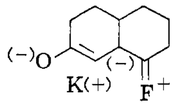
the rate of enolization by a factor of about 3 but reprotonation is slowed by a factor of 35. The forward rates, which involve axial proton loss in (1), (2), and (3), correspond to the anticipated inductive effect of fluorine *vs.* methyl; in the over-all reaction, it is apparent that the transition state in (3) reflects anion stability, while in (2) the reverse is true and the transition state must resemble the ketone.

A different pattern emerges with equatorial proton loss, as seen in the forward rates of the 6β-methyl (entry 8) and 6β-fluoro (entry 9) steroids. Either substituent increases the rate of enolization by a factor of about 10-fold relative to the unsubstituted steroid and, while k_f for 6β- and 6α-methyl are of the same magnitude, the rate of 6α-fluoro is 390× that of 6β-fluoro. As noted previously,[9] the 6β-methyl compound is highly unstable relative to the 6α isomer, and a close resemblance of the transition state in both cases to the common enolate anion would dictate a much faster enolization rate for the β-methyl isomer. The enhanced rate of (8) relative to the nonsubstituted compound may be due to a slight relief of strain in the transition state, or the diaxial 6β-19 methyl–methyl interaction may lead to deformation of the C-6 methylene in the ketonic ground state so that the 6α-proton is not strictly equatorial.

The 6β-fluoro rate increase of 13-fold is very likely primarily an inductive effect, although, as in (8), steric effects may play a small role. Since the over-all K_{eq} for anion formation must be even greater for the unstable isomers (8) and (9) than for the corresponding 6α-substituted compounds, it is clear from the small rate enhancement that the transition state of (9), in contrast to (3), cannot reflect the favorable free-energy factor for anion formation and must resemble the starting ketone. Yet, in enolization the inductive effect of either axial or equatorial fluorine must be essentially equal with respect to the departing proton; therefore, a resonance role must be invoked for fluorine that is operative in the transition state only when fluorine is equatorial. Such a contribution may be formally depicted as



which requires fluorine in the plane of ring B (equatorial) for continuous overlap. We believe the enhanced k_f of (3) relative to (9) and the shift toward enolate anion character in the transition state are due to this resonance contribution while a combination of this effect with inductive delocalization of charge explains the great stability of the fluoro enolate anion.

Enolate stabilization by the 6-methyl group may be attributed to hyperconjugation in common with the usual increased stability of a more substituted olefin. The failure to enhance k_f even with an equatorial methyl group in position for continuous participation may be a general phenomenon as evidenced by the equal enolization rates of nitromethane and nitroethane despite the much greater anion stability of the latter.[10] The parallel between anion stability and enolization rate with equatorial but not axial 6-fluoro suggests that *deviations from a free-energy relationship in other anionic systems* (in particular alicyclic) *containing strong electron-withdrawing groups such as halogen, double bond, nitrile, or carbonyl may be due to favored conformations that do not allow continuous participation of the resonating group.*

The important question of the direction of solvation of the potassium–oxygen ion pair and the extent of this interaction with adjacent methyl groups may be approached from the following observations. The 4-methyl group destabilizes the enolate anion by ~0.7 kcal (3-fold, entry (5)) while a 2α-methyl group (entry (6)) causes a 1.4 kcal destabilization. The equatorial 2α-methyl is essentially in the plane of oxygen in either the ketone or enolate anion; therefore, the effect of 1.4 kcal must arise completely as the result of a marked steric interaction between the solvated ion pair and that methyl group[11] (the electronic effect of methyl at C-2 should be negligible). With respect to the 4-methyl compound the decreased K_{eq} represents a summation of electronic and steric factors. If electronic stabilization of the double bond by methyl is more effective in the neutral unsaturated ketone than in the enolate anion, as appears most likely, the steric interaction of the 4-methyl with the ion pair must be less than 0.7 kcal. *This indicates that the steric requirement of the ion pair may be unsymmetrical about C-2 and C-4 with the greatest bulk directed away from the double bond and the C-4 position and toward C-2.*[12]

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[9] S. K. Malhotra and H. J. Ringold, *J. Am. Chem. Soc.*, **86**, 1997 (1964).

[10] R. G. Pearson and R. L. Dillon, *ibid.*, **75**, 2439 (1953).

