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A MODEL FOR THE PHOTOCHEMICALLY INDUCED VALENCE BOND ISOMERIZATIONS OF THIOPHENES[1]

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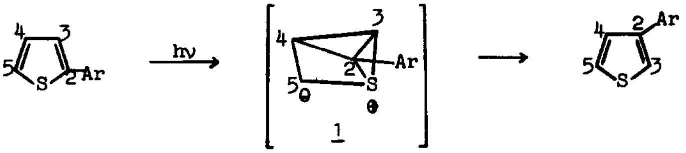
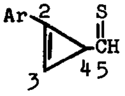
Striking isomerizations of aryl and alkyl substituted thiophenes occur on irradiation with ultraviolet light.[2] A key for the delineation of the mechanisms by which these transformations take place is found in the extensive data available on the rearrangements of isomeric thiophenes.[2] Successful solution of this problem should lead to models applicable for interpreting the rearrangements of other heteroaromatic and benzenoid systems.

A model (1) offered previously[2a] predicted correctly the major products obtained from 2-aryl substituted thiophenes (eq 1). Preference was given to intermediate (transition state?) 1 rather than thioaldehyde 2 arising by bond reorganization. However, as emphasized at the time,[2a]



(1)



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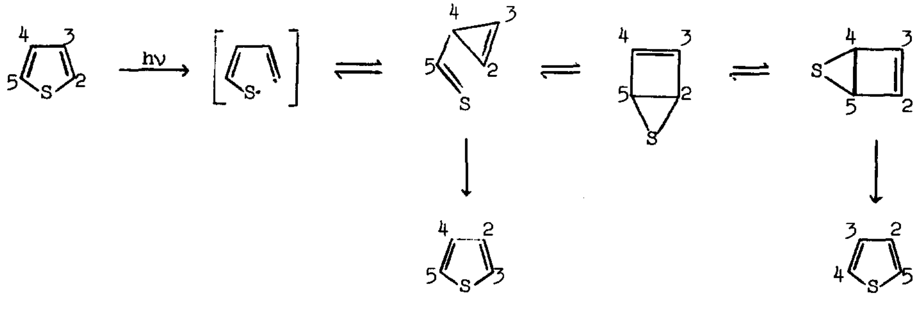
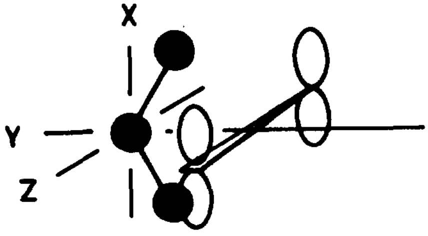
this model failed to explain the rearrangements of a number of 3-substituted thiophenes. In order to encompass all thiophene (as well as furan) rearrangements within a single framework, Van Tamelen and Whitesides[3] recently proposed the scheme shown in eq 2.[3,4] Rationalization of known furan rearrangements required only a cyclopropenyl ketone analogous to 2 (S=O)[3] whereas Dewar intermediates had also to be invoked in the thiophene rearrangements.



(2)

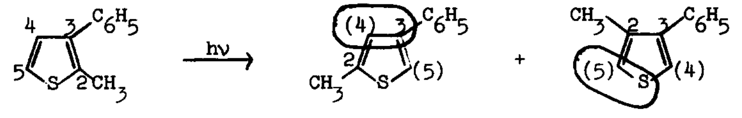
The purpose of the present communication is to recommend a model wherein 1 represents one member of a family of excited state structures. This family consists of the three possible contiguous combinations of atoms wherein a two-atom fragment is wrenched 90° out of the plane formed by the remaining three atoms (3). The three distinct arrangements derived by 90° rotation out of the plane of the ring of S_1-C_2 (=S_1-C_5), C_2-C_3 (=C_4-C_5), and C_3-C_4 (=C_4-C_3) are suggested to provide energetic minima to greatly distorted excited singlet states.[5]



