

# **SYNTHESIS OF COMMERCIAL HERBICIDES**

**parts I-II**

*Joseph V. Urenovitch*

*Dale D. Dixon*



SYNTHESIS OF COMMERCIAL HERBICIDES

by: Joseph Urenovitch

and

Dale Dixon

Copyright © 1971, by the authors.

All rights reserved

This second section lists the methods of preparation  
and lists detailed synthesis procedures which can be used to prepare the  
compounds in each chemical class. In cases where the class is large and

experimental conditions are varied, "NOTICE" alternative procedures are supplied. The

Nothing contained in this MANUSCRIPT shall be construed to constitute a permission or recommendation to practice any invention covered by any patent without license from the patent

owners. Further, the authors do not assume any

liability with respect to the use of, or for

damages resulting from the use of, any information,

apparatus, method or process described in this

MANUSCRIPT.

activity, however, manufacturing information should also prove valuable to engineering, patent and commercial development personnel.

PREFACE

The purpose of this book is to outline and discuss the chemical methods of synthesis of commercial herbicides.

The commercial herbicides are arranged according to chemical classes, and each class is treated as an individual chapter. Every chapter begins with a table which lists the product and chemical name, chemical structure, physical properties, pertinent patents with dates of issuance, and major herbicidal uses of each compound.

The second section of each chapter describes the methods of preparation and lists detailed synthesis procedures which can be used to prepare the compounds in each chemical class. In cases where the class is large and experimental conditions overlap, representative procedures are supplied. The third section of each chapter lists the literature references from which the material in each chapter is extracted.

Since this work is devoted primarily to methods of synthesis, there is no detailed discussion of biological activity.

This book should find extensive use in industrial, governmental and university environments. It should be a valuable source for quickly locating experimental conditions for preparing commercial herbicides and related compounds. In addition it should allow chemists and biologists to quickly survey synthesis work carried out in each chemical class of herbicides. The carefully prepared tables should be useful in observing trends, detecting areas which need further investigation and in preparing new herbicidally active compounds by extending or combining structures of known herbicidal activity. The patent and manufacturing information should also prove valuable to engineering, patent and commercial development personnel.

DR. JOSEPH V. URENOVITCH

Ph.D. Inorganic Chemistry, University of Pennsylvania (A. G. MacDiarmid) 1963.

Postdoctoral Research, Organometallic Chemistry, University of Wisconsin (R. A. West) 1964.

Research Chemist, Olin Mathieson Chemical Corporation; January 1964 - June 1965. Basic research on hydrazine chemistry and carborane chemistry.

Senior Research Chemist, Group Leader and Section Manager, Organic Synthesis Section, Agricultural Chemicals Department; Air Products and Chemicals, Inc. July 1965 - December 1969. Synthesis and development of new biologically active compounds for use as herbicides, insecticides and fungicides.

Has authored six papers in organometallic and inorganic chemistry and five patents dealing with herbicides, insecticides and fungicides.

DR. DALE DIXON

Ph.D. Organic Chemistry, Oregon State University (F. T. Bond) 1968.

Research Chemistry, Organic Synthesis Section, Agricultural Chemicals Department; Air Products and Chemicals, Inc. May 1968 - December 1969. Synthesis and development of new biologically active compounds for use as herbicides, insecticides and fungicides.

Areas of synthetic experience include modification of natural products, preparation of trifluoromethyl heterocyclics and strained ring compounds, studies of reactivities such as methylene generators, imidoyl halides and nitrile oxides, direct fluorination of organics.

Authored two publications in organic chemistry and six patents dealing with pesticides, polymers and fluorochemicals.

