Oxadiaziridines, the Cyclic Form of an Azoxy Group. Synthesis, Valence Isomerism, and Reactivity[1a,b]

FREDERICK D. GREENE AND STEPHEN S. HECHT[1c]

Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

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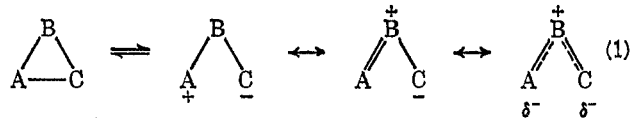
The photolysis of alkyl azoxy compounds RNN(O)R (**11a**, R = *t*-butyl; **11b**, R = *n*-butyl) in pentane affords a new three-membered-ring heterocycle, an oxadiaziridine (**12a**, R = *t*-butyl; **12b**, R = *n*-butyl). The oxadiaziridines revert to the azoxy compounds, $t_{1/2}$ at 28° ≃ 5 hr. The isomerization is catalyzed by acids (fivefold acceleration for **12a** by 1.7 *M* $Cl_2CHCOOH$ in CCl_4) and shows a slight solvent effect (k_{rel} for **12a** in CCl_4, CH_3OH, CH_3NO_2: 1, 2, 2.5). Compound **12a** is reduced to the corresponding azo compound by acidified NaI in acetone; it is generally unreactive toward $LiAlH_4$ or CH_3Li. Compounds **11b** and **12b** are reduced to the corresponding azo compound by $LiAlH_4$. Compound **12b** is reduced by CH_3Li to azobutane and butyraldehyde *n*-butylhydrazone; **11b** reacts with CH_3Li to afford 1-methylazobutane.

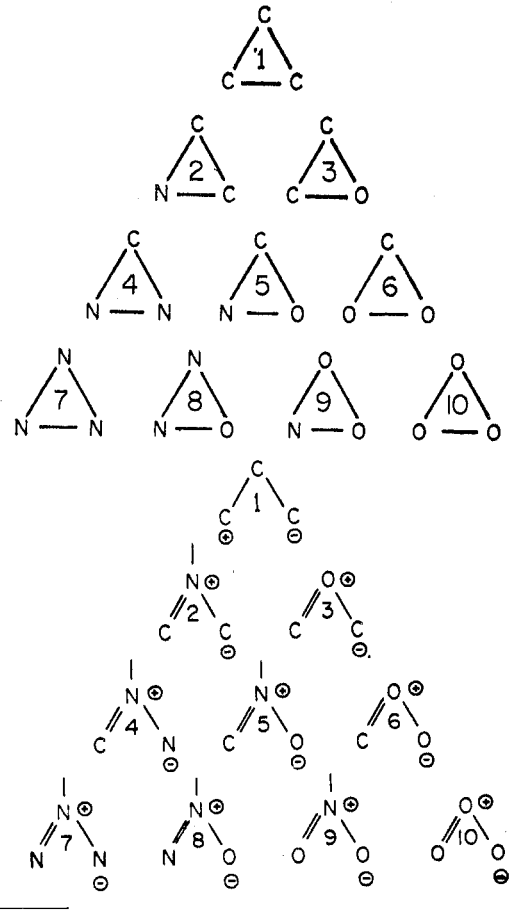
The interconversion of a three-membered ring with an open-chain dipolar form constitutes a type of valence isomerism that has received little attention (eq 1).



(1)

Scheme I illustrates all of the possible combinations for saturated three-membered rings containing carbon, nitrogen, and oxygen and a corresponding dipolar form.[2]

SCHEME I



(1) (a) Supported in part by the National Science Foundation; (b) F. D. Greene and S. S. Hecht, *J. Amer. Chem. Soc.*, **89**, 6761 (1967); (c) National Institutes of Health Predoctoral Fellow, 1965–1968.

(2) The appropriate number of substituents is assumed to be attached to C, N, and O corresponding to the saturated valence states of these atoms.

Systems isolable in covalent form are **1**, **2**, **3**, **4**,[3a] and **5**.[3a,b] Those isolable in dipolar form are **5**,[3a,b] **8**, **9**, and **10**. There is some evidence for the transient existence of dipolar forms **2**,[3c] **3**,[3d] **4**,[3e,f] and **6**.[3g] The ability to exist in a dipolar form is obviously tied to the accommodations for the charges: to the availability of a lone pair on atom B, to the electronegativity of atoms A and C, and to the substituents attached to A and C (eq 1).[4] The relationship between the (isolable) covalent form and a transient dipolar form has been examined for **2**[3c] and **3**,[3d] and in the case of **2** the stereochemistry of the ring-opening reaction (conrotatory) has been established.[3c] For only one of the ten combinations—**5** in the center of the triangle—has it been possible to isolate both the covalent and the dipolar form[3b] for simple substituents.[5]

In recent years, the use of bulky substituents has resulted in the synthesis of small rings of enhanced stability (diaziridinones,[6a] aziridinones,[6b] cyclopropanones[7]). The stabilizing effect of tertiary alkyl substituents in these systems may be due to impeded attack at the carbonyl group, hindrance to concerted ring opening, or more subtle effects. These results encouraged the further examination of adequately hindered, new ring systems. We describe here the synthesis of the oxadiaziridine ring system **8**[8] and a number of reactions of this new class. Interestingly, bulky sub-

