Syntheses, ^{13}C and ^{1}H Nuclear Magnetic Resonance Spectra of Some 1,2,4-Triazine 1- and 2-Oxides

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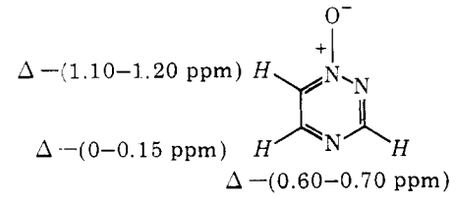
The selective synthesis of 1,2,4-triazine 2-oxide and some of its derivatives is described. The ^{1}H and ^{13}C NMR spectra of these and related compounds are discussed. N-Oxidation of azines causes shielding of the ^{13}C situated ortho and para to the *N*-oxide function and some deshielding of the ^{13}C situated meta to this functional group when viewed *through* an ortho carbon atom. It is suggested that back-donation of the oxide oxygen electrons contributes significantly to the ground state of the 1,2,4-triazine 1- as well as 2-oxides.

Some time ago we described the synthesis of 1,2,4-triazine 1-oxide (**1**) and some of its 3- as well as 5-substituted derivatives, along with structure proofs of 3-amino-5-phenyl- (**2c**) and 3-amino-5,6-diphenyl-1,2,4-triazine 2-oxides.[1]

As these studies suggested, substituted 3-amino-1,2,4-triazines afford, as the major N-oxidation products, the 2-oxides. We have now applied this type of oxidation to 3-amino-1,2,4-triazine (**2a**) (cf. Scheme I) and its 5-methyl derivative (**2b**) and have obtained their respective mono-*N*-oxides (**3a** and **3b**). The ^{1}H NMR spectra of these *N*-oxides



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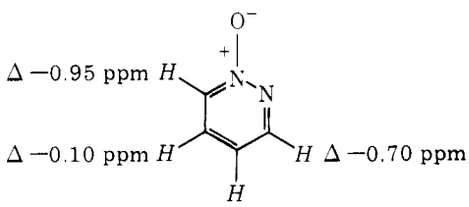

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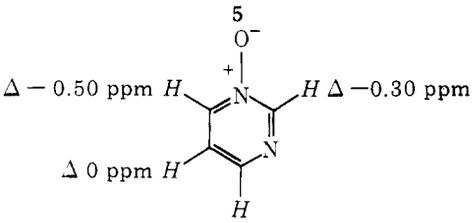

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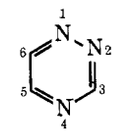
$(\Delta = \delta_{N\text{-oxide}} - \delta_{\text{non-}N\text{-oxidized azine}})$

when compared with those of the starting amines (cf. Table I) show that H-6 becomes more shielded upon N-oxidation by 0.65 and 0.62 ppm (cf. Table II), respectively, while H-5 experiences shielding by only 0.34 ppm. In order to establish the site of N-oxidation in these compounds we took recourse to comparing these chemical shift changes with those that occur upon N-oxidation of several other azines:[1-3]

Clearly, the proton situated on the carbon meta to the *N*-oxide function [bonded via another sp^2 nitrogen; H-3 in pyridazine 1-oxide (**5**), and in 1,2,4-triazine 1-oxide (**1**)] becomes more shielded by 0.60–0.70 ppm upon N-oxidation. The proton bonded to the carbon situated para to the *N*-oxide becomes more shielded by 0.30–0.50 ppm [H-4 in pyridazine 1-oxide (**5**) and in pyrimidine 1-oxide (**6**)].

