# Synthesis and Herbicidal Activity of Small-Ring Compounds

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A series of cycloaliphatic carboxamides was prepared and screened for herbicidal activity. Specific structural requirements for activity were determined. In general, the cyclopropanecarboxamides were more active than the larger ring homologs. One material, N-(3,4-dichlorophenyl)-cyclopropanecarboxamide (cypromid), has been successfully field tested and introduced for commercial use as a selective postemergence herbicide in corn.

The discovery of the postemergence herbicidal activity of several cyclopropanecarboxamides resulted in the initiation of a synthesis and screening program of a broad spectrum of cyclopropane- and other cycloaliphatic carboxamides. Approximately 130 compounds were prepared and evaluated as post- and pre-emergence herbicides. This series enabled certain generalizations to be made for correlation of structure with herbicidal activity. Two compounds, N-(3,4-dichlorophenyl)-cyclopropanecarboxamide (A) and N-(3,4-dichloro-phenyl)-1-methylcyclopropanecarboxamide (B), have been selected for further development and possible commercialization.


(A)   (B)
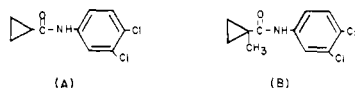
Compound A, which has been given the trivial name cypromid (Clobber), has been introduced as a selective postemergence herbicide in corn. The field development and results have been reported recently (6).
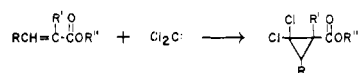
Synthesis of Compounds

Several general routes were utilized for the synthesis of the required intermediate acids and esters. The procedures employed included the following:
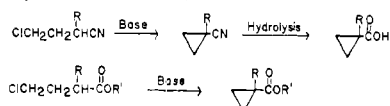
Method A. The addition of diazo compounds (diazomethane, ethyl diazoacetate, etc.) to olefins or α-olefinic esters (3)
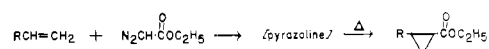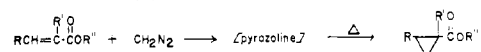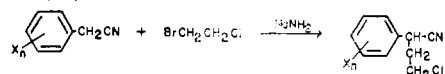

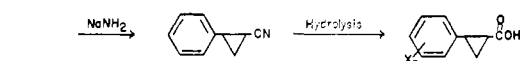**Method B.** Addition of halocarbenes to α-olefinic esters (18).

Method C. Base-induced cyclization of γ-halonitriles or γ-haloesters (16).

Method D. Alkylation of benzyl cyanides with dihaloalkanes followed by cyclization and hydrolysis to the acids (10).

Method E. Cleavage of α-substituted butyrolactones with hydrogen chloride to produce γ-chlorobutyric acids which were esterified with methanol, then cyclized with base to the desired esters (4)
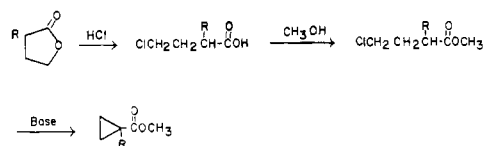
Method F. Base-catalyzed alkylation of monoalkyl-malonic esters with ethylene oxide to produce α-substituted butyrolactones which were then treated as in Method E to give the desired esters.
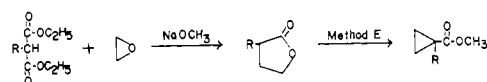
Method G. Alkylation of malonic ester with dihaloalkanes followed by cyclization, hydrolysis, and decarboxylation to the mono acid (15).
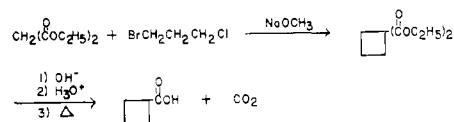
The acids or esters were then converted to the amides or anilides by one of the following methods:

Method X. Reaction of the desired amine or aniline with an acid chloride in the presence of a halogen acid acceptor.

$$RCOCl + R'NH_2 \xrightarrow{\text{Base}} R{-}\underset{\underset{O}{\|}}{C}{-}NHR'$$
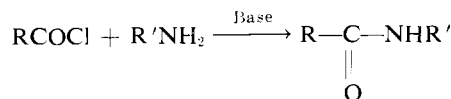
Method Y. Reaction of an acid with an aromatic phosphazo compound.
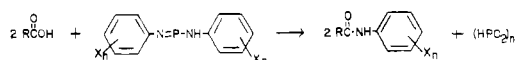
Method Z. Reaction of an ester with the desired aniline and an equivalent of sodium alkoxide (5).
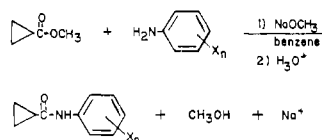
Structures of previously unreported compounds were verified by quantitative elemental determination of three or more elements (accuracy within ±0.3%) and by infrared spectroscopy.