(3) (a) E. Schmitz, "Dreiringe mit Zwei Heteroatomen," Springer-Verlag, New York, N. Y., 1967; (b) W. D. Emmons, *J. Amer. Chem. Soc.*, **79**, 5739 (1957); (c) R. Huisgen, W. Scheer, and H. Huber, *ibid.*, **89**, 1753 (1967); (d) W. J. Linn, O. W. Webster, and R. E. Benson, *ibid.*, **87**, 3651 (1965); (e) R. Huisgen, *Proc. Chem. Soc.*, 357 (1961); (f) *Helv. Chim. Acta*, **50**, 2421 (1967); (g) R. Criegee, A. Kerckow, and H. Zinke, *Chem. Ber.*, **88**, 1878 (1955); P. D. Bartlett and T. G. Traylor, *J. Amer. Chem. Soc.*, **84**, 3408 (1962); see also R. W. Murray, *Accounts Chem. Res.*, **1**, 313 (1968).

(4) The incorporation of the groups of Scheme I into aromatic systems leads to many additional examples: *e.g.*, (a) for dipolar form **3**, see E. F. Ullman and W. A. Henderson, Jr., *J. Amer. Chem. Soc.*, **88**, 4942 (1966); (b) for **4**, see J. Streith and J. M. Cassal, *Tetrahedron Lett.*, 4541 (1968); (c) for dipolar form **7**, see M. J. Perkins, *J. Chem. Soc.*, 3005 (1964); see also M. S. Gibson, *Nature*, **193**, 474 (1962).

(5) With rather specialized substituents,[4] both covalent and dipolar forms have been isolated, *e.g.*, for **3**, see ref 4a.

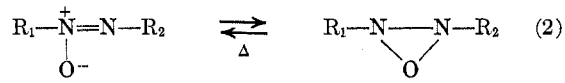
(6) (a) F. D. Greene, J. C. Stowell, and W. R. Bergmark, *J. Org. Chem.*, **34**, 2254 (1969); (b) J. C. Sheehan and J. H. Beeson, *J. Amer. Chem. Soc.*, **89**, 362 (1967).

(7) J. F. Pazos and F. D. Greene, *ibid.*, **89**, 1030 (1967).

(8) The cyclic structure for **8** has appeared in the early literature as a formulation for the azoxy group. In recent times, a diaryloxadiaziridine has been proposed as an intermediate in the Wallach rearrangement of azoxybenzenes to hydroxyaryl azo compounds [M. M. Shemyakin, V. I. Maimind, and Ts. E. Agadzhanyan, *Chem. Ind.* (London) 1223 (1961)]. For further references on the Wallach rearrangement, see E. Buncel, A. Dolenko, I. G. Czizmadia, J. Pincock, and K. Yates, *Tetrahedron*, 6671 (1968), and C. S. Hahn, K. W. Lee, and H. H. Jaffé, *J. Amer. Chem. Soc.*, **89**, 4975 (1967).

stituents do not appear to be essential to the synthesis or stability of this system.

Synthesis of Oxadiaziridines.—Two methods have been examined: photolysis of azoxy compounds[9] and oxidation of azo compounds. Photolysis of azoxy compounds **11a–c** in pentane solution at 10–20° with a Hanovia Type L lamp resulted in ring closure to oxadiaziridines **12a–c.**



(2)

11a, $R_1 = R_2 =$ *t*-butyl
b, $R_1 = R_2 =$ *n*-butyl
c, $R_1 =$ Me; $R_2 =$ *t*-butyl

12a, $R_1 = R_2 =$ *t*-butyl
b, $R_1 = R_2 =$ *n*-butyl
c, $R_1 =$ Me; $R_2 =$ *t*-butyl

Assignment of structure **12** to the photoproducts is based on spectral data (see Table I), molecular weight,

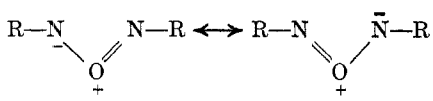
TABLE I

SPECTRAL PROPERTIES OF **11a,b** AND **12a,b**

	Nmr, ppm	Ir, cm^{-1}	Uv, $m\mu$ (ϵ)
11a	1.25 (9 H, s)	1495, s	221 (5535)
	1.46 (9 H, s)	1295	
12a	1.00 (18 H, s)		None
11b	4.17 (2 H, t)	1500	218 (8088)
	3.37 (2 H, t)	1315	
	2.0–0.8 (14 H, m)		
12b	2.63 (4 H, t)		None
	2.0–0.8 (14 H, m)		

volatility, and quantitative thermal isomerization back to the azoxy compounds. Oxadiaziridine **12c** was observed in the photolysis mixture but could not be isolated. Details are given in the Experimental Section.