Table I. ^{1}H Chemical Shifts (δ) of Some 1,2,4-Triazine Reference Compounds



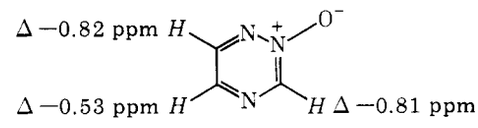
Registry no.	Compd[a]	R_3	R_5	R_6	R_3	R_5	R_6
27531-62-0	**1**[7]	H	H	H	9.00	8.57	8.04
1120-99-6	**2a**[7]	NH_2	H	H	8.28	8.53	8.88
6302-68-7	**2b**[4]	NH_2	CH_3	H	7.36	8.62	8.80
61108-77-8	**10a**[5]	NHR_3[b]	H	H	3.80	8.12	8.56
61108-78-9	**10b**[5]	NHR_3	CH_3	H	3.83	2.38	8.51
61108-79-0	**10c**[5]	NHR_3	Ph	H	3.88	8.10 7.52	9.09
290-38-0	**25**[1]	H	H	H	9.63	8.53	9.24

[a] Superscript numbers refer to the references describing the syntheses of these compounds. [b] $R_3 = CH_2CH_2Cl$.

Thus, the chemical shift changes in the 3-amino-1,2,4-triazines upon N-oxidation clearly establish these compounds as 2-oxides (**3a–c**) (cf. Scheme I).

When the 3-amino-1,2,4-triazine 2-oxides (**3a–c**) were treated with nitrous acid, in the presence of hydrochloric acid, the respective 3-chloro-1,2,4-triazine 2-oxides (**4a–c**) were obtained, while, with nitrous acid in the presence of hydrobromic acid, the 3-bromo-1,2,4-triazine 2-oxide (**7**) was generated. To assure ourselves that we are indeed dealing with the 3-halo compounds, the 3-chloro derivative **4a** was treated with methanolic ammonia, to regenerate the 3-amino compound **3a**.

In order to prepare 1,2,4-triazine 2-oxide (**9**) itself, the 3-bromo derivative (**7**) was treated with hydrazine to form the 3-hydrazino derivative (**8**), which, when oxidized with activated manganese dioxide, afforded a compound $C_3H_3N_3O$. The ^{1}H NMR spectrum of this substance (**9**) (cf. Table II) shows an ABX pattern ($J_{AB} = 3.0$, $J_{AX} = 0.3$ Hz). The most deshielded proton, a broad singlet approaching a doublet, can be assigned to H-3, while H-5 and H-6 resonate at δ 8.00 and 8.42, respectively. The latter two assignments are established by comparison with the chemical shifts of these protons in compounds **4a,b** and **7**. Thus, the substance is the expected 1,2,4-triazine 2-oxide (**9**). A comparison of these proton chemical shifts with those of the corresponding ones in 1,2,4-triazine (**25**) affords the following proton chemical shift differences ($\Delta = \delta_{N\text{-oxide}} - \delta_{\text{non-N-oxidized compound}}$):



Scheme I

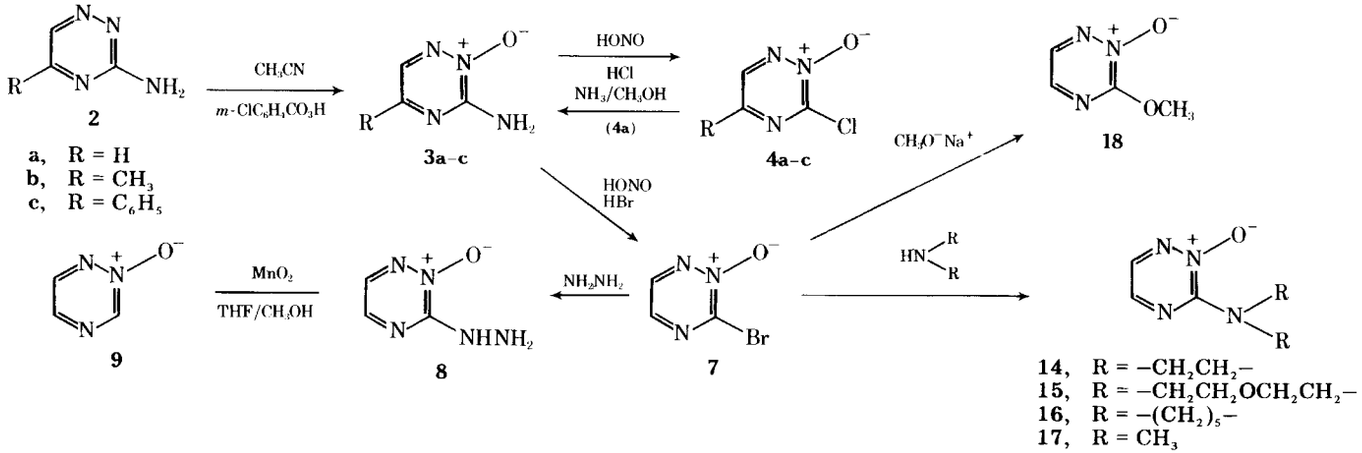
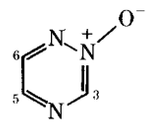