Biological Screening Methods

Postemergence tests were run at a rate of 5 pounds per acre. Seeds were sown in 4-inch clay pots containing a 1:1:1 fertilized mixture of clay loam, peat, and sand. The plants were sprayed 1 week after emergence. The chemical was applied as an emulsion or dispersion in an emulsifier–xylene mixture with water at 60 gallons per acre spray volume and 40 p.s.i. The treated plants were placed in the greenhouse at 85° F. day and 75° F. night temperatures. Plants treated were tomato, alfalfa, wheat, flax, radish, oats, sugar beets, corn, and millet. Ratings were taken 2 weeks after treatment.

Pre-emergence tests were run at a rate of 10 pounds per acre. Flats (10 × 12 × 2.5 inches) were filled with alluvial soil and seeded, and the seeds covered with 0.5 inch of soil. The chemical was dissolved in acetone and sprinkled evenly over the surface. The acetone was allowed to evaporate and the flat was watered thoroughly. The flat was seeded with alfalfa, brome, flax, oats, radish, and sugar beets, then placed in the greenhouse and held at 60° F. night and 70° F. day temperatures. Another flat, treated as described and seeded with corn, coxcomb, cotton, crabgrass, millet, and soybeans, was held at 80° F. day and 70° F. night temperatures. The test was evaluated after 28 days.

Ratings were made on a 0 to 4 basis for each plant species as follows: 0, no effect; 1, 0 to 25% foliage affected; 2, 26 to 75% foliage affected; 3, 76 to 99% foliage affected; and 4, all plants dead.

Total herbicidal activity is recorded in Tables I to IX. This represents a summation of the injury to all the plant species treated. Thus, a chemical which received a rating of 4 on each of the 9 species of plants in the postemergence screen would have a rating of 36. Likewise, a chemical which resulted in total kill in the pre-emergence screen would have a rating of 48 (rating of 4 on each of 12 plant species). In some instances a chemical was screened on less than the usual number of plant species. The activity rating for these materials is represented by the fraction, summation of injury to species treated/4× number of species treated. This method of expressing activity rating is an indication of total activity only and not selectivity.

Results and Discussion

Amides of cyclopropanecarboxylic acids appeared to have the greatest potential as useful herbicides, and a major portion of the research effort was directed toward the synthesis and screening of these materials. The synthesis and screening data for the cyclopropanecarboxamides are compiled in Tables I through V. A study of the biological data indicates that many of the N-aromatic cyclopropanecarboxamides (Tables I and II) possess a high degree of herbicidal activity and in general they are more active than N-aliphatic cyclopropanecarboxamides (Table III). Herbicidal activity appears to be enhanced when the aromatic ring of the anilides is substituted either in the meta or para position or in both positions by halogen, methyl, or trifluoromethyl groups. Substitution in the ortho position by chlorine, bromine, or methyl groups, however, seems to reduce herbicidal activity (particularly postemergence). The N-(3,4-dichlorophenyl)amide is the most active of the series.

The presence of a substituent and the position of the substituent on the cyclopropyl ring also affect herbicidal activity as shown in Table IV. This effect is more clearly illustrated in Table V, in which the 3,4-dichloroanilides of a series of substituted cyclopropanecarboxylic acids are compared. In general, large bulky groups in any position on the cyclopropyl ring drastically reduce herbicidal activity. Activity is greatest when the cyclopropyl ring is unsubstituted or is substituted in the α-position with a relatively small group such as methyl.

The cyclopropanecarboxamides which have outstanding pre-emergence and postemergence activity are summarized in Tables VI and VII, respectively.

