The Photochemistry of Thiophenes. VII. Observations on the Mechanism of Arylthiophene Rearrangements

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Abstract: Photoinduced rearrangement of 2-arylthiophenes proceeds cleanly and irreversibly to 3-arylthiophenes through a photoreorganization reaction. Rearrangement is confined to the thiophene ring and the primary path of rearrangement involves an interchange of the C_2-C_3 carbon atoms without concomitant inversion of the C_4-C_5 carbon atoms as shown by substituent labeling experiments. 3-Arylthiophenes also undergo photochemical rearrangement in the thienyl ring; with 3-phenylthiophene a photochemical "no-reaction reaction" occurs. The rearrangement of 2-arylthiophenes to 3-arylthiophenes is suggested to occur through a species involving valence shell expansion of the sulfur atom in preference to ring opening to a thioaldehyde followed by ring closure. An attempt has been made to correlate these results with other rearrangements reported in the literature.

Under the influence of ultraviolet light, arylthiophenes undergo rearrangements[2a] seemingly unprecedented in the more familar area of thermal reactions. Considerable information has now been accumulated about the photochemical behavior of a number of arylthiophenes.[2b-6] The results of these experiments allow the postulation of a mechanism which rationalizes the experimental observations.

The more readily derived facts about arylthiophene rearrangements are the following. (a) Rearrangement must involve a photoreorganization (valence isomerization) of the thiophene ring with rebonding among the carbon and sulfur atoms. This is confirmed by the ^{14}C labeling experiments carried out with 2-phenylthiophene.[2b,5] Although only explicitly proved for 2-phenylthiophene, this seems a reasonable generalization for other systems studied.

(b) 2-Arylthiophenes rearrange irreversibly to 3-arylthiophenes and do not form any other detectable products.[2a,5,7]
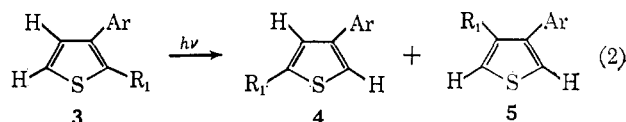
(c) In phenylthiophenes photorearrangement is confined to the thiophene ring and no rearrangement occurs in the aryl substituent.[5,8]

(d) The *major* path of photorearrangement of phenyl-, deuterio-, and methyl-substituted 2-phenylthiophenes involves an interchange of the C_2-C_3 carbon atoms without concomitant inversion of the C_4-C_5 carbon atoms. This conclusion is drawn from collected experimental results (eq 1).[5,6,9]
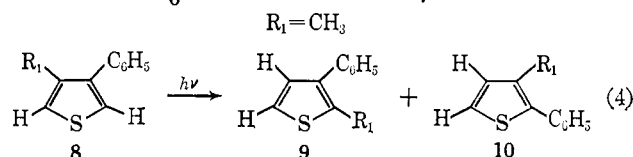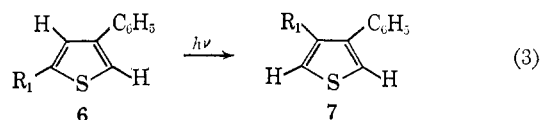
(e) Phenyl-, deuterio-, and methyl-substituted 3-phenylthiophenes exhibit considerable specificity of rearrangement as shown in eq 2–4.[5,6,9,10]

$$\text{(1)}$$

1 → 2
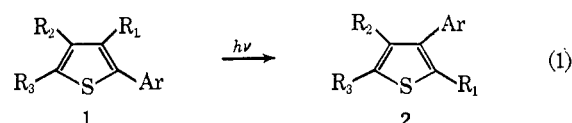
a, Ar = C_6D_5; R_3 = D; R_1 = R_2 = H
b, Ar = C_6H_5; R_3 = CH_3; R_1 = R_2 = H
c, Ar = C_6H_5; R_2 = CH_3; R_1 = R_3 = H
d, Ar = C_6H_5; R_1 = CH_3; R_2 = R_3 = H
e, Ar = C_6H_5; R_2 = C_6H_5; R_1 = R_3 = H

$$\text{(2)}$$

3 → 4 + 5

a, Ar = C_6D_5; R_1 = D
b, Ar = C_6H_5; R_1 = CH_3

$$\text{(3)}$$

6 → 7

$R_1 = CH_3$

$$\text{(4)}$$

8 → 9 + 10

a, R_1 = CH_3
b, R_1 = C_6H_5

An earlier proposal made by us on the basis of evidence then available was that thiophene valence bond isomers **11**, **12**, or **13** analogous to Dewar (**14**), prismane (Ladenburg) (**15**), or benzvalene (**16**) valence bond iso-

