bromide in ether. From this reaction was obtained 11.6 g. (51.3%) of crude 1-cyano-2,2-diethylhydrazine. After several recrystallizations from ethyl acetate using Norite A decolorizing carbon the product melted at 115.5–116.8°.

*Anal.* Calcd. for $C_5H_{11}N_3$: C, 53.07; H, 9.80; N. 37.14. Found: C, 53.35; H, 10.00; N, 37.11.

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## Preparation and Reduction of Methylvinylnitrosamine

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As a part of the investigation of hydrazines and related compounds in this laboratory, attempts were made to prepare 1-methyl-1-vinylhydrazine. One route to the synthesis of this compound appeared to lie through the reduction of methylvinylnitrosamine. This nitrosamine was selected because it has been found that the nitroso group in diallylnitrosamine can be reduced to give the corresponding hydrazine leaving the carbon-carbon bonds intact.[1] Methylvinylnitrosamine was synthesized in 51.7% yield from β-hydroxyethylmethylamine through nitrosation, chlorination, and dehydrohalogenation. It was later found that Workman[2] had prepared methylvinylnitrosamine in a similar manner during the course of a study undertaken to determine the products resulting from the thermal decomposition of β-chloroethylmethylnitrosamine.

Reduction of methylvinylnitrosamine was attempted with a number of reducing agents. The first reactions were carried out with lithium aluminum hydride in ether. Because the desired compound was not obtained, several variations of the hydride reduction were investigated. These included reverse addition of the hydride solution to the nitrosamine solution, change in solvent to tetrahydrofuran, and variation of the amount of hydride. None of these methods gave 1-methyl-1-vinylhydrazine. From the crude reaction mixtures only methylhydrazine and 1-ethyl-1-methylhydrazine were isolated and identified. Other fractions were separated from the reaction mixture but were too small and impure to identify. Reduction with sodium borohydride was also attempted after first verifying that dimethylnitrosamine could be reduced to 1,1-dimethylhydrazine by the borohydride. Small yields were obtained when the reaction was carried out in water at 70° for eight hours. Similar treatment of methylvinylnitrosamine, however, gave no reaction and the compound was recovered unchanged.

Other reducing agents included sodium hydrosulfite in basic solution. Reaction of this reagent with methylvinylnitrosamine gave a 63.5% yield of methylamine which was identified as its oxalate. Traces of ammonia also were produced. Reduction with sodium in liquid ammonia of methylvinylnitrosamine did not give an isolable product. Only a brown solid residue was obtained from this reaction. Catalytic hydrogenation of methylvinylnitrosamine also was attempted a number of times because it seemed to offer an easy method for isolation of the product. Catalysts employed were freshly activated palladium on charcoal, palladium on gum arabic, and platinum oxide. The reductions were run in ethyl alcohol either with a trace of hydrochloric acid or a trace of acetic acid. The solutions from these reductions had the power to reduce potassium iodate but the concentration of the products was such that no volatile products could be isolated. Hydrogenation in ethyl alcohol without acid using platinum oxide catalyst gave a 53.4% yield of ethylmethylnitrosamine.

In the course of an alternative procedure for the preparation of 1-methyl-1-vinylhydrazine, an effort was made to prepare 1-β-chloroethyl-1-methylhydrazine as an intermediate which could be dehydrohalogenated. Reduction of β-chloroethylmethylnitrosamine with lithium aluminum hydride in ether, however, gave a 54.2% yield of crude 1-ethyl-1-methylhydrazine. Similar results were obtained by Wawzonek and Culbertson[3] in the lithium aluminum hydride reduction of *n*-butyl-4-chlor-*n*-butylnitrosamine. The reduction produced mainly 1,1-di-*n*-butylhydrazine and di-*n*-butylnitrosamine.

### EXPERIMENTAL

*β-Hydroxyethylmethylnitrosamine.* To 751.1 g. (10.0 moles) of β-methylaminoethanol (Eastman Kodak Co.) was added approximately 200 ml. of water. While cooling the flask in an ice bath the amine solution was made just acid to litmus with 835 ml. of concd. hydrochloric acid. The solution was then heated to 70–75°, and 793 g. (11.5 moles) of sodium nitrite dissolved in 1 l. of water was added slowly through a dropping funnel. Addition required 2 hr. during which time the reaction mixture was held at the above temperature. Additional small quantities of concentrated hydrochloric acid were added from time to time to keep the solution acidic. After completion of the sodium nitrite addition, the mixture was held at reaction temperature and stirred for an hour longer. It was then cooled to room temperature and the precipitated inorganic salts removed by filtration. Most of the water and ethyl alcohol were removed from the product by means of a rotating vacuum evaporator. Final purification was accomplished by distillation at reduced pressure. The yield of bright yellow β-hydroxyethylmethylnitrosamine was 1019.5 g. (97.9%) boiling at 110.5–111.5°/1.0 mm., $n_D^{25}$ 1.4778.

