
Navy Department - Office of Naval Research

NAVAL RESEARCH LABORATORY

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FR-2879

CHEMISTRY DIVISION - PROTECTIVE COATINGS SECTION

10 July 1946

CHEMICAL STUDIES ON FUNGICIDES - Part II

SYNTHESIS

by

W. E. Weaver and W. M. Whaley

- Report P-2879 -

* * *

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ABSTRACT

The synthesis of 122 compounds intended for fungicidal evaluation is briefly described. Indications of fungicidity accompany most of the compounds. The increasing importance of work of this nature is pointed out.

ABSTRACT

The synthesis of 122 compounds intended for fungicidal evaluation is briefly described. Indications of fungicidity accompany most of the compounds. The increasing importance of work of this nature is pointed out.

INTRODUCTION

A. Authorization

1. The study of fungicides is authorized under Bureau of Ships Project Order No. 152/46 and ONR Project No. 46/46.

B. References

2. (a) NRL Report No. P-2518 dated 15 May 1945.
(b) NRL Report No. P-2611 dated 1 August 1945.
(c) NRL Report No. P-2626 dated 23 August 1945.
(d) NRL Report No. P-2628 dated 28 August 1945.
(e) NRL Report No. P-2653 dated 6 November 1945.
(f) NRL Report No. P-2877 dated 19 June 1946.
(g) Unpublished work of NRL.

C. General

3. The scientific knowledge of fungicides is much poorer than that of bactericides and insecticides. While much work has been done in the field, it is often poorly integrated and unreliable. The survey initiated in these laboratories is an attempt to bring a semblance of order out of relative chaos. A comprehensive study of fungicidal action of organic compounds demands the supplementing of commercially available substances by compounds synthesized in the laboratory. This synthetic work is motivated by the necessity of including all types of compounds in the initial survey and of pursuing promising leads.
4. References (a) to (e) cover the preliminary phases of fungicidal evaluation, the remainder being as yet unreported. Extensive correlation has recently been made between chemical structure and fungicidal activity and reported upon as Part I of this present series of chemical studies (ref.(f)).
5. The purpose of this report is to record the syntheses carried out in the preparation of fungicides, nearly all of which have been evaluated and considered in the reports mentioned previously. Many different types of compounds have been synthesized in the search for new toxicants and several of the more promising groups have been extensively investigated. Most fungicides are inadequate for certain exacting uses such as incorporation into protective coatings, and a particularly powerful toxicant is necessary. Although many compounds synthesized were found to possess no fungicidity, it is to be remembered that an important phase of the work is knowing which types of compounds are not fungicidal. Proper correlation of structure and fungicidity requires a complete knowledge of the activity and inactivity of many compounds.

EXPERIMENTAL

(Note: The accompanying plates present condensed equations for the synthesis of the fungicides discussed.)

6. AMIDES

(1) Salicyl-1-naphthalide. Two-tenths mole of salicylic acid, 0.2 mole of alpha-naphthylamine, 0.25 mole of phosphorus trichloride and 0.25 mole of dimethylaniline were heated on a water bath for 1/2 hour. The hot syrup was poured into 400 cc. of hot dilute hydrochloride acid. The precipitate was recrystallized from alcohol and water and dried over P_2O_5 . Yield: 64% of gray-white crystals, m.p. 180° . Anal. Calcd. for $C_{17}H_{13}NO_2$: N, 5.32. Found: N, 5.39. (Senier and Shepherd, J.C.S., 95, 444 (1909). This compound was not fungicidal.

(2) Salicyl-2-naphthalide was prepared in the same way as the 1-compound. Yield: 80% of light-yellow crystals, m.p. $185-8^\circ$. Anal. Calcd. for $C_{17}H_{13}NO_2$: N, 5.32. Found: N, 5.43. This compound was not fungicidal.

(3) Salicylamide. Salicylyl chloride was prepared by refluxing 0.2 mole of salicylic acid with 0.3 mole of thionyl chloride in 50 cc. of benzene for 4 hours. The excess benzene and thionyl chloride were removed on a water pump. One-tenth mole of this crude salicylyl chloride was added slowly, with shaking, to 30 cc. of 15% ammonia. The precipitate was filtered off and recrystallized from hot water. Yield: 75%, m.p. $125-30^\circ$. This compound was not fungicidal.

(4) p-Salicylylaminobenzoic acid was prepared by adding a suspension of 0.1 mole of salicylyl chloride (crude) in ether to 0.2 mole of p-amino-benzoic acid in ether. The ether was evaporated, the solid dissolved in alkali and precipitated with acid. The white product was filtered and dried over P_2O_5 . Yield: 58%, m.p. above 210° . Anal. Calcd. for $C_{13}H_{11}NO_4$: N, 5.46. Found: N, 5.30. This compound was not fungicidal.

(5) Benzanilide was prepared by adding 0.1 mole of benzoyl chloride in ether to 0.2 mole of aniline dissolved in ether. The white precipitate was filtered and recrystallized from alcohol and water. Yield: 81%, m.p. 163° . This compound was not fungicidal.

(6) Cinnamanilide was prepared in like manner from cinnamoyl chloride. Yield: 99%, m.p. $151-3^\circ$. This compound was not fungicidal.

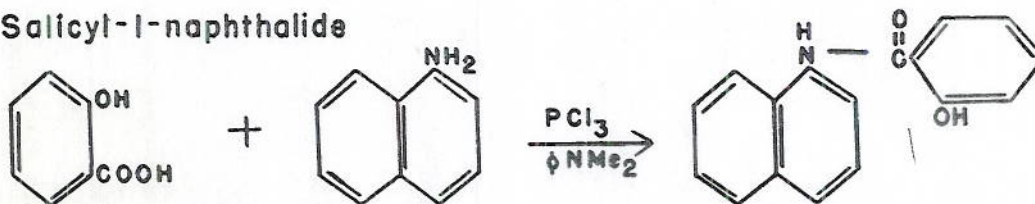
(7) N-Cyclohexylsalicylamide was prepared in like manner from salicylyl chloride (crude) and cyclohexylamine. M.p. $70-5^\circ$. Anal. Calcd. for $C_{13}H_{17}NO_2$: N, 6.40. Found: N, 6.39. This compound was not fungicidal.

(8) Lauranilide. One-tenth mole of lauric acid was refluxed several hours with 0.3 mole of thionyl chloride. The excess thionyl chloride was removed in vacuo and the residue added to an ethereal solution of 0.1 mole of aniline. Yield: 25%, m.p. $72-4^\circ$. This compound was not fungicidal.

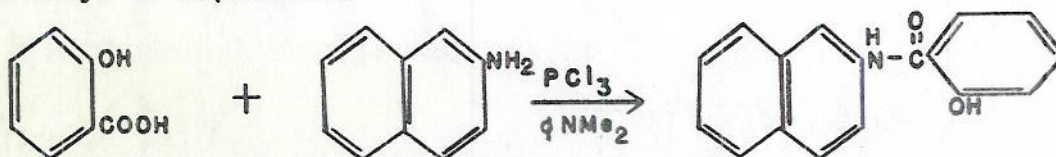
CHEMICAL REACTIONS

6. AMIDES

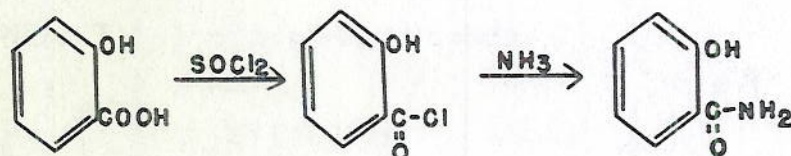
(1) Salicyl-1-naphthalide



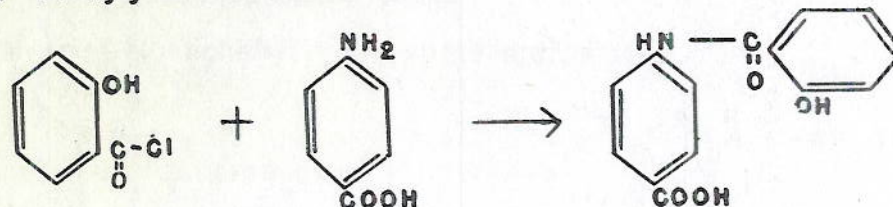
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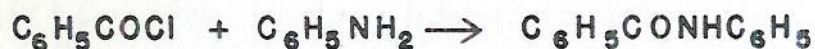
(3) Salicylamide



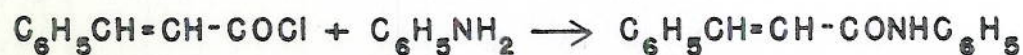
(4) p-Salicylaminobenzoic Acid



(5) Benzanilide

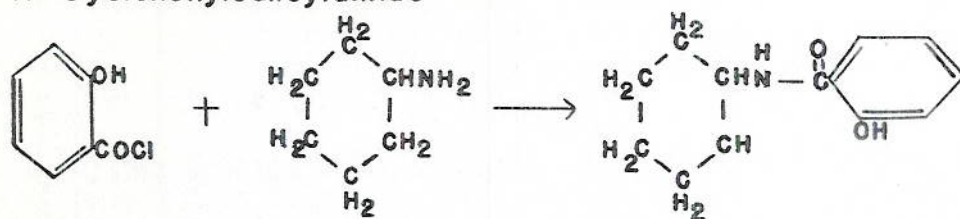


(6) Cinnamanilide



CHEMICAL REACTIONS

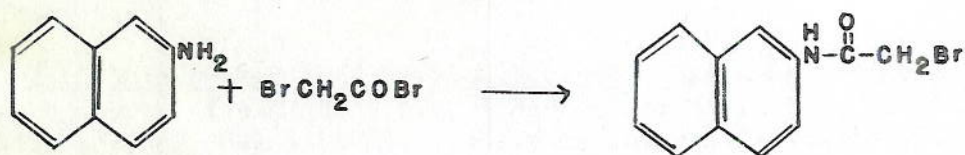
(7) N-Cyclohexylsalicylamide



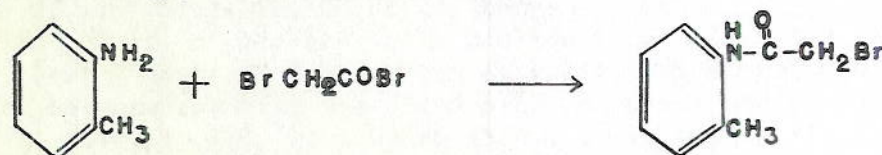
(8) Lauranilide



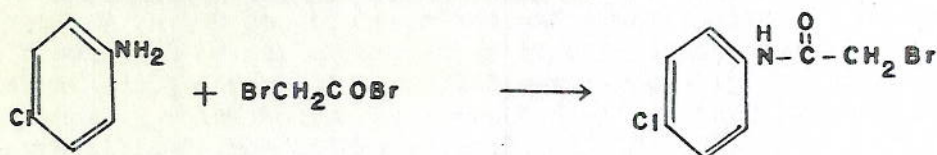
(9) N-(β-Naphthyl)-α-bromoacetamide



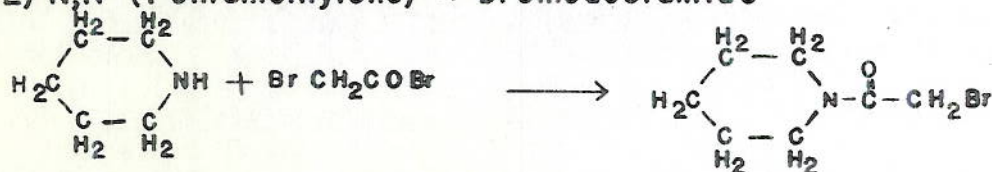
(10) N-(o-Tolyl)-α-bromoacetamide



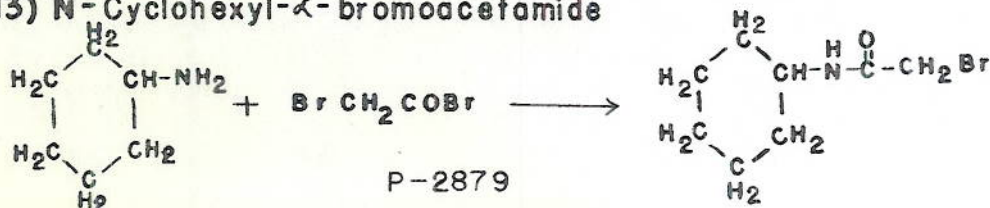
(11) N-(p-Chlorophenyl)-α-bromoacetamide



(12) N,N-(Pentamethylene)-α-bromoacetamide



(13) N-Cyclohexyl-α-bromoacetamide



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Plate 2.

(9) N-(beta-Naphthyl)-alpha-bromoacetamide was prepared by treating a solution of 0.2 mole of beta-naphthylamine in 500 cc. of benzene with 0.1 mole of bromoacetyl bromide in 50 cc. of benzene at room temperature. The mixture was filtered and the solid heated with 500 cc. of alcohol and then cooled. The insoluble hydrobromide was filtered off and discarded. The alcoholic solution was heated and 300 cc. of water added. After cooling, the product was filtered off and dried over P_2O_5 . Yield: 65%, m.p. 125-30°. The compound was lachrymatory when heated. (Lit. m.p. 134°, Stolle, Bergdoll, Luther, Auerhahn and Wacker, J. prakt. Chem., 128, 1 (1930)). This compound was not fungicidal.

(10) N-(o-Tolyl)-alpha-bromoacetamide was synthesized by treating 0.2 mole of o-toluidine in 100 cc. of benzene with 0.1 mole of bromoacetyl bromide in 100 cc. of benzene at room temperature. Water was added and the benzene removed on the steam bath. The mixture was cooled and filtered. The solid was recrystallized from dilute alcohol as small white needles. The compound is sternutatory, lachrymatory and causes burning of the skin. Dried in vacuo over P_2O_5 . Yield: 92%, m.p. 112-13°. (Lit. m.p. 113°, Abenius and Widman, J. prakt. Chem., 38, 298 (1888)). This compound was fairly fungicidal.

(11) N-(p-Chlorophenyl)-alpha-bromoacetamide was prepared like the previous compound. Yield: 83%, m.p. 153-6° (Lit. m.p. 161°, Collet, Bull. soc. chim., (3), 22, 541 (1902)). This compound was fairly fungicidal.

(12) N,N-(Pentamethylene)-alpha-bromoacetamide was prepared by treating 0.2 mole of piperidine in 100 cc. of benzene, with 0.1 mole of bromoacetyl bromide in 100 cc. of benzene while cooling in an ice bath. After standing for several hours, a fair amount of solid formed, which was filtered off. The benzene solution was dried over anhydrous sodium sulfate and distilled. Yield: 32%, b.p. 95°/0.15 mm. (Bath 145°). It is irritating to the skin upon direct contact. This compound was fairly fungicidal.

