

Synthesis and Herbicidal Properties of Substituted 1,4-Dihydro-1,2,4-benzotriazines

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A series of 1,4-dihydro-1,2,4-benzotriazines exhibits slight to moderate herbicidal activity in preemergence and postemergence tests. Postemergence applications of these benzotriazines at 4 lb/acre provided good control of large crabgrass, foxtail millet, redroot pigweed, wild mustard, and tomato, but no selectivity was observed among the various plant species. At 4 lb/acre preemergence, corn, wheat, rice, cotton, and soybean show tolerance, while large crabgrass, foxtail millet, redroot pigweed, common lambsquarters, velvetleaf, and jimsonweed were killed or severely injured. A total of 36 analogues was synthesized, and their herbicidal activities were determined to examine the structure-activity relationships. In general, we found that, among the variations investigated, cyano substitution on the benzo portion, small alkyl at the 1-position, and hydrogens at the 3- and 4-positions led to the most active herbicides.

INTRODUCTION

1,4-Dihydro-1,2,4-benzotriazines represent a new class of preemergence and postemergence herbicides discovered by the authors while exploring the chemistry of acylated dinitrophenylhydrazines. The 1,4-dihydro analogues have been broadly taught as new chemicals, but not specifically as new herbicides (Blatter and Lukaszewski, 1968). Also, the 1,4-diaryl examples have been reported to be stable free radicals (Blatter, 1969). The benzotriazines of this paper were synthesized in four steps (Scheme I). The 2-halogen from commercially available 2-halonitrobenzenes can be readily displaced by alkyhydrazines to provide *N*-phenyl-*N*-alkylhydrazines (B). The usual variety of acylation agents and conditions are suitable for the synthesis of numerous hydrazides (C). These are readily reduced to the *N*-(2-anilino)-*N*-alkyl-*N'*-acylhydrazines (D), which also display significant herbicidal activity. They can then cyclize via acid catalysis to yield the 1,4-dihydro family (E). The herbicidal activity of these benzotriazines was examined during a systematic screening effort for preemergence and postemergence herbicidal activity. This paper presents studies of structure-activity relationships that examine the effects on activity exerted by substituent variations on the benzo portion and on the 3-position of the heterocycle portion and the effects of substitution at each of the three ring nitrogens.

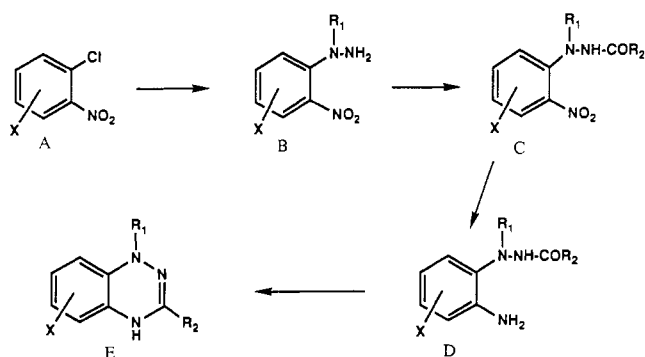
EXPERIMENTAL METHODS

Synthetic Methods. The 2-chloronitrobenzenes used were purchased from commercial sources. The method of Stroh and Scharnov (1965) was used to prepare *n*-propylhydrazine; all other hydrazines were purchased.

Experimental Procedures. ¹H NMR spectra were collected on a Varian T-60 spectrometer using tetramethylsilane as the internal reference. Melting points were determined on a Thomas Hoover oil bath apparatus and are uncorrected. Elemental analyses were performed by Lilly Research Laboratories, Indianapolis, IN.

3-Nitro-4-(1-propylhydrazino)benzotrile. To a solution of 4.75 g (~0.045 mol) of 75% pure *n*-propylhydrazine in 5 mL of anhydrous dimethylformamide was added 3.64 g (0.02 mol) of 4-chloro-3-nitrobenzotrile. After sitting overnight, the solution was diluted with 150 mL of water, precipitating 3.94 g of an orange solid. This was dissolved in methylene chloride and washed with water. After separation of the phases, the organic layer was filtered and evaporated in vacuo to provide 3.88 g (90%) of

Scheme I



product: mp 126–128 °C; ¹H NMR (CDCl₃) δ 7.7 (m, 1 H), 7.4 (m, 1 H), 6.8 (m, 1 H), 4 (s, 2 H), 3.45 (m, 2 H), 1 (m, 3 H).

