(R = Me) 5-methionium derivative, 52133-53-6; **7**, 52133-59-2; **8**, 52133-60-5; **9**, 52133-61-6; **10**, 52133-62-7; **11**, 52133-63-8; **12**, 52133-64-9; **13**, 52133-65-0; **14**, 52133-66-1; ethyl 2,2-diethoxyethylcyanoacetate, 52133-67-2; benzyloxyurea, 2048-50-2; ethyl cyano-α-(2-methyl-1,3-dioxolan-2-ylmethyl)acetate, 52133-68-3; 6-amino-5-carboxymethyluracil, 52133-69-4; *dl*-methionine, 59-51-8.

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A Novel, Directed Synthesis of Unsymmetrical Azoxyalkanes and Azoxyaralkanes from *N,N*-Dihaloamine and Nitroso Precursors[1]

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Received April 19, 1974

A novel, directed synthesis of unsymmetrical azoxyalkanes and azoxyaralkanes from nitroso compounds (RNO) and *N,N*-dichloroamines ($R'NCl_2$) in the presence of methanolic caustic is described. An investigation of the scope of the reaction revealed that the highest yields of azoxy compounds were produced when R is *tert*-alkyl or aryl and R′ is *tert*-alkyl. This method possesses advantages not offered by prior techniques. Possible mechanistic pathways are also discussed.

Aliphatic azoxy compounds are of interest partly because of the powerful physiological activity of some naturally occurring members.[4,5] To date there are only two useful methods for the production of unsymmetrical[6] alkyl or aralkyl azoxy compounds, which give rise to a single, structurally predictable product.[7] The aralkyl types can be generated by reaction of an azoxy tosylate,[8] eq 1, or azoxy

$$ArN(O)=NTs \xrightarrow{RMgCl} ArN(O)=NR \quad (1)$$

fluoride[9] with a Grignard reagent. The other approach involves reaction of alkyl diazotates with alkyl iodides,[10] eq 2.

$$RN=NO^-K^+ \xrightarrow{R'I} RN=N(O)R' \quad (2)$$

Other techniques, including condensation of nitroso compounds with *N*-alkylhydroxylamines,[10-12] eq 3, and oxidation of azo compounds with peracid,[10,11] suffer from lack of specificity, since mixtures of the two possible isomers often result (see below).

$$RNO + R'NHOH \longrightarrow RN(O)=NR' + RN=N(O)R' \quad (3)$$

We herein describe a new route[33] to azoxyalkanes and azoxyaralkanes entailing reaction of an *N,N*-dichloroamine with a nitroso compound in the presence of base. The scope of the reaction and mechanistic aspects are treated, and a comparison of this new method with those of eq 1 and 2 is given.

Results and Discussion

The general procedure used in most cases for the azoxy products involved reaction of a nitroso compound with an *N,N*-dichloroamine in the presence of caustic, eq 4. Equimolar quantities of the nitroso compound and *N,N*-dichloroamine, prepared[13] from the amine and calcium hypochlorite, were dissolved in methanol. After potassium hydroxide was added at about 30°, the reaction mixture was stirred until the color disappeared. In the latter stages of the investigation, we discovered that the procedure could be simplified appreciably by adding sodium hypochlorite to a methanolic solution of the amine and nitroso compound, eq 5. Apparently the hypochlorite serves a dual function—

$$RNCl_2 + R'NO \xrightarrow{OH^-} RN=N(O)R' \quad (4)$$

R = alkyl; R′ = alkyl or aryl

$$RNH_2 + R'NO \xrightarrow{NaOCl} RN=N(O)R' \quad (5)$$

as a chlorinating agent to form the haloamine and as a source of caustic.

