with 300 mL of ether and then poured into 300 mL of 20% aqueous hydrochloric acid. After separation, the ether solution was washed with an additional 300 mL of 20% aqueous hydrochloric acid and was dried over anhydrous magnesium sulfate. The ether was removed under reduced pressure and the residue was distilled at 0.6 Torr to give 4.56 g of a light yellow liquid (bp 107–110 °C at 0.6 Torr; lit.[27] bp 254–257 °C) that crystallized on standing (mp 40.5–41.0 °C; lit.[27] mp 43 °C): 0.0238 mol, 68% yield.

Acknowledgment. We gratefully acknowledge the financial support of the National Science Foundation for this work. We thank Richard J. Bosch for his assistance in this project.

Registry No.—Dimethylformamide, 68-12-2; $C_6H_5CH_2ONO$, 935-05-7.

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1,2,4-Triazine 1- and 2-Oxides. Reactivities toward Some Electrophiles and Nucleophiles

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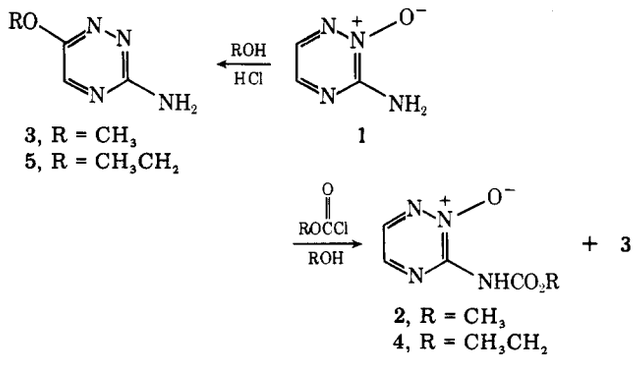
The 3-amino- (**1**), 3-methylamino- (**6**), 3-dimethylamino- (**7**), and methylthio- (**10**) 1,2,4-triazine 2-oxides undergo an addition–elimination reaction with methanol, ethanol, or 2-propanol to give the corresponding 6-alkoxy-1,2,4-triazines. The 1,2,4-triazine 1-oxides do not react with methanol under similar reaction conditions. Reaction of 3-amino-1,2,4-triazine 1-oxide (**14**) with nitrous acid in the presence of hydrobromic acid forms 3-bromo- (**19**) and 3,6-dibromo-1,2,4-triazine 1-oxide (**20**). The 3-methoxy- (**13**), 3-amino- (**14**), 3-methylamino- (**15**), and 3-dimethylamino- (**16**) 1,2,4-triazine 1-oxides react with bromine to give the respective 6-bromo-1,2,4-triazine 1-oxides (**21**–**24**). Possible reaction paths to account for these transformations are proposed.

1,2,4-Triazines have proven to be rather unusual π-deficient heteroaromatic compounds, as exemplified by their facile covalent hydration across the N_4–C_5 bonds,[1] their propensity for acting as dienes in Diels–Alder reactions,[2] and the tendency for ring contraction of their N-alkylated derivatives.[3]

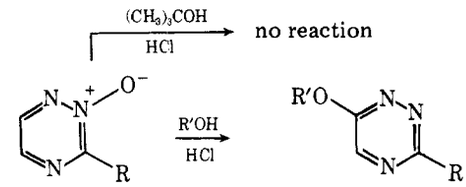
We have described the selective N-1 and N-2 oxidation of several 1,2,4-triazine derivatives[4,5] and now wish to report some interesting chemical transformations of these compounds.

During studies involving the condensation of 3-amino-1,2,4-triazine 2-oxide (**1**) with methanolic methyl chloroformate, the expected urethane (**2**) was the minor product; the



major one is a compound $C_4H_6N_4O$ whose ^1H NMR spectrum shows three singlets (δ 7.94, 5.30 and 4.05 (ppm)), with relative area ratios of 1:2:3. The broad two-proton singlet at δ 5.30 is subject to facile H → D exchange. Thus, we are dealing with either 5- or 6-methoxy-3-amino-1,2,4-triazine (**3**).