[11] See also S. K. Malhotra and F. Johnson, *ibid.*, **87**, 5513 (1965).

[12] It should be noted that with *t*-butyl alcohol as solvent, the oxygen–potassium ion pair of the enolate is undissociated and the degree of negative charge on ring carbons may be minimal. Studies are in progress to determine if the same resonance and steric interaction effects pertain in dissociating solvent systems.

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Reversible Addition of Sulfur Dioxide to Four-Coordinated Metal Complexes[1]

Sir:

The discovery of a synthetic oxygen-carrying system[1b] has led us to a study of the factors which are responsible for reversible oxygenation of metal complexes, both synthetic and natural. A part of this program has been concerned with finding analogies for molecular oxygen in its reversible reaction with the square-planar iridium complex, *trans*-$[\mathrm{IrCl(CO)(Ph_3P)_2}]$.[1b,2] Thus, we have been searching for reactions of the latter with small molecules which would remain *undissociated* in their adducts with the metal complex. These investigations have produced reversible addition compounds of $[\mathrm{IrCl(CO)(Ph_3P)_2}]$ with ethylene,[3] carbon monoxide,[4] and sulfur dioxide, the subject of this paper.

Prior to this investigation, the only known complexes containing SO_2 as ligand were those of the ruthenium–

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[1] (a) Activation of Molecular Oxygen and Related Molecules by Transition Metal Complexes. II. (b) For part I, see L. Vaska, *Science*, **140**, 809 (1963).

[2] L. Vaska and J. W. DiLuzio, *J. Am. Chem. Soc.*, **83**, 2384 (1961).

[3] L. Vaska and R. E. Rhodes, *ibid.*, **87**, 4970 (1965).

[4] L. Vaska, submitted for publication.

ammine series reported by Gleu.[5] Accordingly, it was of interest to explore the reactions of sulfur dioxide also with other transition metal complexes.[6] Recently, a detailed structural and spectral study of the Ru–ammine–SO_2 complexes appeared,[7] establishing that the metal–SO_2 association occurs through sulfur. Two other recent communications, briefly describing two SO_2 derivatives of iron carbonyls,[8a] and a manganese–SO_2 complex,[8b] complete the presently available recorded data on sulfur dioxide complexes of transition metals.[9–11]

[(SO_2)IrCl(CO)(Ph_3P)$_2$]. Benzene or toluene solutions of the yellow complex, [IrCl(CO)(Ph_3P)$_2$], react almost instantly with gaseous SO_2 at 25° producing green solutions from which green crystals are deposited on standing. Best results are obtained when the preparation is carried out in an oxygen-free solution under a pressure of SO_2 in a closed system (*e.g.*, $[Ir] = 2 \times 10^{-2}\ M$ in toluene; p_{SO_2} 700 mm; 25°; 2 hr; 97% yield).

The green crystals of the 1:1 adduct are diamagnetic and stable in air. In benzene, the compound is monomeric. *Anal.* Calcd for $IrClSP_2C_{37}H_{30}O_3$: Ir, 22.8; Cl, 4.2; S, 3.8; P, 7.4; C, 52.6; H, 3.6; O, 5.7; mol wt, 844. Found: Ir, 22.8; Cl, 3.8; S, 3.5; P, 7.2; C, 52.4; H, 3.4; O, 5.7; mol wt, 890 ± 45. The infrared data are given in Tables I and II. The molecular structure of the complex has been recently determined by La Placa and Ibers: the SO_2 is bonded to the metal *via* sulfur which lies at the apex of a tetragonal pyramid.[12]

On heating, the SO_2 adduct loses sulfur dioxide and the complex is reverted to the starting material.

$$[IrCl(CO)(Ph_3P)_2] + SO_2 \underset{\Delta}{\rightleftarrows} [(SO_2)IrCl(CO)(Ph_3P)_2] \quad (1)$$

In toluene solution, enclosed in an atmosphere of SO_2, the reversibility of (1) is evidenced by the color changes which occur when the solution is alternately heated (>100°, green → yellow) and cooled (by removing the heat, yellow → green). In the absence of sulfur dioxide, *e.g.*, by dissolving the SO_2 adduct in boiling benzene (in air), the reverse reaction can be demonstrated by recovering and identifying the starting material. Crystals of [(SO_2)IrCl(CO)(Ph_3P)$_2$] liberate SO_2 on heating above 150°.

