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Synthesis and Herbicidal Activity of 1-Aryl-5-halo- and 1-Aryl-5-(trifluoromethyl)-1*H*-pyrazole-4-carboxamides

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A series of 1-aryl-5-halo- and 1-aryl-5-(trifluoromethyl)-1*H*-pyrazole-4-carboxamides exhibit moderate to strong herbicidal activity in preemergence and postemergence tests. At $^1/_2$ lb/acre, corn, rice, wheat, cotton, and soybean show tolerance, while large crabgrass, foxtail millet, common lambsquarters, redroot pigweed, wild mustard, velvetleaf, jimsonweed, and zinnia were killed or severely injured. A total of 83 5-halo analogues and 47 5-trifluoromethyl analogues were synthesized and their herbicidal activities determined in order to examine the structure–activity relationships. The order of activity at C-5 of the pyrazole ring was $CF_3 > Cl \cong Br > I$. The order of activity involving substitution on the carboxamide moiety was cyclopropyl ≅ methyl > dimethyl > ethyl > isopropyl. Substitution on the benzene ring did not result in any major increase in activity when compared with the corresponding phenyl analogue.

1-Aryl-5-halo-1*H*-pyrazole-4-carboxamides and the corresponding 5-trifluoromethyl analogues represent a new class of preemergence and postemergence herbicides (Beck and Lynch, 1986). The 5-halo derivatives were synthesized in three steps (Scheme I) from ethyl 5-amino-1-aryl-1*H*-pyrazole-4-carboxylate esters (**A**) which were prepared by the reaction of ethyl (ethoxymethylene)cyanoacetate with the appropriate arylhydrazine (Beck et al., 1987 and references therein). The conversion of the amino esters to the halo esters (**B**) by a process involving nonaqueous diazotization was reported in a U.S. Patent (Beck and Lynch, 1986) and a recent publication (Beck et al., 1987). Treatment of the amino esters with nitrosyl chloride in chloroform gave the corresponding chloro esters (**B**, X = Cl). Similar treatment with isopentyl nitrite in the presence of bromine or iodine led to the formation of the bromo and iodo esters (**B**, X = Br and I), respectively. The halo esters were converted to the carboxylic acids (**C**) by base hydrolysis, and the herbicidal halo carboxamides (**D**) were prepared by standard procedures.

The 5-trifluoromethyl analogues were synthesized in three steps (Scheme II) from ethyl 3-ethoxy-2-(trifluoroacetyl)-2-propenate (**A**) (Jones, 1951). Treatment of **A** with the appropriate arylhydrazine under mild conditions led to the formation of pyrazole-4-carboxylate esters **B** (Beck and Lynch, 1986; Beck and Wright, 1987). Saponification gave carboxylic acids **C**, which were converted

Scheme I

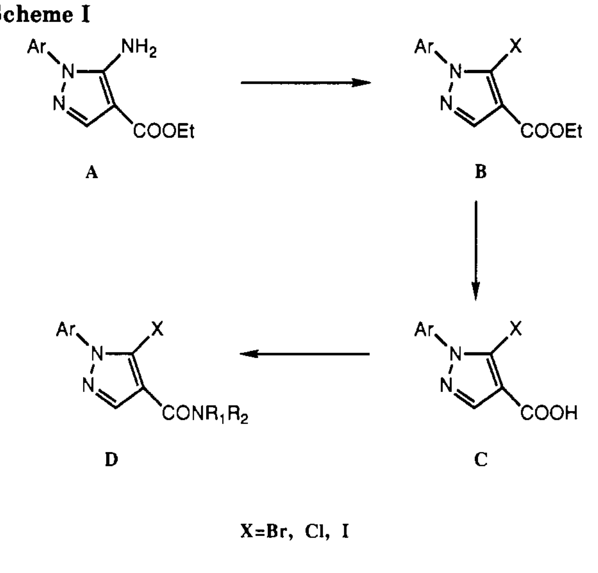
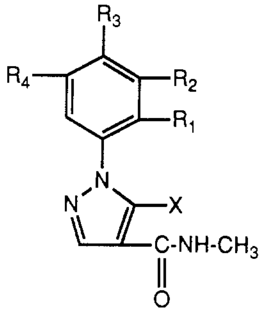