## TABLE OF CONTENTS

### Chapter I - UREA HERBICIDES

|                               |                 |     |
|-------------------------------|-----------------|-----|
| I. Listing of Urea Herbicides | A. Effusent     | 100 |
| II. Methods of Preparation    | B. Berips       | 16  |
| A. Chloroxuron                | C. Triadfon     | 16  |
| B. Fenuron TCA                | D. Silvex       | 16  |
| C. Buturon                    | E. HEDQ         | 17  |
| D. Linuron                    | F. Hepbas       | 18  |
| E. Tandex                     | G. Deltatol     | 19  |
| F. Norea                      | H. Triodostepes | 20  |
| G. DCU                        | I. Mefusin      | 22  |
| H. Bromacil                   | J. Teliferbeeze | 23  |
| I. Trimeturon                 | K. Trifluralin  | 26  |
| III. References               |                 | 32  |

### Chapter II - PHENOXY HERBICIDES

|   |                                       |    |
|---|---------------------------------------|----|
| I. Listing of Phenoxy Herbicides                                | A. S-4-Diethyl-o- <i>p</i> -Allylisom | 39 |
| II. Preparation of Phenoxyacetic and 2-(Phenoxy) Proponic Acids | B. 2-(Phenoxy)ethanol                 | 39 |
| III. Preparation of 4-(Phenoxy)Butyric Acids                    | C. 4-(Phenoxy)butyric acid            | 46 |
| IV. Preparation of Esters of the Phenoxycarboxylic Acids        | D. 2-(Phenoxy)ethoxyacetic acid       | 49 |
| V. Preparation of Amine Salts of the Phenoxycarboxylic Acids    | E. 2-(Phenoxy)ethoxyproponic acid     | 51 |
| VI. Preparation of Amide Derivatives of Phenoxycarboxylic Acids | F. 2-(Phenoxy)ethoxypropanoic acid    | 52 |
| VII. Preparation of 2-(Phenoxy)Ethanol Derivatives              | G. 2-(Phenoxy)ethoxybenzoic acid      | 55 |
| VIII. References  | H. Trifluralin and Benofin            | 58 |

~~CONTENTS~~

Chapter III - CARBAMATE AND THIOCARBAMATE HERBICIDES

|   |    |
|---|----|
| I. Listing of Carbamate and Thiocarbamate Herbicides    | 64 |
| II. Methods of Preparation of Carbamate Herbicides      | 64 |
| A. Betanal  | 64 |
| B. Barban   | 66 |
| C. Terbutol   | 66 |
| D. Sirmate  | 67 |
| III. Methods of Preparation of Thiocarbamate Herbicides | 68 |
| A. EPTC   | 68 |
| B. Pebulate   | 70 |
| C. Diallate   | 70 |
| D. Thionocarbamate                                      | 71 |
| E. Metham   | 73 |
| IV. References  | 75 |

Chapter IV - s-TRIAZINE HERBICIDES

|   |    |
|---|----|
| I. Listing of s-Triazine Herbicides                                     | 81 |
| II. Methods of Preparation  | 81 |
| A. 2,4-Dichloro-6-Alkylamino-s-Triazines                                | 82 |
| B. Symmetrically Substituted 2-Chloro-4,6-Bis(Alkylamino)-s-Triazines   | 83 |
| C. Assymmetrically Substituted 2-Chloro-4,6-Bis(alkylamino)-s-Triazines | 84 |
| D. 2-Alkoxy-4,6-Bis(Alkylamino)-s-Triazines                             | 85 |
| E. 2-Alkylthio-4,6-Bis(Alkylamino)-s-Triazines                          | 89 |
| III. References   | 94 |