Increasing the alicyclic ring to four carbon atoms results in a general decrease in herbicidal activity, shown in the series of cyclobutanecarboxamides listed in Table VIII. A further increase of the ring to five or six carbon atoms causes an even greater decrease in activity. The effect of alicyclic ring size upon herbicidal activity is depicted in Table IX.

The cyclopropanecarboxanilides were shown to inhibit photochemical activity (Hill reaction) of isolated chloroplasts. The Hill reaction involves the ability of plants to oxidize water to molecular oxygen and to

Table I. Herbicidal Activity of Aromatic Cyclopropanecarboxamides

$$\triangleright\text{-}\overset{O}{\underset{}{C}}\text{-N}\overset{R_1}{\underset{R_2}{}}$$

R_1	R_2	M.P., ° C.	Yield, %	Method of Preparation	Post-emergence Activity	Pre-emergence Activity
H	1-Naphthyl	174–5.5	45	E, X	0	16
H	2-Thiazolyl	164–6	24	E, X	21	44
H	2-Pyridyl	86–7.5	19	E, X	15	14
H	2-Pyrimidyl	130–1.5	29	E, X	1	18
CH₃	Phenyl	69–70	91	E, X	18	..
CH₂CH=CH₂	Phenyl	120–3/5 mm.ᵃ	77	E, X	4	35

ᵃ B.p. ° C./mm. Hg.

Table II. Herbicidal Activity of Cyclopropanecarboxanilides
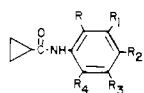
R	R$_1$	R$_2$	R$_3$	R$_4$	M.P., °C.	Yield, %	Method of Preparation	Σ Post-emergence Activity	Σ Pre-emergence Activity
Cl	H	H	H	H	110–11	93	E, X	0	39
F	H	H	H	H	116.5–18	76	E, X	19	...
H	Cl	H	H	H	147–8.5	74	E, X	33	42
H	Br	H	H	H	142–4	93	E, X	27	42
H	F	H	H	H	124–6	84	E, X	34	41
H	I	H	H	H	132–4	82	E, X	20	32
H	H	Cl	H	H	163–5	94	E, X	35	44
H	H	Br	H	H	192–4	96	E, X	21	41
H	H	F	H	H	160–2	93	E, X	26	17
Cl	Cl	H	H	H	137–8	57	E, X	8	21
Cl	H	Cl	H	H	155–6	83	E, X	4	21
Cl	H	H	Cl	H	163–4	82	E, X	5	18
H	Cl	H	Cl	H	172–4	94	E, X	10	8
H	Cl	Cl	H	H	130–1	90	E, Z	36	44
H	Br	Br	H	H	126–8	90	E, X	30/32*	30
F	H	F	H	H	142–3.5	90	E, X	4	6
F	H	H	F	H	103–4	80	E, X	24	25
Cl	H	Cl	H	Cl	210–11	94	E, X	0	4
Cl	H	Cl	Cl	H	170–2	95	E, X	3	18
CH$_3$	H	H	H	H	128.5–30	82	E, X	5	10
H	CH$_3$	H	H	H	100–101	79	E, X	29	15/44
H	H	CH$_3$	H	H	165–6.5	87	E, X (2)	10	11
H	CH$_3$	CH$_3$	H	H	137–9	80	E, X	21	10
H	CH$_3$	H	CH$_3$	H	138–40	80	E, X	1	26
CH$_3$	H	CH$_3$	H	CH$_3$	160.5–2	69	E, X	0	16
CH$_3$	H	H	Cl	H	164–5	82	E, X	0	15
CH$_3$	Cl	H	H	H	175–6	80	E, X	0	5
Cl	H	H	CH$_3$	H	138–9	53	E, X	0	16
CH$_3$	H	H	NO$_2$	H	202–3.5	68	E, X	3	5
Cl	H	NO$_2$	H	H	180–2	45	E, X	1	12
Cl	CF$_3$	H	H	H	117.5–9	67	E, X	0	22
H	CF$_3$	Cl	H	H	121–3	82	E, X	31	30
H	CF$_3$	H	H	H	121–2.5	74	E, X	20	31
H	CH$_3$	Cl	H	H	152–4	95	E, X	27/32	25
H	Cl	CH$_3$	H	H	144–5	82	E, X	29	30
H	CH$_3$O	CH$_3$O	H	H	137–8	47	E, X	10	4
CH$_3$O	H	H	Cl	H	97–9	80	E, X	14	14
H	CH$_3$O	H	H	H	105–6	37	E, X	19	42
H	CH$_3$CONH	H	H	H	181–3	56	A, X	4	0
H	Cyclopropane-carbonyloxy	H	H	H	160–1.5	86	A, X	3	9
H	H	Cyclopropane-carbonylamino	H	H	299–301	66	A, X	3	6
H	H	NO$_2$	H	H	180–2	76	A, X	5	38
H	H	CN	H	H	140–1	89	A, X	18	40
H	H	OH	H	H	208–10	46	A, X	2	0
H	H	C$_2$H$_5$OCO	H	H	161–2.5	90	A, X	2	0
CH$_3$O	H	H	NO$_2$	H	192–4	50	A, X	0	21
CH$_3$	H	Cl	Cl	H	182–3	92	A, X	0	3
CH$_3$	H	CH$_3$	CH$_3$	H	166–7.5	50	A, X	0	0