Table I. Effect of Ring Substituents on 1-Aryl-5-halo- and 1-Aryl-5-(trifluoromethyl)-*N*-methyl-1*H*-pyrazole-4-carboxamides for Preemergence and Postemergence Herbicidal Activity



compd	ring substituent R1	R2	R3	R4	5-pyrazole substituent X	av control rating[a] at 8 lb/acre for all species[b] tested: preemergence	postemergence
1	H	H	Cl	H	CF_3	5.0	5.0
2	H	H	H	H	CF_3	5.0	4.7
3	H	H	Me	H	CF_3	5.0	4.4
4	Cl	H	Cl	H	CF_3	5.0	4.4
5	H	CF_3	H	H	CF_3	5.0	3.5
6	H	Cl	H	H	CF_3	5.0	3.2
7	H	H	OMe	H	CF_3	5.0	1.8
8	H	F	H	H	Br	4.7	3.7
9	H	H	F	H	Br	4.7	2.8
10	Cl	H	H	H	Cl	4.5	4.0
11	Cl	H	Cl	H	Cl	4.5	4.0
12	H	H	Me	H	Br	4.5	3.8
13	H	H	H	H	Br	4.5	3.8
14	H	F	H	H	Cl	4.5	3.8
15	OMe	H	H	H	Cl	4.5	3.7
16	H	Cl	H	H	Br	4.3	3.8
17	H	H	Cl	H	Cl	4.2	3.8
18	F	H	F	H	Cl	4.0	4.5
19	H	Cl	H	H	Cl	4.0	3.8
20	H	CF_3	H	H	Cl	4.0	3.7
21	H	H	H	H	Cl	4.0	2.8
22	Cl	H	H	Cl	Br	3.8	3.8
23	Cl	H	H	Cl	Cl	3.8	3.8
24	H	H	H	H	I	3.8	2.2
25	H	H	F	H	Cl	3.7	4.0
26	H	H	Cl	H	Br	3.7	3.5
27	Cl	Cl	H	H	Cl	3.7	1.7
28	F	H	F	H	Br	3.5	4.2
29	Br	H	Br	H	Cl	3.5	3.5
30	H	Cl	Cl	H	Br	3.3	2.5

[a] Rating scale: 1 = no effect, 2 = slight effect, 3 = moderate effect, 4 = severe effect, 5 = death of plants. [b] Species tested: large crabgrass, foxtail millet, redroot pigweed, velvetleaf, morningglory, and zinnia.

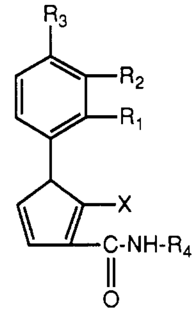
to herbicidal carboxamides **D** utilizing standard procedures.

The herbicidal activity of this subject class was examined during a systematic screening effort for preemergence and postemergence herbicidal activity. This report presents studies of structure–activity relationships, which examine the effect of 5-halo and 5-trifluoromethyl functionality, as well as substituent changes on the aryl ring and carboxamide nitrogen atom, on overall herbicidal activity.

EXPERIMENTAL SECTION

Synthetic Methods. The general synthesis and examples of all carboxamides (melting point and microanalysis) were reported in a U.S. Patent (Beck and Lynch, 1986). The prep-

Table II. Effect of Ring Substituents on 1-Aryl-5-halo- and 1-Aryl-5-(trifluoromethyl)-*N*-alkyl-1*H*-pyrazole-4-carboxamides for Preemergence and Postemergence Herbicidal Activity



