mmol) for 30 min, followed by addition of methyl iodide (0.72 mL, 9.95 mmol). After 3 h, the solvent was evaporated and the residue partitioned between EtOAc (40 mL) and water (7 mL). The EtOAc layer was worked up as usual and subjected to preparative TLC (silica gel, 20 × 20 cm; $CHCl_3$/MeOH, 9:1) to give from the main band on oily mixture, which was further purified by dry distillation (5 torr, 120 °C) to afford 1.13 g (72%) of **3b** as an oil: λ_{max} (95% EtOH) 225 nm (ϵ 7600, infl), 256 (2600, sh); ^{1}H NMR ($CDCl_3$) δ 1.22 (3 H, d, $J_{5\text{-Me},H_5}$ = 6.8 Hz, 5-Me), 1.96 (3 H, s, 6-Me), 2.39 (3 H, s, SMe), 3.32 (3 H, s, N-Me), 3.82 (1 H, q, $J_{H_5,5\text{-Me}}$ = 6.8 Hz, H_5). Anal. Calcd for $C_7H_{13}N_3S$: C, 49.09; H, 7.65; N, 24.54. Found: C, 48.82; H, 7.56; N, 24.84.

2-Ethyl-5-phenyl-1,2,4-triazin-3(2*H*)-one (8). Compound **3a** (825 mg, 3.80 mmol) and DMAD (1.08 g, 7.6 mmol) were combined in toluene (10 mL) in a pressure tube, and the mixture was heated at 110 °C under argon for 15 h. After the mixture cooled, the volatiles were evaporated, and the residue was subjected to preparative TLC (silica gel, 20 × 20 cm; $CHCl_3$/EtOAc, 5:1). The main band was eluted with acetone and the obtained solid distilled (0.1 torr, 140–160 °C) to give 543 mg (71%) of **8**: mp 65–67 °C; λ_{max} (MeOH) 215 nm (ϵ 12900, sh), 293 (13700); ^{1}H NMR ($CDCl_3$) δ 1.40 (3 H, t, J = 7.5 Hz, CH_3 of the ethyl group), 4.20 (2 H, q, J = 7.5 Hz, CH_2), 7.3–8.3 (5 H, m, phenyl), 8.34 (1 H, s, H_6). Anal. Calcd for $C_{11}H_{11}N_3O$: C, 65.66; H, 5.51; N, 20.88. Found: C, 65.68; H, 5.70; N, 21.16.

Registry No. 1a, 28735-27-5; **1b**, 28735-28-6; **1c**, 7275-70-9; **1d**, 28735-31-1; **1e**, 28735-24-2; **1f**, 28735-25-3; **1g**, 28735-21-9; **1h**, 28735-22-0; **2a**, 49597-36-6; **2b**, 49597-47-9; **2c**, 49597-40-2; **2d**, 74930-65-7; **2e**, 49597-35-5; **2f**, 49597-46-8; **2g**, 74930-66-8; **2h**, 74930-67-9; **3a**, 74930-68-0; **3b**, 74930-34-0; **7**, 31947-28-1; **8**, 74930-69-1; methyl iodide, 74-88-4; DMAD, 762-42-5.

Cyclic Azo Dioxides. Synthesis and Properties of Bis(*o*-nitrosobenzyl) Derivatives[1]

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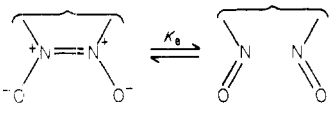
Several cyclic azo dioxides have been prepared by oxidation of the corresponding diamines with sodium tungstate–hydrogen peroxide in ethanol–water: **4** (related to *o,o'*-dinitrosobibenzyl), **8** (related to bis(*o*-nitrosobenzyl) ether), **14** (related to bis(*o*-nitrosobenzyl)amine), **13** (the trifluoroacetate salt of **14**), **12a** and **12b** (the *N*-carbomethoxy and *N*-carbo-*tert*-butoxy derivatives of **14**. In solution the azo dioxides are in equilibrium (K_e) with the corresponding dinitroso forms: K_e increases with decreasing polarity of solvent and with increasing temperature. For azo dioxide **4** in dioxane at 25 °C K_e = 0.18, $\Delta H°$ = 7.09 ± 0.47 kcal mol^{-1}, and $\Delta S°$ = 20.4 cal mol^{-1} deg^{-1}. The azo dioxides decompose at elevated temperatures (>100 °C); azo dioxide **14** is converted to 2-(*o*-nitrosobenzyl)indazole (**15**) in refluxing methylene chloride.

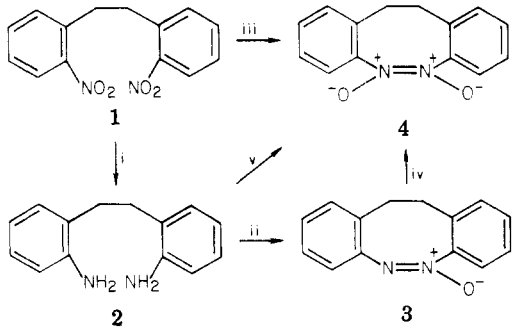
The equilibrium[2,3] between azo dioxides and nitroso species is of much interest: a simple, often facile, electron reorganization interconverts two species of markedly different properties—azo dioxides, which are moderately polar, colorless, and chemically unreactive, and nitroso species which are less polar, colored, and chemically reactive in a variety of ways.[4] For some uses of these substances, control of the equilibrium is complicated by the concentration dependence associated with the dimer ⇄ monomer situation (eq 1). Consequently, we have in-



(1)

vestigated a number of cyclic azo dioxides. In general, the azo dioxide is the more stable form in aliphatic systems.[2,3] Arylnitroso species are largely dissociated in solution[4,5] although they often exist in the azo dioxide form in the solid state. In this paper, we report the synthesis and properties of some cyclic azo dioxides in the aryl series.

Scheme I[a]



[a] (i) Pd/C-H_2NNH_2. (ii) *m*-$ClC_6H_4CO_3H$. (iii) (a) Zn, NH_4Cl; (b) CrO_4^{2-}, H^+. (iv) CF_3CO_3H. (v) WO_4^{2-}-H_2O_2, EtOH-H_2O.

Results

Syntheses. Our initial objective was the synthesis of cyclic azo dioxide **4** (5,6-dihydrodibenzo[*c,g*]-1,2-diazocine *N,N'*-dioxide.) The corresponding azo and azo *N*-oxide were both known,[6] as well as the related diamino and

(1) This investigation was supported by Grant No. CA 23550, awarded by the National Cancer Institute, DHEW.

(2) See: Wajer, A. J. W.; deBoer, T. J. *Recl. Trav. Chim. Pays-Bas* **1972**, *91*, 565 and references cited.

