Table V. Response of Ten Plant Species to Preemergence Applications (Visual Ratings; 1 lb/acre) of Substituted *N,N,α*-Trimethylpyrazole-1-acetamides

Species	9	40	20	16	46
Corn	3	5	1	0	3
Cotton	1	7	2	1	3
Rice	10	9	10	0	9
Soybean	1	6	4	0	1
Barnyardgrass	10	10	7	2	5
Bermudagrass	10	10	10	4	10
Blackgrass	10	10	8	2	6
Johnsongrass	5	7	4	0	5
Tall morningglory	0	0	0	0	0
Velvetleaf	4	0	3	1	2
Averages					
Crops	3.8	6.8	4.3	0.3	4.0
Grassy weeds	8.8	9.3	7.3	2.0	6.5
Broadleaf weeds	2.0	0	1.5	0.5	1.0

Table VI. Compound 9 and 40 Rates (lb AI/acre) Tolerated by Crops (90% of Control Growth) and Required to Control Weeds (90% Inhibition of Growth) in Field Evaluations

	9		40	
Species	Pre	PPI	Pre	PPI
Corn	2.0	>4.0	<0.2	0.3
Cotton	2.0	>4.0	0.2	0.2
Peanut	>4.0	>4.0		
Sorghum	1.0	0.9	0.2	0.2
Soybean	2.0	>4.0	0.8	0.9
Sugarbeet	1.0	1.1	<0.2	0.2
Tomato	>4.0	>4.0	>4.0	>4.0
Common ragweed			1.7	1.9
Lambsquarters	3.2	1.7	0.5	0.7
Redroot pigweed	1.2	1.2	<0.2	<0.2
Stinkgrass			1.7	1.8
Yellow mustard	3.0	2.0		
Average				
Crops	2.3	3.1	0.9	1.0
Weeds	2.5	1.6	1.0	1.2

similar. Compound **16** was less phytotoxic to both crops and weeds than compound **46**.

Activity of compounds **9** and **40** was further evaluated in preplant incorporated and preemergence field applications. Preemergence applications of compound **9** were more phytotoxic to soybean than the incorporated applications (Table VI). The incorporated treatments were more efficacious than the surface treatments. Corn, cotton, peanut, soybean, and tomato exhibited tolerance to compound **9** at rates (1.6 to 2.5 lb/acre) that selectively controlled some annual weeds. Compound **40** was more phytotoxic to both crops and weeds than compound **9**, as expected from greenhouse results. Activity of compound **40** was not altered by application method. Only tomato exhibited tolerance to compound **40** at weed control rates (<2.0 lb/acre). Susceptible plants usually emerged from soil treated with these amides; but they remained stunted, often in the cotyledonary leaf stage. Roots of the injured plants were always bulbous and abnormally short. Secondary roots were usually highly proliferated. These injured plants usually did not die unless exposed to environmental stresses such as severe drying during hot weather.

These results suggest that compound **9** might selectively control annual weeds in a major food crop.

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Herbicidal Activity and Redox Properties of 3-Aryl-6-(perfluoroalkyl)-1,2,4,5-tetrazines and 1,2-Dihydro Derivatives

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1,2-Dihydro-3-aryl-6-(perfluoroalkyl)-*s*-tetrazines (VI) and 3-aryl-6-(perfluoroalkyl)-*s*-tetrazines (VII) show postemergence activity against broadleaf weeds, with little activity on grasses. The responses to light and plant symptoms resulting from foliar applications of VI and VII are similar to those of redox herbicides such as paraquat. The chemical behavior supports this view, i.e., *s*-tetrazines are reversibly reduced to 1,2-dihydro-*s*-tetrazines. The *s*-tetrazines and their 1,2-dihydro derivatives are phytotoxic only when treated plants are in the light; they were relatively inactive in preemergence herbicide tests. In aqueous solution, especially at pH above 7, both VI and VII decompose to redox inactive products that are herbicidally inactive. In general, electron-withdrawing substituents tend to stabilize the tetrazine ring and increase herbicidal activity.