A possible alternative structure, **13**, has not been rigorously excluded but is considered less likely than **12** on the basis of the lack of reactivity of photoproducts **a** and **b** toward 1,3 dipolarophiles and toward water, and the lack of uv absorption. Peracid oxidation of



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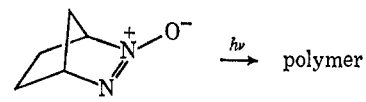
azo compounds is a known method for the synthesis of azoxy compounds. In view of the facile isomerization of oxadiaziridines to azoxy compounds (see section on reactivity) and the peracid oxidation of imines to oxaziridines,[3b] it seemed possible that low-temperature oxidation of azo compounds might first afford oxadiaziridines. Oxidation of azo-*t*-butane[10] with *m*-chloroperbenzoic acid or peracetic acid at 0° showed immediate appearance of azoxy infrared bands and provided no evidence for formation of the oxadiaziridine.

Both the azoxy compounds and the oxadiaziridines are capable, in theory, of existence in *cis* and *trans* forms. Steric considerations suggest the *trans* structure for **11a** and **12a**.[11,12] Nmr comparisons suggest that azoxy-*n*-butane (**11b**) has the *trans* structure. Di-*n*-butyloxadiaziridine could be either *cis* or *trans*. The nmr spectrum is suggestive of a single species. Interconversion of *cis*- and *trans*-*n*-butyloxidiaziridine (*e.g.*, by nitrogen inversion) would be expected to be slow by analogy to diaziridines[13] and oxaziridines.[13]

The photolysis of 2,3-diazabicyclo[2.2.1]-2-heptene N-oxide (**14**)[12] was studied in the hope of preparing a *cis*-substituted oxidiaziridine. Large amounts of uncharacterized polymeric material were obtained. No evidence was found for the presence of the oxadiaziridine.



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Reactivity of Oxadiaziridines.—Thermal isomerization of the oxadiaziridines to the azoxy compounds is facile, quantitative, and first order (Table II). Two

TABLE II

ISOMERIZATION OF OXADIAZIRIDINES TO AZOXYALKANES IN NEUTRAL AND ACIDIC MEDIA

	$t_{1/2}$, min (28°)	
Compd	CCl_4	CCl_4, 1.74 *M* in Cl_2CHCO_2H
12a	290	45
12b	270	70

aspects are of special interest. Firstly, the rates of isomerization for the *t*-butyl compound **12a** and the *n*-butyl compound **12b** are almost the same, implying that the bulky alkyl substituents convey no *special* stabilizing effect in this system. Secondly, the rate of isomerization of **12a** to **11a** is quite insensitive to the polarity of the medium[14] (relative rates: CCl_4, 1; CH_3OH, 2; CH_3NO_2, 2.5) implying that at the transition state of the ring-opening reaction one has not made much progress toward the charge distribution of the azoxy compound.

The stereochemistry of the ring-opening reaction is not known. The spectral properties of the azoxy-*n*-butane obtained from thermal isomerization of **12b** strongly suggest the presence of a single (the starting) isomer, presumably *trans*.

In the stronger acid medium of trifluoroacetic acid, di-*t*-butyloxadiaziridine is rapidly converted to *t*-butyl trifluoroacetate (78% yield). The same reaction is observed with azoxy-*t*-butane (92% yield of the tri-

(9) For the closely related photochemical conversion of nitrones to oxaziridines, see J. S. Splitter and M. Calvin, *J. Org. Chem.*, **30**, 3427 (1965). Photolysis of azoxymethane has been reported [B. G. Gowenlock, *Can. J. Chem.*, **42**, 1936 (1964)] giving C_2H_6, CH_4, N_2, and N_2O. Photolysis of aryl azoxy compounds has been reported to give *o*-hydroxyaryl azo compounds [G. M. Badger and R. G. Butley, *J. Chem. Soc.*, 2243 (1954)].

(10) "Azo-*t*-butane" is 1,1,1′,1′-tetramethylazoethane; "azoxy-*t*-butane" is 1,1,1′,1′-tetramethylazoxyethane.

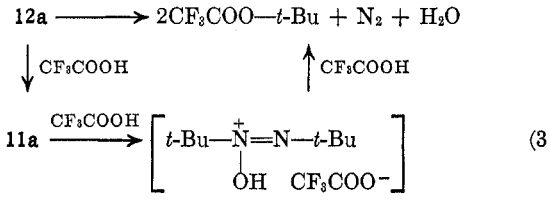
(11) We do not know of any *cis* acyclic aliphatic compounds. The compounds reported by B. T. Gillis and K. F. Schimmel, *J. Org. Chem.*, **27**, 413 (1962), have been reassigned dimeric structures (C. E. Wintner, Ph.D. Thesis, Harvard University, 1963). Cyclic azoxy compounds are known (ref 12).

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

(13) A. Mannschreck and W. Seitz, *Angew. Chem. Int. Ed. Engl.*, **8**, 212 (1969).