11   12   13   14   15   16
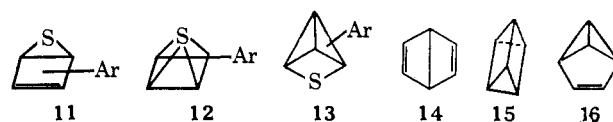
mers of benzene might be involved in the rearrangement.[2] Any mechanisms proposed for a photochemical valence isomerization in an aromatic system must

(1) Royal Dutch Shell Fellow, 1963–1966.
(2) (a) H. Wynberg and H. van Driel, *J. Am. Chem. Soc.*, **87**, 3998 (1965); (b) *Chem. Commun.*, 204 (1966).
(3) H. Wynberg and R. M. Kellogg, 152nd National Meeting of the American Chemical Society, New York, N. Y., Sept 1966.
(4) H. Wynberg, R. M. Kellogg, H. van Driel, and G. E. Beekhuis, *J. Am. Chem. Soc.*, **88**, 5047 (1966).
(5) H. Wynberg, H. van Driel, R. M. Kellogg, and J. Buter, *ibid.*, **89**, 3487 (1967).
(6) R. M. Kellogg and H. Wynberg, *ibid.*, **89**, 3495 (1967).
(7) 2-Alkyl-substituted thiophenes also rearrange to 3-alkyl-substituted thiophenes but in low yield: R. M. Kellogg, J. Dik, and H. Wynberg, unpublished results.
(8) This applies for the various tolylthiophenes and for mesitylthiophenes; this may be inferred but is not explicitly proved for other systems. In the photorearrangement of labeled 2,2'- to 2,3'-dithienyl rearrangement can be detected only in the thienyl ring in which positional isomerization occurs; no rearrangement is found in the migrating ring: R. M. Kellogg, H. van Driel, J. Buter, and H. Wynberg, to be published.
(9) H. Wynberg, G. E. Beekhuis, H. van Driel, and R. M. Kellogg, *J. Am. Chem. Soc.*, **89**, 3498 (1967).
(10) Due to the increased number of major rearrangement products over the 2-phenylthiophenes (eq 1), the assignments of "major" rearrangement products are made with a bit less certainty.

consider the evidence accumulated regarding these intermediates.[11]

The original isolation by van Tamelen and Pappas[12] of a substituted Dewar benzene from photolysis of 1,2,4-tri-*t*-butylbenzene followed by their synthesis of Dewar benzene itself[13] provided an important precedent. The subsequent isolation by Viehe and co-workers[14] from a synthetic procedure of all three benzene valence bond isomers (stabilized by fluorine atoms) provided unambiguous proof of their existence. One or more of these isomers have been subsequently implicated in a number of photochemical rearrangements. Burgstahler and Chien[15] suggested the photorearrangement of *o*-di-*t*-butylbenzene proceeded by valence bond isomerization as did Arnett and Bollinger[16] for 1,2,4,5-tetra-*t*-butylbenzene. Wilzbach and Kaplan[17] postulated valence bond isomerization with *o*-xylene and subsequently showed that photorearrangement of mesitylene involves valence bond isomerization (tested by ^{14}C labeling).[18] These authors have been able to isolate Dewar, prismane, and benzvalene isomers from the photolysis of 1,3,5-tri-*t*-butylbenzene.[19] Several recent reports indicate trapping of valence bond isomers (usually benzvalenes) by reactions with olefins[20,21] and alcohols.[22] The photochemically induced addition of acids to benzvalene-like species has also been reported.[23] Pitts and co-workers recently reported detection of what may be a photoisomer of benzene itself.[24,24a] By proper substitution these isomers are often remarkably stable; hexafluorobenzene gives a stable Dewar benzene upon photolysis[25] and hexamethyl Dewar benzene is now reported to be commercially available.[26] Although the mechanistic paths are far from clear, the very finding of benzenoid valence bond isomers in aromatic photolysis reactions indicates their importance. Bryce-Smith and Longuet-