[(SO_2)RhCl(CO)(Ph_3P)$_2$]. The univalent rhodium complex, *trans*-[RhCl(CO)(Ph_3P)$_2$], isostructural with [IrCl(CO)(Ph_3P)$_2$],[2,3] reacts with SO_2 in solution to give a yellowish green 1:1 adduct which is isostructural with the corresponding adduct of iridium according to the X-ray diffraction patterns and the infrared spectra (Table I) of the two complexes. [(SO_2)RhCl(CO)-(Ph_3P)$_2$] has been characterized by complete elemental analysis, and its other properties are, in general, similar to those described above for the iridium analog.[13]

Table I. Vibrational Frequencies (cm^{-1}) of the SO_2 Ligand in Metal Complexes[a]

Compound	ν_1 (sym str)	ν_3 (asym str)	ν_2 (bend)	Ref
SO_2 solid	1147	1330, 1308	521	15
[RuCl(SO_2)(NH_3)$_4$]Cl	1100	1301, 1278	552	7
[Mn(C_5H_5)(SO_2)(CO_2]^b		1282		8b
[RhCl(SO_2)(CO)(Ph_3P)$_2$]	1057	1214, 1188		This work
[IrCl(SO_2)(CO)(Ph_3P)$_2$]	1048	1198, 1185	559	This work
[Fe_2(SO_2)(CO)$_8$]	1048	1209		8a

[a] Crystals in mull or KBr. [b] In benzene. All ν_1 and ν_3 are strong; ν_2 are medium.

Infrared Spectra and Bonding. The vibrational frequencies of the coordinated SO_2 ligand in the Ir and Rh adducts are listed in Table I, together with those of sulfur dioxide[15] and the SO_2 groups in three complexes reported previously.[7,8]

The sulfur in SO_2 may be regarded as a poor σ donor and as a moderate π acceptor through the availability of empty $d\pi$ (or antibonding $p\pi$) orbitals, a situation which is somewhat analogous to that in carbon monoxide. By analogy with carbonyl complexes,[16] we would expect the S–O stretching frequencies to decrease as the extent of π-electron donation from the metal to the SO_2 group increases. In other words, a lower oxidation state and/or a lower coordination number of the central metal atom imply a lower S–O bond order. Examination of the data in Table I shows that this trend is indeed evident.[17]

Further information about the nature of the sulfur dioxide complexes is obtained from the carbonyl stretching frequencies in the various adducts of [IrCl-(CO)(Ph_3P)$_2$] listed in Table II.[18] It is seen that the addition of SO_2 shifts the ν_{CO} to a higher frequency. Similar shifts are observed with other addenda, and the $\Delta\nu_{CO}$ can be interpreted as a reflection of the extent of oxidation of the univalent complex.[19] Accordingly, [(SO_2)IrCl(CO)(Ph_3P)$_2$] may formally be regarded as a sulfoxylo (SO_2^{2-}) complex of Ir(III) or, perhaps more correctly, as an Ir(II) compound containing formally SO_2^-.[21,22]

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(5) (a) K. Gleu and K. Rehm, *Z. Anorg. Allgem. Chem.*, **227**, 237 (1936); (b) K. Gleu, W. Breuel, and K. Rehm, *ibid.*, **235**, 201, 211 (1938).

(6) The reactions of SO_2 with some complexes of ruthenium, osmium, palladium, and platinum will be reported in a later article.

(7) (a) L. H. Vogt, Jr., Ph.D. Thesis, Rensselaer Polytechnic Institute, Troy, N. Y., 1964; (b) L. H. Vogt, Jr., J. L. Katz, and S. E. Wiberly, *Inorg. Chem.*, **4**, 1157 (1965).

(8) (a) E. H. Braye and W. Hübel, *Angew. Chem.*, **75**, 345 (1963); (b) W. Strohmeier and J. F. Guttenberger, *Chem. Ber.*, **97**, 1871 (1964).

(9) Titanium and zirconium tetrachlorides are reported to form SO_2 adducts or solvates, $2TiCl_4 \cdot SO_2$ and $ZrCl_4 \cdot SO_2$, but it is not known whether or not the metal is associated with the SO_2 group; see ref 10.