Yields of azoxyaralkanes and azoxyalkanes are set forth in Tables I and II, respectively. It is evident that the reaction is sensitive to the nature of the *N,N*-dihaloamine. Tertiary alkyl substituents gave the best results, the primary type provided moderate yields, and secondary groups produced the lowest amount of desired material. Presumably, dehydrohalogenation[14] of the haloamine comprises a competing process, eq 6. Since formation of the *N*-chloroimine

$$\begin{matrix} | \\ HCNCl_2 \\ | \end{matrix} \xrightarrow{OH^-} \begin{matrix} | \\ C=NCl \\ | \end{matrix} \quad (6)$$

should take place more readily with the secondary and primary alkyl groups, the observed yield order, tertiary > primary, secondary, is in accord with this concept. In the case of aliphatic nitroso precursors, only tertiary alkyls were

Table I
Yields of Azoxyaralkanes from C_6H_5NO and $RNCl_2$[a]

Compd	R	Yield, %
1	$CH_3(CH_2)_3$	36[b]
2	$(CH_3)_2CH$	4
3	C_6H_{11}	7[c,d]
4	$(CH_3)_3C$	80[c,e]
5	$(CH_3)_2C(CN)$	72
6	1-Adamantyl	78

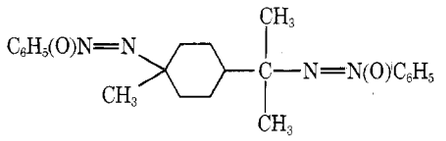
[a] General procedure A. [b] 2:1 molar ratio of $RNCl_2$:C_6H_5NO. [c] Identified by comparison with an authentic sample. [d] 2:1 molar ratio of $RNCl_2$:C_6H_5NO produced a 12% yield. [e] 83% yield from general procedure B.

Table II
Yields of Azoxyalkanes from RNO and $R'NCl_2$

Compd	R	R'	Yield, %
7	1-Adamantyl	$(CH_3)_3C$	54[a]
8	$(CH_3)_3C$	1-Adamantyl	49[a]
9	$(CH_3)_2C(CN)$	$(CH_3)_2C(CN)$	48[a]
10	1-Chloro-1-cyclohexyl	$(CH_3)_2C(CN)$	68
11	1-Cyano-1-cyclohexyl	$(CH_3)_2C(CN)$	65[a]
12	$(CH_3)_2C(CN)$	1-Cyano-1-cyclohexyl	72[a]
13	$(CH_3)_3C$	$(CH_3)_3C$	42

[a] Identified by comparison with an authentic sample.

used, since base-catalyzed isomerization[15a] to oximes occurs readily with the primary and secondary groups. In an investigation of scope, the reaction was applied to formation of a diazoxy type, **14**, from 1,8-diamino-*p*-menthane



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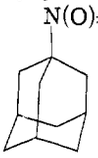
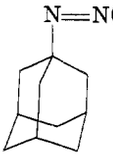
and nitrosobenzene. This appears to be the first disclosure of a diazoxy compound in the aralkyl class. Unsuccessful attempts were made to extend the method to azoxy compounds completely substituted with aromatic nuclei. Treatment of a mixture of nitrosobenzene and aniline with sodium hypochlorite at low temperatures (Dry Ice) resulted in a complex mixture containing none of the desired azoxybenzene. Similarly, no azoxy product was obtained from *o*- or *p*-nitroaniline and nitrosobenzene.

Satisfactory elemental analyses were obtained for all compounds, except **11** and **12**, which appeared to undergo a change which is not understood. The infrared spectra in all cases exhibited strong absorption, characteristic[5] of the azoxy functionality, in the 1300- and 1500-cm^{-1} regions. In addition, nmr was particularly valuable in ascertaining the position of oxygen in the unsymmetrical products. Prior investigations[11,16,17] revealed that protons in the vicinity of the oxidized nitrogen are shifted downfield relative to those near the other nitrogen. Application of this principle to the present studies is summarized in Table III.

Use of chemical evidence was also made for identification. For example, compound **4** yielded phenylazo-*tert*-butane on reduction.

Table III
Nmr Chemical Shifts (δ) of Azoxy Compounds[a]

Compd	Protons: $CH_3CN=$	Protons: $CH_3CN(O)=$
$C_6H_5N(O)=NC(CH_3)_3$	1.20	
$C_6H_5N=N(O)C(CH_3)_3$		1.37
 $N(O)=NC(CH_3)_3$	1.10	
 $N=N(O)C(CH_3)_3$		1.40
$(CH_3)_3CN(O)=NC(CH_3)_3$	1.27	1.47

[a] In CCl_4.