Since 5-ethoxy-3-amino-1,2,4-triazine[6] is known, the reaction was repeated with ethyl chloroformate in ethanol. The resulting ethoxy-3-amino-1,2,4-triazine formed as the major product, along with compound **4**, was compared with an authentic sample of the 3-amino-5-ethoxy-1,2,4-triazine. The latter compound (mp 166–168 °C) is different from the material obtained in this reaction (mp 110–112 °C). Thus, the 3-amino-6-alkoxy-1,2,4-triazines (**3** and **5**) are the major products in these reactions. Since this transformation, does *not* occur upon treatment of 3-amino-1,2,4-triazine or its 1-oxide with methanol and methyl chloroformate, the presence of the 2-oxide function is clearly required. When 3-amino-1,2,4-triazine 2-oxide (**1**) is treated with methanol containing only anhydrous hydrochloric acid, rather than methyl chloroformate, 6-methoxy-3-amino-1,2,4-triazine (**3**) is the only product.



1, R = NH_2
6, R = $NHCH_3$
7, R = $N(CH_3)_2$
10, R = SCH_3

3, R = NH_2; R' = CH_3
5, R = NH_2; R' = CH_3CH_2
8, R = $NHCH_3$; R' = CH_3
9, R = $N(CH_3)_2$; R' = CH_3
11, R = SCH_3; R' = CH_3
12, R = NH_2; R' = $(CH_3)_2CH$

The deoxygenated 6-methxy derivatives (**8, 9**) of 3-methylamino- (**6**) and 3-dimethylamino- (**7**) 1,2,4-triazine 2-oxides are obtained when these compounds are treated with methanolic hydrochloric acid.

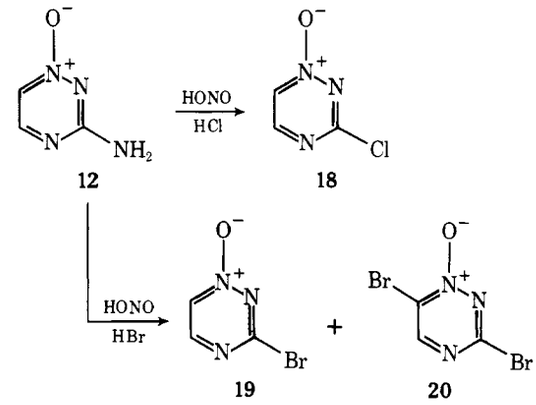
It clearly remains to establish whether a 3-amino substituent is required for this reaction to proceed. When 3-methylthio-1,2,4-triazine 2-oxide (**10**) was reacted with methanolic HCl, the 6-methoxy-3-methylthio-1,2,4-triazine (**11**) was readily obtained (cf. Table I for structure proof).

When either ethyl or isopropyl alcohol is used in place of methanol, the corresponding 6-ethoxy and 6-isopropoxy derivatives (**5, 12**) are formed. *tert*-Butyl alcohol, on the other hand, does not react with these 3-amino-1,2,4-triazine 2-oxides under the same reaction conditions.

It now became of interest to investigate the reactivity of the corresponding 3-substituted 1,2,4-triazine 1-oxides under similar reaction conditions. The necessary compounds **14–16** were prepared by nucleophilic displacement of the 3-methoxy group in 3-methoxy-1,2,4-triazine 1-oxide (**13**) (cf. Experimental Section). 3-Dimethylamino-1,2,4-triazine 1-oxide (**16**) can also be prepared by direct N-oxidation of 3-dimethylamino-1,2,4-triazine (**17**).[7]

None of these 1-oxides react with methanolic HCl under the conditions which yield the 6-alkoxy compounds in the 2-oxides.