| Chapter V - ORGANIC ACID AND ESTER HERBICIDES   |                                     |
|---|-------------------------------------|
| I. Listing of Organic Acid and Ester Herbicides |                                     |
| 100   | A. 2,3,6-TBA                        |
| 100   | B. Benweil D                        |
| 102   | C. Dinoben                          |
| 104   | D. Amitroben                        |
| 105   | E. Picloram                         |
| 106   | F. Napthalene Acetic Acid           |
| 109   | G. Benazolin                        |
| 111   | H. Endothell                        |
| 114   | I. Amitroben and IT-3456            |
| 115   | J. Dechal                           |
| 116   | K. Glenbar                          |
| 117   | L. OCS-21693                        |
| 119   | M. ECT                              |
| 120   | N. Nepetalam                        |
| 125   | O. Alax-85                          |
| 125   | P. Mendok                           |
| 125   | Q. S-04 H9 Jadua - 2g/l/kg A. N. K. |
| 125   | R. Xtra                             |
| 125   | S. Blimexidol                       |
| 125   | T. Amidoon                          |
| 125   | U. GAD                              |
| 125   | V. Saponin                          |
| 125   | W. Saponin                          |
| 125   | X. Saponin                          |
| 125   | Y. Saponin                          |
| 125   | Z. Saponin                          |
| II. Methods of Preparation                      |                                     |
| 100   | A. Trifluralin and Benefin          |
| 125   | B. Blimexidol                       |
| 125   | C. Lignoxol                         |
| 125   | D. Amitroben                        |
| 125   | E. Saponin                          |
| 125   | F. Napthalene Acetic Acid           |
| 125   | G. Blimexidol                       |
| 125   | H. Saponin                          |
| 125   | I. Saponin                          |
| 125   | J. Saponin                          |
| 125   | K. Saponin                          |
| 125   | L. Saponin                          |
| 125   | M. Saponin                          |
| 125   | N. Saponin                          |
| 125   | O. Saponin                          |
| 125   | P. Saponin                          |
| 125   | Q. Saponin                          |
| 125   | R. Saponin                          |
| 125   | S. Saponin                          |
| 125   | T. Saponin                          |
| 125   | U. Saponin                          |
| 125   | V. Saponin                          |
| 125   | W. Saponin                          |
| 125   | X. Saponin                          |
| 125   | Y. Saponin                          |
| 125   | Z. Saponin                          |
| III. References                                 |                                     |
| 125   | A. Amitroben and IT-3456            |
| 125   | B. Blimexidol                       |
| 125   | C. Lignoxol                         |
| 125   | D. Amitroben                        |
| 125   | E. Picloram                         |
| 125   | F. Napthalene Acetic Acid           |
| 125   | G. Blimexidol                       |
| 125   | H. Saponin                          |
| 125   | I. Saponin                          |
| 125   | J. Saponin                          |
| 125   | K. Saponin                          |
| 125   | L. Saponin                          |
| 125   | M. Saponin                          |
| 125   | N. Saponin                          |
| 125   | O. Saponin                          |
| 125   | P. Saponin                          |
| 125   | Q. Saponin                          |
| 125   | R. Saponin                          |
| 125   | S. Saponin                          |
| 125   | T. Saponin                          |
| 125   | U. Saponin                          |
| 125   | V. Saponin                          |
| 125   | W. Saponin                          |
| 125   | X. Saponin                          |
| 125   | Y. Saponin                          |
| 125   | Z. Saponin                          |
| Chapter VI - DINITRONANILINE HERBICIDES         |                                     |
| 125   | A. Amitroben and IT-3456            |
| 125   | B. Blimexidol                       |
| 125   | C. Lignoxol                         |
| 125   | D. Amitroben                        |
| 125   | E. Picloram                         |
| 125   | F. Napthalene Acetic Acid           |
| 125   | G. Blimexidol                       |
| 125   | H. Saponin                          |
| 125   | I. Saponin                          |
| 125   | J. Saponin                          |
| 125   | K. Saponin                          |
| 125   | L. Saponin                          |
| 125   | M. Saponin                          |
| 125   | N. Saponin                          |
| 125   | O. Saponin                          |
| 125   | P. Saponin                          |
| 125   | Q. Saponin                          |
| 125   | R. Saponin                          |
| 125   | S. Saponin                          |
| 125   | T. Saponin                          |
| 125   | U. Saponin                          |
| 125   | V. Saponin                          |
| 125   | W. Saponin                          |
| 125   | X. Saponin                          |
| 125   | Y. Saponin                          |
| 125   | Z. Saponin                          |

|   |     |
|---|-----|
| <u>Chapter III - ORGANIC ACID AND SALT HERBICIDES</u> |     |
| B. Nitralin   | 130 |
| C. Dipropalin   | 133 |
| D. Risalin  | 136 |
| III. References                                       | 140 |
| <u>Chapter VII - AMIDE HERBICIDES</u>                 |     |
| I. Listing of Amide Herbicides                        | 144 |
| II. Methods of Preparation                            | 144 |
| A. Propanil   | 144 |
| B. Cypromid   | 145 |
| C. Solan  | 145 |
| D. Dicryl   | 146 |
| E. Lasso  | 148 |
| F. Ramrod   | 149 |
| G. CDAA   | 150 |
| H. Rootone  | 151 |
| I. Diphenamid   | 154 |
| J. Prefix   | 155 |
| K. N. V. Philips - Duphar PH 40-25                    | 158 |
| III. References                                       | 159 |