In general, for both new and known products, authentic materials were prepared by previously reported routes. Although the condensation of nitroso compounds with hydroxylamines, eq 3, was commonly utilized, isomeric mixtures were obtained in all cases (**7** and **8**, **4** and **18**, **11** and **12**). These results further emphasize the lack of specificity characteristic of this technique. Cyclohexylmagnesium chloride and phenylnitrosohydroxylamine tosylate served as precursors for compound **3**, eq 1. Another approach entailed oxidation of the azo precursor. Freeman[11] noted that reaction of perbenzoic acid with **15** provided **16**,

$$\underset{\mathbf{15}}{C_6H_5N{=}NCH_3} \xrightarrow{C_6H_5CO_3H} \underset{\mathbf{16}}{C_6H_5N(O){=}NCH_3} \qquad (7)$$

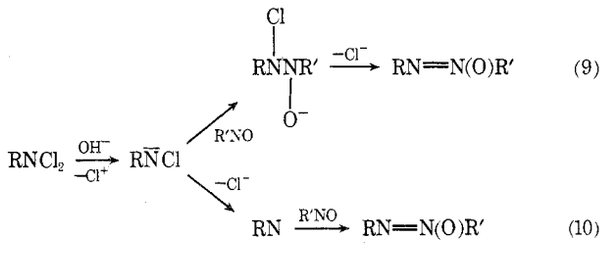
eq 7. An attempt on our part to apply this reaction to the synthesis of **4** from **17** gave isomer **18** instead, eq 8. Factors

$$\underset{\mathbf{17}}{C_6H_5N{=}NC(CH_3)_3} \xrightarrow{C_6H_5CO_3H} \underset{\mathbf{18}}{C_6H_5N{=}N(O)C(CH_3)_3} \qquad (8)$$

favoring the observed site of attack may be the increased inductive effect of *tert*-butyl *vs.* methyl, and steric hindrance[18] by the *tert*-butyl group to reaction on the nitrogen affixed to phenyl.

The geometry of the azoxy compounds is believed to be trans. The nmr spectra of the aralkyl types were quite indicative of the stereochemistry. The ortho protons appeared downfield approximately 0.7 δ from the meta and para ones. If the cis arrangement were present, the ortho protons would be expected to appear upfield with respect to the other aromatic protons.[17a] Also, under the conditions (glpc, 165–200°) generally used for isolation of the azoxyalkyl products, the cis isomer, if present, would be expected to isomerize to the more stable trans form.[16,17]

In relation to the reaction mechanism, several pathways deserve attention. The initial step might consist of nucleophilic attack[14] on the haloamine by hydroxide ion to form



an anion. Subsequent nucleophilic attack on the nitroso entity, which has literature analogy,[15b] could then lead eventually to end product, eq 9. Alternatively, α-elimination would provide a nitrene intermediate[19a] which yields azoxy compound on interaction with nitroso substrate, eq 10. Previous investigators have postulated this type of interaction leading to azoxy formation.[19c] Attempts to trap a nitrene with cyclohexene[20a] or benzene[20b] proved fruitless. In addition, nitrenes can abstract hydrogen to form amines,[19b] or rearrange,[19b] but compounds expected from such reactions were not observed as by-products in our case. A radical pathway should also be considered, eq 11. This ap-

$$RNCl_2 + OH^- \xrightarrow[-Cl^-]{-OH\cdot} R\dot{N}Cl \xrightarrow{R'NO} RN(Cl)-NR'(O\cdot) \xrightarrow{-Cl\cdot} RN{=}N(O)R' \quad (11)$$

proach resembles radical formation in the reaction of alkyl and aryl halides with organometallic reagents,[21a] eq 12. Ni-

$$R'X + R^- \longrightarrow R'\cdot + R\cdot + X^- \quad (12)$$

troso compounds can interact with amino radicals to form stable free radicals. In our case, subsequent loss of a chlorine atom gives rise to azoxy product.

