peak areas to determine relative mole percentages. Material balances, *i.e.*, (olefin$_1$ + cyclopropane$_1$)/(olefin$_2$ + cyclopropane$_2$) = olefin$_1$ (init)/olefin$_2$ (init) were satisfactory, indicating no detectable losses due to side reactions.

Several runs were made with many of the olefins having relative rates close to that of cyclohexene. Reproducibility was good in these cases (±3%), with individual point variations within a run having an average deviation of ±5%. Deviations were somewhat larger with olefins of more dissimilar reactivity. Data were treated by the usual first-order rate expression. No trends in relative rate ratios were observed when points were taken at various stages of reaction.

Registry No.—**1**, 591-49-1; **2**, 1674-10-8; **3**, 591-47-9; **4**, 3742-42-5; **5**, 14072-82-3; **6**, 2228-98-0; **7**, 3685-00-5; **8**, 14116-67-7; **9**, 14072-86-7; **10**, 591-48-0; **11**, 14072-87-8; **12**, 5132-52-5; **13**, 590-66-9; **14**, 142-29-0; **15**, 693-89-0; **16**, 498-66-8; **17**, 628-92-2; **18**, 100-42-5; **19**, 771-98-2; **20**, 95-13-6; iodomethylzinc iodide, 4109-94-8.

1-Aryltetrazoles. Synthesis and Properties

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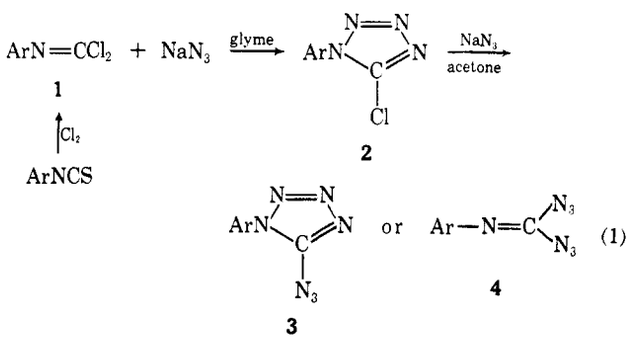
Synthetic routes to 1-aryltetrazoles were studied; the reaction of sodium azide with N-aryldichloroazomethines in dimethoxyethane solvent provides a new general synthesis for 1-aryl-5-chlorotetrazoles. A number of reactions of 1-aryltetrazoles are reported, including rearrangements and an opening of the tetrazole ring. The 1-tetrazolyl group and its 5-substituted derivatives are inductively strongly electron withdrawing (like nitro) but show only small resonance interactions, which vary with the 5 substituent. Four characteristic infrared bands between 950 and 1300 cm^{-1} are assigned to the 1-aryltetrazole system. The molecular structure of 1-aryltetrazoles is discussed on the basis of the infrared and electronic properties.

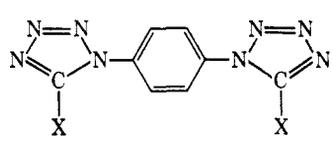
Tetrazoles have been studied extensively since they were first described in 1885[2,3] and have been used in a variety of synthetic and mechanistic programs.[3-5] 1-Aryltetrazoles have been prepared by addition of azide ion to isonitriles and by the reaction of diazonium salts with diformylhydrazine,[3] but with the exception of studies by Fallon and Herbst[6] no generally useful synthesis of 1-aryltetrazoles and their 5-substituted derivatives has been developed.

A. Synthesis. 1. 1-Aryl-5-chloro- and 1-Aryl-5-azidotetrazoles.—We now report a convenient synthesis of 1-aryl-5-chlorotetrazoles from the reaction of N-aryldichloroazomethines (**1**) with sodium azide. In glyme (1,2-dimethoxyethane) as solvent, the chlorotetrazole **2** is isolated in almost quantitative yield, but as was previously reported by Pel'kis and Dunaevs'ka[7a] for N-phenyldichloroazomethine, the use of acetone as solvent leads directly to the 1-aryl-5-azidotetrazole. Similarly when 1-phenyl-5-chlorotetrazole (**2**, Ar = C_5H_6) is treated with sodium azide in acetone, 1-phenyl-5-azidotetrazole is produced[7] (eq 1). Spectral studies, which will be discussed below, suggest that this product has the assigned tetrazole structure **3** rather than the azomethine form **4**, although under certain conditions the two forms may be in equilibrium.



(1)

A large number of N-aryldichloroazomethines can be readily converted to the corresponding 1-aryl-5-chlorotetrazoles by the azide reaction in glyme; in the present study, unsubstituted and nitro- and fluoro-substituted derivatives **2** (Ar = C_6H_5, *m*-, and *p*-C_6H_4F, *o*-,*m*-, and *p*-$C_6H_4NO_2$) as well as the bis derivative **5** have been prepared (see Table I). A



5, X = Cl
6, X = N_3

number of azidotetrazoles was also prepared but not studied further because of poor stability (*e.g.*, **6** is extremely shock sensitive and explodes on rubbing with a spatula.)

On the basis of our observations of this reaction, we consider the mechanisms given in Scheme I to be the most probable and prefer course a. Azide ion reacts rapidly with the dichloroazomethine **1** (probably by an addition–elimination process) to form the chlorotetrazole **2**. The reaction of **2** with azide is considerably slower, but takes place readily in acetone in which the nucleophilic properties of azide ion are enhanced.[8] When freshly precipitated (activated) sodium azide is

(1) This work was presented in part at the 152nd National Meeting of the American Chemical Society, New York, N. Y., Sept 1966.

(2) J. A. Bladin, *Ber.*, **18**, 1544 (1885).

(3) (a) F. R. Benson, *Chem. Rev.*, **41**, 1 (1947); (b) F. R. Benson in "Heterocylic Compounds," R. C. Elderfield, Ed., John Wiley and Sons, Inc., New York, N.Y., 1967, p 1.

(4) (a) R. Huisgen, *Proc. Chem. Soc.*, 357 (1961); (b) R. Huisgen, J. Sauer, and M. Seidel, *Ann.*, **654**, 146 (1962); (c) W. J. Musliner and J. W. Gates, *J. Am. Chem. Soc.*, **88**, 4271 (1966).

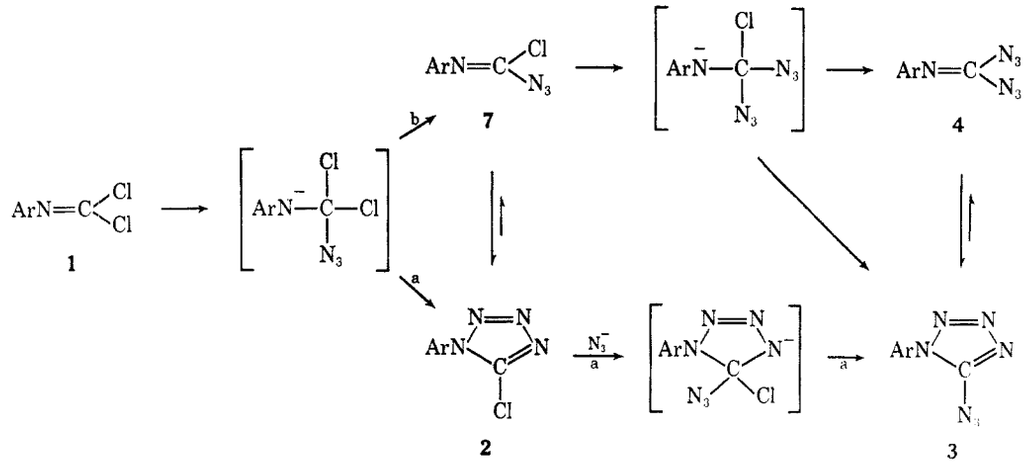
(5) (a) C. Temple, Jr., and J. A. Montgomery, *ibid.*, **86**, 2946 (1964); (b) R. Fusco, S. Rossi, and S. Maiorana, *Tetrahedron Letters*, 1965 (1965); (c) J. H. Boyer and E. J. Miller, *J. Am. Chem. Soc.*, **81**, 4671 (1959).

(6) F. G. Fallon and R. M. Herbst, *J. Org. Chem.*, **22**, 933 (1957)

(7) (a) P. S Pel'kis and Ts. S. Dunaevs'ka, *Mem. Inst. Chem. Acad. Sci. Ukr. SSR*, **6**, 163 (1940); *Chem. Abstr.*, **34**, 5829 (1940); (b) R. Stolle, K. Ehrmann, D. Rieder, H. Wille, H. Winter, and F. Henke-Stark, *J. Prakt. Chem.*, **134**, 282 (1932).

(8) A. J. Parker [*J. Chem. Soc.*, 1328 (1961)] notes that SNAr reactions of azide may occur more than 10^4 times faster in dipolar aprotic solvents such as acetone than in methanol or water.

SCHEME I



used, much more rapid reactions are observed. Under these conditions the active nucleophile may not be free azide ion in solution but rather azide ion attached to a catalytic surface.

Stolle[7b] notes that while **2** reacts with hot aqueous potassium hydroxide, it is unaffected by ethanolic silver nitrate. We have verified this observation. The intervention of azidoazomethine species **4** and **7** in all of these reactions (see Scheme I) cannot be ruled out, but no trace of the normally powerful azide absorption was detected in the infrared spectra (both solid phase and in a variety of solvents) of nine examples of 1-aryl-5-chlorotetrazoles (**2**). Thus the equilibrium (if any) between **2** and **7** strongly favors **2**.

1-Phenyl-5-chlorotetrazole was prepared originally by Stolle[9] by treatment of 1-phenyltetrazole with mercuric acetate followed by chlorine. It was also prepared by diazotizing 1-phenyl-5-aminotetrazole in hydrochloric acid in the presence of copper powder.[7b] Both of these older routes are considerably inferior to the present method which provides a convenient route to many arylchlorotetrazoles from the corresponding aniline derivative.

$$ArNH_2 \rightarrow ArNCS \rightarrow 1 \rightarrow 2$$

2. 1-Aryltetrazoles.—Although the reaction of aryldichloroazomethines with sodium azide provides a convenient and high-yield route to 5-azido- and 5-chloro-1-aryltetrazoles, routes to 1-aryltetrazoles unsubstituted in the 5 position were also needed for another program. Particularly desired were *ortho*-substituted derivatives. The reaction of aryldiazonium salts with diformylhydrazine[10] was reported to give certain 1-aryltetrazoles in fair to modest yields, but like other workers[6] we found the procedure to be generally unsatisfactory. Direct arylation of tetrazole with *o*-nitrochlorobenzene or *o*-nitrofluorobenzene was also not successful in contrast to the corresponding arylation of 1,2,3-triazole.[11]

A convenient route to a variety of substituted 1-aryltetrazoles was developed from the oxidative desulfurization of 5-mercapto-1-aryltetrazoles.[12] As

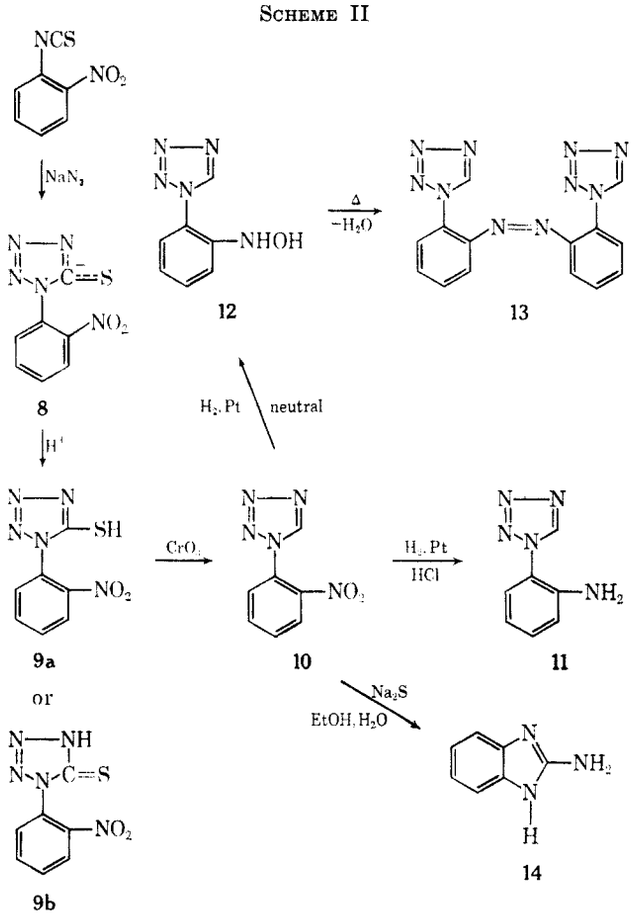
(9) R. Stolle and F. Henke-Stark, *J. Prakt. Chem.*, **124**, 261 (1930).