Higgins have recently attempted a theoretical rationalization of benzenoid photolyses by considering the nature of the first excited singlet and triplet states of benzene.[27] Valence bond isomerizations have been reviewed recently.[28,29]

The literature thus far does not provide examples of heterocyclic analogs to the benzenoid valence bond isomers. Several heterocyclic photorearrangements are known. The best studied is the photorearrangement of 3,5-diphenylisoxazole (17) to 2,5-diphenyloxazole (19) (eq 5) reported by Ullman and Singh.[30] In this case
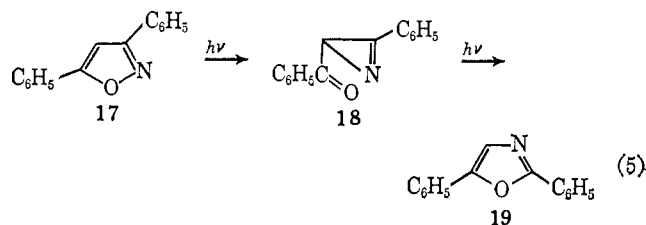
the "valence bond isomer" was shown to be azirine 18, a product of ring opening, which underwent subsequent photochemical ring closure to the product 19. A reaction of formally similar nature is the recently reported photodecarboxylation of sydnone.[31] Other heterocyclic photorearrangements of possible bearing are the transformation of indazoles to benzimidazoles,[32] pyrazoles to imidazoles,[32] and the photo ring closure of 1,2-diamino-1,2-dicyanoethylene and 1,1-diamino-2,2-dicyanoethylene to 4-amino-5-cyanoimidazole.[33] The photoisomerization of pyrazine to pyrimidine in very low yield has been reported.[34]

The recent results obtained for phenyl-, deuterio-, and methyl-labeled 2-phenylthiophenes[4–6,9] are not compatible with any of valence bond isomers 11, 12, or 13 which were suggested by earlier results.[2] Dewar structure 11[35] or prismane structure 12 predict no more than a relative change in the position of the sulfur atom. The carbon atom sequential order will not be changed if rearrangement proceeded through either of these intermediates. Equation 6 shows the predicted labeling results. Rearrangement through valene 13[36]
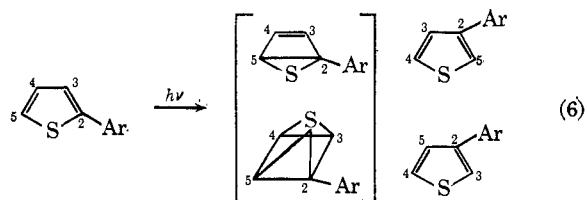
(11) The word "intermediate" is being used here without reference to the stability, lifetime, or energy content of the species indicated. This point will be considered in more detail later in the paper.

(12) E. E. van Tamelen and S. P. Pappas, *J. Am. Chem. Soc.*, 84, 3789 (1962).

(13) E. E. van Tamelen and S. P. Pappas, *ibid.*, 85, 3297 (1963).

(14) H. G. Viehe, R. Merényi, J. F. M. Oth, J. R. Senders, and P. Valange, *Angew. Chem.*, 76, 922 (1964).

(15) A. W. Burgstahler and P. L. Chien, *J. Am. Chem. Soc.*, 86, 2940 (1964).

(16) E. M. Arnett and J. M. Bollinger, *Tetrahedron Letters*, 3803 (1964).

(17) K. E. Wilzbach and L. Kaplan, *J. Am. Chem. Soc.*, 86, 2307 (1964).

(18) L. Kaplan, K. E. Wilzbach, W. G. Brown, and S. S. Yang, *ibid.*, 87, 675 (1965).

(19) K. E. Wilzbach and L. Kaplan, *ibid.*, 87, 4004 (1965).

(20) K. E. Wilzbach and L. Kaplan, *ibid.*, 88, 2066 (1966); R. Srinivasan and K. A. Hill, *ibid.*, 87, 4653 (1965). Srinivasan and Hill report an addition of Dewar benzene to cyclobutene.

(21) D. Bryce-Smith, A. Gilbert, and B. H. Orger, *Chem. Commun.*, 512 (1966).