(10) T. C. Waddington in "Non-Aqueous Solvents," T. C. Waddington, Ed., Academic Press, Inc., New York, N. Y., 1965, pp 253–284.

(11) We cite here only the cases in which the SO_2 ligand is bonded to the transition metal and to no other atom or group; for an interesting SO_2 insertion reaction, see J. P. Bibler and A. Wojcicki, *J. Am. Chem. Soc.*, **86**, 5051 (1964).

(12) S. J. La Placa and J. A. Ibers, *Inorg. Chem.*, 5, 405 (1966).

(13) The formation of the Rh–SO_2 adduct is slower, however, and it dissociates more readily than the Ir complex. These observations agree with the established trend that the Rh(I) complexes are more stable toward oxidative additions than the corresponding compounds of Ir(I).[3,14]

(14) Unpublished results.

(15) R. N. Wiener and E. R. Nixon, *J. Chem. Phys.*, **25**, 175 (1956).

(16) See, for example, L. E. Orgel, *Inorg. Chem.*, **1**, 25 (1962).

(17) A full discussion of the vibrational spectra of these and other SO_2 complexes in relation to their structures will be given elsewhere.[6]

(18) An analogous but less extensive list is available for the adducts of [RhCl(CO)(Ph_3P)$_2$]; the interpretation is the same as cited for the iridium case. The ν_{CO} in the Rh–SO_2 adduct is 2034 cm^{-1}.

(19) This interpretation, cited previously,[1b,2,20] and based on the data on several dozens of adducts of [IrCl(CO)(Ph_3P)$_2$], will be elaborated in a future article.

(20) L. Vaska and J. W. DiLuzio, *J. Am. Chem. Soc.*, **84**, 679 (1962).

(21) In this case, the observed diamagnetism would result from pairing the unpaired spin of SO_2^- with that of Ir(II) of d^7 configuration.

Table II. Carbonyl Stretching Frequencies (cm^{-1}) in Iridium Complexes[a]

L in [(L)IrCl(CO)(Ph$_3$P)$_2$]	ν_{CO}
. . .	1956
O$_2$	2000
D$_2$	2003
H$_2$S	2013
SO$_2$	2020
HCl	2024
CH$_3$I	2054
I$_2$	2065
Br$_2$	2075
Cl$_2$	2078

[a] Crystals in Nujol or halocarbon mull.

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(22) NOTE ADDED IN PROOF. A recent paper describes a novel type SO$_2$ complex, a dimeric SO$_2$-bridged cobalt compound, K$_6$[(CN)$_5$Co-(SO$_2$)Co(CN)$_5$], which points to a further analogy between SO$_2$ and CO complexes of transition metals: A. A. Vlček and F. Basolo, *Inorg. Chem.*, 5, 156 (1966).

(23) Deceased Oct 4, 1962.

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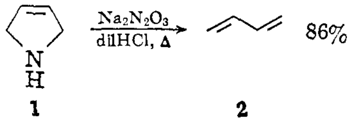
Dienes from 3-Pyrrolines.
A Stereospecific Deamination

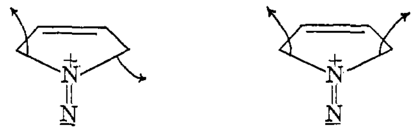
Sir:

We wish to report that dienes are generated in high yield from 3-pyrrolines by treatment with nitrohydroxylamine, as illustrated by the prototype **1** → **2**. The availability of 3-pyrrolines from pyrroles makes this reaction potentially useful from a synthetic viewpoint, particularly because it proceeds with *complete stereospecificity.*



1 **2**

Concerted fragmentation of the five-membered ring might occur either with conrotation or with disrotation[1] of the ends of the developing diene system.[2] In Figure 1 these alternatives are illustrated for the presumed diazene intermediate[3] from 3-pyrroline. Since the process on the left (during which the entire molecule becomes twisted) is at every stage characterized by a twofold axis of symmetry and the right-hand process by a plane of symmetry, we choose to describe them as "axisymmetric" and "sigmasymmetric," respectively.[4]

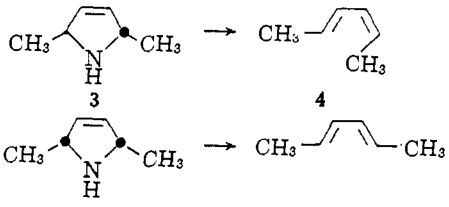


axisymmetric sigmasymmetric

Figure 1. Possible fragmentation modes in 3-pyrroline deamination.