compd	ring substituent R1	R2	R3	5-pyrazole substituent X	amide substituent	av control rating[a] at 8 lb/acre for all species[b] tested: preemergence	postemergence
31	H	H	H	CF_3	c-Pr	5.0	5.0
32	H	H	Cl	CF_3	c-Pr	5.0	5.0
33	Cl	H	Cl	CF_3	c-Pr	5.0	5.0
34	H	H	H	CF_3	Bu	5.0	5.0
35	H	CF_3	H	CF_3	c-Pr	5.0	4.8
36	F	H	F	Cl	c-Pr	5.0	4.8
37	H	H	Me	CF_3	Et	5.0	4.7
38	H	H	Me	CF_3	c-Pr	5.0	4.4
39	H	H	H	CF_3	Et	5.0	4.2
40	H	H	Cl	CF_3	Et	5.0	4.0
41	H	H	OMe	CF_3	c-Pr	5.0	3.7
42	H	H	H	CF_3	Pr	5.0	3.4
43	H	Cl	H	CF_3	c-Pr	4.8	3.7
44	H	H	H	Cl	c-Pr	4.7	3.0
45	H	H	OMe	CF_3	Et	4.7	1.7
46	Cl	H	Cl	CF_3	H	4.5	2.5
47	H	Cl	H	CF_3	Et	4.5	2.2
48	Cl	H	Cl	Br	c-Pr	4.4	3.7
49	H	H	Cl	CF_3	H	4.4	2.7
50	Cl	H	Cl	Cl	c-Pr	4.3	3.5
51	H	H	Cl	Cl	c-Pr	4.3	3.5
52	H	H	H	CF_3	*i*-Pr	4.0	1.7
53	H	Cl	H	Cl	c-Pr	3.8	3.0
54	H	F	H	Br	c-Pr	3.8	2.7
55	Cl	H	Cl	CF_3	c-Pr	3.8	2.2
56	H	F	H	Cl	Et	3.5	2.7
57	H	Me	Me	Cl	c-Pr	3.5	2.2
58	H	CF_3	H	Cl	c-Pr	3.0	4.5
59	H	H	H	CF_3	H	3.0	2.2

[a] Rating scale: 1 = no effect, 2 = slight effect, 3 = moderate effect, 4 = severe effect, 5 = death of plants. [b] Species tested: large crabgrass, foxtail millet, redroot pigweed, velvetleaf, morningglory, and zinnia.

Scheme II

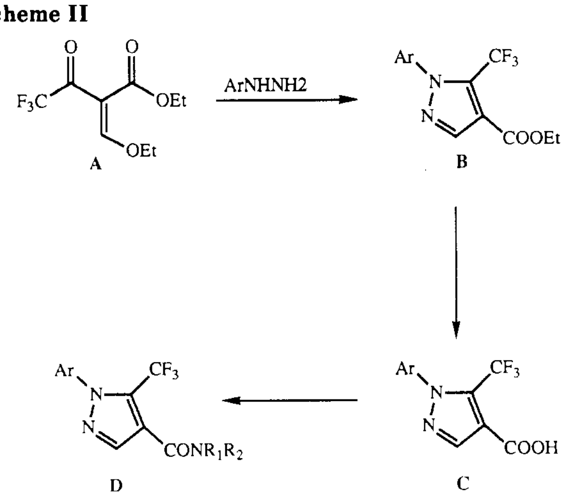
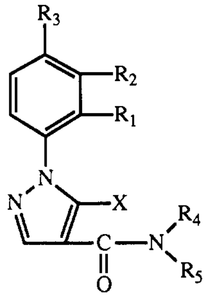


Table III. Effect of Ring Substituents on 1-Aryl-5-halo- and 1-Aryl-5-(trifluoromethyl)-*N*,*N*-dialkyl-1*H*-pyrazole-4-carboxamides for Preemergence and Postemergence Herbicidal Activity