(22) L. Kaplan, J. S. Ritscher, and K. E. Wilzbach, *J. Am. Chem. Soc.*, 88, 2881 (1966).

(23) E. Farenhorst and A. F. Bickel, *Tetrahedron Letters*, 5911 (1966).

(24) J. K. Foote, M. H. Mallon, and J. N. Pitts, Jr., *J. Am. Chem. Soc.*, 88, 3698 (1966).

(24) (a) Note Added in Proof: This product, formed upon gas-phase photolysis of benzene at 1849 A, has been shown to be primarily fulvene: H. R. Ward, J. S. Wishnok, and P. D. Sherman, Jr., *ibid.*, 89, 162 (1967); L. Kaplan and K. E. Wilzbach, *ibid.*, 89, 1030 (1967). Authentic unsubstituted benzvalene has been isolated in the liquid-phase photolysis of benzene: K. E. Wilzbach, J. S. Ritscher, and L. Kaplan, *ibid.*, 89, 1031 (1967). For a "Mobius" benzene intermediate see E. Farenhorst, *Tetrahedron Letters*, 6465 (1966).

(25) I. Haller, *J. Am. Chem. Soc.*, 88, 2070 (1966).

(26) *Chem. Eng. News*, 44, No. 28, 20 (1966); W. Schäfer, *Angew. Chem.*, 78, 716 (1966).

(27) D. Bryce-Smith and H. C. Longuet-Higgins, *Chem. Commun.*, 593 (1966).

(28) E. E. van Tamelen, *Angew. Chem.*, 77, 759 (1965).

(29) H. G. Viehe, *ibid.*, 77, 768 (1965).

(30) E. F. Ullman and B. Singh, *J. Am. Chem. Soc.*, 88, 1844 (1966).

(31) C. H. Krauch, J. Kuhls, and H. J. Peik, *Tetrahedron Letters*, 4043 (1966).

(32) H. Tiefenthaler, W. Dörscheln, H. Göth, and H. Schmid, *ibid.*, 2999 (1964).

(33) J. P. Ferris and L. E. Orgel, *J. Am. Chem. Soc.*, 88, 1074 (1966).

(34) F. Lahmani, N. Ivanoff, and M. Magat, *Compt. Rend.*, 263, 1005 (1966).

(35) Besides aromatic photolysis results, the reported ring closure of cyclopentadiene to tricyclo[2.1.0]hex-2-ene might serve as precedent for Dewar thiophene formation: J. I. Brauman, L. E. Ellis, and E. E. van Tamelen, *J. Am. Chem. Soc.*, 88, 846 (1966).

(36) Both results from photolysis of aromatic hydrocarbons and diene photolyses provide precedent for a valene. Valenes have been identified in liquid-phase butadiene photolysis: I. Haller and R. Srinivasan, *J. Chem. Phys.*, 40, 1992 (1964), and in the photolysis of $\Delta^{3,5}$-cholestadiene: W. E. Dauben and F. G. Willey, *Tetrahedron Letters*, 893 (1962).

would be expected to proceed as shown in eq 7. The exact mechanism of rearrangement of **13** to the 3-arylthiophene is not obvious, but for rearrangement to occur the sulfur atom must become bonded to *either* the C_3 or C_4 positions because of their equivalence in **13**.
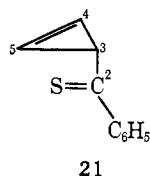

$$(7)$$
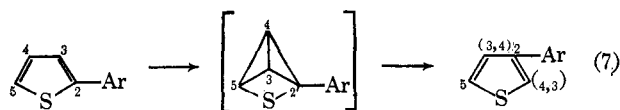
Even allowing for a sizeable substituent effect one would still expect appreciable equilibration when a methyl substituent is on the C_3 or C_4 position. This is not observed.[9] Thus valene **13** seems unlikely because of the predicted symmetry.[37]

