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(30) The lower limit of visual detectability of a cyclic dinitroso alkane can be set at 10^{-3} *M*. For example, under spectrophotometric conditions an absorbance of 0.05, a path length of 5 cm, and an ϵ of 10.5 correspond to this concentration.[4f] Dinitroso *trans*-**13** absorbs in the visible at λ_{max} 645 nm (96% EtOH) with ϵ 53. A 1.2×10^{-3} *M* solution is an unambiguous pale blue, unnoticeable at 1.2×10^{-4} *M*. (cf. Experimental Section for comparisons with dinitroso *cis*-**13**.)

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(32) (a) Models indicate that a twisted acyl group R_2 (**32**) is sterically less demanding than the corresponding methyl function. Although conformational free-energy differences for the acyl group are to our knowledge not available, tabulated values for CH_3, COCl, and CO_2CH_3 support the ordering i > ii; cf. E. L. Eliel, N. L. Allinger, S. J. Angyal, and G. A. Morrison, "Conformational Analysis", Interscience, New York, N.Y., 1965, pp 436–442. (b) For an analysis of the conformations of acyclic azoxy alkanes as a function of substituent bulk, see ref 9b.

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(46) Compound **7** in solution has been described only as the ring-closed azo dioxide in several studies.[10]

(47) The possibility that low concentrations of dinitroso alkane are rapidly diverted to the corresponding dioximes[1a] or are destroyed by reaction with solvent at high temperatures cannot be ruled out at present.

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Convenient Synthesis of Bicyclic and Polycyclic Cis Azo *N,N'*-Dioxides

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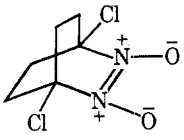
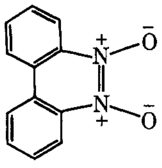
Two methods for the synthesis of bicyclic and polycyclic cis azo N,N'-dioxides are described. Oxidation of azo alkanes with trifluoroperacetic acid afford their corresponding azo N,N'-dioxides, while chlorination of 1,4-dioximes give the α,α'-dichloro azo N,N'-dioxides. Structures of all new compounds are supported by spectral data and elemental analysis.

One of the distinct properties of *C*-nitroso compounds is their tendency to dimerize to form azo N,N'-dioxides. The acyclic dimers can exhibit cis–trans configurational isomerism with the trans isomer generally being more stable than the cis isomer. Although many examples of trans azo dioxides are known, there are very few examples reported of cis azo dioxides. Certain cyclic azo N,N'-dioxides can only exist in their cis form, e.g., the azo dioxides **1–3**,[1,2] and are obtained by the ring closure of their corresponding bis nitroso precursors. In connection with other work we needed bicyclic and polycyclic cis azo N,N'-dioxides and would like to report convenient synthetic routes to these compounds.[3]



1



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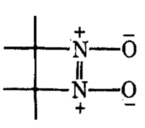


3

The key intermediate to the synthesis of the azo dioxide **8** is 2,3-diazabicyclo[2.2.1]hept-2-ene (**6**), which was prepared in high yield according to Scheme I. The Diels–Alder adduct of cyclopentadiene and ethyl azodicarboxylate was hydrogenated and the product **4** was hydrolyzed with strong base in ethylene glycol.[4] Oxidation of the crude reaction mixture with 30% hydrogen peroxide gave the bicyclic azo compound **6** in overall 97% yield from **4**. This observation is in contrast to Snyder's report of the formation of the cis azoxy compound **7** in 73% yield[5] from **5** under similar conditions. The monoxide could, however, be easily obtained in 80% yield by *m*-chloroperbenzoic acid oxidation of the azo compound **6**.[6] The use of hydrogen peroxide for oxidation of hydrazines, such as **5**, has a distinct advantage