(3) Greene, F. D.; Gilbert, K. E. *J. Org. Chem.* **1975**, *40*, 1409.

(4) (a) Smith, P. A. S. "Open-Chain Nitrogen Compounds", W. A. Benjamin, New York, 1966; Vol. II, Chapter 13. (b) Metzger, H.; Meier, H. "Methoden der Organischen Chemie (Houben-Weyl)"; Muller, E., Ed.; Georg Thieme Verlag: Stuttgart, 1971; Band 10/1, Chapter 3; Seidenfaden, W. *Ibid.*, Chapter 4. (c) Feuer, H., Ed. "The Chemistry of the Nitro and Nitroso Groups"; Interscience: New York, 1969, Parts I and II; Boyer, J. H. *Ibid.*, Part I, Chapter 5.

(5) (a) Keussler, V.; Luttke, W. *Z. Electrochem.* **1959**, *63*, 614. (b) Cox, R. H.; Hamada, M. *Org. Magn. Reson.* **1979**, *12*, 322.

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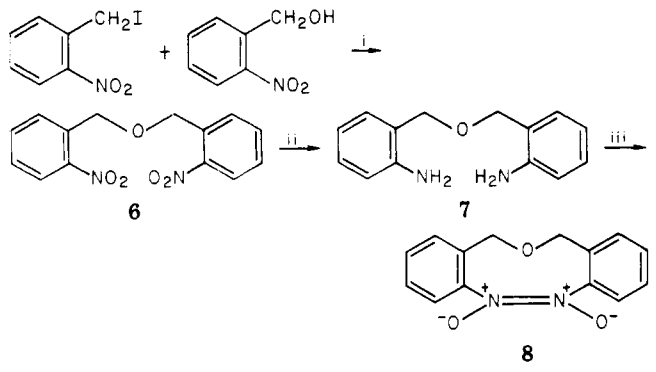
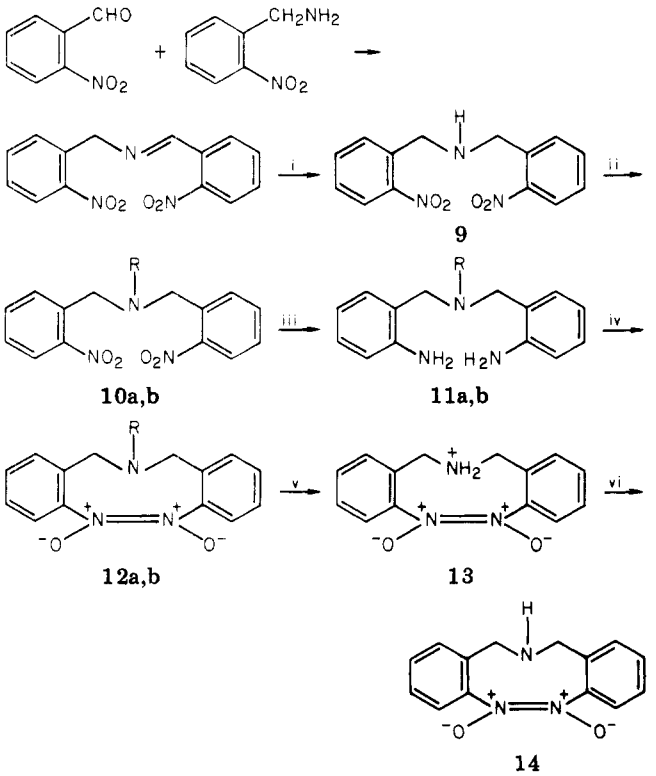
Scheme II[a]



[a] (i) Ag_2O. (ii) $Pd/C-H_2NNH_2$. (iii) $WO_4^{2-}-H_2O_2$, EtOH-H_2O.

Scheme III[a,b]



[a] (i) HCl, $[BH_3CN]^-$. (ii) $ClCOOCH_3$ or $(t\text{-BuOCO})_2O$. (iii) $Pd/C-H_2NNH_2$. (iv) $WO_4^{2-}-H_2O_2$. (v) CF_3COOH. (vi) OH^-. [b] a, R = $COOCH_3$; b, R = COO-*t*-Bu.

dinitro species (easily made by an oxidative coupling of *o*-nitrotoluene).[7] Three ways (iii, iv, and v in Scheme I) have been found for the synthesis of azo dioxide **4**. Overall yields (~20%) are similar for the three paths; product purification was easiest with the tungstate–hydrogen peroxide route (v). A difficulty with this oxidative route is that the azo dioxide **4** is in equilibrium with the dinitroso form (discussed below), which is subject to further oxidation.

A second system investigated was **5** in which A is an oxygen or a nitrogen bridging atom. The oxygen-bridged system was synthesized by the route shown in Scheme II. Here, oxidation of diamine to azo dioxide could only be effected by the tungstate–hydrogen peroxide route (~20% yield).

(6) (a) Paudler, W. M.; Zeiler, A. G. *J. Org. Chem.* **1969**, *34*, 3237. (b) Yanagida, A.; Gansser, C. *Ann. Chim. (Paris)* **1973**, [14] *8*, 391.
(7) Fogassy, E.; Zolyomi, G. Hungarian Patent 149 380; *Chem. Abstr.* **1963**, *58*, 5570e.

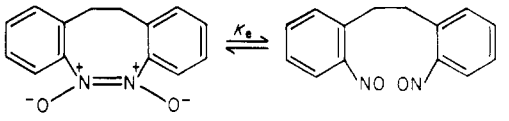
Table I

azo dioxide 8 $\overset{K_e{}^a}{\rightleftharpoons}$ dinitroso 8

solvent	K_e[b]	solvent	K_e[b]
nitrobenzene-d_5	0.6	Me_2SO	0.07
$CDCl_3$	0.3		

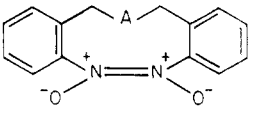
[a] Determined by NMR. [b] At 27 °C.

Table II



solvent	temp, °C	K_e	$\Delta H°$,[a] kcal/mol	$\Delta S°$,[a] eu
dioxane[b]	13.51	0.117		
	27.19	0.199	7.09 ± 0.47	20.4 ± 2.1
	46.51	0.400		
nitrobenzene[b]	17.69	0.068		
	35.47	0.131	6.82 ± 0.28	18.1 ± 1.3
	65.80	0.368		
nitrobenzene-d_5[c]	29.55	0.1		

[a] Calculated from the full data (Table IV). [b] By use of the UV-vis method. [c] By use of the NMR method.