compd	ring substituent R_1	ring substituent R_2	ring substituent R_3	5-pyrazole substituent X	amide substituent R_4	amide substituent R_5	av control rating[a] at 8 lb/acre for all species[b] tested: preemergence	postemergence
60	Cl	H	Cl	CF_3	Me	Me	5.0	5.0
61	H	H	Cl	CF_3	Et	Et	5.0	4.8
62	H	H	Cl	CF_3	Me	OMe	5.0	4.7
63	H	H	Cl	CF_3	Me	Me	5.0	4.5
64	H	H	H	CF_3	Me	OMe	5.0	4.4
65	H	H	H	CF_3	Me	Et	5.0	3.8
66	H	H	H	CF_3	Et	Et	4.8	4.7
67	H	H	Me	CF_3	Me	OMe	4.8	4.5
68	H	H	Me	CF_3	Et	Et	4.7	4.4
69	H	H	H	CF_3	Me	Me	4.5	3.2
70	H	F	H	Cl	Me	Me	4.2	4.0
71	H	H	OMe	CF_3	Me	OMe	4.2	3.4
72	H	Cl	H	Cl	Me	Me	4.0	3.2
73	Cl	H	Cl	Br	Me	Me	4.0	3.0
74	H	Cl	H	CF_3	Me	OMe	4.0	2.8
75	H	CF_3	H	CF_3	Me	OMe	3.7	3.4
76	H	CF_3	H	CF_3	Et	Et	3.7	2.7
77	H	Cl	H	Br	Me	Me	3.5	3.5
78	H	H	H	Br	Me	Me	3.5	2.4

[a] Rating scale: 1 = no effect, 2 = slight effect, 3 = moderate effect, 4 = severe effect, 5 = death of plants. [b] Species tested: large crabgrass, foxtail millet, redroot pigweed, velvetleaf, morningglory, and zinnia.

aration of the halo esters and carboxylic acids was described in the same patent and in a publication (Beck et al., 1987). The synthesis of trifluoromethyl esters and carboxylic acids was described in the same patent and in a publication (Beck and Wright, 1987).

Biological Methods. Compounds were evaluated at 8 lb/acre as preemergence and postemergence herbicides. The test plants were large crabgrass (*Digitaria sanguinalis*), foxtail millet (*Setaria italica*), redroot pigweed (*Amaranthus retroflexus*), velvetleaf (*Abutilon theophrasti*), morningglory (*Ipomoea* spp.), and zinnia (*Zinnia elegans*).

In the preemergence and postemergence tests, each compound was dissolved in a spray solution containing acetone–ethanol (1:1 ratio) with Toximul R and S surfactants added and then diluted with deionized water. Toximul R is a blend of calcium sulfate and nonionic surfactants. Toximul S is a hydrophilic emulsifier that when combined with Toximul R provides a superior emulsion for the herbicide formulations. For the preemergence tests, the spray solution was sprayed on soil immediately after the test species were planted. Approximately 3 weeks after spraying, the herbicidal activity of the compound was determined by visual observation of the treated area in comparison with untreated controls. These observations are reported on a scale of 1–5, where 1 = no effect, 2 = slight effect, 3 = moderate effect, 4 = severe effect, and 5 = death of plants.

For the postemergence tests, developing plants were sprayed about 2 weeks after the seeds were sown. Approximately 2 weeks after spraying, the herbicidal activity of the compound was determined by visual observation of the treated plants in comparison with the untreated controls. The rating scale was the same as that for the preemergence tests.

The herbicidal activities presented in Tables I–III are average control ratings for all six species tested at 8 lb/acre for both the preemergence and postemergence tests.

In addition to the 8 lb/acre tests, several compounds with prominent preemergence activity were retested at $^1/_2$ and 1 lb/acre on a broad spectrum of grass and broadleaf species. As well as the six species listed above, other plant species evaluated included corn (*Zea mays*), rice (*Oryza sativa*), wheat (*Triticum aestivum*), alfalfa (*Medicago sativa*), cucumber (*Cucumis sativus*), cotton (*Gossypium hirsutum*), sugarbeet (*Beta vulgaris*), soybean (*Glycine max*), tomato (*Lycopersicon esculentum*), barnyardgrass (*Echinochloa crus-galli*), wild oat (*Avena fatua*), common lambsquarters (*Chenopodium album*), jimsonweed (*Datura stramonium*), and wild mustard (*Brassica kaber*). The herbicidal activities presented in Table IVA for crops and Table IVB for weeds are average control ratings for all 20 species tested at $^1/_2$ and 1 lb/acre in this preemergence test.