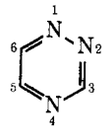
Table II. ^{1}H NMR[a] and Analytical Data of Some 1,2,4-Triazines



Registry no.	Compd	Mol formula	Substituents			^{1}H NMR, δ			Mp, °C	Calcd, %			Found, %		
			R_3	R_5	R_6	R_3	R_5	R_6		C	H	N	C	H	N
61177-95-5	**3a**	$C_3H_4N_4O$	NH_2	H	H	8.28	8.19	8.23	200–201	32.15	3.16	49.27	31.92	3.34	49.47
61177-96-6	**3b**	$C_4H_6N_4O$	NH_2	CH_3	H	8.18	2.61	8.18	168–169	38.10	4.80	44.41	38.08	4.89	44.44
61177-97-7	**12a**	$C_8H_7N_4OCl$	NHR	H	H	3.81	7.23	7.84	106–108	34.40	4.04	37.09	34.31	4.06	32.17
61177-98-8	**12b**	$C_6H_9N_4OCl$	NHR	CH_3	H	3.81	2.39	7.71	150 dec	38.21	4.81	29.71	38.16	4.82	29.68
61177-99-9	**12c**	$C_{11}H_{11}N_4OCl$	NHR	Ph	H	3.87	7.98 7.50	8.33	165 dec	52.70	4.42		52.89	4.51	
61202-85-5	**4a**	$C_3H_2N_3OCl$	Cl	H	H		7.98	8.46	84–85	27.39	1.53	31.95	27.68	1.70	31.41
61178-00-5	**4b**	$C_4H_4N_3OCl$	Cl	CH_3	H		2.55	8.32	72–74	33.01	2.77	28.87	33.01	2.78	28.90
61178-01-6	**4c**	$C_9H_6N_3OCl$	Cl	Ph	H		8.01 7.55	8.88	153–155	52.06	2.91		52.21	3.05	
61178-02-7	**7**	$C_3H_2N_3OBr$	Br	H	H		7.86	8.45	100–103	27.39	1.53	31.95	27.68	1.70	31.41
61178-03-8	**18**	$C_4H_5N_3O_2$	OCH_3	H	H	4.24	7.76	8.12	108–110	37.39	3.96	33.07	37.72	4.00	33.10
61178-04-9	**17**	$C_5H_8N_4O$	NMe_2	H	H	3.30	7.76	7.86	73–75	42.85	5.71	40.00	42.72	5.74	40.14
61178-05-0	**15**	$C_7H_{10}N_4O_2$	NC_4H_8O	H	H	3.88	7.81	8.02	122–124	46.15	5.49	30.77	46.19	5.53	30.70
61178-06-1	**16**	$C_8H_{12}N_4O$	NC_5H_{10}	H	H	3.64 1.59	7.66	7.79	52–55	53.33	6.66	31.11	53.20	6.54	31.19
61178-12-9	**14a**	$C_5H_6N_4O$	NC_2H_4	H	H	2.60	7.82	8.16	97–99	43.48	4.38	40.56	43.57	4.42	40.59
61178-08-3	**14b**	$C_6H_8N_4O$	NC_2H_4	CH_3	H	2.59	2.44	8.02	90–92	47.36	5.30	36.82	47.38	5.31	36.71
61178-09-4	**8**	$C_3H_5N_5O$	$NHNH_2$	H	H		8.34	8.38	163–164	28.36	3.96	55.10	28.46	3.98	55.38
59323-39-6	**9**	$C_3H_3N_3O$	H	H	H	8.82	8.00	8.42	82.5–84	37.11	3.09	43.29	37.04	3.17	43.11

[a] Chemical shifts in δ (ppm), dilute solutions in $CDCl_3$, except for the 3-amino derivatives, which are recorded as dilute solutions in CD_3SOCD_3.