Scheme I

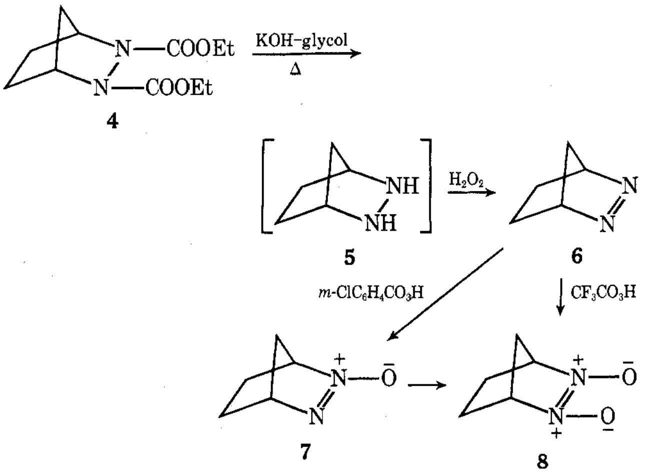


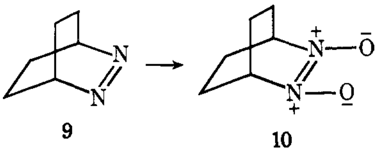
Table I
Physical Data of Bicyclic and Polycyclic Azo *N,N'*-Dioxides

Azo dioxide[a]	Yield,[b] %	Mp, °C (crystn solvent)	Ir,[c] cm^{-1}	Uv,[d] nm (ϵ)	NMR,[e] δ
8	75, 90[f]	153–154 dec ($CHCl_3$–C_6H_{12})	1485, 1420	265 (7850)	1.97 (d, J = 11 Hz, 1 H) 2.25 (br s, 4 H) 2.53 (d, J = 11 Hz, 1 H) 4.8 (br s, 2 H)
10	71	236–237 dec ($CHCl_3$)	1490, 1420	264 (8800)	1.8–2.4 (m, 8 H) 4.8 (br s, 2 H)
12	72	184–185 ($CHCl_3$–C_6H_6)	1495, 1430	271 (7000)	2.0 (s, 2 H), 2.36 (s, 3 H), 2.98 (br s, 1 H), 4.7 and 4.75 (singlets, 2 H)
16	91[g]	236–238 dec (C_2H_5OH)	1440, 1395	274 (7100)	1.72 and 2.1 (AB quartet, J = 12 Hz, $\Delta\nu_{AB}$ = 23 Hz, 2 H), 3.0–3.4 (m, 8 H)
18	7[g]	234–234.5 dec (CH_3CN)	1445, 1400[h]	273[i]	[i]
1[j]		165 dec (C_2H_5OH)	1445, 1395[h]	270 (7800)	[i]

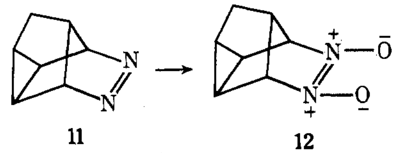
[a] Correct elemental analyses were obtained for all new compounds. [b] Unless stated otherwise the yield are from the corresponding cyclic azo compounds and are unoptimized. [c] Unless indicated otherwise the ir spectra were recorded in $CHCl_3$. [d] In C_2H_5OH. [e] In $CDCl_3$ with Me_4Si as an internal standard. [f] From the azoxy compound 7. [g] By chlorination of the corresponding 1,4-dioxime. [h] In KBr. [i] Not sufficiently soluble. [j] Earlier work, ref 11.

over the cupric chloride and the mercuric oxide methods in that it is less cumbersome and affords the azo compounds in high yield (see Experimental Section).[4,7,8]

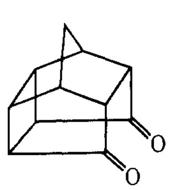
Treatment of the azo compound **6** or its monoxide **7** with *m*-chloroperbenzoic and peracetic acid under a variety of conditions failed to give the dioxide **8**.[9] This is presumably due to the fact that the positively charged nitrogen in monoxide **7** considerably decreases the reactivity at the neighboring nitrogen to further oxidation. The oxidations of **6** and **7** to the dioxide **8** were accomplished,[10] however, in 75 and 95% yield, respectively, by use of trifluoroperacetic acid in methylene chloride. That the method of preparation of azo dioxides is general was demonstrated by high-yield conversion of the bicyclic and the quadricyclic azo compounds **9** and **11**[7,8] to the corresponding dioxides **10** and **12**.