With the discovery of the phytotoxic properties of the dipyridylium herbicides, paraquat and diquat, and by the knowledge that the one-electron transfer which is reversed by oxygen is intimately involved in their mode of biological action (Homer et al., 1960) interest in redox systems has increased. Investigations in our laboratories showed that 3-aryl-6-(perfluoroalkyl)-1,2,4,5-tetrazines and their 1,2-

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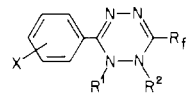
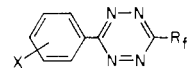
Table I. 1,2-Dihydro-3-aryl-6-(perfluoroalkyl)-1,2,4,5-tetrazines: Properties and Test Results



Compd	X	R^1	R^2	R_f	Mp, °C	Phytotoxicity index from foliar spray[a] Large crabgrass 1[b]	Large crabgrass 2[c]	Pigweed 1	Pigweed 2
1	H	H	H	CF_3	159-161	9	9	9	9
2	H	H	CH_3	CF_3	133-136	0	1	8	8
3	H	CH_3	CH_3	CF_3	75-78	0	0	0	0
4	H	H	H	C_2F_5	161-163	9	9	9	9
5	H	H	H	C_3F_7	162-164	5	9	9	9
6	3-CH_3	H	H	CF_3	116-120	9	9	9	9
7	4-CH_3	H	H	CF_3	188-191	9	9	9	9
8	3,4-$(CH_3)_2$	H	H	CF_3	149-152	9	9	9	9
9	3,4-CH=CHCH=CH—	H	H	CF_3	203-205	8	9	9	9
10	4-$C(CH_3)_3$	H	H	CF_3	116-119	7	9	9	9
11	4-Cl, 3,5-$(CH_3)_2$	H	H	CF_3	197-200	9	9	9	9
12	2-F	H	H	CF_3	155-157	0	4	6	9
13	4-Cl	H	H	CF_3	175-177	9	9	9	9
14	4-Cl	H	H	C_2F_5	157-159	9	9	9	9
15	4-Cl	H	H	C_3F_7	140-143	9	9	9	9
16	3-CF_3	H	H	CF_3	132-134	6	9	9	9

[a] 0 = no effect; 9 = complete control. [b] Rate 1: sprayed to run-off with 250 ppm active ingredient. [c] Rate 2: sprayed to run-off with 2500 ppm active ingredient.

Table II. 3-Aryl-6-(perfluoroalkyl)-1,2,4,5-tetrazines: Properties and Test Results



Compd	X	R_f	Mp, °C	Phytotoxicity index from foliar spray[a] Large crabgrass 1[b]	Large crabgrass 2[c]	Pigweed 1	Pigweed 2
17	H	CF_3	154-156	8	8	9	9
18	H	C_2F_5	117-120	5	9	9	9
19	H	C_3F_7	87-89	7	9	7	9
20	3-CH_3	CF_3	64-66	8	9	9	9
21	4-CH_3	CF_3	152-154	9	9	9	9
22	3,4-$(CH_3)_2$	CF_3	65-67	9	9	9	9
23	3,5-$(CH_3)_2$	CF_3	125-128	2	9	9	9
24	3,4-CH=CHCH=CH—	CF_3	189-192	8	8	9	9
25	4-$C(CH_3)_3$	CF_3	73-75	9	9	9	9
26	4-Cl 3,5-$(CH_3)_2$	CF_3	133-135	9	9	9	9
27	2-F	CF_3	68-71	0	3	0	9
28	4-Cl	CF_3	92-94	9	9	9	9
29	4-Cl	C_2F_5	84-86	6	9	9	9
30	4-Cl	C_3F_7	62-64	8	9	9	9
31	3-CF_3	CF_3		1	9	7	9
32	3,4-Cl_2	CF_3	90-92	7	9	9	9
33	4-NO_2	CF_3	129-131	7	7	9	9

[a,b,c] Defined as in Table I.