Anal. Calcd for C₁₀H₁₂N₄O₂: C, 54.54; H, 5.49; N, 25.44. Found: C, 54.34; H, 5.39; N, 25.44.

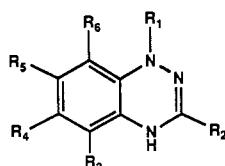
4-(1-Methylhydrazino)-3-nitrobenzotrile. To a solution of 3.65 g (0.02 mol) of 4-chloro-3-nitrobenzotrile in 50 mL of ethanol was added ~3 g (≥0.04 mol) of methylhydrazine. The solution was heated at 100 °C for 30 min and developed yellow crystals while cooling. This suspension was diluted with 200 mL of water and the resulting solid filtered. Recrystallization from methanol yielded 3.2 g: mp 130–133.5 °C; ¹H NMR (CDCl₃ + DMSO-*d*₆) δ 7.65 (m, 1 H), 7.45 (m, 1 H), 6.9 (m, 1 H), 4.25 (s, 2 H), 3.2 (s, 3 H).

Anal. Calcd for C₈H₈N₄O₂: C, 50.00; H, 4.20; N, 29.15. Found: C, 50.21; H, 4.00; N, 29.44.

Trifluoroacetic Acid, 2-(4-Cyano-2-nitrophenyl)-2-propylhydrazide. To a solution of 2.3 g (0.0105 mol) of the phenylhydrazine in 75 mL of methylene chloride was added 2.6 g (0.012 mol) of trifluoroacetic anhydride. After 10 min, the solvent was removed in vacuo to give a yellow solid, which was recrystallized from hexane/ethyl acetate to yield 2.9 g (92%) of product: mp 135–137 °C; ¹H NMR (CDCl₃ + DMSO-*d*₆) δ 7.75 (m, 1 H), 7.5 (m, 1 H), 7.1 (m, 1 H), 3.45 (m, 2 H), 1.6 (m, 2 H), 9 (m, 3 H).

Anal. Calcd for C₁₁H₁₁F₃N₄O₃: C, 45.58; H, 3.51; N, 17.72. Found: C, 45.86; H, 3.47; N, 17.87.

Trifluoroacetic Acid, 2-(2-Amino-4-cyanophenyl)-2-propylhydrazide. A solution of 2.75 g (0.009 mol) of the preceding hydrazide in 100 mL of ethanol containing 0.27 g of 5% Pd/C was hydrogenated in a calibrated Parr apparatus until 3 equiv of hydrogen was taken up. The reaction mixture was then filtered, and the solvent was removed in vacuo to give a dark red oil. Crystallization from hexane/chloroform gave 2.37 g (95%) of orange solid: mp 135.5–137 °C; ¹H NMR (CDCl₃ + DMSO-*d*₆)

Table I. Substituent Effects on 1,4-Dihydro-1-alkyl-1,2,4-benzotriazines for Preemergence and Postemergence Herbicidal Activity

compd	ring substituents						mp, °C	av control rating at 8 lb/acre for all species tested	
	R ₁	R ₂	R ₃	R ₄	R ₅	R ₆		preemergence	postemergence
1	Pr	H	H	CN	H	H	110-112	5.0	4.8
2	Me	H	H	CN	H	H	130-133	4.7	4.3
3	Me	H	CN	H	H	H	153-154.5	4.2	4.0
4	Pr	H	H	CF ₃	H	H	80-84.5	4.2	3.8
5	Me	H	H	SO ₂ NH ₂	H	H	188-191	4.2	2.5
6	Me	H	H	CO ₂ Et	H	H	118-119	4.0	4.2
7	H	H	H	CF ₃	H	H	86-87.5	4.0	3.2
8	Pr	CF ₃	H	CN	H	H	141-143	4.0	2.0
9	Me	H	H	CF ₃	H	H	124	3.8	4.3
10	Me	CF ₃	H	H	Cl	H	85-88	3.7	3.3
11	Me	Me	H	CF ₃	H	H	94-98	3.7	3.3
12	Me	CF ₃	H	CN	H	H	210-213	3.7	1.8
13	Me	CF ₃	H	CF ₃	Cl	H	64-68	3.5	2.3
14	Me	CF ₃	H	CF ₃	H	H	66-67.5	3.5	1.3
15	Me	CF ₂ CF ₂ H	H	CF ₃	H	H	52	3.3	2.0
16	Pr	Me	H	CF ₃	H	H	185-190 (dec)	3.2	3.2
17	Me	CONHMe	H	CF ₃	H	H	202-205	3.2	1.0
18	Me	CF ₂ CF ₃	H	CF ₃	H	H	71-78	2.8	1.0
19	Me	CF ₃	H	CO ₂ Et	H	H	117.5-119	2.5	1.3
20	Me	CF ₃	H	Cl	H	H	61.5-62.5	2.2	3.8
21	Me	H	H	SO ₂ Me	H	H	172-174	2.0	2.0
22	Me	CF ₃	H	SO ₂ Me	H	H	213-215	1.8	1.0
23	Me	Ph	H	CF ₃	H	H	124	1.5	2.2
24	H	CF ₃	H	CF ₃	H	NO ₂	158-161	1.0	3.0
25	Me	CH ₂ O-2,4-Cl ₂ C ₆ H ₃	H	CF ₃	H	H	96-97	NT ^a	2.7
26	Me	CF ₃	H	CF ₃	H	NH ₂	~140 (dec)	1.0	2.2
27	Me	H	H	H	H	NO ₂	144.5-146	1.0	1.8
28	Me	OH	H	CF ₃	H	H	192-194	1.0	1.8
29	Me	CO ₂ Et	H	CF ₃	H	H	179	1.0	1.0
30	Me	CF ₃	H	SO ₂ NH ₂	H	H	204.5-207	1.0	1.0
31	Me	CF ₃	H	SO ₂ NMe ₂	H	H	157.5-159	1.0	1.0
32	Me	<i>t</i> -Bu	H	CF ₃	H	H	113-115	1.0	1.0
33	Me	H	H	CF ₃	H	NO ₂	152-155	1.0	1.0

