisonicotinate. The methyl 2-nitroisonicotinate (0.273 g., 0.0018 mole) was reduced by refluxing with excess iron filings in 1 ml. of a solution of 12*N* HCl in methanol (1:5). After 2 hr. the black mixture was filtered and the filtrate neutralized with methanolic sodium hydroxide solution. The solution was evaporated to dryness and extracted with ether. The ether was evaporated to obtain plates, 89 mg. (39%). After recrystallization from benzene, the crystals were pale yellow, m.p. 149.5–151°.

Anal. Calcd. for $\text{C}_7\text{H}_8\text{N}_2\text{O}_2$: C, 55.24; H, 5.30. Found: C, 55.90; H, 5.27.

2-Aminoisonicotinic acid hydrazide. Methyl 2-aminoisonicotinate (0.046, 0.0003 mole) was refluxed for 2 hr. with excess 85% hydrazine hydrate in 0.6 ml. of ethanol. On cooling, needles were obtained; yield 14 mg. (31%), m.p. 194.5–195°.

Anal. Calcd. for $\text{C}_6\text{H}_8\text{N}_4\text{O}$: C, 47.35; H, 5.30. Found: C, 47.93; H, 5.28.

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(5) R. H. Wiley and J. L. Hartman, *J. Am. Chem. Soc.*, **73**, 494 (1951).

(6) E. V. Brown, *J. Am. Chem. Soc.*, **76**, 3167 (1954).

Reaction of D-Glucamine with Aromatic Nitro and Halogen Compounds

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Tamm³ has shown that *N*-glucosides of some

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(2) Fellow of the American Foundation for Pharmaceutical Education, 1953–55.

(3) I. Tamm, K. Folkers, C. H. Shunk, and F. L. Horsfall, *J. Exptl. Med.*, **99**, 227(1954); I. Tamm, *Science*, **120**, 847(1954).

halogenated benzimidazoles possess low inhibitory properties against virus multiplication in the chick embryo. The condensation of activated nitro- and halogen-substituted benzenes with D-glucamine was therefore attempted as a method of obtaining *N*-aryl-D-glucamines for antiviral testing. A recent review⁴ of the nucleophilic replacements of activated aromatic nitro and halogen groups indicated the feasibility of the proposed reaction, but also that unexpected products could be obtained. Other reports by Folkers *et al.*,⁵ however, described the condensations under a nitrogen atmosphere of various glycamines with activated nitro and halogen compounds such as 1,2-dinitro-4,5-dichlorobenzene and 2-nitrochlorobenzene, and the expected *N*-arylglycamines were obtained.

A reaction between D-glucamine and *p*-nitrochlorobenzene was found to occur in boiling pyridine, with replacement of the halogen, as might be expected. A 14% yield of *N*-*p*-nitrophenyl-D-glucamine resulted; no reaction took place in ethanol-sodium acetate, however, den Otter⁶ has reported that 2,4-dinitrochlorobenzene and D-glucamine react in ethanol in the presence of sodium acetate to form *N*-2,4-dinitrophenyl-D-glucamine in unspecified yield. On repeating this experiment we obtained a 77% yield of material which melted 16° higher than previously reported but gave a correct carbon-hydrogen analysis. In boiling pyridine, however, the product was 2,4-dinitroaniline (69% yield in 2 hr.).

Similarly, primary amines were obtained from the reaction of D-glucamine in pyridine with 1,3,5-trinitrobenzene, 2,4,6-trinitrotoluene, 3-nitro-4-chlorobenzoic acid, 3-nitro-4-chlorobenzamide, *p*-dinitrobenzene, *p*-nitrobenzenesulfonamide, and 2-chloro-5-nitrobenzenesulfonamide. The reaction of *m*-dinitrobenzene with D-glucamine gave only 3% of *m*-nitroaniline after 18 hr. in boiling pyridine, but a larger yield (20%) of 3,3'-dinitroazobenzene was obtained. The same reaction with *m*-dinitrobenzoic acid, however, gave no evidence of oxidation-reduction; a 15% yield of 3-amino-5-nitrobenzoic acid was the only product isolated. Another instance of oxidation-reduction was observed in the reaction of *p*-dinitrobenzene with D-glucamine in ethanol-sodium acetate. A 3% conversion to *p*-nitroaniline took place, and a 3% yield of 4,4'-dinitroazobenzene was also obtained.