#### Chapter VIII - NITRILE HERBICIDES

|                                  |     |
|----------------------------------|-----|
| I. Listing of Nitrile Herbicides | 162 |
| II. Methods of Preparation       | 162 |
| A. Diphenatrile                  | 162 |
| B. Dichlobenil                   | 165 |
| C. Bromoxynil and Ioxynil        | 167 |

|  |            |
|--|------------|
| <b>III. References</b>                                   | <b>172</b> |
| <b>Chapter IX - QUATERNARY AMMONIUM SALT HERBICIDES</b>  |            |
| <b>I. Listing of Quaternary Ammonium Salt Herbicides</b> | <b>174</b> |
| <b>II. Methods of Preparation</b>                        | <b>174</b> |
| A. Paraquat  | 174        |
| B. Diquat  | 175        |
| C. Chlormequat   | 176        |
| D. Penar   | 177        |
| <b>III. References</b>                                   | <b>178</b> |
| <b>Chapter X - HETEROCYCLIC HERBICIDES</b>               |            |
| <b>I. Listing of Heterocyclic Herbicides</b>             | <b>181</b> |
| <b>II. Methods of Preparation</b>                        | <b>181</b> |
| A. Amitrole  | 181        |
| B. BH-584  | 182        |
| C. Pyrichlor   | 182        |
| D. Maleic Hydrozide                                      | 186        |
| E. Pyrazon   | 187        |
| F. Dazomet   | 188        |
| G. PH 40-21  | 188        |
| <b>III. References</b>                                   | <b>190</b> |

**Chapter XI - AROMATIC ETHER HERBICIDES**

|  |            |
|--|------------|
| <b>I. Listing of Aromatic Ether Herbicides</b> | <b>192</b> |
| <b>II. Methods of Preparation</b>              | <b>192</b> |

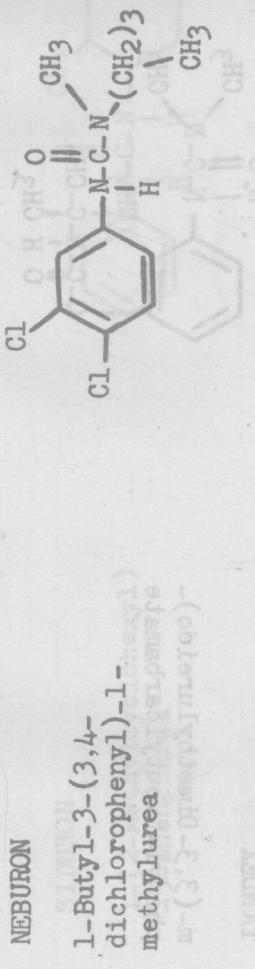
|   |  |            |
|---|--|------------|
| <b>III.</b>   | <b>References</b>  | <b>193</b> |
| A.  | Nitrofen   | 192        |
| B.  | Preforan   | 193        |
| <b>III.</b>   | <b>References</b>  | <b>193</b> |
| <b>Chapter XII - PHENOL AND PHENOL DERIVATIVE HERBICIDES</b>    |  |            |
| <b>I.</b>   | <b>Listing of Phenol and Phenol Derivative Herbicides</b>    | <b>196</b> |
| <b>II.</b>  | <b>Methods of Preparation</b>                                | <b>196</b> |
| A.  | 4,6-Dinitro-o-Alkylphenols                                   | 196        |
| B.  | Tribonate  | 198        |
| C.  | Pentachlorophenol  | 200        |
| <b>III.</b>   | <b>References</b>  | <b>206</b> |
| <b>Chapter XIII - ORGANOPHOSPHORUS HERBICIDES</b>               |  |            |
| <b>I.</b>   | <b>Listing of Organophosphorus Herbicides</b>                | <b>209</b> |
| <b>II.</b>  | <b>Methods of Preparation</b>                                | <b>209</b> |
| A.  | Folex  | 209        |
| B.  | DEF  | 212        |
| C.  | NIA 10637  | 219        |
| D.  | Betasan  | 220        |
| E.  | Phosphon   | 221        |
| F.  | Zytron   | 222        |
| <b>III.</b>   | <b>References</b>  | <b>224</b> |
| <b>Chapter XIV - ORGANOARSENIC AND ORGANOMERCURY HERBICIDES</b> |  |            |
| <b>I.</b>   | <b>Listing of Organoarsenic and Organomercury Herbicides</b> | <b>227</b> |
| <b>II.</b>  | <b>Methods of Preparation</b>                                | <b>227</b> |
| O.  | Bromoxynil and Ioxynil                                       | 227        |

