distance of 2.333 A seems to be too high for a normal single bond, much like the corresponding S–S bond in IIb, since the sum of the single-bond covalent radii for S and Se (1.04 and 1.17 A, respectively[8]) is 2.21 A. (Comparable S–Se bond lengths in other compounds have apparently not been determined experimentally.) Similarity to IIb is also shown in the smooth elimination of *selenium* on treatment with mercuric acetate in acetone–acetic acid at room temperature, regenerating IV in high yield. Peracetic acid gives the same result. On the whole it seems apparent that Vb contributes more than Va to the structure, just as IIb is more important than IIa; the S–Se bond distance is *less* than the S–S distance, whereas the "normal" S–Se distance of 2.21 A (sum of covalent radii) is *greater* than the normal S–S bond distance of 2.08 A. Selenium is accommodated in the thiothiophthene system without distortion.[9]

**Acknowledgment.** The authors are indebted to Mrs. Maryellen Kish and Mr. N. R. Nelson for technical assistance.

[8] S. C. Abrahams, *Quart. Rev.* (London), **10**, 417, 429 (1956).

[9] Selenium compounds that may be related to thiothiophthene have been reported, without structure analysis, by G. Traverso [*Ann. Chim.*, 47, 3 (1957)] and M. Sanesi and G. Traverso [*Chem. Ber.*, **93**, 1566 (1960)].

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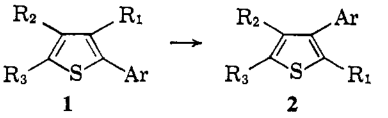
## The Photochemistry of Thiophenes. III. Photochemical Rearrangements of Arylthiophenes

*Sir:*

The results of photochemically induced rearrangement of a large number of unsymmetrically disubstituted arylthiophenes coupled with previous $^{14}$C evidence[1] allow significant extension and refinement of our recent mechanistic proposals.[1-3]

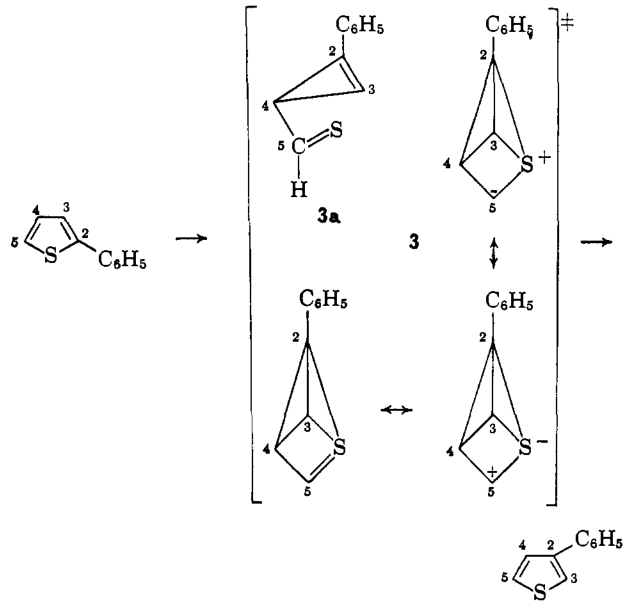


(1)

**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

With 2-arylthiophenes **1a–e**, products **2a–e** account for 80% or more of the rearranged materials (eq 1);[4] the balance of the products are the other positional isomers and starting material.[5] The major rearrangement path (80% or more) thus involves, as shown in eq 1, specific $C_2$–$C_3$ inversion without concomitant $C_4$–$C_5$ inversion of the thiophene ring carbons.

A prediction, at this stage, of the exact geometry of the state(s) responsible for rearrangement is difficult.[6] A series of sufficiently complex equilibria between postulated valene, Dewar, and/or prismane type structures[1-3] allow rationalization of the products formed (or indeed of any rearrangement products!) but fail to predict adequately the observed specificity of this photoreorganization. More logical, we think, are structures **3a** and **3** which provide a useful qualitative framework for rationalization of the observations. Form **3a**, a thioaldehyde, would clearly offer the simplest explanation though little ground-state stability would be predicted.[7] Structures **3** involve active participation of the sulfur 3d orbitals.



In unsymmetrically disubstituted 3-phenylthiophenes further changes in the carbon atom sequential order occur, as shown in eq 2–4.[4,5,8] Selectivity of rearrangement is again observed, but is of a different nature than that observed with 2-phenylthiophenes. In these rearrangements intermediates similar to **3** could play an important role but do not provide a necessarily unique rationalization of the results.

In the superficially similar rearrangement of an isoxazole to an oxazole, Ullman and Singh[9] have isolated, as a true photochemical intermediate, an azirine analogous to **3a**. Participation of the sulfur 3d orbitals of our **3a** with the carbon–carbon double bond

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[1] The phenyl group remains attached to the same carbon atom during rearrangement. H. Wynberg and H. van Driel, *Chem. Commun.*, 204 (1966). We assume this holds true for all arylthiophenes although this is unequivocally proved only with 2-phenylthiophene.