Possible mechanisms for the production of primary aromatic amines from these reactions include the following: (a) Reaction of the aryl halides

with pyridine to form arylpyridinium salts, followed by ammonolytic cleavage to primary amines; (b) Decomposition of D-glucamine to form ammonia which then attacks the halides or nitro compounds to form amines; (c) Formation of the *N*-aryl-D-glucamines, followed by decomposition to primary amines; (d) Direct reduction of nitro to amino groups when halogen is absent.

The first possibility is apparently a factor in the reaction; 2,4-dinitrochlorobenzene, for instance, forms a brown solid in refluxing pyridine which melts with decomposition about 200° above the melting point of the 2,4-dinitrochlorobenzene. The second possible course is also involved, since D-glucamine definitely liberates ammonia on refluxing in pyridine. Approximately 50% of the D-glucamine is decomposed by this treatment in 18 hr. The third possibility is unlikely, since formation of glucamines was in no case accompanied by primary amines, even with shorter reaction times. Definite evidence is at hand for the fourth mechanism with the simultaneous formation of azo compounds in two instances. No azo compound was found, however, when *m*-dinitrobenzene was refluxed with cyclohexylamine in pyridine, which implies that the sugar moiety is involved where reduction reactions are possible.

EXPERIMENTAL

The melting points listed are uncorrected. The elemental analyses were carried out at the Weiler and Strauss Micro-analytical Laboratory, Oxford, England.

D-Glucamine. The high pressure hydrogenation procedure of Holly *et al.*^{5a} was employed, giving a product of m.p. 122-126°. This agrees with the recorded value, which indicates a purity of approximately 80%.

N-4-Nitrophenyl-D-glucamine. D-Glucamine (5.0 g., 0.028 mole) and *p*-nitrochlorobenzene (5.0 g., 0.032 mole) were refluxed with 15 ml. of anhydrous pyridine for 18 hr. After cooling and decanting from a black tar, the resulting solution was diluted with 15 ml. of water; yellow needles of *p*-nitrochlorobenzene precipitated. The filtrate was then steam distilled until 250 ml. of distillate was collected, the residue was concentrated to about 20 ml., and a fine, yellow powder appeared after chilling. This was filtered, washed with water, and recrystallized from methanol to give 1.2 g. (14.4%) of yellow needles of *N*-4-nitrophenyl-D-glucamine, m.p. 155-158°.

Anal. Calcd. for C₁₂H₁₈N₂O₇: C, 47.68; H, 6.00. Found: C, 47.62; H, 6.21.

N-2,4-dinitrophenyl-D-glucamine. D-Glucamine (4.0 g., 0.022 mole), 2,4-dinitrochlorobenzene (5.0 g., 0.025 mole), and anhydrous sodium acetate (5.0 g., 0.061 mole) were refluxed with 250 ml. of absolute ethanol for 5 hr. The solution was concentrated to about 50 ml. and 25 ml. of water was added. The hot aqueous solution was quickly extracted with two 25-ml. portions of carbon tetrachloride and chilled overnight. The product separated as yellow, crystalline rosettes, and after recrystallization from methanol weighed 5.9 g. (76.8% yield) and melted at 165-167°. Further recrystallization from methanol gave a m.p. of 167-169°.

Anal. Calcd. for C₁₂H₁₇N₃O₉: C, 41.50; H, 4.94. Found: C, 41.23; H, 4.66.

Reaction of D-glucamine with p-dinitrobenzene: In pyridine. D-Glucamine (4.0 g., 0.022 mole) and *p*-dinitrobenzene (3.7 g., 0.022 mole) were refluxed with 15 ml. of anhydrous pyridine for 18 hr. After dilution with water and steam dis-

(4) J. F. Bunnett and R. E. Zahler, *Chem. Revs.*, **49**, 273 (1951).