The simplest mechanism consistent with the observed rearrangement patterns of substituted 2-arylthiophenes is a ring opening–ring closure reaction (eq 8) formally similar to that observed by Ullman and Singh.[30] The ring opening would involve concerted breaking of the C_2–S bond and bonding between C_2 and C_4 thus forming, in the case of 2-phenylthiophene, thioaldehyde **20**. This thioaldehyde (or thioketone in the case of a 5-substituted phenylthiophene) could rearrange to the 3-phenyl-

$$(8)$$

20
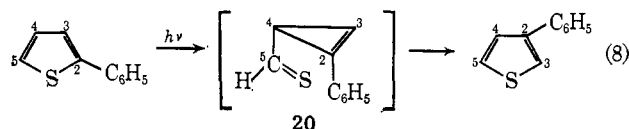
thiophene by formation of a S–C_3 bond with concomitant breaking of the C_3–C_4 bond. This mechanism can satisfactorily explain the major rearrangement paths of phenyl-, deuterio-, and methyl-substituted arylthiophenes.[38]

Closer consideration of the experimental results suggests that eq 8 is a gross simplification. Species **20**, whether ground state or still possessing excess energy (see below), is an aliphatic thioaldehyde, a type of compound usually predicted to be very unstable.[39] For a species such as **20** to lead to such a clean rearrangement is remarkable. One might qualitatively expect that in the case of a 5-substituted arylthiophene, the formation of a more stable thioketone as intermediate would lead to a cleaner rearrangement proceeding in higher yield. This is not observed.[9] A more serious objection is that ring opening must lead to thioaldehyde **20** instead of expectedly more stable phenyl thioketone **21**. Since **21** predicts equilibration of the C_4–C_5 positions,

21

rather than migration of the phenyl group, it cannot be a major intermediate despite its seemingly greater likelihood.

An alternative and attractive explanation of the rearrangement involves the possibility of valence shell expansion of the sulfur atom. If the sulfur 3d orbitals are allowed to interact with the presumably more activated C_2–C_3 carbons (the double bond of **20**), one obtains intermediate **22** (eq 9). Concerted rearrangement of **22** in the obvious manner leads to the rearranged 3-phenylthiophene with the requisite inversion of the C_2–C_3 carbon atoms. Intermediate **22** provides a use-

22

$$(9)$$
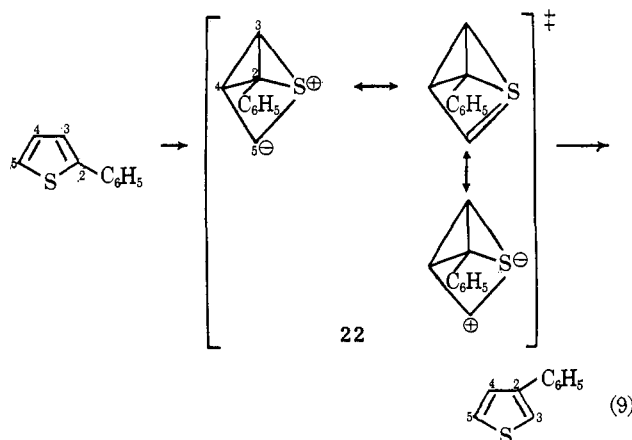
ful qualitative description of the species leading to rearrangement and possesses advantages over thioaldehyde **20** in that its formation and subsequent rearomatization proceed in a predictable manner. Moreover, **22** would rearrange to one product, whereas other types of reactions might be expected from thioaldehyde **20**. The present information allows no absolute decision between **20** and **22** although we definitely favor the latter. No obvious precedent for excited-state participation in the manner indicated in **22** exists to our knowledge. In ground-state reactions intermediates similar to **22** have been postulated in connection with studies of d orbital resonance. Thus, base-catalyzed deuterium exchange has been observed with bicyclo-[2.2.1]heptane-1-sulfonium ion presumably through an intermediate geometrically similar to **22**.[40]

Ground-state resonance structures of thiophene involving d orbital resonance have been postulated by both Schomaker and Pauling[41] and Longuet-Higgins[42] and these proposals have been further considered by Jaffé.[43] On the basis of the discussion of Jaffé,[43] the preferred resonance structure of **22** would be the ylid form bearing the positive charge on sulfur. Ground-state ylids of this sort are well known and a number have been characterized.[44] The observation that the rate of rearrangement increases in polar media could also suggest a charged intermediate species. It should be recognized that any structures drawn, *i.e.*, ground state, excited singlet, vibrational ground state, can be no more

(37) One can with enough imagination, time, and paper rationalize virtually *any* product through sufficiently complex equilibria of intermediates 11, 12, and 13. Thus far, however, we have been unable to predict the observed specificity of rearrangement by these efforts. Although complex equilibria can be postulated, the intricate paths one is forced to consider approach the point of sublime ridiculousness.

