source of the rate retardation: the high barriers calculated and measured for acyclic hydroxylamines indicate that the electronegativity of the oxygen atom also plays a very important role.

Registry No.—*N,N*-Dimethylhydroxylamine, 5725-96-2; *N,N*-dibenzylhydroxylamine, 621-07-8; *N*-methylisoxazolidine, 22445-44-9.

References and Notes

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Regiospecific Synthesis of Unsymmetrical Azoxy Compounds (Diazene *N*-Oxides)[1a]

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A directed synthesis is described of unsymmetrical azoxy compounds by condensation of nitroso substrates with *N,N*-dihaloamino derivatives in the presence of different types of promoters. Products bearing a variety of substituents, including aryl, alkyl, carboxylate, carbonamide, and halogen groups, are produced in fair to high yield. Evidence is presented that the reaction can proceed by several mechanistic pathways, depending upon the promoter.

Until 1974 there were only two useful methods for the regiospecific synthesis of azoxyalkanes and alkylazoxyarenes.[2,3] Other methods are not regiospecific[4a,b] or are impractical when electron-withdrawing groups are present.[4c] Recently,[5] we described the regiospecific synthesis of azoxyalkanes and alkylazoxyarenes by condensation of an *N,N*-dichloro amine with a nitroso compound in the presence of caustic (eq 1)

$$RNCl_2 + R'NO \longrightarrow RN{=}N(O)R' \qquad (1)$$

but the method is not useful if product or starting material is sensitive to basic conditions.

We herein report that the condensation of *N,N*-dihalo amine derivatives and tertiary alkyl or aryl nitroso compounds can be effected by a wide variety of promoters, generally in fair to excellent yields. It is probable that several mechanistic pathways pertain, depending upon the promoter.

Results and Discussion

By the condensation of a tertiary alkyl or aryl nitroso substrate with an *N,N*-dihalo amine derivative, various types of azoxy compounds (Table I) have been prepared. In addition to the base-sensitive ester (**3**), amide (**5**), and acyl derivative (**4**), we have synthesized members containing two azoxy moieties (**10** and **11**) (Table II), and the interesting compound "chloroazoxobenzene" (**8**) in a yield superior to that reported in the only other published procedure.[6]

The method also works with *N,N*-dibromo compounds as shown in Table III. Only two dibromoamino derivatives, a dibromo amide and dibromo amine, were investigated. In general *N,N*-dibromo substrates provide considerably higher yields than the corresponding *N,N*-dichloro counterparts. The *N,N*-dibromo amide, however, gave poorer results, presumably owing to its instability (decomposition even below 0 °C). This method for the synthesis of azoxy compounds is limited mainly by the availability of the nitroso precursor and the lack of success with aromatic *N*-halo amines. An attempt by us to N,N-dichlorinate *m*-nitroaniline was not fruitful, and exposure of sulfanilic acid to hypochlorite yielded the corresponding azo compound.[7]

Since primary and secondary nitrosoalkanes preferentially exist as the oxime tautomers, we were able to use only tertiary alkyl or aryl nitroso compounds. With the intent of circumventing this deficiency, we prepared the haloazoxy compounds **6** and **12** in order to replace subsequently the halogen with hydrogen. Attempted reductions with Zn, $CrCl_2$, Bu_3SnH, $NaBH_4$, and HI yielded intractable material in all cases. Sodium cyanoborohydride proved to be unreactive, even toward the azoxy moiety.

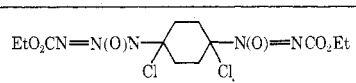
A convenient synthesis of azoxyalkenes is desirable, since several natural products[8] such as **13** contain α,β unsaturation, for which type there are only a few published syntheses.[9] Experiments aimed at producing such compounds from pre-

Table I. Diazene *N*-Oxide Syntheses

Product	Promoter	R'N(O) = NR R	R'	Yield, %
1[a]	CuCl	*n*-Bu	Ph	83
2[a]	CuCl	C_6H_{11}	Ph	58
3	CuCl	CO_2Et	Ph	65
3	CuCN	CO_2Et	Ph	90
3	KI	CO_2Et	Ph	71
4	CuCl	PhCO	Ph	75
5	CuCl	Me_2NCO	Ph	51
6	CuCl	*t*-Bu		38
7[a]	CuCl	*t*-Bu	Ph	44
7	KI	*t*-Bu	Ph	79
8	CuCN	Cl	Ph	25
8	KI	Cl	Ph	60
9	CuCN	PhCO	*t*-Bu	25

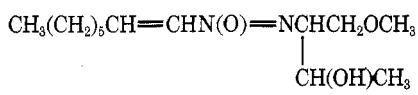
[a] Identified by comparison with an authentic sample, ref 5.