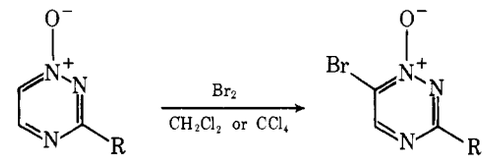
As previously reported,[5] diazotization of 3-amino-1,2,4-triazine 2-oxide affords the 3-halo derivatives. When this reaction was applied to 3-amino-1,2,4-triazine 1-oxide, the corresponding 3-halo (chloro or bromo) derivatives (**18, 19**) were obtained. In addition to the formation of the 3-bromo derivative, a dibromo compound ($C_3HN_3OBr_2$) was also formed. The structure of this material is readily established by comparison of the ^1H NMR spectrum of compound **19** with that of the dibromo derivative. The chemical-shift assign-



ments for H_5 (δ 8.50) and H_6 (τ 8.11) of the protons in compound **19** are consistent with our results described earlier.[4] Since it is well known that replacement of a hydrogen by bromine on an aromatic ring has only a small effect on the chemical shift of a proton on the ortho carbon, the singlet (δ 8.63) observed in the ^1H NMR spectrum of the dibromo compound **20** must be due to H_5. Thus, we are dealing with 3,6-dibromo-1,2,4-triazine 1-oxide (**20**).

An obvious extension of this dibromination reaction led us to examine the bromination of several 3-substituted 1,2,4-triazine 1-oxides.

When the 1-oxides of 3-amino- (**14**), 3-methylamino- (**15**), 3-dimethylamino- (**16**), or 3-methoxy- (**13**) 1,2,4-triazines are

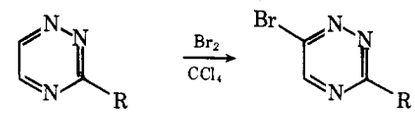


13, R = OCH_3
14, R = NH_2
15, R = $NHCH_3$
16, R = $N(CH_3)_2$

21, R = OCH_3
22, R = NH_2
23, R = $NHCH_3$
24, R = $N(CH_3)_2$

treated with bromine in carbon tetrachloride or methylene chloride, in the presence of triethylamine, the corresponding monobromo derivatives **21–24** are obtained in excellent yields. The question as to whether we are again dealing with 6-bromo derivatives or not is readily answered by a comparison of the ^1H NMR chemical shifts of these bromo derivatives with those of their precursors (cf. Table I). Since the chemical shifts of the aromatic protons in these bromo compounds are in the region δ 8.10–8.30, these compounds are the 6-bromo derivatives (**21–24**). Further confirmation of these assignments is found in a comparison of the ^{13}C chemical shifts of 3-methoxy-1,2,4-triazine 1-oxide (**13**) (δ_c (ppm): C_3, 166.5; C_5, 154; C_6, 124.5) with those of the 6-bromo derivative **21** (δ_c (ppm): C_3, 164; C_5, 156; C_6, 119).[8]

These facile bromination reactions prompted us to examine two non-N-oxidized 1,2,4-triazines, the 3-methoxy (**25**) and 3-dimethylamino (**17**) derivatives. In the former instance, no



17, R = $N(CH_3)_2$
25, R = OCH_3

26, R = $N(CH_3)_2$
No reaction

ring bromination occurred, while, in the latter one, a monobromo derivative **26** was obtained. The structure of this compound was readily established by a comparison of its ^1H NMR spectrum with that of the starting material (cf. Table I).

Mechanistic Considerations. The unique deoxygenative 6-alkoxylation of the 3-substituted 1,2,4-triazine 2-oxides