*β-Chloroethylmethylnitrosamine.* A solution of 312.3 g. (2.5 moles) of β-hydroxyethylmethylnitrosamine in 600 ml. of dry thiophene-free benzene was prepared and cooled to

(1) Unpublished results.
(2) W. R. Workman, *Dissertation Abstr.*, **15**, 1733 (1955).
(3) S. Wawzonek and T. P. Culbertson, *J. Am. Chem. Soc.*, **81**, 3367 (1959).

−10 to −15° in a Dry Ice–acetone bath. To this solution was added with constant stirring, 333.1 g. (2.8 moles) of clear white thionyl chloride from a dropping funnel. After addition was completed, the solution was allowed to warm. When the temperature reached 10°, evolution of nitrogen oxides was noted and 159 g. (1.5 moles) of anhydrous sodium carbonate was added to neutralize the acid formed in the reaction. The mixture was then heated under reflux for 3 hr. No further reaction as shown by the evolution of sulfur dioxide was noted. After allowing the mixture to cool, the solid inorganic salts were filtered off and washed with benzene. The benzene solution and washings were concentrated on a rotating vacuum evaporator. Vacuum distillation of the residual yellow liquid gave 202.1 g. (66% yield) of β-chloroethylmethylnitrosamine boiling at 77–78°/2 mm.; $n_D^{25}$ 1.4797.

*Anal.* Calcd. for $C_3H_7N_2OCl$: C, 29.4; H, 5.8; N, 22.9; Cl, 28.9. Found: C, 29.6; H, 6.1; N, 23.4; Cl, 28.4.

When pyridine was used as the base in the reaction the yield was increased to 92.5% but it was found that even repeated careful vacuum fractional distillation could not rid the product of the pyridine-sulfur dioxide complex which contaminated it.

*Methylvinylnitrosamine.* A solution containing 165 g. of 85% potassium hydroxide (2.5 moles) in 700 ml. of absolute methyl alcohol was cooled to 10°. While the solution was stirred and held below 35°, 245 g. (2.0 moles) of β-chloroethylmethylnitrosamine was slowly added through an addition funnel. The reaction mixture turned cloudy as addition progressed and solid potassium chloride began to precipitate. Addition was completed in about 1 hr. and the reaction mixture was then refluxed for 1 hr. before being allowed to stand for 16 hr. The precipitated potassium chloride was removed by filtration and the filtrate carefully neutralized with concentrated hydrochloric acid. Additional potassium chloride which formed was filtered and the combined precipitates were washed with methyl alcohol and chloroform. The washings and the filtrate were combined. At this point, 300 ml. of chloroform and 500 ml. of water were added to the filtrate. The chloroform layer (rich in the product) was removed and the water–methyl alcohol layer was extracted twice more with 100-ml. portions of chloroform. Finally, one more liter of water was added to the water–methyl alcohol phase and this was extracted with two more 50-ml. portions of chloroform. At this point the chloroform extract was free of the yellow color of the product. The combined chloroform extracts were dried over calcium sulfate. The drying agent was removed and the chloroform separated from the crude product by distillation through a vacuum-jacketed Vigreux column. The residual yellow liquid was then distilled through the same column at reduced pressure giving a yield of methylvinylnitrosamine of 138.9 g. (80.5%) boiling at 50–52°/30 mm.; $n_D^{25}$ 1.4920.

*Anal.* Calcd. for $C_3H_6N_2O$: C, 41.8; H, 7.0; N, 32.4. Found: C, 41.7; H, 6.9; N, 32.4.

*Reduction of methylvinylnitrosamine with lithium aluminum hydride.* In a system provided with a stirrer and drying tube, 26.6 g. (0.70 mole) of lithium aluminum hydride was added to 400 ml. of dry ether in an atmosphere of dry nitrogen. When the hydride had become dispersed and partially dissolved, 30.1 g. (0.35 mole) of methylvinylnitrosamine in 50 ml. of dry ether was added dropwise at such a rate as to keep the ether at a slow reflux. Addition required 1.5 hr. The mixture was allowed to stir for 2 hr. longer before the complex and excess lithium aluminum hydride were decomposed by the cautious addition of 60 ml. of water. The solid aluminum hydroxide and lithium hydroxide precipitates were removed by filtration. Vacuum distillation of the filtrate removed most of the ether and gave a yield of 18.6 g. of slightly yellow liquid reaction products. These were further purified by drying over sodium hydroxide and vacuum distillation. The distillate from this step was again dried over barium oxide for 20 hr. and distilled under vacuum. By distillation of the resulting material through a center-rod column (30 cm.) under reduced pressure at a reflux ratio of 10:1, two fractions were obtained. The first (b.p. 43–47°/230 mm., yield 7.2 g.) was contaminated with ether and gave an oxalate with a melting point of 163–163.5°. It was identified as methylhydrazine oxalate by a mixed melting point with an authentic sample of methylhydrazine oxalate. Combustion analyses also agreed with those for methylhydrazine oxalate. The second fraction (b.p. 48–50°/215–230 mm., yield 4.33 g.) was identified as 1-ethyl-1-methylhydrazine. The oxalate of this material melted at 110.5–111.5° and showed no depression in a mixed melting point with an authentic sample of 1-ethyl-1-methylhydrazine oxalate.