To distinguish between these possibilities it was necessary to obtain 2,5-disubstituted 3-pyrrolines of known stereochemistry. Thus the dimethyl derivative was prepared by zinc–hydrochloric acid reduction of 2,5-dimethylpyrrole.[5] Reported to be pure *trans*-2,5-dimethyl-3-pyrroline, the Δ^3 fraction of the product was shown in this laboratory to be a 1:3.5 *cis*:*trans* mixture.[6] The isomers were separated by fractional crystallization of their *p*-toluenesulfonamides and recovered by reductive cleavage with sodium in liquid ammonia.[7]

Deaminated in the manner described for **1**, *trans*-2,5-dimethyl-3-pyrroline (**3**) yielded *cis,trans*-2,4-hexadiene (**4**) and the *cis*-pyrroline **5** gave *trans,trans*-2,4-hexadiene (**6**); in neither experiment were traces of the other geometrical isomers detectable by vapor chromatography. *Hence both fragmentations occurred in the sigmasymmetric fashion.* Though in principle the *cis*-pyrroline was subject to a second sigmasymmetric mode of decomposition leading to *cis,cis*-2,4-hexadiene, the nonoccurrence of this process is not surprising in light of the severe methyl–methyl repulsion it would have entailed.



3 **4**
5 **6**

Woodward and Hoffmann's beautiful and far-reaching theory[1,8] regarding the influence of orbital symmetries over the course of organic reactions can be brought to bear on the present problem. Figures 2 and 3 are orbital correlation diagrams corresponding respectively to axisymmetric and sigmasymmetric decomposition of the diazene from 3-pyrroline.[9] Correlation of a bonding with an antibonding orbital characterizes the former, but not the latter process. Thus sigmasymmetric fragmentation should occur, in harmony with experiment.[10–12]

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(1) R. B. Woodward and R. Hoffmann, *J. Am. Chem. Soc.*, **87**, 395 (1965).

(2) The literature on fragmentations related to **1** → **2** appears to be contradictory regarding the question of stereochemistry (*cf.* the discussion of this point by L. A. Carpino, *ibid.*, **84**, 2196 (1962)).

(3) D. M. Lemal and T. W. Rave, *ibid.*, **87**, 393 (1965).

(4) The terms "conrotatory" and "disrotatory," which aptly describe electrocyclic processes, would lose clarity if applied indiscriminately to fragmentation or cycloaddition reactions (particularly in cases more complex than the present one). "Axisymmetric" and "sigmasymmetric" are intended to describe *any* concerted reaction whose transition state possesses a twofold (or higher) axis or mirror plane, respectively. *Cf.* the less restrictive definition of the former term in Webster's Third New International Dictionary, G. and C. Merriam Co., Springfield, Mass., 1961.

(5) G. G. Evans, *J. Am. Chem. Soc.*, **73**, 5230 (1951).

(6) The nmr spectrum (D$_2$O) of the 3-pyrroline, free of double bond isomers, displayed a *pair* of doublets in the methyl region. Hydrogenation of this liquid over Adams catalyst in acetic acid gave a product resolvable into two peaks by vapor chromatography (though the 3-pyrrolines themselves were not separable on any of a variety of columns); the retention time of the minor component matched that of *cis*-2,5-dimethylpyrrolidine.[5]

(7) I. Photaki and V. du Vigneaud, *J. Am. Chem. Soc.*, **87**, 908 (1965), and references contained therein.

(8) R. Hoffmann and R. B. Woodward, *ibid.*, **87**, 2046, 4388, 4389 (1965); R. B. Woodward and R. Hoffmann, *ibid.*, **87**, 2511 (1965).

(9) Though the arrangement of orbital energy levels is only approximate, neither refinement of their spacing nor changes in the assumed hybridizations at nitrogen alter the argument based on Figures 2 and 3.

(10) The same theoretical conclusion was reached independently by Hoffmann and Woodward, who have derived selection rules for fragmentations of this type (Abstracts, 150th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 1965, p 8S).