9 **10**



11 **12**



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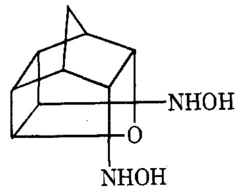

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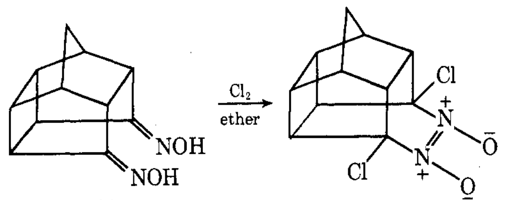
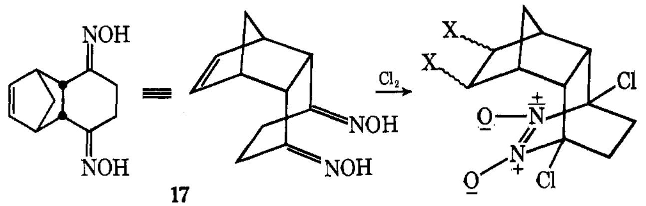
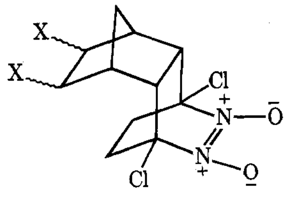


14 **16**

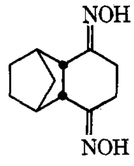


17

18, X = Cl
21, X = H



19, X = Cl
22, X = H

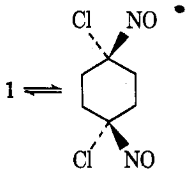


20

The bridgehead dichloro azo dioxide **1** has been prepared by chlorination of 1,4-cyclohexanedione dioxime.[11] We have now extended the utility of this reaction further in synthesizing polycyclic α,α'-dichloro azo *N,N'*-dioxides **16**, **18** and **21**. Treatment of cage diketone **13** with hydroxylamine gave the bis oxime **14** in 92% yield in contrast to Cookson's report of exclusive formation of oxa bird cage compound **15**.[12,13] A suspension of the dioxime **14** in a solution of excess chlorine in ether at low temperature afforded cleanly the cage azo dioxide **16** in over 90% yield. While the 60-MHz NMR spectrum was able to resolve only the apical proton as an AB quartet, the 300-MHz spectrum[14] afforded complete resolution of all of the different protons, thus supporting the proposed structure **16** (see Experimental Section). Similarly, chlorination of suspensions of tricyclic bis oximes **17**[15] and **20**[16] gave high-melting azo dioxides **18** and **21** in poor yields, along with blue liquids which decomposed to a complex mixure during isolation. The stereochemistry of the azo dioxides **18** and **22** has not been rigorously established but is preferred over the alternative structures **19** and **22** on the basis of steric approach of chlorine from the least hindered side.[17,18]

The structures proposed for all of the azo *N,N'*-dioxides prepared are in accord with their analytical and spectral properties (Table I). They are characterized by a pair of strong infrared bands between 1350 and 1500 cm^{-1} and strong π–π* ultraviolet absorption between 260 and 275 nm.

The bicyclic azo dioxide 1 on heating in a variety of solvents develops a deep blue color (characteristic of nitroso compounds). Color formation is reversible and is dependent on temperature and solvent, indicating its equilibrium with bis nitroso isomer **23.** In contrast to this observation other bicyclic and polycyclic azo dioxides showed no color when they were heated in a variety of solvents.[19] Slow heating of the azo dioxides, in solid state, resulted in charring at their melting point.[20]



23

Although direct irradiation of the azo dioxides **8, 10,** and **12** gave complex mixtures, these compounds have been found to be remarkably stable to sensitized photolysis. Like 3,3,4,4-tetramethyldiazatine 1,2-dioxide (**3**), the cis azo *N,N'*-dioxides are expected to have very low energy triplet states. Their efficiency as low energy triplet quenchers will be described elsewhere.[2,21]

Experimental Section[22]

2,3-Diazabicyclo[2.2.1]hept-2-ene (6). This azo compound was obtained as a white, crystalline solid by a modified procedure of Gassman and Mansfield.[4]