(38) The possibility of a ring-opening sequence was first brought to our attention during a seminar at Princeton University, Feb 12, 1966.

(39) For a typical reference on the preparation of aliphatic thioaldehydes, see: W. Schroth, F.Billig, and H. Langguth, *Angew. Chem.*, 77, 919 (1965). The first stable thioaldehyde was reported by R. B. Woodward, *et al.*, *J. Am. Chem. Soc.*, 82, 3800 (1960). More examples of stable thioaldehydes (in aromatic systems) have recently been reported: S. McKenzie and D. H. Reid, *Chem. Commun.*, 401 (1966).

(40) W. von E. Doering and A. K. Hoffmann, *J. Am. Chem. Soc.*, 77, 521 (1955).

(41) V. Schomaker and L. Pauling, *ibid.*, 61, 1769 (1939).

(42) H. C. Longuet-Higgins, *Trans. Faraday Soc.*, 45, 173 (1949).

(43) H. H. Jaffé, *J. Phys. Chem.*, 58, 185 (1954).

(44) (a) C. K. Ingold and J. A. Jessop, *J. Chem. Soc.*, 713 (1930); (b) A. W. Johnson and R. B. La Count, *J. Am. Chem. Soc.*, 83, 417 (1961); (c) A. W. Johnson, V. J. Hruby and J. L. Williams, *ibid.*, 86, 918 (1964).

than schematic representations of the actual species involved as long as the energy content is unknown.[45]

The energy content of the species responsible for rearrangement is difficult to estimate. At no time have we ever detected traces of intermediates by gas chromatography or ultraviolet spectroscopy under conditions used. Thus, any species involved must be relatively short lived. It is conceivable that with flash spectroscopy intermediates could be detected. The intermediate(s) involved may never reach a ground state but undergo rearrangement while still possessing excess energy. If they were to rearrange thermally, a temperature effect on the rearrangement might be expected; this is not observed.[5] If rearrangement of the intermediate involved reabsorption of light it should have a detectable ultraviolet absorption in a nonabsorbing region of the parent compound (unless it is photosensitized). If the intermediate lifetime is sufficiently short, the absorption would, of course, not be detected by normal ultraviolet techniques. The nature of the electronic states involved in these rearrangements cannot be determined from the present information. The ultraviolet absorption spectrum of 2-phenylthiophene has a strong absorption at 282 mμ (ϵ 13,400 in cyclohexane) and absorption continuing to shorter wavelengths. Although comments have been made, no detailed analysis of the spectrum of 2-phenylthiophene has been carried out.[46] In analogy to thiophene, the 282-mμ band may be the $\pi-\pi^*$ absorption shifted to longer wavelengths.[47] The position and intensity of the n$-\pi^*$ band is not known. 3-Phenylthiophene has two maxima in cyclohexane, one at 227 mμ (ϵ 15,300) and the other at 259 mμ (ϵ 13,700). The nature of the photophysical decay processes in 2- and 3-phenylthiophene are obviously different because 2-phenylthiophene has little phosphorescence while 3-phenylthiophene displays a strong phosphorescence.[5a] Similar differences in fluorescence and phosphorescence spectra have been observed with the diphenylthiophenes.[5] Detailed analysis of the relative importance of the various photophysical and photochemical processes is not possible at this time. The question of whether the rearrangement occurs in the excited singlet (or a vibrationally excited ground state derived by internal conversion), an excited triplet, or a short-lived ground-state intermediate is open. Intuition suggests rearrangement through an excited singlet or a vibrationally excited ground state. This idea is very qualitatively supported by the absence of an oxygen effect on the rearrangement.

The relationship between valence species 13, thioaldehyde 20, and valene species 22 should be noted. Thioaldehyde 20, by participation of the sulfur 3d orbitals with the C_2-C_3 double bond, forms 22 or by concerted cycloaddition with the C_2-C_3 double bond may form valene 13 or the isomeric valene with the phenyl at the
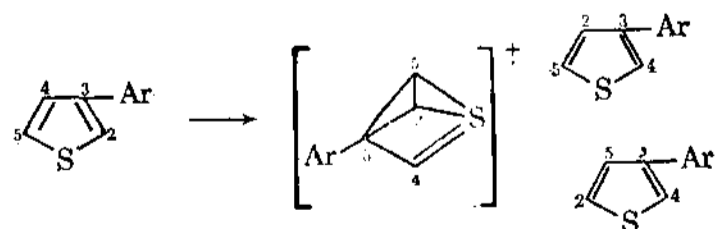
bridgehead position. This interrelation of these different intermediates may be of considerable importance.