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

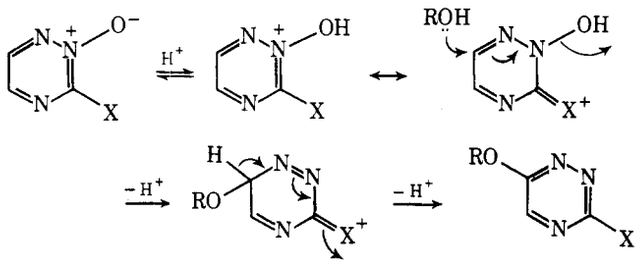
Compd no.	Mol Formula	Substituents[d] R_3	Substituents[d] R_6	Registry no.	Chemical Shifts[a] R_3	R_5	R_6	mp, °C
2[b]	$C_5H_6N_4O_3$	$NHCO_2CH_3$	H	63196-97-4	3.85 9.30	8.00	8.15	136–138
3	$C_4H_6N_4O$	NH_2	OCH_3	63196-98-5	5.30	7.94	4.05	119–120
5	$C_5H_8N_4O$	NH_2	OCH_2CH_3	63196-99-6	5.24	7.99	4.46	110–112
6[b]	$C_4H_6N_4O$	$NHCH_3$	H	63197-00-2	3.20 3.25	7.80	7.80	130–131
8	$C_5H_8N_4O$	$NHCH_3$	OCH_3	63197-01-3	3.02 3.08	7.96	4.02	99–101
9	$C_6H_{10}N_4O$	$N(CH_3)_2$	OCH_3	63197-02-4	3.20	7.96	4.02	10–12
10[b]	$C_4H_5N_3OS$	SCH_3	H	63197-03-5	2.70	8.03	8.26	94–96
11	$C_5H_7N_3OS$	SCH_3	OCH_3	63197-04-6	2.78	8.18	4.16	5–6
12[c]	$C_6H_{10}N_4O$	NH_2	$OCH(CH_3)_2$	63197-05-7	5.11	7.96	5.36 1.38	102–104
15[c]	$C_4H_6N_4O$	$NHCH_3$	H	63197-06-8	3.03 5.90	8.14	7.55	164–165.5
18[c]	$C_3H_2N_3OCl$	Cl	H	63197-07-9		8.55	8.09	40–41
19[c]	$C_3H_2N_3OBr$	Br	H	63197-08-0		8.50	8.11	64–66
20[c]	$C_3HN_3OBr_2$	Br	Br	63197-09-1		8.63		113–115
21[c]	$C_4H_4N_3O_2Br$	OCH_3	Br	63197-10-4	4.08	8.61		133–135
22[c]	$C_3H_3N_4OBr$	NH_2	Br	63197-11-5	7.90	9.00		130 dec
23[c]	$C_4H_5N_4OBr$	$NHCH_3$	Br	63197-12-6	3.03 5.68	8.34		185–187
24[c]	$C_5H_7N_4OBr$	$N(CH_3)_2$	Br	63197-13-7	4.21	8.33		176–177
26[c]	$C_5H_7N_4Br$	$N(CH_3)_2$	Br	63197-14-8	3.28	8.14		66–67.5

[a] δ (ppm), $CDCl_3$, [b] N_2-oxide. [c] N_1-oxide. [d] R_5 = H. [e] Satisfactory analytical values (±0.3% for C, H. N) were reported for all compounds in table.

Table II. Experimental Variables for the Syntheses of Various 6-Alkoxy 3-Substituted 1,2,4-Triazines

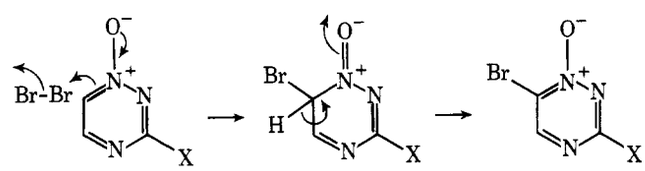
Compd	Reaction time (h)	Temp, °C	% yield	mp, °C
3	0.5	64.5	71	119–120
5	0.5	78.4	64	110–112
8	0.2	64.5	50	99–101
9	0.2	64.5	51	10–12
11	4	64.5	90	5–6
12	36	82.4	65	102–104

warrants some mechanistic speculation. Since the reaction does not depend upon possible amine–imine tautomerization, and since the 3-dimethylamino as well as 3-methylthio 2-oxides react, any mechanistic considerations involving this phenomenon can be eliminated. Furthermore, since all of the functional groups situated at C_3 are electron donating, and because an acidic medium as well as the presence of a 2-rather than 1-oxide group is required for this transformation to occur, the following reaction path can be reasonably proposed:

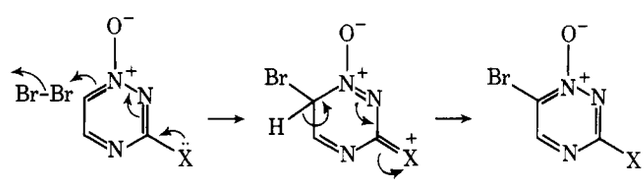


The formation of the 3-substituted 6-halo-1,2,4-triazine 1-oxides from the corresponding 3-substituted 1-oxides, in conjunction with the observation that the same transformation does not take place on the 3-methoxy-1,2,4-triazine, while it occurs in the 3-dimethylamino 1,2,4-triazine, might well be accounted for by either one or both of the following two paths:

Path a



Path b



In view of the observation that 3-methoxy-1,2,4-triazine does not react with bromine under these conditions, while the 3-dimethylamino derivative does, this may simply reflect the greater contribution of path b in the latter instance. The N-1 oxide would simply facilitate electrophilic substitution of C-6, beyond the activation possible by a 3-methoxy substituent.

These new substitution and addition–deoxygenation reactions on the 1,2,4-triazine ring system offer facile routes to functionally substituted 3,6- and 6-substituted 1,2,4-triazines, compounds needed for the syntheses of various potential antibiotics. Further studies of these *N*-oxides and their synthetic utility are in progress.

Experimental Section

Mass spectra were recorded with a Hitachi Perkin-Elmer RMU-6M instrument on all new compounds. Their molecular ions and frag-

mentation patterns are consistent with the indicated structures. A Varian HA-100 instrument was used to record the ^1H NMR and a Perkin-Elmer R-26 instrument to record ^{13}C NMR spectra. Melting points are corrected. Elemental analyses were performed by Atlantic Microlab, Inc., Atlanta, Georgia, and the Analytical Services Laboratory, Department of Chemistry, The University of Alabama.

Reaction of 3-Amino-1,2,4-triazine 2-Oxide (1) with Methyl Chloroformate in Methanol. To a solution of 500 mg (4.46 mmol) of 3-amino-1,2,4-triazine 2-oxide (1) in 150 mL of dry CH_3OH was added 843 mg (8.9 mmol) of methyl chloroformate. The solution was refluxed for 4 h, after which time an excess of $NaHCO_3$ was added and refluxing was continued overnight. The solution was evaporated to dryness and the residue was sublimed to give a pale-yellow solid. This solid was chromatographed on grade III silica gel with $CHCl_3$ as eluant to give 337 mg (60%) of 6-methoxy-3-amino-1,2,4-triazine (3) and 157 mg (2) of 3-methoxycarbonylamino-1,2,4-triazine 2-oxide (2).

A similar procedure using ethyl chloroformate and dry CH_3CH_2OH gave 406 mg (65%) of 6-ethoxy-3-amino-1,2,4-triazine (5), along with 123 mg (15%) of 3-ethoxycarbonylamino-1,2,4-triazine 2-oxide (4).

3-Methylamino-1,2,4-triazine 2-Oxide (6). Into a solution of 350 mg (3.0 mmol) of 3-bromo-1,2,4-triazine 2-oxide in 50 mL of dry tetrahydrofuran (THF) was bubbled gaseous methylamine. The solution, which immediately became yellow, was stirred for an additional 10 min. Evaporation to dryness gave a yellow solid which was crystallized from 50% petroleum ether/THF to give 190 mg (75%) of 3-methylamino-1,2,4-triazine 2-oxide (6).