(10) O. Dimroth and G. deMontnollin, *Ber.*, **43**, 2907 (1910).

(11) R. A. Carboni, J. C. Kauer, W. R. Hatchard, and R. J. Harder, *J. Am. Chem. Soc.*, **89**, 2626 (1967).

(12) M. Freund and T. Paradies [*Ber.*, **34**, 3110 (1901)] reported the oxidative desulfurization of 1-phenyltetrazole-5-thiol.

SCHEME II



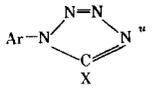
shown in Scheme II,[13] *o*-nitrophenyl isothiocyanate reacts rapidly with warm aqueous sodium azide[14] to form the 1-(*o*-nitrophenyl)tetrazole thiolate anion **8**, which, on acidification, gives the unstable mercaptotetrazole **9**.[15] Chromic acid oxidation of **9** yields

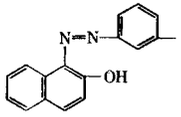
(13) In this phase of the work, *o*-nitrophenyl derivatives were studied more extensively and consequently will be used in the discussion, but the majority of reactions have also been applied to other aryl derivatives.

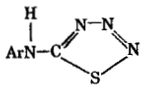
(14) Excessive heating of the solution must be avoided.

(15) (a) E. Lieber, C. N. R. Rao, C. N. Pillai, J. Ramachandran, and R. D. Hites [*Can. J. Chem.*, **36**, 801 (1958)] have reported that the infrared spectra of these compounds in the solid state support the tetrazolinethione formulation **9b** rather than the tautomeric mercaptotetrazole **9a**. Our spectral correlations also suggest that these compounds are not normal 1-aryltetrazoles. However, for convenience in tabulation, the 5-mercaptotetrazole nomenclature will be maintained. Similar arguments have been made for the existence of 5-hydroxy-1-aryltetrazoles in the tautomeric tetrazolin-5-one (lactam) form.[15b] (b) J. P. Horwitz, B. E. Fisher, and A. J. Tomasewski, *J. Am. Chem. Soc.*, **81**, 3076 (1959).

TABLE I
SYNTHESES AND PROPERTIES OF 1-ARYLTETRAZOLES AND THIATRIAZOLES



Ar	X	Mp,[a] °C	Solvent for recrystln	Method of prepn,[b] % yield	Ultraviolet solvent[c] λmax, mμ	Ultraviolet solvent[c] εmax	Formula	Calcd, % C	Calcd, % H	Calcd, % N	Calcd, % Other	Found, % C	Found, % H	Found, % N	Found, % Other
					A. 1-Aryltetrazoles										
C_6H_5	Cl	123.4–124.6[d]	Benzene–hexane	A1 (92)	227 (E)	6040	$C_7H_5ClN_4$	46.6	2.79	31.1	Cl 19.6	46.6	2.94	31.3	19.3
m-FC_6H_4	Cl	104–105	Benzene–hexane	A1 (98)	264 (I)	1520	$C_7H_4ClFN_4$	42.3	2.03	28.2	F 9.6	42.0	2.14	28.1	9.6
					227	7040									
p-FC_6H_4	Cl	88	Benzene–hexane	A1 (79)	228 (I)	6440	$C_7H_4ClFN_4$	42.3	2.03	28.2	F 9.6	42.2	2.25	28.2	9.7
o-$O_2NC_6H_4$	Cl	88.8–89.6	Benzene–hexane	A1 (73)[e]	251 (E)	5660	$C_7H_4ClN_5O_2$	37.3	1.79	31.1	Cl 15.7	37.7	2.11	30.8	15.4
m-$O_2NC_6H_4$	Cl	130.4–132.2	Benzene–hexane	A1 (84–99)	255 (E)	7280	$C_7H_4ClN_5O_2$	...	...	31.1	Cl 15.7	...	...	31.3	15.6
					215	17,200								31.2	
p-$O_2NC_6H_4$	Cl	98.0–99.4	Benzene–hexane	A1 (56); B1 (83)[f]	260 (E)	12,000	$C_7H_4ClN_5O_2$	...	...	31.1	Cl 15.7	...	...	31.1	15.7
p-C_6H_4 (bistetrazole)	Cl	213 dec	Acetone, precipitd with pentane	A1 (57)[g]	234 (E)	14,250	$C_8H_4N_8Cl_2$	34.0	1.4	39.6	Cl 25.1	34.7	2.0	39.4	23.9
m-$H_2NC_6H_4$	Cl	109.0–109.9	Benzene–hexane	B2a[h]	306 (E)	2570	$C_7H_6ClN_5$	43.0	3.10	35.8	Cl 18.1	43.4	3.27	36.4	18.3
					228	13,900									
As hydrochloride		199–200 dec	Washed with ether	B2a (82)	307 (E)	2250	$C_7H_6ClN_5 \cdot HCl$	36.2	3.04	30.2	Cl 30.6	36.5	3.21	31.3	29.6
					229	12,900									
p-$H_2NC_6H_4$	Cl	146.1–147.2	Benzene	B2a (83)	262 (E)	9280	$C_7H_6ClN_5$	43.0	3.10	35.8	Cl 18.1	43.4	3.28	35.4	17.6
	Cl	204–205 dec	Benzene	B3 (63)	472 (E); 300; 265; 226	15,700; 8310; 10,800; 41,300	$C_{17}H_{11}ClN_6O$	58.2	3.17	24.0	Cl 10.1	58.7	3.18	24.2	9.5
C_6H_5	N_3	96–96.7[i]	Methanol	A2 (77)	240 (E)	14,000	$C_7H_5N_7$	...	...	...	...	...	...	...	...
m-FC_6H_4	N_3	86–88	Benzene–pentane	A2 (100)	240 (E)	12,150	$C_7H_4FN_7$	41.0	1.97	...	F 9.3	41.4	2.36	...	8.7
p-FC_6H_4	N_3	86.0–86.5	Benzene–hexane	A2 (100)	238 (E)	11,600	$C_7H_4FN_7$	41.0	1.97	...	...	40.8	2.42	...	...
												41.0	2.19		
p-C_6H_4 (bistetrazole)	N_3	205 (detonates)[j]	Acetone	A2 (over 80%)	...	...	$C_8H_4N_{14}$	...	...	66.2	...	...	...	65.8	...
p-$O_2NC_6H_4$	N_3	128.6–129.4	Methanol	A2 (62)	291 (E); 213 sh	12,380; 12,100	$C_7H_4N_8O_2$	36.2	1.74	...	...	36.1	1.79	...	...
m-FC_6H_4	OH	157.3–158.5	Benzene	*k*	281 sh (E)	1640	$C_7H_5FN_4O$	46.7	2.80	31.1	F 10.6	46.6	2.62	31.1	10.4
					275 sh	2850					mw 180				176 (DMSO, fp)
					247	10,800									
p-FC_6H_4	OH	201.5–202	Benzene	*k*	285 (E)	840	$C_7H_5FN_4O$	...	...	31.1	F 10.6	...	...	30.7	10.4
					275	1830					mw 180				339 (benzene, bp)
					247	9300									168 (DMSO, fp)
m-FC_6H_4[l]	SH	148–148.5	From aqueous sodium hydroxide solution with dilute HCl	A3 (92)	292 (E)	5650	$C_7H_5FN_4S$	42.8	2.57	28.6	F 9.7	42.9	2.68	27.7	9.6
					270	4830					S 16.4	42.7	2.55	28.0	16.3
					219	14,500					mw 196				387 (benzene, fp)
															196 (DMSO, fp)
p-FC_6H_4	SH	157.5–158.5[l,m]	As above	A3 (91)	290 (E)	5120	$C_7H_5FN_4S$	42.8	2.57	28.6	F 9.7	42.4	2.64	28.0	9.0
					263	7970					S 16.4			28.3	15.9
					220	10,750					mw 196				185 (DMSO, fp)
o-$O_2NC_6H_4$	SH	119.8–120.4	From aqueous sodium hydroxide solution with dilute HCl	A3 (45–63)	242 (E)	12,250	$C_7H_5N_5SO_2$	37.7	2.26	31.4	...	37.5	2.38	30.8	
					327	1360									
m-$O_2NC_6H_4$	SH	129.8–130.1	As above	A3 (94)	289 (E)	6120	$C_7H_5N_5O_2S$	37.7	2.26	30.4	S 14.3	37.5	2.50	30.6	14.1
					254	9420									
					215	23,000									
p-$O_2NC_6H_4$	SH	138–139.5[n]	As above	A3 (73)	338 (E)	4500	$C_7H_5N_5O_2S$	37.7	2.26	30.4	S 14.3	38.1	2.39	30.9	14.5
					257	13,100						38.1	2.25	30.8	