Table II. Bis Diazene *N*-Oxides[a]

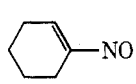
Product	Structure	Yield, %
10		75
11	$PhN(O)=N(CH_2)_2N=N(O)Ph$	46

[a] CuCl promoter.

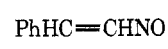
formed nitroso olefins were unsuccessful since the precursors either polymerize readily, as does **14**,[10] or exist as stable dimeric azo dioxides, as does **15**[11] (insoluble). Attempted base-catalyzed dehydrohalogenation of both **6** and **12** yielded none of the desired *tert*-butylazoxyalkene, only intractable tars.



13



14



15

Mechanistic Considerations. The condensation of nitrosobenzene with *N,N*-dichloro-*tert*-butylamine to form **7** was chosen as the standard system for the mechanistic study. This compound is produced in poorer yield than many of the others, possibly owing to competing elimination of dichloro amine from *t*-$BuNCl_2$ to form isobutylene. It has been shown[12] that tertiary alkyl *N,N*-dichloro amines can undergo such a transformation in the presence of a variety of promoters, including cuprous chloride, triethylamine, potassium iodide, and ferrous chloride. In spite of this limitation, the synthesis of *tert*-butylazoxybenzene was chosen as the standard owing to the ease of estimation of the percent yields and the absence of competing reactions, other than the above-mentioned elimination. There is no possibility of dehydrohalogenation, as with a primary or secondary alkyl *N,N*-dichloro amine, or nucleophilic attack on the carbonyl function, as with *N,N*-dichlorourethane. Indeed, when *N,N*-dichlorourethane was stirred with CuCN under the usual reaction conditions, product was formed whose ir and NMR spectra indicated the presence of ethyl cyanoformate. A run with nitrosobenzene and *N,N*-dichloro-*n*-butylamine in the absence of promoter yielded only starting material.

The yields of **7** and **3** obtained with various promoters are

Table III. Effect on Diazene *N*-Oxide Yield of Variation in $X(RNX_2)^a$

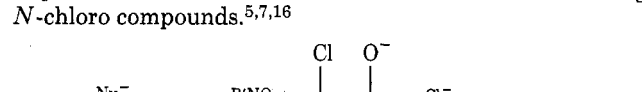
Compd	RN = N(O)R' R	R'	Yield, %, when X = Cl	Br
7	*t*-Bu	Ph	44	90
6	*t*-Bu		38	69
3	CO_2Et	Ph	65	47
12	*t*-Bu	$(CH_3)_2CBr$		70

[a] CuCl promoter.

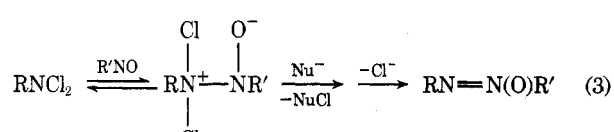
Table IV. Effect of Promoter on Diazene *N*-Oxide Yields

Promoter	Yield, % 7	3
Ag^0	57	
AgCl	11	
CuCl	49	65
$CuCl_2$	15	
CuCN	53	90
CuBr	53	
CuI	58	
Cu_2S	54	
$FeCl_2$	35	40
$FeSO_4$	~5	
CoBr	81	
$CoSO_4$	~2	
KI	79	
Et_3N	55	
NaCN	18	35
AgCN		68
$AgClO_4$		0
AgOAc		41

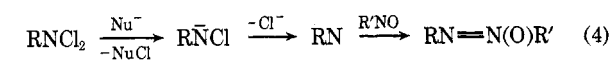
set forth in Tables IV–VI. The good results obtained with Et_3N, NaCN, and KI suggest nucleophilic attack on positive halogen in the *N,N*-dichloro amine, eq 2[13] or 3. Nucleophilic attack on the nitroso entity is known to occur.[14] As a mechanistic probe[15] for the validity of eq 2, the sodium salt of *N*-monochlorourethane, $(EtO_2CNCl)^-Na^+$, was allowed to react with nitrosobenzene in the absence of promoter. Formation of a complex mixture containing urethane and no more than 15–20% of **3** suggests that eq 2 does not represent a major pathway. Interpretation is difficult since some nitrene might be arising from the salt. A more likely possibility entails involvement of a nitrene,[5] eq 4. Nitrenes have previously been implicated as intermediates in various reactions entailing *N*-chloro compounds.[5,7,16]



