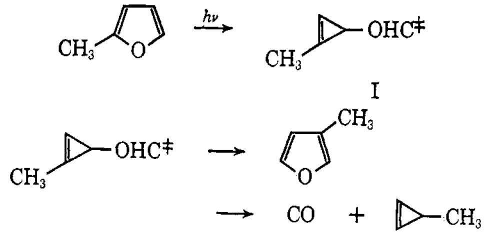
chromatographic column with those of an authentic sample.[7]

Hg($^3P_1$) sensitization of 3-methylfuran[8] led to decarbonylation ($\Phi_{CO} = 1.0 \pm 0.1$) as the only observable process. The cyclopropene that was formed in this instance was entirely 1-methylcyclopropene. Hg($^3P_1$) sensitization of 2-methyl-4,5-dihydrofuran gave methyl cyclopropyl ketone and other photoproducts derived from it by secondary processes.[9] The maximum quantum yield for the disappearance of 2-methyl-4,5-dihydrofuran was nearly unity. Irradiation or photosensitization of methyl cyclopropyl ketone gave no detectable yield of 2-methyl-4,5-dihydrofuran.[10]

The results of the decarbonylation process in furans can be shown to be consistent with the results of the isomerization reaction if it is postulated that the same cyclopropenecarboxaldehyde acts as the intermediate for both reactions. From 2-methylfuran, the intermediate is presumably I. The sum of the quantum yields for reactions 2b and 2c accounts for 80% of the photons that were absorbed. It follows that the reverse of reaction 2a cannot involve more than 20% of the excited molecules. *The reversal of reaction 2a that is considered here, as well as the transformation of I to 3-methylfuran, are processes which involve the carry-over of energy from the initial photochemical ring contraction.* The possibility that either of these reactions involves the absorption of a second photon can be excluded since the steady-state concentration of the cyclopropenecarboxaldehydes in any of these systems is below the limit of detectability by infrared spectroscopy (0.01% of the furan present). At the low conversions that were used in this study, less than 1 photon in 10,000 would have been available to sensitize or excite the intermediate. It is noteworthy too that the scission of the ring in 2-methylfuran does not occur to a significant extent between the oxygen and C-5. Such an isomerization would have given a ketone which would have been detected.[11]



(2a)

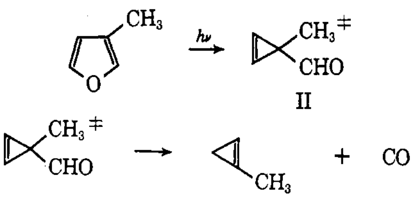
I

(2b)

(2c)

The photointermediate from 3-methylfuran can only be II as the alternative ring-contraction path would lead to I, which presumably would give only 3-methylcyclopropene. The fact that Φ_{CO} has a maximum value of unity when Hg($^3P_1$) was used as a sensitizer indicates that reaction 3a is not a reversible process (as defined above) under the present conditions.

In 2-methyl-4,5-dihydrofuran, the ring-contraction reaction gives an isolable product. Since the initially absorbed photons were wholly accounted for, this ring-contraction reaction evidently does not proceed reversibly, nor does the ring-contracted product revert to 2-methyl-4,5-dihydrofuran by a photochemical process.[12]



(3a)

II

(3b)

These data show that the alkylfurans studied here undergo both photochemical valence tautomerization and decarbonylation in the gas phase. The primary ring contraction takes place in a specific direction, presumably due to the directive influence of the methyl substituent. The carry-over of the initial excitation energy causes the intermediate carbonyl compound to revert to the furan ring system with a low efficiency, again in a specific way (2-alkyl to 3-alkyl, but not *vice versa*).

Many of the features of the photorearrangements of the furans seem to be present in the thiophenes although, as already noted, there is no compelling evidence to show that they are wholly related. The photoreactions of 3,5-diphenylisoxazole appear to be unique in that (i) the initial ring contraction is photochemically reversible and the transformation from isoxazole → intermediate → oxazole or isoxazole requires two photons, (ii) the presence of two distinct chromophores (*i.e.*, isoxazole and phenyl) complicates the interpretation of the photoprocess as pointed out by Ullman and Singh,[5] and (iii) the net photoisomerization reaction leads to the preferential migration of an aryl group from the 3 to the 2 position, emphasizing the strong influence of the nitrogen atom in the ring.

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(8) The authors thank Dr. D. M. Burness of the Eastman Kodak Co. for a generous sample of 3-methyl-2-furoic acid from which the 3-methylfuran was prepared.