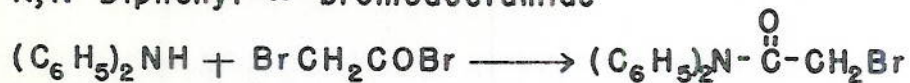
(13) N-Cyclohexyl-alpha-bromoacetamide. Cyclohexylamine (0.2 mole) was dissolved in 100 cc. of dry ether and treated with 0.1 mole of bromoacetyl bromide in 50 cc. of dry ether at room temperature. The reaction was violent and the reagent was added very gradually. After evaporation of the ether, a white solid was extracted with dilute hydrochloric acid and recrystallized from dilute alcohol. Yield: 55%, m.p. 110-11°. This compound was fairly fungicidal.

(14) N,N-(Diphenyl)-alpha-bromoacetamide was prepared like the previous compound. Yield: 19%, m.p. 38-40°. This compound was not fungicidal.

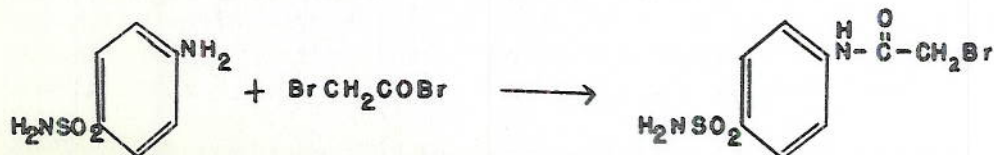
(15) N-(p-Sulfamylphenyl)-alpha-bromoacetamide. One-tenth mole of sulfanilamide and 20 cc. of pyridine were dissolved in 100 cc. of acetone and treated with 0.1 mole of bromoacetyl bromide in 50 cc. of ether. The mixture was concentrated on the steam bath. The gum obtained was not soluble in hot alcohol, but on boiling in alcohol, it was transformed into a white solid, which was recrystallized from 80% acetic acid and dried over P_2O_5 . Yield: 65%, m.p. 240-2°d. (Lit. m.p. 218°, Bergmann and Haskellberg, J.A.C.S., 63, 2243 (1941)). This compound was not fungicidal.

CHEMICAL REACTIONS

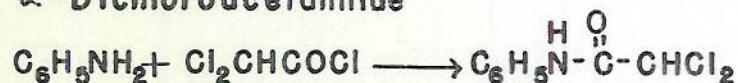
(14) N,N-Diphenyl- α -bromoacetamide



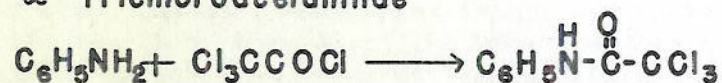
(15) N-(p-Sulfamylphenyl)- α -bromoacetamide



(16) α -Dichloroacetanilide



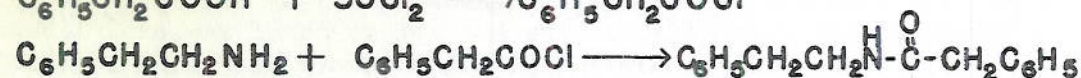
(17) α -Trichloroacetanilide



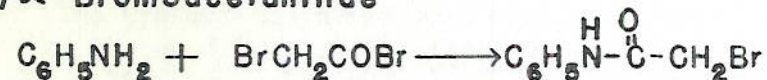
(18) α -Bromopropionanilide



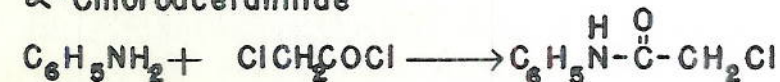
(19) N-Phenylacetyl- β -phenylethylamine



(20) α -Bromoacetanilide



(21) α -Chloroacetanilide



(16) alpha-Dichloroacetanilide was prepared by treating 0.2 mole of aniline in benzene with 0.1 mole of dichloroacetyl chloride at room temperature. Water was added to dissolve the salt, the mixture shaken and filtered. The air-dried product melted at 100°. It was recrystallized from dilute alcohol as white prisms. Yield: 84%, m.p. 113-15°. (Lit. m.p. 117°, Cech, Ber., 9, 339 (1876); Pawlewski, Ber., 32, 1426 (1899)). This compound was not fungicidal.

(17) alpha-Trichloroacetanilide was prepared by treating 0.2 mole of aniline in dry ether with 0.1 mole of trichloroacetyl chloride at room temperature. The ether was allowed to evaporate at room temperature, 100 cc. of water added and heated to boiling; then sufficient alcohol was added to bring the solid into solution while hot. On cooling, the white crystals were removed by filtration. Yield: 80%, m.p. 88-90° (Lit. m.p. 94-5°, Judgson, Ber., 3, 783 (1870)). This compound was not fungicidal.

(18) alpha-Bromopropionanilide was prepared like the previous compound. Yield 81% of white crystals. M.p. 95-8° (Lit. m.p. 99°, Tigerstedt, Ber., 25, 2919 (1892)). This compound was not fungicidal.

(19) N-Phenylacetyl-beta-phenylethylamine. One-half mole of phenylacetic acid, 0.75 mole of thionyl chloride and 300 cc. of benzene were heated gently in a 1-liter flask fitted with a reflux condenser and a gas absorption trap. After 1 hour, the mixture was heated to boiling to complete the reaction, then distilled under reduced pressure. Yield of phenylacetyl chloride, 88%, b.p. 94°/15 mm. (Bath 130°). One-quarter mole of beta-phenylethylamine was mixed with 0.75 mole of sodium hydroxide in 100 cc. of water and cooled in an ice-bath while 0.25 mole of phenylacetyl chloride was dropped in with stirring. After standing several hours, the mixture was filtered and washed with water. The product was recrystallized from dilute alcohol. Yield: 83%, m.p. 91-2°. This compound was not fungicidal.

(20) alpha-Bromoacetanilide. Four-tenths mole of aniline in 100 cc. of benzene was cooled in an ice-bath and 0.2 mole of bromoacetyl bromide slowly added. Care was taken to add the acid bromide very slowly since the reaction was violently exothermic. At the end of the reaction period the flask was filled with white solid. Water was added, the undissolved solid filtered off and washed several times with dilute hydrochloric acid and water. The product was dried over P₂O₅ in vacuo. Yield: 100%, m.p. 129-30°. The compound is very irritant to the skin. (Lit. m.p. 131°, Abenius, J. prakt. Chem., (2) 40, 428 (1889)). This compound was very fungicidal.

(21) alpha-Chloroacetanilide was prepared by treating 0.4 mole of aniline in 100 cc. of benzene with 0.2 mole of chloroacetyl chloride with cooling. After completion, the reaction mixture set to a solid mass. Water was added, the solid filtered and washed with hydrochloric acid and ice-water, and dried in vacuo over P₂O₅. Yield: 91% of white solid, m.p. 127-8°. (Lit. m.p. 134.5°, Holmberg and Psilanderhielm, J. prakt. Chem., (2) 82, 442 (1910)). This compound was fairly fungicidal.

(22) N-(p-Tolyl)-alpha-bromoacetamide was prepared like the above compound and recrystallized from dilute alcohol. Yield: 97%, m.p. 167-8°. (Lit. m.p. 164°, Abenius, J. prakt. Chem., (2) 40, 433 (1889)). This compound was fairly fungicidal.

(23) N-(p-Carboxyphenyl)-alpha-bromoacetamide was prepared by treating 0.1 mole of p-amino-benzoic acid and 10 g. of pyridine in 100 cc. of dry ether with 0.1 mole of bromoacetyl bromide at room temperature. After evaporation of the ether on the steam-bath, water was added to the dark residue and the solid filtered off. This product was decolorized with Nuchar, recrystallized from dilute alcohol and dried over P₂O₅ in vacuo. Yield: 21% of brown solid, m.p. 205-8°. This compound was not fungicidal.

(24) N-(p-Acetoxyphenyl)-alpha-bromoacetamide. One-tenth mole of p-amino-acetophenone was dissolved in 200 cc. of chloroform in a 500 cc. 3-necked flask equipped with stirrer, dropping-funnel and thermometer. Eight grams of pyridine was added and the mixture cooled in an ice-salt bath. One-tenth mole of bromoacetyl bromide was added dropwise over a period of 15 minutes. Water was added and the yellow precipitate filtered off and washed well with water and dried in a vacuum oven at 45°. Yield: 88% of light-yellow needles, m.p. 152-3°. This compound was fairly fungicidal.

(25) N,N-Dibutyl-alpha-bromoacetamide was prepared by treating 0.2 mole of dibutylamine in 100 cc. of benzene with 0.1 mole of bromoacetyl bromide, with cooling. After standing overnight, ether was added to the mixture and it was filtered. The filtrate was dried over anhydrous sodium sulfate and distilled. Yield: 62% of brownish liquid, b.p. 102-5°/0.3 mm. (bath 140-5°). This compound was fairly fungicidal.

7. ORGANOMERCURIALS

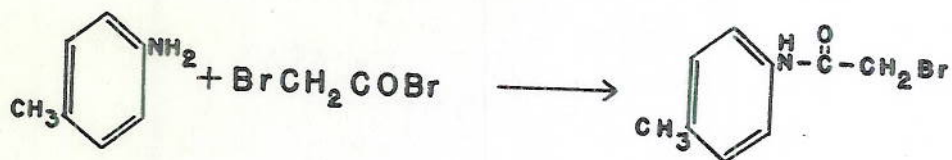
(1) beta-Naphthylmercuric chloride was prepared from beta-naphthylamine through the intermediate diazonium chloride-mercuric chloride double salt. The details of the reaction are given in Org. Syn., Coll. Vol. II, 432. Yield: 10% m.p. above 250°. This compound was not fungicidal.

(2) alpha-Naphthylmercuric chloride was prepared like the previous compound. It was quite soluble in acetone and was recrystallized from dilute acetone as pink biaxial plates. Yield: 14%, m.p. 191-3°. (Lit. m.p. 191°, Nesmeyanov, Ber., 62, 1010 (1929)). This compound was fairly fungicidal.

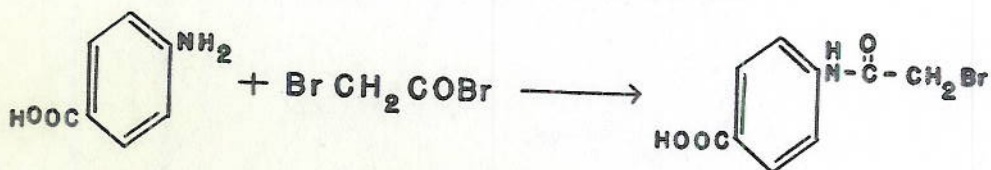
(3) p-Aminophenylmercuric acetate was prepared by dissolving 0.8 mole of mercuric acetate in 1280 cc. of water and adding 1.6 moles of aniline. A clear yellow solution resulted which after 1 hour began a slow deposition of large yellow crystals. After standing overnight, the product was filtered, washed with water and dried over P₂O₅. Yield: 96%, m.p. 165°. (Lit. m.p. 167°, Dimroth, Ber., 35, 2039, (1902)). Anal. Calcd. for C₈H₉NO₂Hg: Hg, 57.05. Found: Hg, 57.17. This compound was fairly fungicidal.

CHEMICAL REACTIONS

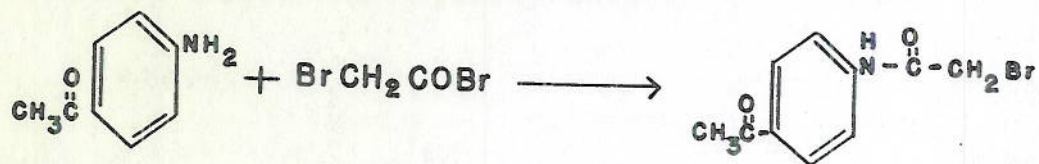
(22) N-(p-Tolyl)- α -bromoacetamide



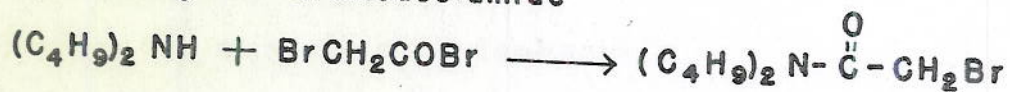
(23) N-(p-Carboxyphenyl)- α -bromoacetamide



(24) N-(p-Acetophenyl)- α -bromoacetamide

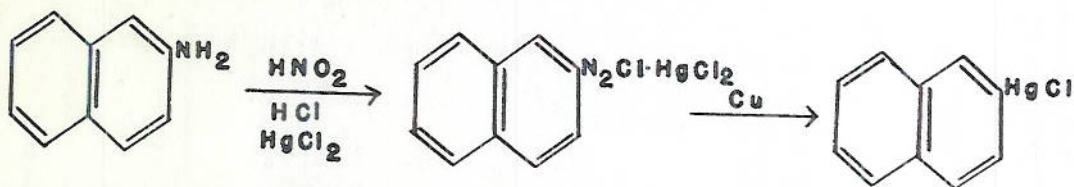


(25) N,N-Dibutyl- α -bromoacetamide

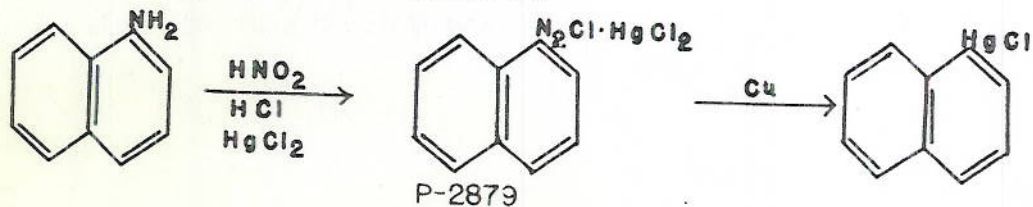


7. ORGANOMERCURIALS

(1) β -Naphthylmercuric chloride

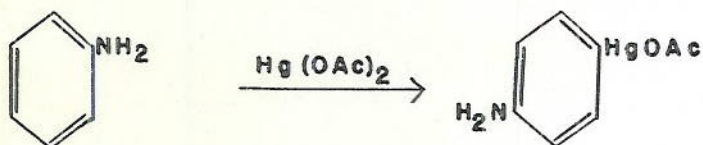


(2) α -Naphthylmercuric chloride

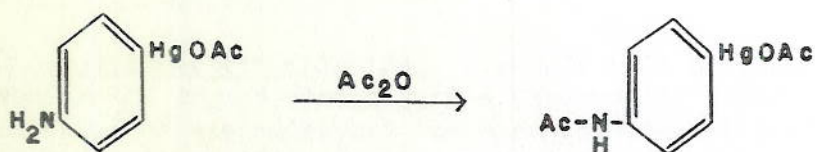


CHEMICAL REACTIONS

(3) p-Aminophenylmercuric acetate



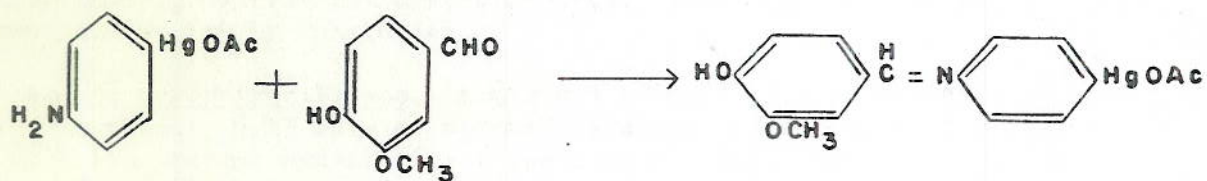
(4) p-Acetylamino phenylmercuric acetate