|  |                       |     |
|--|-----------------------|-----|
| <b>A.</b>  | <b>DSMA</b>           | 227 |
| <b>B.</b>  | <b>CMA</b>            | 232 |
| <b>C.</b>  | <b>CPA</b>            | 237 |
| <b>D.</b>  | <b>Cacodylic Acid</b> | 238 |
| <b>E.</b>  | <b>PMA and PMP</b>    | 241 |
| <b>III. References</b>                                   |                       | 242 |
| <br><u>Chapter XV - MISCELLANEOUS ORGANIC HERBICIDES</u> |                       |     |
| <b>I. Listing of Miscellaneous Organic Herbicides</b>    |                       | 245 |
| <b>II. Methods of Preparation</b>                        |                       | 245 |
| <b>A.</b>  | <b>Sindone</b>        | 245 |
| <b>B.</b>  | <b>Tritac</b>         | 247 |
| <b>C.</b>  | <b>TCBC</b>           | 248 |
| <b>D.</b>  | <b>Sulfasan</b>       | 249 |
| <b>III. References</b>                                   |                       | 250 |
| <br><u>Chapter XVI - INORGANIC HERBICIDES</u>            |                       |     |
|  |                       | 251 |

TABLE I

| PRODUCT NAME | CHEMICAL NAME  | CHEMICAL STRUCTURE | PHYSICAL PROPERTIES | U.S. PATENTS     | HERBICIDAL USES                                    |
|--------------|--|--------------------|---------------------|------------------|--|
| FENURON      | 3-Phenyl-1,1-dimethylurea                            |                    | m.p. 133-134°       | 2,655,447 (1953) | Brush control                                      |
| FENURON TCA  | 3-(p-Chlorophenyl)-1,1-dimethylurea trichloroacetate |                    | m.p. 65-68°         | 2,782,112 (1957) | Brush control and temporary soil sterilization     |
| MONURON      | 3-(p-Chlorophenyl)-1,1-dimethylurea trichloroacetate |                    | m.p. 174-175°       | 2,655,445 (1953) | Pre-emergence control of broadleaf and grass weeds |
| DIURON       | 3-(3,4-Dichlorophenyl)-1,1-dimethylurea              |                    | m.p. 78-81°         | 2,782,112 (1957) | Soil sterilization                                 |

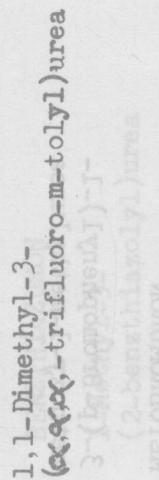
## NEBURON



m.p. 102-103°

2,655,447  
(1953)Pre-emergence control  
of broadleaf and  
grass weedsGORTON, J. T., J. R.  
3,3'-Dichloro-1-methoxy-  
1,1-dimethylurea

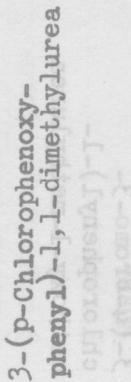
## FLUOMETURON



m.p. 163-164°

Brit.  
94,779  
(1963)Pre-emergence control  
of broadleaf and  
grass weedsGORTON, J. T., J. R.  
3,3'-Dichloro-1-methoxy-  
1,1-dimethylurea