As mentioned earlier, the two principal literature methods for directed synthesis of unsymmetrical azoxy compounds are represented by eq 1 and 2. The former is useful only for aralkyl types containing primary and secondary alkyl groups. Equation 2 appears to work satisfactorily when R'I is primary or secondary but poorly when R'I is tertiary. The present method is characterized by simplicity, and is useful for aralkyl and alkyl types. It works best with *tert*-alkyl groups, and thus nicely complements eq 1 and 2. In addition, versatility is displayed in the preparation of unsymmetrical azoxy derivatives containing α-cyano and α-chloro groups. The halogen-containing type appears promising as a source, *via* dehydrohalogenation, of analogs of naturally occurring materials. A number of naturally occurring azoxy compounds contain α,β unsaturation,[5,17] *e.g.*, **19**. Only a few methods[22] are currently available for synthesis of the conjugated types.

$$CH_3(CH_2)_5CH{=}CHN(O){=}NCH(CH(OH)CH_3)CH_2OCH_3$$

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Experimental Section

Materials. In general, high-purity commercial chemicals were used directly.

Analytical Procedures. Infrared spectra were recorded on a Perkin-Elmer 137 spectrophotometer with neat samples or potassium bromide pellets with the 1601.8-cm^{-1} band of polystyrene for calibration. Nmr spectra were taken with a Varian Model T-60 (parts per million with tetramethylsilane as internal standard). Gas chromatography was conducted with a Varian Aerograph Hy-Fi 1700, 10 ft × 0.25 in. column, 15% UCON 50HB2000 and 5% NaOH on Chromosorb W.

Quantitative glpc was accomplished by comparison of peak areas of solutions of crude products with those of solutions of authentic materials. Positive chlorine content was determined by standard iodometric titration.[23] Melting and boiling points are uncorrected. The elemental analyses were performed by Baron Consulting Co., Orange, Conn., and Dr. Ronald E. White.

***N,N*-Dichloroamines.** A literature procedure[13] was followed, providing yields in excess of 90%. Removal of methylene chloride provided the crude product, which was used without further purification. Iodometric titration was employed for analysis of the solid or liquid material.

General Procedures for Azoxy Compounds. A. To a solution of the nitroso compound (0.01 mol) in 35 ml of methanol (*tert*-butyl alcohol was used for **7**) was added the crude *N,N*-dichloroamine (0.01 mol). The solution was stirred at ambient temperatures (with compounds **5, 9, 10, 11,** and **12,** the reaction temperature was maintained at 0°) while 2.3 ml of 50% potassium hydroxide solution was added dropwise over a 15-min period. An exotherm was noted, and the reaction mixture was allowed to stir for an additional 30 min, or until the blue color of the nitroso compound disappeared. The reaction mixture was then poured into water and extracted with ether. The ethereal solution was washed with water and dried over $CaCl_2$. After solvent was removed, the compound was purified by distillation, glpc, or column chromatography (alumina with chloroform as eluent).

B. 1. Commercial sodium hypochlorite (28.6 ml, 0.7 *N*) was added dropwise to a solution of nitrosobenzene (1.07 g, 10 mmol) and *tert*-butylamine (0.73 g, 10 mmol) in 110 ml of methanol. The reaction mixture was stirred for 2 hr, and then poured into water. The mixture was extracted with ether, and the organic layer was washed with water and then dried over $CaCl_2$. After the ether was removed, product **4** was isolated in 83% yield.

2. To a solution of 1,8-diamino-*p*-methane (0.85 g, 5 mmol) and nitrosobenzene (1.07 g, 10 mmol) in 110 ml of methanol was added dropwise 28.6 ml of sodium hypochlorite solution (0.7 *N*). After completion of the addition, the reaction mixture was stirred for 2 hr and then poured into water. The mixture was extracted with ether, and the ethereal solution was washed with water and then dried over $CaCl_2$. After the ether was removed, the brown residue was chromatographed on an alumina column with chloroform as eluent, yield 1.4 g (75%) of a yellow oil: ir (neat) 1496 (N=N), 1285 (NO), 768, and 685 cm^{-1}; nmr (CCl_4) δ 8.10 (m, 4 H), 7.40 (m, 6 H), 1.00–2.10 (m, 18 H).