(9) It is believed that the secondary products were formed from a "hot" methyl cyclopropyl ketone molecule that was the primary product. A detailed report of the photochemistry of this system, as well as of methylcyclopropyl ketone,[10] will be published elsewhere.

(10) I. Haller and R. Srinivasan, unpublished work.

(11) Thus, in the sensitized photolysis of 2,5-dimethylfuran, the formation of 2-methylcyclopropenyl methyl ketone by a ring contraction has been reported (ref 1, p 4813, footnote 7).

(12) A referee has put forward the point of view that "the failure of methyl cyclopropyl ketone to ring expand photochemically appears to have no bearing on the question of possible ring expansion of vibrationally excited cyclopropenecarboxaldehyde." While we do not necessarily disagree, we wished to see if a parallel existed between the 2,3-dihydrofuran–cyclopropylcarboxaldehyde system and the isoelectronic cyclopentene–vinylcyclopropane system. The thermal and photochemical relationships that have been observed[13,14] in the latter case are well known.

(13) W. A. Gibbons, W. F. Allen, and H. E. Gunning, *Can. J. Chem.*, **40**, 568 (1962).

(14) M. C. Flowers and H. M. Frey, *J. Chem. Soc.*, 3574 (1961).

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Stereospecific Interconversions of Optically Active Sulfoxides, Sulfilimines, and Sulfoximines[1]

Sir:

A previous paper[2] reported the stereospecific interconversions of sulfoxide (+)-I and sulfilimine (−)-II. The reaction (+)-I → (−)-II was found to occur with 98% and of (−)-II → (+)-I with 96% stereospecificity and inversion of configuration at sulfur. That (+)-I and (−)-II had opposite configurations at sulfur was

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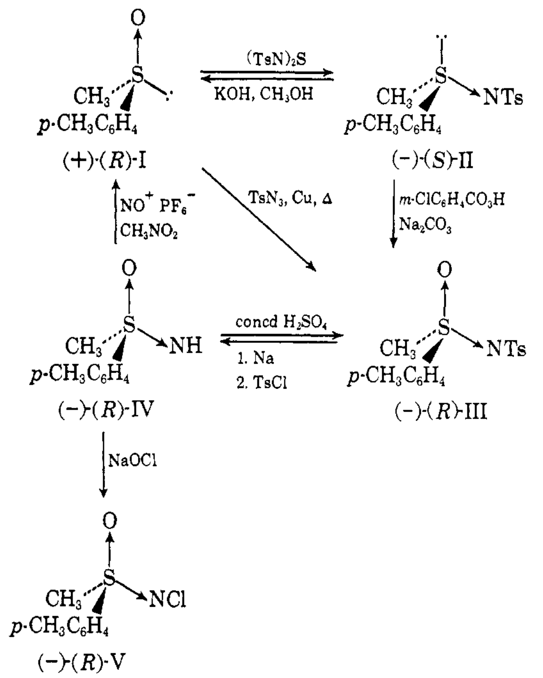
(1) This investigation was supported by U. S. Public Health Service Research Grant No. GM 12640-04 from the Department of Health, Education, and Welfare.

(2) J. Day and D. J. Cram, *J. Am. Chem. Soc.*, **87**, 4398 (1965).

suggested by the opposite signs of the Cotton effects in their similarly shaped optical rotatory dispersion (ORD) spectra. Since (+)-I possesses an *R* configuration,[3] (−)-II was assigned the *S* configuration.[2] We now wish to report the interconversions of the sulfoxide, sulfilimine, and sulfoximines formulated. These transformations can be made to go with high stereospecificity, and they complete three new cycles of reactions useful in establishing configurational relationships and preparing optically active derivatives of sulfur.