(14) See S. Brownstein, *Can. J. Chem.*, **38**, 1590 (1960), and references cited therein; see also E. M. Kosower, "An Introduction to Physical-Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1968, Chapter 2.6–2.8.

fluoroacetate), possibly *via* a route such as that shown in eq 3. In this medium (CF_3COOH), di-*n*-butyloxa-

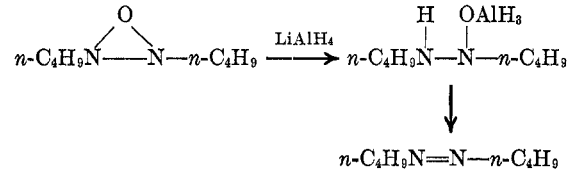


(3)

diaziridine is isomerized to azoxy compound. In contrast to azoxy-*t*-butane, azoxy-*n*-butane is unchanged by trifluoroacetic acid after 24 hr at room temperature.[15]

Reduction Reactions.—Di-*t*-butyloxadiaziridine is converted to azo-*t*-butane[10] (95%) by the action of acidified sodium iodide in acetone. This reaction can be used to assay samples of the oxadiaziridine. (However, spectral methods of assay are simpler.)

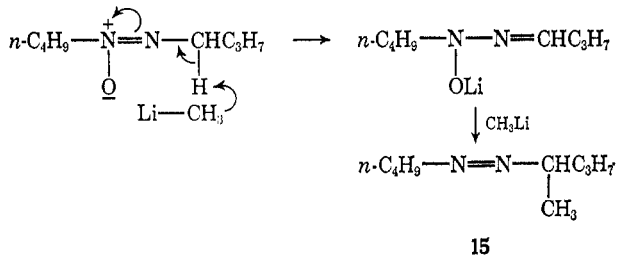
Di-*t*-butyloxadiaziridine is not reduced by lithium aluminum hydride in ether at room temperature. Di-*n*-butyloxadiaziridine is reduced to azobutane in 40% yield.



The same pattern is seen with lithium aluminum hydride and the azoxy compounds; the di-*t*-butyl derivative is recovered unchanged, while azoxy-*n*-butane is converted to azo-*n*-butane in 80% yield.

Reactions with Methyllithium.—The reaction of di-*t*-butyloxadiaziridine with methyllithium at room temperature proceeds sluggishly. Interruption of the reaction after 1 hr at room temperature gives a 7% yield of azo-*t*-butane,[10] while the remainder of the material is oxadiaziridine and azoxy-*t*-butane[10] (resulting from isomerization). Azoxy-*t*-butane, when treated under the same conditions, is slowly reduced to the azo compound (9% after 18 hr at 25°).

When azoxy-*n*-butane is mixed at 0° with a solution of methyllithium, a vigorous reaction takes place with evolution of gas and development of an orange color. Quenching results in decolorization and the isolation of 1-methyl-azobutane (**15**) in 30% yield as the single major product. The presence of the corresponding C_9 hydrazones is also indicated (see Experimental Section). The reaction of di-*n*-butyloxadiaziridine with



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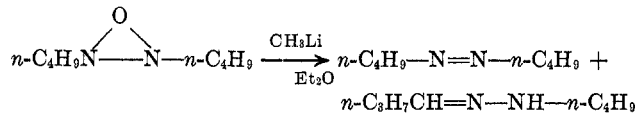
methyllithium follows a different course. In this case, the major products are found to be azo-*n*-butane (50%) and butyraldehyde *n*-butylhydrazone (25%). The



hydrazone may arise by isomerization of azo-*n*-butane or by extraction of an α hydrogen at an intermediate stage.

A number of conditions which gave no reaction with the oxadiaziridines and the azoxy compounds are summarized in the Experimental Section.

Experimental Section

Azo-*n*-butane.[16]—An aqueous solution of sodium hypochlorite (80 ml, 1.5 *M*) was added at 0° with stirring to a mixture of NaOH (5.0 g, 0.125 mol) and di-*n*-butylsulfamide (obtained from the reaction of *n*-butylamine and sulfuryl chloride,[16] mp 118–120°, 12 g, 0.058 mol) in 20 ml of pentane and stirred 2 hr at 25°. The mixture was extracted with three 50-ml portions of pentane and the pentane layer was dried ($MgSO_4$) and concentrated. The residue was distilled at 77° (30 mm) giving 5.0 g (59%) of azo-*n*-butane: ir (CCl_4) 2960, 2865, 1465, 1430, 1380 cm^{-1}; nmr (CCl_4) 3.72 ppm (4 H, triplet), 2.0–0.8 ppm (14 H, multiplet).

Azoxy-*n*-butane (11b).—To a solution of azo-*n*-butane (4.0 g, 0.028 mol) in methylene chloride (50 ml) was added a peracetic acid solution (10 ml, 4.9 *M* peracid in acetic acid) dropwise. The mixture was stirred for 2 hr at 0–10° and poured into 200 ml of water. The layers were separated, and the methylene chloride layer was washed with saturated aqueous solutions of $NaHSO_3$, $NaHCO_3$, and NaCl in 200-ml portions and dried ($MgSO_4$). Concentration and distillation [105° (20 mm)] gave azoxy-*n*-butane (**11b**) (2.09 g, 35%): ir (CCl_4) 2950, 2925, 2860, 1500, 1460, 1450, 1430, 1419, 1315, 1205 cm^{-1}; nmr (CCl_4) 4.17 (2 H, triplet), 3.37 (2 H, triplet), 2.0–0.8 ppm (14 H, multiplet); uv (EtOH) λ_{max} 218 mμ (ϵ 8088), 278 (53).