*Reduction of methylvinylnitrosamine with sodium hydrosulfite.* A solution of 8.1 g. (0.1 mole) of methylvinylnitrosamine in 400 ml. of a 1:1 mixture of ethyl alcohol and 20% aqueous sodium hydroxide was prepared. The solution was stirred for 0.5 hr. under a stream of nitrogen before 42.03 g. (0.2 mole) of solid sodium hydrosulfite was added in one portion. The temperature was kept at 58° throughout the addition and subsequent 5-hr. stirring period. No evolution of gas was noted. The mixture was allowed to stand for 16 hr. and the product then removed along with the water and ethanol by vacuum distillation to dryness. The distilled material had an amine-like odor but did not reduce potassium iodate in 6*N* hydrochloric acid solution. Oxalic acid (0.1 mole) was added to the distillate, the mixture stirred to effect solution, and the aqueous ethanol removed by evaporation. An oxalate salt (10.3 g., 65.5% based on methylamine) was obtained which melted at 171–173°. A mixed melting point with an authentic sample of methylamine oxalate showed no depression. Free amine liberated with alkali from the oxalate salt gave an infrared spectrum identical to that of methylamine.

*Catalytic hydrogenation of methylvinylnitrosamine.* A Parr Instrument Company series 3910 low-pressure hydrogenation apparatus was employed. In a typical experiment run without acid, the 500-ml. hydrogenation bottle was charged with 8.6 g. (0.1 mole) methylvinylnitrosamine, 100 ml. of absolute ethyl alcohol and a pinch of platinum oxide catalyst. The bottle was pressurized to 50 lbs. with hydrogen and shaking was begun. After 20 hr. no further uptake of hydrogen took place. Total hydrogen uptake was 12.8 lbs. (0.16 mole). The catalyst was then removed and the ethyl alcohol was stripped. Distillation of the residue gave 3.95 g. (53.4%) of a yellow liquid boiling at 78–79°/47 mm. The material was identified as ethylmethylnitrosamine by comparison of its infrared spectrum with that of an authentic sample of ethylmethylnitrosamine. The ethyl alcohol strippings smelled of an amine or hydrazine and had faint reducing power but no hydrazine could be isolated.

*Reduction of β-chloroethylmethylnitrosamine with lithium aluminum hydride.* A solution was prepared by adding 38 g. (1.0 mole) of powdered lithium aluminum hydride to 500 ml. of dry ether. The solution was blanketed with nitrogen, stirred, and 61.3 g. (0.5 mole) of β-chloroethylmethylnitrosamine was added in 50 ml. of ether at such a rate as to keep the ether at slow reflux. Addition required 2 hr. The mixture was stirred for 0.5 hr. after completion of addition and then allowed to stand for 16 hr. The complex and excess hydride were decomposed by the careful addition of 75 ml. of water with constant stirring. After stirring for an hour the inorganic solids were filtered off and washed three times with small portions of ether. The ether was then stripped to yield 29.4 g. (54.2%) of crude product. This was further purified by distillation under reduced pressure to yield a liquid boiling at 29°/61 mm. in 5.2 g. yield. This material was identified as 1-ethyl-1-methylhydrazine by comparison of its infrared spectrum with that of an authentic sample. A small amount of higher boiling material also was obtained from the distillation but was not identified. Material collecting in the Dry Ice trap during the distillation was

treated with oxalic acid in ether to give 11.4 g. of an oxalate melting at 110–111.3°. This compound was identified as 1-ethyl-1-methylhydrazine oxalate by a mixed melting point with an authentic sample.