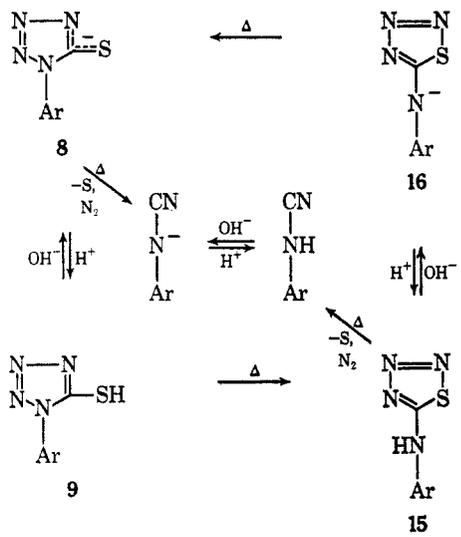
C_6H_5	H	66.5–67.3[o]	CCl_4	A3a (46)	237 (E)	9150	$C_7H_6N_4$	...	...	...	...	...	...	...	...
m-FC_6H_4	H	65.5–66	Ethanol–water, CCl_4	A3a (28)[p]	279 (E)	1140	$C_7H_5FN_4$	51.2	3.07	34.1	F 11.6	50.8	3.50	34.1	11.4
					271	1800									
					236	9080									
p-FC_6H_4	H	92.5–93.5	Ethanol–water, CCl_4	A3a (54)	236 (E)	8000	$C_7H_5FN_4$	51.2	3.07	34.1	F 11.6	50.7	3.28	34.0	12.0
											mw 164				163 (CH_3CN, bp)
o-$O_2NC_6H_4$	H	85–86	Ethanol	A3b (47–62)	250 (E)	5080	$C_7H_5N_5O_2$	44.0	2.64	36.6	...	44.2	2.73	36.8	...
m-$O_2NC_6H_4$	H	109–109.5	Acetone–water or CCl_4	A3b (57)	300 (E)	1070	$C_7H_5N_5O_2$	44.0	2.64	36.7	...	44.0	2.86	36.1	...
					230	18,200						44.0	3.02	36.4	
p-$O_2NC_6H_4$	H	182–184[q]	Acetone–water	A3b (30)	272 (E)	14,400	$C_7H_5N_5O_2$	...	...	...	...	...	...	...	...
		208 dec (block)	Acetone	B1 (82)											
o-$H_2NC_6H_4$	H	88.6–89.2	Hexane	B2a (56)	305 (E)	3200	$C_7H_7N_5$	52.2	4.38	43.5	...	51.9	4.24	43.6	...
					220	13,000									
m-$H_2NC_6H_4$	H	94.5–96.0	Water	B2a (60)	310 (E)	2400	$C_7H_7N_5$	52.2	4.38	43.5	...	52.5	4.18	43.2	...
					236	19,800								42.8	
p-$H_2NC_6H_4$	H	145–145.5[r]	Water	B2a (43)	278 (E)	9230	$C_7H_7N_5$	52.2	4.38	43.5	...	52.1	4.20	43.1	...
												52.1	4.80	42.9	
o-$NHOHC_6H_4$	H	138.8–140.6	Ethanol	B2b-1 (72)	298 (E)	2580	$C_7H_7N_5O$	47.5	3.98	39.5	mw 177	47.6	4.22	40.0	173 (acetone, bp)
															182
	H	244.8	Dimethyl sulfoxide	B2b-2 (50)	452 (A)	474	$C_{14}H_{10}N_{10}$	52.8	3.17	44.0	...	52.8	3.25	43.7	...
					328	17,520									
					235	15,610									
Bis(*m*-FC_6H_4)	–SS–	119.3–119.7	Ethanol–water and CCl_4	A3a (23)[s]	None (E), strong absorption below 210		$C_{14}H_8F_2N_8S_2$	43.1	2.07	28.7	F 9.7	42.8	2.03	28.2	10.3
											S 16.4				15.9
											mw 390				427 (benzene, bp)
Bis(*p*-FC_6H_4)	–SS–	143.5–144	Ethanol–water and CCl_4	A3a (27)[s]	As above		$C_{14}H_8F_2N_8S_2$	43.1	2.07	28.7	F 9.7	43.1	2.57	28.7	10.0
											S 16.4				16.2
					B. Thiatriazoles										
															
o-$O_2NC_6H_4$		114.2–114.7	Benzene–hexane	B5 (51)	356 (E)	4410	$C_7H_5N_5SO_2$	37.7	2.26	31.4	...	37.9	2.29	31.0	...
					282	10,630		...	...	...	...	37.8			
					236	10,680									
m-FC_6H_4		127–127.5	Ethanol–water	B5 (53)	300 (E)	13,200	$C_7H_5FN_4S$	42.8	2.57	...	F 9.7	42.4	2.63	...	9.6
					240	8900									
p-FC_6H_4		126–127[t]	Ethanol–water	B5 (53)	300 (E)	9650	$C_7H_5FN_4S$	42.8	2.57	...	F 9.7	42.3	2.50	...	8.9
					288	10,000									
					239	7800									

[a] Melting points are corrected. [b] Letter and numeral designation refer to procedure listed in Experimental Section. Any modification in conditions or unusual results are given in footnotes. [c] Solvents used are: E, ethanol; I, isooctane; W, water; A, acetonitrile. Infrared and nmr spectra were also obtained on most of the compounds (see discussion in Experimental Section). [d] Lit.[9] mp 124°. [e] Sodium chloride removed by filtration and solvent removed under reduced pressure. [f] *Para* orientation in nitration verified by comparison to authentic product from azide preparation. Typical A_2B_2 pattern was noted for proton nmr in aromatic ring. [g] Product and sodium chloride precipitated; washed with water before recrystallization. [h] Aniline is liberated from hydrochloride in almost quantitative yield. [i] Lit.[7a] mp 99°. [j] *WARNING:* This compound is extremely sensitive to shock or friction and detonates with violence; it should be handled only in small quantities behind shields. [k] Prepared by oxidation of corresponding mercaptotetrazole with potassium permanganate followed by heating with base; M. Freund and H. Hempel, *Ber.*, **28**, 80 (1895), and R. Stolle and F. Henke-Stark, *J. prakt. Chem.*, **124**, 261 (1930). [l] See ref 15; for simplicity the mercapto form is used in table. [m] Lit.[38] mp 154–155°. [n] Lit.[36] mp 148°. [o] See ref 12: lit. mp 66.5–67.3; λ_{max} 236 (ϵ) 9300. [p] The corresponding disulfide isolated as by-product in 17% yield. [q] The melting point is a function of the rate of heating; lit. mp. 205° dec;[12] 183–185°, 190° dec (R. Huisgen and H. J. Koch, *Ann.*, **591**, 200 (1955). [r] Lit.[12] mp 155°. [s] Disulfide is by-product in certain preparations of corresponding tetrazole by oxidation of 1-(fluorophenyl)-5-mercaptotetrazole. It was easily separated from the much more soluble tetrazole by recrystallization. [t] Lit.[38] mp 127–128°. [u] Registry no.: Ar = *m*-FC_6H_4, X = OH (**9a** form), 14320-30-0; Ar = *m*-FC_6H_4, X = OH (**9b** form), 14213-08-2; Ar = *p*-FC_6H_4, X = OH (**9a** form), 14213-07-1; Ar = *p*-FC_6H_4, X = OH (**9b** form), 14213-09-3; Ar = C_6H_5, X = H, 5378-52-9; Ar = *m*-FC_6H_4, X = H, 14210-80-1; Ar = *p*-FC_6H_4, X = H, 14210-81-2; Ar = *m*-$O_2NC_6H_4$, X = H, 14213-10-6; Ar = *p*-$O_2NC_6H_4$, X = H, 14213-11-7; Ar = *m*-$H_2NC_6H_4$, X = H, 14213-12-8; Ar = *p*-$H_2NC_6H_4$, X = H, 14213-13-9; Ar = bis(*m*-FC_6H_4), X = –SS–, 14213-14-0; Ar = bis(*p*-FC_6H_4), X = –SS–, 14213-15-1.

o-nitrophenyltetrazole (**10**) in 50–60% yield.[16] This compound in turn can be reduced catalytically in dilute acid to the aniline **11**. When the catalytic hydrogenation is carried out under neutral conditions, only the hydroxylamine **12** is obtained. On standing in solution or on warming, this hydroxylamine readily undergoes dehydration to produce the azobenzene **13**. An attempt to reduce the *o*-nitrophenyltetrazole **10** with sodium sulfide in aqueous ethanol resulted in displacement of nitrogen from the tetrazole ring to produce 2-aminobenzimidazole (**14**).

We find that the mercaptotetrazole **9** rearranges rapidly in refluxing benzene to the thiatriazole **15** (Scheme III). This reaction appears to be the reverse

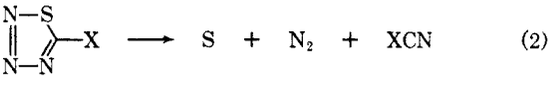
SCHEME III



Ar = *o*-nitrophenyl

of the rearrangement of 5-anilino-1,2,3,4-thiatriazole to 1-phenyl-5-mercaptotetrazole in basic solution reported by Lieber, Pillai, and Hites.[17] When **15** is dissolved in cold base and the solution immediately acidified, unchanged **15** is precipitated. However, when the basic solution is warmed, rearrangement of anion **16** to **8** occurs and, on acidification of the solution, only **9** is obtained. These reactions are summarized in Scheme III.

On long heating of **15** in benzene or of **8** in aqueous base, nitrogen and sulfur are lost and *o*-nitrophenylcyanamide (*o*-nitrocarbanilonitrile) is obtained[18] (eq 2). This reaction is also applicable to the synthesis of phenyl- and *m*- and *p*-fluorophenylcyanamide, but yields are poor, apparently because of the instability of the product. This is yet another example of the facile thermal cleavage of 5-substituted thiatriazoles to yield nitrogen, sulfur, and a substituted nitrile. This reaction and the recent elegant syntheses of alkyl

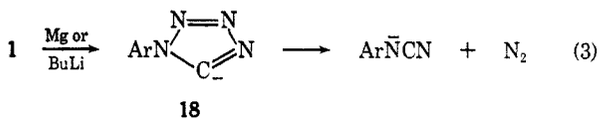


(2)

cyanates[19] and cyanogen isothiocyanate[20] by the thermolysis of the corresponding thiatriazoles suggest that this thermolysis reaction may have general utility for the preparation of compounds with cyano groups on oxygen, sulfur, and nitrogen functions.

B. Chemical Reactions of 1-Aryl-5-chlorotetrazoles.—Very little has been reported on the chemistry of 1-aryl-5-chlorotetrazoles.[3] Recently, nucleophilic replacement of the chlorine by phenolate anions was reported and utilized in a valuable synthetic procedure for dehydroxylation of phenols.[4c] The 5-chlorotetrazole ring is not affected by catalytic reduction; a nitro group on the aryl ring can be catalytically hydrogenated to produce the corresponding aniline (**2**, Ar = $C_6H_4NH_2$), which undergoes normal diazotization and coupling with β-naphthol. 1-Phenyl-5-chlorotetrazole is easily nitrated in the phenyl ring with fuming nitric acid. The position of nitration is chiefly *para*, as is reported for some other aryl tetrazoles.[12,21]

Decomposition of the tetrazole ring in 1-phenyl-5-chlorotetrazole occurs chemically from attack by magnesium or butyllithium. No indication of a Grignard or lithium reagent was found on carbonation of the reaction mixture; the product isolated was phenylcyanamide. A reasonable route to such a product is through the anion **18**[22,23] (eq 3). Reaction of 1-phenyl-5-chlorotetrazole with triphenylphosphine in refluxing benzene also occurs with nitrogen evolution, but the product is complex and appears to contain N-phenylcyanamide. Stolle[7b] noted that reaction of this same tetrazole with sodium in ethanol resulted in the destruction of the tetrazole ring.



(3)

C. Thermal Decomposition Studies.—The thermal decomposition of tetrazoles has received considerable attention. 2,5-Disubstituted tetrazoles are a source of the 1,3-dipolarophiles,[4] $R\bar{N}N{=}{+}CX$. Recently a careful study of the thermolysis of 5-aryltetrazoles[24] showed that ionization of the tetrazole was an important factor in the rate of decomposition and was influenced considerably by solvent. No satisfactory correlations with substituents were apparent. When thermally decomposed, 1,5-diaryltetrazoles were shown to rearrange to diarylcarbodiimides and 2-arylbenzi-

(16) In the corresponding oxidations of 5-(*m*- and *p*-fluorophenyl)tetrazoles some disulfide was isolated (see Table I).

(17) E. Lieber, C. N. Pillai, and R. D. Hites, *Can. J. Chem.*, **35**, 832 (1957).

(18) Lieber and co-workers[17] noted a "violent" decomposition on heating unsubstituted 5-anilino-1,2,3,4-thiatriazole and the formation of nitrogen, sulfur, and an unidentified crystalline solid.

(19) K. A. Jensen and A. Holm, *Acta. Chem. Scand.*, **18**, 826 (1964); K. A. Jensen, M. Due, and A. Holm, *ibid.*, **19**, 438 (1965); D. Martin, *Angew. Chem. Intern. Ed. Engl.*, **3**, 311 (1964).

(20) E. Lieber, E. Oftedahl, and C. N. R. Rao, *J. Org. Chem.*, **28**, 194 (1963).

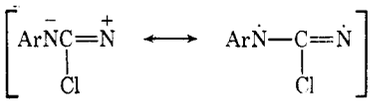
(21) J. v. Braun and W. Rudolph, *Ber.*, **74**, 264 (1941).