## CHLOROXON



m.p. 151-152°

3,060,235  
(1962)Pre-emergence control  
of broadleaf and  
grass weedsGORTON, J. T., J. R.  
3,3'-Dichloro-1-methoxy-  
1,1-dimethylurea

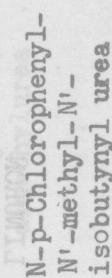
## PROBAN



m.p. 84-85°

2,867,520  
(1959)Pre-emergence selective  
control of weeds in  
cereal cropsGORTON, J. T., J. R.  
3,3'-Dichloro-1-methoxy-  
1,1-dimethylurea

## BUTURON



m.p. 148-149°

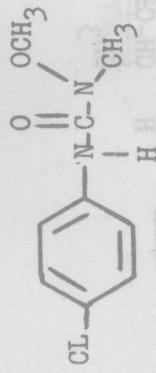
3,149,955  
(1964)Pre-emergence selective  
control of weeds in  
cereal cropsGORTON, J. T., J. R.  
3,3'-Dichloro-1-methoxy-  
1,1-dimethylurea

## KOMATUMON

m.p. 83-85°

(J. D. Q.)  
S. D. Q. 231Emulsion of propanil  
bis-emulsion control

MONOLINURON

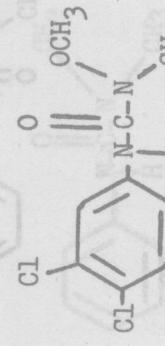


3-(*p*-Chlorophenyl)-1-methoxy-1-methylurea

m.p. 83-84°

2,960,534  
(1960)

Pre-emergence control  
of broadleaf and  
grass weeds



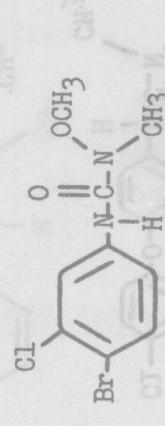
3-(3,4-Dichlorophenyl)-  
1-methoxy-1-methylurea

m.p. 93-94°

2,960,534  
(1960)

Pre-and Post-  
emergence control of  
broadleaf and grass  
weeds

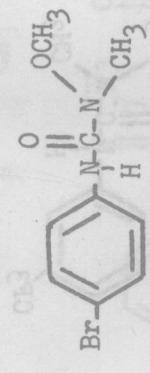
MALORAN



m.p. 94-96°

SWISS  
405,821  
(1966)

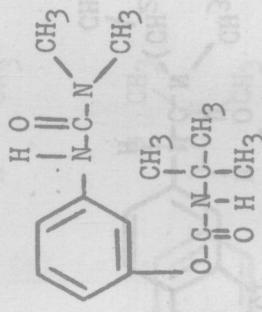
Pre-emergence control  
of broadleaf and  
grass weeds



m.p. 95-96°

2,793,224  
(1955)

Pre-emergence control  
of broadleaf and  
grass weeds  
of pre-planting soil  
pre-emergence control

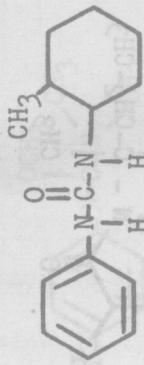


TANDEX

*m*-(3,3-Dimethylureido)-  
phenyl-t-butylcarbamate  
3,434,822  
(1969)

Soil sterilization

grass weeds  
or pre-planting soil  
pre-emergence control



SIDURON  
1-(2-Methylcyclohexyl)  
-3-phenylurea

### Pre-emergence control of grass weeds

3,309,192  
(1967)

M.P.133-138°

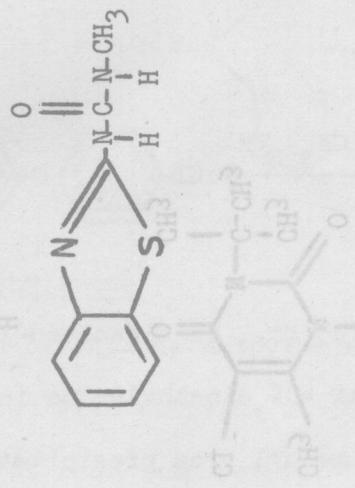
BENZTHIAZUON

### 1-Methyl-3-(2-benzthiazolyl)urea

Pre-emergence  
selective control  
of weeds in corn,  
beets and cotton

Brit.  
1,004,469  
(1965)