3-Methylthio-1,2,4-triazine 2-Oxide (10). Into a solution of 500 mg (2.8 mmol) of 3-bromo-1,2,4-triazine 2-oxide in 250 mL of anhydrous ether was bubbled gaseous methyl mercaptan. The solution was stirred overnight. Excess Na_2CO_3 was added and stirring was continued for an additional hour. The solution was filtered and the solvent evaporated. The residue was triturated with 50 mL of hexane, filtered, and sublimed at 100 °C/0.05 Torr to give 350 mg (87%) of 3-methythio-1,2,4-triazine 2-oxide (10).

6-Alkoxy 3-Substituted 1,2,4-Triazines from 3-Substituted 1,2,4-Triazine 2-Oxides. (General procedure, cf. Table II for experimental variables.) In a typical experiment, a solution of 500 mg (4.5 mmol) of 3-amino-1,2,4-triazine 2-oxide in 50 mL of dry MeOH saturated with HCl was refluxed for 30 min. Excess sodium carbonate was added and refluxing was continued for 30 min. The mixture was filtered and the filtrate was evaporated to dryness. The residue was sublimed at 90 °C/0.05 Torr to give 400 mg (71%) of 6-methoxy-3-amino-1,2,4-triazine (3).

3-Amino-1,2,4-triazine 1-Oxide (14). To 2.54 g (0.02 mol) of 3-methoxy-1,2,4-triazine 1-oxide (13) was added to 40 mL of methanolic NH_3. The mixture was heated in a sealed tube at 100 °C for 4–5 h. After allowing the mixture to come to room temperature, 1.75 g of product (14) was collected by filtration. An additional 0.48 g of 12 could be obtained by evaporating the mother liquor and extracting the residue with 20 mL of $CHCl_3$; total yield 98%.

3-Methylamino-1,2,4-triazine 1-Oxide (15). A mixture of 3-methoxy-1,2,4-triazine 1-oxide (13) (650 mg, 5.0 mmol) and 10 mL of 5% $MeNH_2$ in MeOH was heated in a sealed tube at 90 °C for 1 h. After cooling, 500 mg of 15 was collected by filtration. Additional product (150 mg) could be obtained by evaporating the mother liquor and extracting the residue with 10 mL of $CHCl_3$. An analytical sample was prepared by sublimation at 105–110 °C/0.01 Torr.

3-Chloro-1,2,4-triazine 1-Oxide (18). To 6 mL (30 mmol) of warm 5 N HCl was added 330 mg (2.9 mmol) of 3-amino-1,2,4-triazine 1-oxide (14). The stirred reaction mixture was cooled to 5 °C and 414 mg (6.0 mmol) of $NaNO_2$ dissolved in 2 mL of H_2O was added dropwise (5 min). After 5 min of additional stirring, 10 mL of $CHCl_3$ was added and the mixture was allowed to come to room temperature. The layers were separated and the aqueous portion was extracted with additional $CHCl_3$ (3 × 10 mL). The combined $CHCl_3$ extracts were dried over Na_2SO_4, filtered, and evaporated in vacuo. The residue was chromatographed on alumina (grade III) with $CHCl_3$ to give 90 mg of 18 (24%). An analytical sample was prepared by sublimation at 30–40 °C/0.01 Torr.

Reaction of 3-Amino-1,2,4-triazine 1-Oxide (14) with HNO_2/HBr. To 448 mg (4.0 mmol) of 14 was added 6 mL (27 mmol) of 4.5 N HBr. The clear solution was cooled to 5 °C and 552 mg (8.0 mmol) of $NaNO_2$ in 2 mL of H_2O was added dropwise (5 min). After 5 min of stirring, 10 mL of $CHCl_3$ was added. The reaction was worked up as above to give 120 mg of 19 (17%) and 50 mg of 20 (5%). Both 19 and 20 were further purified by vacuum sublimation.