[2] H. Wynberg and H. van Driel, *J. Am. Chem. Soc.*, **87**, 3998 (1965).

[3] H. Wynberg and R. M. Kellogg, 152nd National Meeting of the American Chemical Society, New York, N. Y., Sept 10–16, 1966.

[4] Photolysis conditions were approximately those previously described.[2] Extrapolation of product ratios to zero time indicated products **2** to be the first products of rearrangement and not those of secondary photolysis. Small quantities of the other isomers appear to be formed in the primary photolysis.

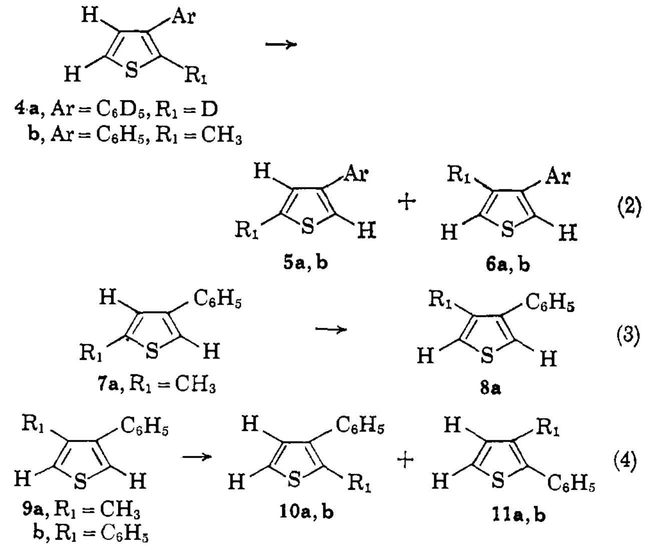
[5] All products have been unambiguously identified by comparison of infrared, ultraviolet, and/or nmr spectra with those of authentic samples. The synthesis, separation, and identification will be included in the full paper.

[6] This is particularly true if rearrangement occurs in an excited state or even in a highly vibrationally excited ground state. Thus far we have been unable to detect any ground-state intermediates either directly or by trapping experiments. Lacking other evidence, we assume rearrangement through an energetic species.

[7] For a representative reference on thioaldehydes, see W. Schroth, F. Billig, and H. Langguth, *Angew. Chem.*, 77, 919 (1965).

[8] For 3-phenylthiophene itself these rearrangements become examples of photochemical "no-reaction" reactions.

[9] E. F. Ullman and B. Singh, *J. Am. Chem. Soc.*, **88**, 1844 (1966). See also a sydnone rearrangement: C. H. Krauch, J. Kuhls, and H. J. Piek, *Tetrahedron Letters*, **34**, 4043 (1966).



**4a**, Ar = $C_6D_5$, $R_1$ = D
**b**, Ar = $C_6H_5$, $R_1$ = $CH_3$

**5a,b** **6a,b** (2)

**7a**, $R_1$ = $CH_3$ **8a** (3)

**9a**, $R_1$ = $CH_3$
**b**, $R_1$ = $C_6H_5$
**10a,b** **11a,b** (4)

provides **3**. Alternatively, cycloaddition of the carbon–sulfur double bond with the carbon–carbon double bond forms a sulfur-bridged bicyclobutane (valene),[1] the implicit symmetry of which fails to rationalize the specific 2-arylthiophene rearrangements.

The observed tendency for 1,2 shifts in benzenoid photorearrangements[10] bears striking similarity to our results and those of Ullman.[9] The isolation of reasonably stable Dewar,[11] prismane, and valene structures[12] with only end ultraviolet absorption leads one to question if these species provide a complete explanation of the rearrangements. The possibility of ring opening has not been considered in the literature. In this connection the formation of a benzene structure by thermal rearrangement of a dicyclopropene,[13] an analog of **3a** or Ullman's azirine, is of more than passing interest.

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(10) *o*-Xylene gives, in addition to other products, *m*- and *p*-xylene in an 11:1 ratio in the first 20 min of reaction: K. E. Wilzbach and L. Kaplan, *J. Am. Chem. Soc.*, **86**, 2307 (1964). Mesitylene gives 1,2,4-trimethylbenzene: L. Kaplan, K. E. Wilzbach, W. G. Brown, and S. S. Yang, *ibid.*, **87**, 675 (1965). *o*-Di-*t*-butylbenzene is reported to give mostly 1,3-di-*t*-butylbenzene in the first 6 hr of reaction: A. W. Burgstahler and P. L. Chien, *ibid.*, **86**, 2940 (1964). In other benzenoid photorearrangements a 1,2 shift cannot be readily distinguished; see, *e.g.*, E. M. Arnett and J. M. Bollinger, *Tetrahedron Letters*, **50**, 3803 (1964).