(5) (a) F. W. Holly, E. W. Peel, R. Mazingo, and K. Folkers, *J. Am. Chem. Soc.*, **72**, 5416 (1950); (b) F. W. Holly, E. W. Peel, J. J. Cahill, F. R. Koniuszy, and K. Folkers, *J. Am. Chem. Soc.*, **74**, 4047 (1952); (c) C. H. Shunk, F. R. Koniuszy, and K. Folkers, *J. Am. Chem. Soc.*, **74**, 4251 (1952).

(6) H. den Otter, *Rec. trav. chim.*, **56**, 1196 (1937).

tillation, the aqueous concentrate yielded 0.5 g. (16.5%) of *p*-nitroaniline, m.p. 148–149° (lit.⁷ m.p. 147°). The *N*-acetyl derivative melted at 214–215° (lit.⁷ m.p. 215°). In ethanol-sodium acetate. *D*-Glucamine (4.0 g., 0.022 mole), *p*-dinitrobenzene (3.7 g., 0.022 mole), and anhydrous sodium acetate (4.0 g.) were refluxed with 250 ml. of absolute ethanol for 5 hr. Conventional methods of isolation gave 0.1 g. (3.3%) of *p*-nitroaniline, m.p. 146–148°. The original aqueous solution also gave 0.1 g. of orange needles, m.p. 190–192°. Further recrystallizations failed to raise this m.p., which corresponds to that of 4,4'-dinitroazobenzene (lit.⁸ m.p. 192°). The carbon-hydrogen analysis, however, checks for 4,4'-dinitroazobenzene (lit.⁹ m.p. 222°).

Anal. Calcd. for $C_{12}H_8N_4O_5$ (Azoxy): C, 50.00; H, 2.80. Calcd. for $C_{12}H_8N_4O_4$ (Azo): C, 52.95; H, 2.96. Found: C, 52.83; H, 3.04.

The product obtained was orange-red in color, while the azo compound is reported to be orange-red and the azoxy compound lemon yellow. The ultraviolet absorption spectrum of the product showed a maximum at 342 μ , which corresponds to the maximum of the azo compound reported by Szego.¹⁰

Reaction of D-Glucamine with m-dinitrobenzene. *D*-Glucamine (4.0 g., 0.022 mole) and *m*-dinitrobenzene (3.7 g., 0.022 mole) were refluxed with 15 ml. of anhydrous pyridine for 18 hr. After dilution with water, steam distillation, and extraction of the residue with chloroform-carbon tetrachloride (1:1), a solid resulted from the residual solution, which was washed with dilute sulfuric acid and recrystallized from benzene and ligroin to give 0.6 g. (20%) of orange needles of 3,3'-dinitroazobenzene, m.p. 145.5–147.5° (lit.⁹ m.p. 149–150°).

Anal. Calcd. for $C_{12}H_8N_4O_4$: C, 52.95; H, 2.96. Found: C, 52.91; H, 2.98.

The dilute sulfuric acid extract of the impure solid was made basic and chilled, giving 0.1 g. (3.3%) of *m*-nitroaniline, m.p. 107–111° (lit.⁷ m.p. 114°). The *N*-acetyl derivative melted at 151–153° (lit.¹¹ m.p. 155°).

Reaction of D-glucamine with 1,3,5-trinitrobenzene. *D*-Glucamine (5.0 g., 0.028 mole) and 1,3,5-trinitrobenzene (5.0 g., 0.024 mole) were refluxed with 20 ml. of anhydrous pyridine for 18 hr. By common purification procedures was obtained 0.2 g. of yellow needles, m.p. 138–140° (from aqueous ethanol) which was insoluble in dilute acid. Salkowski¹² lists a m.p. of 138° for 2,6-dinitroaniline, for which the yield is 5.0%.

Anal. Calcd. for $C_8H_5N_3O_4$: C, 39.33; H, 2.75. Found: C, 39.28; H, 2.75.