Table III. ^{13}C Chemicals Shifts (δ ppm) of Some 1,2,4-Triazines and Their *N*-Oxides[a]

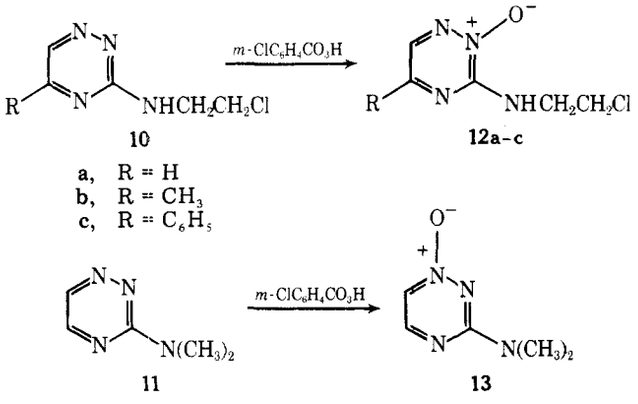


Position of *N*-oxidation —N-ox—	Substituents	Registry no.	C_3	C_5	C_6	Substituent carbon
N-2	None (9)		132	143	143	
None	3-OCH_3 (19)	28735-22-0	164	150	143	54
None	3-OCH_3, 6-CH_3 (20)	61178-10-7	163	150	152	54
N-1	3-OCH_3 (21)	27531-67-5	166.5	154	124.5	55.5
N-2	3-OCH_3 (18)		152.5	130	135.5	57
None	3-NH_2 (2a)		161	148	139	
None	3-NH_2, 5-CH_3 (24)	6302-68-7	161	157	139	20
N-1	3-NH_2 (23)	61178-11-8	162	153	119	
N-2	3-NH_2 (3a)		151	132	134	
None	3-NMe_2 (22)	53300-17-7	160	148	138	36
N-1	3-NMe_2 (13)	61178-07-2	161	152	120	36
N-2	3-NMe_2 (17a)		151	132	133	39

[a] ^{13}C spectra were taken with a Hitachi Perkin-Elmer R-26 spectrometer; δ (ppm) from Me_4Si. The spectra of the amino compounds were obtained as 1.5 M solutions in Me_2SO-d_6; all of the others were obrained as 1.5 M solutions in $CDCl_3$. The pulse intervals were 16 s, and a pulse angle of 50° with a total of about 500 scans per spectrum. All spectra were wide-band proton decoupled.

The selective N-2 oxidation of the 3-amino-1,2,4-triazines (**2a–c**) in contrast to the N-1 oxidation of 3-methoxy-1,2,4-triazines prompted us to examine the N-oxidation of some 3-alkylamino- (**10**) and 3-dimethylamino- (**11**) 1,2,4-triazines. In the former instances (cf. Scheme II) the N-oxidation again

Scheme II



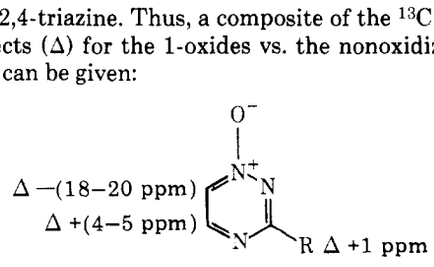
afforded the 2-oxides (**12a–c**) as established by a comparison of the proton chemical shifts with those of the nonoxidized compounds (**10a–c**), while the 1-oxide (**13**) was obtained in the latter instance.[6] Thus, it appears that a *3-amino–3-imino tautomerism* must be possible in order for *N-2 oxidation* to occur on these 1,2,4-triazines, while the absence of this possibility causes N-oxidation to occur at N-1.