^a NT, not tested.

δ 7.2 (m, 1 H), 6.85 (m, 2 H), 4.7 (s, 2 H), 3.2 (m, 2 H), 1.5 (m, 2 H), 1.0 (m, 3 H).

Anal. Calcd for C₁₂H₁₃F₃N₄O: C, 50.35; H, 4.58; N, 19.57. Found: C, 50.25; H, 4.53; N, 19.52.

1,4-Dihydro-1-propyl-3-(trifluoromethyl)-1,2,4-benzotriazine-6-carbonitrile (8). To a solution of 0.5 g (0.0017 mol) of the preceding aminohydrazide in 5 mL of ethanol was added 1 drop of concentrated hydrochloric acid. After 10 min, the solvent was removed in vacuo to give an orange solid. Recrystallization from hexane/methylene chloride provided 0.43 g (94%) of orange crystals: mp 148-150 °C. As with most examples of this series, a sharp NMR spectrum was not obtainable until MeOD was added to the sample; these compounds have a considerable degree of unpaired-electron character and display concomitant paramagnetic broadening. ¹H NMR (CDCl₃ + MeOD) δ 6.8 (m, 1 H), 6.2 (m, 1 H), 5.9 (m, 1 H), 3.0 (m, 2 H), 1.55 (m, 2 H), 0.9 (m, 3 H).

Anal. Calcd for C₁₂H₁₁F₃N₄: C, 53.73; H, 4.13; N, 20.89. Found: C, 53.60; H, 4.37; N, 20.74.

4-(2-Formyl-1-propylhydrazino)-3-nitrobenzonitrile. A solution of 1.2 g (0.0055 mol) of 3-nitro-4-(1-propylhydrazino)benzonitrile (above) in 6 mL of formic acid was heated at 100 °C for 15 min and then evaporated in vacuo. Stirring this into 100 mL of water and a small amount of ether/hexane yielded a bright yellow solid: 1.15 g (84%); mp 129-131 °C; ¹H NMR (DMSO-*d*₆) δ 9.9 (s, 1 H), 7.9 (m, 2 H), 7.3 (m, 1 H), 3.4 (m, 2 H), 1.5 (m, 2 H), 0.9 (m, 3 H).

Anal. Calcd for C₁₁H₁₂N₄O₃: C, 53.22; H, 4.87; N, 22.57. Found: C, 52.97; H, 4.65; N, 22.45.

1,4-Dihydro-1-propyl-1,2,4-benzotriazine-6-carbonitrile (1). A solution of 1.61 g (0.0065 mol) of 4-(2-formyl-1-propylhydrazino)-3-nitrobenzonitrile (above) in 100 mL of ethanol containing 0.3 g of 5% Pd/C was hydrogenated in a Parr shaker until 3 equiv of hydrogen was taken up. The suspension was filtered, and 4 drops of 5 N hydrochloric acid was added to the filtrate. After 10 min, the solvent was removed in vacuo; the residue was re-dissolved in a minimum volume of methanol, diluted with 100 mL of water, and neutralized with dilute ammonium hydroxide. The resulting orange solid was filtered to yield 1.14 g (77%) of product: mp 109-110 °C. This compound demonstrated too much paramagnetic broadening to afford a definitive ¹H NMR in a variety of solvents.