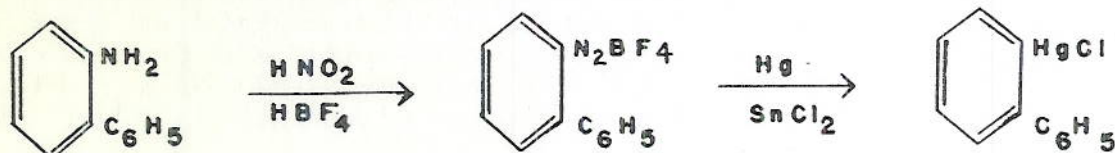
(5) 4-Acetoxymercuri-(2'-hydroxybenzylidene)-aniline



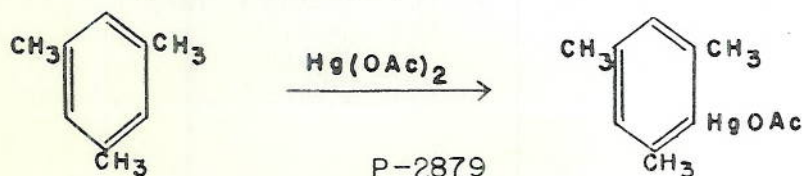
(6) 4-Acetoxymercurivanillideneaniline



(7) o-Xenylmercuric chloride



(8) Acetoxymercurimesitylene



P-2879

(4) p-Acetylaminophenylmercuric acetate was prepared by allowing 70 g. of p-aminophenylmercuric acetate to stand at room temperature in 150 g. of acetic anhydride for 1 week. A white powder slowly formed which was recrystallized from acetone. Yield: 60%, m.p. 121-2° (Jacobs and Heidelberger, J.B.C., 20, 515 (1915)). Anal. Calcd. for $C_{10}H_{11}NO_3Hg$: Hg, 50.91. Found: Hg, 50.9. This compound was fairly fungicidal.

(5) 4-Acetoxymercuri-(2'-hydroxybenzylidene)-aniline was prepared by heating 0.1 mole of p-aminophenylmercuric acetate with 0.6 mole of salicylaldehyde until solution was effected. The solution solidified on cooling, was washed with 500 cc. of alcohol, filtered and washed again with alcohol and ether. Yield: 67% of yellow crystals, m.p. 170-5°. This compound was not fungicidal.

(6) 4-Acetoxymercurivanillidene aniline was prepared like the previous compound. Yield: 50% of yellow product, m.p. above 250° d. This compound was slightly fungicidal.

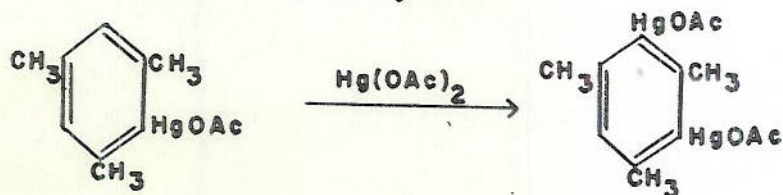
(7) o-Xenylmercuric chloride. One-half mole of o-aminodiphenyl was dissolved in 250 cc. of alcohol. One hundred and fifty cc. of concentrated hydrochloric acid was added and the warm solution stirred a few minutes until it suddenly solidified into a thick paste. One hundred and ten cc. of 45% fluoboric acid was added. The mixture was stirred at 5° or less and diazotized with an aqueous solution of 0.5 mole of sodium nitrite. The light-yellow product was collected, washed with alcohol and ether and dried over P_2O_5 . Yield: 79% of o-xenyldiazonium borofluoride. (Dunker, Starkey and Jenkins, J.A.C.S., 58, 2308 (1936)). A mixture of 10 g. of o-xenyldiazonium borofluoride, 10 g. of mercuric chloride and 100 cc. of glacial acetic acid was added slowly to a mixture of 10 g. of mercuric chloride, 16 g. of stannous chloride dihydrate, and 100 cc. of acetone. At the end of 2 hours' stirring, there was a milky suspension which was filtered. The residue contained 19 g. of very impure product, which was recrystallized from acetone and water as tiny white crystals. Yield: 46%, m.p. 167-8° (Lit. m.p. 165-7°, Courtat and Bastani, Compt. rend., 203, 197 (1936)). This compound was fairly fungicidal.

(8) Acetoxymercurimesitylene. A mixture of 0.33 mole of mesitylene, 200 cc. of methanol, 0.33 mole of mercuric acetate and 40 cc. of glacial acetic acid (to prevent hydrolysis of the mercuric salt) was refluxed for 50 hours. The residue in the flask was filtered off and constituted diacetoxymercurimesitylene. The yellow filtrate was mixed with an equal volume of water, which caused a heavy layer to separate. On standing several days, the layer crystallized and was filtered off. The product was recrystallized from dilute methanol and dried over P_2O_5 in vacuo. Yield: 54%, m.p. 97-100°. (Lit. m.p. 103°, Smith and Taylor, J.A.C.S., 57, 2370 (1935)). This compound was very fungicidal.

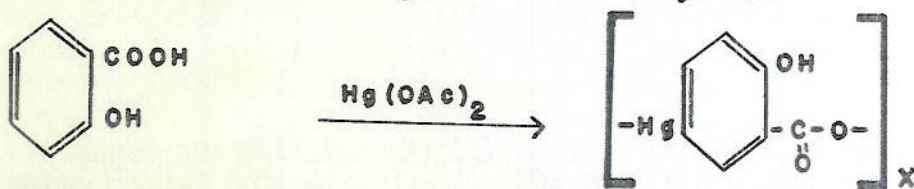
(9) Diacetoxymercurimesitylene was obtained as a by-product in the synthesis of acetoxymercurimesitylene. It was purified by boiling with 100 cc. of methanol, cooling, filtering, and drying in vacuo at 110°. Yield: 11%, m.p. 230° (Smith and Taylor, J.A.C.S., 57, 2370 (1935)). This compound was slightly fungicidal.

CHEMICAL REACTIONS

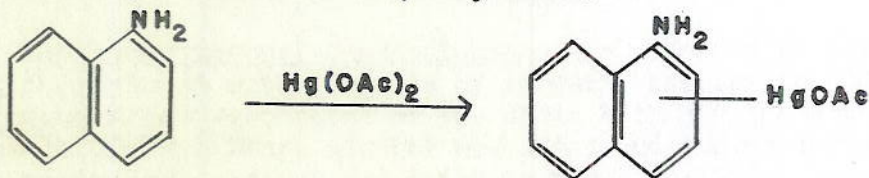
(9) Diacetoxymercurimesitylene



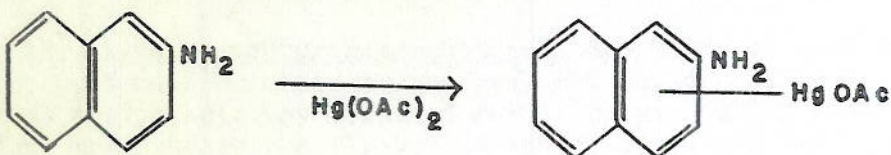
(10) 5-Hydroxymercurisalicylic acid anhydride



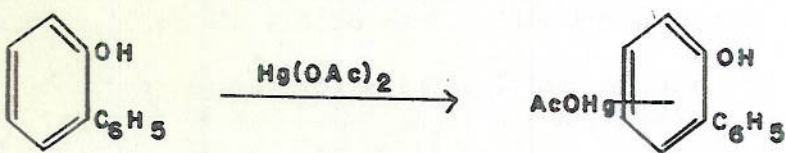
(11) Acetoxymercuri- α -naphthylamine



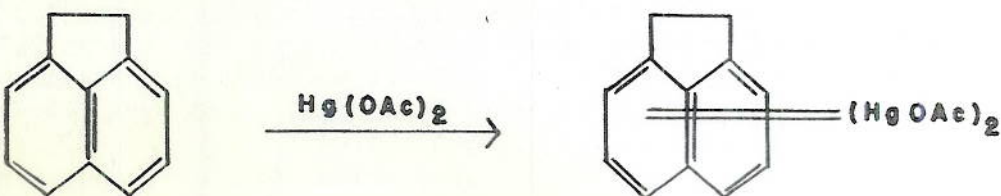
(12) Acetoxymercuri- β -naphthylamine



(13) Acetoxymercuri-o-phenylphenol



(14) Diacetoxymercuriacenaphthene



(10) 5-Hydroxymercurisalicyclic acid anhydride. Sixty grams of salicylic acid in 1 liter of water and 160 cc. of 10% sodium hydroxide was heated to boiling and, while stirring, treated with a solution of 208 g. of mercuric acetate in 1 liter of water and 40 cc. of glacial acetic acid. A brown color appeared during the brief induction period, then precipitation of an orange solid occurred. The solid was filtered out, washed with water and dried in vacuo at 105°. Yield: 74% of light pink powder, m.p. over 300°. The position of the mercury on the ring was proved by replacing it with a nitro group. (Brenans and Rapiilly, *Compt. rend.*, 193, 55 (1931)). This compound was slightly fungicidal.

(11) Acetoxymercuri-alpha-naphthylamine was prepared by adding a solution of 0.2 mole of alpha-naphthylamine in 150 cc. of hot alcohol to a solution of 0.1 mole of mercuric acetate in 350 cc. of 70% alcohol, containing 3 cc. of glacial acetic acid. There was almost immediate formation of many small crystals. It was shaken for 1 hour, filtered, washed with methanol and dried in vacuo at 105°. Yield: 65% of pink crystals, m.p. above 300°. The position of the mercury on the ring has not been determined. The compound was fairly fungicidal.

(12) Acetoxymercuri-beta-naphthylamine was prepared like the previous compound. Yield: 83%, m.p. 190°. The position of the mercury on the ring has not been determined. This compound was fairly fungicidal.

(13) Acetoxymercuri-o-phenylphenol was prepared by treating 0.2 mole of o-phenylphenol with 0.1 mole of mercuric acetate in 500 cc. of methanol. The methanol was evaporated on the steam bath and the excess o-phenylphenol steam distilled. Ethyl alcohol was added and the mercurial was filtered off, washed with alcohol and dried in vacuo at 100°. Yield 42%, m. p. over 300°. This compound is possibly contaminated with the dimercurated derivative. The compound was very fungicidal.

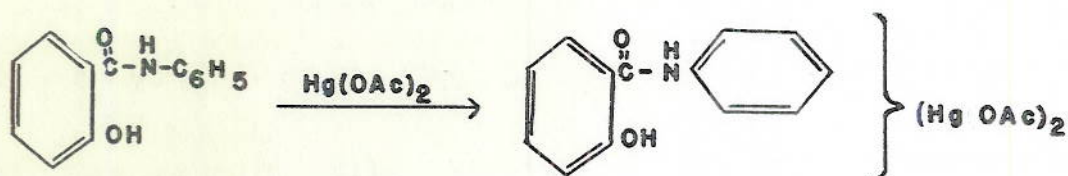
(14) Diacetoxymercuriacenaphthene. A mixture of 0.15 mole of acenaphthene, 0.15 mole of mercuric acetate, 250 cc. of methanol, and 10 cc. of glacial acetic acid was refluxed for 12 hours, during which time the solid product appeared in the flask. It was filtered off and dried in vacuo at 100°. Yield: 20%, m.p. darkens over 230°. Anal. Calcd. for $C_{16}H_{14}O_4Hg_2$: Hg, 59.7. Found: Hg, 58.5. Goswami and Das-Gupta (*J. Indian Chem. Soc.*, 8, 475 (1931)) claim monosubstitution on mercurating acenaphthene with mercuric acetate in acetic acid. This compound was not fungicidal.

(15) Diacetoxymercurisalicylanilide was prepared by allowing 0.1 mole of salicylanilide and 0.1 mole of mercuric acetate in 250 cc. of methanol to stand over night. The solid material was collected, washed and dried. Yield: 31%, m.p. above 300°. Anal. Calcd. for $C_{17}H_{15}NO_6Hg_2$: Hg, 54.8. Found: Hg, 53.5. This compound was not fungicidal.

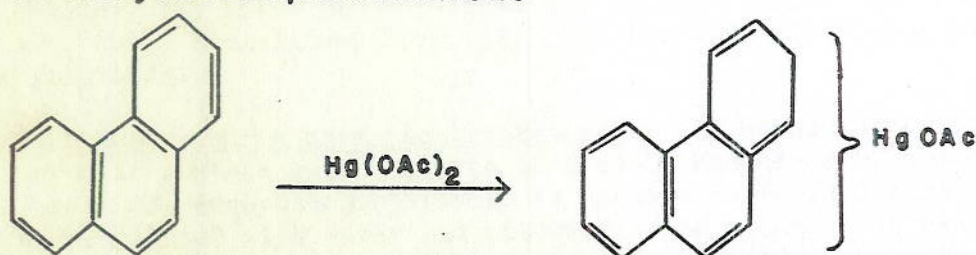
(16) Acetoxymercuriphenanthrene was prepared by refluxing a mixture of 0.2 mole of phenanthrene and 0.2 mole of mercuric acetate in 300 cc. of methanol with stirring for 60 hours. The product was filtered out, recrystallized from ethanol and dried in vacuo at 90°. Yield: 17%, m.p. above 300°. Anal. Calcd. for $C_{16}H_{12}O_2Hg$: Hg, 45.8. Found: Hg, 47.3. This compound was not fungicidal.