(2)



(3)



(4)

The anion of the metal salt might be functioning as the nucleophile with the metal ion assuming the role of the Friedel–Crafts catalyst, either polarizing the nitroso bond or facilitating the removal of Cl^- in the last step. This conjecture is supported by the increase in yield of product **3** from AgCN vs. NaCN. Since nitroso compounds form stable complexes with certain metal ions,[17] such Lewis acid catalysis seems

Table V. Diazene *N*-Oxides from Ag^0 [a]

$C_6H_5N(O)=NR$		
Compd	R	Yield, %
7	*t*-Bu	60
2	C_6H_{11}	30
13[b]	*i*-Pr	17
1[b]	*n*-Bu	33

[a] $RNCl_2$:C_6H_5NO:Ag (Tollens') = 1:1:2 molar ratio, CH_3OH solvent. [b] See ref 5.

reasonable. In any event, in the absence of a reducing agent the presence of a nucleophile is necessary, as shown by the inability of $AgClO_4$ to promote the reaction.

The efficacy of silver metal, redox metal salts, and MgI_2/Mg as promoters suggests that a second reaction pathway is operative, namely a one-electron transfer from the reducing agent, eq 5. The nitrogen-centered radical then attacks the nitroso group to produce a nitroxide which yields product on loss of a chlorine atom. Freshly precipitated silver metal gives a substantial yield of product, in accord with published observations that *N*-chloro amines yield nitrogen radicals upon treatment with this reagent.[18] That the neutral silver is the promoter and not the generated silver chloride is shown by the small yield obtained with performed silver chloride. The superiority of cuprous chloride over cupric chloride lends credence to our contention since cuprous ion should be the weaker Lewis acid. The combination of MgI_2 and Mg, which presumably generates IMg, afforded **7** in 25% yield. Supporting this mechanism is the observation that radicals add to nitroso compounds yielding azoxy products,[19a] eq 6. Iodide ion, besides being a good nucleophile, is also a reducing agent, and may be playing both roles. Nucleophilic attack on positive chlorine would yield iodine monochloride which disproportionates to free iodine. Alternatively, the promoter may function as a one-electron reducing agent as in eq 5. There are examples[19b] of iodide reacting with dichloro amines to yield products best interpreted by means of a radical scheme. Although azo **16**, eq 7, could result from nitrene dimerization, peroxide **17** is more adequately accounted for on the basis of radical precursors, eq 8–10. The redox salts, ferrous sulfate and cobaltous sulfate, were also explored. Product resulted in both cases, but in very low yield. The insolubility of these salts in acetonitrile, or anion specificity,[20] could be a factor. Most of the data can be accommodated by a radical mechanism involving electron transfer reagents.

$$RNCl_2 + Ag^0 \xrightarrow{-AgCl} R\dot{N}Cl \xrightarrow{R'NO} RN(O\cdot)-NR'(Cl) \xrightarrow[-AgCl]{Ag^0} RN{=}N(O)R' \quad (5)$$

$$F_2N\text{-}C_6H_4\text{-}NO \xrightarrow{\cdot NF_2} F_2N\text{-}C_6H_4\text{-}N(O){=}NF \quad (6)$$

$$PhCH(R)NCl_2 \xrightarrow{I^-} PhCH(R)N{=}NCHR(Ph) \quad (7)$$

16

$$Ph_3NCl_2 \xrightarrow{I^-} Ph_3COOCPh_3 \quad (8)$$

17

$$Ph_3CNCl_2 \xrightarrow{I^-} Ph_3C\dot{N}Cl \xrightarrow{-NCl} Ph_3C\cdot \xrightarrow{O_2} \mathbf{17} \quad (9)$$

$$Ph_3CNCl_2 \xrightarrow[-NCl_2^-]{I^-} Ph_3C\cdot \xrightarrow{O_2} \mathbf{17} \quad (10)$$

In conclusion, the condensation of *N,N*-dihalo compounds with tertiary alkyl or aryl nitroso compounds can be effected with a wide variety of promoters, and probably can occur by several mechanistic pathways, depending on the promoter. The evidence suggests that reaction takes place initially by an ionic pathway, promoted by a nucleophile, or by a free-radical route, promoted by redox metal ions or neutral metals. Some flexibility in the choice of reaction conditions is thus possible. Hence, base-sensitive compounds can be prepared using a redox metal salt, and compounds sensitive to the presence of radicals or reducing agents can be synthesized using a nucleophile as promoter.

