The covalent nature of the S–Cl bond in chlorosulfuranes **1** and **6a–e** is indicated by the presence of a molecular ion at m/e 278 in the field desorption mass spectrum of **1** and by several NMR comparisons. The ^1H NMR peaks for the proton ortho to sulfur in the disubstituted ring of **1** and the analogous protons in **6a–e** occur at lower field than δ 9.10. The analogous protons occur at higher field than δ 8.35 for the ionic fluoroborates or trifluoromethanesulfonates. The separation between the two *gem*-dimethyl signals is consistently more than 25 Hz for covalent derivatives, including alkoxysulfurane analogs of the chlorosulfuranes, and less than 15 Hz for the ionic species. The NMR of **1** in $CDCl_3$ is independent of the concentration of added tetraethylammonium chloride from 0 to 2.25 M. This evidence for the covalent character of the S–Cl bond parallels that from earlier studies[3a] of unisolated chlorosulfuranes studied in solution by ^1H NMR.

The relative rate constants for hydrolysis of **1** (1), **6a** (0.3), **6b** (1.15), **6c** (2.8), **6d** (1.54), and **6e** (26.0) show that substituents, Y, in the fused-ring system are much more effective than those, X, in the freely rotating aromatic ring ($\rho_Y = 2.0$, $\rho_X = 0.3$). Both are positive, consistent with the operation of an associative mechanism involving the development of negative charge on sulfur in a transition state resembling **5**. There are 24 stereoisomers (12 pairs of enantiomers) of the general octahedral structure **5**, and the somewhat arbitrary choice of **5** for illustration in Scheme I will be discussed in a later paper. Known analogs of **5** include the SF_5^- species reported by Christe[5a] and Muetterties.[5b]

The silver assisted ionization of Scheme I initiates a dissociative route for displacement via sulfonium salt **4**. If this ionization can be considered to proceed with retention of configuration at sulfur and the further reaction with hydroxyl ion is considered to proceed to give **4** and **2** by the stereochemical route demonstrated for the basic hydrolysis of acyclic alkoxy sulfonium salts,[6] the relationship between **1** and **2** is established as that shown in Scheme I. Associative displacement of the chloride of **1** by hydroxide, under the same conditions used for the competitive rate studies, proceeds to give **2** of the same configuration with less than 9% racemization. This direct displacement must therefore also proceed with retention of geometry.

The synthesis of **2** by a Grignard displacement[7a] on menthyl (S)-benzenesulfinate ($[\alpha]D$ −202°, acetone; lit.[8] $[\alpha]D$ −206°, acetone), a reaction known to proceed with inversion,[7b] completes the definition of stereochemistry as that shown in Scheme I. Enantiomeric purities[9] of **1** and **2** were determined by the method of Pirkle[10] using (S)-(+)-1-(10-methyl-9-anthryl)-2,2,2-trifluoroethanol[11] (**7**) in $CDCl_3$ to provide the chiral medium in which the methyl signals for enantiomers of **1** and **2** were clearly resolved.[12,13]

Acknowledgment. This research was supported in part by a grant from the National Science Foundation, MPS71-03222, and in part by a grant from the National Institutes of Health (CA-13963).

References and Notes

(1) Paper XVIII in a series of papers on sulfuranes. For paper XVII see J. C. Martin and J. A. Franz, *J. Am. Chem. Soc.*, in press.

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(6) C. R. Johnson and D. McCants, Jr., *J. Am. Chem. Soc.*, **87**, 5404 (1965); R. Tang and K. Mislow, *ibid.*, **91**, 5644 (1969).

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(8) J. Jacobus and K. Mislow, *J. Am. Chem. Soc.*, **89**, 5228 (1967).

(9) We have assumed optical and enantiomeric purity to be identical.

(10) W. H. Pirkle and S. D. Beare, *J. Am. Chem. Soc.*, **90**, 6250 (1968).

(11) We are indebted to W. H. Pirkle and D. Sikkenga for a sample of this material.

(12) The methyl signals for **1** (Scheme I) were at lower field than those for its enantiomer by about 9 Hz while those for (R)-**2** were at higher field than those of (S)-**2** by about 7 Hz in the presence of 0.18 M **7**.