CHEMICAL REACTIONS

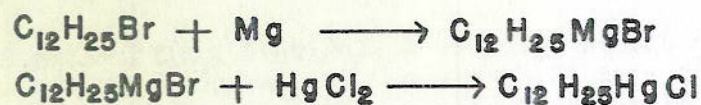
(15) Diacetoxymercurisalicylanilide



(16) Acetoxymercuriphenanthrene



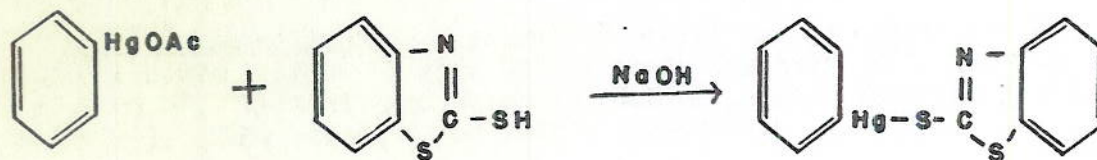
(17) Laurylmercuric chloride



(18) Phenylmercuric Iodide



(19) Phenylmercuric mercaptobenzothiazole



(20) Amylmercuric bromide



(17) Laurylmercuric chloride. A solution of 0.1 mole of dodecyl bromide in 200 cc. of dry ether was treated with 0.125 mole of magnesium turnings and heated 1 hour. The reaction was difficult to start and was initiated with a small crystal of iodine. After reaction, the dark solution was decanted and heated 1 hour with 0.11 mole of mercuric chloride. There was very vigorous boiling during the reaction, and formation of a white solid. After standing over night, the mixture was treated with water and dilute hydrochloric acid, then filtered. The white solid was recrystallized from methyl cellosolve as gleaming waxy plates. Since an alkyl bromide was used for the reaction with mercuric chloride, the product was undoubtedly a mixture of bromide and chloride. Yield: 79%, m.p. 110-12°. (Slotta and Jacobi, J. prakt. Chem., 120, 280 (1929)). This compound was not fungicidal.

(18) Phenylmercuric iodide. A mixture of 0.2 mole of phenylmercuric acetate and 0.7 mole of sodium iodide in 500 cc. of 95% alcohol was refluxed for 16 hours, during which time the solid never entirely dissolved. After cooling, the solid was collected and dried. Yield: 65%, m.p. 267-9°. (Lit. m.p. 269°, Nesmejanow, Ber., 62, 1013 (1929)). This compound was fairly fungicidal.

(19) Phenylmercuric mercaptobenzothiazole. Five-hundredths mole of phenylmercuric acetate was dissolved in dioxane and mixed with a solution of 0.05 mole of mercaptobenzothiazole in aqueous sodium hydroxide. The mixture was diluted with water and filtered. The product was recrystallized from dioxane and water as white crystals. Yield: 59%, m.p. 153-5°. Anal. Calcd. for $C_{13}H_9NS_2Hg$: Hg, 45.2. Found: Hg, 44.5. This compound was fairly fungicidal.

(20) n-Amylmercuric bromide. A solution of 0.2 mole of n-amyl bromide in 200 cc. of dry ether was treated with 0.25 mole of magnesium turnings and heated 1 hour. The reaction started immediately and spontaneously, but turned very black. The ethereal solution was decanted carefully into 0.22 mole of mercuric bromide, and heated several hours. The mixture was treated with water and dilute hydrochloric acid, then filtered. The solid was recrystallized from methyl cellosolve and water. Yield: 68%, m.p. 118°. (Lit. m.p. 122°, Vaughen, Spahr and Nieuwland, J.A.C.S., 55, 4206 (1933)). This compound was slightly fungicidal.

8. THIO AND SELENOCYANATES

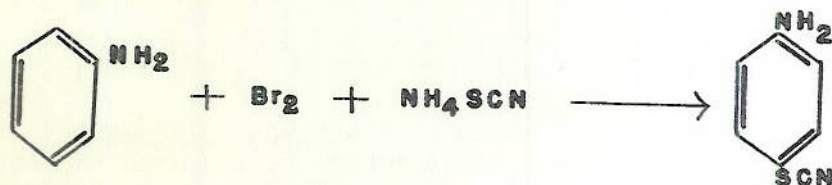
(1) p-Thiocyananiline was prepared according to the method of Org. Syn. Vol. I, p.574 (1941). Yield: 30% of white crystals, m.p. 56-7°. (Lit. m.p. 56.5°. Hartzell and Wilcoxon, Contrib. Boyce Thomson Inst., 6, 269 (1934)). This compound was fairly fungicidal.

(2) Butyl thiocyanate was prepared by refluxing 0.5 mole of butyl bromide and 0.5 mole of potassium thiocyanate in 200 cc. of alcohol for six hours. The alcohol was taken off under vacuum and the product distilled. Yield: 71% of colorless liquid with alliaceous odor, slowly turning yellow. B.p. 84°/30 mm., $n_D^{24} = 1.4623$. This compound was very fungicidal.

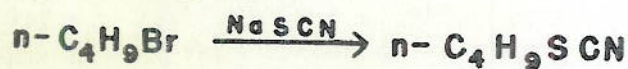
CHEMICAL REACTIONS

8. THIO AND SELENOCYANATES

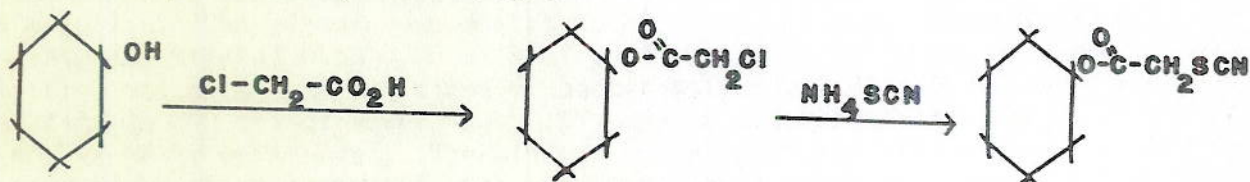
(1) p-Thiocyanoaniline



(2) Butyl thiocyanate



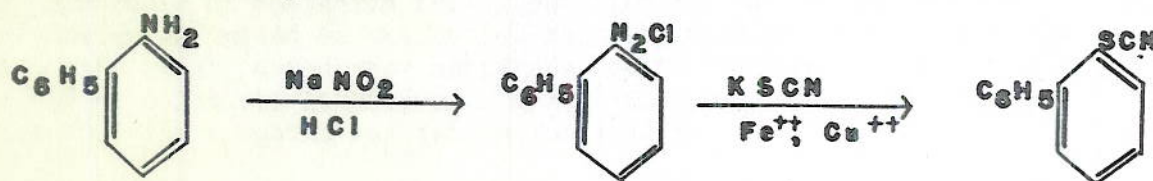
(3) Cyclohexyl thiocyanacetate



(4) Benzyl thiocyanate



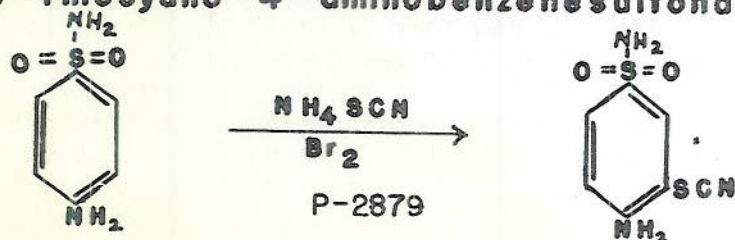
(5) o-Xenyl thiocyanate



(6) Lauryl thiocyanate



(7) 3-Thiocyano-4-aminobenzenesulfonamide



(3) Cyclohexyl thiocyanacetate was prepared from the intermediate cyclohexyl chloroacetate, which in turn resulted from the azeotropic refluxing of 0.67 mole of chloroacetic acid, 0.87 mole of cyclohexanol and 150 cc. of benzene. After washing with sodium carbonate and drying over anhydrous sodium sulfate, the product was distilled. Yield of cyclohexyl chloroacetate was 77% of colorless liquid, b.p. 113-14°/20 mm. (bath 145-150°). One-quarter mole of this product, 0.3 mole of ammonium thiocyanate and 200 cc. of ethanol were refluxed for 0.5 hour. The ammonium bromide was filtered out and the filtrate diluted with water. The oil which separated was distilled. Yield: 74% of clear, odorless liquid, b.p. 115-6°/0.3 mm. (bath 140°), $n_D^{24} = 1.4965$. Anal. calcd. for $C_9H_{13}NO_2S$: N, 7.03. Found: N, 7.33. This compound was slightly fungicidal.

(4) Benzyl thiocyanate was prepared by warming 0.4 mole of benzyl chloride and 0.5 mole of ammonium thiocyanate with 200 cc. of alcohol. The reaction was completed in a few minutes. Ice and water were added to the reaction mixture and the yellow precipitate collected and dried over P_2O_5 in vacuo. Yield: 93%, m.p. 36°. (Lit. m.p. 41°, Hartzell and Wilcoxon, loc. cit.) This compound was slightly fungicidal.

(5) o-Xenyl thiocyanate. One-quarter mole of o-venylamine, 100 cc. of water and 26 g. of conc. hydrochloric acid were warmed with stirring to effect solution. The mixture was cooled to 0°, 75 g. of conc. hydrochloric acid added, and treated with 0.25 mole of sodium nitrite in 60 cc. of water. Seventy-five cc. of a molar solution of copper sulfate, 0.43 mole of ferrous sulfate in 200 cc. of water, and 0.27 mole of potassium thiocyanate in 55 cc. of water were added. The mixture was stirred and allowed to stand over night, then extracted with petroleum ether and distilled. Yield: 38% of a yellow liquid, b.p. 124-5°/0.3 mm. (bath 165-70°), $n_D^{24} = 1.6323$. Anal. Calcd. for $C_{13}H_9NS$: N, 6.63. Found: N, 5.62. According to the analysis the purity is about 80%, in accord with U. S. Patent 2,281,692. This compound was fairly fungicidal.

(6) Lauryl thiocyanate was prepared by refluxing 0.2 mole of lauryl bromide, 0.25 mole of potassium thiocyanate and 100 cc. of ethanol for 4 hours. Water was added to the cooled reaction mixture, the product was extracted with ether, dried over anhydrous sodium sulfate and distilled. Yield: 71% of colorless liquid, b.p. 133-8°/0.25 mm. (bath 165-70°), $n_D^{24} = 1.4670$. The compound was fairly fungicidal.

(7) 3-Thiocyano-4-aminobenzenesulfonamide. Two-tenths mole of sulfanilamide and 0.6 mole of ammonium thiocyanate were dissolved in 200 cc. of methanol, cooled in an ice-salt bath, and 0.2 mole of bromine dissolved in 40 cc. of methanol saturated with sodium bromide was added dropwise over a period of about 45 minutes with stirring. Fifty cc. of methanol was added and stirring continued for 2 hours while the mixture came up to room temperature. Sufficient water was added to dissolve the solid in the reaction flask. The mixture was then made alkaline with sodium carbonate, with the formation of a yellow precipitate. The product was collected, recrystallized from methanol and water and dried. Yield: 77%, m.p. 150°. Anal. Calcd. for $C_7H_7N_3O_2S_2$: N, 18.34. Found: N, 17.8. (Lit. m.p. 161-2°, Kaufmann and Buckmann, Arch. Pharm., 279, 194 (1941)). This compound was not fungicidal.

(8) alpha-Thiocyanoacetanilide was prepared by refluxing 0.15 mole of alpha-bromoacetanilide (prepared as previously described) and 0.17 mole of ammonium thiocyanate in 200 cc. of 95% ethanol for a short time. Water was added, the precipitate collected, washed with water and dried over P_2O_5 . Yield: 100% of white powder, m.p. 84-5°. (Lit. m.p. 86°, Wheeler and Merriam, J.A.C.S., 23, 286 (1901)). This compound was fairly fungicidal.

(9) Octyl thiocyanate was prepared by refluxing 0.2 mole of octyl bromide and 0.25 mole of ammonium thiocyanate in 250 cc. of ethanol for 15 hours. The ethanol was partially removed by distillation and the residue was poured into water. The oil was extracted with ether-benzene, dried over sodium sulfate, the solvent removed in vacuo and the product distilled. Yield: 82% of colorless liquid, b.p. 108-9°/5 mm. (bath 140-5°), $n_D^{24} = 1.4650$. This compound was not fungicidal.

(10) Decyl thiocyanate was prepared like the above compound. Yield: 86% of colorless liquid, b.p. 121-2°/2.5 mm. (bath 145-50°), $n_D^{24} = 1.4650$. This compound was not fungicidal.

(11) 2,4-Dinitrophenyl thiocyanate was prepared by refluxing 0.15 mole of 2,4-dinitrochlorobenzene with 0.16 mole of ammonium thiocyanate in 500 cc. of 95% ethanol for 6.5 hours. At the end of this time a clear, brown solution was present, but after cooling and standing overnight, beautiful yellow leaflets separated. The ethanol was partly removed by distillation, water was added and the crude product filtered out. It was recrystallized from dilute alcohol as light-yellow crystals and dried over P_2O_5 . Yield: 79%, m.p. 137°. This compound was not fungicidal.

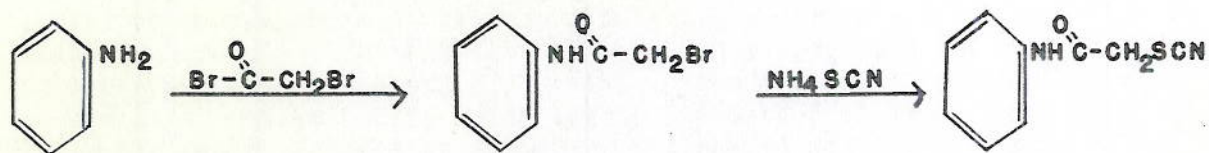
(12) Ethyl thiocynoacetate was prepared by refluxing 0.6 mole of ethyl bromoacetate (prepared as described below) and 0.8 mole of ammonium thiocyanate in 600 cc. of alcohol for a brief time. There was almost immediate formation of ammonium bromide crystals. After filtering, the bulk of the alcohol was removed by vacuum distillation, water was added and the oily layer was extracted with ether. The ethereal extract was dried and distilled. Yield: 65% of colorless liquid, b.p. 97°/5 mm., (bath 125°), $n_D^{24} = 1.4725$. Anal. Calcd. for $C_5H_7NO_2S$: N, 9.76. Found: N, 9.69. This compound was very fungicidal.