Anal. Calcd for C₁₁H₁₂N₄: C, 65.97; H, 6.04; N, 27.98. Found: C, 65.81; H, 5.80; N, 27.77.

Trifluoroacetic Acid, 2-(2-Amino-5-chlorophenyl)-2-methylhydrazide. The requisite *o*-nitrophenyl precursor was prepared. Since the ring chlorine was sensitive to the usual hydrogenation conditions, the following alternative procedure was followed: 1.84 g (0.006 mol) of starting material was dissolved in 35 mL of ethanol containing 0.2 g of 5% Pd/C. To this was added 0.5 g (0.015 mol) of anhydrous hydrazine, resulting in effervescence and a mild exotherm. After cooling to room temperature, the reaction was allowed to stand 1 h and was filtered, and the solvent was removed in vacuo to give 1.6 g of orange solid.

This was triturated with very dilute hydrochloric acid to pH 1-2 and then filtered to give 1.27 g (79%) of essentially pure product. It was recrystallized from hexane/ether: mp 139.5-140

Table II. Postemergence Herbicidal Activity of Prominent Compounds at 1, 2, and 4 lb/Acre on Six Plants^a

compd	rate, lb/acre	control rating for plants					
		lcg	ftm	rrpw	tmt	mgj	wmu
1	1	4	4	4	4	2	5
	2	3	5	3	5	2	5
	4	5	5	5	5	3	5
2	1	3	4	3	4	2	5
	2	5	4	4	5	2	5
	4	5	5	5	5	3	5
3	1	3	3	2	1	1	2
	2	3	4	3	2	1	3
6	1	3	4	2	2	2	4
	2	4	5	4	3	2	4
	4	4	5	4	4	3	5
10	1	1	1	2	1	1	2
	2	1	1	3	1	2	2
	4	1	1	3	2	2	4

^a Key for plants: lcg, large crabgrass; ftm, foxtail millet; rrpw, redroot pigweed; tmt, tomato; mgj, morningglory; wmu, wild mustard.

^oC; ¹H NMR (CDCl₃) δ 7.1 (m, 1 H), 6.8 (m, 1 H), 6.5 (m, 1 H), 4.3 (m, 2 H), 3.0 (s, 3 H).

Anal. Calcd for C₉H₉ClF₃N₃O: C, 40.39; H, 3.39; N, 15.70. Found: C, 40.66; H, 3.53; N, 15.70.

7-Chloro-1,4-dihydro-1-methyl-3-(trifluoromethyl)-1,2,4-benzotriazine (10). One drop of concentrated hydrochloric acid was added to a solution of 1.5 g (0.0056 mol) of trifluoroacetic acid, 2-(2-amino-5-chlorophenyl)-2-methylhydrazide (above) in 20 mL of ethanol. This was warmed briefly (~50 °C) then stored overnight at -10 °C. Solvent was removed in vacuo to give a brown oil which was extracted with 100 mL of 2-methylbutane. Evaporation of the extract gave 1.3 g (93%) of pure product as a yellow powder: mp 85–88 °C; ¹H NMR could not be obtained due to paramagnetic broadening.

Anal. Calcd for C₉H₇ClF₃N₃: C, 43.31; H, 2.83; N, 16.83. Found: C, 43.04; H, 2.71; N, 16.55.

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*), tomato (*Lycopersicon esculentum*), morningglory (*Ipomoea* spp.), and wild mustard (*Brassica kaber*).

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 sulfonate and nonionic surfactants. Toximul S is a hydrophilic emulsifier than when combined with Toximul R provides a superior emulsion for the herbicide formulations. The acetone-ethanol solvent system constituted 8% of the final spray solution, while the Toximul R and S surfactants only constituted 0.2% of the final spray solution. 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 containers 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 test.

The herbicidal activities presented in Table I 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 postemergence activity were retested at 1, 2, and 4 lb/acre on the same six test plants. The herbicidal effects for six compounds with postemergence activity are presented in Table II.