(13) We propose extension of the R–S nomenclature system[14,15] to trigonal bipyramidal molecules using the usual sequence rules,[14] by viewing the molecule along the apical axis with the higher ranking of the *two apical ligands* at the nearer end of that axis. (For a distorted trigonal bipyramid the most nearly collinear pair of bonds joining ligands to the central atom is designated the apical axis.) The chirality of the molecule is then defined in terms of the sequence of equatorial ligands in the usual way.[14] By this convention the chlorosulfurane pictured in Scheme I is (S)-(+)-**1**. The validity of this assignment rests, of course, on the arguments outlined in the text.

(14) R. S. Cahn, C. Ingold, and V. Prelog, *Angew. Chem., Int. Ed. Engl.*, **5**, 385 (1966), proposed a nomenclature system for the specification of molecular chirality which has been generally accepted. They explicitly refrained (p 410) from considering trigonal bipyramidal molecules since no compounds were known at that time whose chirality depended on the configurational stability of the central atom of such a structure. Since 1966 reports have appeared of a spiro derivative of hypervalent selenium by B. Lindgren, *Acta Chem. Scand.*, **26**, 2560 (1970); a spirophosphorane by D. Hellwinkel, *Chem. Ber.*, **99**, 3628 (1966); and phosphoranes bearing chiral ligands by J. F. Brazier, J. Ferekh, A. Munoz, and R. Wolf, *C. R. Acad. Sci.*, **272**, 1521 (1971), and J. Ferekh, J. F. Brazier, A. Munoz, and R. Wolf, *ibid.*, **270**, 865 (1970).

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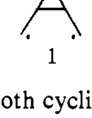
Generation of Photochemical Species on Ground, Excited Singlet, and Triplet Hypersurfaces in Barrelene Photochemistry[1,2]

Sir:

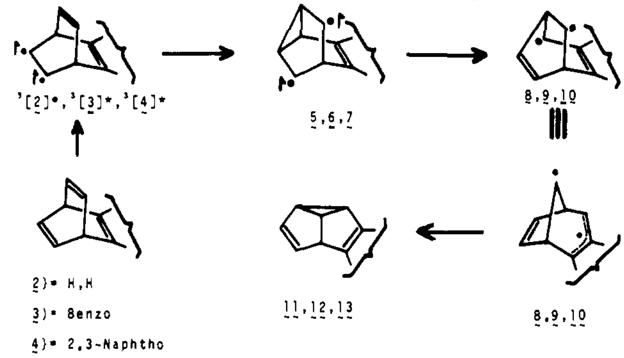
The di-π-methane rearrangement[3] has developed into one of the most general of photochemical reactions and its mechanism has been the subject of considerable study.[4] The cyclopropyldicarbinyl diradical species **1** has been postulated[4] to be involved in both cyclic and acyclic examples of the rearrangement. In the specific examples of the di-π-methane rearrangements of barrelene (**2**), benzobarrelene (**3**), and 2,3-naphthobarrelene (**4**) the mechanism[5] in Chart I is seen to involve the triplet cyclopropyldicarbinyl diradicals **5**, **6**, and **7**.



1

That such cyclopropyldicarbinyl diradical species should lead onward to di-π-methane products poses a dilemma, since ground[6a-d] and excited[6e,f] state precedent give no evidence of such rearrangements but rather suggest that dirad-

Chart I. Mechanism of the Di-π-methane Rearrangement



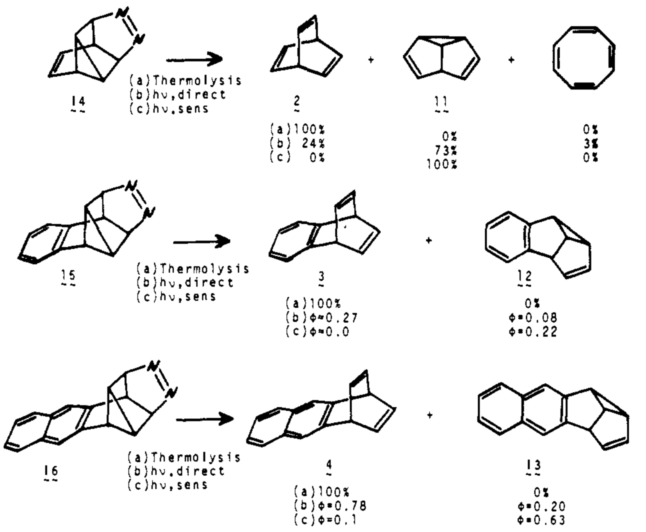
ical species such as **1** instead undergo Grob fragmentation[7] to give 1,4-pentadienes, in this case reactant barrelenes.