(22) Substitution of the bromine of 1-phenyl-5-bromotetrazole by phenylhydrazine is reported, but reaction of 1-phenyl-5-iodotetrazole with methylmagnesium iodide followed by benzoyl chloride is reported to give only N-phenyl-N-benzoylcyanamide and N_2.[7b,9]

(23) R. A. Olofson [private communication; see *J. Am. Chem. Soc.*, **88**, 4266 (1966)] finds that deuterium exchange of the 5-H of tetrazoles proceeds 10^6 faster than the rate of decomposition. However, direct comparison of results is not possible since our conditions involve irreversible anion formation whereas in the exchange experiment the anion is formed reversibly, probably in low concentration. In addition, magnesium, magnesium halide, or lithium halide in our system could promote decomposition of anion **18**; alternatively a concerted attack–decomposition not involving **18** could explain the results.

(24) J. H. Markgraf, S. H. Brown, M. W. Kaplinsky, and R. G. Peterson, *J. Org. Chem.*, **29**, 2629 (1964).

midazoles.[25] 1-Aryl-5-chlorotetrazoles cannot give a stablized 1,3-dipolar intermediate on loss of nitrogen and would not be expected to undergo the rearrangement found for 1,5-diaryltetrazoles because of predicted low stability of the intermediate **19**.



19

The decomposition of 1-aryl-5-chlorotetrazole occurs rapidly at 170–180° and 1 mole of nitrogen is evolved. The rate of nitrogen evolution is first order. No tractable decomposition product was isolated or trapped by a variety of reagents such as nitriles or olefins. Rate of decomposition studies (by following nitrogen evolution, see Tables II and III) show that

TABLE II
THERMAL DECOMPOSITION OF TETRAZOLES. THE EFFECT OF SOLVENT AND CATALYST ON 1-PHENYL-5-CHLOROTETRAZOLE (5×10^{-3} MOLE IN 100 ML OF SOLVENT) DECOMPOSITION AT 171 ± 1°

Solvent	Catalyst (ml)	Average rate constant, $k_1 \times 10^2$, min^{-1}	Relative rate
$HOCH_2CH_2OCH_2CH_2OH$	...	1.16	1.0
		1.11	
	H_2O (2)	1.15	1.0
		1.15	
	1 *N* $CuSO_4$ (2)	2.97	2.6
		2.54	
	1 *N* $FeCl_3$ (2)	1.45	1.3
	1 *N* NaOH (2)	0.88	0.8
	Cuprex, Cu powder	0.69	0.6
	Quartz powder	1.11	1.0
$EtOCH_2CH_2OCH_2CH_2OH$	...	2.52	2.2
$BuOCH_2CH_2OCH_2CH_2OH$	...	2.97	
C_6H_5CN	...	3.69	3.2
Nujol	...	9.04	7.9

TABLE III
EFFECT OF SUBSTITUENT ON RATE OF DECOMPOSITION OF 1-ARYLTETRAZOLES (3–4 MMOLES) IN $BuOCH_2CH_2OCH_2CH_2OH$ (100 ML) AT 175 ± 1°

ArN₄CX[a]		Average rate constant, $k_1 \times 10^2$, min^{-1}	Relative rate
1-Ar	5-X		
C_6H_5	Cl	2.97	1.0
m-$H_2NC_6H_4$	Cl	2.26–1.62	0.7
p-$H_2NC_6H_4$	Cl	2.23–1.69	0.7
m-$O_2NC_6H_4$	Cl	56–70	22
p-$O_2NC_6H_4$	Cl	79–92	29
C_6H_5	SO_2CH_3	1.81–1.63	0.6
C_6H_5	SCH_3	2.09–1.95	0.7
C_6H_5	SO_3K	1.10–0.99	0.4
C_6H_5	CH_3	0.04	0.01
C_6H_5	NH_2	0.10	0.03
C_6H_5	C_6H_5	0.08	0.03
C_6H_5	*p*-$O_2NC_6H_4$	0.02	0.07
p-$O_2NC_6H_4$	C_6H_5	0.24	0.08

[a] Registry no.: 1-Ar = C_6H_5, 5-X = CH_3, 14213-16-2; 1-Ar = C_6H_5, 5-X = NH_2, 5467-78-7.

decomposition is an order of magnitude faster in nonpolar solvents (mineral oil) than polar solvents (alcohol). No significant catalytic or surface effects are found; the largest effect observed is doubling of the rate by addition of copper salts. An electron-withdrawing substituent in the aromatic ring increases the rate of decomposition, but the effect is small; from the small number of substituents examined (*meta*- and *para*-amino and nitro), no quantitative correlation is apparent.

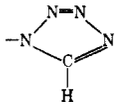
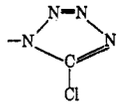
The rate of decomposition of the azido–azomethine form should be different from the tetrazole form; solvent and substituents do influence the position of equilibrium, but without much more extensive studies no definite conclusion about the mechanism of decomposition of tetrazoles can be drawn.[26]

D. Electronic Properties of Tetrazoles.—The electron density in tetrazoles has been calculated[27] and compared with dipole moment measurements.[28] Unfortunately, tautomeric equilibria (both tetrazole–azidoazomethine and proton position equilibria) complicate the nmr measurements and no definite picture of the electron density was obtained.

As pointed out earlier, electrophilic reagents attack the *para* position in the phenyl ring of aryltetrazoles. A phenyl ring in the 1 position of the tetrazole appears more susceptible to attack than one in the 5 position.[21] In electrophilic substitution, *para* orientation to a substituent with unshared electrons is expected and usually found, even when the substituent is inductively a strong electron-withdrawing group [for example, $N(CF_3)_2$],[29] because, in attack by an electrophilic reagent, the requirements to stabilize a transition state by resonance conjugation override all other factors.

Quantitative data on the electronic character of tetrazoles have been obtained by standard pK_a measurements on the anilines (Table IV) and F^{19} nmr measurements on the aryl fluorides substituted in the *meta* and *para* positions by tetrazoles (Table V). The substituent parameters, calculated by the usual methods,[30] are summarized in Table VI; the data obtained for tetrazoles substituted in the 1 position by the aryl group and in the 5 position by H, Cl, N_3, disulfide, OH,

TABLE IV
IONIZATION CONSTANTS AND SUBSTITUENT PARAMETERS FOR ANILINES, WATER AT 25°, $RC_6H_4NH_3^+ \rightleftharpoons RC_6H_4NH_2 + H^+$

R		λ_{max}	pK_a	σ^a
	*meta*	297	2.90	0.60
	para	267	2.97	0.57
	*meta*	294	2.58	0.72
			2.55	
	para	256	2.61	0.70

[a] Calculated using values of pK_a for anilinium ion as 4.56 and $\rho = +2.767$.

(25) (a) P. A. S. Smith and E. Leon, *J. Am. Chem. Soc.*, **80**, 4647 (1958); (b) J. Vaughan and P. A. S. Smith, *J. Org. Chem.*, **23**, 1909 (1958).

(26) I. Ugi and R. Huisgen [*Ber.*, **91**, 531 (1958)] have studied the mechanism of decomposition of arylpentazoles and have shown that they can decompose from both the pentazole and open-chain aryldiazo–azide forms and that the rate of decomposition is enhanced by electron-withdrawing substituents.

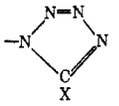
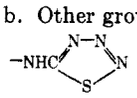
(27) A. J. Owen, *Tetrahedron*, **14**, 237 (1961).

(28) (a) M. H. Kaufman, F. M. Ernsberger, and W. S. McEwan, *J. Am. Chem. Soc.*, **78**, 4197 (1956); (b) K. A. Jensen and A. Friediger, *Kgl. Danske Videnskab. Selskab, Mat-fys. Medd.*, **20**, No. 20, 1 (1943).

(29) W. A. Sheppard and F. S. Fawcett, *J. Am. Chem. Soc.*, **87**, 4341 (1965).

(30) (a) See W. A. Sheppard, *ibid.*, **87**, 2410 (1965); (b) The use of σ_I and σ_R parameters to evaluate the contribution by inductive and resonance effects is described by R. W. Taft, Jr., *J. Phys. Chem.*, **64**, 1805 (1960).

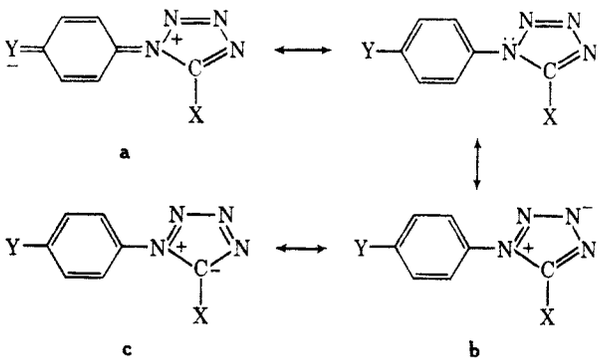
TABLE V
F19 NMR CHEMICAL SHIFTS FOR FC_6H_4Z

Group		Isomer	δ at infinite dilution relative to C_6H_5F in solvent, ppm: Benzene[a]	Dioxane[a]	Acetonitrile[a]	Acetone[a]	Methanol[a]	CCl_3F[b]
a. Tetrazoles	X							
	H	*meta*	3.28	2.96	3.23	3.17	3.83	I[c]
		para	1.61	1.22	2.06	1.72	2.52	I
	Cl	*meta*	3.44	3.21	3.51	3.36	3.94	I
		para	3.63	3.42	4.29	4.03	4.61	I
	N_3	*meta*	I	3.03	3.28	3.15	3.52	I
		para	1.99	1.93	2.90	2.59	2.94	I
	bis(–SS–)	*meta*	I	3.53	3.81	3.63	I	I
		para	I	3.68	4.44	4.13	I	I
	–SH	*meta*	I	2.46	2.61	2.43	2.59	I
		para	I	1.58	2.59	2.02	2.39	I
	–OH	*meta*	I	I	I	2.61	2.91	I
		para	I	I	I	0.98	0.14	I
b. Other groups								
		*meta*	I	2.46	2.39	2.23	2.39	I
		para	I	−4.60	−4.34	−4.97	−4.43	I
–NHCN		*meta*	2.06	1.67	2.00	1.83	1.99	I
		para	−7.01	−7.79	−7.36	−7.66	−7.36	I
$-N{=}CCl_2$		*meta*	...	...	...	...	...	1.42
S		*para*	...	...	...	...	...	−3.15
‖		*meta*	I	...	1.44	1.14	...	I
$-NHCNH_2$		*para*	I	...	−2.50	−3.76	...	I

[a] Calibrations run at 20, 10, and 5% concentration using 5% 1,1,2,2-tetrachloro-3,3,4,4-tetrafluorocyclobutane as internal standard. Chemical shift values for C_6H_5F relative to internal standard: benzene, −35; dioxane, −15; acetonitrile, +32; acetone, +15; methanol, +12 Hz at 56.4 mHz. [b] Trichlorofluoromethane used as solvent and internal calibrant. Chemical shift value of C_6H_5F relative to CCl_3F is 6382 Hz. [c] I—too insoluble for nmr measurements. [d] Registry no.: Z = –NHCN (*meta*), 14213-18-4; Z = –NHCN (*para*), 14213-19-5; Z = $-N{=}CCl_2$, (*meta*), 14213-20-8; Z = $-NHC(=S)NH_2$ (*meta*), 458-05-9; Z = $-NHC(=S)NH_2$ (*para*), 459-05-2.

or SH are reported; values for some other substituents are also given. From comparison of σ_m or σ_I values, the 1-tetrazoles all appear to be inductively strongly electron-withdrawing (of the same order as a nitro group but not so strong as a trimethylammonium), suggesting that the 1-nitrogen has lost considerable electron density and is highly positive in character. As expected, the 5-chloro substituent enhances this inductive effect (see Scheme IV and discussion below).