III. P. 265°



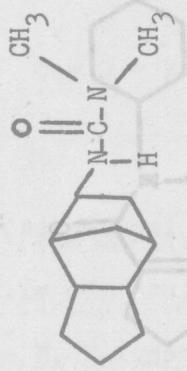
NOREA

3-(Hexahydro-4,7-methanoindan-5-yl)-1,1-dimethylurea

Pre-emergence  
control of broadleaf  
and grass weeds

3,150,179  
(1964)

172°

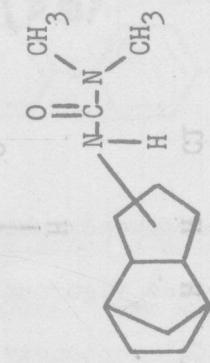


H-210  
N-[or 2-(4,5,6,7,8,9-hexahydro-4,7-methanoindanyl)]-N'-dimethylurea

Pre-emergence control  
of broadleaf and  
grass weeds

Ger.  
1,200,062  
(1965)

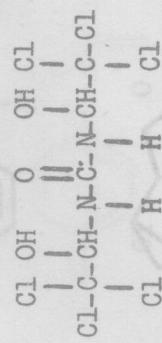
m.p. 154-156°



**MONOCOT**

DCU

1,3-Bis(1-hydroxy-2,2-dichloroethyl)urea



(Semicarbazide  
penta(chloro-1-methylurea))<sub>2</sub>

1-(5-Chloro-2-methyl-5-oxo-1-phenyl-1,3-dihydro-1H-pyrazole-4-yl)-1-methylurea

LENACIL

3-Cyclohexyl-6,7-dihydro-1H-cyclopentapyrimidine-2,4-(3H,5H)-dione

(5-Chloro-1-methyl-5-oxo-1-phenyl-1,3-dihydro-1H-pyrazole-4-yl)-1-methylurea

TERBACIL

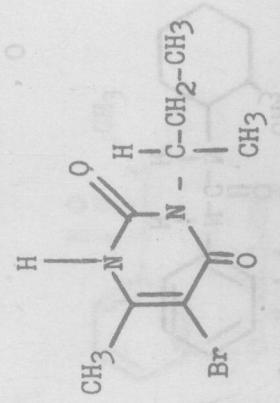
3-t-Butyl-5-chloro-6-methyluracil

METOBROMON

(5-Persulfato-2,4-dimethyl-3,4-dihydro-1H-pyrazole-1,3-dione)

BROMACIL

5-Bromo-3-sec-butyl-6-methyluracil



m.p. 200°

2,619,416  
(1952)

Pre-emergence control  
of grasses and broadleaf weeds

Sugarcane  
or paddytest 92%

He-susReuse couple  
Pre and Post-

m.p.  
315.5-316.5°

Brit.  
968,662  
(1964)

Selective control  
of weeds in  
sugarbeets

Pre-emergence control  
of broadleaf weeds

Selective control  
of weeds in various  
fruit

3,235,357  
(1966)

Pre-emergence control  
of grasses and  
control of postemergence  
herbicides on various  
grasses weeds

m.p.  
175-177°

3,235,357  
(1966)

Selective control  
of weeds in various  
fruits

Pre-emergence  
couple of sugar  
beneReuse

m.p.  
2,730,390  
(1966)

Pre-emergence  
couple of sugar  
beneReuse

3,235,357  
(1966)

Soil sterilization

m.p.  
3,300,385  
(1966)

Pre-emergence  
couple of sugar  
beneReuse

General plant  
growth control

b.p. 155-160°  
at 14mm  
Brit. 904, 706  
3, 280, 190  
(1966)

TRIMETURON

N-(*p*-Chlorophenyl)-  
N,N-dimethyl-  
O-methylisourea