Anal. Calcd for $C_8H_{18}N_2O$: C, 60.76; H, 11.39; N, 17.72. Found: C, 60.70; H, 11.49; N, 17.85.

2,3-Diazabicyclo[2.2.1]-2-heptene N-Oxide (14).—A solution of 2,3-diazabicyclo(2.2.1]-2-heptene[17] (288 mg, 3.0 mmol) in methylene chloride (10 ml) was added at 0° to a methylene chloride (15 ml) solution of 85% *m*-chloroperbenzoic acid (800 mg, 4.0 mmol) and stirred at 25° for 3 hr. Neutralization (by 8 g of K_2CO_3, and stirring at room temperature for an additional 16 hr), filtration, and concentration at reduced pressure yielded 200 mg (57%) of crude **14**. Pure material (mp 87–89°) could be obtained either by sublimation, by recrystallization from hexane, or by collection from glpc. Azoxy compound **14** has the following spectral properties: ir ($CHCl_3$) 3000, 2960, 1500 (s), 1465, 1365, 1352, 1300 (w), 1285, 1252, 1180, 1121 cm^{-1}; uv (EtOH) λ_{max} 228 (ϵ 6000); nmr[18] ($CDCl_3$) 4.61 (2 H, singlet), 2.30–1.50 ppm (6 H, multiplet); mass spectrum, *m/e* (relative intensity), 112 (32, molecular ion), 68 (100), 67 (74), 39 (30).

Anal. Calcd for $C_5H_8N_2O$: C, 53.57; H, 7.14; N, 25.00; mol wt, 112. Found: C, 53.56; H, 7.13; N, 25.02; mol wt (cryoscopic in benzene), 122.

Di-*t*-butyloxadiaziridine (12a).—Azoxy-*t*-butane (**11a**)[18] [1,1-1′,1′-tetramethylazoxybutane] (12.0 g, 0.076 mol) was irradiated in 250 ml of purified pentane using a Hanovia Type L high-pressure lamp. The quartz inner-well was cooled with cold water. The solution was degassed (N_2 stream) and the photolysis was followed by disappearance of the uv band at 221 mμ (complete in 3 hr). The pentane was removed at reduced pressure at room temperature yielding a residue of crude di-*t*-butyloxadiaziridine (**12a**), 9.0 g. Analysis by glpc (5 ft × 0.25

(15) For a study of the effect of strong acids on primary and secondary azoxyalkanes, see R. Biela, H. Horing, and W. Pritzkow, *J. Prakt. Chem.*, **36**, 197 (1967); see also B. W. Langley, B. Lythgoe, and L. S. Rayner, *J. Chem. Soc.*, 4191 (1952).

(16) E. Schmitz and R. Ohme, *Angew. Chem. Int. Ed. Engl.*, **4**, 433 (1965).

(17) S. G. Cohen, R. Zand, and C. Steel, *J. Amer. Chem. Soc.*, **83**, 2895 (1961). In this preparation, it is necessary to follow exactly Cohen's procedure for the hydrolysis of the diester to the hydrazo compound. Oxidation of the hydrazo compound to the title compound was most efficiently accomplished by the copper(I) chloride method cited by Cohen.

(18) J. P. Freeman, *J. Org. Chem.*, **28**, 2508 (1963).

in., 20% SE-30, 100°) showed one major peak, which was collected and had infrared spectrum and retention time identical with those of azoxy-*t*-butane.

Small portion of **12a** (0.3–0.5 g) were purified one at a time by trap-to-trap distillation at room temperature and 0.1 mm. The distillation gave a mixture of di-*t*-butyloxadiaziridine (**12a**) and azoxy-*t*-butane (**11a**), the latter forming during work-up and distillation. This mixture was separated by chromatography on alumina using a water-cooled column and a 100:1 alumina: substrate ratio with pentane as eluent (order of elution: oxadiaziridine, azoxy-*t*-butane). The chromatography was successful with Woelm activity grade I neutral alumina and Merck acid-washed alumina. Di-*t*-butyloxadiaziridine (**12a**) has the following physical properties: nmr (CCl_4) 1.00 ppm (singlet); ir (CCl_4) 2970, 2925, 2850, 1475, 1452, 1380, 1365, 1230, 1205 cm^{-1}; mass spectrum *m/e* (relative intensity) 87 (7), 57 (100), 41 (40).

Anal. Calcd for $C_8H_{18}N_2O$: C, 60.76; H, 11.39; N, 17.72; mol wt, 158. Found: C, 60.62; H, 11.33; N, 17.70; mol wt (cryoscopic in benzene), 166.