That the 3-halo substituents in the 2-oxides (**4a, 7**) are, as expected, subject to facile nucleophilic displacement reactions was shown by their conversion to 3-ethylenimino- (**14a**), 3-morpholino- (**15**), 3-piperidino- (**16**), 3-dimethylamino- (**17**), and 3-methoxy- (**18**) 1,2,4-triazine 2-oxides under very mild conditions (room temperature, 5–10 min).

The ^{13}C chemical shifts of 1,2,4-triazines as well as their 1- and 2-oxides and derivatives have never been examined. To confirm our structural assignments and to develop background information for more detailed studies, we obtained the ^{13}C spectra of some of the compounds (cf. Table III).

3-Methoxy-1,2,4-triazine (**19**) has, as anticipated, four carbon signals. The relaxation time of the most deshielded carbon (164 ppm) is much longer than that of any of the others (relative peak heights 1:4 for C_3 vs. C_5 or C_6 under our experimental conditions) and is, consequently, assigned to C-3, while the most shielded peak (54 ppm) is clearly due to the methoxyl carbon atom. The remaining two peaks (143 and 150 ppm, respectively) must now be assigned. Since it is well known[9] that C-methylation causes deshielding of the methyl group bearing carbon by 8–10 ppm, we examined the ^{13}C spectrum of 3-methoxy-6-methyl-1,2,4-triazine (**20**). The peaks due to C_3 as well as the methoxyl carbon in compound **20** still have the same chemical shift in this derivative as in compound **19**, while the 143-ppm peak is not only shifted to 152 ppm, but its relaxation time is also considerably lengthened (relative peak heights 1:2 for C_6 vs. C_5 under our experimental conditions). Thus, C-6 resonates at 143 ppm and C-5 at 150 ppm in 3-methoxy-1,2,4-triazine (**19**). Similar comparisons of the 3-amino-1,2,4-triazines again show that C-6 is more shielded than C-5. Thus, the shielding sequence of the ^{13}C nuclei in these 1,2,4-triazines is C-3 < C-5 < C-6.

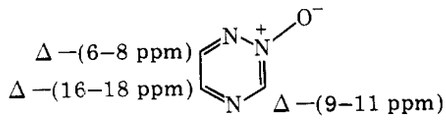
The ^{13}C spectrum of 3-methoxy-1,2,4-triazine 1-oxide (**21**) shows the long relaxation time peak at 166.5 ppm, ascribable to C-3, along with absorptions at 154.0 and 124.5 ppm, respectively. The former is clearly due to C-5 while the latter, with increased relaxation time, must be due to C-6, the carbon ortho to the *N*-oxide function. Thus N-1 oxidation causes shielding (Δ 18 ppm) of C-6, while having little effect (some deshielding, Δ 2–5 ppm) on the other carbon atoms. Similar effects occur in the N-1 oxides of 3-amino- and 3-dimethylamino-1,2,4-triazine. Thus, a composite of the ^{13}C chemical shift effects (Δ) for the 1-oxides vs. the nonoxidized 1,2,4-triazines can be given:



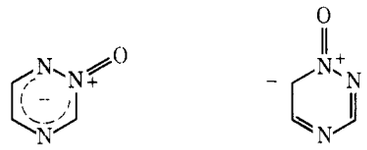
(negative numbers indicate shielding)

The ^{13}C carbons in 3-methoxy-1,2,4-triazine 2-oxide (**18**) in comparison to the non-N-oxidized compound **19** are all more shielded. The lowest intensity peak (longest relaxation time) is again assigned to C-3 (152.5 ppm). This peak has become more shielded by 11 ppm with respect to the non-N-oxidized compound. While the C-5 and C-6 chemical shifts of all of the 2-oxides examined are very similar (Δ 0–5 ppm),

a comparison of these chemical shifts with those of the corresponding non-N-oxidized compounds is nevertheless possible and establishes that C-5, upon 2-oxidation, becomes more shielded by 16–18 ppm, while C-6 experiences a shielding of 6–8 ppm. Thus the following composite can be drawn ($\Delta = \delta_{^{13}C\ N\text{-oxide}} - \delta_{^{13}C\ \text{nonoxidized compound}}$):