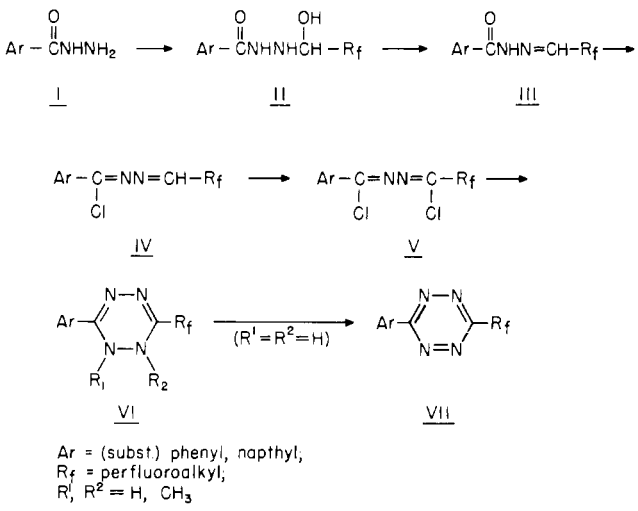
dihydro derivatives were active as herbicides (Pilgram and Skiles, 1975). Some correlations of herbicidal activity and redox properties with change of position and nature of substituents in the *s*-tetrazines have emerged from these studies.

MATERIALS AND METHODS

Chemical Methods. Treatment of a variety of aroylhydrazides, I (Scheme I), with perfluorinated aliphatic aldehydes (or their hydrates or hemiacetals) gave 2-(1-hydroxyperfluoroalkyl)aroylhydrazides, II, from which perfluorinated aliphatic aldehyde aroylhydrazones, III, were produced by dehydration (thionyl chloride or heat). Treatment of both II and III with thionyl chloride at reflux produced 1-aryl-1-chloro-4-(perfluoroalkyl)azines, IV, which on treatment with chlorine in carbon tetrachloride or glacial acetic acid afforded 1-aryl-1,4-dichloro-4-(perfluoroalkyl)azines, V. Reaction of V with hydrazine hydrate, methylhydrazine, or 1,2-dimethylhydrazine gave the 1,2-dihydro-3-aryl-6-(perfluoroalkyl)-1,2,4,5-tetrazines, VI, from which the 3-aryl-6-(perfluoroalkyl)-1,2,4,5-tetrazines, VII, were obtained by oxidation with ferric chloride, hydrogen peroxide, or sodium nitrite.

The methods for the preparation of 1,2-dihydro-3-aryl-6-(perfluoroalkyl)-1,2,3,4-tetrazines, VI, and 3-aryl-6-(perfluoroalkyl)-1,2,4,5-tetrazines, VII, are described below for the synthesis of 1,2-dihydro-3-(4-chlorophenyl)-6-(heptafluoropropyl)-1,2,4,5-tetrazine, **15**, and 3-(4-chlorophenyl)-6-(heptafluoropropyl)-1,2,4,5-tetrazine, **30**; these methods were applicable for the synthesis of all *s*-tetrazines, **17–33** (Table II), and 1,2-dihydro derivatives, **1–16** (Table I).

Scheme I



1,2-Dihydro-3-(4-chlorophenyl)-6-(heptafluoropropyl)-1,2,4,5-tetrazine (15). *a. Heptafluorobutyraldehyde-4-chlorobenzoylhydrazone.* A mixture containing 84.5 g (0.50 mol) of 4-chlorobenzhydrazide, 20 drops of concentrated hydrochloric acid, and 140 g (0.62 mol) of heptafluorobutyraldehyde ethyl hemiacetal in 600 mL of ethanol was refluxed for 18 h. The cooled reaction mixture was filtered to give 145 g (83%) of product, mp 138–140 °C. Anal. Calcd for $C_{11}H_6ClF_7N_2O$: C, 37.7; H, 1.7; N, 8.0. Found: C, 37.6; H, 1.6; N, 8.0.

b. 1-Chloro-1-(4-chlorophenyl)-4-(heptafluoropropyl)azine. A solution containing 144 g (0.41 mol) of the above hydrazone in 500 g of thionyl chloride and ten drops of dimethylformamide was refluxed for 8 h and concentrated under reduced pressure. The residual amber liquid was distilled to give 144.5 g (96%) of the chloroazine; bp 73–75 °C (0.03 mm). Anal. Calcd for $C_{11}H_5Cl_2F_7N_2$: C, 35.8; H, 1.4; Cl, 19.2; N, 7.6. Found: C, 35.8; H, 1.4; Cl, 19.0; N, 7.6.