Di-*n*-butyloxadiaziridine (12b) was prepared using the same procedure as for **12a**, above. After 2 hr of irradiation the ultraviolet maxima had disappeared. Removal of solvent and analysis of the mixture by glpc (5 ft × 0.25 in., 20% SE-30, 100°) showed two major peaks corresponding in retention time to azo-*n*-butane (14%) and azoxy-*n*-butane (**11b**) (86%). Chromatography on alumina (alumina:substrate = 100:1, pentane: methylene chloride eluent 50:50) resulted in elution of di-*n*-butyloxadiaziridine (**12b**) as the first fraction. Samples were found to be contaminated with 10% azo-*n*-butane. Trap-to-trap distillation of the crude mixture at 25° (0.01 mm) resulted in separation of di-*n*-butyloxadiaziridine (**12b**) and azo-*n*-butane from azoxy-*n*-butane (**11b**). Samples free of azo compound were prepared by rapidly mixing the crude mixture with *m*-chloroperbenzoic acid solution at 0° in methylene chloride and working up quickly at 0°. This converted azo-*n*-butane to azoxy-*n*-butane (**11b**) which was then separated from di-*n*-butyloxadiaziridine (**12b**) by either chromatography or distillation. Spectral properties: nmr (CCl_4) 2.63 ppm (4 H, triplet), 0.8–2.0 (14 H, multiplet); ir (CCl_4) 2945, 2915, 2857, 1466, 1387 cm^{-1} (infrared and nmr spectra identical with those of azoxy-*n*-butane were obtained by heating a sample at 90° for 4 min).

Anal. Calcd for $C_8H_{18}N_2O$: C, 60.76; H, 11.39; N, 17.72. Found: C, 60.58; H, 11.38; N, 17.67.

Photolysis of N-*t*-butyl-N′-methyldiimide N-oxide (1,1-dimethylethaneazoxymethane) (11c)[18,19] was carried out under the same conditions described for **12a** and **12b** [1.5 g (0.013 mol) of **11c** in 250 ml of pentane]. The uv max of **11c** disappeared after 2.5 hr. Concentration yielded a residue of 0.5 g, shown by glpc (5 ft, 20% SE-30, 100°) to be a mixture of at least 11 components: 50% corresponded to a mixture of two unsymmetrical azoxy compounds and 1-methyl-2-*t*-butyloxadiaziridine (**12c**), 22% was a mixture of low-boiling components, and 27% was a mixture of less volatile material. The infrared spectrum of the crude mixture showed characteristic azoxy bands, which increased in intensity on heating of a sample in a sealed tube for 5 min at 90°. The nmr of the crude material showed, in addition to a multiplet at 1.40–1.10 ppm, singlets at 3.10 ppm (3 H), 2.62 (3 H), 1.50 (9 H), and 1.00 (9 H). After standing overnight, the signals at 2.62 and 1.00 ppm (**12c**) disappeared with enhancement of the peaks at 3.10 and 1.50 ppm (**11c**). A weak signal was also observed at 3.95 ppm. Alumina chromatography yielded the high-boiling components of the mixture as a first fraction (elution with pentane). A second pentane fraction contained a complex mixture of products. Elution with methylene chloride yielded the azoxy compound. The nmr spectrum of the less volatile components showed a multiplet between 1.0 and 1.4 ppm. No signals were observed further downfield. This excludes dimers with N-methyl linkages.

Photolysis of 2,3-Diazabicyclo[2.2.1]-2-heptene N-Oxide (14).—A degassed solution of **14** (15 mg, 0.13 mmol) in 250 ml of spectroquality cyclohexane was irradiated with a Hanovia Type L high-pressure lamp. After 0.5 hr, the ultraviolet maximum due to the azoxy compound had disappeared. Heating of a portion of the photolysis solution at reflux for 0.5 hr effected no return of the azoxy ultraviolet absorption. Concentration under reduced pressure yielded a residue (13 mg) which contained some solid material which did not melt below 300°. Attempted sublimation of the residue was unsuccessful. Examination of the residue by glpc (8 ft × 0.25 in., 20% SE-30, 150°) showed no peaks other than solvent. Photolysis in Freon (188 mg **14** in 250 ml) and in octane (100 mg **14** in 250 ml) gave essentially the same results. Neither cyclopentene nor bicyclopentane was observed by glpc of the photolysis solution (octane solvent).

Isomerizations of Di-*t*-butyloxadiaziridine and Di-*n*-butyloxadiaziridine.—Isomerization of di-*t*-butyloxadiaziridine to azoxy-*t*-butane can be followed by nmr (disappearance of singlet at 1.00 ppm with appearance of singlets at 1.25 and 1.46 ppm), ir (appearance of bands at 1500 and 1300 cm^{-1}), and uv (appearance of band at 221 mμ). In the case of di-*n*-butyloxadiaziridine, the triplet centered at 2.60 ppm disappears with appearance of two triplets centered at 3.40 and 4.17 ppm. The thermal isomerization of di-*t*-butyloxadiaziridine was found to be essentially quantitative by comparison of the intensity of the ultraviolet absorption at 221 mμ after isomerization (ε 5501) with that of azoxy-*t*-butane (ε 5535). Analysis of this material by vpc (5 ft × 0.25 in., 20% SE-30, 100°) showed only one peak, identical in retention time and infrared spectrum with those of azoxy-*t*-butane. The rates of isomerization of di-*t*-butyloxadiaziridine and di-*n*-butyloxadiaziridine were followed by integration of nmr peaks, and the half-lives reported in the text for the thermal reaction were obtained from first-order plots.