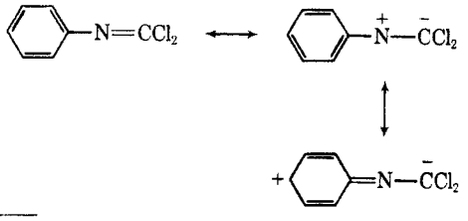
SCHEME IV



The variations in σ_I values are not surprising since σ_I values obtained from F19 measurements often are significantly less than those obtained from reactivity or pK_a measurements.[31] However, from inspection of the σ_p or σ_R values, no simple conclusion can be drawn about the resonance interactions from the 1 position of the tetrazole ring. Small electron return by resonance is seen from the pK_a measurements, but the F19 nmr measurements show both donation and withdrawal depending on the substituent in the 5 position. Resonance interactions to feed electron density into the aromatic ring can be described by **a** and are important in stabilizing the transition state for *para* attack in electrophilic substitution. Withdrawal of electron density by contributing forms such as **b** and **c** makes the tetrazole inductively electron withdrawing. The π-inductive mechanism[32] can cause enhancement of this electron withdrawal in the *para* position, but other secondary effects such as ring currents or p–π interactions[30a] can also contribute and cause small variations. The greater inductive effect of 5-chlorotetrazoles relative to tetrazole supports this picture since the inductive effect of chlorine should enhance the contribution of form **c**.

The interpretation of the parameters for the mercapto- and azidotetrazoles is discussed below in the section on molecular structure. However, measurements of substituent parameters for a series of 2- and 5-substituted tetrazoles are needed for a clear picture of the electron density in the rest of the tetrazole ring.

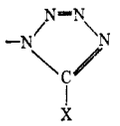
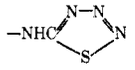
The σ values were also measured for several other groups found in intermediates or by-products of the tetrazole preparations or reactions. The N,N-dichloroazomethine group, $N{=}CCl_2$, is very similar to the



(31) R. W. Taft, E. Price, I. R. Fox, I. C. Lewis, K. K. Andersen, and G. T. Davis, *J. Am. Chem. Soc.*, **85**, 709 (1963).

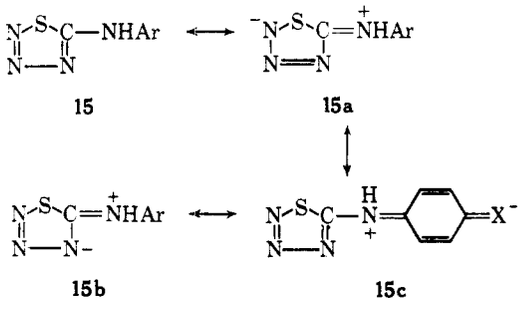
(32) M. J. S. Dewar, "Hyperconjugation," The Ronald Press Co., New York, N. Y., 1962.

TABLE VI
SUBSTITUENT PARAMETERS FOR TETRAZOLES AND RELATED GROUPS

Substituent		Method[a]	σ_m	σ_p	σ_I	σ_R or σ_R^0
a. Tetrazoles	X					
	H	A	0.60	0.57	0.57	−0.03
		F	0.52	0.50	0.54	−0.04
	Cl	A	0.72	0.70	0.69	−0.02
		F	0.60	0.61	0.58	0.03
	N_3	F	0.54	0.54	0.55	−0.01
	SH	F	0.45	0.45	0.45	0
	OH	F[b]	0.39	0.33	0.45	−0.12
	bis(-SS-)	F	0.63	0.64	0.62	0.02
b. Other groups						
$-NO_2$		A[c]	0.71	1.27	0.68	0.67
		F[d]	0.67	0.78	0.56	0.22
$-N(CF_3)_2$		A[e]	0.47	0.53	0.44	0.06
		F[e]	0.49	0.50	0.49	0.01
$-\overset{+}{N}(CH_3)_3$		A[f]	0.85	0.75	0.82	−0.11
		F[d]	0.87	0.82	0.93	−0.11
$-C_6H_5$		A[g]	0.12	0.11	0.14	−0.04
		F[d]	0.04	−0.01	0.08	−0.09
$-N{=}CCl_2$		F[h]	0.21	0.13	0.29	−0.16
$-N{=}C{=}O$		F[e,h]	0.27	0.19	0.36	−0.17
$-NHCN$		F	0.21	0.06	0.37	−0.31
		F	0.30	0.19	0.42	−0.23
$-NHC(=O)CH_3$		F[d]	0.13	0.02	0.24	−0.22
$-NHC(=S)NH_2$		F	0.22	0.16	0.29	−0.13

[a] A from pK_a of anilinium ions. F from F^{19} nmr chemical shift measurements in CH_3CN unless indicated otherwise. [b] Solvent acetone. [c] See ref 41. [d] See ref 31 and 42. [e] See ref 29. [f] J. D. Roberts, R. A. Clement, and J. J. Drysdale, *J. Am. Chem. Soc.*, **73**, 2182 (1951). [g] E. A. Braude and F. C. Nachod, "Determination of Organic Structures by Physical Methods," Academic Press Inc., New York, N. Y., 1955, p 590. [h] Solvent CCl_3F.

isocyanate group—electron withdrawing by induction but electron donating by resonance. This similarity suggests that contribution from the resonance forms shown is not important. The N-cyanoamino group, NHCN, is more deactivating inductively than an amide group, but is still strongly electron donating by resonance. The aminothiatriazole group, $NHCN_3S$, is also similar to an amide but shows even larger inductive deactivation. Lieber and co-workers[33] suggested from ultraviolet measurements that this group is strongly electron withdrawing both inductively and by resonance and proposed resonance contributions by ionic structures such as **15a** and **15b**. However, no



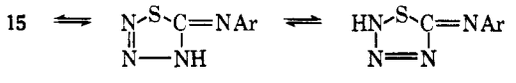
15 **15a**

15b **15c**

Ar = C_6H_4S

(33) E. Lieber, J. Ramachandran, C. N. R. Rao, and C. N. Pillai, *Can. J. Chem.*, **37**, 563 (1959).

forms can be drawn that would suggest resonance deactivation of the aromatic ring while the normal electron donation of the unshared electron pair on nitrogen into the aromatic ring is possible (**15c**) and could compete with donation into the thiatriazole ring. The contribution of forms **15a** and **15b** cannot be large since the σ_R value for the aminothiatriazole group is comparable to that of an amide. The enhanced σ_I value for this group could be from a ring current in the thiatriazole ring. However tautomeric structures **15d** and **15e** could also be present in solution. Indeed, the



15d **15e**

similarity of substituent parameters for the thiatriazole to dichloroazomethine and isocyanate groups suggests that these tautomeric forms **15d** and **15e** (with azomethine structure) do make a significant contribution. Solvents appear to shift the tautomeric equilibrium (note solvent effects in Table V).

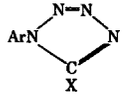
E. Infrared Spectral Correlations.—The infrared spectra of approximately 30 1-aryltetrazole derivatives were examined both in the solid state and in solution during the course of this work (see Table VII). Four prominent absorption bands at approximately 1210, 1090, 1000, and 960 cm^{-1} were observed in these tetrazoles. In the 5-chlorotetrazoles the bands were shifted by 10–20 cm^{-1} to higher frequency, while in the 5-azidotetrazoles and the 5-disulfides only small variable shifts were observed. In most cases the first three bands were strong and the 960-cm^{-1} band was medium to weak, a characteristic band pattern which was usually easy to identify.

These correlations apparently are limited to 1-aryltetrazoles since a number of other tetrazoles which were examined (unsubstituted and 2-substituted) failed to show the band pattern. In addition, the pattern was not shown clearly for the six 5-mercaptotetrazoles studied, giving credence to the view of Lieber[17] that these compounds are not normal 5-mercaptotetrazoles. Lieber and co-workers[15] have noted that these 5-mercaptotetrazoles, which they characterize as tetrazolinethiones, exhibit medium intensity absorptions at about 1210 and 1170 and at 1270–1300 cm^{-1}. We also observe these bands in the mercaptotetrazoles as well as strong bands at about 1040 and 990 cm^{-1}.

A similar question on the molecular structure of 1-aryl-5-hydroxytetrazoles has been discussed by Horwitz and co-workers.[15b] They report that such compounds exhibit strong infrared absorption in potassium bromide at 5.87–5.83 μ (1704–1714 cm^{-1}) and conclude that the 1-aryl-5-hydroxytetrazoles in the solid state are best represented by the tautomeric tetrazolin-5-one formulation with considerable intermolecular association through hydrogen bonding. We, too, find the strong carbonyl absorption at *ca.* 1710–1720 cm^{-1} in potassium bromide wafers as well as in carbon disulfide solution. The absorption is displaced to *ca.* 1740 cm^{-1} in acetonitrile. In addition, the pattern of absorptions in the region of 950–1300 cm^{-1} is unlike that which we described above for normal 1-aryltetrazoles (see Table VII). The absorptions are, how-

