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PHOTOISOMERIZATION OF BIS(TRIFLUOROMETHYL)THIOPHENES

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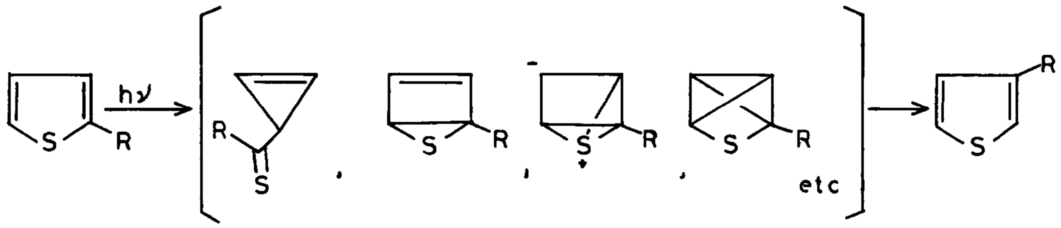
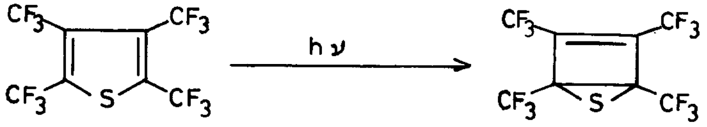
Summary: The photolysis of 2,3-bis(trifluoromethyl)thiophene gave an equilibrium mixture of 2,3- and 3,4-bis(trifluoromethyl)Dewar thiophenes, while that of 2,5-bis(trifluoromethyl)thiophene gave 2,4-bis(trifluoromethyl)-thiophene, which seemed to be formed through an intermediate other than the Dewar form.

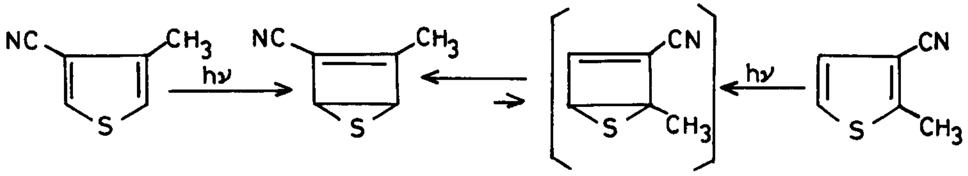
The photoreaction of thiophene derivatives has long been investigated since the photoisomerization of 2-arylthiophene to 3-arylthiophene was first reported.1) A number of valence bond isomers of thiophene have been proposed as intermediates for the isomerization.2)



Among these, a cyclopropenylthioketone intermediate proposed by Couture et al. based on the fact that the photolysis of a thiophene in the presence of a primary amine gives a pyrrole compound, was believed to be the most probable one.3) However, any of these intermediates had not been isolated, until a Dewar type isomer was obtained by the photoreaction of tetrakis(trifluoromethyl)thiophene.4) The remarkable stability of this Dewar thiophene can be explained as due to the presence of the trifluoromethyl groups; perfluoroalkyl group generally stabilize a strained ring system.5)

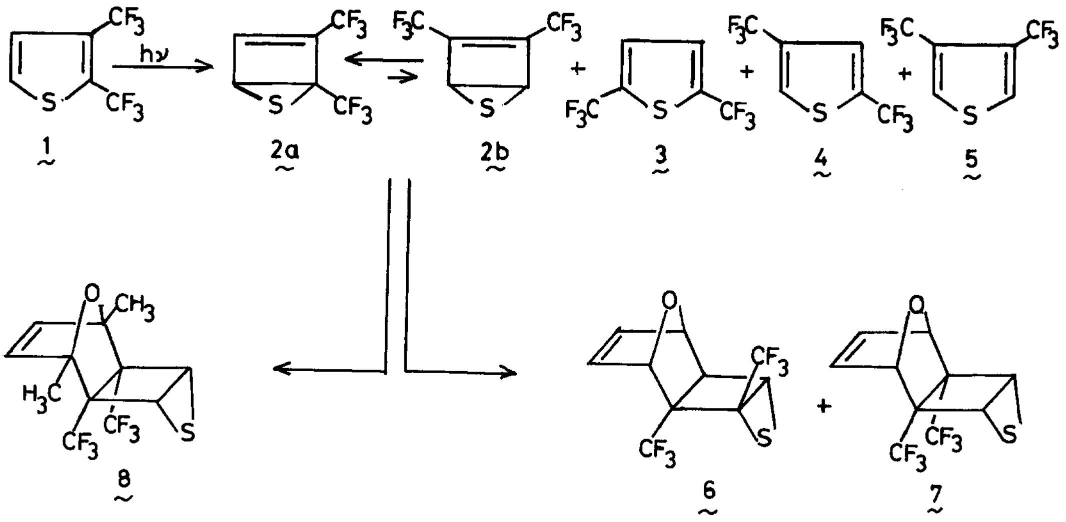


A few years after the isolation of the Dewar thiophene mentioned above, methylcyanothiophenes were reported to give a Dewar isomer on photolysis.$^{6)}$ In this case, a pull-push interaction of cyano and methyl groups is believed to take part in the stabilization of the Dewar isomer. Thus, pertrifluoromethylation is not neccessary for the isolation of a Dewar thiophene.



Therefore, we planned to examine the photoisomerization of bis(trifluoromethyl)thiophenes to determine the substituent effects of trifluoromethyl groups and found that one isomer gave a Dewar isomer on photolysis and the other isomer gave rearranged thiophene but not through a Dewar isomer.