Table III. Herbicidal Activity of Aliphatic Cyclopropanecarboxamides

R_1	R_2	M.P., ° C.	Yield, %	Method of Preparation	Post-emergence Activity	Pre-emergence Activity
H	H	124–6	60	E, X (17)	5	15
H	CH₃	55–7	88	E, X	0	28
H	CH₂—CH=CH₂	35–6	80	E, X	2	0
H	CH₂CH₂OH	43–5	77	E, X	0	6
H	C(CH₃)₃	137–9	81	E, X	0	0
H	CH₂—C≡CCH₂Cl	78.5–80	58	E, X	14	32
H	CH₂CO₂C₂H₅	77–8	29	E, X	0	6
H	Cyclopropyl	111–2	69	E, X (8)	0	11
H	Cyclopentyl	115–6	61	E, X	4	0
H	Cyclohexyl	138–9.5	78	E, X (1)	2	7
C₄H₉	C₄H₉	104–7/5 mm.ᵃ	74	E, X	9	11
—CH₂—CH₂—O—CH₂—CH₂—		42–3	77	E, X	2	15

ᵃ B.p. ° C./mm. Hg.

Table IV. Herbicidal Activity of Cyclopropanecarboxamides Containing Substituents on the Cyclopropyl Ring

R_1	R_2	R_3	R	M.P., ° C.	Yield, %	Method of Preparation	Σ Post-emergence Activity	Σ Pre-emergence Activity
CH₃	H	H	2,6-Dimethylphenyl	128–30	70	A, X	0	21
CH₃	H	H	H	148.5–50.5	60	F, X (3)	0	0
CH₃	H	H	2,6-Dichlorophenyl	147–9	16	A, X	. . .	21
CH₃	H	H	2,5-Dimethylphenyl	84–5	68	A, X	19	47
CH₃	H	H	2-Methyl-5-chlorophenyl	74–6	27	A, Z	21	44
CH₃	H	H	3-Chlorophenyl	118–20	24	A, Z	31/32	40
CH₃	H	H	3,4-Dichlorophenyl	132–4	85	F, X	36	45
C₂H₅	H	H	3,4-Dichlorophenyl	97–8.5	71	F, X	34	17
C₂H₅	H	H	Phenyl	94–5	65	F, X	17	0
C₂H₅	H	H	3-Chlorophenyl	93–94.5	70	F, X	20	39
C₂H₅	H	H	2-Methyl-5-chlorophenyl	79–80	65	F, X	20	45
C₂H₅	H	H	2,5-Dimethylphenyl	88.5–89.5	60	F, X	21	44
C₂H₅	H	H	2-Pyridyl	94–5/2 mm.ᵃ	22	F, X	8	2
C₄H₉	H	H	Phenyl	88–89	50	F, X	3	0
C₄H₉	H	H	2,5-Dimethylphenyl	61.5–63	55	F, X	5	33
C₄H₉	H	H	3-Methylphenyl	68.5–70	60	F, X	3	0
C₄H₉	H	H	2-Methyl-5-chlorophenyl	47.5–48.5	65	F, X	3	26
C₄H₉	H	H	3-Chlorophenyl	97–8	55	F, X	0	0
C₄H₉	H	H	3,4-Dichlorophenyl	118.5–20	87	F, X	2/28	0
CH₃S	H	H	Phenyl	31–2	60	E, X	3	12
CH₃S	H	H	2-Methyl-5-chlorophenyl	86–7	58	E, X	7	4
CH₃S	H	H	2,5-Dimethylphenyl	132–4/1 mm.ᵃ	62	E, X	0	14
CH₃S	H	H	3,4-Dichlorophenyl	99–100	60	E, X	16	11
2,4-Dichlorophenoxy	H	H	Phenyl	73–5	35	E, Y	0	0
2,4-Dichlorophenoxy	H	H	3,4-Dichlorophenyl	95–6	33	E, X	0	0
CH₃O	H	H	2-Methyl-5-chlorophenyl	88–9	43	C, Z	4	40
CH₃O	H	H	2,5-Dichlorophenyl	87.5–9	66	C, Z	0	0