The rearrangements of 3-arylthiophenes are of a complexity even surpassing those of the 2-arylthiophenes. 3-Phenylthiophene is characterized by its complete failure to revert to the 2-substituted isomer. Yet apparently upon photolysis the carbon atoms in the thiophene ring rearrange in a "no-reaction reaction" as shown with 2-deuterio-3-pentadeuteriophenylthiophene.[4,6] With phenyl-, deuterio-, and methyl-substituted 3-arylthiophenes the systematic pattern of the major rearrangement paths shown in eq 2-4 may be seen. Again, only 3-arylthiophenes are formed except in the case of 3,4-disubstituted thiophenes (eq 4) where 2-aryl-substituted thiophenes are formed as products. The rearrangement patterns observed do not allow formulation of a mechanism in the manner used for 2-arylthiophenes. The mechanism suggested with 2-arylthiophenes fails to explain the products of 3-arylthiophene rearrangements. Other steric or electronic factors may be in operation which cause a change in the manner of rearomatization or, indeed, a totally different mechanism may be involved with the 3-arylthiophenes.[48]
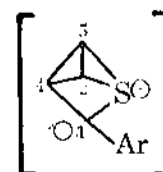
The formation of all possible isomers in the photolysis of the phenylmethylthiophenes,[9] even though one isomer predominates, emphasizes the complexity of arylthiophene rearrangements. These other isomers appear to be formed in the primary photochemical step and are not products of secondary photolysis.[9] The discussions thus far have attempted to rationalize the major products but have not explained the formation of these minor ones. Other relatively minor paths must be operating during the rearrangements, and the intermediates they may involve are completely unpredictable from the present information. All of the thiophene valence bond isomers might be involved or variations of essentially the same intermediate may be responsible. The present results simply do not allow solution of these problems and this must be the object of further extensive study.

Qualitatively the rearrangements of arylthiophenes, especially 2-arylthiophenes, appear to fall in a middle position between benzenoid photorearrangements and the complete ring opening reaction reported by Ullman and Singh.[3u] While the benzenoid and heterocyclic systems which have been studied must differ greatly in the nature of the excited states involved, they do possess

(45) One tempting generalization would be that heteroaromatic systems containing elements of the third row of the periodic table (with empty d orbitals) undergo rearrangement via similar photoexcited states. The report that diphenylfurans fail to undergo phenyl group migrations, A. Padwa and R. Hartman, J. Am. Chem. Soc., 88, 3759 (1966), suggests that sulfur must play a role in photorearrangement that cannot be fulfilled by oxygen.

(46) V. N. Ivanova, Zh. Obshch. Khim., 28, 1238 (1958); Chem. Abstr., 52, 19448e (1958). L. Bruzzi, J. Degani, and A. Tundo, Boll. Sci. Fac. Chim. Ind. Bologna, 19, 40 (1961); Chem. Abstr., 55, 23040a (1961).

(47) S. Gronowitz, Advan. Heterocyclic Chem., 1, 14 (1963).

(48) A scheme capable of explaining the rearrangement products is

plus invoking

formed in the case of 3,4-disubstituted thiophenes. Although capable of explaining the results, the formation of the requisite valence bond isomers is difficult to rationalize.

in common the ability to undergo photoisomerizations. They also possess in common the fact that a specific turning over of two atoms appears to be the major rearrangement result. In benzenoid systems o-xylene gives, in addition to elimination products, m- and p-xylene in 11:1 ratio during the first 30 min of photolysis.[17] Furthermore, mesitylene forms 1,2,4-trimethylbenzene exclusively upon photolysis,[18] and o-di-t-butylbenzene is reported to give mostly m-di-t-butylbenzene in the first 6 hr of reaction.[15] In other systems, specific inversion of two carbons could have occurred but cannot, by the nature of the labeling, be distinguished.[16] Obviously the benzenoid systems have not been completely elucidated, and the mechanism of rearrangement may vary from system to system. In t-butyl systems relief of strain has been cited as a driving force for rearrangement[15] but this obviously is not a

prerequisite. Of the various valence bond isomers considered for benzenoid photochemical rearrangements, it is perhaps surprising that ring opening to form a dicyclopropenyl, an analog of Ullman's azirine or thioaldehyde 20, has not been considered. A dicyclopropenyl can theoretically lead to the observed rearrangement products in benzenoid systems and as a description of the excited species leading to rearrangement could be considered. In this regard the formation of a benzene derivative by thermal rearrangement of a dicyclopropenyl is of considerable interest.[49]