TABLE VII

MAJOR INFRARED ABSORPTION BANDS FOR 1-ARYLTETRAZOLES FROM 950 TO 1270 CM^{-1}



Ar[f]	X	Medium	Absorption bands,[a] cm^{-1}												
C_6H_5	H	KBr		*1208s*	1192m	1176w		*1094s*		1080w	1048m			*999/996s*	*962s*
		CS_2		*1199s*	1179w	1171w		*1087s*			1037m			*996s*	*951m*
		CH_3CN		*1206s*				*1094s*		1080w				*997s*	*961m*
		Acetone[d]		*d*				*d*		1080m	1037ms			*997s*	*959m*
m-C_6H_4F	H	KBr	1244s[e]	*1193s*	1174m	1157w		*1093s*		1045w	1034w			*1008/1004s*	*962m*
		CS_2	1238s[e]	*1179s*		1149w		*1082s*						*998s*	*948w*
		CH_3CN	1234s[e]	*1181s*		1152m		*1089s*						*1009/1003s*	*959m*
		Acetone[d]		*d*				*d*						*1007/1002s*	*955m*
p-C_6H_4F	H	KBr	1244s[e]	*1213s*	1185m	1160m		*1101/1094s*		1043m				*1002s*	*969m*
		CS_2	1241s[e]	*1196m*	1186m	1152m		*1084s*			1027m			*996s*	*950w*
		CH_3CN	1234s[e]	*1181s*		1152m		*1089s*						*1009/1003s*	*957m*
		Acetone		*d*				*d*						*1007/1002s*	*955m*
o-$C_6H_4NH_2$	H	KBr		*1205s*	1188m	1166w	1144m	*1100s*		1047w				*1003s*	*971m*
m-$C_6H_4NH_2$	H	KBr	1262s	*1205s*	1190s	1168m		*1095s*		1051m	1016m			*994s*	*970m*
p-C_6H_4-NH_2	H	KBr		*1205s*		1168s		*1092s*		1038m	1015m			*996m*	*966m*
o-C_6H_4-NHOH	H	KBr		*1198s*		1165m	1122w	*1094s*		1033m	1019m			*996s*	*971m*
m-$C_6H_4NO_2$	H	KBr		*1218s*	1189m			*1094/1090s*		1053m	1012m			*998m*	*965m*
p-C_6H_4-NO_2	H	KBr		*1212s*			1110m	*1088s*						*993s*	*955m*
o,o'-azobenzenebis-	H	KBr	1228w	*1205s*	1165m		1129s	*1086s*		1042w	1024m			*996s*	*959m*
C_6H_5	Cl	KBr		*1242s*	1171w			*1113s*		1073m	1040m			*1015s*	*975m*
		CS_2		*1244s*				*1100m*		1075w	1055w	1040w		*1016m*	*973m*
		CH_3CN		*1244s*	1176w			*1113s*		1080m				*1015s*	*979ms*
		Acetone[d]		*d*				*1107s*				1044mw		*1015s*	*977s*
m-C_6H_4F	Cl	KBr		*1269s*[c?] *1260s*	1188s	1155w		*1115s*		1081/1075m		1042m		*1007w*	*977ms*
		CS_2		*1269*[c?]*/1261s*	1215w	1193s	1155m	*1100s*			1058m	1039w		*1005w*	*971m*
		CH_3CN		*1263s*		1193s	1159m	*1110s*						*1006m*	*978s*
		Acetone		*1261s*			1157m	*1107s*		1069m		1045m		*1007w*	*977m*
p-C_6H_4F	Cl	KBr	1261m[e]	*1245s*	1221s	1156s		*1113/1110s*		1069w	1032s			*1012s*	*978s*
		CS_2		*1250/1238s*			1156m	*1106/1095m*		1058w	1032m			*1013m*	*974w*
		CH_3CN		*1250/1227s*			1159s	*1113/1099s*						*1013m*	*979m*
		Acetone		*1269/1255s,br*			1159s	*1111s*		1067m		1036s		*1014s*	*978s*
m-C_6H_4-NH_2	Cl	KBr		*1224s*			1161m	*1113s*		1075m		1047ms		*995s*	*985m*
p-C_6H_4-NH_2	Cl	KBr		*1244s*			1179m	*1113m*		1089w	1072w	1040w		*1007s*	*982m*
o-$C_6H_4NO_2$	Cl	KBr		*1242s*		1168w	1148w	*1098s*			1066w	1042w		*1021m*	*975m*
m-$C_6H_4NO_2$	Cl	KBr		*1247s*		1164w		*1110/1102s*		1083m	1073w	1049m		*1003w*	*978m*
p-$C_6H_4NO_2$	Cl	KBr		*1247s*			1172w	*1113m/1100s*		1067m	1029m			*1010s*	*979m*
p-C_6H_4 bis-	Cl	KBr	1259m	*1242s*	1228m		1121m	*1096s*		1071m	1038m			*1007s*	*979ms*
C_6H_5	SCH_3	KBr		*1245s*	1167w			*1096s*		1078s	1064w	1044m		*1015ms* *988ms*	*978s*
C_6H_5	SO_2CH_3	KBr	1269w	*1233w*	1159s			*1107mw*		1074m	1055m			*1018m* *964s*	*955s*
C_6H_5	SO_3K	KBr		*1253/1245s*	1174m	1160w	1152m	*1114s*	1100w	1083s	1073m	1050w	1037mw	*1016m* *990w*	*975w*
C_6H_5	C_6H_5	KBr		*1271s*	1182w	1163m	1147s	*1107s*	1068s	1053m	1038w	1026m		*1008s*	*987m*
C_6H_5	*p*-C_6H_4-NO_2	KBr		*1263m*	1168mw		1134m	*1109s*	1075m		1013m	1006m		*1000s*	*968w*
C_6H_5	N_3	KBr		*1196s*	1175w	1107w		*1088s*		1071m				*1010m*	*984m*
	N_3	CS_2		*1195s*				*1094s*		1083m	1066m	1046w		*1018m*	*982m*
	N_3	CH_3CN		*1199s*				*1099/1090s*			1071m			*1015m*	*985m*
	N_3	Acetone		*d*	1174m			*d*			1069s			*1016s*	*983m*
p-$C_6H_4NO_2$	N_3	KBr		*1181s*	1121m		1106m	*1089s*			1040m			*1004m*	*978mw*
	N_3	CS_2		*1186s*			1111m	*1086s*			1065m			*1013m*	*976w*

		CH_3CN			*1195s*			1110m	*1093s*		1081sh			*1011m*		*981m*
		Acetone			*1172m*				*d*		1035w			*1012s*		*980m*
m-C_6H_4F	N_3	KBr			*1205s*	1179s	1160m	1155w	*1094ms*	1084m		1069m		*1000w*		*983w*
		CS_2			*1212s*	1179s	1157m		*1096s*	1086m	1069m			*1005w*		*981w*
		CH_3CN			*1216s*	1183s	1160m		*1104s*	1096m	1076w			*1006w*		*985w*
		Acetone			*d*	1172s	1157s		*1102m*		1074s			*1005m*		*983m*
p-C_6H_4F	N_3	KBr	1241s[c]		*1206s*		1159m		*1109/1095m*		1084m			*1013m*		*981w*
		CS_2	1239s[c]		*1192s*		1157m	1105w	*1093m*		1075mw			*1015mw*		*981w*
		CH_3CN	1241s[c]	1228s[c]	*1199s*		1160s	1110m	*1098s*					*1013w*		*986w*
		Acetone			*d*		1160s	1109m	*d*		1079m			*1015m*		*985mw*
bis(*m*-C_6H_4F)	–SS–	KBr	1261/1255s[c]		*1196s*		1157m		*1094s*	1084m	1059m	1040w		*1006w*		*982/977w*
		CS_2[b]	1269s[c]		*1236s*		1156m		*1100w*			1044w				*994m*
		CH_3CN	1269s[c]	1239m	*1190s*		1159m	1117m	*1096m*					*1006w*		*982w*
		Acetone	1261s[c]		*1176s*		1156s		*1116m*	1076w	1058s	1043m		*1006m*		*980w*
bis(*p*-C_6H_4F)	bis(–SS–)	KBr			*1227vs*		1157ms	1105m	*1093m*	1066w	1056w	1031m		*1012m*		*986w*
		CS_2[b]			*1238s*		1157m		*1006w*			1031w		*1012mw*		*987w*
		CH_3CN			*1230vs*		1160s		*1099ms*					*1013m*		*985m*
		Acetone			*d*		1157s		*1109w,br*	1081w	1061m	1033m		*1013s*		*980w,br*
C_6H_5	SH	KBr			*1277/1271s*	1209ms		*1156w*		1102/1093w	1073w		*1049s*	1002mw		*982s*
		CS_2			*1269s*	1208s		*1153w*		1101/1093w	1071w		*1044s*	1002w		*982s*
		CH_3CN[b]														
		Acetone			*1269s*			*d*		1102s			*d*			*985s*
m-C_6H_4F	SH	KBr		1253s[c]	*1242s*		1176s	*1151m*		1090m	1076w		*1048s*	1006w		*996s*
		CS_2		1267s[c]	*1247s*		1183s	*1156m*		*d*			*1042s*	1022m	1006w	*996s*
		CH_3CN		1264s[c]	*1242ms*		1182s	*1157m*		1096w			*d*		1007w	*993m*
		Acetone		1262ms[c]	*d*		1176m	*1156ms*			1081m		*1043s*		1005w	*988m*
p-C_6H_4F	SH	KBr		1272s[c]	*1236s*	1215ms		*1159ms*		1096mw	1082m		*1048ms*		1018mw	*993s*
		CS_2[b]		1282m[c]	*1236s*	1218w		*1160m*		1101w	1084w		*1055/1044m*		1022w	*993m*
		CH_3CN		1266s[c]	*1228s*	1212m		*1159m*					*d*			*992m*
		Acetone		1272s[c]	*d*			*1159m*		*d*			*1047s*		1014w	*988s*
o-C_6H_4-NO_2	SH	KBr			*1266m*	1227m		*1160m*	1140m	1101m	1080m		*1045s*	1020w	1008w	*989s*
		CS_2[b]														
		CH_3CN		1287s	*1263w*	1212m			1144w	1101w			*1047s*[d]			*987s*
		Acetone		1292s	*1263w*				1145m	*d*			*1047s*	1019w		*985s*
m-$C_6H_4NO_2$	SH	KBr			*1274s*	1221m		*1163w*	1102w	1086m			*1051s*			*998m*
		CS_2			*1274s*	1222m		*d*	1101w	1086m			*1057m*			*1000m*
		CH_3CN			*1266s*	1224ms		*1167w*	1094m				*d*			*992m*
		Acetone			*1266s*	*d*		*d*					*1044s*	1003w		*987m*
p-$C_6H_4NO_2$	SH	KBr			*1275ms*	1218m		*1176w*	1127w	1113m	1087m		*1045s*	1010w		*993ms*
		CS_2			*1274m*	1216m		*1174w*		1113m	1087m		*1044s*	1015w		*992m*
		CH_3CN			*1271s*	1211m		*d*		1113m	1093w		*d*	1012w		*982ms*
		Acetone			*1269s*	*d*		*d*		1111m	1082w		*1044s*	1012w		*985s*
C_6H_5	OH	KBr	1720[e]		*1241m*		1155m	*1149s*		1106w	1082m		*1060/1050s*	991m		*973s*
m-C_6H_4F	OH	KBr	1715[e]		*1232/1220s*		1161ms	*1148ms*		1103m			*1057ms*	1037m		*971s*
		CS_2	1718[e]		*1256s/1241m*	1214m	1157m	*1149/1142s*					*1055m*			*978/968s*
						1199s										
		CH_3CN	1745[e]		*1230s*			*1157s*		1096m			*d*			*963s*
		Acetone	*d*		*d*			*1160s*					*1056s*	1033ms		*960s*
p-C_6H_4F	OH	KBr	1712[e]		*1258s*	1199s		*1143s*			1078m/1065ms		*1050s*		1004m	*971s*
		CS_2[b]	1715[e]		*1235s*	*d*		*1161/1147s*					*1058br*			*968br*
		CH_3CN	1742[e]		*1245s*	1192m		*1148s*					*1050s,br*			*968/960s*
		Acetone	*d*		*d*	*d*	*d*	*1147s*					*1053/1038s*			*966/959s*

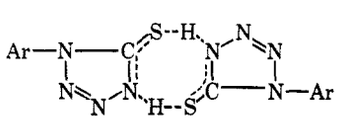
[a] Absorption bands assigned as characteristic of 1-aryltetrazoles are italicized. See discussion part E. Absorption intensities: s = strong; m = medium; w = weak; br = broad; sh = shoulder. [b] Very low solubility; detectable absorption bands are noted. [c] C–F absorptions. [d] Solvent interference. [e] Carbonyl absorption frequency. [f] Registry no.: Ar = C_6H_5, X = SCH_3, 1455-92-1; Ar = C_6H_5, X = SO_2CH_3, 3206-44-8; Ar = C_6H_5, X = SO_3K, 14213-25-3; Ar = C_6H_5, X = C_6H_5, 7477-73-8; Ar = C_6H_5, X = *p*-$C_6H_4NO_2$, 14213-27-5; Ar = C_6H_5, X = SH (**9a** form), 86-93-1; Ar = C_6H_5, X = SH (**9b** form), 1437-66-7; Ar = C_6H_5, X = OH (**9a** form), 1483-17-6; Ar = C_6H_5, X = OH (**9b** form), 5097-82-5.

ever, very similar to those of the 1-aryl-5-mercaptotetrazoles, suggesting that the heterocyclic nuclei of these two classes of compound are very similar. This question will be discussed further in the next section.

The four 5-anilino-1,2,3,4-thiatriazoles examined exhibited strong absorptions at 1270–1300 and 1070–1100 cm^{-1} and weaker absorptions at 930–950 cm^{-1}, which have been assigned by Lieber to skeletal vibrations of the thiatriazole ring. In addition these compounds exhibited the strong absorptions at *ca.* 1550–1600 cm^{-1} that were observed by Lieber.[15a] (The band at *ca.* 1700 cm^{-1}, tentatively assigned by Lieber to an exocyclic C=N absorption, was absent in the four compounds reported here.)