ᵃ B.p. ° C./mm. Hg.

Table IV. (Continued)

R₁	R₂	R₃	R	M.P., °C.	Yield, %	Method of Preparation	Σ Post-emergence Activity	Σ Pre-emergence Activity
CH₃O	H	H	3,4-Dichlorophenyl	89–91	60	C, Z	23/32	43
H	CH₃	H	2,5-Dimethylphenyl	181–2	17	A, Z	0	1
H	CN	H	3-Chlorophenyl	136–8	27	A, Z	0	0
H	CH₃	CH₃	2-Methyl-5-chloro-phenyl	132–3	90	A, X	0	0

Table V. Effect of Substituents on the Cyclopropyl Ring upon Herbicidal Activity of N-(3,4-Dichlorophenyl)cyclopropanecarboxamides


R₁	R₂	R₃	M.P., °C.	Yield, %	Method of Preparation	Σ Post-emergence Activity	Σ Pre-emergence Activity
H	H	H	130–1	90	E, Z	36	42
CH₃	H	H	132–4	85	F, X	36	45
Cl	H	H	95–6	79	E, X	26	34
CH₃O	H	H	89–91	60	C, Z	23/32	43
C₄H₉	H	H	118.5–20	87	F, X	2/28	0
Phenyl	H	H	123–5	48	A, X	0	0
C₂H₅	H	H	97–8.5	71	F, X	34	17
CH₃S	H	H	99–100	60	E, X	16	11
2,4-Dichloro-phenyl	H	H	95–6	33	E, X	0	0
H	CH₃	H	93–4	88	C, X	30	25
H	Phenyl	H	168–70	58	D, X	0	0
H	4-Pyridyl	H	241–3	29	A, Z	0	0
H	2-Pyridyl	H	145–6	17	A, Z	0	0
H	Cl	Cl	159.5–61	34	B, X	0	0
H	CH	CH₂C(CH₃)₃	155–7/1 mm.ᵃ	40	A, X	0	0

ᵃ B.p. °C. mm. Hg.

Table VI. Best Pre-emergence Compounds (Primary screen)

Structure	Activity Rating	Structure	Activity Rating
	47		44
	45		44
	45		43
	44		42
	44		42
			42
			40

assimilate carbon dioxide. Isolated chloroplasts when illuminated in the presence of certain oxidants cause reduction of the oxidant with formation of oxygen, thereby simulating photosynthesis. If ferricyanide is the oxidant, the reaction may be depicted as

$$4K_3Fe(CN)_6 + 4K^+ + 2H_2O \xrightarrow[\text{chloroplasts}]{\text{light}} 4K_4Fe(CN)_6$$

$$+ 4H^+ + O_2$$
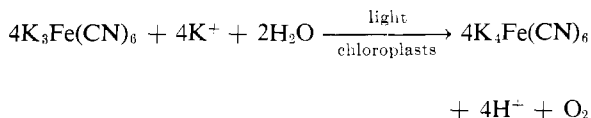
Certain types of herbicides (phenylureas, amides, phenyl carbamates, s-triazines, and nitrophenols) inhibit this reaction (7, 9, 11, 13, 14) and the degree of inhibition may be measured and expressed as the molar concentration of herbicide required to inhibit the reaction by 50% (I_{50} values).