A slow stream of nitrogen was bubbled for 30 min through 50 ml of warm ethylene glycol in a 500-ml three-necked flask fitted with a constant-pressure dropping funnel and a reflux condenser equipped with a Drierite tube to protect from atmospheric moisture. The solution was stirred with a magnetic stirrer and potassium hydroxide (17 g) was added. When the potassium hydroxide had dissolved the solution was heated to 125°, and the diethyl 2,3-diazabicyclo[2.2.1]heptane-2,3-dicarboxylate (**4**,[4] 13.5 g) was dropped in rapidly, maintaining the reaction temperature between 125 and 130°. The reaction mixture was stirred at ca. 125° for 1.5 hr and then diluted with 100 ml of water. The resulting solution was cooled and to the stirring solution was added dropwise 30% hydrogen peroxide solution (100 ml, excess) at room temperature. The reaction mixture was stirred for 2 hr,[23] diluted with water, and extracted with methylene chloride. The extract was washed with saturated aqueous sodium sulfite solution and water and dried. Removal of the solvent afforded the azo compound **6** as a dirty white solid (5.2 g, 97%). Recrystallization from pentane afforded white crystals: mp 98–99° (lit.[4] mp 99.5–100°); δ ($CDCl_3$) 0.7–1.8 (m, 6 H), 4.49 (broad s, 2 H).

2,3-Diazabicyclo[2.2.2]oct-2-ene (9). The 4-phenyl-2,4,6-triazatricyclo[5.2.2.0^{2,6}]undeca-3,5-dione[24] (2.2 g) in a 1:1 mixture of ethylene glycol–water (100 ml) was refluxed with potassium hydroxide pellets (3.3 g) under a slow stream of nitrogen. After 5 hr the reaction mixture was cooled and 30% hydrogen peroxide (20 ml) was adde carefully. The solution was stirred for 30 min and then refluxed for 1 hr. The aniline formed during the reaction was removed by steam distillation. The resulting product was diluted with water and extracted with chloroform. The organic layer was dried and removal of the solvent, under reduced pressure, at room temperature gave the bicyclic diazo compound **9** as a light brown solid (700 mg, 76%). The product was purified by preparative tlc (silica, chloroform–methanol, 9:1) and crystallization from *n*-hexane gave colorless needles: mp 145–146° (lit.[7] mp 146–147°); δ ($CDCl_3$) 1.2–2.1 (m, 8 H), 5.1 (broad s, 2 H).

6,7-Diazaquadricyclo[3.2.1.1^{3,8}.0^{2,4}]non-6-ene (11). The homoconjugate Diels–Alder adduct of ethyl azodicarboxylate to norbornadiene was hydrolyzed with potassium hydroxide according to Moriarty's method.[8a] The product was oxidized with 30% hydrogen peroxide as above and there was obtained the tetracyclic azo compound **11** as a thick oil which solidified on standing (1.06 g, 87%). This was homogenous on TLC (silica) in a variety of solvent systems and its spectral data were identical with that reported in the literature.[8]

Oxidation of the Cyclic Azo Compounds to Azo *N,N'*-Dioxides with Trifluoroperacetic Acid. A general method for the formation of cyclic azo dioxides from the azo compounds is given below.

Trifluoroperacetic acid was prepared from trifluoroacetic anhydride (46.2 g, 0.22 mol) in methylene chloride (50 ml) and 98% hydrogen peroxide (5.4 ml) according to Hart's[25] method. The crude 2,3-diazabicyclic compound **6** (9.6 g, 0.1 mol) in methylene chloride (21 ml) was added dropwise to an ice-cooled, stirring methylene chloride solution of trifluoroperacetic acid. The reaction mixture was stirred in the ice bath for 3 hr and at room temperature for an additional day. The oxidized reaction mixture was taken in a 1-l. beaker, cooled to 0°, and stirred with aqueous sodium bisulfite solution until it gave a negative test to potassium iodide–starch paper. The solution was neutralized carefully with saturated aqueous sodium bicarbonate and filtered. Continuous extraction of the filtrate with chloroform for 2 days furnished TLC-pure azo dioxide **8** (10.2 g, 80%) as a dirty white, crystalline solid. Decolorization with Norit A and recrystallization from chloroform–hexane afforded **8** as shining white microcrystals (9.5 g, 75%), mp 153–154° dec.

Anal. Calcd for $C_5H_8N_2O_2$: C, 46.87; H, 6.29; N, 21.87; mol wt, 128. Found: C, 46.81; H, 6.39; N, 21.96; mol wt, 125.3.[26]

All azo dioxides are white, crystalline solids.