(13) Amyl thiocyanate was prepared by refluxing 0.25 mole of amyl bromide and 0.3 mole of ammonium thiocyanate in 105 cc. of methanol for 1.5 hours. Half the methanol was then removed by distillation, water was added and the mixture extracted with ether-benzene. The extract was dried over anhydrous sodium sulfate and distilled. Yield: 74% of colorless liquid, b.p. 88-9°/17 mm. (bath 128-30°), $n_D^{24} = 1.4641$. This compound was very fungicidal.

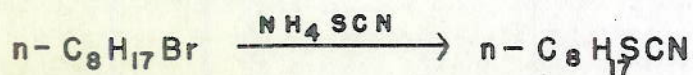
(14) Phenacyl thiocyanate was prepared by refluxing 0.25 mole of phenacyl chloride and 0.3 mole of ammonium thiocyanate in 250 cc. of alcohol for one hour. Ammonium chloride crystals were formed as soon as reflux temperature was reached. After filtration, the excess alcohol was

CHEMICAL REACTIONS

(8) α -Thiocyanoacetanilide



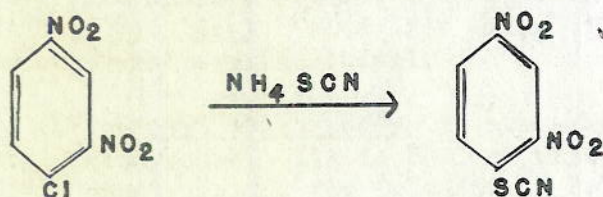
(9) Octyl thiocyanate



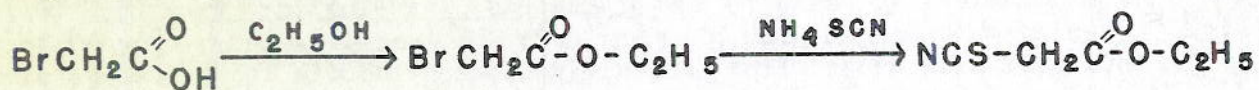
(10) Decyl thiocyanate



(11) 2,4-Dinitrophenyl thiocyanate



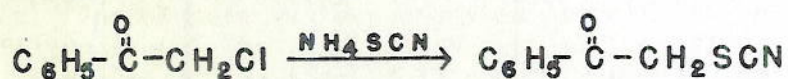
(12) Ethyl thiocyanoacetate



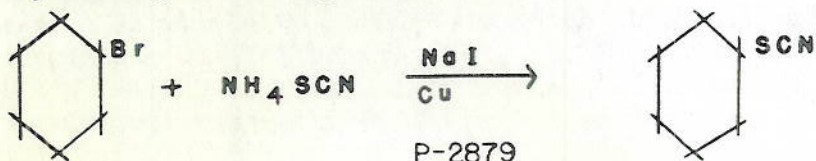
(13) Amyl thiocyanate



(14) Phenacyl thiocyanate



(15) Cyclohexyl thiocyanate



removed by distillation, water was added and the crystalline precipitate collected and dried. Yield: 77% of light yellow needles, m.p. 63-5° (Lit. m.p. 73°, Hartzell and Wilcoxon, Contrib. Boyce Thomson Inst., 6, 269 (1934)). This compound was very fungicidal.

(15) Cyclohexyl thiocyanate. Conventional methods for preparing aliphatic thiocyanates were unsuccessful when used to prepare this compound. Refluxing chlorocyclohexane with ammonium thiocyanate in ethanol failed to yield any product. The substitution of lead thiocyanate for ammonium thiocyanate was also of no avail. Use of sodium thiocyanate with a catalytic amount of sodium iodide according to the method of Wohl, Ber., 39, 1951 (1906), again resulted in failure. Cyclohexyl iodide and ammonium thiocyanate in ethanol yielded a product largely contaminated with the iodide. Cyclohexyl thiocyanate was finally prepared by refluxing 0.25 mole of cyclohexyl bromide, 0.3 mole of ammonium thiocyanate, 0.5 g. of metallic copper (powder) and 0.5 g. of sodium iodide in 250 cc. of alcohol for 20 hours. The excess alcohol was removed by distillation, water was added and the oil extracted with ether. The extract was dried over anhydrous sodium sulfate and distilled. Yield: 23% of colorless liquid, b.p. 82°/7 mm. (bath 123°), $n_D^{24} = 1.5038$. Anal. Calcd. for $C_7H_{11}NS$: N, 9.95. Found: N, 10.03. The compound was not fungicidal.

(16) Hexyl thiocyanate was prepared according to the method used for octyl thiocyanate. Yield: 62%, colorless liquid, b.p. 87-9°/10 mm. (bath 120°). Anal. Calcd. for $C_7H_{13}NS$: N, 9.79. Found: N, 9.64. This compound was very fungicidal.

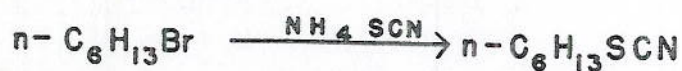
(17) Heptyl thiocyanate was prepared according to the method used for octyl thiocyanate. Yield: 58%, colorless liquid, b.p. 103°/10 mm. (bath 135°). Anal. Calcd. for $C_8H_{15}NS$: N, 8.91. Found: N, 8.88. This compound was not fungicidal.

(18) 2-Hydroxy-5-nitrobenzyl thiocyanate was prepared by refluxing 0.1 mole of 2-hydroxy-5-nitrobenzyl chloride and 0.15 mole of ammonium thiocyanate in 150 cc. of alcohol for several hours, followed by dilution with 1 liter of water and filtration. The product was recrystallized from dilute alcohol as small, light-yellow crystals. Yield: 72%, m.p. 145-7°. This compound was not fungicidal.

(19) Butyl selenocyanate. Potassium selenocyanate was prepared by treating 1.0 mole of potassium cyanide in 150 cc. of water with 1.0 gram-atom of powdered selenium metal. There was an easily controlled evolution of heat. The mixture was concentrated to half its original volume by boiling, filtered while hot and the rest of the water removed in vacuo over P_2O_5 . The product was recrystallized from 200 cc. of alcohol, using 200 cc. of ether to complete the precipitation. Yield: 47%, light-pink powder, (Schiellerup, Ann., 109, 125 (1859)). The salt was more conveniently prepared in an alcoholic medium from which it was directly crystallized. (Birckenbach and Kellermann, Ber., 58, 790 (1925)). Butyl selenocyanate was prepared by refluxing 0.25 mole of butyl bromide and 0.3 mole of potassium selenocyanate in 250 cc. of alcohol for six hours. The alcohol

CHEMICAL REACTIONS

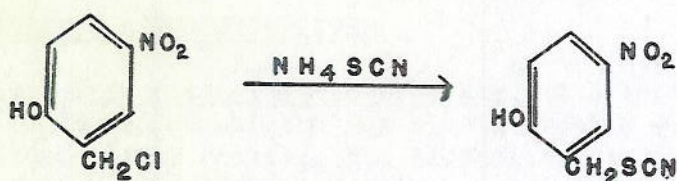
(16) Hexyl thiocyanate



(17) Heptyl thiocyanate



(18) 2-Hydroxy-5-nitrobenzyl thiocyanate



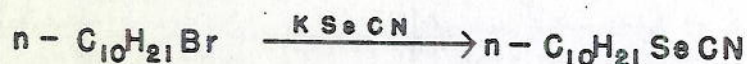
(19) Butyl selenocyanate



(20) Hexyl selenocyanate

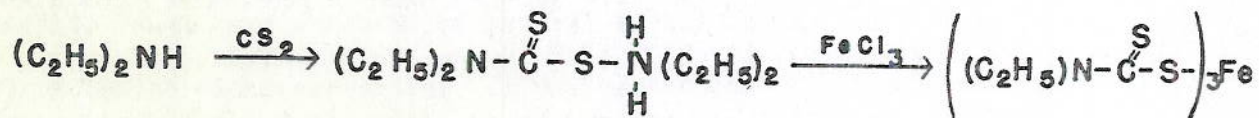


(21) Decyl selenocyanate



9. CARBAMIC ACID DERIVATIVES

(1) Ferric diethyldithiocarbamate



was removed by distillation, water was added and the mixture extracted with ether-benzene. The extract was dried over anhydrous sodium sulfate and distilled. Yield: 44% of yellow liquid with repugnant odor, b.p. 88-90°/13 mm. (bath 125°). Anal. Calcd. for C_5H_9NSe : N, 8.65. Found: N, 8.71. This compound was very fungicidal.

(20) Hexyl selenocyanate. This was prepared like the previous compound. Yield: 62% of yellow liquid with repugnant odor, b.p. 87-9°/10 mm. (bath 120°). Anal. Calcd. for $C_7H_{13}NSe$: N, 9.79. Found: N, 9.64. This compound was very fungicidal.

(21) Decyl selenocyanate was prepared according to the method used for butyl selenocyanate. Yield: 67%, colorless liquid with unpleasant odor, b.p. 97-8°/0.2 mm. (bath 150°). Anal. Calcd. for $C_{11}H_{21}NSe$: N, 5.69. Found: N, 5.44. This compound was slightly fungicidal.

9. CARBAMIC ACID DERIVATIVES

(1) Ferric diethyldithiocarbamate. A solution of 0.2 mole of diethylamine in 75 cc. of alcohol was slowly treated with 0.1 mole of carbon disulfide. After cooling, the alcoholic solution of diethylammonium diethyldithiocarbamate was treated with 0.1 mole of ferric chloride hexahydrate. There was immediate formation of a heavy black precipitate, with considerable evolution of heat. The precipitate was filtered, washed with water and dried. Yield: 100% of black crystals. Anal. Calcd. for $C_{15}H_{30}N_3S_6Fe$: Fe, 11.2. Found: Fe, 12.0. This compound was slightly fungicidal.

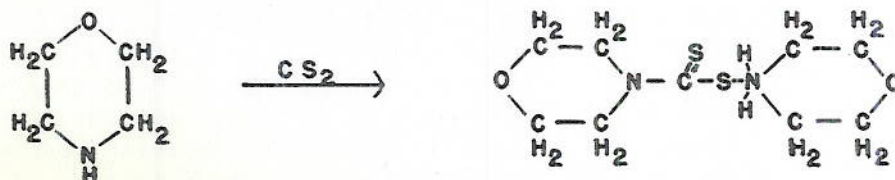
(2) Dimorpholine dithiocarbamate was prepared by treating 0.5 mole of morpholine dissolved in 500 cc. of water with 0.25 mole of carbon disulfide. After the vigorous reaction subsided, the white product was collected and dried; d. 170°. Anal. Calcd. for $C_9H_{18}N_2O_2S_2$: N, 11.2. Found: N, 11.0. This compound was not fungicidal,

(3) Dimorpholinethiuram disulfide was prepared by treating the previously described compound with 0.125 mole of bromine in aqueous sodium bromide, while stirring vigorously. The solid product was filtered off and dried. Yield: 12%, m.p. 134-5°. Anal. Calcd. for $C_{10}H_{16}N_2O_2S_4$: N, 8.61; S, 39.5. Found: N, 8.40; S, 39.4. This compound was not fungicidal.

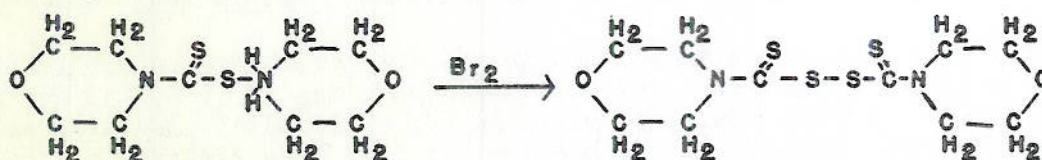
(4) Ethylene thiourea. One-half mole of ethylenediamine dissolved in 100 cc. of water was treated with 0.5 mole of carbon disulfide, and allowed to react over a period of several weeks, during which time it slowly solidified into a white mass. This compound corresponded to ethylenediamine dithiocarbamate. It was heated in 300 cc. of water on the steam bath for 5 days, until no more hydrogen sulfide was evolved. After cooling in the refrigerator, the small white crystals were filtered off and dried over P_2O_5 . Yield: 55%, m.p. 197-8°. After recrystallizing from water, m.p. 200-3°. (Lit. m.p. 194°, Hofmann, Ber., 5, 240 (1872)).

CHEMICAL REACTIONS

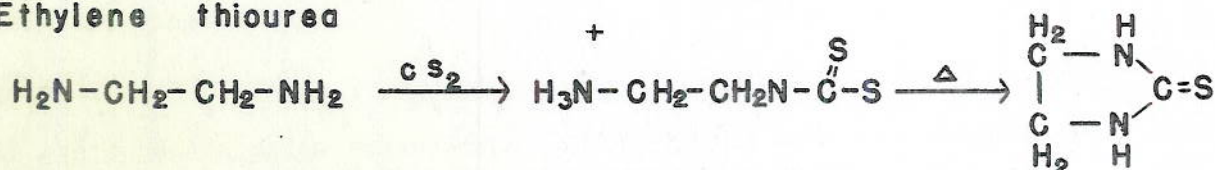
(2) Dimorpholinedithiocarbamate



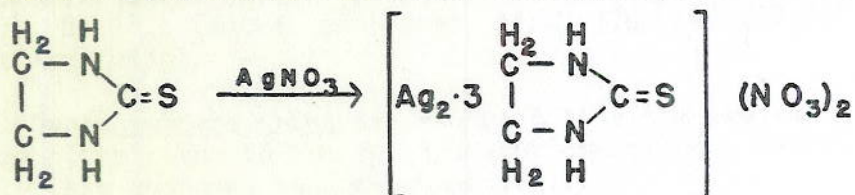
(3) Dimorpholinethiuram disulfide



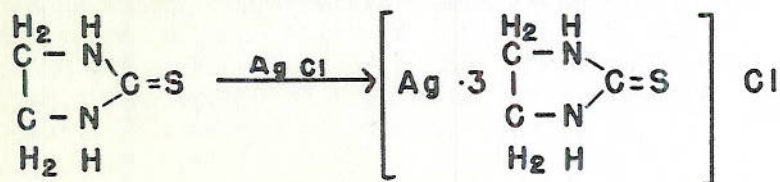
(4) Ethylene thiourea



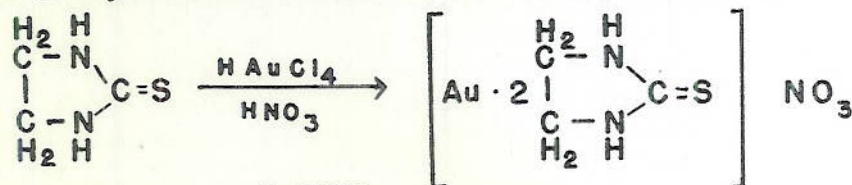
(5) Tris (ethylenethiocarbamido) diargentous nitrate



(6) Tris (ethylenethiocarbamido) argentous chloride



(7) Bis (ethylenethiocarbamido) aurous nitrate



(5) Tris-(ethylenethiocarbamido)-diargentous nitrate was prepared by treating an aqueous solution of 8.5 g. of silver nitrate with a solution of 10 g. of ethylene thiourea in 2 liters of water. An amorphous white precipitate formed which dissolved on heating and crystallized out as white needles on cooling. Yield: 60%, m.p. 230-3° d. (Lit. d. 200°, Morgan and Burstall, J.C.S., 1943 (1928)). This compound was not fungicidal.