c. 1-(4-Chlorophenyl)-1,4-dichloro-4-(heptafluoropropyl)azine. A solution containing 140 g (0.379 mol) of the above chloroazine in 250 mL of carbon tetrachloride was saturated at 30 °C with chlorine. After 20 days, the reaction mixture was concentrated to a yellow oil, 149 g (97%). Anal. Calcd for $C_{11}H_4Cl_3F_7N_2$: N, 6.9. Found: N, 6.8.

d. Preparation of 15. To a chilled (0 °C) solution of 139 g (0.344 mol) of the above crude dichloroazine in 700 mL of ethanol was added dropwise (15 min) with stirring a solution of 35.1 g (1.107 mol) of 95% hydrazine in 200 mL of ethanol. After 3 h at ambient temperature, the reaction mixture was concentrated under reduced pressure, washed well with water, dried, and recrystallized from benzene–hexane (1:1) to give 59 g (47%) of **15**, a yellow solid; mp 140–142 °C. Anal. Calcd for $C_{11}H_6ClF_7N_4$: C, 36.4; H, 1.7; N, 15.4. Found: C, 36.4; H, 1.7; N, 15.3.

3-(4-Chlorophenyl)-6-(heptafluoropropyl)-1,2,4,5-tetrazine, 30. To a cooled (5 °C) solution containing 34 g (93.8 mmol) of **15** in 200 mL of glacial acetic acid was added dropwise with stirring a solution containing 34 g (0.50 mol) of sodium nitrite in 75 mL of water. The reaction mixture which became deep red in color was stirred for 1 h at ambient temperature, poured into 1 L of ice–water, and filtered. The filter cake was washed with water, dried, and recrystallized from hexane to give 31 g (93%) of **30**, a purple-red crystalline solid; mp 62–64 °C. Anal. Calcd for $C_{11}H_4ClF_7N_4$: C, 36.6; H, 1.1; N, 15.5. Found: C, 36.7; H, 1.1; N, 15.5.

Biological Methods. The postemergence herbicidal activity was detected by spraying the foliage of 10-day-old pigweed plants and 7-day-old crabgrass plants to run-off with 250 and 2500 ppm solutions of the test compounds designated rate 1 and rate 2 in Tables I and II. The sprayed plants were held in chambers with fluorescent light (43 000 lux) at 21–23 °C and watered as needed for 10 days twice daily. Phytotoxicity of the test compound was then rated visually on a 0–9 scale, with 0 indicating no effect, 9 indicating complete control.

Compounds showing appreciable activity in the initial postemergence screen (Tables I and II) were included in additional tests involving variable rate spray applications. Each chemical was applied in a logarithmic dilution from a maximum of 10 lb/acre to a minimum of 0.02 lb/acre to the foliage of seedlings planted in rows in 3-in. pots kept in standard 6 × 24 in. trays. Results with these tests evaluated 2 weeks after foliar treatment are presented in Tables III and IV.

To gain insight into the mode of action of the *s*-tetrazines, a special laboratory test was designed to compare the activity of one analogue, **1**, with Paraquat-Cl (1,1-dimethyl-4,4′-dipyridylium dichloride) and 2,4-dinitrophenol. Plantings of pigweed and crabgrass were sprayed to run-off at the rates of 1 and 10 lb/acre. The pigweed was in the four-leaf stage and the crabgrass in the early two-leaf stage.