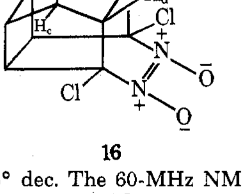
2,3-Diazabicyclo[2.2.1]hept-2-ene 2-Oxide (7). A solution of the diazo compound **6** (200 mg) in chloroform (20 ml) was stirred at room temperature with *m*-chloroperbenzoic acid (1.4 g) for 2 hr, and was then refluxed for 1 day. The reaction mixture was cooled and the excess peracid destroyed with 10% aqueous sodium sulfite. The organic layer was washed with 10% aqueous sodium bicarbonate and water and dried. Removal of the solvent under reduced pressure afforded a semisolid residue which by TLC and GLC was found to be only one compound. The product was purified by preparative tlc (silica, chloroform–methanol, 9:1) and there was obtained **7** (180 mg, 80%) as easily sublimable white crystals: mp 93–95° (lit.[6] mp 93–95°); ν_{max} (CCl_4) 1515 cm^{-1}; λ_{max} (MeOH) 228 nm; δ ($CDCl_3$) 4.7 (broad s, 2 H), 1.5–2.4 (m, 6 H).

The azoxy compound **7** was oxidized in 90% yield to the azo dioxide **8** with trifluoroperacetic acid in methylene chloride.

Treatment of Cage Diketone 13 with Hydroxylamine Hydrochloride. Formation of Dioxime 14. A solution of the diketone **13** (20 g) and hydroxylamine hydrochloride (60 g) in ethanol (400 ml) and pyridine (200 ml) was heated under reflux for 4 hr, during which time most of the product crystallized out. The reaction mixture was cooled, stripped of the solvents under vacuum, and diluted with excess of water. The dioxime **14** was filtered, washed with water, and dried, mp 302–304° dec (lit.[13a] mp 302° dec). The yield of the dioxime was 24.3 g (92%). Sublimation at 120° (0.03 mm) afforded the analytical sample, mp 303–305° dec.

Anal. Calcd for $C_{11}H_{12}N_2O_2$: C, 64.69; H, 5.92; N, 13.72. Found: C, 64.59; H, 5.82; N, 14.03.

Reaction of Cage Dioxime 14 with Chlorine. Formation of Dichloro Azo Dioxide 16. The dioxime **14** (20.4 g) was suspended in dry ether (1 l.) in a 2-l., three-necked flask equipped with a gas bubbler, a thermometer, and a drying tube. The reaction mixture was cooled in a Dry Ice–acetone bath and chlorine gas (ca. 20 g) was gently bubbled through the stirring suspension in the dark. The reaction mixture was warmed slowly to 10–15° and further stirred for 1.5 hr at this temperature. The white crystalline azo dioxide **16** was filtered and washed with ether, cold 5% aqueous sodium hydroxide, and water. The dried product weighed 22 g (91%, TLC pure). Recrystallization from ethanol gave **16** as white needles (19 g), mp 236–238° dec. The 60-MHz NMR ($CDCl_3$) spectrum showed apical protons as an AB quartet at δ 1.72 (H_a) and 2.10 (H_b) (J = 12 Hz, $\Delta\nu_{AB}$ = 23 Hz, 2 H) and a multiplet between δ 3.0 and 3.4 (8 H).



16

The 300-MHz NMR spectrum ($CDCl_3$) exhibited signals at δ 1.70 (d, J = 12 Hz, 1 H, H_a), 2.08 (d, J = 12 Hz, 1 H, H_b), 3.07 (s, 2 H, bridgehead protons H_c), 3.1–3.2 (m, 4 H, cyclobutyl protons), and 3.24–3.30 (m, 2 H, H_d).

Anal. Calcd for $C_{11}H_{10}Cl_2N_2O_2$: C, 48.40; H, 3.66; Cl, 26.00; N, 10.23. Found: C, 48.32; H, 3.60; Cl, 25.71; N, 10.33.