(6) Tris-(ethylenethiocarbamido)-argentous chloride. A freshly prepared sample of 7.0 g. of silver chloride was dissolved in an aqueous solution of 20.0 g. of ethylene thiourea. Several liters of water were used and were concentrated on the steam bath to 200 cc. The hot solution was decolorized with Nuchar and filtered. On cooling, a mass of white crystals separated which were dried over P₂O₅ in vacuo. Yield: 80%, m.p. 167-8° on recrystallization from water. (Lit. m.p. 168°. Morgan and Burstall, loc. cit.). This compound was not fungicidal.

(7) Bis-(ethylenethiocarbamido)-aurous nitrate was prepared by adding a solution of 2.0 g. of auric chloride to a hot solution of 3.0 g. of ethylene thiourea, followed by the addition of excess nitric acid. After cooling, the crystals were filtered off and dried. Yield: 100%, m.p. 172-4°. (Lit. m.p. 173° d., Morgan and Burstall, loc. cit.). This compound was not fungicidal.

10. OXIMES

(1) Acetophenone oxime was prepared by mixing 0.5 mole of acetophenone in 60 cc. of methanol with 0.85 mole of hydroxylamine hydrochloride and 0.75 mole of sodium acetate in 100 cc. of water. After 1.5 months in the refrigerator, large white crystals were filtered off and dried. Yield: 86%, m.p. 58-9°. (Huckel and Sachs, Ann., 498, 166 (1932)). This compound was not fungicidal.

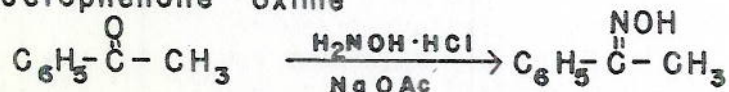
(2) Cyclohexanone oxime was prepared like the preceding compound by allowing it to stand in the refrigerator overnight. Yield: 89%, m.p. 88-90°. This compound was not fungicidal.

(3) Fenchone oxime was prepared according to the method used for acetophenone oxime, the reaction time being twelve hours. Yield: 50%, m.p. 155°. The melting point of this compound varies with the rate of heating and was easily lowered by the presence of small amounts of impurities. The method of Org. Syn., Coll. Vol. II, 313 was tried without success. The method of Rimini, (Gazz., 26, II, 502 through Cockburn, J.C.S., 75, 503 (1899)), consisted in heating 0.5 mole of fenchone, 0.8 mole of hydroxylamine hydrochloride and 150 g. of sodium hydroxide in 300 cc. of alcohol on the steam bath. After a few hours, another 0.4 mole of hydroxylamine hydrochloride was added and heating continued for several hours. Water was added and the mixture was extracted with ether. The extract was dried and evaporated, yielding an oil. The product was obtained by adding 300 cc. of ligroin, cooling to -70° and filtering. Yield: 11% of product melting at 110-20°. Another method was tried where- in 1.0 mole of fenchone, 1.75 moles of hydroxylamine hydrochloride and

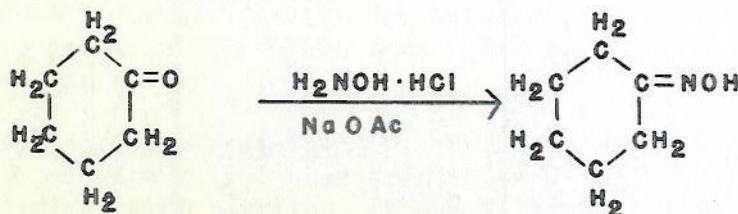
CHEMICAL REACTIONS

10. OXIMES

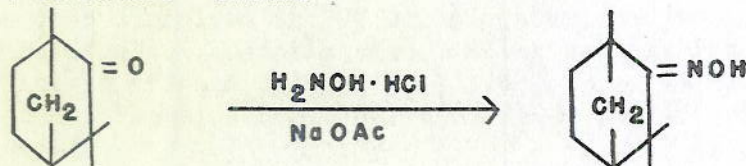
(1) Acetophenone oxime



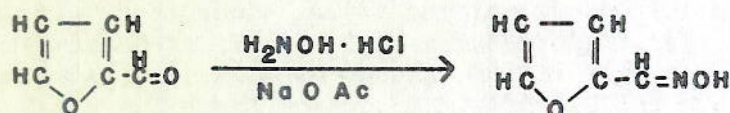
(2) Cyclohexanone oxime



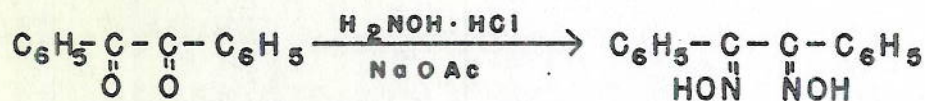
(3) Fenchone oxime



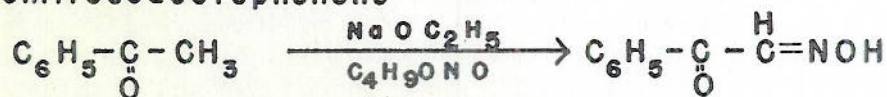
(4) Furfuraldoxime



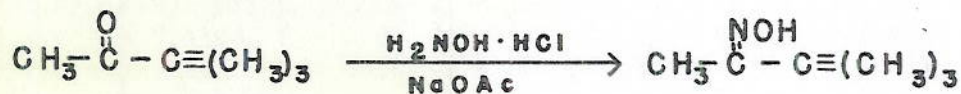
(5) Benzildioxime



(6) Isonitrosoacetophenone



(7) Pinacolone oxime



1.5 moles of anhydrous sodium acetate in 250 cc. of methanol were alternately boiled and stored in the refrigerator daily for one week. Water was added to dissolve the inorganic salts, the product filtered off and dried in vacuo over P_2O_5 . Yield: 22% of product melting at $130-40^\circ$. This compound was not fungicidal.

(4) Furfuraldoxime. One-half mole of furfural in 45 cc. of methanol was mixed with a solution of 0.87 mole of hydroxylamine hydrochloride and 0.75 mole of sodium acetate in 90 cc. of water. While standing in the refrigerator for one week, long needles of the oxime were formed. They were recrystallized from dilute alcohol, after decolorizing with charcoal. Yield: 33%, m.p. 90° . This compound was not fungicidal.

(5) Benzil dioxime was prepared according to the method used for acetophenone oxime. An oil was obtained, from which alcohol precipitated white crystals of the alpha form. Yield: 7%, m.p. $230-5^\circ$. This compound was not fungicidal.

(6) Isonitrosoacetophenone. One gram-atom of sodium was dissolved in 500 cc. of alcohol and then treated at 0° with 1 mole of acetophenone and 1.0 mole of butyl nitrite. It was allowed to stand in the refrigerator for five days, after which 300 cc. of ether was added. The heavy red precipitate of sodium salt was filtered off, washed with ether and air-dried. It was then dissolved in 300 cc. of water, cooled to 5° , and treated with 1.0 mole of glacial acetic acid. After cooling for 0.5 hours, the product was filtered off and dried. Yield: 44%, m.p. $127-9^\circ$. (Lit. m.p. 127° , Claisen and Manasse, Ber., 20, 656, 2194 (1887)). This compound was not fungicidal.

(7) Pinacolone oxime was prepared by reacting 0.25 mole of pinacolone, 0.25 mole of hydroxylamine hydrochloride and 75 g. of sodium acetate in 400 cc. of 50% alcohol. After warming to 50° for a short time, the mixture was placed in the refrigerator overnight, the white crystals filtered out and dried over P_2O_5 in vacuo. Yield: 77%, m.p. $74-5^\circ$. (Lit. m.p. $74-5^\circ$, Janny and Scholl, Ann., 338, 116 (1905); m.p. $77-8^\circ$, Markownikow, Ber., 32, 1448 (1899)). This compound was fairly fungicidal.

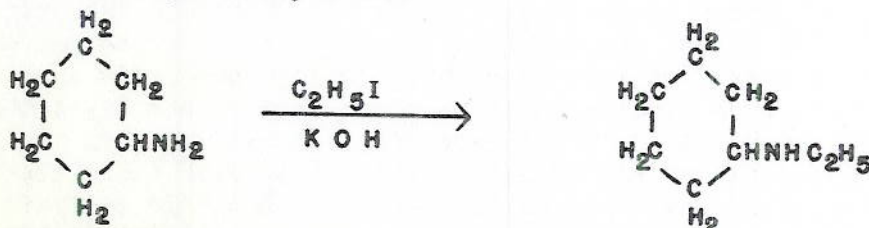
11. AMINES AND NITRILES

(1) N-Ethylcyclohexylamine was prepared by adding 0.25 mole of cyclohexylamine with 0.5 mole of potassium hydroxide in 250 cc. of 95% ethanol to 0.5 mole of ethyl iodide. Two to three minutes after the addition was completed a violent reaction set in, with the separation of a solid and then a liquid which slowly crystallized. More alcohol was added and the mixture refluxed for two hours. Most of the alcohol was removed by distillation, water was added, the mixture extracted with ether-benzene and dried over anhydrous sodium sulfate. On distillation, instead of the expected N,N-diethylcyclohexylamine, a product boiling at $60-3^\circ/20$ mm. was obtained. $n_D^{20} = 1.4494$, $d = 0.82$. These data show the compound to be N-ethylcyclohexylamine. MR: calcd.: 40.7. Found: 41.5. Yield 20%. This compound was very fungicidal.

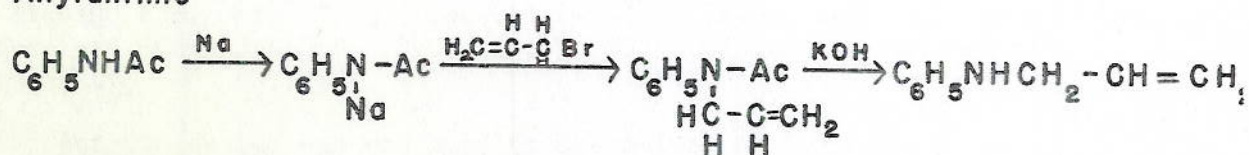
CHEMICAL REACTIONS

II. AMINES AND NITRILES

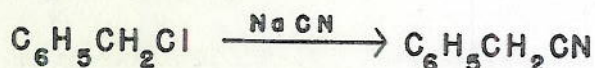
(1) N-Ethylcyclohexylamine



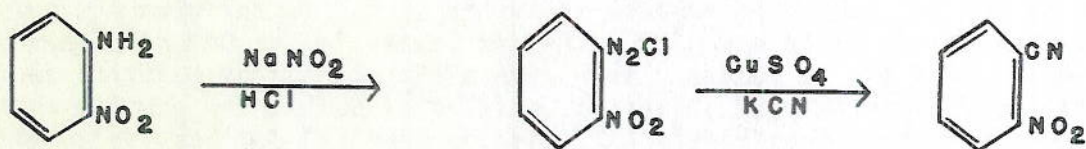
(2) Allylaniline



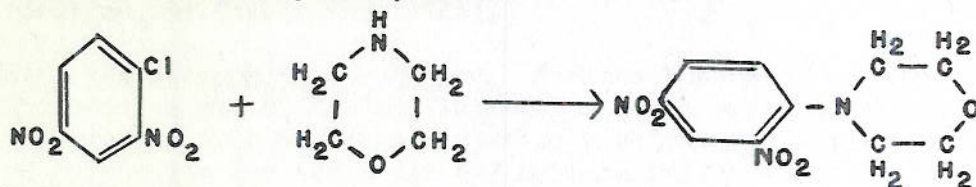
(3) Benzyl cyanide



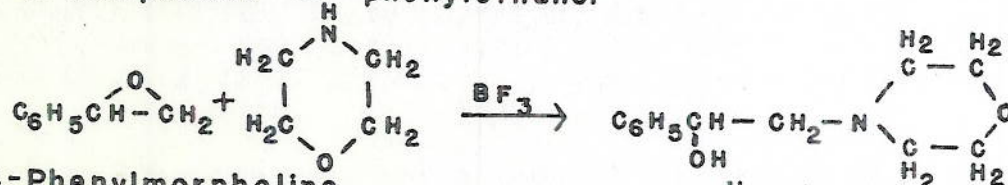
(4) 2-Nitrobenzonitrile



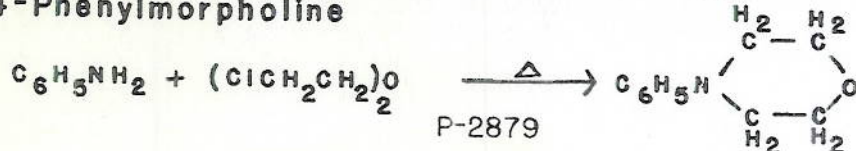
(5) 2,4-Dinitrophenylmorpholine



(6) β-N-Morpholino-α-phenylethanol



(7) 4-Phenylmorpholine



P-2879

Plate 13.

(2) Allylaniline. One-half mole of acetanilide, thoroughly dried, 500 cc. of xylene and 0.5 mole of sodium were placed in a 1-liter 3-necked, round-bottomed flask equipped with a stirrer and heated on an oil bath. When the sodium melted a sudden reaction took place and stirring and heating were stopped. The fluffy white solid (sodium acetanilide) was transferred to a 2-liter, 3-necked, round-bottomed flask equipped with a stirrer and dropping funnel. Then 0.7 mole of allyl bromide was added during 0.5 hour while gently heating the flask in the oil bath (reflux temperature). Refluxing was continued for three hours longer, during which time the solid became amorphous and the liquid turned brown. After standing overnight the xylene was distilled off, 60 g. of potassium hydroxide in 500 cc. of ethanol was added and the mixture refluxed eight hours. Most of the ethanol was distilled off, the reaction mixture acidified with hydrochloric acid and steam-distilled until all the residual xylene was removed. The residue was made alkaline with 20% sodium hydroxide and steam-distilled. The yellow layer in the distillate was separated and distilled. Yield: 60% of colorless liquid, b.p., 111°/22 mm. (bath 145-50°). (Hepp, Ber., 10, 327 (1877); Carnahan and Hurd, J.A.C.S., 52, 4586, (1930)). This compound was not fungicidal.