5, A = O or NR

Synthesis of **5** (A = NR) is shown in Scheme III. The bridging nitrogen was protected as a carbamate for the oxidation sequences. Both the carbomethoxy and carbo-*tert*-butoxy groups were examined. Oxidative cyclization of **11a** and **11b** to the azo dioxides **12a** and **12b** was achieved by the tungstate–hydrogen peroxide method in ~20% yield. Efforts to synthesize **12a** from the azoxy derivative by trifluoroperacetic acid (one of the ways used to make azo dioxide **4**) were unsuccessful.

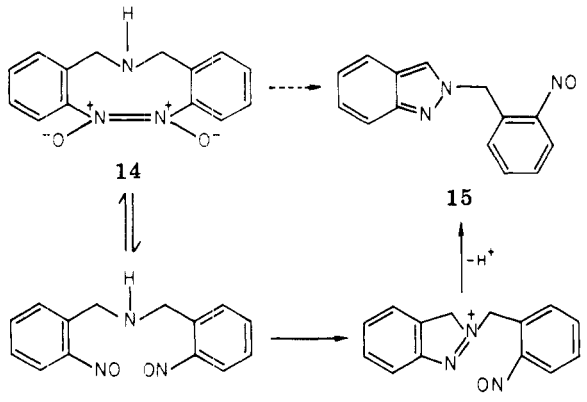
Removal of the carbomethoxy group (acid, base, trimethylsilyl iodide, or lithium thiomethoxide) was troublesome, in some instances due to attack on the azo dioxide moiety (e.g., lithium thiomethoxide in HMPA reacts rapidly with **12a** resulting in destruction of the azo dioxide group). Success was achieved with the carbo-*tert*-butoxy group; brief exposure of **12b** to trifluoroacetic acid afforded the trifluoroacetate salt **13**, which was converted to the free base **14**.

Properties. The azo dioxides **4**, **8**, **12a,b**, **13** and **14** are colorless solids. In organic solvents, compounds **4**, **8**, and **12a,b** are in rapid reversible equilibrium with the dinitroso forms. Solutions of the compounds in polar solvents (e.g., methanol) are colorless, indicating little or none of the (less polar) nitroso form. In less polar solvents some dissociation (ring opening) to dinitroso (blue to blue-green in solution) takes place (see Table I).

Effect of Temperature. As expected, higher temperatures increase K_e; at elevated temperatures further changes occur.

At room temperature the proton NMR of **4** in nitrobenzene-d_5 shows peaks for the methylene hydrogens of both the dinitroso form (broad singlet) and the azo dioxide form. The methylene hydrogens of the latter appear as an A_2B_2 quartet, consistent with the conformation expected from models—a tub shape with a large dihedral angle

Scheme IV



between the plane of the N_2O_2 moiety and the plane of each benzene ring. Partial coalescence is observed between 95–105 °C. Brief heating to 100 °C and cooling regenerates the peaks in the original intensity. Higher temperatures result in decomposition, precluding an accurate determination of the coalescence temperature but pointing to a value of approximately 125 °C, corresponding to an activation energy for ring opening for azo dioxide **4** of ~20 kcal/mol. [The K_e at 125 °C, extrapolated from the data of Table II (see below) is 1.9.] Activation energies for dissociation of primary and secondary aliphatic azo dioxides are in the range 18–25 kcal/mol.[8]

Azo dioxides **8** and **12a,b** also show reversible changes in the proton NMR upon being warmed and cooled in organic solvents. Here, too, elevated temperatures result in decomposition, affording dark solutions and intractable product mixtures.

A more simple result is observed with azo dioxide **14**. Refluxing in methylene chloride results in clean conversion to **15** (eq 2), assigned the structure shown on the basis of

$$\underset{\mathbf{14}}{C_{14}H_{13}N_3O_2} \rightarrow \underset{\mathbf{15}}{C_{14}H_{11}N_3O} \qquad (2)$$

the physical data (IR, ^{1}H NMR, ^{13}C NMR, UV, high-resolution mass spectrum) summarized in the Experimental Section. In the elucidation of the structure two aspects were of particular help: the high-resolution mass spectrum showed a strong molecular ion at *m/e* 237 and a base peak at *m/e* 118 of composition $C_7H_6N_2$ (the protonated indazole ion); the UV spectrum corresponded closely to the summation of the UV spectra for *o*-nitrosotoluene and 2-methylindazole (but not 1-methylindazole).[9] The probable route of formation of **15** involves ring-opening of **14** to a dinitroso compound (Scheme IV) and intramolecular reaction of the secondary amine and a nitroso group with dehydration, followed by proton loss.

Equilibrium Study of Azo Dioxide 4. This system was examined by two methods (UV–vis and NMR) in three solvents over the temperature range 13–70 °C. The UV–vis method, monitoring the nitroso band at ~785 nm, is the better of the two. The principal results are summarized in Table II; more complete results are given in Table IV in the Experimental Section.

Table III

$$RN(O)=N(O)R \overset{K_e}{\rightleftharpoons} 2RNO$$

R[a]	solvent	$\Delta G°$ (20 °C), kcal/mol	$\Delta H°$, kcal/mol	$\Delta S°$, eu
cyclohexyl[b]	C_6H_6	8.6	20.6	41
2,4,6-$Br_3C_6H_2$[b]	C_6H_6	−0.2	10.9	38
2,4,6-$(CH_3)_3C_6H_2$[b]	C_6H_6	1.5	12.1	36
4-$CH_3C_6H_4$[c]	CD_3COCD_3	−0.8[d]	~7[e]	~35[e]
C_6H_5[c]	CD_3COCD_3	−0.1[d]		

[a] Trans azo dioxides. [b] Reference 5a. [c] Reference 5b. [d] −40 °C. [e] Estimated value; see text.

Some azo dioxide–dinitroso equilibria data from other systems are summarized in Table III. Entropy factors for azo dioxide ⇄ nitroso systems are resonably well-behaved: with acyclic azo dioxides (aromatic or aliphatic), $\Delta S°$ favors the nitroso species by ~40 eu; with cyclic azo dioxides, $\Delta S°$ is expected to be considerably less[10] [$\Delta S° \simeq 20$ eu for a bicyclic azo dioxide, and $\Delta S° \simeq 20$ eu for azo dioxide **4** (Table I)].