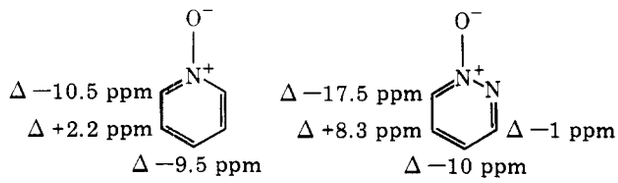


Since the ortho and para positions in the 1- as well as 2-oxides become more shielded in comparison to the nonoxidized compounds, this functional group is increasing the electron density at these positions in the 1,2,4-triazine ring system.[10] Consequently, resonance contributing structures involving back-donation of electrons from the oxygen must contribute significantly to the ground states of these *N*-oxides. Since C-5 in the 2-oxides also experiences shielding upon N-2 oxidation, structure **26** may well best represent the ground-state structure of these 2-oxides while **27** describes the apparent lesser degree of back-donation in the 1-oxides.

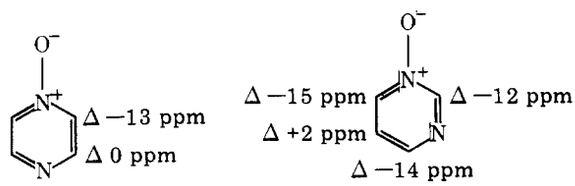


26 **27**

The ^{13}C NMR spectra of some pyridine[11] and pyridazine *N*-oxides[12] have also been recently described. In these compounds shielding effects similar to those observed in the 1,2,4-triazine *N*-oxides occur:



In order to complete the "picture" we obtained the ^{13}C spectra of the *N*-oxides of pyrazine (**28**) and pyrimidine (**29**). The differences in the ^{13}C chemical shifts ($\delta_{N\text{-oxide}} - \delta_{\text{non-}N\text{-oxide}}$) of the various ring carbons are as follows.



The chemical shift effect on the carbon atoms in these azines upon N-oxidation can now be summarized. (1) Carbons ortho and para to the *N*-oxide function become more *shielded* (9–20 ppm). (2) Carbons meta to the *N*-oxide *through* a *carbon* bond become slightly *deshielded* (0–8 ppm). (3) Carbons meta to the *N*-oxide *through* a *nitrogen* bond become slightly *shielded* (1–6 ppm). A comparison of these effects with those in the corresponding ^1H NMR spectra points to the interesting difference between the chemical shift changes on the carbon and proton meta to the *N*-oxide through a carbon atom, where in the ^1H NMR none or a small *shielding* effect is observed while in the carbon NMR none or a *deshielding* effect is present.

Conclusion

This study has afforded synthetic means to selectively prepare 1,2,4-triazine 1- and 2-oxides.

The ^{13}C chemical shifts of a series of azine *N*-oxides have been related to their azine precursors. A combination of ^{13}C and ^1H NMR can be employed to unequivocally establish sites of N-oxidation in azines.

Experimental Section[13]

The 3-amino-1,2,4-triazines (**2a–c**) were prepared as described in ref 7, the 3-(2-chloroethylamino)-1,2,4-triazines as described in ref 5. The dimethylamino-1,2,4-triazine 1-oxide was prepared by the method of Paudler and Chen.[6]

Table II lists the necessary analytical data for the new compounds prepared in this study.

Preparation of 3-Amino-1,2,4-triazine 2-Oxides (3a, b). In a typical experiment, 7.00 g (3.40 mmol) of 85% *m*-chloroperbenzoic acid dissolved in 60 ml of reagent grade acetonitrile was added dropwise (10 min) to 2.85 g (26.0 mmol) of 3-amino-1,2,4-triazine (**2a**) in 120 ml of acetonitrile. The reaction mixture was heated at 70–75 °C for 3.0 h and allowed to come to room temperature. The reaction mixture was then evaporated in vacuo and the residue triturated with 100 ml of ether. The suspension was filtered and the solid washed with ether (3 × 20 ml) and benzene (2 × 20 ml) to give 2.63 g (80%) of **3a.** Compounds **3b** could be prepared in 80% yield by a similar procedure. Compounds **3a** and **3b** could be further purified by vacuum sublimation (0.1 Torr, 130 °C) or by recrystallization from acetonitrile.