3-Methoxy-6-bromo-1,2,4-triazine 1-Oxide (21). To 127 mg (1.0 mmol) of 3-methoxy-1,2,4-triazine 1-oxide (13) dissolved in 40 mL of CH_2Cl_2 was added 2 mL of 2.2 M Br_2 in CCl_4 and 140 mg (1.0 mmol) of annydrous K_2CO_3. The mixture was stirred at room temperature overnight and then heated at 40–50 °C for 1.0 h. The mixture was filtered and the filtrate evaporated in vacuo. The residue was chromatographed on neutral alumina (grade III) with 50% $CHCl_3/C_6H_6$ to give 100–120 mg of 21 (50–60%). An analytical sample was prepared by sublimation at 60 °C/0.01 Torr.

6-Bromo-3-amino-1,2,4-triazine 1-Oxide (22). To 222 mg (2.0 mmol) of 3-amino-1,2,4-triazine 1-oxide (14) dissolved in 150 mL of CH_2Cl_2 and 25 mL of reagent grade CH_3CN was added 3 mL of 2.2 M Br_2 (6.6 mmol) in CCl_4. The mixture was stirred at room temperature for 0.5 h and 420 mg (30 mmol) of anhydrous K_2CO_3 was added. After it was stirred for an additional 0.5 h, the mixture was filtered and evaporated in vacuo. The residue was triturated with 10 mL of CH_2Cl_2 and filtered to give 380 mg of 22 (100%). Compound 22 was further purified by sublimation at 130 °C/0.01 Torr.

6-Bromo-3-methylamino-1,2,4-triazine 1-Oxide (23). To 126 mg (1.0 mmol) of 3-methylamino-1,2,4-triazine 1-oxide (15) dissolved in 40 mL of 50% CH_2Cl_2/CCl_4 was added 1 mL of 2.2 M Br_2 (2.2 mmol) in CCl_4, followed by 0.2 mL (1.4 mmol) of Et_3N in 2 mL of CH_2Cl_2. The mixture was stirred at room temperature overnight and then evaporated in vacuo, and the residue was chromatographed on alumina (grade III) with $CHCl_3$. Sublimation of the major component at 110 °C/0.01 Torr gave 142 mg of 23 (70%).

6-Bromo-3-dimethylamino-1,2,4-triazine 1-Oxide (24). To 140 mg (1.0 mmol) of 3-dimethylamino-1,2,4-triazine 1-oxide (16) in 30 mL of CCl_4 was added 1.5 mL of 2.2 M Br_2 (3.3 mmol) in CCl_4 followed by 0.2 mL (1.4 mmol) of Et_3N in 2 mL of CH_2Cl_2. The mixture was stirred at room temperature for 0.5 h and then evaporated in vacuo. The residue was chromatographed on neutral alumina (grade III) with 50% $C_6H_6/CHCl_3$. The major component was sublimed at 110 °C/0.01 Torr to give 165 mg of 24 (77%).

6-Bromo-3-dimethylamino-1,2,4-triazine (26). To 310 mg (2.5 mmol) of 3-dimethylamino-1,2,4-triazine (14) dissolved in 30 mL of CCl_4 was added 2.5 mL of 2 M Br_2 (5.0 mmol) in CCl_4 followed by 0.4 mL (3 mmol) of Et_3N. After stirring overnight, the mixture was evaporated in vacuo. The residue was chromatographed on alumina (grade III) with 50% $C_6H_6/CHCl_3$. The major component was sublimed at 40 °C/0.01 Torr to give 252 mg of 26 (50%).

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Registry No.—1, 61177-95-5; 7, 61178-04-9; 13, 27531-67-5; 14, 61178-11-8; 16, 61178-07-2; methyl chloroformate, 79-22-1; ethyl chloroformate, 541-41-3; 3-bromo-1,2,4-triazine 2-oxide, 61178-02-7; methylamine, 74-89-5; methyl mercaptan, 74-93-1; methanol, 67-56-1; ethanol, 64-17-5; 2-propanol, 67-63-0.

References and Notes

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(8) It should be mentioned that the relaxation time of C_6 in the bromo derivatives is extremely long. All ^{13}C NMR spectra were taken as 1.5 M solutions in $CDCl_3$. A Perkin-Elmer R-26 instrument was used.