With aliphatic azo dioxides in the absence of strain factors the $\Delta H°$ term favors the azo dioxide form over the nitroso form by approximately 20 kcal/mol.[11] With ortho-substituted aryl azo dioxides both forms may be present in solution.[5a] Aromatic azo dioxides with hydrogen in the 2- and 6-positions are largely dissociated in solution at 20 °C; a recent study indicates a K_e of ~1.2 M^{-1} for nitrosobenzene and ~5 M^{-1} for *p*-nitrosotoluene in acetone-d_6 at −40 °C. With an estimated value of $\Delta S° \approx 35 \pm 5$ eu,[10] this corresponds to a $\Delta H°$ of ~7 kcal/mol. Comparison of this value with the $\Delta H°$ of 11–12 kcal/mol for the 2,6-disubstituted nitrosobenzenes[5a] is suggestive of a few kilocalories per mole greater resonance stabilization in the nitrosoaryl unit than in the azo dioxide aryl unit. (A measure of this resonance stabilization in nitrosobenzene is the free energy of activation for rotation around the C–N bond—7.7 kcal/mol for nitrosobenzene in acetone-d_6 at 25 °C).[5b]

For cyclic azo dioxide **4** (Table II), in addition to the above factors, the $\Delta H°$ will also include ring strain effects. The overall strain in 1,3,5-cyclooctatriene, a possible model for azo dioxide **4**, is small (3.5 kcal/mol).[12] Thus, the observed $\Delta H°$ of 7 kcal/mol for **4**, a monoortho-substituted system, seems in reasonable accord with expectations.

In summary, these results show that cyclic diaryl azo dioxides are accessible systems of moderate thermal stability. The ring-opening equilibrium constant, K_e, should be subject to considerable variation as a function of substituent.[13]

Experimental Section

2,2′-Diaminobibenzyl was prepared by catalytic reduction of the dinitro compound;[7] mp 65–66 °C (lit.[14] mp 66–67 °C).

5,6-Dihydrodibenzo[*c,g*]-1,2-diazocine *N*-Oxide (3). To a solution of 2,2′-diaminobibenzyl (1.00 g, 4.69 mmol) in 40 mL of methylene chloride at 0 °C was added a solution of *m*-

(8) See: Chaudhry, A. V.; Gowenlock, B. G. *J. Chem. Soc. B* **1968**, 1083 and references cited.

(9) For the UV spectra of 1- and 2-methylindazole see: Rousseau, V.; Lindwall, H. G. *J. Am. Chem. Soc.* **1950**, *72*, 3047. For the UV spectrum of *o*-nitrosotoluene, see: Tsuzuki, Y.; Uemura, T.; Hirasawa, N. *Chem. Ber.* **1941**, *74*, 616. The full spectrum of **15** fits closely to the calculated summation of the spectra of 2-methylindazole and *o*-nitrosotoluene. For ^{13}C NMR of indazoles, see: Bouchet, P.; Fruchier, A.; Joncheray, G. *Org. Magn. Reson.* **1977**, *9*, 716.

(10) See: for example Table II, the first three entries (see also ref 2 and 3). With acyclic azo dioxides the major factor in $\Delta S°$ is the translational terms associated with one dimer dissociating to two monomers. With cyclic azo dioxides the main factors are the greater rotational possibilities in the dissociated (ring-opened) form compared with the more restricted cyclized form. For an estimation of entropy changes, see: Benson, S. W. "Thermochemical Kinetics"; Wiley-Interscience: New York, 1976; Chapter 2.

(11) With cis azo dioxides, $\Delta H° \simeq 18$ kcal/mol.

(12) Turner, R. B.; Mallon, B. J.; Tichy, M.; Doering, W. v. E.; Roth, W. R.; Schröder, G. *J. Am. Chem. Soc.* **1973**, *95*, 8605.

(13) Holmes, R. R., et al. *J. Org. Chem.* **1965**, *30*, 3837.

(14) Ruggli, P.; Dinger, A. *Helv. Chim. Acta* **1939**, *22*, 908.

chloroperbenzoic acid (Aldrich; 85%, 3.01 g, 14.8 mmol) in 50 mL of methylene chloride at a rate such that the reaction mixture did not exceed 5 °C. After the addition, the reaction was stirred at 0 °C for 2 h. Ammonia was bubbled through the solution for 15 min, the ammonium salts were filtered, and the filtrate was concentrated under reduced pressure. The brown solid remaining was recrystallized from CCl_4 to give 0.413 g of tan needles, a mixture of the *N*-oxide and *N,N'*-dioxide by TLC. Preparative thin-layer chromatography (silica gel, $CHCl_3$ eluent) of a 76-mg fraction gave 56 mg (R_f 0.7) of the *N*-oxide, **3**, as white needles (mp 166–167 °C), after recrystallization from ethyl acetate (lit.[6b] mp 166–167 °C): IR ($CHCl_3$) 1467 (vs), 1340 cm^{-1} (w); mass spectrum, *m/e* 224 (M^+); UV (*i*-PrOH) 240 nm (ϵ 11 000), 308 (1500.)

5,6-Dihydrodibenzo[*c,g*]1,2-diazocine *N,N'*-Dioxide (4). (a) From the Dinitro Compound. 2,2'-Dinitrobibenzyl (2.00 g, 7.4 mmol) and NH_4Cl (1.76 g, 33 mmol) were added to 100 mL of ethanol and 10 mL of water. While the mixture was stirred, freshly activated zinc dust (10.2 g, 0.16 mol) was added over 5 min (the temperature rose to 40 °C). After 25 min the solution was filtered through Celite. The solvent was evaporated under reduced pressure to 5 mL. Water (30 mL) was added and the mixture reduced to 10 mL. The temperature was not allowed to exceed 25 °C during these solvent-removal steps. To the resulting slurry at 0 °C were added 40 mL of water and 4.5 mL of concentrated sulfuric acid. To this mixture was added rapidly a solution of sodium dichromate (1.02 g, 3.9 mmol) in 5 mL of water at 0 °C. The mixture was vigorously swirled for 3 min and then rapidly filtered. The green solids were taken up in 200 mL of boiling benzene and filtered. Evaporation to a small volume (20 mL), cooling, and filtration gave 197 mg (17%) of azo dioxide **4** as tan crystals (contaminated with a minor amount of the *N*-oxide) which was purified by preparative thin-layer chromatography (silica gel, $CHCl_3$ eluent; azo dioxide **4**, R_f 0.2; azoxy **3**, R_f 0.7) and recrystallized from acetone: mp 154–155 °C dec; IR ($CHCl_3$) 2995 (m), 1480 (m), 1445 (m), 1410 (s), 1385 (s), 1305 (w), 1200 (s), 1175 (m), 1110 (w), 950 (d, s), 770 cm^{-1} (s); NMR ($CDCl_3$) δ 3.20 (A_2B_2, 4 H), 7.0–7.5 (m, 8 H); UV (dioxane at 25 °C) 292 nm (ϵ 9200);[15] visible spectrum (dioxane at 25 °C) 783 nm (ϵ 19);[15] (nitrobenzene) 790 nm (ϵ 11, i.e., 10% dinitroso); mass spectrum, *m/e* (relative intensity) 241 (0.89), 240 (5.21, M^+), 223 (29, M – OH), 221 (25), (18, M – NO), 206 (33), 205 (32), 195 (27), 194 (39), 193 (65), 192 (43), 180 (40, M – 2 NO), 179 (46), 178 (68), 177 (24), 176 (16), 165 (100), 120 (69), 92 (63), 91 (44), 77 (48), 76 (39), 63 (62), 51 (54), 30 (29).