Preparation of 3-Chloro-1,2,4-triazine 2-Oxides (4a–c). In a typical experiment, 2.76 g (0.04 mol) of $NaNO_2$ in 9 ml of H_2O was added dropwise (20 min) to a solution of 1.12 g (0.01 mol) of compound **3a** in 17 ml (0.10 mol) of 6 N HCl cooled to 0 °C. After the addition was complete, 30 ml of $CHCl_3$ was added and the reaction mixture was allowed to come to room temperature. The $CHCl_3$ was separated and additional $CHCl_3$ (4 × 30 ml) extractions were made. The combined $CHCl_3$ extracts were dried over anhydrous Na_2SO_4, filtered, and evacuated in vacuo. The residue was sublimed at 55–60 °C (0.01 Torr) to give 440 mg (34%) of **4a.** Compounds **4b** and **4c** were prepared by a similar procedure in 32 and 26% yields, respectively.

Preparation of 3-Bromo-1,2,4-triazine 2-Oxide (7). To a solution of 1.12 g (0.01 mol) of 3-amino-1,2,4-triazine 2-oxide (**3a**) in 100 ml of 2 N HBr was added, dropwise, at 0 °C, a solution of 4.14 g (0.12 mol) of $NaNO_2$ in 20 ml of water. The solution was refrigerated overnight and extracted with $CHCl_3$ (5 × 100 ml). The combined extracts were washed with 50 ml of saturated aqueous Na_2CO_3 solution and dried over anhydrous Na_2SO_4. The $CHCl_3$ was evaporated and the residue sublimed at 60 °C (0.05 Torr) to give 1.0 g (47%) of 3-bromo-1,2,4-triazine 2-oxide (**7**).

Preparation of 3-Hydrazino-1,2,4-triazine 2-Oxide (8). To a solution of 1.0 g (5.7 mmol) of 3-bromo-1,2,4-triazine 2-oxide (**7**) in 200 ml of dry tetrahydrofuran was slowly added 0.27 g (0.85 mol) of hydrazine (97%) in 10 ml of dry CH_3OH. The solution was stirred for 30 min and the yellow solid was removed by filtration. Evaporation of the filtrate gave an orange solid which could be recrystallized from CH_3CH_2OH to yield 0.5 (69%) of 3-hydrazino-1,2,4-triazine 2-oxide (**8**).

Preparation of 1,2,4-Triazine 2-Oxide (9). To a solution of 0.2 g (1.4 mmol) of compound **8a** dissolved in 200 ml of dry tetrahydrofuran was added 5 g of activated MnO_2 and the slurry was stirred for 4.5 h. The solution was filtered through Celite and the filtrate was evaporated to dryness to give a yellow-brown oil which crystallized upon standing. Sublimation at room temperature and at 0.1 Torr yielded 40 mg (27%) of 1,2,4-triazine 2-oxide (**9**) as a white solid.

Preparation of 3-(2-Chloroethylamino)-1,2,4-triazine 2-Oxides (12a–c). In a typical experiment, 900 mg (4.4 mmol) of 85% *m*-chloroperbenzoic acid dissolved in 30 ml of anhydrous $CHCl_3$ was added to 640 mg (3.7 mmol) of compound **10b** in 40 ml of anhydrous $CHCl_3$. The reaction mixture was stirred at room temperature overnight and heated at 50–5 °C for 70 min. The cooled $CHCl_3$ solution was washed first with a solution of 0.65 g (4.6 mmol) of K_2CO_3 in 50 ml of H_2O followed by 2 × 20 ml of H_2O. The remaining $CHCl_3$ solution was dried over anhydrous Na_2SO_4, filtered, and evaporated in vacuo. The residue was chromatographed on neutral alumina (grade III) using $CHCl_3$–CH_2Cl_2 (1:1) as eluent to give 530 mg (77%) of **12b.** Compounds **10a** and **10c** were isolated in 51 and 35% yields, respectively, by similar procedures. Analytical samples were obtained by vacuum sublimation.