F. Molecular Structure.—We have alluded several times in the above discussions to the question of tautomeric equilibria between the tetrazole and azidoazomethine forms (see, for example, **2** and **7** or **3** and **4**) and the mercaptotetrazole *vs.* tetrazolinethione forms (see **9a** and **9b**). For 1-aryltetrazoles and 1-aryl-5-chlorotetrazoles no azide absorption is observed in the infrared either in the solid state or in a variety of solvents including acetone and trifluoroacetic acid. For the 1-azidotetrazole, criteria other than azide absorption band are needed. In these cases, however, the absorption bands between 960 and 1210 cm^{-1} characteristic of 1-aryltetrazoles are present. Furthermore the electronic properties (σ_m and σ_p) of the 5-azidotetrazole group are intermediate between those of the tetrazole and 5-chlorotetrazole groups (see Table VI). Solvent studies on the F^{19} nmr chemical shift for the aryl fluorides show no abnormal behavior relative to the other tetrazoles (see Table V). We conclude that if an equilibrium exists between the azidomethine and tetrazole forms, it must lie very far on the side of the tetrazole both in the solid state and in solution for all 1-aryltetrazoles examined in the present study.

The position of the hydrogen atom in the mercaptotetrazoles is not as clearly defined. The infrared studies suggest that the normal 1-aryltetrazole system is not present. The electronic character of the group also supports this conclusion since the inductive effect (σ_I 0.45) of the group is significantly less than that of other 5-substituted tetrazoles (particularly note the disulfides for comparison; however both groups show no resonance effect) and the solvent effects on F^{19} chemical shifts vary from the pattern for other tetrazoles (see Table V). The molecular weight is that of a dimer in benzene but that of a monomer (or less because of ionization) in dimethyl sulfoxide. We conclude that this tetrazole system may exist as a hydrogen-bonded dimer, **20** (like carboxylic acids), in the



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solid state or in weakly polar solvents. In this dimeric form the tetrazole ring has lost a certain amount of the resonance properties characteristic of the 1-aryltetrazole system so that the 1-nitrogen is not so positive.

As discussed above, the 1-aryl-5-hydroxytetrazoles have also been reported to exist as the tautomeric tetrazolin-5-one in the solid state because of a strong infrared absorption at *ca.* 1710 cm^{-1} assigned to the carbonyl function;[15b] we have confirmed this observation for several 1-aryl-5-hydroxytetrazoles. The substituent parameters for the 5-hydroxytetrazole group (σ_I 0.45 and σ_R −0.12) indicate that the 1-nitrogen has less positive character than in the other tetrazoles with the unshared pair of electrons more available for resonance contribution to the phenyl ring. Thus, the heterocyclic ring is much less aromatic and more like an amide group (σ_I 0.24 and σ_R −0.22). However, the molecular weight in benzene is that of a dimer; hydrogen-bonded association should be more effective in the hydroxytetrazole than in the mercaptotetrazole (like carboxylic compared to thiocarboxylic acids) with the proton more closely associated with the ring nitrogen than with the oxygen.

Experimental Section

All melting points are corrected. Proton nmr spectra were obtained with a Varian A-60 spectrometer. Saturated deuteriochloroform solutions with tetramethylsilane as an internal standard were used unless otherwise noted. Peak center positions are reported as $\tau = 10 - \delta_H$ ppm; the number of protons (by integration) is given in brackets. Infrared spectra were determined in potassium bromide wafers with a Perkin-Elmer 21 spectrophotometer unless otherwise noted. Prominent peaks are noted. Ultraviolet spectra were determined in ethanol unless otherwise noted.

Starting Materials.—Activated sodium azide[34] was prepared by a simplified procedure obtained from Dr. F. D. Marsh of this laboratory. A solution of 10 g of commercial sodium azide in 30 ml of water was treated with 1.0 g of hydrazine hydrate. The solution was stirred for 15 min and was filtered into 400 ml of acetone. The precipitated sodium azide was separated by filtration, washed with acetone, and dried with a stream of nitrogen. It was stored in a tightly stoppered bottle under nitrogen and was used within 2 weeks.

Aryl isothiocyanates were prepared from the corresponding anilines and thiophosgene.[35a] N-Aryldichloroazomethines were generally prepared by chlorination of the corresponding aryl isothiocyanates;[35b] N-(*m*-nitrophenyl)dichloroazomethine was prepared by chlorination of *m*-nitrophenylformanilide in thionyl chloride.[36]

N-(*o*-Nitrophenyl)dichloroazomethine.—Only the following procedure gave a satisfactory product. A solution of 50 g of *o*-nitrophenylisothiocyanate in 1 l. of methylene chloride was treated overnight with a slow stream of chlorine. Nitrogen was passed through the reaction mixture to remove excess chlorine. The solution was filtered and the filtrate was concentrated at reduced pressure using a water pump protected by a trap cooled to −80°. The resulting viscous oil slowly crystallized. (The oil must not be warmed above 30°. Vigorous exothermic decomposition occurs above this temperature.) The crystals were dried on a clay plate. The crude N-(*o*-nitrophenyl)dichloroazomethine weighed 24.5 g after washing with hexane. Recrystallization from methylene chloride–hexane produced colorless crystals (21.4 g, 34%) which melted at 81.5–82.5°: $\lambda_{max}^{cyclohexane}$ 303 mμ (ε 2650), 250 (6720).

Anal. Calcd for $C_7H_4Cl_2N_2O_2$: C, 38.4; H, 1.84; N, 12.8; Cl, 32.4; mol wt, 219. Found: C, 39.1; H, 2.21; N, 13.0; Cl, 32.7; mol wt, 219 (cryoscopic benzene).

N-(*p*-Fluorophenyl)dichloroazomethine [bp 77° (9 mm), $n^{25}D$ 1.5440] was prepared by chlorination of the *m*-fluorophenyl isothiocyanate in dichloromethane at 25° and is also a new compound in this class.

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Anal. Calcd for $C_7H_4Cl_2FN$: C, 43.8; H, 2.10; F, 9.9; Cl, 36.9. Found: C, 44.0; H, 2.06; F, 10.6; Cl, 37.0.

A. Synthesis. 1. 1-Aryl-5-chlorotetrazoles.—The following example illustrates the general method used to prepare 1-aryl-5-chlorotetrazoles. All 1-aryl-5-chlorotetrazoles prepared by this method are reported in Table I with yields, physical and spectral properties, and analytical data. Any major modification in method or work-up is indicated in a footnote.

A solution of 19.2 g (0.010 mole) of N-(*p*-fluorophenyl)dichloroazomethine in 25 ml of dimethoxyethane was stirred overnight with 0.70 g (0.011 mole) of activated sodium azide. The solution was poured into a large excess of ice water. The resulting light-colored solid was separated by suction filtration, washed with water, and air dried. The crude 1-(*p*-fluorophenyl-5-chlorotetrazole), mp 87–88°, was obtained in yield of 1.59 g (79%) and was purified by recrystallization from benzene–hexane mixture to white crystals, mp 88°.

2. 1-Phenyl-5-azidotetrazole (3, Ar = C_6H_5).—A solution of 5.40 g of **2** (Ar = C_6H_5) in 100 ml of acetone was treated with 13 g of commercial sodium azide. (Activated sodium azide was used in most of the other preparations.) The solution was stirred and heated to reflux overnight. The mixture was filtered and solvent was removed from the filtrate under reduced pressure. The residue was recrystallized from methanol to yield 4.30 g (77%) of 1-phenyl-5-azidotetrazole, mp 96–96.7° (lit.[7] mp 99°).

This reaction underwent no apparent reversal when a solution of **3** (Ar = C_6H_5) in acetone was heated to reflux for 3 days with a large excess of tetraethylammonium chloride monohydrate.

3. 1-Aryl-5-mercaptotetrazoles.[15]—Most of these compounds were prepared by the standard literature procedures.[12] However, a modified procedure was required for the *o*-nitro derivative.

1-(*o*-Nitrophenyl)-5-mercaptotetrazole.[15]—A solution of 18 g (0.1 mole) of recrystallized *o*-nitrophenyl isothiocyanate in 50 ml of warm chloroform was placed in a round-bottom flask equipped with a mechanical stirrer and reflux condenser and mounted on the steam bath. A solution of 15 g of sodium azide in 50 ml of water was added to the stirred solution. After the initial exothermic reaction subsided, the steam was turned on and the stirred solution was heated to reflux for 0.5–1.5 hr. (The optimum time, which varied with the purity of the isothiocyanate, was determined for each batch.) The solution was cooled and filtered. The aqueous layer was separated and acidified with 10 ml of 37% hydrochloric acid. The precipitate of crude yellow thiol containing some *o*-nitrophenylcyanamide was separated by suction filtration, washed with distilled water, and air dried. The crude solid was slurried with 200 ml of benzene and allowed to stand for 1–3 days. The mixture was filtered and the pure 1-(*o*-nitrophenyl)-5-mercaptotetrazole was washed with benzene and was air dried: yield, 10–14 g (45–63%). A portion recrystallized by careful acidification (hydrochloric acid) of a solution in very dilute sodium hydroxide melted at 119.8–120.4°: ν_{max} 3040, 2900, 2750, 1600, 1580, 1525, 1393, 1340, 1290, 1044, 986, 856, 793, 743, 718, 696, and 662 cm^{-1}.

4. 1-Aryltetrazoles by Oxidation of 1-Aryl-5-mercaptotetrazole.—The following modifications of the procedure of Freund and Paradies[12] were found convenient for the preparation of a variety of 1-aryltetrazoles (see Table I; method B was found more suitable for certain thermally sensitive 5-mercaptotetrazoles).

Method A Illustrated for 1-Phenyltetrazole.—A stirred solution of 44.5 g (0.25 mole) of 1-phenyl-5-mercaptotetrazole in 350 ml of hot acetic acid was cooled to 70° and 50 g (0.50 mole) of solid chromic acid was added in portions while maintaining the temperature at 60–75°. After an additional 10 min at 70–75°, the product was poured onto a mixture of 1 kg of ice and 500 ml of dichloromethane in a 4-l. beaker. An aqueous solution of 200 g of sodium hydroxide was added continuously with stirring. The solution was brought to pH 7 with sodium carbonate solution. The solution was extracted with methylene chloride and the extract was washed with sodium carbonate solution and dried with magnesium sulfate. Solvent was removed under reduced pressure and the residue was recrystallized from carbon tetrachloride to yield 16.8 g (46%) of 1-phenyltetrazole, mp 66.5–67.3 (lit.[12] mp 66.5–67.3°).

Method B Illustrated for 1-(*o*-Nitrophenyl)tetrazole (10).—A solution of 30 g (0.135 mole) of *o*-nitrophenyl-5-mercaptotetrazole in 350 ml of acetic acid was treated with a solution of 20 g (0.20 mole) of chromic acid in 35 ml of water while maintaining the temperature at 35–40° with a cooling bath. The solution was allowed to stand for 1 hr and was worked up as above. Evaporation of the solvent produced 12–16 g (47–62%) of crude 1-(*o*-nitrophenyl)tetrazole, mp 79.5–82°. Recrystallization from ethanol afforded yellow crystals: mp 85–86°; nmr τ 0.92 (1), 2.05, 2.10 (4) symmetrical multiplets. When this compound was reduced with sodium sulfide in boiling aqueous ethanol, it lost nitrogen to form 2-aminobenzimidazole.

B. Chemical Reactions of 5-Aryltetrazoles. 1. Nitration.—To a stirred solution of 10.0 g (0.0554 mole) of 1-phenyl-5-chlorotetrazole in 90 ml of 90% nitric acid was added 30 ml of red fuming nitric acid and the mixture was warmed on the steam bath for 5 min. The solution was then poured onto ice and the solid product filtered, washed thoroughly with water, and air dried. The crude 1-(*p*-nitrophenyl)-5-chlorotetrazole (10.3 g, 83% yield, mp 91–94°) was recrystallized from benzene–hexane to give 8.20 g (66%) of pale yellow plates, mp 95.5–97.0°. The melting point rose to 98.0–99.4° after additional recrystallizations. The *para* orientation was proved by comparison of the infrared and proton nmr spectra with those of authentic samples of 1-(*m*- and *p*-nitrophenyl)-5-chlorotetrazole, prepared from the corresponding N-(nitrophenyl)dichloroazomethines. Analytical data are given in Table I.