The present communication reports the following: (a) the generation of the cyclopropyldicarbinyl diradicals postulated in the barrelene, benzobarrelene, and 2,3-naphthobarrelene rearrangements; (b) observation that the ground state diradicals do indeed undergo Grob fragmentation to the corresponding barrelenes; (c) the finding that appropriately designed triplet diradicals, in contrast, lead preferentially to the corresponding semibullvalenes; (d) multiplicity control leading the excited singlet diradical instead to barrelenes.

The azo compounds **14, 15,** and **16,** selected as precursors to the desired cyclopropyldicarbinyl diradicals **5, 6,** and **7,** were synthesized by homo Diels-Alder addition of ethyl azodicarboxylate to barrelene, benzobarrelene, and 2,3-naphthobarrelene, respectively, followed by saponification and oxidation.[8] The azo compounds were obtained crystalline with melting points of 36-38° (for **14**), 85-89° dec (for **15**), and 110-112° dec (for **16**).

Thermolysis at 60-80° of the azo compounds **14, 15,** and **16** led in each case to the corresponding barrelene (note Chart II). This is the expected reaction of a cyclopropyldicarbinyl diradicaloid species based on literature precedent.[6] The reaction is in effect a ground state ${}_2\sigma_s + {}_2\sigma_s + {}_2\sigma_s$ cycloreversion (a designation[9] equivalent to terming the transition state as Hückel[10] with six electrons) and is expected to be concerted. Nevertheless, the transition state can be envisaged as a good model for the cyclopropyldicarbinyl diradical, consisting of this diradical in juxtaposition to a single nitrogen molecule. Hence these experiments define the behavior of ground state cyclopropyldicarbinyl diradicals.

Chart II



In contrast, the photochemical reactions of azo compounds **14, 15,** and **16** led to the corresponding barrelenes **2, 3,** and **4** and semibullvalenes **11, 12,** and **13,** with the ratio depending on multiplicity. As outlined in Chart II, the sensitized runs led predominately to semibullvalenes while direct photolysis showed an enhanced preference for formation of barrelene product.

The first point to note is that the sensitized reaction, where a triplet diradical (**5, 6,** and **7**) is expected, leads to the same photochemistry observed in the sensitized irradiation of the three barrelenes. Since these triplet diradicals (**5, 6,** and **7**) previously were postulated as involved in the di-π-methane rearrangement of barrelenes to semibullvalenes, the present independent generation of these diradicals with resulting semibullvalene formation is in accord with and supports the di-π-methane mechanism.

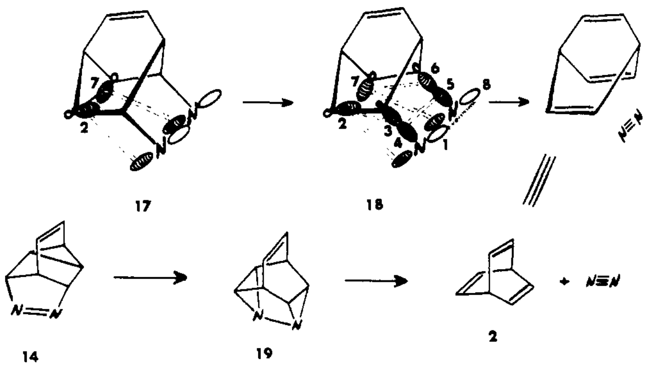
The greater tendency of the azo compounds to give barrelene on direct irradiation compared to the sensitized runs suggests that intersystem crossing of the azo compounds is inefficient. Hence it is S_1 which exhibits a preference for barrelene formation.