Chlorination of 1,4-Dioxime 17. Formation of Tetrachloro Azo Dioxide 18. The tricyclic dioxime **17** (5 g) was suspended in dry ether (150 ml) in a three-necked flask equipped with a gas bubbler, a thermometer, and a drying tube. The reaction mixture was cooled to −40° and chlorine gas was bubbled through it. The contents of the flask were stirred for 90 min and then allowed to warm to room temperature. The solid was filtered. The greenish-blue filtrate was neutralized with solid sodium bicarbonate and washed with water. The organic layer was dried and evaporation of the solvent gave a blue semisolid residue which decomposed on standing for a few hours.

The solid obtained above, containing unreacted dioxime **17** and the azo dioxide **18**, was stirred with 5% sodium hydroxide in the cold. After 1.5 hr the solution was filtered and the filtrate was acidified (pH 6) with glacial acetic acid to furnish 1.8 g of recovered dioxime, mp 191–192° dec. The solid residue was washed with water and dried to give crude azo dioxide **17** (ca. 300 mg, 7%). The product was decolorized with Norit A and recrystallized from acetonitrile to afford colorless microcrystals of **17**, mp 234–234.5° dec.

Anal. Calcd for $C_{11}H_{12}Cl_4N_2O_2$: C, 38.15; H, 3.47; Cl, 41.10; N, 8.10. Found: C, 38.34; H, 3.57; Cl, 40.93; N, 8.00.

Chlorination of Dioxime 20. Formation of Azo Dioxide 21. A suspension of dioxime **20** (500 mg) in ether at −40° was treated with chlorine gas. Work-up as above afforded the azo dioxide **21** as a white solid: mp 226–230° dec (10 mg); λ_{max} (EtOH) 273 nm; mass spectrum (70 eV) m/e 278, 276 (M^+), 248, (M − NO), 218, 216 (M − 2NO), 183, 181 (M − 2NO − Cl).

Acknowledgments. The author is thankful to Dr. E. F. Ullman for helpful discussions.

Registry No.—**4**, 18860-71-4; **6**, 2721-32-6; **7**, 22509-00-8; **8**, 36335-10-1; **9**, 3310-62-1; **10**, 36479-80-8; **11**, 16104-45-3; **12**, 54142-91-5; **13**, 2958-72-7; **14**, 54142-92-6; **16**, 54142-93-7; **17**, 54142-94-8; **18**, 54142-95-9; **20**, 54142-96-0; **21**, 54142-97-1; 4-phenyl-2,4,6-triazatricyclo[5.2.2.0^{26}]undeca-3,5-dione, 30169-55-2; trifluoroperacetic acid, 359-48-8; hydroylamine hydrochloride, 5470-11-1; chlorine, 7782-50-5.

References and Notes

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(2) (a) E. F. Ullman and P. Singh, *J. Am. Chem. Soc.*, **94**, 5077 (1972). (b) P. Singh, D. G. B. Boocock, and E. F. Ullman, *Tetrahedron Lett.*, 3935 (1971).

(3) When this work was in progress, Professor Snyder reported the mass spectral data of bicyclic azo dioxides **8** and **10**. A method for the synthesis of these azo dioxides, however, was not described. J. P. Snyder, M. L. Heyman, and V. T. Bandurco, *Tetrahedron Lett.*, 4693 (1971).

(4) P. G. Gassman and K. T. Mansfield, "Organic Syntheses", Collect. Vol. V, H. E. Baumgarten, Ed., Wiley, New York, N.Y., 1973, p 96.

(5) V. T. Bandurco and J. P. Snyder, *Tetrahedron Lett.*, 4643 (1969). Professor Snyder has now kindly informed us that the azoxy compound **7** is formed only when the hydrazine **5** is oxidized with hydrogen peroxide under vigorous conditions: J. P. Snyder, V. T. Bandurco, F. Darack, and H. Olsen, *J. Am. Chem. Soc.*, **96**, 5158 (1974).

(6) F. D. Greene and S. S. Hecht, *Tetrahedron Lett.*, 575 (1969).

(7) (a) S. G. Cohen and R. Zand, *J. Am. Chem. Soc.*, **84**, 586 (1962). (b) Convenient azo alkane synthesis by oxidation of semicarbazides with copper halide has recently been reported: M. Heyman, V. T. Bandurco, and J. P. Snyder, *Chem. Commun.*, 297 (1971).