On the day of treatment half the plants were kept in a dark chamber for 5 h immediately prior to treating. After treatment these same plants were placed in the dark chamber for 24 h at which time they were evaluated. The

Table III. Response of Four Broadleaf Weed Species to Foliar Applications of 1,2-Dihydro-1,2,4,5-tetrazines[a]

Compd	Curly dock	Fiddleneck	Wild mustard	Pigweed
1		+5.0	3.5	0.9
4		−0.5	−0.5	−0.5
5		−0.5	−0.5	−0.5
6	+5.0		−0.6	−0.6
7	2.8		−0.6	0.7
8	+10.0		2.4	5.6
9	+5.0		+5.0	1.2
10	+5.0		−0.6	0.8
11	+5.0		+5.0	+5.0
12	+5.0		+5.0	1.2
13		−0.5	−0.5	−0.5
14			−0.02	−0.02
15			−0.02	−0.02
16	+2.0		0.6	0.5

[a] Given as lb/acre causing 90% growth inhibition. The symbols (+) and (−) indicate respectively "greater than" and "less than". Compounds were applied with continuous logarithmic dilution within the range of 10 lb/acre to 0.02 lb/acre.

Table IV. Response of Four Broadleaf Weed Species to Foliar Applications of *s*-Tetrazines[a]

Compd	Curly dock	Fiddleneck	Wild mustard	Pigweed
17		−1.0	−1.0	−1.0
18		−0.5	−0.5	−0.5
19	+5.0		−0.5	2.8
20	+5.0		−0.5	−0.5
21	+5.0		−0.6	−0.6
22	+10.0		−1.3	−1.3
24	+5.0		+5.0	+5.0
25	+5.0		−0.6	0.9
26	+5.0		−0.6	0.8
27	+5.0		3.8	2.3
28		−0.5	−0.5	−0.5
29			−0.02	0.02
30			0.08	−0.02
32	+5.0		+5.0	1.6

[a] Defined as in Table III.

Table V. Effect of Light on Herbicidal Activity of 1,2-Dihydro-3-phenyl-6-(trifluoromethyl)-1,2,4,5-tetrazine (1) in Foliar Applications[a]

	Continuous light				Continuous dark				Dark then light			
	Crabgrass		Pigweed		Crabgrass		Pigweed		Crabgrass		Pigweed	
Compd	1[b]	10[b]	1	10	1	10	1	10	1	10	1	10
1[c]	9	9	9	9	0	0	0	0	9		9	
Paraquat-Cl[d]	9	9	9	9	0	0	0	0	9		9	
2,4-Dinitrophenol[c]	9	9	9	9	9	9	9	9	9		9	
Control	0	0	0	0	0	0	0	0	0		0	

[a] 0 = no effect; 9 = complete control. [b] Rate applied in lb/acre. [c] Solvent, acetone. [d] Solvent, water.

other half of the plants were kept in the light continuously before and after treatment. Those that had been in the dark were placed in the light after reading at 24 h and observed for regrowth and other changes. The results are recorded in Table V.

Weed species mentioned in this paper are: large crabgress (*Digitaria sanguinalis*), pigweed (Amaranthus spp., mixture of species), barnyardgrass (*Echinochloa crusgalli*), downey brome (*Bromus tectorum* L.), curly dock (*Rumex crispus* L.), fiddleneck (*Amsinckia douglasiana*), wild mustard (*Brassica arvensis*).

Physical-Chemical Methods. Polarographic measurements were obtained using a Radiometer Polariter (Type PO4) together with a Dropping Mercury Electrode Assembly (E65) and a Drop Life Timer (DLT-1). Polarograms were measured by the Tast method in which the current is recorded only during the final part of the mercury drop life. *s*-Tetrazines and 1,2-dihydro derivatives were examined as ca. 10^{-4} M solutions in 25% (v/v) ethanolic 0.1 M potassium phosphate buffer containing 0.002% (v/v) Triton X-100 as a polarographic maximum suppressor and at a temperature of 25 °C. The compounds were insufficiently soluble to be examined in water alone. Solutions were prepared by dissolving the material in 25 mL of ethanol and adding 50 mL of 0.2 M potassium phosphate (pH 6.39) and then water up to the 100 mL mark of a volumetric flask. The final pH was 7.00. As oxygen polarographic waves interfere with the measurements, solutions were deoxygenated by bubbling with nitrogen for at least 15 min, after which the above system had no interfering waves in the +0.1 to −1.7 V (SCE) region (+0.35 to −0.145 V, NHE scale).