Table VI. Diazene *N*-Oxides from Silver Acetate

$C_6H_5N(O)=NR$		
Compd	R	Yield, %
7	*t*-Bu	42
2	C_6H_{11}	28
3	CO_2Et	55

Experimental Section

Infrared spectra were recorded on a Beckman IR-8 or a Perkin-Elmer 137 spectrophotometer. NMR spectra were taken on a Varian T-60A with tetramethylsilane as internal standard. Positive halogen content was determined by iodometric titration.[21] Melting and boiling points are uncorrected. Elemental analyses were performed by Baron Consulting Co., Orange, Conn.

***N,N*-Dimethylurea** was prepared by a published procedure.[22a]

***N,N*-Dichloro amines and amides** were prepared by a literature method.[23] After removal of solvent, the crude products were used without further purification.

Potassium salt of monochlorourethane (18) was prepared by a literature method.[24]

Trichloramine was prepared by a published procedure.[21] The methylene chloride solution was used without further purification.

***N,N*-Dibromo-*tert*-butylamine.** A solution of sodium hydroxide (30 g, 0.75 mol) and bromine (48 g, 0.3 mol) in water (150 ml) was stirred in an ice bath as *tert*-butylamine (15.3 g, 0.2 mol) in methylene chloride (200 ml) was added dropwise. The mixture was stirred for 5 h. The organic phase was removed, the aqueous phase was washed with methylene chloride, and the combined organic portion was dried over calcium chloride. Evaporation of solvent yielded product, red oil, 27 g (58%). Iodometric titration indicated the positive halogen content to be 100% of theory.

***N,N*-Dibromourethane.** A modified literature procedure was followed.[25] Silver acetate (25.1 g, 0.15 mol), suspended in carbon tetrachloride (400 ml), was stirred in an ice–salt bath as bromine (24 g, 0.15 mol) in carbon tetrachloride was added dropwise. After 10 min of stirring in the absence of light, urethane (4.5 g, 0.05 mol) was added and the mixture was stirred for 75 min at room temperature. The suspension was filtered, and evaporation of solvent yielded product, red oil (13.8 g, 100%). Iodometric titration indicated the positive halogen content to be 94% of theory.

1-Chloro-1-nitrosocyclohexane was prepared according to a published procedure.[26] The crude product was used.

***trans,trans*-1,4-Dichloro-1,4-dinitrosocylohexane** was prepared according to a literature method.[27]

2-Bromo-2-nitrosopropane was prepared according to a published procedure.[28] The undistilled product was used.

General Procedure for Diazene *N*-Oxides 1–13. The nitroso compound (0.01 mol) and the dihaloamino compound (0.01 mol) were stirred in acetonitrile (50 ml). In the synthesis of **9**, 0.005 mol of the tetrachlorodiamine was used. For **10**, trichloramine (0.01 mol) was added as a 0.7 M solution in methylene chloride. The promoter (0.01 mol of KI, Et_3N, AgCN, or NaCN; 0.02 mol of the others) was added and the mixture was stirred at room temperature overnight. In the cases of **5**, **10**, **11**, and **12**, the mixture was stirred at 0 °C for the first hour. The mixture was then poured into 500 ml of water. In the synthesis of **8**, the product was isolated by filtration. In the other cases, the water solution was extracted repeatedly with Et_2O. The combined extract was washed with H_2O, then with saturated aqueous NaCl, and dried over $CaCl_2$. Evaporation of solvent yielded the crude product as a brown oil. Compounds **8** and **9** were purified by crystallization. Products **1–6**, **11**, and **12** were chromatographed on silica gel with elution by benzene–petroleum ether (3:7). In the synthesis of **7** for the mechanistic studies, the crude product was held under reduced pressure at ca. 70 °C to remove unreacted *N,N*-dichloro-*tert*-butylamine, the only remaining impurity being nitrosobenzene. The percentage of product **7** in this mixture was estimated by comparison of

the integral of the *tert*-butyl singlet (δ 1.4) with the integral for the phenyl absorption (δ 8.2–7.0) in the NMR spectrum.