(8) (a) R. M. Moriarty, *J. Org. Chem.*, **28**, 2385 (1963); (b) R. C. Cookson, S. S. H. Gilani, and I. D. R. Stevens, *J. Chem. Soc. C*, 1905 (1967).

(9) Traces of the azo dioxide **8** were formed (TLC analysis) when the azoxy compound **7** was refluxed with a large excess of peracetic acid in methylene chloride.

(10) The R_f value of **8** on TLC was identical with that of its authentic sample in a variety of solvents. The author is highly thankful to Professor Snyder for a generous gift of the azo dioxide **8** for comparison.

(11) (a) O. Piloty and H. Steinbock, *Chem. Ber.*, **35**, 3101 (1902); (b) H. Rheinboldt and M. Dewald, *Justus Liebigs Ann. Chem.*, **455**, 300 (1927).

(12) R. C. Cookson, E. Crundwell, R. R. Hill, and J. Hudec, *J. Chem. Soc.*, 3062 (1964).

(13) Other workers have independently arrived at the same conclusion: (a) T. Sasaki, S. Eguchi, and T. Kiriyama, *Tetrahedron Lett.*, 2651 (1971); (b) J. P. Snyder, M. L. Heyman, and E. N. Suciu, *J. Org. Chem.*, **40**, 1395 (1975).

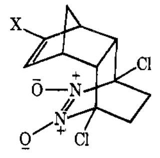
(14) I am thankful to Professor M. Anteunis, Organic Chemistry Department, State University of Gent, Gent, Belgium, for recording the 300-MHz nmr spectrum.

(15) (a) W. Albrecht, *Justus Liebigs Ann. Chem.*, **348**, 31 (1906); (b) A. Wassermann, *J. Chem. Soc.*, 1511 (1935).

(16) O. Diels and K. Alder, *Justus Liebigs Ann. Chem.*, **460**, 108 (1928).

(17) For a similar argument on stereochemistry of the azo dioxide **21** see ref 13b.

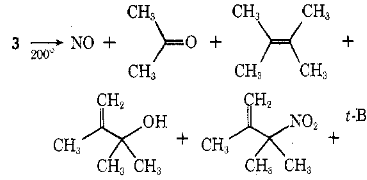
(18) We are yet unable to dehalogenate or dehydrohalogenate the compound **18** to unsaturated azo dioxide **24**, which should be capable of exhibiting an interesting through-space interaction of the two chromophores.



24a, X = H
b, X = Cl

(19) Ethanol solution of **1** (2 × 10^{-3} M) at 25° contains, at equilibrium, ca. 1% of the dinitroso compound **23**. Solutions of other azo dioxides are estimated to contain <0.05% of their open dinitroso isomers under similar conditions: P. Singh and E. F. Ullman, to be submitted for publication.

(20) The greenish-blue color obtained by heating 3,3,4,4-tetramethyldiazetine 1,2-dioxide (**3**) at its melting point is considered due to dissolved oxides of nitrogen. Thermolysis of **3** gives a complex mixture of which six compounds have been tentatively identified: P. Singh and E. F. Ullman, unpublished observations.



(21) P. Singh and E. F. Ullman, presented at the 167th National Meeting of the American Chemical Society, Los Angeles, Calif., April 1974, Abstract ORGN 78.

(22) Melting points were determined in capillary tubes with a Thomas-Hoover Uni-Melt apparatus and are uncorrected. Solutions in organic solvents were dried over anhydrous magnesium sulfate. Uv spectra were recorded on a Cary 15 spectrophotometer and ir spectra were run on a Perkin-Elmer spectrophotomer. The NMR spectra were recorded on a Varian T-60 machine and the values are given in δ parts per million downfield from tetramethylsilane as internal standard.

(23) Further heating of the reaction mixture for 2 hr did not give any azoxy compound **7** (TLC and GLPC analysis); cf. ref 5.

(24) A. B. Evnin, D. R. Arnold, L. A. Karnischky, and E. Strom, *J. Am. Chem. Soc.*, **92**, 6219 (1970).

(25) H. Hart, R. M. Lange, and P. M. Collins, "Organic Syntheses", Collect. Vol. V, H. E. Baumgarten, Ed., Wiley, New York, N.Y., 1973, p 598.

(26) Determined in benzene with a Macrolab vapor pressure osmometer.