In the conversion of (+)-(*R*)-I to (−)-(*S*)-II, substitution of N,N′-bis(*p*-toluenesulfonyl)sulfodiimide[4] for the N-sulfinyl-*p*-toluenesulfonamide used previously[2] gave under the same reaction conditions the same result. Oxidation of sulfilimine (−)-(*S*)-II of maximum rotation with *m*-chloroperbenzoic acid in the presence of sodium carbonate in acetone at 25° (24 hr) gave after chromatography of the products on silica gel (ether–pentane) a 55% yield of nonfractionally crystallized sulfoximine, (−)-(*R*)-III, $[\alpha]^{25}_{546}$ −168.5° (*c* 0.80, acetone), which after repeated recrystallization from dichloromethane–ether gave product, $[\alpha]^{25}_{546}$ −172.5° (*c* 0.80, acetone), mp 159.0–160.5°.[5,6] Nitrenation (no mechanism implied) of sulfoxide (+)-(*R*)-I of maximum rotation with tosyl azide and freshly prepared copper powder in refluxing methanol (until nitrogen evolution stopped) by the Kwart–Khan method[7] gave after chromatography on silica gel (ether) 38–65% yields of nonfractionally crystallized (−)-(*R*)-III, $[\alpha]^{25}_{546}$ −165.6° (*c* 0.80, acetone). The material of $[\alpha]^{25}_{546}$ −172.5° (*c* 0.80, acetone) was demonstrated to be essentially optically pure (see below), and hence the oxidation was 98% and the nitrenation was 96% stereospecific. The ORD spectrum of (−)-(*R*)-III in ethanol gave principle maxima at 239 mμ ($[\phi]$ −47,500°) and 226.5 mμ ($[\phi]$ +54,900°), and $[\phi]$ was zero at 233 and 216 mμ. The curve resembles more that of sulfilimine (−)-(*S*)-II rather than that of sulfoxide (+)-(*R*)-I, as expected. This cycle of transformations formally demonstrates that, of the three reactions I → II (or II → I), II → III, and I → III, one must occur with inversion and the other two with retention, or all three must go with inversion. Since II → III and I → III are both electrophilic substitution reactions and reflect attack on the electron pair of sulfur, these transformations very probably occur with retention. This conclusion is compatible with that reached from ORD comparisons. Thus, reactions I ⇄ II go with inversion of configuration, and this deduction is compatible with the nucleophilic character of the substitutions at sulfur.

The second cycle of reactions involved III ⇄ IV. Treatment of (−)-(*R*)-III of maximum rotation with concentrated sulfuric acid[8] for 15 min at 25° gave a colorless solution which was dissolved in water and taken to pH 9. The solution was extracted with chloroform, and the chloroform was evaporated to give in nearly quantitative yield (−)-(*R*)-IV, $[\alpha]^{25}_{546}$ −38.5° (*c* 1.58, acetone), mp 55–59°. Recrystallization of this material from methylene dichloride–hexane gave essentially optically pure (−)-(*R*)-IV,[5] $[\alpha]^{25}_{546}$ −39.9° (*c* 1.03, acetone), mp 57–59°. This compound in ethanol gave an ORD spectrum with maxima at 275 ($[\phi]$ +292°), 271 (−250°), 268 (−125°), 263 (−584°), 261 (−533°), and 256 mμ (−790°), and $[\phi]$ was zero at 281 and 273 mμ. Treatment of (−)-(*R*)-IV of maximum rotation with sodium in refluxing benzene followed by tosyl chloride gave after chromatography on silica gel (benzene–ether) a 62% yield of nonfractionally crystallized (−)-(*R*)-III, $[\alpha]^{25}_{546}$ −166.3°, 96% optically pure. The nmr and ir spectra of this material were identical in detail with those of an authentic sample.[9] Since neither of these two reactions involves substitution at sulfur, the configuration was undoubtedly preserved.

The third cycle of transformations was completed by conversion of sulfoximine (−)-(*R*)-IV to sulfoxide (+)-(*R*)-I by a new reaction. Treatment of (−)-(*R*)-IV of 98% optical purity with 1 equiv of nitrosyl hexafluorophosphate in nitromethane for 5 min at 25° resulted in an exothermic, gas-producing (probably nitrous oxide) reaction.[10] The solution was mixed with dilute sodium bicarbonate and extracted with chloroform, and the resulting sulfoxide was chromatographed on silica gel (benzene–ether) to a give a 20% yield (not maximized) of (+)-(*R*)-I, $[\alpha]^{25}_{546}$ +175.0° (*c* 1.145, acetone), mp 71–75° (nonfractionally crystallized material). This reaction occurred with at least 98% stereospecificity and completes a link in the chain of reactions (+)-I → (−)-III → (−)-IV → (+)-I. Since the maxi-

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[3] K. Mislow, M. M. Green, P. Laur, J. T. Melillo, T. Simmons, and A. L. Ternay, Jr., *J. Am. Chem. Soc.*, **87**, 1958 (1965)

[4] W. Wucherpfennig and G. Kresze, *Tetrahedron Letters*, 1671 (1966).

[5] All new compounds gave elemental analyses within 0.3% of theory and nmr spectra compatible with the assigned structures.

[6] Optically active sulfilimines previously have been oxidized to active sulfoximines with potassium permanganate [G. Kresze and B. Wustrow, *Chem. Ber.*, **95**, 2652 (1962)]. The same workers also observed that this reagent oxidized aromatic methyl groups.