The *N*-acetyl derivative melted at 193–195° after four recrystallizations from aqueous ethanol (lit.¹³ m.p. 197°). The 4-bromo derivative was also prepared, using a large excess of bromine-potassium bromide in water; m.p. 156–159° (lit.¹⁴ m.p. 160°). The *N*-acetyl derivative of 3,5-dinitroaniline melts at 191°,¹⁵ while an excess of bromine converts 3,5-dinitroaniline to the tribromo derivative, m.p. 235°.¹⁶

Reaction of D-glucamine with 2,4,6-trinitrotoluene. *D*-Glucamine (4.0 g., 0.022 mole) and 2,4,6-trinitrotoluene (5.0 g., 0.022 mole) in similar fashion gave two products of m.p. 169–171° and 148–153° after fractionation from acetic acid and recrystallization from aqueous ethanol. The m.p. of

the first product corresponds to that of 4-amino-2,6-dinitrotoluene (lit.¹⁷ m.p. 171°) and the second to 2-amino-4,6-dinitrotoluene (lit.¹⁷ m.p. 155°). The 0.1 g. of the combined isomers represents a 2.3% conversion.

Reaction of D-glucamine and 2,4-dinitrochlorobenzene. *D*-Glucamine (4.0 g., 0.022 mole) and 2,4-dinitrochlorobenzene (5.0 g., 0.025 mole) were refluxed with 15 ml. of anhydrous pyridine for 18 hr. After dilution with water and steam distillation was obtained 2.2 g. (54.3%) of yellow 2,4-dinitroaniline, m.p. 178.5–180°. A mixed melting point with an authentic sample showed no depression. A second run of this reaction in which the time of refluxing was shortened to 2 hr. gave 2.8 g. (69%) of 2,4-dinitroaniline, with no evidence of accompanying decomposition.

D-Glucamine and 3,5-dinitrobenzoic acid. *D*-Glucamine (4.0 g., 0.022 mole) and 3,5-dinitrobenzoic acid 4.7 g., 0.022 mole) were allowed to react in the same manner to give a solid which melted at 192–202° and weighed 0.6 g. It was converted to an ethyl ester, m.p. 92–94°, which agrees with that¹⁸ for the ethyl ester of 3,5-dinitrobenzoic acid.

An acid extract also gave 0.6 g. of solid after neutralization which melted at 206–208°, and was converted to an ethyl ester which melted at 155–156°. Hubner¹⁹ lists 209–210° as the melting point of 3-amino-5-nitrobenzoic acid and 155° for its ethyl ester. The 0.6 g. obtained represents a yield of 14.8%. The *N*-acetyl derivative melted at 294–295°.

Anal. Calcd. for $C_9H_8N_2O_5$: C, 48.22; H, 3.60. Found C, 48.13; H, 3.49.

D-Glucamine and 4-chloro-3-nitrobenzoic acid. *D*-Glucamine (4.0 g., 0.022 mole) and 4-chloro-3-nitrobenzoic acid (4.5 g., 0.022 mole) were refluxed with 15 ml. of anhydrous pyridine for 18 hr. After dilution with water, steam distillation, and removal of tar, the tar was extracted with methanol. The extract was evaporated, and the residue was dissolved in ethyl acetate to give a high-melting solid after evaporation. This was extracted with dilute sulfuric acid which was neutralized, giving 0.2 g. of material melting at 186–188°. Brill²⁰ lists 186–187° as the m.p. of *p*-aminobenzoic acid, and a mixed melting point with an authentic sample gave no depression. This amount represents a 0.7% yield.

The acid-extracted solid, which was soluble in base, was recrystallized several times from methanol to give 0.8 g. of bright yellow product, m.p. 273–277°. The material could not be purified further by recrystallization, nor could a pure *N*-acetyl derivative be prepared. Bogert²¹ lists 284° as the melting point of 3-nitro-4-aminobenzoic acid, and assuming it to be somewhat impure, a 19.5% yield was recovered.