Reactions with Trifluoroacetic Acid. A. Azoxy-*t*-butane (50 mg, 0.32 mmol) was mixed with 2.5 ml of trifluoroacetic acid. An immediate exothermic reaction took place with evolution of gas. Nmr of the solution showed a singlet at 1.47 ppm. The mixture was diluted with H_2O and extracted with ether. The ether phase was washed (saturated aqueous K_2CO_3), dried ($MgSO_4$), and concentrated. The residue (vpc, one peak) was identified as *t*-butyl trifluoroacetate by comparison of retention time and ir and nmr spectra with those of an authentic sample. The yield was 92% (based on 2 mol of *t*-butyl trifluoroacetate produced for every 1 mol of azoxy-*t*-butane consumed).

B. Di-*t*-butyloxadiaziridine (24.0 mg, 0.15 mmol) was added slowly to 0.5 ml of trifluoroacetic acid. Reaction took place immediately and resulted in formation of *t*-butyl trifluoroacetate (84% yield).

C. Azoxy-*n*-butane (50 mg, 0.32 mmol) was added to trifluoroacetic acid (0.5 ml). Some heat was evolved, but there was no evolution of gas as in the case of azoxy-*t*-butane. No change was observed in the nmr spectrum after 24 hr at room temperature. [It should be noted, however, that the chemical shift of the methylene groups adjacent to the azoxy functionality is somewhat different in trifluoroacetic acid (3.83 and 4.66 ppm) than in a neat sample (3.40 and 4.17 ppm)].

D. Di-*n*-butyloxadiaziridine (50 mg, 0.32 mmol) was mixed with trifluoroacetic acid (0.5 ml) at 0° in an nmr tube and allowed to come to 20°. The oxadiaziridine gradually disappeared over a period of 80 min with appearance of triplets at 3.83 and 4.66 ppm, corresponding to azoxy-*n*-butane. In addition to this, two smaller triplets were observed centered at 4.20 and 4.69 ppm. The acid was destroyed by addition of solid K_2CO_3. Concentration yielded 47 mg of material which showed 80% azoxy-*n*-butane by glpc (5 ft × 0.25 in., 20% SE-30, 100°) in addition to 20% material of shorter retention time, which remains unidentified.

Reactions with Lithium Aluminum Hydride. A. Di-*t*-butyloxadiaziridine (100 mg, 0.63 mmol) was added at room temperature to a slurry of lithium aluminum hydride (40 mg, 1.0 mmol) in ether (5 ml). No signs of reaction were observed. Stirring was continued at room temperature for 1 hr and the mixture was quenched by cautious addition of H_2O. The ether phase was dried ($MgSO_4$) and concentrated, yielding 60 mg of material which was a mixture of di-*t*-butyloxadiaziridine (40%) and azoxy-*t*-butane (60%) by nmr. When **azoxy-*t*-butane** was subjected to the same conditions, it was recovered unchanged.

B. Azoxy-*n*-butane (510 mg, 3.2 mmol) was added in portions at room temperature to a slurry of lithium aluminum hydride (192 mg, 5.0 mmol) in 25 ml of ether. There was a slightly exothermic reaction for the first 20 min. Stirring was continued for 50 min more. The reaction mixture was quenched by cautious addition of H_2O. The ether phase was dried ($MgSO_4$) and concentrated yielding 364 mg (80%) of azo-*n*-butane, identified by comparison of infrared and nmr spectra with those of authentic material.

C. Di-*n*-butyloxadiaziridine was converted to azo-*n*-butane in 40% yield under the above conditions.

(19) J. G. Aston and D. M. Jenkins, *Nature*, **167**, 863 (1951).

Reaction of Di-*t*-butyloxadiaziridine with Sodium Iodide in Acetone. A. Titration.—Di-*t*-butyloxadiaziridine (21 mg, 0.13 mmol) was added to a degassed, saturated solution of sodium iodide in acetone (10 ml) containing 1 ml of 1.0 *N* HCl. An immediate dark red color appeared and the solution was stirred for 5 min at room temperature under N_2. Titration of the iodine with 0.020 *N* $Na_2S_2O_3$ solution gave an average value of 90% "active oxygen" for samples known to contain 90% di-*t*-butyloxadiaziridine by uv spectrum. When this procedure was employed with azoxy-*t*-butane as substrate, some coloration of the solution (yellow) was observed.

B. Product Identification.—Di-*t*-butyloxadiaziridine (100 mg, 0.63 mmol) was added at room temperature to a saturated solution of sodium iodide in acetone containing 1 drop of concentrated HCl. The mixture was stirred for 5 min at room temperature. The red color was dissipated by addition of a few drops of saturated aqueous $Na_2S_2O_3$. The ether layer was washed (aqueous NaOH) and examined by glpc (5 ft × 0.25 in., 20% SE-30, 100°). The yield of azo-*t*-butane was 95% by calibration with a known amount of decane.