Anal. Calcd for $C_{14}H_{12}N_2O_2$: C, 69.98; H, 5.04; N, 11.66. Found: C, 69.79; H, 4.97; N, 11.47.

(b) From the *N*-Oxide (3). To a solution of trifluoroacetic anhydride (0.3 mL, 2.1 mmol) in 4 mL of methylene chloride at 0 °C was added 90% hydrogen peroxide (0.065 mL, 2.4 mmol). The solution was warmed to room temperature and cooled back to 0 °C. A solution of the *N*-oxide **3** (361 mg, 1.61 mmol) in 6 mL of methylene chloride was added and the mixture stirred at 0 °C for 24 h. The mixture was treated with gaseous ammonia for 15 min, diluted with 20 mL of methylene chloride, and extracted (3 × 5 mL) with water. The organic layer was dried ($MgSO_4$) and the solvent removed under reduced pressure. The resulting solid was chromatographed on a 2000-μm silica gel plate with chloroform eluent, affording 206.3 mg of azo dioxide **4** (53%) as white cubic crystals, mp 155–156 °C. Also obtained were 33 mg (8%) of 2,2'-dinitrobibenzyl and 10 mg (3%) of the *N*-oxide **3**.

(c) From the Diamine 2. To a cooled solution of 2,2'-diaminobibenzyl (816 mg, 3.84 mmol) and 178 mg of sodium tungstate dihydrate in 20 mL of 70% ethanol–water was added 2.67 g of 30% hydrogen peroxide. The mixture was stirred for 24 h, and then 25 mL of 1:1 saturated NaCl/H_2O along with an equivalent volume of methylene chloride was added. The aqueous layer was extracted with small portions of methylene chloride, and the organic fractions were combined, dried (K_2CO_3), and concentrated in vacuo. The resulting oil was taken up in acetone and cooled to give 169 mg (18.5%) of the azo dioxide **4**, mp 155–156 °C.

(15) These extinction coefficient values correspond to 18% dissociation.

Table IV. K_e Values at Various Temperatures in Dioxane, Nitrobenzene, and Nitrobenzene-d_5

$$\text{azo dioxide } 4 \underset{}{\overset{K_e}{\rightleftharpoons}} \text{dinitroso}$$

Dioxane[a,b]

C_0 = 0.0203 M [temp, °C (K_e)]: 13.51 (0.117), 14.71 (0.121), 16.71 (0.132), 18.66 (0.145), 20.71 (0.158), 24.31 (0.185), 27.76 (0.212), 34.01 (0.270)

C_0 = 0.0162 M [temp, °C (K_e)]: 27.19 (0.199), 29.26 (0.217), 32.36 (0.244), 35.99 (0.280), 41.36 (0.340), 46.51 (0.400)

Nitrobenzene[a,c]

C_0 = 0.0238 M [temp, °C (K_e)]: 17.69 (0.068), 25.09 (0.090), 35.47 (0.131), 46.46 (0.189), 56.36 (0.270), 65.80 (0.368)

C_0 = 0.0238 M [temp, °C (K_e)]: 17.69 (0.069), 25.09 (0.090), 35.47 (0.133), 46.46 (0.193), 56.36 (0.270), 65.80 (0.368)

Nitrobenzene-d_5[d]

C_0 = 0.09 M [temp, °C (K_e)]: 29.55 (0.10), 69.55 (~0.5)

[a] Extinction coefficient for pure dinitroso calculated as 108 M^{-1} cm^{-1} from the K_e measured by the NMR method. [b] UV_{max} 783 nm (dinitroso). [c] UV_{max} 790 nm (dinitroso). [d] K_e determined by NMR.

Variable-Temperature Visible and NMR Spectra of Azo Dioxide 4. Determination of K_e for Azo Dioxide–Nitroso Equilibrium. Reagent grade dioxane was purified by passage through a column of activated neutral alumina. Reagent grade nitrobenzene was purified by being washed with 2 N sodium hydroxide, water, 5% HCl, and then water. It was dried ($MgSO_4$) and distilled from P_2O_5, the middle fraction boiling at 117 °C (54 mmHg) being collected. Nitrobenzene-d_5 (Aldrich, 99 atom % D) was used as obtained. All solutions were degassed and sealed from the atmosphere prior to use. The equilibrium constant at each temperature was determined by integration of the methylene protons for the two species (3.3 ppm for azo dioxide **4** and 4.5 ppm for the dinitroso form).

Variable-temperature visible spectra were taken with a water-jacketed Guilford Model 222 spectrophotometer. Corrections for solvent expansion upon heating were made for absorbances in both solutions by using either the coefficient of cubical expansion (dioxane)[16a] or the relation for changes of density with temperature (nitrobenzene).[16b] The value for the extinction coefficient for the 783-nm band of the dinitroso compound **4** (108 M^{-1} cm^{-1}) was calculated from the equilibrium constants determined by the NMR method. Assigned errors in the thermodynamic parameters were determined by calculation of the quantities using the maximum probable errors in the derived extinction coefficient. The results are given in Tables II and IV.

***o*-Nitrobenzyl Iodide.** *o*-Nitrotoluene was converted to the benzyl bromide[17] and the bromide (not isolated) to the iodide,[18] mp 74–75 °C (lit.[18] mp 73–75 °C).

Bis(*o*-nitrobenzyl) Ether (6). To a mixture of 11.19 g (0.073 mol) of *o*-nitrobenzyl alcohol,[19] 23.06 g (0.087 mol) of *o*-nitrobenzyl iodide, and 20.00 g of silver oxide, under nitrogen, was added 100 mL of dry DMF. The slurry was stirred overnight under N_2. Me_2SO (100 mL) was added, and the solution was heated on a steam bath, filtered through Celite, and cooled. Filtration and recrystallization from ethyl acetate afforded 11.39 g of the ether as white crystals: mp 160.5–161.0 °C; NMR ($CDCl_3$) δ 8.20–7.26 (m, 8), 5.06 (s, 4); IR (KBr) 1515, 1342, 1109 cm^{-1}; mass spectrum (70 eV), *m/e* (relative intensity) 163 (6), 152 (6), 136 (39), 120 (45), 92 (25), 78 (100), 65 (32).

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Anal. Calcd for $C_{14}H_{12}N_2O_3$: C, 58.33; H, 4.20; N, 9.72. Found: C, 58.35; H, 4.26; N, 9.73.