Table X presents the data comparing the I_{50} values of cyclopropanecarboxanilides with other herbicides known to be Hill reaction inhibitors. Previously described techniques were employed (12), with the exception that the ferricyanide reduction was followed

colorimetrically. These data indicate that the cyclopropanecarboxanilides compare favorably with some of the best-known Hill reaction inhibitors.

Acknowledgment

Table VII. Best Postemergence Compounds (Primary screen)

Structure	Activity Rating
(cyclopropanecarboxanilide, CH₃, 3,4-Cl₂)	36
(cyclopropanecarboxanilide, 3,4-Cl₂)	36
(cyclopropanecarboxanilide, 4-Cl)	35
(cyclopropanecarboxanilide, CH₃, 3-Cl)	31/32
(cyclopropanecarboxanilide, 2-F)	34
(cyclopropanecarboxanilide, C₂H₅, 3,4-Cl₂)	34
(cyclopropanecarboxanilide, 3-Cl)	33
(cyclopropanecarboxanilide, 3-Cl, 4-CF₃)	31
(cyclopropanecarboxanilide, CH₃, 3,4-Cl₂)	30

Table IX. Herbicidal Activity of Anilides of Alicyclic Acids

$$R-\underset{\underset{O}{\|}}{C}-NHR'$$

R	R' = 3,4-dichlorophenyl Post	R' = 3,4-dichlorophenyl Pre	R' = 3-chlorophenyl Post	R' = 3-chlorophenyl Pre	R' = phenyl Post	R' = phenyl Pre
cyclopropyl	36	44	33	42		
cyclobutyl	28	27	21	22	13	15
cyclopentyl	7	11	3	1	6	0
cyclohexyl	1	9	--	--	--	--

Table VIII. Herbicidal Activity of Cyclobutanecarboxamides

R	R₁	R₂	M.P., °C.	Yields,[a] %	Σ Post-emergence Activity	Σ Pre-emergence Activity
—CH₂C≡CCH₂Cl	H	H	60–1	37	14	4
C₆H₁₁	H	H	121–3	59	13	15
—CH₂(CH₂)₃CH₂—	H	H	89–91/1 mm.[b]	64	3	0
—CH₂CH₂OCH₂CH₂—	H	H	96–7/1 mm.[b]	55	2	26
Cyclohexyl	H	H	113.5–14	80	7	4
C(CH₃)₃	H	H	124–5	36	0	1
CH₂CH=CH₂	H	H	54–55.5	52	6	3
1-Naphthyl	H	H	147–7.5	53	4	2
CH₂C₆H₅	H	H	76–7.5	85	10	0
2-Pyrimidyl	H	H	126–9/1 mm.[b]	30	..	21
2-Thiazolyl	H	H	132–3	39	..	23
3,4-Cl₂C₆H₃	H	H	102–4	75	28	27
C₆H₅	Br	H	89–90	75	9	2
3,4-Cl₂C₆H₃	Br	H	97–8	72	12	16
3,4-Cl₂C₆H₃	H	COOH	182–3	87	2	9

[a] All compounds prepared by reaction of appropriate acid chloride with appropriate amine.
[b] B.p. °C. mm. Hg.