Reactions with Methyllithium. A. Di-*t*-butyloxadiaziridine (146 mg, 0.92 mmol) was added at room temperature under N_2 to a stirred ether solution of methyllithium (1.25 ml of a 1.6 *N* solution). Stirring was continued for 1 hr at room temperature and the mixture was quenched by cautious addition of H_2O. Drying ($MgSO_4$) and concentration yielded 96 mg (65%) of a mixture of azoxy-*t*-butane, azo-*t*-butane, and di-*t*-butyloxadiaziridine in the ratio of 63:10:27 by integration of nmr peaks. Subjection of azoxy-*t*-butane to these conditions resulted in 9% reduction to azo-*t*-butane after 18 hr at room temperature.

B. Azoxy-*n*-butane (125 mg, 0.79 mmol) was added at 0° under N_2 to an ether solution of methyllithium (2.0 ml, 1.6 *M*). A vigorous reaction took place with evolution of gas and development of an orange color. After the bubbling had ceased (5 min), the reaction mixture was quenched by cautious addition of H_2O. Drying ($MgSO_4$) of the ether phase and concentration yielded a residue (66 mg) which was analyzed by glpc (2 ft × 0.25 in., 20% SE-30, 80°).

There were four peaks having relative retention times (intensity) of 0.43 (60%), 0.67 (2%), 0.86 (14%), and 1.0 (24%). The 14 and 24% peaks are thought to be the corresponding C_9 hydrazones. The mass spectrum of the 24% peak shows a molecular ion of 156 and the ir spectrum of the combined peaks shows NH absorption and a weak –C=N band. The nmr of the crude mixture shows a triplet centered at 6.83 ppm corresponding to the "aldehydic" hydrogen of the hydrazone. The 60% peak was identified as 1-methylazobutane (**15**) by comparison of its spectral properties with those of an authentic sample prepared by the method of Spialter:[20] ir (CCl_4) 2980, 2940, 2880, 1465, 1455, 1375 cm^{-1}; nmr (CCl_4) 3.66 ppm [triplet (2 H) superimposed on a multiplet (1 H)], 2.0–0.8 ppm, [multiplet (17 H) which includes a doublet (J = 6 cps) centered at 1.15 ppm]; mass spectrum m/e (relative intensity) 156 (9, molecular ion), 71 (47), 57 (36), 43 (100), 41 (39).

Anal. Calcd for $C_9H_{20}N_2$: C, 69.23; H, 12.82. Found: C, 69.15; H, 12.72.

C. Di-*n*-butyloxadiaziridine (82 mg, 0.52 mmol) was added at 0° under N_2 to a solution of methyllithium in ether (1.6 ml, 1.6 *M*). There was no color change or evolution of gas. Stirring was continued for 5 min and the mixture was quenched by cautious addition of H_2O. The ether phase was dried ($MgSO_4$) and concentrated yielding a residue of 49 mg. Analysis of this mixture by glpc (2 ft × 0.25 in., 20% SE-30, 80°) and nmr indicated that it was a mixture of azo-*n*-butane (75%) and *n*-butyraldehyde *n*-butylhydrazone (25%). The latter was identified by comparison with an authentic sample obtained by the method of Beringer.[21]

Conditions Which Gave No Reaction with the Oxadiaziridine and Azoxy Systems.—(a) Azoxy-*t*-butane and di-*t*-butyloxadiaziridine were recovered unchanged (except for isomerization of the latter) after stirring with magnesium and ethanol at room temperature for 24 hr. (b) Azoxy-*t*-butane and di-*t*-butyloxadiaziridine were recovered unchanged (except for isomerization) after stirring with triethyl phosphite for 24 hr at room temperature. (c) Azoxy-*t*-butane, azoxy-*n*-butane, di-*t*-butyloxadiaziridine, and di-*n*-butyloxyadiaziridine were shown to be inert to further oxidation by *m*-chloroperbenzoic acid (3–6 hr, room temperature, in CH_2Cl_2). (d) Azoxy-*t*-butane, azoxy-*n*-butane, di-*t*-butyloxadiaziridine, and di-*n*-butyloxadiaziridine could be recovered unchanged (except for isomerization) after 3 hr of stirring in an ethanol solution at room temperature under 1 atm of hydrogen with 10% Pd–C as catalyst. (e) Azoxy-*t*-butane was recovered unchanged after stirring for 24 hr at room temperature with 6 *M* aqueous NaOH. Di-*t*-butyloxadiaziridine showed only isomerization to the azoxy compound under these conditions. (f) Di-*n*-butyloxadiaziridine did not undergo reaction at room temperature with furan, norbornylene, phenyl isocyanate, or diazomethane.

Registry No.—**11a**, 16649-52-8; **11b**, 17697-56-2; **12a**, 18857-00-6; **12b**, 24766-60-7; **14**, 22509-00-8; **15**, 24766-62-9.

(20) L. Spialter, D. H. O'Brien, G. L. Untereiner, and W. A. Rush, *J. Org. Chem.*, **30**, 3278 (1965).

(21) F. M. Beringer, J. A. Farr, Jr., and S. Sands, *J. Amer. Chem. Soc.*, **75**, 3984 (1953).