(3) Benzyl cyanide was prepared by the method of Org. Syn., Coll., Vol. I, 107 (1941). Yield: 77%, b.p. 101-3°/10 mm., $n_D^{30} = 1.5202$. This compound was not fungicidal.

(4) 2-Nitrobenzonitrile. One-half mole of o-nitroaniline and 1 mole of concentrated hydrochloric acid were stirred together until the white hydrochloride formed. Two liters of water were added all at once. Then 0.5 mole of sodium nitrite in 200 cc. of water was added during 40 minutes, with stirring. A solution of 125 g. of copper sulfate and 140 g. of 96% potassium cyanide in 750 cc. of water, heated to 90°, was added slowly and with vigorous stirring to the diazonium salt over a period of one hour. The reaction mixture was heated to boiling, filtered, the tar extracted with boiling water, and the filtrate cooled. The light-brown product was collected, washed with water and dried over P₂O₅ in vacuo. Yield: 38%, m.p. 107-8° (Lit. m.p. 109°. Bogert and Hand, J.A.C.S., 24, 1031 (1902)). This compound was fairly fungicidal.

(5) 2,4-Dinitrophenylmorpholine. Fifteen-hundredths mole of 2,4-dinitrochlorobenzene and 0.5 mole of morpholine were mixed together. Much heat was evolved with the development of a bright red color. One-quarter mole of morpholine was added and the mixture refluxed for one hour. On cooling, cold dilute hydrochloric acid was added and the red solid filtered off, recrystallized from dilute alcohol and dried over P₂O₅ in vacuo. Yield: 83% of orange-red crystals, m.p. 118-9°. (Lit. m.p. 118-9°, Harra-dence and Lyons, J. Proc. Roy. Soc. N.S. Wales, 70, 406 (1937)). This compound was not fungicidal.

(6) beta-N-Morpholino-alpha-phenylethanol was prepared by treating a solution of 0.2 mole of phenylethylene oxide in 250 cc. of morpholine with boron trifluoride gas for 10 minutes. Much heat developed. After standing

for one hour, 1 liter of 5% sodium acetate solution was added and the mixture extracted twice with ether. The combined extracts were dried over anhydrous sodium sulfate and distilled. Yield: 49%, b.p. 134°/.3 mm. (bath 170°). The product solidified at room temperature. The compound was prepared previously using a phosphoric acid catalyst by Emerson (J.A.C.S., 67, 516 (1945)). This compound was not fungicidal.

(7) 4-Phenylmorpholine was prepared by heating 0.5 mole of dichlorodiethyl ether and 1.5 moles of aniline in an oil bath. The initial reaction took place violently on reaching 155° and heating was continued at 200° for two hours. After cooling, benzene was added and the insoluble aniline hydrochloride filtered off. The benzene extract was evaporated, the residue dissolved in methanol and decolorized with Nuchar. The methanolic solution was then cooled and stirred while water was slowly dropped in. The small light-tan crystals were recrystallized from acidic dilute methanol as white crystals. Yield: 18%, m.p. 50° (Lit. m.p. 53°, Cretcher, Koch and Pittenger, J.A.C.S., 47, 1173 (1925)). This compound was not fungicidal.

12. HALOGENATED COMPOUNDS

(1) Benzyl iodide was prepared by allowing 0.25 mole of benzyl chloride and 0.25 mole of sodium iodide in 250 cc. of acetone to stand overnight. The acetone was removed by distillation, water was added and the mixture extracted with ether-benzene. The ethereal extract was dried over anhydrous sodium sulfate and distilled. Yield: 35%, b.p. 88-9°/9 mm. (bath 110°). (Lit. b.p. 93°/10 mm. Whitmore and Thurman, J.A.C.S., 51, 1491 (1929)). This compound was fairly fungicidal.

(2) 2-Hydroxy-5-nitrobenzyl chloride was prepared by the method of Buehler, Kirchner and Deebel, Org. Syn., 20, 59 (1940). Yield: 55%, m.p. 122-7°. This compound was not fungicidal.

(3) 2,3-Diiodopropanol-1. Twenty-one-hundredths (0.21) mole of allyl alcohol (redistilled) and 0.2 mole of iodine in chloroformic solution were mixed and allowed to stand for two days. The dark-brown solution was washed with 10% sodium hydroxide and water, and the chloroform evaporated in a stream of air. The dark-brown product was dissolved in alcohol, precipitated with iced water, filtered, washed with very dilute potassium hydroxide and then with water. Yield: 80%, m.p. 41.5 - 2.5° (Lit. m.p. 45°, Herz, Ber., 40, 2898 (1907)). The product rapidly decomposed in the air.

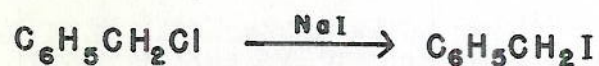
(4) Glycerol-1,3-dichlorohydrin was prepared according to the method of Org. Syn., Coll. Vol. I, 292 (1941). Yield: 20%, b.p. 82-4°/23 mm. This compound was slightly fungicidal.

(5) 1,3-Diiodopropanol-2 (Iothion). A mixture of 0.15 mole of glycerol-1, 3-dichlorohydrin and 0.32 mole of potassium iodide moistened with water was heated at 130-40° with frequent stirring for two hours. The crude product was washed with sodium thiosulfate solution and filtered. Yield: 48% of colorless liquid, $n_D^{25} = 1.6118$, $d = 2.42$ (Lit. $d = 2.4$, Lusignani, Boll, chim. farm., 78, 557 (1939)). This compound was slightly fungicidal.

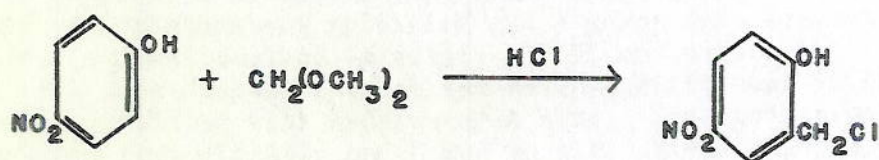
CHEMICAL REACTIONS

12. HALOGENATED COMPOUNDS

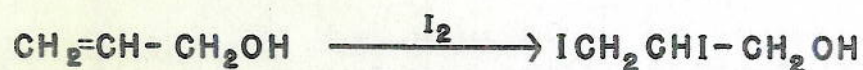
(1) Benzyl iodide



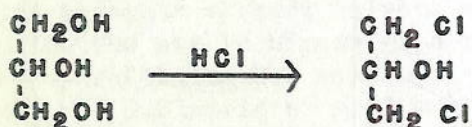
(2) 2-Hydroxy-5-nitrobenzyl chloride



(3) 2,3-Diiodopropanol-1



(4) Glycerol-1,3-dichlorohydrin



(5) 1,3-Diiodopropanol-2



(6) Acetylene diiodide



(6) Acetylene diiodide. Two-tenths mole of iodine in 75 cc. of absolute alcohol was treated for twenty hours with acetylene, agitating occasionally. The mixture was poured into ice-water containing enough sodium hydroxide to decolorize the iodine. The product was filtered, washed with very dilute alkali and water, recrystallized from dilute alcohol and dried over P_2O_5 . Yield: 64% of bright yellow crystals, m.p. 66° (Lit. m.p. 72° , Biltz, Ber., 30, 1200 (1897)). This compound was very fungicidal.

13. ARLOXY ACIDS

(1) Salicylanilide-O-acetic acid. An attempt to synthesize this compound from salicylanilide and bromoacetic acid was unsuccessful, presumably because of saponification of the bromoacetic acid. It was prepared by refluxing 0.15 mole of salicylanilide, 0.32 mole of chloroacetic acid and 100 cc. of 20% sodium hydroxide (0.5 mole) for two hours on a steam bath. On cooling, the mixture was acidified and a gummy mass separated, which was filtered out, redissolved in dilute alkali and neutralized with carbon dioxide. The precipitate of unreacted salicylanilide was filtered out and the filtrate acidified with hydrochloric acid. The product was collected, recrystallized from ethanol, and dried in air. Yield: 44%, m.p. 156° (Lit. m.p. 157° , Cohn, J. prakt. Chem., 168, 404 (1899)). Anal. Calcd. for $C_{15}H_{13}NO_4$: N, 5.16. Found: N, 4.97. This compound was not fungicidal.

(2) o-Xenoxyacetic acid. Attempts to prepare this compound with equivalent proportions of o-phenylphenol, alkali and bromoacetic acid were unsuccessful, as were attempts using the same quantities of reactants in concentrated aqueous or alcoholic alkali. Heating o-phenylphenol and chloroacetic acid together without solvent or alkali at 180° for seven hours, or refluxing the two in pinene also resulted in failure. It was finally prepared by refluxing 0.2 mole of o-phenylphenol, 0.2 mole of chloroacetic acid and 0.21 mole of sodium hydroxide in 500 cc. of ethanol for 3.5 hours. The sodium chloride was filtered off and most of the ethanol removed at atmospheric pressure. Ether-benzene was added to the residue, the product extracted with sodium carbonate and obtained upon acidification. Yield: 68% of white solid, m.p. 102° , N.E.: Calcd.: 228. Found: 232. This compound was not fungicidal.

(3) o-Xenoxy-alpha-pronionic acid was prepared in the same way. Yield: 49%, m.p. $108-11^\circ$. The N.E. indicated a purity of 80%. This compound was not fungicidal.

(4) beta-Naphthoxyacetic acid was prepared by refluxing 0.33 mole of beta-naphthol, 0.5 mole of chloroacetic acid, and 3 moles of potassium hydroxide in 1 liter of water for three hours. The hot solution was acidified, the precipitate collected, redissolved in alkali and precipitated by addition of acid. Yield: 76% of white solid, m.p. 150° . (Lit. m.p. 156° , Spitzer, Ber., 34, 3192 (1901)). N.E.: Calcd.: 202. Found: 206. This compound was not fungicidal.

(5) Quinoline-8-oxoacetic acid. One and one-half moles of freshly prepared sodium ethoxide in 2 liters of absolute alcohol was treated with 0.68 mole of 8-hydroxyquinoline and refluxed for one hour. A concentrated alcoholic solution of 0.68 mole of chloroacetic acid was added in small portions and the mixture heated for 12 hours on the steam-bath. All the alcohol was removed by evaporation, the residue dissolved in 1.5 liters of water and the mixture treated with carbon dioxide. The unreacted phenol precipitated (0.2 mole), was removed, and the filtrate evaporated to dryness. The dry residue was extracted with ether to remove the rest of the phenol. The residue was dissolved in hot water and excess barium chloride solution added to precipitate the barium salt, which was treated with sulfuric acid and the barium sulfate filtered off. Excess silver nitrate solution was added and the tan precipitate was collected, suspended in water and treated with hydrogen sulfide until no more precipitation occurred. After filtration the filtrate was concentrated, cooled, and the yellow needles were collected and dried over P_2O_5 in vacuo. Yield: 25%, m.p. 163° d. (Lit. m.p. 176° , Nagel, Monatsh., 18, 32 (1897)). This compound was not fungicidal.

14. QUATERNARY SALTS

(1) Octylhexamethylenetetraminium bromide was prepared by treating a solution of 0.25 mole of hexamethylenetetramine in a minimum of chloroform with 0.25 mole of octyl bromide. After standing for five months, the solid was collected, washed with chloroform, and air-dried. Yield: 30% of white solid, m.p. 203° d. This compound was not fungicidal.

(2) Decylhexamethylenetetraminium bromide was prepared like the previous compound. M.p. 205° d. This compound was not fungicidal.

(3) Benzylhexamethylenetetraminium chloride was prepared in the same way except that the reaction was completed overnight. M.p. 203° d. Anal. Calcd. for $C_{13}H_{19}N_4Cl$: N, 21.05. Found: N, 21.17. This compound was not fungicidal.

(4) Laurylpyridinium iodide was prepared by heating 0.5 mole of lauryl iodide and 0.2 mole of pyridine in 50 cc. of dioxane on the steam bath for six hours. The solvent was removed under reduced pressure and the solid was shaken with a mixture of absolute ether and petroleum ether which caused it to liquify. The liquid was separated and dried in vacuo over P_2O_5 . Yield: 96% of yellow solid, m.p. $75-80^\circ$.

15. ESTERS

(1) Ethyl bromoacetate was prepared by refluxing 2.0 moles of bromoacetic acid in 500 cc. of alcohol for five hours, with 2 cc. of concentrated sulfuric acid added as catalyst. After washing out the acid, the solution was distilled. Yield: 60%, b.p. $70-2^\circ/32$ mm. This compound was fairly fungicidal.

(2) Cyclohexyl chloroacetate. The preparation of this compound was described under cyclohexyl thiocynoacetate.

CHEMICAL REACTIONS

14. QUATERNARY SALTS

(1) Octyl hexamethylenetetraminium bromide



(2) Decyl hexamethylenetetraminium bromide



(3) Benzylhexamethylenetetraminium chloride



(4) Laurylpyridinium iodide

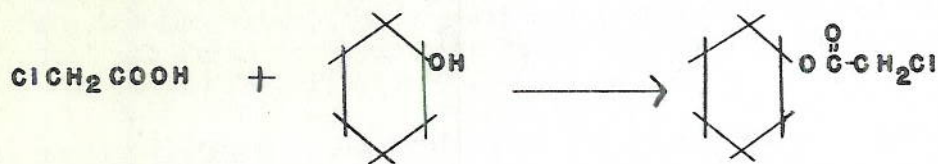


15. ESTERS

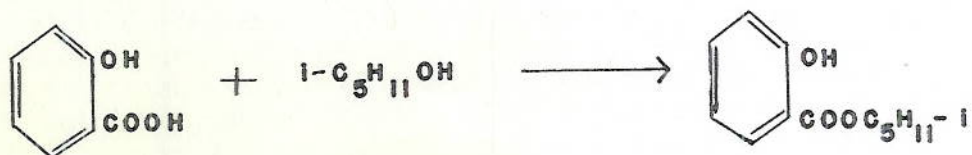
(1) Ethyl bromoacetate



(2) Cyclohexyl chloroacetate



(3) Isoamyl salicylate



(3) Isoamyl salicylate was prepared by azeotropically refluxing 0.25 mole of salicylic acid and 0.4 mole of isoamyl alcohol in 150 cc. of benzene, using 1 drop of conc. sulfuric acid as catalyst. After refluxing 40 hours, iced water and ether were added to the mixture, which was then washed with 10% sodium carbonate. The ether-benzene was dried over anhydrous sodium sulfate and distilled. Yield: 15%, b.p. 105-8°/0.5 mm. (bath 140°), $n_D^{23} = 1.5037$. (Lit. $n_D^{20} = 1.5060$). This compound was not fungicidal.