Table III. Preemergence Herbicidal Activity of Prominent Compounds at 1, 2, and 4 lb/Acre on Crops^a

compd	rate, lb/acre	control rating for plants						
		corn	cttn	sybn	whet	sgbt	rice	tmt
1	1	1	1	1	1	4	1	1
	2	1	1	1	1	5	1	2
	4	1	2	2	2	5	4	5
2	1	1	1	1	1	4	2	1
	2	1	1	1	1	5	3	2
	4	1	1	1	3	5	3	5
3	1	1	1	1	1	2	1	2
	2	2	2	2	2	3	1	2
6	1	2	1	1	1	2	1	2
	2	2	2	2	2	2	1	3
	4	2	2	2	1	5	2	3
8	1	1	1	1	1	3	1	1
	2	1	1	1	1	4	2	1
	4	1	1	1	2	4	2	4
10	1	1	1	1	1	3	1	1
	2	1	1	1	1	4	1	3
	4	1	1	1	1	5	1	4
12	1	1	1	1	1	3	1	1
	2	1	1	1	1	3	1	3
	4	1	1	2	3	4	4	3

^a Key for crops: cttn, cotton; sybn, soybean; whet, wheat; sgbt, sugarbeet; tmt, tomato.

Table IV. Preemergence Herbicidal Activity of Prominent Compounds at 1, 2, and 4 lb/Acre on Weeds^a

compd	rate, lb/acre	control rating for weeds								
		lcg	ftm	woa	wmu	rrpw	clq	vel	jw	mgj
1	1	3	1	1	1	2	1	2	1	1
	2	5	5	1	1	4	1	3	1	2
	4	5	5	3	1	5	5	5	5	3
2	1	5	4	1	1	2	5	1	1	1
	2	5	5	1	1	4	5	4	4	2
	4	5	5	3	2	5	5	5	5	1
3	1	3	1	2	1	1	2	2	2	1
	2	4	2	3	2	2	2	2	2	3
	4	1	1	1	2	2	1	1	1	1
6	1	1	1	2	2	3	1	1	3	1
	2	1	1	2	2	3	1	1	3	2
	4	1	3	1	3	2	2	1	3	2
8	1	4	1	1	1	1	3	1	3	1
	2	4	3	1	1	3	4	3	4	1
	4	4	3	1	1	3	4	4	5	1
10	1	1	1	1	5	1	5	3	3	3
	2	2	1	1	4	1	5	3	4	4
	4	3	2	2	4	4	5	4	5	3
12	1	4	3	1	1	1	1	2	1	1
	2	5	5	2	1	3	3	3	3	1
	4	5	5	4	1	4	4	3	4	1

^a Key for weeds: lcg, large crabgrass; ftm, foxtail millet; woa, wild oat; wmu, wild mustard; rrpw, redroot pigweed; clq, common lambsquarters; vel, velvetleaf; jw, jimsonweed; mgj, morningglory.

Several compounds with prominent preemergence activity were retested at 1, 2, and 4 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*), cotton (*Gossypium hirsutum*), sugarbeet (*Beta vulgaris*), soybean (*Glycine max*), wild oat (*Avena fatua*), common lambsquarters (*Chenopodium album*), jimsonweed (*Datura stramonium*), and velvetleaf (*Abutilon theophrasti*). The herbicidal activities presented in Table III A for crops and in Table IV for weeds are control ratings for the 16 species tested at 1, 2, and 4 lb/acre in this preemergence test.

RESULTS AND DISCUSSION

In general, many of these benzotriazine compounds at 8 lb/acre exhibit slight to moderate 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. At 2–4 lb/acre, the 1-methyl- and 1-propyl-1,4-dihydro-1,2,4-benzotriazine-6-carbonitrile compounds and the 1,4-dihydro-1-methyl-1,2,4-benzotriazine-6-carboxylic acid, ethyl ester compound (see Table I) severely injured or killed large crabgrass, foxtail millet, redroot pigweed, wild mustard, and tomato. These compounds appear to be contact herbicides, and no selectivity was observed between the various plant species. Although mode of action studies were not conducted, the postemergence activity of these compounds resembled symptoms exhibited by known substituted phenylurea herbicides.

These compounds at 8 lb/acre also exhibit slight to moderate preemergence herbicidal activity on grass and broadleaf species. These compounds do not prevent germination or emergence of plants. Injury symptoms observed were growth inhibition and 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 benzotriazines are slow-acting as preemergence herbicides. Again, plant injury symptoms observed with a preemergence application of these compounds also resemble symptoms exhibited by known phenylurea herbicides.