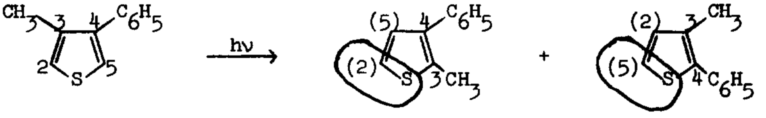
The three-atom fragment lies in the xz plane, the two-atom fragment in the yz plane. Darkened circles represent tops of p-lobes. If S is at a terminal position of the three-atom fragment then 3 equals generalized 1. (3)

This presumption has qualitative foundation. The very observation of valence bond isomerization implicates drastic geometrical distortion of the molecule in the excited state.[6] Structures such as 1 give a "reasonable" sigma framework for the topography represented by 3; however, generalized 3 (which includes 1) differs in that it is presumed to be stabilized by a Möbius-like overlap[7] of the basis set of p orbitals of the benzenoid system after twisting of the sigma framework. There is adequate reason to believe that this may lead to excited state stabilization.[8,9] An equivalent view of 3 is that it represents a tightly complexed $\pi 4_a + \pi 2_s$ system[10] with antiaromatic characteristics disposing it for excited state stabilization.[11]

This view allows a consistent interpretation of thiophene rearrangement results, particularly of the previously inexplicable rearrangements of phenylmethylthiophenes.[12] Net "turning-over" of a C_2-C_3 fragment occurs in 2-arylthiophenes (eq 3). Examples of competitive processes are given in eqs 4,5 where "turning-over" of the encircled fragments leads to the indicated major products. The numbers in parentheses represent atoms that have not been traced unequivocally by substituent or ^{14}C labelling experiments. In most cases such experiments are too complicated to be carried out with profit. However, the interpretation given explains



(3)



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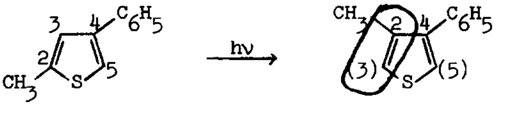

(5)

adequately not only the rearrangements illustrated in eqs 1 and 3-5 but also other known rearrangements.[2] This model corrects a deficiency of the Van Tamelen-Whitesides scheme (eq 2) wherein a Dewar structure is used to explain those rearrangements not interpretable by 1 [or a thioaldehyde(ketone), which gives the same results]. Thus the latter scheme cannot predict 2-methyl-4-phenylthiophene as a major product from 2-methyl-3-phenylthiophene. No such difficulty is encountered with the model proposed here.

In summary, the present theory proposes that excitation of the thiophene chromophore produces drastic geometrical distortion of the ring and that the geometry implicated by 3 provides a degree of stabilization to that distorted species. Subsequent collapse to starting material or rearrangement product may occur. A prediction of the dominant rearrangement process of the several available to an unsymmetrically substituted thiophene is difficult if not impossible since this is a subtle and complicated function of the substituent pattern. Usually "turning-over" of C_2-C_3 occurs (equivalent to 1); for such rearrangements subsequent bond reorganisation to a more stable thioaldehyde(ketone) might provide a lower energy pathway to products. This is particularly true with furans where the extremely stable carbonyl system develops.[13,14]

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3. E.E. van Tamelen and T.H. Whitesides, J. Amer. Chem. Soc. 93, 6129 (1971); see also E.E. van Tamelen, Angew. Chem. 77, 759 (1965).
4. Thioaldehydes(ketones) (i.e. 2, eq 1) are claimed as ubiquitous, presumably ground state, intermediates on the basis of low yield conversions of alkylthiophenes to pyrroles when irradiated in solutions of primary amines: A. Couture and A. Lablanche-Combier, Tetrahedron 27, 1059 (1971); A. Couture and A. Lablanche-Combier, Chem. Comm., 891 (1971). Structures related to 1 were rejected on the remarkable grounds that an amine fails to attack nucleophilically at a tertiary carbon atom. A more logical path involving attack at secondary C-5 of 1 was not considered. The products from this path are the same as those obtained from a free thioaldehyde(ketone).
5. (a) There is evidence that the singlet excited state of 2-phenylthiophene is directly responsible for the photochemical rearrangement: R.M. Kellogg and H. Wynberg, Tetrahedron Letters, 5895 (1968).
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