Anal. Calcd for $C_{22}H_{28}N_4O_2$: C, 69.44; H, 7.42; N, 14.73. Found: C, 69.72; H, 7.70; N, 14.48.

Characterization of Azoxy Products. *N*-*n*-Butyl-*N'*-phenyldiazine *N'*-oxide (**1**): nmr (CCl_4) δ 8.08 (m, 2 H), 7.40 (m, 3 H), 3.54 (m, 2 H), 0.8–1.60 (m, 7 H); ir (neat) 1485 (N=N), 1295 (NO), 773 and 685 cm^{-1} (aromatic).

Anal. Calcd for $C_{10}H_{14}N_2O$: C, 67.38; H, 7.92; N, 15.72. Found: C, 67.04; H, 7.84; N, 15.42.

N-2-Propyl-*N'*-phenyldiazine *N'*-oxide (**2**): nmr (CCl_4) δ 8.04 (m, 2 H), 7.37 (m, 3 H), 4.30 (m, 1 H), 1.23 (d, 6 H); ir (CCl_4) 1470 (N=N), 1310 (NO), 780 cm^{-1} (aromatic).

N-Cyclohexyl-*N'*-phenyldiazine *N'*-oxide (**3**): nmr (CCl_4) δ 8.08 (m, 2 H), 7.40 (m, 3 H), 4.18 (m, 1 H), 2.20–1.30 (m, 10 H); ir (neat) 1470 (N=N), 1295 (NO), 780 and 690 cm^{-1} (aromatic).

Anal. Calcd for $C_{12}H_{16}N_2O$: C, 70.56; H, 7.90; N, 13.71. Found: C, 70.41; H, 8.08; N, 13.53.

N-*tert*-Butyl-*N'*-phenyldiazine *N'*-oxide (**4**): nmr (CCl_4) δ 7.90 (m, 2 H), 7.14 (m, 3 H), 1.20 (s, 9 H); ir (neat) 1475 (N=N), 1290 (NO), 782 and 696 cm^{-1} (aromatic).

Anal. Calcd for $C_{10}H_{14}N_2O$: C, 67.38; H, 7.92; N, 15.72. Found: C, 67.61; H, 8.15; N, 15.38.

N-2-(2-Cyanopropyl)-*N'*-phenyldiazine *N'*-oxide (**5**): nmr (CCl_4) δ 8.00 (m, 2 H), 7.40 (m, 3 H), 1.60 (s, 6 H); ir (neat) 2225 (C≡N), 1470 (N=N), 1310 (NO), 782 and 698 cm^{-1} (aromatic).

Anal. Calcd for $C_{10}H_{11}N_3O$: C, 63.47; H, 5.86; N, 22.21. Found: C, 63.73; H, 5.97; N, 22.44.

N-1-Adamantyl-*N'*-phenyldiazine *N'*-oxide (**6**), white powder: mp 96–97.5°; nmr (CCl_4) δ 8.01 (m, 2 H), 7.33 (m, 3 H), 2.10 (s, 9 H), 1.64 (s, 6 H); ir (KBr) 1478 (N=N), 1285 (NO), 780 and 690 cm^{-1} (aromatic).

Anal. Calcd for $C_{16}H_{20}N_2O$: C, 74.96; H, 7.86; N, 10.93. Found: C, 74.62; H, 7.89; N, 11.08.

N-*tert*-Butyl-*N'*-1-adamantyldiazine *N'*-oxide (**7**): nmr (CCl_4) δ 1.96 (s, 9 H), 1.52 (s, 6 H), 1.10 (s, 9 H); ir (neat) 1480 (N=N), 1280 cm^{-1} (NO).

Anal. Calcd for $C_{14}H_{24}N_2O$: C, 71.14; H, 10.24; N, 11.85. Found: C, 71.40; H, 9.96; N, 12.04.

N-1-Adamantyl-*N'*-*tert*-butyldiazine *N'*-oxide (**8**): nmr (CCl_4) δ 1.95 (s, 9 H), 1.65 (s, 6 H), 1.40 (s, 9 H); ir (neat) 1500 (N=N), 1298 cm^{-1} (NO). *Anal.* Calcd for $C_{14}H_{24}N_2O$: C, 71.14; H, 10.24; N, 11.85. Found: C, 71.38; H, 10.34; N, 11.78.