Our one-electron, three-dimensional calculations[5a] reveal excited state minima roughly corresponding to the cyclopropyldicarbinyl diradical (**5**) and the allylic diradical (**8**). The first minimum is poised above a ground state surface leading back to barrelene while the second hovers over the ground state surface leading to semibullvalene. Thus, presently from T_1 there seems to be preferential accumulation of the allylic diradicals (**8, 9,** and **10**) and decay to product semibullvalenes, while from S_1 there is formation of the cyclopropyldicarbinyl diradicals (**5, 6,** and **7**) with subsequent decay to barrelenes. The allylic diradical has greater electron-electron separation while the cyclopropyldicarbinyl diradical is more compressed. Hence the multiplicity dependence accords with the point made earlier that S_1 tends to have a wave function composed of ionic, two-electron terms and favors tight geometries,[11] in contrast to T_1 which is covalent and prefers extended geometries.[11]

Another conclusion derives from the high ratio of semibullvalenes to barrelenes in sensitized photolyses of the azo compounds. We can conclude that any inefficiency in barrelene photochemistry is in formation of the cyclopropyldicarbinyl diradicals and not subsequent steps. This, again, reveals the triplet cyclopropyldicarbinyl diradical to proceed onward with efficiency to the allylic diradical.

The reaction of S_1 to give barrelenes is formally orbitally forbidden (although ground state allowed; note above). However, in the spirit of "minimization of forbiddenness" as discussed by us earlier,[12] we note that the reaction forbiddenness becomes decreased by overlap of the π-system of the azo moiety with the three-ring σ bond 2-7 (Chart III). A simple way of seeing this is to picture the forbidden reaction instead as proceeding in two steps, the first involving

Chart III



$_2\sigma_s + {}_2\pi_s$ cycloaddition (excited state allowed) followed by nitrogen disengagement which is also excited state allowed (eight electrons, Hückel) or equivalently a reverse $_2\sigma_s + {}_2\pi_s + {}_2\sigma_s + {}_2\pi_s$.[13]

Thus, the concept of generating species on photochemical hypersurfaces has again proven of utility in determining photochemical details.[16] In this instance the diradical postulated 8 years ago[5a] has proven a reality.

Acknowledgment. Support of this research by the National Science Foundation and the U.S. Army Research Office is gratefully acknowledged.

References and Notes

(1) This is paper number 98 of our photochemical series.

(2) For paper number 95 note H. E. Zimmerman and G. E. Keck, *J. Am. Chem. Soc.*, **97**, 3527 (1975).

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(7) For leading references note C. A. Grob, *Angew. Chem.*, **81**, 543 (1969).

(8) All new compounds which were thermally stable analyzed satisfactorily. Spectral and chromatographic data were used to ensure homogeneity of the azo compounds. Full synthetic and experimental detail will be presented in our full paper.

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(10) (a) H. E. Zimmerman, *J. Am. Chem. Soc.*, **88**, 1564 (1966); (b) *Acc. Chem. Res.*, **4**, 272 (1971).

(11) (a) H. E. Zimmerman and G. A. Epling, *J. Am. Chem. Soc.*, **94**, 3647, 8749 (1972). (b) J. Michl, *Mol. Photochem.*, **4**, 243, 257, 287 (1972). (c) This same point has been made recently by Salem.[11d] (d) L. Salem and C. Rowland, *Angew. Chem., Int. Ed. Engl.*, **11**, 92 (1972).

(12) H. E. Zimmerman, *Acc. Chem. Res.*, **5**, 393 (1972).

(13) As noted earlier by us,[10b] and most recently by Day,[14] the Hückel–Möbius and generalized Woodward–Hoffmann treatments[15] are perfectly analogous, since the number of sign inversions in a pericyclic transition state is simply equal to the number of antara components in the generalized Woodward–Hoffmann rule.

(14) A. C. Day, *J. Am. Chem. Soc.*, **97**, 2431 (1975).

(15) Reference 9, p 169.

(16) For a recent example of the nonphotochemical generation of rearranging excited states, note H. E. Zimmerman and G. E. Keck, *J. Am. Chem. Soc.*, **97**, 3527 (1975).

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Oxygenation of the Nitrosyl Ligand in Complexes of Iridium

Sir:

Synthetic and structural studies of metal-nitrosyl complexes have recently attracted considerable attention because of their importance in developing an understanding of reactions of small molecules which play significant roles in living systems or in industrial catalytic reactions. The chemical reactivity of the coordinated nitrosyl ligand depends on its mode of bonding.[1] While many complexes with linear M-N-O bonds and with ν(NO) usually greater than 1850 cm^{-1} react with nucleophiles such as OH$^-$ or N$_3^-$,[2] certain complexes with bent M-N-O bonds undergo electrophilic attack. These latter sparsely studied reactions include protonation[3] to form the coordinated nitroxyl (HNO) or hydroxylamine ligands and oxidation with nitric oxide[4] or dioxygen. In the presence of bases five-coordinate nitrosyl complexes can be oxygenated to form nitro complexes[5] or mixtures of nitro and nitrato complexes.[6,7] It has been suggested recently that ν(NO) may serve as a useful criterion for predicting whether oxygenation will give MNO$_2$ or MNO$_3$ products, namely, that complexes with low ν(NO) (1600-1710 cm^{-1}) give MNO$_2$ complexes, while complexes with ν(NO) at higher frequencies (1710-1765 cm^{-1}) give MNO$_3$ complexes.[6] Our observations indicate that ν(NO) is not a useful criterion.

Table I. Selected Infrared Spectral Data[a] (cm^{-1}) for Ir(PPh$_3$)$_2$(CO)ClX(NO) and Experimentally Observed Rate Constants for the Reaction Ir(PPh$_3$)$_2$(CO)ClX(NO) + O$_2$ → Ir(PPh$_3$)$_2$(CO)ClXNO$_3$ at 25°C and Partial Pressure of O$_2$ at 619 Torr

X	ν(CO)	ν(NO)	$10^3 k_{obsd}$, (sec^{-1})
I	2055	1550	184.
Br	2059, 2040 sh	1560, 1530	40.4
	2020,		
Cl[b,f]	2060, 2040 sh	1560, 1520	8.25
NCS[c]	2055	1545	6.68
NCO[d]	2040	1540	3.42
N$_3$[e]	2050	1540	1.59

[a] In KBr. [b] Bands in CH$_2$Cl$_2$ at 2057, 1535 cm^{-1}. [c] ν(NCS) at 2090 cm^{-1}. [d] ν(NCO) at 2225 cm^{-1}. [e] ν(N$_3$) at 2030 cm^{-1}. [f] ν(Ir–Cl) at 307 307 (w) and 200 (vw) cm^{-1}.

We report herein the synthesis of a new class of iridium nitrosyl complexes with NO stretching frequencies in the 1520-1560-cm^{-1} region (among the lowest yet reported for metal nitrosyls) and the oxygenation of these complexes exclusively to nitrato complexes.

The crystal structure of [Ir(PPh$_3$)$_2$(CO)(NO)Cl]BF$_4$ (**1**), determined by Ibers and Hodgson,[8] revealed the first example of a metal-nitrosyl complex with a bent M-N-O bond. Rather surprisingly reports on the reactions of **1** have not appeared. Compound **1** (previously reported as an 18-electron complex)[9] was carbonylated to give [Ir(PPh$_3$)$_2$(CO)$_2$Cl(NO)]BF$_4$ (**2**), a 1:1 electrolyte in nitromethane.[10] Compound **2** has ν(CO) at 2070, 2023, and 1980 cm^{-1}, ν(NO) at 1680 cm^{-1}, and ν(BF$_4$) at 1060 cm^{-1}.

Addition of solutions of LiCl or HCl in methanol to violet dichloromethane solutions of **1** gave immediate decoloration. Partial evaporation of solvent with a stream of nitrogen led to crystallization of yellow-green Ir(PPh$_3$)$_2$(CO)(NO)Cl$_2$. Other coordinating anions X$^-$ added as Li$^+$, Na$^+$, K$^+$, or NH$_4^+$ salts gave the products shown in Table I. These nitrosyl complexes, which are nonconducting in nitromethane, are soluble in benzene, chloroform, or dichloromethane and are only slightly soluble in methanol or hexane. The complexes are structurally analogous to the aryldiazo complexes, Ir(PPh$_3$)$_2$(CO)ClX(N$_2$Ar), reported by Haymore and Ibers.[11] Compared to the ν(NO) for **1** at 1700 cm^{-1}, the ν(NO) for the complexes Ir(PPh$_3$)$_2$(CO)ClX(NO) (**3**) are in the 1520-1560-cm^{-1} region.

Like other complexes formed by the addition of nucleophiles to five-coordinate Ir(III) complexes,[12] it is likely that **3** initially has an octahedral structure with the added ligand X trans to the trans directing NO$^-$ ligand and with PPh$_3$ ligands trans to each other. In an ionizing solvent, however, extensive rearrangement may be expected.[12e] The complexes have ν(CO) at 2050 ± 10 cm^{-1}.