Tollens' Silver. Concentrated ammonia solution (about 50 ml) was added to a suspension of silver oxide[22b] (2.4 g) in water (30 ml) until the solid dissolved. Then 37% formaldehyde (40–50 ml) was added slowly with stirring and cooling in order to precipitate the silver metal. The solid was filtered and washed repeatedly with water, and then with methanol until free of formaldehyde.

7 from *t*-BuNCl$_2$–C$_6$H$_5$NO–Mg–MgI$_2$.[29] After a mixture of magnesium turnings (0.96 g, 0.013 mol) in 50 ml of tetrahydrofuran was warmed to 50 °C, iodine (1.68 g, 0.04 mol) was added in small amounts over a period of 1 h. The mixture slowly turned light brown in color. Then the mixture was cooled to room temperature and added to a solution of nitrosobenzene (1.07 g, 0.01 mol) and *N,N*-dichloro-*tert*-butylamine (1.44 g, 0.01 mol) in 50 ml of THF. The mixture became dark brown in color. Stirring was continued overnight. The mixture was then poured into 250 ml of water, and sodium thiosulfate (0.01 mol) was added until the color became lighter. The product was extracted into ether and dried over calcium chloride. Ether was removed by vacuum distillation and product was then distilled, bp 60–80 °C (0.5 mm), yield 25%. The properties (NMR, ir) of this fraction were identical with those of an authentic sample of **7**.

Characterization of Diazene *N*-Oxides. 1, 2, and **7** were identified by comparison with authentic samples.[5]

***N*-Ethylcarboxyl-*N'*-phenyldiazene *N'*-Oxide (3):** mp 37–38 °C; bp 112–114 °C (0.25 mm); NMR ($CDCl_3$) δ 1.37 (t, CH_3, 3.2 H), 4.42 (q, CH_2, 1.9 H), 7.50 (m, Ph, 3.0 H), 8.15 (m, Ph, 1.9 H); ir (neat) 1755 (C=O), 1490 (N=N), 1450 (NO), 1240 (C–O), 780, 695 cm^{-1} (Ph).

Anal. Calcd for $C_9H_{10}N_2O_3$: C, 55.65; H, 5.19; N, 14.43. Found: C, 55.38; H, 5.05; N, 14.49.

***N*-Benzoyl-*N'*-phenyldiazene *N'*-Oxide (4):** mp 50–52 °C; NMR ($CDCl_3$) δ 8.20 (m, Ph, 2.24 H), 7.94 (m, Ph, 1.9 H), 7.50 (m, Ph, 5.9 H); ir (neat) 1700 (C=O), 1580 (Ph), 1470 (N=N), 1430 (NO), 1230, 1320 (C–N), 781, 690 cm^{-1} (Ph).

Anal. Calcd for $C_{13}H_{10}N_2O_2$: C, 69.00; H, 4.46; N, 12.39. Found: C, 68.97; H, 4.66; N, 12.64.

***N*-Dimethylcarbamyl-*N'*-phenyldiazene *N'*-Oxide (5):** mp 44–46 °C; NMR ($CDCl_3$) δ 8.18 (m, Ph, 2.0 H), 7.53 (m, Ph, 3.4 H), 3.06 (s, CH_3, 2.7 H), 2.87 (s, CH_3, 3.0 H); ir (neat) 1680 (C=O), 1480 (N=N), 1430 (NO), 1370 (CH_3), 791, 695 cm^{-1} (Ph).

Anal. Calcd for $C_9H_{11}N_3O_2$: C, 55.95; H, 5.74; N, 21.75. Found: C, 55.70; H, 5.52; N, 21.83.

***N*-*tert*-Butyl-*N'*-chlorocyclohexyldiazene *N'*-Oxide (6):** bp 53–54 °C (0.25 mm); NMR ($CDCl_3$) δ 1.0–2.8 (m, aliphatic), 1.30 (s, C_4H_9); ir (neat) 1490 (N=N), 1440 (NO), 1350 cm^{-1} (*t*-C_4H_9).

Anal. Calcd for $C_{10}H_{19}N_2OCl$: C, 54.91; H, 8.76; N, 12.81; Cl, 16.21. Found: C, 55.17; H, 8.93; N, 13.01; Cl, 16.45.