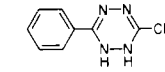
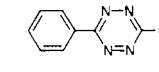
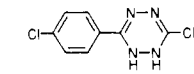
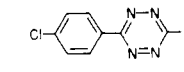
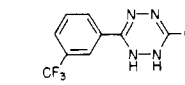
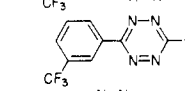
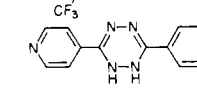
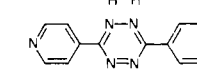
The half-wave potentials ($E_{1/2}$) are the mean values calculated from polarograms obtained with both decreasing and increasing voltage axes. $E_{1/2}$ values on the SCE scale have been converted to the NHE scale by addition of 248 mV, the difference between the two scales at 20 °C using aqueous solutions. It has been assumed that this difference is the same for the 25% ethanolic solutions used here, and consequently the $E_{1/2}$ (NHE) values quoted are precise but not necessarily accurate (Table VI).

The rate of decomposition of 3-phenyl-6-(trifluoromethyl)-1,2,4,5-tetrazine, **17**, was calculated from delayed scan spectra obtained using Unicam SP-8000 and SP-800 spectrophotometers.

RESULTS AND DISCUSSION

For the 1,2-dihydro-*s*-tetrazines, VI, and *s*-tetrazines, VII, the data in Tables I, II, III, and IV indicate sufficient activity only on broadleaf weeds. In the VI series, 1,2-disubstitution, as in **3**, was detrimental to activity; the corresponding monosubstituted analogue, **2**, was moderately active, whereas the unsubstituted VI compounds in which $R^1 = R^2 = H$ were most active. None of the compounds VI and VII where the substituent on phenyl is in the ortho position relative to the tetrazine ring possessed activity. Para substitution resulted in highest activity, slightly more so than meta substitution. In general, lower activity appears to be associated with the alkyl substituted members of VI and VII, whereas electron-withdrawing groups increased overall activity. For example, the 4-chlorine substituent on phenyl of **13** greatly increased activity on broadleaf weeds and produced some activity on grasses. In a given series, VI or VII, the level of activity of the pentafluoroethyl analogue ($R_f = C_2F_5$) was higher than that of the heptafluoropropyl ($R_f = C_3F_7$) and trifluoromethyl ($R_f = CF_3$) analogues.

Table VI. Polarographic Half-Wave Potentials, $E^1/_2$, of *s*-Tetrazines and 1,2-Dihydro Derivatives in 25% (v/v) Ethanolic Potassium Phosphate Buffer (0, 1 M, pH 7,0)

Compd	Structure	$E^1/_2$ (vs. NHE) in mV
1		+102
17		+100
13		+94
28		+98
16		+113
31		+116
34[a]		+57
35[a]		+55

[a] Prepared according to Dallacker (1961).

The response to light and plant symptoms resulting from foliar applications of 1 (Table V) were just like those with Paraquat-Cl and quite different from the effects of 2,4-dinitrophenol. Compound 1 and Paraquat-Cl were phytotoxic only when treated plants were in the light.

The mode of action of paraquat ion, denoted BP^{2+} in eq 1 involves biochemical one-electron reduction to the monocationic radical $BP^{+}\cdot$, which can then be oxidized back to BP^{2+} by molecular oxygen. In principle, both reduction steps of eq 1 are possible; however, the reducing

$$BP^{2+} \overset{+e}{\rightleftarrows} BP^{+}\cdot \overset{+e}{\rightleftarrows} BP \qquad (1)$$

power of plant photosystem I is only sufficient to convert BP^{2+} to $BP^{+}\cdot$. The redox potentials of the $BP^{2+}/BP^{+}\cdot$ couples for the herbicidally active dipyridylium salts are all in the range of −325 to −500 mV (vs. the normal hydrogen electrode, NHE), i.e., between the redox potentials of the $NADP^+$/NADPH and NAD^+/NADH couples. For example, paraquat is reversibly reduced to the monocation