Further work both on the mechanism of the rearrangement as well as the scope and application to other systems is currently under way and will be the subject of future reports.

(49) R. Breslow, "Molecular Rearrangements," Vol. 1, P. de Mayo, Ed., Interscience Publishers, Inc., New York, N. Y., 1963, pp 243–245.

Transannular and Interannular Effects in 1,8-(1',8')-Naphthalylnaphthalene and Related Compounds[1]

William C. Agosta

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Abstract: Reactions at the nonaromatic carbon atoms of 1,8-(1',8')-naphthalylnaphthalene and related compounds lead either to oxygen bridging (as 2) or formation of a transannular carbon–carbon bond (as 10). Spectral evidence indicates considerable electronic interaction between the two formally insulated naphthalene chromophores.

In 1,8-(1',8')-naphthalylnaphthalene[2,3] (1) and related compounds of the same carbon skeleton, there is available a single, rather rigid conformation free of distorted bond angles. We wish to discuss here two general consequences of this arrangement which are reflected in the chemical and physical properties of these molecules. The first of these is a marked tendency for transannular reactions to occur, leading either to direct carbon–carbon bonding between the two nonaromatic carbon atoms or, alternatively, to formation of an oxygen bridge between these centers. The well-investigated peri interactions of simple naphthalenes[4] provide ample precedent for such reactions; the results described below demonstrate that they are highly favored, and indeed appear to be unavoidable, in the rigid array of 1. A second property we find to be general in these molecules is electronic interaction between the two classically insulated naphthalene systems as evidenced by their abnormal spectral properties.

We consider first reactions of 1 leading to transannular oxygen bridging. Treatment of the diketone with a variety of nucleophiles leads to formation of hemiketals of the general structure 2. In no case have

1

2

3, X = H
4, X = CH₃
5, X = OH
9, X = NHNH₂
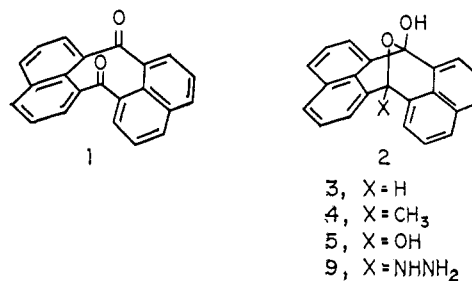
we observed normal reaction of the second carbonyl group, and the ketol–hemiketal equilibrium appears to lie far to the side of the bridged product. Infrared spectra of all these substances show strong hydroxyl absorption and are transparent in the carbonyl region. Thus, sodium borohydride reduction of 1 furnishes 3 as the only isolable product, and reaction of the diketone with excess methyllithium gives only the corresponding methyl hemiketal 4. Similarly, acid-catalyzed hydration of 1 leads in high yield to the stable hydrate 5, a compound which sublimes unchanged at 190° in vacuo and is not dehydrated by prolonged treatment with p-toluenesulfonic acid and refluxing benzene in a water separator. Exposure of the dione to typical Clemmensen reduction conditions yields only the hydrate 5, as does attempted reduction with hydriodic acid and red phosphorus in acetic acid at 145° over 2 days. Failure to isolate reduction products from these reac-

(1) A portion of this work has appeared in preliminary form: W. C. Agosta, Tetrahedron Letters, 3635 (1966).

(2) R. L. Letsinger and J. A. Gilpin, J. Org. Chem., 29, 243 (1964).

(3) The systematic name for this compound is 7H,14H-cycloocta-[1,2,3-de:5,6,7-d'e']dinaphthalene-7,14-dione.

(4) A timely review of this topic has appeared: V. Balasubramaniyan, Chem. Rev., 66, 567 (1966).