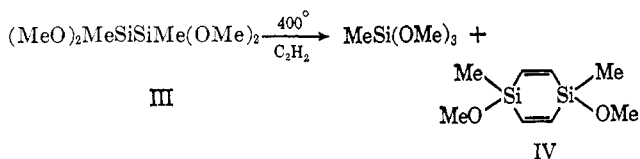


cal anion, IIa is not stable at room temperature. Disproportionation may be occurring to give the dianion of Ia. We are presently searching for evidence for the formation of this dianion.

Octamethyl-1,4-disilacyclohexadiene gives a small concentration of IID with difficulty. A partially resolved spectrum of 11 multiplets split into 9 lines has been resolved to date. The hfs is 5.32 and 0.18 G which is assigned to the C-Me and Si-Me hydrogens, respectively. The tetraethyl derivative Ic gives a spectrum of nine broad lines which is consistent with coupling to eight methylene protons (hfs 1.93 G). The tetraphenyl derivative Ib is easily reduced, presumably to the dianion. Only an unresolved singlet has been obtained to date with Ib.

All spectra were obtained in DME at Dry Ice-acetone temperatures and are due to the free ions. Further studies on the structure of the ion pairs^{1a} are in progress.

Vapor-phase (400°) thermolysis of *sym*-dimethyltetramethoxydisilane (III)¹² in the presence of excess acetylene gave the disilacyclohexadiene IV (60%, bp



100–101° (40 mm)) as a single isomer (SiOMe, SiMe, and -CH at 6.63, 9.85, and 3.08, respectively). *Anal.* Calcd for C₈H₁₆O₂Si₂: C, 48.0; H, 8.00; Si, 28.0; mol wt, 200. Found: C, 47.3, 47.8; H, 7.94, 8.17; Si, 28.1, 28.1; mol wt, 200 (mass spectrometry).

Treatment of IV with ethereal MeMgBr gave Ia, bp 158–159° (SiMe and -CH at τ 9.90 and 3.16, respectively). *Anal.* Calcd for C₈H₁₆Si₂: C, 57.2; H, 9.52; Si, 33.3; mol wt, 168. Found: C, 57.2, 57.1; H, 9.62, 9.95; Si, 33.3, 33.5; mol wt, 168 (mass spectrometry). Compounds Ic (bp 170–172° (40 mm)) and Id (mp 71–72.5°) were prepared by the general procedure previously described¹² for Ib.

cation of benzene actually should be compared to IIa, but this radical is unknown. However, the theoretical spin density distribution is identical in the radical anion and cation.

(12) (a) W. H. Atwell and D. R. Weyenberg, *J. Organometal. Chem.* (Amsterdam), **5**, 594 (1966); (b) *Chem. Eng. News*, 30 (Sept 4, 1967).

Edward G. Janzen, John B. Pickett
Department of Chemistry, University of Georgia
Athens, Georgia 30601

William H. Atwell
Organometallic Research Laboratory
Dow Corning Corporation, Midland, Michigan 48640
Received March 12, 1968

Photoisomerization of 2-Alkylfurans to 3-Alkylfurans

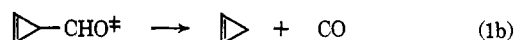
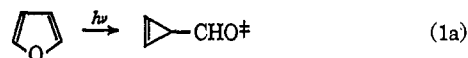
Sir:

In our earlier work on the photochemistry of furan, we had shown that in the vapor phase, on sensitization by mercury (³P₁) atoms¹ or on direct irradiation,² an efficient decarbonylation process takes place. In the sensitized reaction, this was postulated to proceed

(1) R. Srinivasan, *J. Am. Chem. Soc.*, **89**, 1758, 4812 (1967).

(2) H. Hiraoka and R. Srinivasan, *J. Chem. Phys.*, in press.

through an initial valence tautomerization to 2-cyclopropenecarboxaldehyde³ (1a). If eq 1a were reversed,



it is possible to regenerate furan in one of two ways which would not be equivalent when a substituent is present. The net reaction, in principle, would lead to a 3-substituted furan from a 2-substituted furan, or *vice versa*. Such over-all transformations (e.g., from 2-aryl to 3-aryl) under the influence of light have been observed in thiophenes,⁴ although it is not possible to relate them to the furan system since a ring-contracted product from a reaction analogous to eq 1a or 1b has not been observed in the former instance. Both the analog of eq 1a and its reverse reaction have been reported in the photochemistry of 3,5-diphenylisoxazole,⁵ but the resemblance seems to be superficial, as will be pointed out later in this communication.