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## The Schmidt Reaction between 1,1,3-Triphenylpropyne-2-ol-1 and Hydrogen Azide[1]

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In connection with other work, now discontinued, the Schmidt reaction between 1,1,3-triphenylpropyne-2-ol-1 (I) and hydrogen azide has been investigated. The product, identified as the anilide (III) of β-phenylcinnamic acid by an independent synthesis from β-phenylcinnamoyl chloride and aniline, is also obtained from β-phenylbenzalacetophenone (II) and hydrogen azide in the presence of sulfuric acid. The Meyer-Shuster rearrangement of I to II, a preparative method for II, apparently occurs in the transformation of I to III. Migration of a phenyl group rather than a diphenylvinyl group from carbon to nitrogen also occurs, in agreement with an earlier observation that migration of a vinyl group in a Schmidt reaction was not found.[3]

$$\underset{\text{I}}{(C_6H_5)_2C(OH)C{\equiv}CC_6H_5} \xrightarrow{H_2SO_4} \underset{\text{II}}{(C_6H_5)_2C{=}CHCOC_6H_5}$$

$$\text{I or II} \xrightarrow[HN_3]{H_2SO_4} \underset{\text{III}}{(C_6H_5)_2C{=}CHCONHC_6H_5}$$

### EXPERIMENTAL[4]

*Preparation of the anilide* (III) *from* I. To a suspension of 1.5 g. (0.023 mole) of sodium azide in 10 ml. of chloroform cooled in an ice bath, 3.0 ml. (0.055 mole) of concd. sulfuric acid was added slowly. A solution of 3.30 g. (0.0116 mole) of 1,1,3-triphenylpropyne-2-ol-1 (I)[5] in 15 ml. of chloroform was added during 45 min. at room temperature. After stirring for an additional 45 min., the mixture was poured on 100 g. of ice, and extracted with ether. Evaporation of solvents gave an oil which was dissolved in benzene and applied to a column of alumina (Alcoa grade F-20). Elution with benzene gave yellow-green, red, and light yellow bands. The first two were removed from the column with benzene and the third with acetone. On evaporation of solvents, tars were obtained from the first two but the third gave a colorless solid, m.p. 139–140°, 0.53 g. (15%), after two recrystallizations from a mixture of benzene and ligroin, identified as the anilide (III) of β-phenylcinnamic acid.

*Anal.* Calcd. for $C_{21}H_{17}NO$: C, 84.19; H, 5.71; N, 4.67. Found: C, 84.87; H, 5.45; N, 4.63.

*Preparation of the anilide* (III) *from* II. To 3.5 g. (0.0124 mole) of β-phenylbenzalacetophenone (II), m.p. 91–92°,[6] in 30 ml. of chloroform and 1 ml. (0.018 mole) of concd. sulfuric acid a solution of hydrogen azide (excess) in 37 ml. of chloroform was added dropwise over a period of 30 min. as the temperature was kept below 35°. Stirring was continued for 1 hr., the mixture was washed with water, and the organic layer evaporated on a waterbath. Recrystallization of the residue from a mixture of benzene and ligroin gave 1.45 g. (40%) of product, m.p. 137–138°.

Oxidation of III in acetone by potassium permanganate gave benzophenone, m.p. 48° (86%) and acid alcoholysis gave impure ethyl β-phenylcinnamate, b.p. 280°, $n_D^{25.5}$ 1.6010[7] and aniline, isolated as its hydrochloride, m.p. and mixture m.p. 197.5–199° (88%).

*Hydrogenation of the anilide* (III). A solution of 0.21 g. (0.007 mole) of III in 25 ml. of ethanol which contained 15 mg. of platinum oxide was treated with hydrogen at room temperature and normal pressure for 20 hr. After filtration and evaporation of the solvent 0.19 g. (91%) of a white solid, m.p. 180–181° was obtained. One recrystallization from aqueous ethanol gave the anilide of β,β-diphenylpropionic acid, 0.16 g. m.p. 181–182°.[8]

*Anal.* Calcd. for $C_{21}H_{19}NO$: C, 83.68; H, 6.35; N, 4.65; O, 5.38. Found: C, 83.09; H, 6.29; N, 4.67; O, 5.53.

*Preparation of the anilide* (III). After the vigorous reaction brought about by adding 4.5 g. (0.02 mole) of β-phenylcinnamic acid[7] to 14.7 g. (0.12 mole) of thionyl chloride had subsided the mixture was refluxed for 30 min., and excess thionyl chloride was removed by distillation. Ten milliliters of benzene followed by a solution of 5 ml. (0.09 mole) of aniline in 45 ml. of benzene was added to the residue. After a few minutes at room temperature the mixture was washed with ligroin to precipitate the anilide of β-phenylcinnamic acid which was removed by filtration, washed with ligroin, and recrystallized from a mixture of benzene and ligroin as a colorless solid, 4.0 g. (67%), m.p. and mixture m.p. with III prepared from I or II, 133.5–134.0°.

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## Reaction of Thiophosgene with Azide Ion[1]

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In consideration of additional methods for the preparation of 5-substituted amino-1,2,3,4-thia-

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