RESULTS AND DISCUSSION

In general, these compounds at 8 lb/acre exhibit slight to severe postemergence herbicidal activity on grass and broadleaf species. Symptoms observed were necrosis or burning of plant tissue about 2–3 days after spraying, and susceptible species died after about 7–9 days. These compounds are contact herbicides, and no selectivity was observed between the various plant species.

These compounds at 8 lb/acre also exhibit moderate to severe preemergence herbicidal activity on grass and broadleaf species. The compounds do not prevent germination or emergence of the plants. Injury symptoms observed were growth inhibition and slight chlorosis about 5–7 days after the plants emerge, followed by necrosis and eventual death of the susceptible plants after 14–17 days. In general, these pyrazole carboxamides are slow-acting preemergence herbicides.

At $^1/_2$ lb/acre, preemergence activity was observed on both grasses and broadleaves. Several crops such as corn, rice, wheat, cotton, and soybean (Table IVA) were tolerant at 1 lb/acre while several weeds such as common lambsquarters, large crabgrass, foxtail millet, redroot pigweed, wild mustard, jimsonweed, zinnia, and velvetleaf (Table IVB) were controlled. As for other crops, cucumber and tomato were intermediate in tolerance while alfalfa and sugarbeet were injured severely. As for other weeds, barnyardgrass and morningglory were injured slightly to moderately and wild oat appeared tolerant.

Three chemical parameters were examined in this study. These were (1) halogen vs trifluoromethyl at C-5, (2) carboxamide substitution, and (3) substituent effects on the benzene ring. With regard to the first parameter, the order of activity was $CF_3 > Cl \cong Br > I$. The first nine compounds in Tables IVA,B all involve trifluoromethyl substitution, which illustrates the superiority of that functional group over a halogen at the 5-position. The order of activity at the carboxamide nitrogen atom was cyclopropyl ≅ methyl > ethyl > isopropyl. Unsubstituted and *N*-aryl-substituted carboxamides were essentially inactive in both series. Substitution on the benzene ring did not result in any major increase in activity in either series. Halogen substituents such as 4-Cl, 4-F, and 2,4-F_2 did, in certain cases, yield carboxamide derivatives, which showed slightly increased activity when compared to the corresponding phenyl analogue.

Table IV. Preemergence Herbicidal Activity of Prominent Compounds at $^1/_2$ and 1 lb/acre

A. Crops[a]

compd	rate, lb/acre	control rating[b] for crops: corn	cttn	sybn	wheat	alfa	sgbt	rice	cucm	tmto
31	$^1/_2$	2.0	4.0	4.0	3.0	5.0	5.0	4.0	5.0	5.0
	1	3.5	5.0	5.0	4.0	5.0	5.0	4.0	5.0	5.0
41	$^1/_2$	1.0	1.0	1.0	1.0	5.0	5.0	2.0	4.0	1.0
	1	1.0	3.0	2.5	1.0	5.0	5.0	3.5	5.0	5.0
32	$^1/_2$	1.0	2.0	2.0	1.0	5.0	5.0	2.0	4.0	4.0
	1	1.0	1.5	2.0	1.5	5.0	5.0	1.5	4.0	5.0
62	$^1/_2$	1.0	1.0	1.0	1.0	5.0	5.0	3.0	3.0	4.0
	1	1.0	1.5	2.0	1.0	5.0	5.0	3.5	3.5	5.0
1	$^1/_2$	1.0	1.0	1.0	1.0	5.0	5.0	2.0	3.5	3.0
	1	2.0	2.0	2.5	2.0	5.0	5.0	3.5	5.0	5.0
61	$^1/_2$	1.0	1.0	1.0	1.0	5.0	5.0	1.0	2.0	4.0
	1	1.0	1.0	1.0	1.5	5.0	5.0	1.0	4.5	4.5
33	$^1/_2$	1.0	1.0	1.0	1.0	4.0	5.0	2.0	4.0	4.0
	1	1.0	1.0	1.0	1.5	5.0	5.0	2.0	5.0	5.0
35	$^1/_2$	1.0	1.0	1.0	2.0	4.0	5.0	2.0	3.0	2.0
	1	1.5	1.0	1.5	3.0	4.5	5.0	3.0	4.5	4.0
2	$^1/_2$	1.0	2.0	1.0	2.0	5.0	5.0	2.0	4.0	1.0
	1	1.0	2.0	2.0	1.5	4.5	5.0	1.5	4.0	2.0
14	$^1/_2$	1.0	1.0	1.0	1.0	2.0	4.0	2.0	3.0	3.0
	1	1.5	1.5	2.0	1.5	4.0	4.0	2.5	4.0	3.5
18	$^1/_2$	1.0	1.0	1.0	1.0	4.0	4.0	1.0	3.0	2.0
	1	1.0	1.0	2.0	1.5	4.5	4.0	2.0	3.5	2.5
28	$^1/_2$	1.0	1.0	1.0	1.0	3.0	3.0	2.0	2.0	2.0
	1	1.5	1.5	1.0	1.0	4.0	4.0	2.0	3.5	2.5