Preparation of 3-Aziridino-1,2,4-triazine 2-Oxides (14a). In a typical experiment, 0.70 ml (13.0 mmol) of aziridine dissolved in 15 ml of CH_2Cl_2 was added dropwise to 750 mg (5.6 mmol) of compound **7a** in 50 ml of CH_2Cl_2 cooled in an ice bath. After the addition, the ice bath was removed and the reaction mixture was stirred for 0.5 h. The reaction mixture was washed with a solution of 0.79 g (5.6 mmol) of

K_2CO_3 in 10 ml of H_2O. The CH_2Cl_2 was separated and additional CH_2Cl_2 (5 × 25 ml) extracts were made. The combined CH_2Cl_2 extracts were dried over anhydrous Na_2SO_4, filtered, and evaporated in vacuo at room temperature. The residue was chromatographed on a short column of neutral alumina (grade III) and eluted with $CHCl_3$ to give 730 mg (95%) of **14a**. An analytical sample was prepared by sublimation at 50 °C (0.01 Torr). A similar procedure gave compound **14b** in 90% yield.

Preparation of 3-Morpholino-1,2,4-triazine 2-Oxide (15). To a solution of 100 mg (5.7 mmol) of 3-bromo-1,2,4-triazine 2-oxide (**7**) in 25 ml of dry tetrahydrofuran was added 99.4 mg (1.14 mmol) of morpholine as a solution in 5 ml of dry tetrahydrofuran. The solution was stirred for 10 min during which time it became bright yellow and the solid which formed was removed by filtration. The filtrate was evaporated to give a yellow solid. This was recrystallized from 50:50 petroleum ether (bp 30–60 °C)–cyclohexane to give 90 mg (93%) of 3-morpholino-1,2,4-triazine 2-oxide (**15**) as yellow needles.

Preparation of 3-Piperidino-1,2,4-triazine 2-Oxide (16). To a solution of 100 mg (0.57 mmol) of 3-bromo 1,2,4-triazine 2-oxide (**7**) in 25 ml of dry tetrahydrofuran was added a solution of 97 mg (1.1 mmol) of piperidine in 5 ml of tetrahydrofuran. The solution was stirred for 10 min during which time it became bright yellow and the solid which formed was removed by filtration. The filtrate was evaporated and the residue was recrystallized from petroleum ether–cyclohexane to give 100 mg (95%) of 3-piperidino-1,2,4-triazine 2-oxide (**16**), as a fluffy, yellow solid.

Preparation of 3-Dimethylamino-1,2,4-triazine 2-Oxide (17). To a solution of 200 mg (1.5 mmol) of 3-bromo-1,2,4-triazine 2-oxide (**7**) in 50 ml of CH_2Cl_2 was bubbled gaseous dimethylamine. The solution became immediately yellow and was stirred for 10 min. The solution was evaporated and the residue sublimed to give a bright yellow solid. This material was recrystallized from tetrahydrofuran to give 200 mg (93%) of 3-dimethylamino-1,2,4-triazine 2-oxide (**17**) as yellow needles.

Preparation of 3-Methoxy-1,2-4-triazine 2-Oxide (18). To a solution of 0.564 g (5.7 mmol) of triethylamine in 25 ml of dry CH_3OH was added 0.5 g (2.85 mmol) of 3-bromo-1,2,4-triazine 2-oxide (**7**). The solution was stirred until TLC (alumina $CHCl_3$) showed that no starting material was left (3 h). The solution was evaporated and the residue, dissolved in 1 ml of $CHCl_3$, was passed through a short column of alumina (15 g) (grade III) and eluted with $CHCl_3$. The solvent was then evaporated below 40 °C and under reduced pressure. The residue was sublimed to yield 60 mg (10%) of 3-methoxy-1,2-4-triazine 2-oxide (**18**).

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Registry No.—Aziridine, 151-56-4; morpholine, 110-91-8; piperidine, 110-89-4; dimethylamine, 124-40-3; methanol, 67-56-1.

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