Table X. Inhibition of Hill Reaction of Isolated Chloroplasts by Herbicides

Herbicide	Common Name	Molar Concentration for I_{50}	Chloroplast Source
Cyclopropane carboxanilides			
N-(3,4-Dichlorophenyl)-α-methylcyclopropanecarboxamide	...	2.7×10^{-7}	Alaska pea
N-(3,4-Dichlorophenyl)cyclopropanecarboxamide	Cypromid	5.7×10^{-7}	Alaska pea
N-(3,4-Dichlorophenyl)-β-methylcyclopropanecarboxamide	...	1.1×10^{-6}	Alaska pea
N-(3,4-Dichlorophenyl)-α-methoxycyclopropanecarboxamide	...	3.2×10^{-6}	Alaska pea
Other acylanilides			
N-(3,4-Dichlorophenyl)-2-methylpentanamide	Karsil	5.8×10^{-7}	Turnip
N-(3,4-Dichlorophenyl)propionamide	Stam	2.5×10^{-6}	Alaska pea
N-(4-Chlorophenyl)-2-methylpentanamide	4-CPMP	6.4×10^{-6}	Turnip
N-(3-Chlorophenyl)-2-methylpentanamide	3-CPMP	7.8×10^{-6}	Turnip
N-Phenyl-2-methylpentanamide	PMP	4.5×10^{-5}	Turnip
Urea			
1-n-Butyl-3-(3,4-dichlorophenyl)-1-methylurea	Neburon	2.2×10^{-7}	Turnip
3-(3,4-Dichlorophenyl)-1,1-dimethylurea	Diuron	3.3×10^{-7}	Turnip
		1.8×10^{-7}	Alaska pea
3-(3,4-Dichlorophenyl)-1-methylurea	DMU	6.0×10^{-7}	Turnip
3-(p-Chlorophenyl)-1,1-dimethylurea	Monuron	4.1×10^{-6}	Turnip
3-Phenyl-1,1-dimethylurea	Fenuron	2.8×10^{-5}	Turnip
Triazines			
2-Chloro-4-(2-propylamino)-6-ethylamino-3-triazine	Atrazine	2.5×10^{-7}	Alaska pea
2-Chloro-4,6-bis(isopropylamine)-s-triazine	Propazine	4.3×10^{-6}	Turnip
2-Chloro-4,6-bis(ethylamino)-s-triazine	Simazine	5.9×10^{-6}	Turnip
2-Methoxy-4,6-bis(ethylamino)-s-triazine	Methoxysimazine	9.3×10^{-6}	Turnip
2-Chloro-4,6-bis(diethylamino)-s-triazine	Chlorazine	2.7×10^{-4}	Turnip
Miscellaneous			
3-Cyclohexyl-5,6-trimethyleneuracil	...	8.5×10^{-7}	Turnip
5-Bromo-3-sec-butyl-6-methyluracil	Bromacil	1.4×10^{-6}	Turnip
5-Bromo-3-isopropyl-6-methyluracil	Isocil	2.7×10^{-6}	Turnip
Isopropyl N-(3,4-dichlorophenyl)carbamate	3,4-DCIPC	3.3×10^{-5}	Turnip
Isopropyl N-(3-chlorophenyl)carbamate	3-CIPC	2.9×10^{-4}	Turnip
Isopropyl N-phenylcarbamate	IPC	1.2×10^{-3}	Turnip
4,6-Dinitro-O-sec-butylphenol	DNBP	1.3×10^{-5}	Turnip

Literature Cited

(1) Brown, W. G. (to Commercial Solvents Corp.), U. S. Patent 2,784,226 (March 5, 1957).
(2) Bunce, S. C., Cloke, J. B., *J. Am. Chem. Soc.* **76**, 2244 (1954).
(3) Burger, A., Yost, W., *Ibid.*, **70**, 2198 (1948).
(4) Cannon, G. W., Santilli, A. A., Shenian, P., *Ibid.*, **81**, 1660 (1959).
(5) DeFeo, R. J., Strickler, P. D., *J. Org. Chem.* **28**, 2915 (1963).
(6) Dubrovin, K. P., "Clobber, a New Post-Emergence Herbicide," North Central Weed Control Conf., East Lansing, Mich., December 1964.
(7) Good, N. E., *Plant Physiol.* **36**, 788 (1961).
(8) Hart, H., Curtis, O. E., Jr., *J. Am. Chem. Soc.* **78**, 112 (1956).
(9) Hilton, J. L., Monaco, T. J., Moreland, D. E., Gentner, W. A., *Weeds* **12**, 129 (1964).
(10) Knowles, E. C., Cloke, J. B., *J. Am. Chem. Soc.* **54**, 2028 (1932).

(11) Moreland, D. E., USDA, North Carolina State College, Raleigh, N. C., unpublished data.
(12) Moreland, D. E., Hill, K. L., J. AGR. FOOD CHEM. **7**, 832 (1959).
(13) Moreland, D. E., Hill, K. L., *Weeds* **10**, 229 (1962).
(14) *Ibid.*, **11**, 55 (1963).
(15) Organic Syntheses, Coll. Vol. **III**, 213 (1954).
(16) *Ibid.*, p. 221.
(17) Schlatter, M. J., *J. Am. Chem. Soc.* **63**, 1733 (1941).
(18) Woodworth, R. C., Snell, P. S., *Ibid.*, **79**, 2542 (1956).