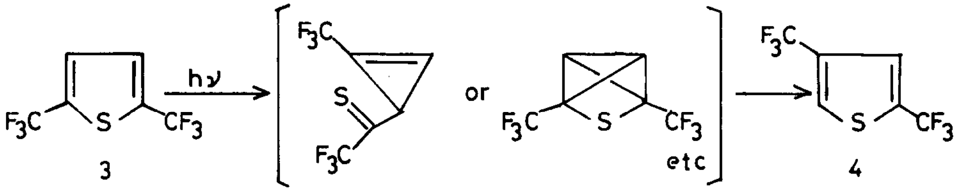
Gas-phase irradiation of 2,3-bis(trifluoromethyl)thiophene (**1**) by a low pressure Hg lamp (Rayonet Photochemical Reactor 2537Å) in a quartz vacuum line and separation by preparative gas chromatography gave a mixture of Dewar thiophenes (**2a** and **2b**) (**2a**/**2b**=8/1)$^{7)}$ as a yellowish highly volatile oil, and isomerized thiophenes **3**,**4**,**5** with the recovery of **1**. The Diels-Alder reaction of this mixture of Dewar thiophenes **2a** and **2b** with furan at room temperature gave two adducts, **6**$^{8)}$ and **7**$^{9)}$, but the ratio of these products was different from that of the starting Dewar isomers. The ratio of **6** and **7** was found to be affected by the reaction conditions. Furthermore, the Diels-Alder reaction of this Dewar mixture with 2,5-dimethylfuran gave only one product **8**.$^{10)}$



The process of this addition reaction with 2,5-dimethyl furan was followed by ^{19}F-nmr. The signal of **2b** disappeared immediately after addition of 2,5-dimethyl furan; at the same time, the signals of **8** appeared, and then the signals of **2a** decreased gradually as those of **8** increased. Finally, the signals of **2a** and **2b** disappeared completely and only new signals of **8** were observed.

From these results, it was confirmed that Dewar isomers **2a** and **2b** form a equilibrium mixture and the equilibrium is inclined to **2a**, probably because the steric and dipole repulsion between the trifluoromethyl groups on **2a** is smaller than that of **2b**. However, the reactivity of **2b** as a dienophile in the Diels-Alder reaction seems higher than **2a** because of the electron withdrawing effect of two trifluoromethyl groups on the olefin and because of unfavorable repulsion of the trifluoromethyl group on the bridge-head of **2a** toward the diene component. Therefore, furan reacts with **2b** favorably, and in particular, 2,5-dimethylfuran, a sterically bulky diene, gives the adduct **8** exclusively.

In contrast to 2,3-bis(trifluoromethyl)thiophene (**1**), irradiation of 2,5-bis(trifluoromethyl)thiophene (**3**) under the same conditions gave no Dewar isomers, but 2,4-bis(trifluoromethyl)thiophene (**4**) was isolated with the recovery of **3**. Compound **4** could not be formed by walk-mechanism of sulfur atom[11] in the Dewar isomer of **3** but through a cyclopropenylthioketone isomer or one of the tricyclic isomers shown below.[2]



3,4-Bis(trifluoromethyl)thiophehe (**5**) exhibits an ultraviolet absorption at 226nm, a much shorter wavelength than that of any of the other trifluoromethylated thiophenes. The photolysis of **5** gave only a trace of **4**, as detected by g.l.c.

In conclusion, two trifluoromethyl groups are sufficient for formation of Dewar thiophenes, provided they are placed in proper positions in the ring. Another type of isomerization not through a Dewar thiophene was observed, depending on the positions of the trifluoromethyl groups.

References

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2. see Y. Kobayashi, and I. Kumadaki, "Advances in Heterocyclic Chemistry" Ed. by A. Katritzky, Academic Press. Vol. 31, p. 169 (1982).
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7. **2a**: ^{1}H-nmr(CDCl$_3$)δ; 4.23(1H, m), 7.04(1H, m). ^{19}F-nmr(CDCl$_3$)ppm: 4.76 (3F, sept), 2.78(3F, m). **2b**: ^{1}H-nmr(CDCl$_3$)δ: 4.16(2H, s). ^{19}F-nmr (CDCl$_3$) ppm: 2.92(6F, s). High resolution mass spectrum Calcd. for $C_6H_2F_6S$, 219.9781. Found: 219.9806.
8. **6**: Colourless oil. bp 98-102/20mmHg. ^{1}H-nmr(CDCl$_3$)δ: 2.71(1H, s) 3.82(1H, bs), 5.04(1H, bs), 5.38(1H, bs), 6.54(2H, bs). ^{19}F-nmr(CDCl$_3$)ppm 1.64(3F, bs). -4.03(3F, bs). High resolution mass spectrum Calcd. for $C_{10}H_6F_6OS$, 288.0043. Found: 288.0045.
9. **7**: Colurless cryst. mp 83-85°C (n-hexane). 1H-nmr(CDCl$_3$)δ: 3.53(2H, bs), 5.08(2H, bs), 6.63(2H, bs). ^{19}F-nmr(CDCl$_2$)ppm: -0.75(6F, s). High resolution mass spectrum $C_{10}H_6F_6OS$, 288.0042. Found: 288.0035.
10. **8**: Colourless cryst. mp 104-106°C (n-hexane). 1H-nmr(CDCl$_3$)δ: 1.73(6H, s), 3.52(2H, bs), 6.40(2H, bs). ^{19}F-nmr(CDCl$_3$)ppm: -158(6F, s). High resolution mass spectrum Calcd. for $C_{12}H_{10}F_6OS$, 316.0356. Found: 316.0361.
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