Several compounds not included in Table I also were synthesized and tested for herbicidal activity. 1,4-Dihydro-1-methyl-3-(trifluoromethyl)pyrido[3,2-*e*]-1,2,4-triazine monohydrochloride (mp 255–258 °C) only showed slight to moderate activity postemergence at 8, 4, 2, and 1 lb/acre. 2-Formyl-1,2-dihydro-6-(trifluoromethyl)-1,2,4-benzotriazine (mp 202–203 °C) showed slight activity preemergence but was not active postemergence when tested at 8 lb/acre. 1,4-Dihydro-1,4-dimethyl-3,6-bis(trifluoromethyl)-1,2,4-benzotriazine (mp 56–58 °C) was not active at 8 lb/acre either preemergence or postemergence. None of these compounds was nearly as active as the compounds that are prominent in Tables II–IV.

At 1–4 lb/acre, preemergence activity was observed on both monocots and dicots. Several crops such as corn, wheat, rice, cotton, and soybean were tolerant or injured slightly at 4 lb/acre, while several weeds such as large crabgrass, foxtail millet, redroot pigweed, common lamb-quarters, velvetleaf, and jimsonweed were controlled. As for other crops, tomato was moderately to severely injured, while sugarbeet, the most sensitive crop tested, was generally killed at 2–4 lb/acre. Other weeds including wild mustard, wild oat, and moringlory were more tolerant to these compounds and were injured only slightly to moderately at 4 lb/acre.

Although synthetic and stability considerations precluded a total exploration of the activity parameters of this series, several generalizations appear valid. Structural variations that diminish preemergence herbicidal activity have roughly the same effect on postemergence activity. R₁ should be a small alkyl group, such as methyl or *n*-propyl, rather than hydrogen. Preferred R₂ substituents are

hydrogen, methyl, or a small electron-withdrawing group. R₄ should be an electron-withdrawing group, preferably cyano or trifluoromethyl. Alkylation at the 4-position of the triazine ring eliminated all activity in our single example. Variations at R₃, R₅, and R₆ were too few to permit meaningful conclusions.

It should be noted that the ultimate utility of this series is diminished by its paramagnetic character. This was manifested for many of the compounds by severe broadening in portions of the ¹H NMR spectra and was usually reversible by addition of CD₃OD. The presence of an unpaired electron in the case of 1,4-dihydro-1-methyl-3-(trifluoromethyl)-6-cyano-1,2,4-benzotriazine was subsequently confirmed by an ESR experiment. Analogues that exhibited the greatest ¹H NMR broadening also displayed the shortest storage life, occasionally measured in minutes. The most stable compounds had storage lives of weeks at room temperature, with eventual decomposition to malodorous brown tars. Attempts to stabilize these dihydrobenzotriazines via salt formation were unsuccessful.

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Registry No. 1, 130200-63-4; 2, 130200-64-5; 3, 130200-65-6; 4, 130200-66-7; 5, 130200-67-8; 6, 130200-68-9; 7, 130200-69-0; 8, 130246-82-1; 9, 130200-70-3; 10, 130200-71-4; 11, 130200-72-5; 12, 130200-73-6; 13, 130200-74-7; 14, 130200-75-8; 15, 130200-76-9; 16, 130200-77-0; 17, 130200-78-1; 18, 130200-79-2; 19, 130200-80-5; 20, 130200-81-6; 21, 130200-82-7; 22, 130200-83-8; 23, 130200-84-9; 24, 130219-73-7; 25, 130200-85-0; 26, 130200-86-1; 27, 130200-87-2; 28, 130200-88-3; 29, 130200-89-4; 30, 130200-90-7; 31, 130200-91-8; 32, 130200-92-9; 33, 130200-93-0; 3-nitro-4-(1-propylhydrazino)benzotrile, 130200-94-1; *n*-propylhydrazine, 5039-61-2; 4-chloro-3-nitrobenzotrile, 939-80-0; 4-(1-methylhydrazino)3-nitrobenzotrile, 130200-95-2; methylhydrazine, 60-34-4; trifluoroacetic acid, 2-(4-cyano-2-nitrophenyl)-2-propylhydrazide, 130200-96-3; trifluoroacetic anhydride, 407-25-0; trifluoroacetic acid, 2-(2-amino-4-cyanophenyl)-2-propylhydrazide, 130200-97-4; 4-(2-formyl-1-propylhydrazino)-3-nitrobenzotrile, 130200-98-5; trifluoroacetic acid, 2-(2-amino-5-chlorophenyl)-2-methylhydrazide, 130200-99-6.