radical with an $E_{1/2}$ of -432 mV (vs. NHE) (Elofson and Edsberg, 1957), the latter value corresponds to -680 mV vs. the saturated calomel electrode (SCE). On the other hand, the reversible polarographic half-wave potential for both $NADP^+/NADPH$ and $NAD^+/NADH$ couples is -320 mV (NHE) at pH 7 and 30 °C (Rodkey, 1955; Rodkey and Donovan, 1959). As the dipyridylium salts appear to interact with photosystem I between $NADP^+$ and P430, photosynthesis research workers have thought that redox herbicide activity would be confined to those compounds with a potential between -325 mV (i.e., $NADP^+/NADPH$ couple) and ca. -500 mV (vs. NHE), which is the potential of the most reducing compound (known as P430) of photosystem I. Recent experiments (Dawson, 1972) with naphtho- and heterocyclic quinone herbicides (Entwistle and Devlin, 1971, 1972); (Entwistle et al., 1972) have shown that redox potentials for these quinones are significantly more positive (+70 to -225 mV) than those for the dipyridylium herbicides, which have a similar mode of action. Substituted 1,4-benzo- and naphthoquinones play a vital role in the respiratory and photosynthetic elements of biological systems (Morton, 1971). These quinones, acting as electron acceptors, are reversibly reduced to hydroquinones (Morton, 1971; Schmidt-Mende and Rumberg, 1968) or possibly semiquinones (Cox et al., 1970; Stiehl and Witt, 1969) when functioning in vivo. The chloroplast reduction process of a quinone, denoted Q in eq 2, therefore also involves transfer of protons as well as electrons. This function is linked to the formation of adenosine triphosphate that occurs during respiration

$$Q \overset{+e\ +H}{\rightleftharpoons} QH\cdot \overset{+e\ +H}{\rightleftharpoons} QH_2 \qquad (2)$$

(Morton, 1971) and photosynthesis (Böhme and Cramer, 1972).

The range of redox potentials for a number of tetrazines is much more positive (Table VI) than those found for both the dipyridylium salts and the quinones. The half-wave potentials of the tetrazines and their 1,2-dihydro derivatives are the same (within experimental error), indicating the thermodynamic reversibility of the redox process. As expected, no waves between +135 mV and +55 mV were found in the polarograms of the N^1-monomethyl- and N^1,N^2-dimethyl-1,2-dihydro-*s*-tetrazines, **2** and **3**, as reaction analogous to eq 2 is not applicable. In contrast to the reduced forms of the dipyridylium and quinone herbicides, the 1,2-dihydro-*s*-tetrazines, denoted TH_2 in the cyclic scheme, are only slowly oxidized by molecular oxygen in aqueous solution. Thus, the cyclic process should be much slower than for dipyridylium salts in chloroplasts, and the rate of herbicidal activity should be reduced accordingly.

Another difference in behavior concerns the instability of the tetrazines in aqueous solution, especially as the pH is increased above 7. Although stable in ethanol, the tetrazines decompose in 25% ethanolic phosphate buffer. For example, in ethanol the electronic spectrum of **17** has two peaks at 273 nm (ϵ 18 600) and at 524 nm (ϵ 480); in 25% ethanolic phosphate buffer these maxima shift to 276 and 512 nm, respectively. At pH 7.0, the 276 and 512 nm maxima gradually decrease in intensity and isosbestic points appear at 261 nm and also at about 300 and 310 nm. As the reaction proceeds the last two points disappear and that at 261 nm becomes less well defined; a new isosbestic point appears at ca. 230 nm. It is evident that at least one intermediate is formed between **17** and the final product, which has a maximum at 252 nm. In 25% ethanolic potassium phosphate, the half-life of a 10^{-4} M solution of **17** at 25 °C is: 9.0 h at pH 6.25, 3.3 h at pH 7.00, and ca. 0.5 min at pH 8.00.

In the approximately pH 7 environment of a chloroplast, the tetrazines and dihydrotetrazines should decompose to redox inactive products and it is not surprising that treated plants can slowly recover in spite of the initial scorching. That the decomposition products are indeed herbicidally inactive has been indicated by the observation that a solution of **17** which had been kept at pH 7 for 24 h showed no herbicidal activity when applied to crabgrass and pigweed foliage at a dosage of 1 lb/acre.

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