Bis(*o*-aminobenzyl) Ether (7). To a stirred solution of 16.30 g (56.6 mmol) of bis(*o*-nitrobenzyl) ether (**6**) and 382 mg of 10% Pd/C in 300 mL of 95% ethanol was added 16.48 g (0.28 mol) of 85% hydrazine hydrate. The solution was stirred 15 min at room temperature and then refluxed for 1 h. The cooled solution was filtered through Celite and concentrated in vacuo. The resulting yellow oil was taken up in ether and extracted with salt water. The ether extract was dried, concentrated in vacuo, dissolved in hot ligroin/benzene (10/1) and cooled. The collected product was recrystallized to yield 12.00 g (93%) of the diamine **7**: mp 67–68 °C; NMR ($CDCl_3$) δ 7.36–6.51 (m, 8), 4.43 (s, 4), 4.06 (br s, 4); IR (KBr) 3460, 3380, 1610, 1493, 1458, 1036 cm^{-1}; mass spectrum (70 eV), *m/e* (relative intensity) 228 (6.7), 123 (16.8), 106 (100.0), 77 (16.7).

Azo Dioxide 8. To a suspension of bis(*o*-aminobenzyl) ether (**7**; 1.027 g, 4.5 mmol) and 193 mg of sodium tungstate dihydrate in 14 mL of 70% ethanol–water was added 3.00 g of 30% hydrogen peroxide dropwise. The mixture was stirred for 24 h at room temperature, poured into 50 mL of 5% HCl, and extracted with three portions of chloroform. The chloroform extracts were dried ($MgSO_4$) and concentrated in vacuo. The resulting residue was briefly heated in 20 mL of acetone and allowed to cool, yielding 237 mg (20.5%) of the azo dioxide **8**: mp 123 °C dec; NMR (Me_2SO d_6) δ 7.72–7.25 (m, 8), 5.93 (s, methylene of dinitroso, small peak), 4.73 (br s, 4); IR (KBr) 1422, 1385, 1218, 1119, 942, 765 cm^{-1}; mass spectrum (70 eV), *m/e* (relative intensity) 256 (0.4), 181 (6.7), 165 (4.2), 120 (76.5), 92 (99.7), 64 (100.0), 39 (59.8); UV max (95% C_2H_5OH) 281.4 nm (log ϵ 3.96).

Anal. Calcd for $C_{14}H_{12}N_2O_3$: C, 65.61; H, 4.72; N, 10.93. Found: C, 65.20; H, 4.70; N, 10.85.

Bis(*o*-nitrobenzyl)amine (9). A solution of 8.69 g (657.2 mmol) of *o*-nitrobenzylamine[20] and 8.69 g (75.5 mmol) of *o*-nitrobenzaldehyde[21] in 100 mL of benzene was refluxed in a Dean–Stark apparatus for 2 h. When the mixture cooled, the anil precipitated; recrystallization from ethanol gave 14.53 g (89%) of product: mp 154–154.5 °C; IR (KBr) 1640, 1610, 1572, 1515, 1382, 1345, 1325, 849, 793, 732 cm^{-1}; NMR ($CDCl_3$) δ 8.80 (br s, 1), 8.07–7.23 (m, 8), 5.20 (br s, 2). Dry HCl gas was bubbled through a solution of 14.53 g of the anil in 300 mL of dry THF. The resultant warm suspension was cooled to room temperature, 2.39 g of sodium cyanoborohydride (90–95%) in 90 mL of dry methanol was added, and the mixture was stirred for 30 min.[22] The solvent was removed in vacuo, and the residue was taken up in methylene chloride and extracted with 150 mL of 0.1 N NaOH. The organic fraction was dried (K_2CO_3), concentrated, and crystallized from ethanol to give 13.54 g (92.5%) of diamine **9**: mp 98–99 °C (lit.[23] mp 99–100 °C); IR (KBr) 3255, 1612, 1575, 1515, 1340, 867, 792 cm^{-1}; NMR ($CDCl_3$) δ 7.97–7.25 (m, 8), 4.08 (s, 4), 2.10 (br s, 1).

***N*-(Carbomethoxy)bis(*o*-nitrobenzyl)amine (10a).** To an ice-cooled solution of 5.063 g (17.6 mmol) of bis(*o*-nitrobenzyl)-amine in 150 mL of methylene chloride and 185 mL of 0.1 N NaOH was added 3.53 g of methyl chloroformate. The two-phase system was stirred at ice temperature for 1 h and then acidified with 10% HCl. The methylene chloride layer was separated, and the aqueous layer was washed with small portions of methylene chloride. The organic fractions were combined, dried ($MgSO_4$), concentrated in vacuo, and crystallized from ethanol to yield 5.49 g (90%) of **10a**: pale yellow crystals; mp 151–152 °C; IR (KBr) 1697, 1512, 1460, 1321, 1250, 790 cm^{-1}; NMR ($CDCl_3$) δ 8.18–7.25 (m, 8), 4.90 (s, 4), 3.75 (s, 3); mass spectrum (70 eV), *m/e* (relative intensity) 225 (3.6), 179 (11.7), 151 (12.9), 136 (96.2), 120 (13.5), 105 (26.0), 91 (29.2), 78 (100.0).

***N*-(Carbomethoxy)bis-(*o*-aminobenzyl)amine (11a).** To a solution of 5.098 g (14.77 mmol) of *N*-(carbomethoxy)bis(*o*-nitrobenzyl)amine (**10a**) and 164 mg of 10% Pd/C in 130 mL of methanol was added hydrazine hydrate (85%, 4.356 g, 73.96 mmol). The hot solution was filtered through Celite and concentrated in vacuo. The resulting mass was partitioned between methylene chloride and water/salt. The organic phase was dried (K_2CO_3) and concentrated in vacuo, and the residue was crystallized from CCl_4–pentane: yield >95%; white crystals; mp 122 °C; IR (KBr) 3450, 3370, 1673, 1632, 1485, 1460, 1250, 750 cm^{-1}; NMR ($CDCl_3$) δ 7.20–6.53 (m, 8), 4.32 (s, 4), 4.10 (br s, 4), 3.75 (s, 3); mass spectrum (70 eV), *m/e* (relative intensity) 285 (10.7), 179 (55.1), 147 (31.0), 121 (14.0), 106 (100.0), and 77 (24.1).

6*H*-5,7-Dihydrodibenzo[*c*,*h*]-1,2,6-triazonine *N*-Oxide. Oxidation of the diamine **11a** by the MCBPA procedure (see procedure for **3**) afforded the azoxy compound in 49% yield after recrystallization from CH_3OH: mp 143–144 °C; IR (KBr) 1700, 1460 (br s) 1400, 1273, 1249, 1192, 1128, 765, 750 cm^{-1}; NMR ($CDCl_3$) 7.87–7.08 (m, 8), 4.78 (d, 2), 4.53 (d, 2), 3.42 (d, 3); mass spectrum (70 eV), *m/e* (relative intensity) 297 (1.0), 280 (5.6), 248 (7.8), 220 (16.6), 190 (26.2), 181 (23.5), 175 (23.8), 145 (11.4), 118 (23.8), 89 (64.0), 77 (76), 65 (100.0), 51 (91.7), 39 (97.3).