Azoxyisobutyronitrile (**9**), white crystals: mp 35–37° [lit.[24] mp 37°]; ir (KBr) 2222 (C≡N), 1496 (N=N), 1298 cm^{-1} (NO).

N-2-(2-Cyanopropyl)-*N'*-1-(1-chlorocyclohexyl)diazine *N'*-oxide (**10**): nmr (CCl_4) δ 2.32 (m, 4 H), 1.62 (s, 12 H); ir (neat) 2220 (C≡N), 1498 (N=N), 1293 (NO), 768 cm^{-1} (CCl).

Anal. Calcd for $C_{10}H_{16}ClN_3O$: C, 52.28; H, 6.97; N, 18.29. Found: C, 52.13; H, 7.07; N, 18.24.

N-2-(2-Cyanopropyl)-*N'*-1-(1-cyanocyclohexyl)diazine *N'*-oxide (**11**): nmr (CCl_4) δ 1.90–2.32 (m, 10 H), 1.70 (s, 6 H); ir (neat) 2223 (C≡N), 1500 (N=N), 1292 cm^{-1} (NO).

Anal. Calcd for $C_{11}H_{16}N_4O$: C, 59.98; H, 7.32; N, 25.44. Found: C, 60.00; H, 7.75; N, 24.90.

On standing for several weeks, there was a change in the ir spectrum.

N-1-(1-Cyanocyclohexyl)-*N'*-2-(2-cyanopropyl)diazine *N'*-oxide (**12**): nmr (CCl_4) δ 1.90–2.34 (m, 10 H), 2.10 (s, 6 H); ir (neat) 2222 (C≡N), 1496 (N=N), 1295 cm^{-1} (NO).

Anal. Calcd for $C_{11}H_{16}N_4O$: C, 59.98; H, 7.32; N, 25.44. Found: C, 59.30; H, 7.75; N, 24.46.

On standing for several weeks, there was a change in the ir spectrum.

Azoxyisobutane (**13**): bp 46–50° (20–25 mm) [lit.[11] bp 50° (20 mm)]; nmr (CCl_4) δ 1.47 (s, 9 H), 1.27 (s, 9 H).

1-Cyano-*N*-cyclohexylhydroxylamine. A previous method[25] was employed: 65% yield, mp 134–136° after recrystallization (lit.[25] mp 136–137°).

2-Cyano-*N*-(2-propyl)hydroxylamine. A literature procedure[25] was used: 48% yield, mp 102.5–104° after recrystallization (lit.[25] mp 98–99°).

1-Cyano-1-nitrosocyclohexane. A previous method[26] was employed to obtain the nitroso compound as a blue solid, 60% yield, mp 36–37° (lit.[26] mp 37–37.5°).

2-Cyano-2-nitrosopropane. A literature procedure[26] was used to obtain the nitroso compound as a white powder, 34% yield, mp 48–50° (lit.[27] mp 53°).

1-Chloro-1-nitrosocyclohexane. A previous method[28] was employed to obtain the product, blue liquid, 90% yield, which was used without further purification. In another run, attempted distillation resulted in a minor explosion and fire.

1-Nitrosoadamantane. A literature procedure[29] was used with the corresponding hydroxylamine as precursor, 84% yield, mp 172–175° (lit.[29] mp 179.5°).

2-Methyl-2-nitrosopropane. A previous method[30] was employed with the corresponding hydroxylamine (prepared by the method of Stetter and Smulders[29]) as precursor, 72% yield, mp 81–82° [lit.[30] mp 83–84°].