D-Glucamine and 4-chloro-3-nitrobenzamide. Carrying out the same procedure as above, using 4.5 g. (0.022 mole) of 4-chloro-3-nitrobenzamide, 1.0 g. (25%) of yellow 4-amino-3-nitrobenzamide was isolated from the aqueous concentrate and recrystallized from aqueous acetone. The m.p. was 224–227° (lit.²² m.p. 226–227°), and the *N*-acetyl derivative melted at 240–241° in a sealed tube (lit.²¹ m.p. 239.5°).

D-Glucamine and p-nitrobenzenesulfonamide. Submitting 4.5 g. (0.022 mole) of *p*-nitrobenzenesulfonamide to the same procedure, the aqueous concentrate yielded 2.8 g. of unreacted sulfonamide and another material which was extracted with acid and neutralized to pH 6. A precipitate of 0.2 g. (5.2%) of sulfanilamide was obtained which melted at 162–164°.

D-Glucamine and 2-chloro-5-nitrobenzenesulfonamide. A similar reaction with 5.2 g. (0.022 mole) of 2-chloro-5-nitrobenzenesulfonamide gave a solid which was extracted with

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- (8) A. Werner and E. Stiasny, *Ber.*, **32**, 3272 (1899).
- (9) S. Goldschmidt and L. Strohmeyer, *Ber.*, **65**, 2463 (1932).
- (10) L. Szego, *Ber.*, **62**, 736 (1929).
- (11) Br. Pawlewski, *Ber.*, **31**, 661 (1898).
- (12) H. Salkowski, *Ann.*, **174**, 273 (1874).
- (13) H. Salkowski, *Ber.*, **10**, 1695 (1877).
- (14) P. Austen, *ibid.*, **9**, 919 (1886).
- (15) J. Blanksma and G. Verberg, *Rsc. trav. chim.*, **53**, 988 (1934).
- (16) J. Blanksma, *Rec. trav. chim.*, **28**, 97 (1909).

- (17) A. Holleman and J. Boeseken, *Rec. trav. chim.*, **16**, 426 (1897).
- (18) G. Malone and E. Reid, *J. Am. Chem. Soc.*, **51**, 3424 (1929).
- (19) H. Hubner, *Ann.*, **222**, 81 (1884).
- (20) H. Brill, *J. Am. Chem. Soc.*, **43**, 1320 (1921).
- (21) M. Bogert and L. Wise, *J. Am. Chem. Soc.*, **34**, 700 (1912).
- (22) P. Thieme, *J. prakt. Chem.*, **43**, 451 (1891).

acetone and ethyl acetate to give 0.2 g. of solid melting at 205–208° after several recrystallizations from aqueous methanol. Fischer²³ gives 207° as the melting point of 2-amino-5-nitrobenzenesulfonamide. The yield was 4.2%, and 0.3 g. of unreacted sulfonamide was also recovered.

Cyclohexylamine and m-dinitrobenzene. Cyclohexylamine (3.0 g., 0.030 mole) and *m*-dinitrobenzene (5.0 g., 0.030 mole) were subjected to the same conditions, and the resulting aqueous concentrate was extracted with benzene. Evaporation of the extract to a tar and extraction with dilute sulfuric acid gave 0.02 g. (0.5%) of *m*-nitroaniline after neutralization; m.p. 104–109°. A mixed melting point with an authentic sample gave no depression. The acid-extracted tar was recrystallized from aqueous ethanol, and 4.7 g. of unreacted *m*-dinitrobenzene, m.p. 88–90°, was recovered.

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(23) P. Fischer, *Ber.*, 24, 3788 (1891).

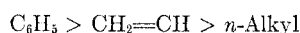
Vinyl Derivatives of the Metals.