(4) Fenchyl bromoacetate was prepared in the same way using 0.3 mole of fenchyl alcohol (prepared by reduction of fenchone with sodium and amyl alcohol) and 0.25 mole of bromoacetic acid. Yield: 58%, b.p. 84-6°/0.5 mm. (bath 115-20°).

16. NITRO COMPOUNDS

(1) 1,3,6,8-Tetranitrocarbazole was prepared by slowly adding 10 g. of carbazole to 120 g. of fuming nitric acid during the course of 1 hour. The dark-green mixture was evaporated on the steam-bath and the yellow residue recrystallized from nitrobenzene and dried over P₂O₅. Yield: 43%, m.p. 280°. (Lit. m.p. 285°. Ziersch, Ber., 42, 3300 (1909)). This compound was not fungicidal.

(2) 2-(2-Nitrovinyl)-furan. The method of Thiele and Lander (Ann., 369, 300 (1909)), could not be repeated. The compound was prepared by adding 0.4 mole of nitromethane to a cooled solution of 0.2 mole of furfural in 100 cc. of ethanol and then introducing 0.44 mole of sodium hydroxide in ethanol over a period of 1 hour, keeping the temperature below 15°. Enough water was added to dissolve the brown precipitate and the mixture was slowly added, with rapid stirring, to 120 cc. of conc. hydrochloric acid in 180 cc. of water. The precipitate was filtered off, washed several times with water and dried over P₂O₅. Yield: 61%, m.p. 72.5°. (Lit. m.p. 74-5°, T. and L., loc. cit.; Lange and Hambourger, J.A.C.S., 53, 3865 (1931)). This compound was not fungicidal.

(3) m-Nitroacetophenone was prepared according to the method of Org. Syn., Coll. Vol. II, 434. There was difficulty in controlling the temperature and the reaction took longer than was desirable (4 hours). When poured into ice and water, the product was gummy. It was recrystallized from alcohol and dried in vacuo over P₂O₅. Yield: 15%, m.p. 73-5°. This compound was fairly fungicidal.

(4) p-Nitrodiphenyl. p-Nitroaniline was converted to p-nitrophenyldiazonium borofluoride according to the method used for o-xenyldiazonium borofluoride (see under o-xenylmercuric chloride). Yield: 71% of stable salt. p-Nitrodiphenyl was prepared by refluxing 0.05 mole of p-nitrophenyldiazonium borofluoride, 0.15 mole of acetic anhydride and 0.125 mole of powdered copper in 200 cc. of dry benzene. After refluxing several minutes, evolution of nitrogen began and the reaction proceeded vigorously while being cooled externally. After a few minutes the reaction subsided and the mixture was refluxed for 0.5 hour longer, filtered, the filtrate washed with sodium carbonate solution and dried over anhydrous sodium sulfate. The solution was evaporated on the steam bath and the solid was recrystallized from 90% alcohol. Yield: 70%, m.p. 110-12°. This compound was not fungicidal.

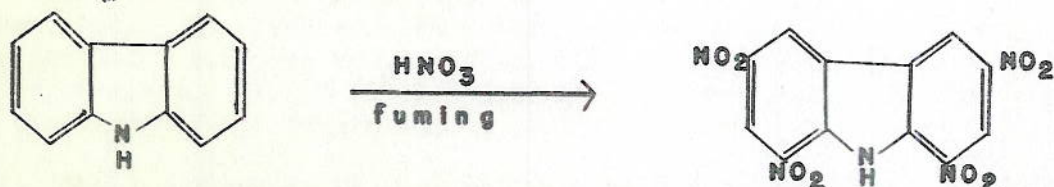
CHEMICAL REACTIONS

(4) Fenchyl bromoacetate

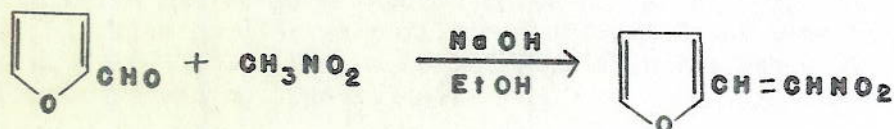


16. NITRO COMPOUNDS

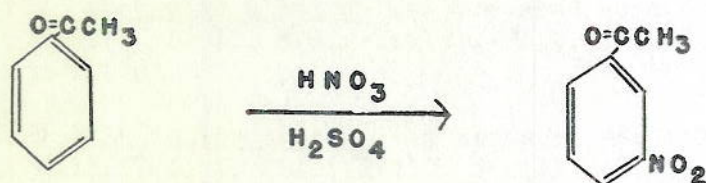
(1) 1,3,6,8,- Tetranitrocarbazole



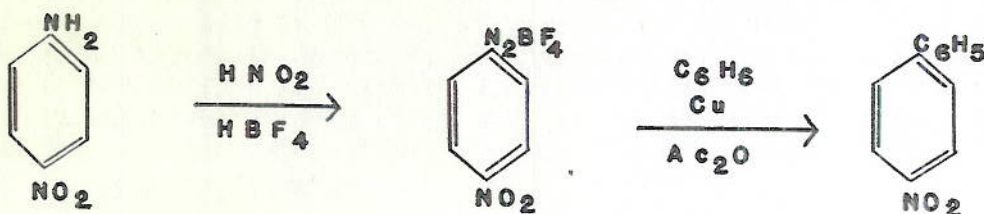
(2) 2- (2- Nitrovinyl) - furan



(3) m- Nitroacetophenone



(4) p- Nitrodiphenyl



17. HYDRAZONES AND SEMICARBAZONES

(1) Furfural phenylhydrazone was prepared by allowing a mixture of 0.3 mole of phenylhydrazine, 0.2 mole of furfural and 70 g. of sodium acetate in 200 cc. of water to stand overnight. The precipitate was collected, dissolved in ethanol and water, decolorized with Nuchar and recrystallized. Yield: 55% of red-brown, unstable crystals, m.p. 85-6°. This compound was not fungicidal.

(2) Cyclohexanone phenylhydrazone was prepared in the same way. Yield: 58% of slowly decomposing, yellow crystals, m.p. 70-3°. This compound was not fungicidal.

(3) Furfural semicarbazone was prepared by dissolving 0.33 mole of redistilled furfural in 10% ethanol and adding 0.33 mole of semicarbazide hydrochloride. The light-yellow precipitate which formed immediately was collected and dried over P_2O_5 . Yield: 92%, m.p. 197-8°. (Lit. m.p. 202-3° Knopfer, Monatsh., 31, 95 (1910); m.p. 190°, Wolff, Ann., 394, 101 (1912)). This compound was not fungicidal.

(4) Cyclohexanone semicarbazone was prepared by dissolving 0.33 mole of cyclohexanone in 500 cc. of water and adding 0.33 mole of semicarbazide hydrochloride and 60 g. of sodium acetate. After standing overnight, the beautiful white needles were filtered off and dried over P_2O_5 . Yield: 100%, m.p. 169-71°. (Lit. m.p. 166-7°, Zelinsky, Ber., 30, 1541 (1897)). This compound was not fungicidal.

18. ALDEHYDES AND KETONES

(1) Pelargonic aldehyde was prepared according to the method of Org. Syn., Coll. Vol. II, 323. Yield: 38%, b.p. 90°/40 mm. This compound was not fungicidal.

(2) 1,3-Dichloroacetone was prepared according to the method of Org. Syn., Coll. Vol. I, 211 (1941). Yield: 54%, b.p. 170°. This compound was very fungicidal.

(3) Butyrolin. Ethyl butyrate was prepared azeotropically by refluxing 2.0 moles of butyric acid, 4.0 moles of ethyl alcohol and 2.0 g. of p-toluenesulfonic acid in 350 cc. of benzene for 15 hours. After washing with sodium carbonate solution, the reaction mixture was dried over anhydrous sodium sulfate and distilled. Yield: 58%, b.p. 107°, $n_D^{20} = 1.3895$. Butyrolin was prepared from ethyl butyrate by the method of Org. Syn., Coll. Vol. II, 114, Yield: 50%, b.p. 80-3°/13 mm. (bath 119°). This compound was not fungicidal.

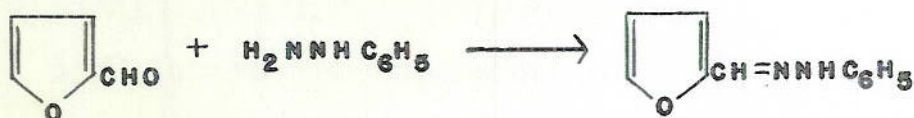
19. MISCELLANEOUS COMPOUNDS

(1) 2,3-Dichloro-1,4-naphthoquinone was prepared by dissolving 0.11 mole of naphthalene tetrachloride in 200 cc. of concentrated nitric acid

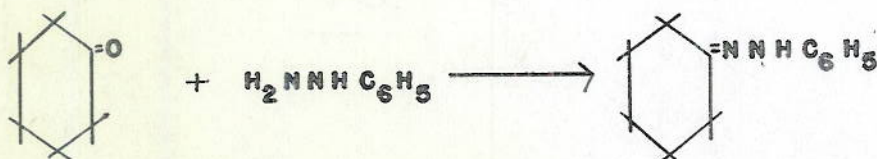
CHEMICAL REACTIONS

17. HYDRAZONES AND SEMICARBAZONES

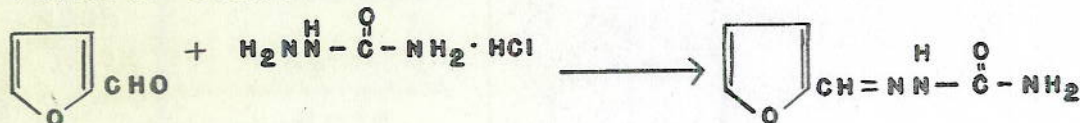
(1) Furfural phenyl hydrazone



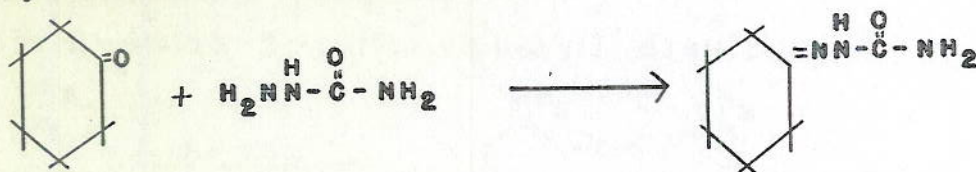
(2) Cyclohexanone phenylhydrazone



(3) Furfural semicarbazone

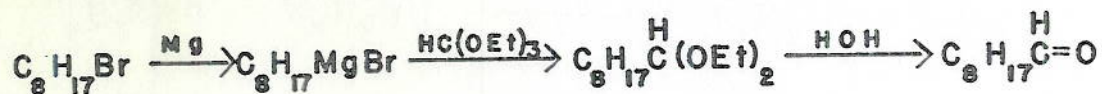


(4) Cyclohexanone semicarbazone

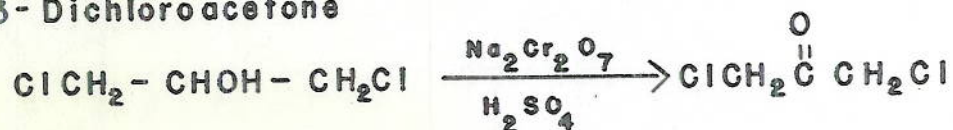


18. ALDEHYDES AND KETONES

(1) Pelargonic aldehyde

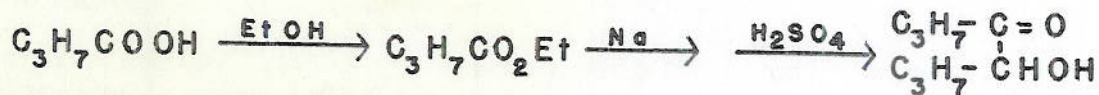


(2) 1,3-Dichloroacetone



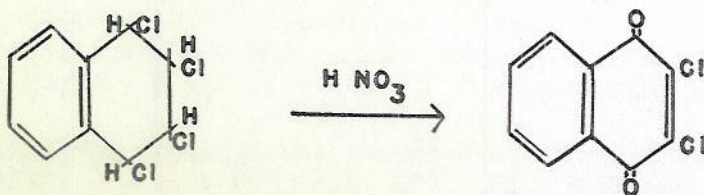
CHEMICAL REACTIONS

(3) Butyrolin

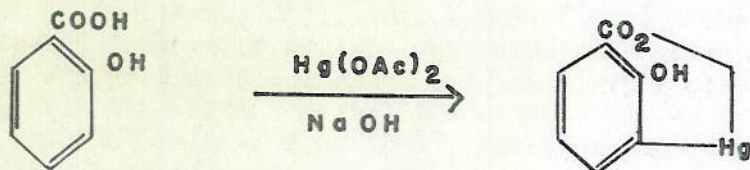


19. MISCELLANEOUS COMPOUNDS

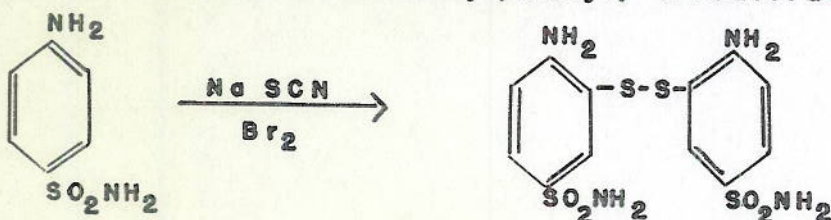
(1) 2,3-Dichloro-1,4-naphthoquinone



(2) Mercuric salicylate



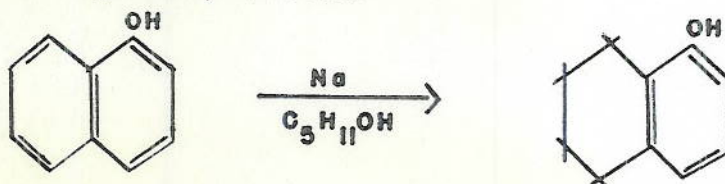
(3) Bis(2-amino-5-sulfamylphenyl) disulfide



(4) Benzaldehyde



(5) 5-Hydroxytetralin



RECOMMENDATIONS

23. The following recommendation is made:

(a) That efforts to discover persistent, effective and non-deleterious fungicides continue.

ACKNOWLEDGMENTS

24. Grateful acknowledgment is made of the services of Lt.(j.g.) Dorothy Molnar, USNR, who performed most of the analyses, and of Mr. Irving Eggert, who drew the plates for this report.