[7] H. Kwart and A. A. Khan, *J. Am. Chem. Soc.*, **89**, 1950 (1967), prepared N-benzenesulfonyl-S,S-dimethylsulfoximine.

[8] H. R. Bentley and J. K. Whitehead, *J. Chem. Soc.*, 2081 (1950), first reported hydrolysis of N-arenesulfonylsulfoximines to give sulfoximines.

[9] J. K. Whitehead and H. R. Bentley, *ibid.*, 1572 (1952), first used this procedure for conversion of S,S-dimethylsulfoximine into N-toluenesulfonyl-S,S-dimethylsulfoximine.

[10] Nitrous oxide has been postulated as leaving group in the thermal decomposition of N-nitrosoaziridines; see W. Rundel and E. Müller, *Chem. Ber.*, **96**, 2528 (1963), and R. D. Clark and G. K. Helmkamp, *J. Org. Chem.*, **29**, 1316 (1964).

mum rotation of (+)-I is known, the maximum rotations of (−)-III and (−)-IV are known, and the stereospecificity of each reaction can be inferred. The conversion of (−)-IV to (+)-I must have followed the same stereochemical course as was observed for the nitrenation reaction of (+)-I to give (−)-III. Since (−)-IV → (+)-I involves substitution at nitrogen and not at sulfur, it very likely proceeds with retention of configuration at sulfur and provides one more piece of interlocking evidence for the configurational assignments to compounds and stereochemical paths for their interconversions.

The discovery of the reaction (−)-(*R*)-IV → (+)-(*R*)-I provides a convenient route for the preparation of optically active sulfoxides not available through the usual Grignard synthesis or the platinium complex resolution.[11] Racemic sulfoxides can be readily converted in good yield by treatment with hydrazoic acid[12] into sulfoximines which in turn are basic enough to be resolvable as salts of optically active sulfonic acids.[13] Finally, optically active sulfoximines can be converted stereospecifically to optically active sulfoxides.

Another reaction broadens the use of optically active sulfoximines as interesting reaction intermediates. Treatment of sulfoximine (−)-(*R*)-IV in aqueous solution with 1 equiv of cold sodium hypochlorite gave (−)-(*R*)-V as an oily precipitate which was extracted with chloroform. The organic layer was dried and evaporated to give (−)-(*R*)-V in 60% yield, mp 66–68.5°, $[\alpha]^{25}{}_{546}$ −266° (*c* 1.35, acetone), which when recrystallized from ether–hexane gave mp 67.5–68.5°, $[\alpha]^{25}{}_{546}$ −264.4° (*c* 0.63, acetone).[5,14] A final recrystallization from acetone did not alter the physical constants. The stability of the sulfoximine group, coupled with the fact that both N-metallo and N-chloro derivatives are readily prepared, suggests that these substances can be used to prepare a large variety of compounds by electrophilic or nucleophilic substitution on nitrogen. Such possibilities are being actively explored.

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(11) A. C. Cope and E. A. Caress, *J. Am. Chem. Soc.*, **88**, 1711 (1966).

(12) (a) J. K. Whitehead and H. R. Bentley, *J. Chem. Soc.*, 1572 (1952); (b) F. Misani, T. W. Fair, and L. Reiner, *J. Am. Chem. Soc.*, **73**, 459 (1951).

(13) R. Fusco and F. Tenconi, *Chim. Ind.* (Milan), **47**, 61 (1965); *Chem. Abstr.*, **62**, 10357*h* (1965).

(14) The authors have not found any examples of N-chlorosulfoximines in the literature, but note that N-bromo-S,S-dimethylsulfoximine has been prepared by direct bromination [see R. Appel, H. W. Fehlhaber, D. Hänssgen, and R. Schöllhorn, *Chem. Ber.*, **99**, 3108 (1966)].

(15) National Institutes of Health Postdoctoral Fellow, University of California at Los Angeles, 1966–1967.