(11) E. E. van Tamelen and S. P. Pappas, *J. Am. Chem. Soc.*, **85**, 3297 (1963). The hexamethyl derivative is now commercially available: *Chem. Eng. News*, **44**, No. 28, 20 (1966).

(12) See, for example, K. E. Wilzbach and L. Kaplan, *J. Am. Chem. Soc.*, **87**, 4004 (1965).

(13) R. Breslow in "Molecular Rearrangements," Vol. 1, P. de Mayo, Ed., Interscience Publishers, Inc., New York-London, 1963, pp 243–245. This reaction is also mentioned by E. E. van Tamelen, *Angew. Chem.*, 77, 759 (1965).

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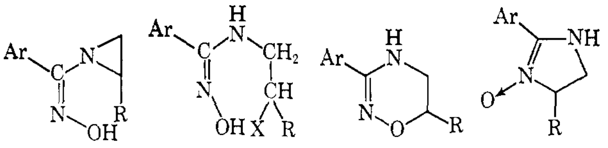
## A New Synthesis of 1,2,4-Oxadiazine Derivatives from 1-Aroylaziridine Oximes

*Sir:*

The protic and Lewis acid catalyzed isomerization of different types of aziridine derivatives is a well-documented phenomenon.[1]

We now wish to report on the acid-catalyzed isomerization of 1-aroylaziridine oximes, a new class of compounds, leading to the derivatives of the little known 1,2,4-oxadiazine.

The 1-aroylaziridine oximes (Ia–e)[2] were prepared, under conditions where the aziridine ring opening is least likely to occur, by treating equimolar proportions of the appropriate benzonitrile oxides with ethylen- or propylenimine in ether.



I II III IV

I and IIIa, Ar = 4-chlorphenyl, R = H
b, Ar = phenyl, R = H
c, Ar = 3,4-dichlorophenyl, R = H
d, Ar = phenyl, R = $CH_3$,
e, Ar = 3-nitrophenyl, R = H
IIa, Ar = 4-chlorophenyl, R = H, X = Cl
b, Ar = 4-chlorophenyl, R = H, X = Br

When 1-(4-chlorobenzoyl)aziridine oxime [Ia; mp 176–178°; infrared spectrum (Nujol): absorptions at 3200 (moderate), 1635 (moderate), 1590 $cm^{-1}$ (weak); nmr spectrum:[3] singlet at $\delta$ 2.27 (four protons), multiplet centered at 7.58 (four protons), singlet at 9.7 (one exchangeable proton)] thus prepared was heated for a short period with enough concentrated hydrochloric acid to bring it into solution, the mixture then evaporated to dryness, and the residue dissolved in a minimum quantity of water and rendered strongly alkaline, an isomeric compound (mp 160–162°; molecular weight by mass spectral determination[4] 196) was isolated. Its infrared spectrum exhibits absorptions at 3300 (moderate) and 1590 $cm^{-1}$ (strong), and its nmr spectrum[3] carries a pair of $A_2B_2$ multiplets centered at $\delta$ 3.57 and 3.93, respectively, a broad singlet at 6.38 (one exchangeable proton), and a multiplet centered at 7.56 (four protons). These physical data would fit in with either of the two structures, IIIa and IV (Ar = 4-chlorophenyl, R = H), possible for this isomeric compound.

Structure IV was eliminated on the following grounds. Treatment of this compound with triphenylphosphine, triethyl phosphite, or phosphorus oxychloride in refluxing benzene left it unchanged, whereas if structure IV (Ar = 4-chlorophenyl, R = H) were correct it should have been smoothly deoxygenated to 2-(4-chlorophenyl)-$\Delta^2$-imidazoline. Secondly, if this compound possesses the N-oxide structure IV (Ar = 4-chlorophenyl, R = H), then its mass spectrum should exhibit a peak at *m/e* 180 (M − 16 ion peak) arising from the loss of an oxygen atom.[5] Actually its mass spectrum contains no peak in the region between *m/e* 153 and 196, and is compatible with the alternate structure IIIa. Finally, IIIa was synthesized by a different method. Condensation of 4-chlorobenzo-

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(1) H. W. Heine, *Angew. Chem. Intern. Ed. Engl.*, **1**, 528 (1962), and references cited therein.

(2) Satisfactory elemental analyses were obtained for all the new compounds reported herein.

(3) A Varian A-60 instrument was used with $CD_3COCD_3$ as solvent and TMS as internal standard.

(4) We are grateful to Dr. H. Hürzeler of CIBA Ltd., Basle, Switzerland, for the determination and interpretation of the mass spectrum.

(5) T. A. Bryce and J. R. Maxwell, *Chem. Commun.*, 206 (1965); A. Chatterjee, P. L. Majumder, and A. B. Ray, *Tetrahedron Letters*, 159 (1965).