III. Vinylmercuric Halides

DIETMAR SEYFERTH

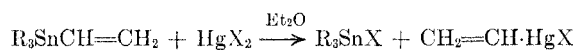
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Recent studies of vinyltin compounds^{1,2} have shown that a vinyl group connected to a tin atom is quite labile, and its position in the Kharasch-type cleavage series for organotin compounds was shown to be:



Manulkin³ reported the cleavage of tetraalkyltin compounds by mercuric halide in alcoholic solution to give a mixture of trialkyltin halide and dialkyltin dihalide with the corresponding alkylmercuric halide.

We have utilized the observed lability of the vinyl-tin bond to prepare the vinylmercuric halides, reported here for the first time, by preferential cleavage of the vinyl group from alkylvinyltin compounds with mercuric chloride, bromide, or iodide:



The method of Manulkin was modified as described in the experimental part of this study. Our Soxhlet method of carrying out this reaction has the advantage that this usually quite vigorous reaction is moderated, and that only small quantities of solvent are required. This method is particularly useful when the extremely insoluble mercuric iodide is used.

(1) D. Seyferth and F. G. A. Stone, *J. Am. Chem. Soc.*, 79, 515 (1957).

(2) D. Seyferth, *J. Am. Chem. Soc.*, in press; cf. Abstracts of Papers Presented at the 131st A.C.S. Meeting, Miami, April 1957, p. 16-M.

(3) Z. M. Manulkin, *J. Gen. Chem. (U.S.S.R.)*, 16, 235 (1946).

The three vinylmercuric halides, their melting points, and their analytical data are listed in Table I. Work utilizing these compounds in other organometallic syntheses is in progress.

TABLE I
VINYL MERCURIC HALIDES, $CH_2=CH-HgX$

X	M.p., °C.	Analyses ^a	
		Calcd., %	Found, %
Cl	185–186	Hg: 76.24	75.92
Br	168–170	Hg: 65.22	65.12
I	150–151.5	C: 6.77	6.96
		H: 0.85	0.91
		I: 35.80	36.04

^a Analyses were performed by the Schwarzkopf Micro-analytical Laboratory, Woodside, N. Y.

EXPERIMENTAL

The preparation of vinylmercuric bromide is described as an example of the technique used.

A solution of 25.7 g. (0.1 mole) of *n*-butyltrivinyltin in 200 ml. of ether was prepared in the still pot of a Soxhlet extraction apparatus. A Soxhlet thimble was filled with 36.0 g. (0.1 mole) of mercuric bromide and placed in the apparatus. The cycling of ether was continued for about 20 hr. until all of the mercuric bromide had been brought to reaction. During the course of the reaction white platelets of vinylmercuric bromide crystallized in the still pot.

The solution was cooled and filtered, concentrated to about one third of its original volume and filtered again to give 20.0 g. of vinylmercuric bromide, a yield of 65%. Recrystallization of a small sample from ether gave analytically pure compound. Fractional distillation of the liquid residue gave 20.5 g. (66.1% yield) of the new compound, *n*-butyldivinyltin bromide, b.p. 72° at 0.75 mm. to 70° at 0.6 mm., d_4^{25} 1.529, n_D^{25} 1.5221.

Anal. Calcd. for $C_8H_{16}BrSn$: C, 31.01; H, 4.88; MR_D , 61.85. Found: C, 31.11; H, 5.03; MR_D , 61.80.

Vinylmercuric chloride was prepared in the same manner using di-*n*-butyldivinyltin and mercuric chloride. Vinylmercuric iodide was obtained from the reaction of *n*-butyltrivinyltin with red mercuric iodide. The reaction proceeded exceedingly slowly due to the insolubility of mercuric iodide. After the ether had been cycled for 2 days only 3 g. of vinylmercuric iodide had crystallized.

Under identical conditions no reaction was observed between tetraalkylgermane, $(CH_2=CH)_4Ge$, and mercuric chloride.

The vinylmercuric halides are stable with respect to atmospheric oxygen and moisture; therefore no special precautions are required. Because of the known high toxicity of $RHgX$ compounds,⁴ all operations were carried out in a good hood.

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(4) E. Krause and A. v. Grosse, "Die Chemie der metallorganischen Verbindungen," Borntraeger, Berlin, 1937, p. 130.

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