Azo Dioxide (12a). Oxidation of the diamine **11a** by the tungstate–H_2O_2 procedure (see **4**, procedure c) afforded the azo dioxide **12a** in 21% yield after recrystallization from acetonitrile: white crystals; mp 144–145 °C dec; IR (KBr) 1685, 1463, 1445, 1409, 1393, 1308, 1237, 1215, 1105, 762 cm^{-1}; NMR ($CDCl_3$) δ 7.75–7.05 (m, 8), 5.40–4.90 (br m, 2), 4.25–3.90 (br m, 2), 3.82 (s, 3); mass spectrum (70 eV), *m/e* (relative intensity) 313 (0.2), 221 (3.9), 177 (6.7), 150 (11.9), 119 (27.0), 91 (46.8), 77 (100.0), 65 (75.4), 50 (87.8), 39 (93.2); UV max (95% C_2H_5OH) 268.0 nm (log ϵ 4.06), 217.0 (4.19).

Anal. Calcd for $C_{16}H_{15}N_3O_4$: C, 61.33; H, 4.82; N, 13.41. Found: C, 61.45; H, 4.90; N, 13.36.

***N*-(Carbo-*tert*-butoxy)bis(*o*-nitrobenzyl)amine (10b).** To a solution of bis(*o*-nitrobenzyl)amine (**9**; 25.00 g, 0.087 mol) in 200 mL of dry $CHCl_3$ was added di-*tert*-butyl dicarbonate (21.52 g, 0.096 mol) in 50 mL of $CHCl_3$. The solution was stirred overnight in the absence of moisture. The solution was concentrated in vacuo, and the resulting yellow oil was taken up in ligroin/benzene (10/1) to give, upon cooling, 32.80 g of pale yellow solid, mp 105–106.5 (97%). Recrystallization from ethanol afforded pale yellow crystals: mp 106–106.5; IR (KBr) 2990, 1700, 1610, 1528, 1410, 1402, 1370, 1360, 1348, 1338, 1275, 1268, 1167, 895, 795, 735 cm^{-1}; NMR ($CDCl_3$) δ 8.20–7.23 (m, 8), 4.86 (s, 4), 1.42 (s, 9).

Anal. Calcd for $C_{19}H_{21}N_3O_6$: C, 58.90; H, 5.46; N, 10.84. Found: C, 58.70; H, 5.36; N, 10.66.

***N*-(Carbo-*tert*-butoxy)bis(*o*-aminobenzyl)amine (11b).** This was prepared by reduction of the dinitro derivative **10b** by the hydrazine hydrate–Pd/C method described above for **11a**. Recrystallization from ligroin gave white crystals: 12.40 g (91%); mp 101 °C; IR (KBr) 3440, 3400, 3340, 3240, 2978, 1678, 1640, 1460, 1418, 1250, 1165, 883, 765 cm^{-1}; NMR ($CHCl_3$) δ 7.30–6.57 (m, 8), 4.25 (br s, 8), 1.45 (s, 9).

Anal. Calcd for $C_{19}H_{25}N_3O_2$: C, 69.69; H, 7.69; N, 12.83. Found: C, 69.71; H, 7.64; N, 12.54.

Azo Dioxide 12b. To a mixture of *N*-(carbo-*tert*-butoxy)-bis(*o*-aminobenzyl)amine (**11b**; 2.088 g, 6.38 mmol) and sodium tungstate dihydrate (292 mg, 0.88 mmol) in 40 mL of H_2O–ethanol (10 mL of H_2O and filled to the 40-mL mark with 95% ethanol) was added 30% hydrogen peroxide (4.366 g). The mixture was stirred for 2.5 days after which 25 mL of saturated, aqueous NaCl followed by an equal volume of methylene chloride was added. The aqueous layer was washed with small portions of CH_2Cl_2. The organic fraction was dried (K_2CO_3) and concentrated in vacuo. The orange-yellow residue was taken up in ether and cooled, affording 0.51 g (22.5%) of white crystals: mp 153–154 °C dec, after recrystallization from $CH_3OCH_2CH_2OCH_3$; IR (KBr) 2990, 1690, 1463, 1422, 1400, 1362, 1247, 1175, 960, 778 cm^{-1}; NMR ($CDCl_3$) δ 7.97–7.12 (m, 8), 5.53–4.96 (br m, 2), 4.38–3.77 (br m, 2), 1.58 (s, 9); UV max (95% C_2H_5OH) 280 nm (log ϵ 3.99), 206.5 (4.26); mass spectrum (70 eV), *m/e* (relative intensity) 254 (4.1), 238 (2.0), 207 (3.1), 135 (8.3), 120 (23.9), 92 (20.1), 77 (9.3), 65 (27.6), 57 (100.0), 41 (37.4).

Azo Dioxide (14). To a solution of azo dioxide **12b** (200 mg) in 5 mL of CH_2Cl_2 under nitrogen was added 5 mL of trifluoroacetic acid with stirring. After 12 min, the solution was concentrated in vacuo at room temperature. The residue was taken up in 10 mL of water and made alkaline by the addition of $NaHCO_3$; the water solution was extracted several times with

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CH_2Cl_2. The organic fraction was dried (K_2CO_3) and concentrated in vacuo. The resulting oily residue was crystallized from CH_2Cl_2/ether to yield 78 mg (55%) of azo dioxide **14**: mp 115–117 °C dec; IR (KBr) 3325, 1483, 1447, 1418, 1392, 1208, 952, 777, 768 cm^{-1}; NMR ($CDCl_3$) δ 7.33–7.05 (m, 8), 4.02 (br s, 4), 1.80 (br s, 1); mass spectrum (70 eV), *m/e* (relative intensity) 237 (23.9), 220 (67.6), 180 (45.1), 152 (14.85), 118 (100.0), 89 (57.0), 77 (36.0), 65 (56.5), 51 (40.3), 39 (61.8); UV max (95% C_2H_5OH) 278 nm (log ϵ 3.98), 208 (4.26).

Anal. Calcd for $C_{14}H_{13}N_3O_2$: C, 65.87; H, 5.13; N, 16.46. Found: C, 66.09; H, 5.02; N, 16.18.