Condensation of Nitroso Compounds with Hydroxylamines.[11,29] Equimolar quantities of the nitroso compound (0.01 mol) and hydroxylamine derivative (0.01 mol) were refluxed in absolute ethanol with catalytic amounts (0.01 g) of potassium hydroxide. After 3 hr, the color had changed from blue to light yellow. The reaction mixture was poured into water and extracted with ether. The organic layer was washed and then dried over $CaCl_2$. After the solvent was removed, the products were collected (glpc). Mixtures synthesized included **7** and **8** (64% yield, 1:1 molar ratio), **4** and **18** (30% yield, 1:2 molar ratio), and **11** and **12** (72% yield, 1:1 molar ratio), In addition, the symmetrical compound **9** was obtained in 41% yield. Since attempts to separate certain pairs of isomers by glpc proved unsuccessful, **7** and **8** and **11** and **12** were analyzed as mixtures. Compounds **4** and **18** were readily separated by glpc and were analyzed individually.

Reduction of *N*-*tert*-Butyl-*N'*-phenyldiazine *N'*-Oxide.[31] To a solution of *N*-*tert*-butyl-*N'*-phenyldiazine *N'*-oxide (**4**, 0.2 g, 1.1 mmol) in 10 ml of ether was added $LiAlH_4$ (0.1 g, 2.6 mmol). After the mixture was refluxed overnight, it was poured into methanol. Water was added and the mixture was extracted with ether. The ethereal solution was washed, dried with $MgSO_4$, and freed of ether. Essentially a quantitative yield of phenylazo-*tert*-butane was obtained. Identification was accomplished by comparison with an authentic sample prepared by the method of Fowler:[32] nmr (CCl_4) δ 7.40–7.81 (m, 5 H), 1.19 (s, 9 H); ir (neat) 1590, 770, and 690 cm^{-1}.

Oxidation of Phenylazo-*tert*-butane with Perbenzoic Acid.[11] To a solution of phenylazo-*tert*-butane (0.3 g, 1.8 mmol) in 10 ml of methylene chloride chilled to 0° was added 10 ml of methylene chloride containing perbenzoic acid (0.4 *N*). The mixture was allowed to stand overnight in a refrigerator. Then a 10% solution of KI was added, followed by sodium thiosulfate until the purple color of iodine disappeared. The organic layer was separated, washed first with $NaHCO_3$ solution and then with water, and dried over $CaCl_2$. The solvent was removed, leaving 0.22 g of a light yellow liquid. The major product was isolated by glpc and identified as *N'*-*tert*-butyl-*N*-phenyldiazine *N'*-oxide (**18**): 40% yield; ir (neat) 1495 (N=N), 1300 (NO), 770 and 690 cm^{-1}; nmr (CCl_4) δ 7.80 (m, 2 H), 7.04 (m, 3 H), 1.37 (s, 9 H).

Anal. Calcd for $C_{10}H_{14}N_2O$: C, 67.38; H, 7.92; N, 15.72. Found: C, 67.57; H, 7.83; N, 15.55.

Phenylazo-2-cyano-2-propane and Perbenzoic Acid. Attempted oxidation of phenylazo-(2-cyano-2-propane with perbenzoic acid (conditions identical with those for oxidation of phenylazo-*tert*-butane to **18**) failed to produce the desired conversion to **5**. Starting material was recovered.

***N*-Cyclohexyl-*N'*-phenyldiazine *N'*-Oxide (3).** A previous method[8] was employed to produce the desired azoxy compound in 36% yield: ir (neat) 1470 (N=N), 1295 (NO), 780 and 690 cm^{-1}; nmr (CCl_4) δ 8.08 (m, 2 H), 7.40 (m, 3 H), 4.18 (m, 1 H), 2.20–1.30 (m, 10 H).

Anal. Calcd for $C_{12}H_{16}N_2O$: C, 70.56; H, 7.90; N, 13.71. Found: C, 70.41; H, 8.08; N, 13.53.

Acknowledgment. We are grateful to the National Science Foundation and the Center for Great Lakes Studies (Contribution No. 107) for support of this work, and to Dr. Ronald E. White for helpful discussions.

Registry No.—**1**, 52123-78-1; **2**, 52123-65-6; **3**, 52123-66-7; **4**, 52123-67-8; **5**, 52123-68-9; **6**, 52123-69-0; **7**, 52123-70-3; **8**, 52123-71-4; **9**, 52123-72-5; **10**, 52123-73-6; **11**, 52123-74-7; **12**, 52123-75-8; **13**, 16649-52-8; **14**, 52123-76-9; **18**, 52123-77-0.

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