1,4-Dichloro-1,4-bis(*N*-ethylcarboxylazo)cyclohexane *N',N'*-Dioxide (10): mp 136–139 °C; NMR ($CDCl_3$) δ 4.08 (q, OCH_2, 3.9 H), 2.77 (s, CCH_2, 7.8 H), 1.40 (t, CH_3, 6.3 H); ir ($CHCl_3$) 1750 (C=O), 1500 (N=N), 1450 (NO), 1200 cm^{-1} (CO).

Anal. Calcd for $C_{12}H_{18}O_6N_4Cl_2$: C, 37.42; H, 4.71; N, 14.55; Cl, 18.41. Found: C, 37.67; H, 4.69; N, 14.74; Cl, 18.69.

1,2-Bis(*N*-phenylazo)ethane *N',N'*-Dioxide (11): mp 155–156 °C; NMR ($CDCl_3$) δ 8.14 (m, Ph, 3.7 H), 7.13 (m, Ph, 6.9 H), 4.18 (s, CH_2, 3.4 H); ir (Nujol) 1470 (N=N), 1430 (NO), 790, 690 cm^{-1} (Ph).

Anal. Calcd for $C_{14}H_{14}N_4O_2$: C, 62.2; H, 5.2; N, 20.7. Found: C, 61.9; H, 5.3; N, 20.7.

***N*-Phenyl-*N'*-chlorodiazene *N*-Oxide (8):** bp 68–70 °C (0.6 mm) [lit.[6] bp 57 °C (0.5 mm)]; NMR[30] (CCl_4) δ 7.2–8.2 (m, Ph); ir (neat) 1475 (N=N), 1430 cm^{-1} (NO); mass spectrum *m/e* (rel intensity) 156 (51) (M^+), 112 (73) ($M^+ - N_2O$), 107 (100) ($M^+ - NCl$).

Anal. Calcd for $C_6H_5ClN_2O$: C, 46.03; H, 3.22; N, 17.89. Found: C, 45.92; H, 3.40; N, 17.82.

***N*-Benzoyl-*N'*-*tert*-butyldiazene *N'*-Oxide (9):** mp 43–45 °C; NMR ($CDCl_3$) δ 7.84 (m, Ph, 1.8 H), 7.53 (m, Ph, 3.1 H), 1.68 (s, *t*-C_4H_9, 9.1 H); ir ($CHCl_3$) 1720 (C=O), 1600 (Ph), 1480 (N=N), 1450 cm^{-1} (NO).

Anal. Calcd for $C_{11}H_{14}N_2O_2$: C, 64.05; H, 6.86; N, 13.58. Found: C, 64.06; H, 6.80; N, 13.41.

***N*-*tert*-Butyl-*N'*-bromoisopropyldiazene *N'*-Oxide (12):** bp 96–99 °C (50 mm); NMR (CCl_4) δ 2.15 (s, $CBrCH_3$, 6.1 H), 1.30 (s, *t*-C_4H_9, 8.9 H); ir (neat) 1490 (N=N), 1450 (NO), 1360 cm^{-1} (*t*-C_4H_9).

Anal. Calcd for $C_7H_{15}N_2OBr$: C, 37.68; H, 6.78; N, 12.56; Br, 35.81. Found: C, 37.40; H, 6.65; N, 12.32; Br, 36.11.

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Registry No.—**3,** 56751-20-3; **4,** 56751-21-4; **5,** 56751-22-5; **6,** 58426-22-5; **7,** 52123-67-8; **8,** 40946-24-5; **9,** 58426-23-6; **10,** 58426-24-7; **11,** 58438-07-6; **12,** 58426-25-8; *N,N*-dimethylurea, 598-94-7; monochlorourethane K salt, 16844-21-6; trichloramine, 10025-85-1; *N,N*-dibromo-*tert*-butylamine, 51655-36-8; *N,N*-dibromourethane, 51066-06-9; 1-chloro-1-nitrosocyclohexane, 695-64-7; *trans-trans*-1,4-dichloro-1,4-dinitrosocyclohexane, 58426-26-9; 2-bromo-2-nitrosopropane, 7119-91-7; nitrosobenzene, 586-96-9; *N,N*-dichloro-*tert*-butylamine, 2156-72-1.

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