2. Reduction. a. To Aniline.—In a control experiment, 0.5 g of 1-phenyl-5-chlorotetrazole in a solution of 100 ml of absolute alcohol containing 0.5 g of PtO_2 was recovered unchanged from shaking under 40-lb hydrogen pressure for 2 hr.

A 1.0-g sample of 1-(*m*-nitrophenyl)-5-chlorotetrazole in 100 ml of absolute ethanol containing 1.0 ml of 9 *N* HCl in anhydrous ethanol and 0.3 g of PtO_2 with hydrogenated in a Parr shaker at 40-lb hydrogen pressure for 2 hr. The catalyst was removed by filtration and the ethanol evaporated. The solid residue after trituration with ether weighed 0.58 g (mp 199–200° dec and was characterized as the hydrochloride of 1-(*m*-aminophenyl)-5-chlorotetrazole. The free aniline was obtained by treatment of the hydrochloride with sodium carbonate and was recrystallized from benzene–hexane. In larger scale hydrogenations the product was partly insoluble and was extracted from the catalyst with dilute hydrochloric acid.

b. Partial Reduction of *o*-Nitro Derivatives. 1. 1-(*o*-N-Hydroxylaminophenyl)tetrazole (12).—A solution of 14.8 g of **10** in 100 ml of warm ethanol was catalytically hydrogenated at 40 psi with 0.2 g of 10% palladium-on-charcoal catalyst. The resulting solution was filtered and the solvent was removed at room temperature under reduced pressure. The residue was rapidly recrystallized from ethanol to yield 9.9 g of 1-(*o*-N-hydroxylaminophenyl)tetrazole. A portion recrystallized from ethanol melted at 138.8–140.6°. The product was rapidly converted to the corresponding azo compound **13** in hot solvents. This reaction also appeared to occur slowly at room temperature in ethanol.

2. *o,o'*-Bis(1-tetrazolyl)azobenzene (13).—A solution of 0.5 g of the hydroxylamine **12** in 0.5 ml of N,N-dimethylformamide was heated for 3 hr on the steam bath. The solution was cooled, 3 ml of ethanol was added, and the orange crystalline product was separated by filtration. After recrystallization from hot dimethyl sulfoxide, the product melted with decomposition at 244.8°.

3. Diazotization and Coupling.—A solution of 0.46 g (0.0020 mole) of 1-(*m*-aminophenyl)-5-chlorotetrazole in 0.5 ml of sulfuric acid and 0.5 ml of glacial acetic acid was diazotized in the usual manner with 0.25 g of sodium nitrite and 0.5 ml of water. Excess nitrite was decomposed with 0.25 g of sulfamic acid in 5 ml of water and the diazonium solution was added to 1.0 g (0.010 mole) of β-naphthol in 50 ml of 95% ethanol. The orange precipitate (0.7 g) was separated by filtration, extracted in ethyl acetate, and precipitated by slow addition of pentane. The 1-[*m*-(β-hydroxynaphthylazo)phenyl]-5-chlorotetrazole (0.44 g, mp 204–205° dec) was further purified for analysis by recrystallization from benzene.

4. Reaction with Magnesium or Butyllithium.—A solution of 3.61 g of 1-phenyl-5-chlorotetrazole in 10 ml of tetrahydrofuran was added to 0.5 g of magnesium in 5 ml of tetrahydrofuran under dry nitrogen. A crystal of iodine and 1 drop of isopropyl alcohol did not initiate reaction, but after refluxing for several hours part of the magnesium was consumed. The solution was cooled and dry CO_2 passed over the surface. No reaction was apparent. The solution was hydrolyzed with

dilute ammonium sulfate and the ether layer separated. No product was isolated from the aqueous phase on acidification, but 2.41 g of oil was obtained from the ether. This oil crystallized on standing, mp 40–45°, and was identified as N-phenylcyanamide, containing small amounts of impurity, by comparison of infrared spectra with that of an authentic sample.

From reaction of 3.28 g (0.0182 mole) of 1-phenyl-5-chlorotetrazole in 40 ml of ether with 13.4 ml of 1 *M* butyl lithium solution in hexane (0.020 mole of butyllithium) at −10°, followed by CO_2 treatment and hydrolysis, 1.15 g of crude N-phenylcyanamide was obtained.

5. Rearrangements of 1-Aryl-5-mercaptotetrazoles (9).—A mixture of 10 g of the 1-(*o*-nitrophenyl)-5-mercaptotetrazole (**9**) and 150 ml of benzene was heated to reflux for no more than 45 min. The solvent was removed under reduced pressure at room temperature and the yellow solid residue was triturated with 10 ml of acetone. The mixture was filtered to remove sulfur and solvent was removed from the filtrate under reduced pressure. The residue was rapidly recrystallized from 75 ml of boiling benzene (Darco) to which 5 ml of hexane was added. The yellow crystalline 5-(*o*-nitroanilino)-1,2,3,4-thiatriazole (5.08 g, 51%) melted at 114.2–114.7°: ν_{max} 1609, 1590, 1548, 1502, 1470, 1334, 1320, 1270, 1216, 1170, 1146, 1094, 1070, 972, 931, 869, 825, 782, 744, and 698 cm^{-1}. By acidification of a solution of **16** in *warm* base, the mercaptotetrazole **9** was obtained.

By the slow addition of hexane to the mother liquors from the recrystallization of **15**, 2.25 g (26%) of *o*-nitrophenylcyanamide was obtained. This compound could also be obtained in high yield by heating **15** overnight in refluxing benzene. The *o*-nitrophenylcyanamide melted at 148.8–149.8° (lit. mp 146°[37a] and 152–153°[37b]) and exhibited characteristic infrared absorptions for NH, C≡N, and NO_2 at 3230, 2260, and 1530/1340 cm^{-1}, respectively.

For preparation of phenyl- and *m*- and *p*-fluorophenylaminothiatriazoles, a modified literature procedure[17,38] (addition of ethanol as solvent was necessary) was most satisfactory because the rate of isomerization of the mercaptotetrazole appeared, from infrared studies, to proceed at a comparable rate to that of decomposition to cyanamide. The physical and analytical data on the fluorophenylthiatriazoles are given in Table I.

N-Phenylcyanamide and N-(*p*-fluorophenyl)cyanamide were obtained in very low yield from decomposition of the corresponding 5-aryl-1-mercaptotetrazoles in refluxing benzene. The *m*-fluorophenylcyanamide was obtained in approximately 40% yield.[39] The products were isolated by evaporation of the solvent, extraction with cold dilute sodium hydroxide solution, and acidification with cold dilute hydrochloric or acetic acid. The poor yields in these cases relative to that from *o*-nitrophenylcyanamide are attributed to the low stability of the products in the reflexing benzene.

Anal. Calcd for $C_7H_5FN_2$: F, 14.0; N, 20.6. Found (for *meta* isomer): F, 13.7, 13.6; N, 20.0; mp 68–68.5°. Found (for *para* isomer): F, 13.7, 13.6; N, 20.4, 20.8; mp 82.1–82.8°.

C. Thermal Decomposition Studies.—The 1-phenyl-5-chlorotetrazole was decomposed in the temperature range of 150–200°, neat and in solvents such as ethylene glycol, diethyl maleate, mineral oil, benzonitrile, 2-(2-butoxyethoxy)ethanol, dicyclopentadiene, and trichlorobenzene. Only brown-to-black resins or dark oils were obtained and no tractable product could be isolated.

Kinetic studies on rate of nitrogen evolution were carried out by measuring nitrogen evolution from a tetrazole using a sealed system connected to a gas buret. The tetrazole sample (about 1 g) was added to approximately 100 ml of solvent held at constant temperature by a refluxing solvent bath; 95–100% of the theoretical amount of nitrogen was obtained for a completed reaction. A first-order rate constant to ±10%, was found between 20 and 70% of nitrogen evolution. The first-order rate constants for nitrogen evolution in a series of decompositions showing solvent, catalyst, and substituent effects are given in Tables II and III.

D. Physical and Spectral Measurements. 1. Ionization Constants.—The ionization constants of the anilines were determined by spectrophotometric measurement in water at 25° as described previously,[40] following the procedure of Bryson.[41] Data are given in Table IV.

2. Nmr Calibrations.—The F^{19} nmr calibrations were carried out as described previously[30,31] in acetonitrile containing 5% *p*-difluorobenzene or in benzene, dioxane, acetonitrile, acetone, or methanol containing 5% 1,1,2,2-tetrachlorotetrafluorocyclobutane as internal calibrant. (Samples were not of sufficient solubility to be calibrated in trichlorofluoromethane or other solvents of low polarity.) Measurements were made at three or four concentrations (40, 20, 10, and 5%) and the chemical shift was obtained by extrapolation to infinite dilution. Data are reported in Table V.

3. Substituent Parameters.—The Hammett σ constants were calculated by the standard methods[30,42] from the ionization constant data. Substituent constants were calculated from the F^{19} Nmr chemical shift data using the procedure described by Taft and co-workers.[30,31,43] The σ_I, σ_R parameters were calculated according to Taft.[31] The data are reported in Tables IV and VI.

Registry No.—**1** (Ar = *o*-$NO_2C_6H_4$), 14213-48-0; **1** (Ar = *p*-FC_6H_4), 14210-24-3; **2** (Ar = C_6H_5), 14210-25-4; **2** (Ar = *m*-FC_6H_4), 14210-26-5; **2** (Ar = *p*-FC_6H_4), 14210-27-6; **2** (Ar = *o*-$O_2NC_6H_4$), 14210-28-7; **2** (Ar = *m*-$O_2NC_6H_4$), 7025-13-0; **2** (Ar = *p*-$O_2NC_6H_4$), 14210-30-1; **2** (Ar = *m*-$H_2NC_6H_4$), 14210-31-2; **2** (Ar = *m*-$H_2NC_6H_4$) HCl, 14210-32-3; **2** (Ar = *p*-$H_2NC_6H_2$), 14210-33-4; **2** (Ar = $C_{16}H_{12}N_2O$), 14210-34-5; **3** (Ar = C_6H_5), 14210-35-6; **3** (Ar = *m*-FC_6H_4), 14210-36-7; **3** (Ar = *p*-FC_6H_4), 14210-37-8; **3** (Ar = *p*-$O_2NC_6H_4$), 14210-38-9; **5**, 14210-39-0; **6**, 14518-73-1; **9a**, 14210-40-3; **9b**, 14210-41-4; **9** (Ar = *m*-FC_6H_4), **9a** form, 14210-42-5; **9** (Ar = *p*-FC_6H_4), **9a** form, 14210-43-6; **9** (Ar = *m*-$O_2NC_6H_4$), **9a** form, 14210-44-7; **9** (Ar = *p*-$O_2NC_6H_4$), **9a** form, 14210-45-8; **9** (Ar = *m*-FC_6H_4), **9b** form, 14210-46-9; **9** (Ar = *p*-FC_6H_4), **9b** form, 1544-79-2; **9** (Ar = *m*-$O_2NC_6H_4$), **9b** form, 7025-16-3; **9** (Ar = *p*-$O_2NC_6H_4$), **9b** form, 14210-49-2; **10**, 14210-50-5; **11**, 14210-51-6; **12**, 14210-52-7; **13**, 14320-29-7; **15** (Ar = *o*-$O_2NC_6H_4$), 14213-04-8; **15** (Ar = *m*-FC_6H_4), 14213-05-9; **15** (Ar = *p*-FC_6H_4), 1544-80-5; N-phenylcyanamide, 622-34-4; *o*-nitrophenylcyanamide, 5465-98-5.

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