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The Induced Oxidation of Cobalt(II) Mesoporphyrin IX Dimethyl Ester by Unsaturated Hydrocarbons[1]

Sir:

We wish to report the induced oxidation of cobalt(II) mesoporphyrin IX dimethyl ester, Co(II)MPIXDME, by unsaturated hydrocarbons. Addition of unsaturated hydrocarbons to a freshly prepared solution of Co(II)MPIXDME in various organic solvents results in an immediate shift of the Soret band from 393 to 411 mμ due respectively to Co(II)- and Co(III)MPIXDME.[2–4] The metal oxidation is followed by porphyrin degradation. Similar results have been obtained which show that Fe(II) in hemoglobin also undergoes oxidation with subsequent porphyrin degradation.[5]

The initial step in the reaction sequence, however, is olefin to metal coordination as shown by the isomerization of *cis*-2-butene to *trans*-2-butene by Co(II)-MPIXDME.[6] Co(II)MPIXDME has a d^7 electron configuration and is square planar. Olefin complexation along the coordinately unsaturated *z* axis leads to a d^7 octahedral structure which eventually undergoes oxidation to form the d^6 octahedral Co(III)MPIXDME.[7] This coordination is probably π-complex formation[8] between the olefin and Co(II)MPIXDME without cobalt oxidation.[9] Examples of this type of nonoxidative olefinic–metal coordination are known.[10]

The unsaturated hydrocarbons which induce the oxidation of Co(II)MPIXDME in chloroform are categorized into two classes. Class I hydrocarbons, which cause an immediate spectral shift, consist of unsaturated hydrocarbons with an isolated double or triple bond such as cyclohexene, 1-heptene, 1-pentene, 1-hexyne, 1-octyne, and 1,5- and 1,3-cyclooctadienes. Class II hydrocarbons, which cause a slow spectral shift, consist of unsaturated hydrocarbons with conjugated double or triple bonds such as diphenylacetylene, stilbene, 1,4-diphenyl-1,3-butadiene, acrylonitrile, and fumaric and maleic acids. Conjugated systems are less reactive due probably to resonance energy considerations which lead

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(1) Presented in part at the Xth International Conference on Coordination Compounds, Nikko, Japan, Sept 1967.

(2) The Soret band is a very intense absorption found in highly conjugated pyrrole-type systems. The position of the Soret band is dependent upon metal oxidation states: J. E. Falk, "Porphyrins and Metalloporphyrins," Elsevier Publishing Co., New York, N. Y., 1964; D. G. Whitten, E. W. Baker, and A. H. Corwin, *J. Org. Chem.*, **28**, 2363 (1963). We have reconfirmed cobalt oxidation by magnetic susceptibility measurements. The oxidation reactions were also carried out in an inert atmosphere and in oxygen- and air-saturated solutions as well as under usual atmospheric reaction conditions. These reactions were carried out in darkness, in the Cary spectrophotometer cell block, and in light (natural and fluorescent), and in various solvents such as benzene, ethyl acetate, thiophene, chloroform, ethanol, and methanol. Under all conditions, no immediate oxidation occurred unless unsaturated hydrocarbons were added.

(3) J. F. Taylor, *J. Biol. Chem.*, **135**, 569 (1940).

(4) V. Caglioti, P. Silvestroni, and C. Furlani, *J. Inorg. Nucl. Chem.*, **13**, 95 (1960).

(5) M. Tsutsui, K. Suzuki, J. Sadai, and R. Velapoldi, to be published.

(6) *cis*- and *trans*-2-butenes in a chloroform solution of Co(II)-MPIXDME and in chloroform were allowed to stand for several hours at room temperature in sealed capsules. Butene analyses were carried out using a Perkin-Elmer Model 54GC with an ethyl malonate on Chromosorb P column. No *trans* to *cis* isomerization was observed. This stereospecificity is not unexpected and only verifies the fact that *cis*-2-butene is not as sterically hindered in complexing with Co(II)-MPIXDME as the *trans* isomer. No isomerizations were observed in the blank runs. The usual Soret band shift was observed in the *cis*–*trans* isomerization.

(7) The crystal-field stabilization energies for d^7 octahedral structures are only slightly below those for d^7 square planar with ligands of strong ligand fields. Square-planar to octahedral structural conversions are common using a d^7 square-pyramidal structure as an intermediate: F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1958, pp 57, 203; J. M. Pratt and R. J. P. Williams, *J. Chem. Soc., Sect. A*, 1291 (1967).

(8) J. Chatt and L. A. Duncanson, *J. Chem. Soc.*, 2939 (1953).

(9) Co(II)MPIXDME dissolved in purified cyclohexene is stable and is not oxidized to Co(III)MPIXDME.

(10) E. O. Fischer and H. Werner, "Metal π-Complexes," Vol. I, Elsevier Publishing Co., New York, N. Y., 1966; J. Halpern, *Ann. Rev. Phys. Chem.*, **16**, 103 (1965); M. A. Bennett, *Chem. Rev.*, **62**, 611 (1962); D. N. Lawson, J. A. Gibson, and G. Wilkinson, *J. Chem. Soc., Sect. A*, 1733 (1966).