We have now observed that 2-methylfuran and 2,5-dimethylfuran photoisomerize to 3-methylfuran and 2,4-dimethylfuran, respectively, under a variety of conditions. Thus, in the vapor phase, direct irradiation or mercury (³P₁) sensitization of 2-methylfuran gave, in addition to CO, 3-methylcyclopropene, and 1,3-butadiene, the identification of which was previously described,¹ an isomeric product (mol wt 82 by mass spectrometry) whose infrared spectrum showed two intense absorptions at 723 and 772 cm⁻¹, in agreement with the reported spectrum⁶ of 3-methylfuran. The material was found to be identical with an authentic sample of 3-methylfuran⁷ in its retention time on a vapor phase chromatograph and in its infrared spectrum. Irradiation of 2-methylfuran in solution (concentration ~1%) in ether also gave 3-methylfuran.

The quantum yields for the formation of 3-methylfuran and CO + C₄H₆ from 2-methylfuran were dependent on the total pressure in the system, the former increasing slightly with increased pressure and the latter behaving in an inverse manner. The total quantum yield for the photoreaction reached a maximum of 0.80 ± 0.15 at 26 torr when Hg(³P₁) was used as a sensitizer. The presence of an eightfold excess of oxygen decreased the quantum yield for the photoisomerization by a factor of four. The fact that the formation of the product was not scavenged completely rules out a free-radical mechanism, *i.e.*, one in which the methyl group migrated from the 2 to the 3 position as a free radical.

Direct irradiation of 2,5-dimethylfuran in the vapor phase gave many isomeric products (mol wt 96 by mass spectrometry) but only one of these was found not to possess a carbonyl group. Its infrared spectrum (gas) showed an intense absorption at 782 cm⁻¹ and subsidiary absorptions at 742 and 730 cm⁻¹. The material was identified as 2,4-dimethylfuran by the comparison of its infrared spectrum and its retention time on a

(3) R. Srinivasan, paper presented at the IUPAC Symposium on Organic Photochemistry at Enschede, Holland, July 1967.

(4) H. Wynberg, R. M. Kellogg, H. van Driel, and G. E. Beekhuis, *J. Am. Chem. Soc.*, **89**, 3501 (1967), and earlier references therein.

(5) E. F. Ullman and B. Singh, *ibid.*, **88**, 1844 (1966).

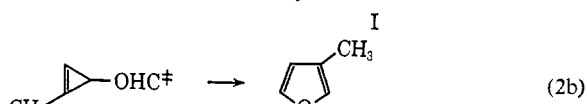
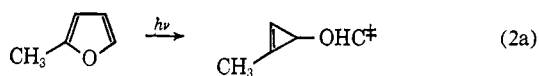
(6) M. Fetizon and J. Guy, *Compt. Rend.*, 1182 (1958).

(7) The authors thank Drs. E. Payo and C. Rivas of the Instituto Venezolano de Investigaciones Científicas, Caracas, Venezuela, for a generous gift of this material.

chromatographic column with those of an authentic sample.⁷

Hg(³P₁) sensitization of 3-methylfuran⁸ led to decarbonylation ($\Phi_{\text{CO}} = 1.0 \pm 0.1$) as the only observable process. The cyclopropene that was formed in this instance was entirely 1-methylcyclopropene. Hg(³P₁) 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

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(³P₁) was used as a sensitizer indicates that reaction 3a is not a reversible process (as defined above) under the present conditions.

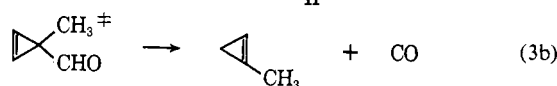
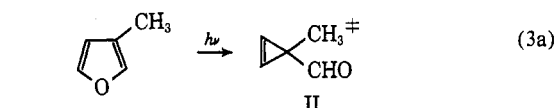
In 2-methyl-4,5-dihydrofuran, the ring-contraction reaction gives an isolable product. Since the initially

(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).



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

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 \rightarrow intermediate \rightarrow 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.

(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).

H. Hiraoka, R. Srinivasan

IBM Watson Research Center
Yorktown Heights, New York 10579

Received October 28, 1967

Stereospecific Interconversions of Optically Active Sulfoxides, Sulfilimines, and Sulfoximines¹

Sir:

A previous paper² reported the stereospecific interconversions of sulfoxide (+)-I and sulfilimine (-)-II. The reaction (+)-I \rightarrow (-)-II was found to occur with 98% and of (-)-II \rightarrow (+)-I with 96% stereospecificity and inversion of configuration at sulfur. That (+)-I and (-)-II had opposite configurations at sulfur was

(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).