B. Weeds[c]

compd	rate, lb/acre	control rating[b] for weeds: bygr	colq	wimu	lacg	rrpw	vele	jiwe	ftmi	mngy	wioa	zinn
31	$^1/_2$	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	1.0	5.0
	1	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	4.0	5.0
41	$^1/_2$	3.0	5.0	5.0	4.0	5.0	5.0	2.0	2.0	3.0	2.0	4.0
	1	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	4.5	2.0	5.0
32	$^1/_2$	4.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	1.0	1.0	4.0
	1	4.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	1.0	5.0
62	$^1/_2$	2.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	2.0	2.0	5.0
	1	3.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	1.5	2.0	5.0
1	$^1/_2$	3.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	3.0	1.0	4.0
	1	4.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	4.5	1.5	5.0
61	$^1/_2$	1.0	5.0	5.0	5.0	5.0	5.0	5.0	4.0	4.0	3.0	3.0
	1	3.5	5.0	5.0	5.0	5.0	5.0	5.0	5.0	4.5	2.5	3.5
33	$^1/_2$	2.0	5.0	5.0	4.0	5.0	4.0	4.0	3.0	3.0	2.0	5.0
	1	3.5	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	1.5	4.5
35	$^1/_2$	3.0	5.0	4.0	4.0	5.0	5.0	4.0	2.0	2.0	1.0	3.0
	1	3.5	5.0	4.5	5.0	5.0	5.0	4.5	4.5	2.5	2.0	4.0
2	$^1/_2$	1.0	5.0	5.0	5.0	5.0	5.0	5.0	4.0	4.0	2.0	4.0
	1	2.5	4.5	4.5	4.5	4.5	4.5	4.5	4.0	3.5	2.0	4.5
14	$^1/_2$	2.0	4.0	5.0	2.0	5.0	1.0	2.0	4.0	4.0	4.0	3.0
	1	4.0	4.0	4.5	3.5	5.0	3.0	3.0	4.5	4.0	4.0	4.0
18	$^1/_2$	2.0	3.0	4.0	1.0	3.0	2.0	2.0	3.0	4.0	2.0	2.0
	1	1.5	3.5	4.0	1.5	4.5	1.5	2.5	4.5	4.0	3.5	3.5
28	$^1/_2$	1.0	3.0	2.0	1.0	4.0	1.0	2.0	3.0	3.0	3.0	2.0
	1	2.0	3.5	4.0	1.5	5.0	1.0	2.5	4.0	4.0	4.0	3.5

[a] Key for crops: wheat = wheat, alfa = alfalfa, cucm = cucumber, cttn = cotton, sgbt = sugarbeet, sybn = soybean, tmto = tomato. [b] Rating scale: 1 = no effect, 2 = slight effect, 3 = moderate effect, 4 = severe effect, 5 = death of plants. [c] Key for weeds: bygr = barnyardgrass, ftmi = foxtail millet, lacg = large crabgrass, wioa = wild oat, colq = common lambsquarters, mngy = morningglory, jiwe = jimsonweed, rrpw = redroot pigweed, vele = velvetleaf, wimu = wild mustard, zinn = zinnia.

LITERATURE CITED

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