Trifluoroacetate salt 13 was prepared in a manner similar to that for the "free" amine. The residue after removal of the trifluoroacetic acid was taken up in THF (dry) and cooled to give white crystals: 80% yield; mp 99–100 °C; IR (KBr) 3440 (br), 1600, 1455, 1423, 1397, 1205, 1180, 1135, 955, 772, 737 cm^{-1}; NMR (DCO_2D) 7.93–7.40 (m, 8), 5.08–4.35 (A_2B_2, 4, J = 14 Hz); mass spectrum (70 eV), *m/e* (relative intensity) 237 (11.2), 220 (32.2), 205 (10.2), 180 (22.0), 152 (7.5), 118 (39.9), 89 (31.3), 77 (20.8), 69 (52.6), 51 (61.7), 45 (100.0).

2-(*o*-Nitrosobenzyl)indazole (15). A solution of 39 mg of **14** in 3 mL of CH_2Cl_2 was refluxed under N_2 for 2 h. The solution was concentrated in vacuo, and the resulting oil was taken up in a small amount of CH_2Cl_2, placed on an alumina preparative thick-layer plate, and eluted with 75% ether/25% pentane (R_f 0.8) to give 31 mg of a green oil which was crystallized from CCl_4–pentane: pale yellow powder; mp 108.5–109 °C; IR ($CHCl_3$) 1632, 1505, 1437, 1312, 1170, 1159, 1140, 1087 cm^{-1}; IR (KBr) 1630, 1528, 1270, 1212, 1172, 1150, 1010, 805, 769, 760, 748 cm^{-1}; NMR (CD_3COCD_3) δ 8.46 (s, 1), 7.96–7.08 (m, 7), 7.01 (s, 2), 6.46–6.26 (d, 1, J = 8, 1 Hz); mass spectrum (70 eV), *m/e* (relative intensity) 237 (30.4), 220 (89.6), 205 (24.1), 180 (49.8), 152 (16.1), 118 (100.0), 103 (33.3), 89 (57.2), 57 (54.5), 43 (54.2); UV max (95% C_2H_5OH) 285 nm (log ϵ 4.10), 220 (4.15); UV min 240 (log ϵ 3.4); ^{13}C (CD_3COCD_3) δ 160.4,[24] 150.1,[24] 140.5,[24] 137.9, 131.8, 129.3, 126.4, 125.0, 122.2, 121.4, 118.3, 107.3, 53.0; high-resolution mass spectrum, *m/e* (relative intensity, composition, calcd *m/e*) 89.039 (27.4, C_7H_5, 89.039), 103.041 (32.5, C_7H_5N, 103.042), 118.052 (100, $C_7H_6N_2$, 118.053), 180.079 (24.4, $C_{13}H_{10}N$, 180.081), 220.084 (68.5, $C_{14}H_{10}N_3$, 220.087); calcd for $C_{14}H_{11}N_3O$ (M^+) *m/e* 237.090, found *m/e* 237.088 (relative intensity 69.1).

Registry No. **1**, 16968-19-7; **2**, 34124-14-6; **3**, 40754-26-5; **4**, 74808-60-9; **6**, 42467-41-4; **7**, 74808-61-0; **8**, 74808-62-1; **9**, 74808-63-2; **10a**, 74808-64-3; **10b**, 74808-65-4; **11a**, 74808-66-5; **11b**, 74808-67-6; **12a**, 74808-68-7; **12b**, 74808-69-8; **13**, 74808-71-2; **14**, 74808-70-1; **15**, 74808-72-3; *o*-nitrobenzyl alcohol, 612-25-9; *o*-nitrobenzyl iodide, 29872-21-7; *o*-nitrobenzylamine, 1904-78-5; *o*-nitrobenzaldehyde, 552-89-6; *o*-nitro-*N*-(*o*-nitrobenzylidene)benzylamine, 74808-73-4; methyl chloroformate, 79-22-1; 6*H*-5,7-dihydrodibenzo[*c*,*h*]-1,2,6-triazine *N*-oxide, 74808-74-5; di-*tert*-butyl dicarbonate, 24424-99-5; nitrosocyclohexane, 2696-95-9; 1-nitroso-2,4,6-tribromobenzene, 45860-18-2; 1-nitroso-2,4,6-trimethylbenzene, 1196-12-9; *p*-nitrosotoluene, 623-11-0; nitrosobenzene, 586-96-9.

(24) Quaternary carbon.

Ene-Type Reaction through the Intermediacy of the 1,4-Dipolar Ion in the Reaction of Tetracyanoethylene with Nucleophilic Double Bonds in Liquid Sulfur Dioxide

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The expected [2 + 2] cycloadduct from the reaction of tetracyanoethylene with 1-methoxycyclohexene in liquid sulfur dioxide underwent a previously unrecognized reaction to give 1-methoxy-6-(1,1,2,2-tetracyanoethyl)-cyclohexene. Further isomerization of this ene-type product with sulfur dioxide gave the isomeric 1-methoxy-2-(1,1,2,2-tetracyanoethyl)cyclohexene. The [2 + 2] cycloadduct is therefore a kinetic product which exists in equilibrium with the 1,4-dipolar ion precursor. Under thermodynamic conditions the dipolar ion provides a more stable ene-type product, the isomeric enol ether, and small amounts of 1,2,3,4,5,6,7,8,9,10-decahydro-8a-methoxy-9,9,10,10-tetracyanophenanthrene and 1,1-dimethoxy-2-(1,1,2,2-tetracyanoethyl)cyclohexane. The latter two products are the result of trapping of the dipolar ion with 1-methoxycyclohexene and methanol, respectively. Under similar conditions, cyclohexanone and tetracyanoethylene in liquid sulfur dioxide gave 2-(1,1,2,2-tetracyanoethyl)cyclohexanone.

Unlike typical internally stabilized heteroallyl 1,3-dipolar ions,[1] the dipolar ions in which charges are separated by an sp^3-hybridized carbon atom possess electrophilic and nucleophilic ends and react with appropriate dipolarophiles with a predictable orientation.[2] Recently, we reported that the 1,3-dipolar ions, resulting from the electrophilic attack of nitrosonium ion on nucleophilic double bonds of trisubstituted olefins as well as of certain enols, could be trapped by a carbonyl group of ketones and aldehydes to give novel heterocyclic structures.[3] A different type of 1,3-dipolar ion, generated by the reaction of sulfur dioxide with an enol ether, could be trapped by the enol ether itself.[2] Surprisingly, more detailed investigation of the behavior of nucleophilic double bonds in liquid sulfur dioxide revealed that the corresponding dipolar ions, although present in too low concentration to be detected spectroscopically, had a rich chemistry of their own.[2-6] It became evident that the initially formed π complexes of sulfur dioxide with a typical olefin would isomerize to the dipolar σ complex (albeit short-lived) only if the positive charge in the σ complex could develop on a tertiary carbon atom.[4] The dipolar ions were in equilibrium with the isomeric allylic sulfinic acids, formed reversibly by the abstraction of the allylic hydrogens by the negative charge of the dipolar ion. This facile intramolecular hydrogen abstraction, resembling an ene reaction, provided a basis

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