

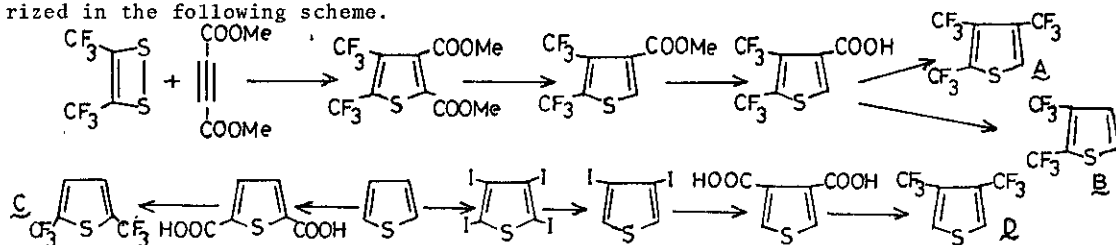
PHOTOISOMERIZATION OF TRIFLUOROMETHYLATED THIOPHENES

Yoshiro Kobayashi, Kosuke Kawada, Akira Ando, and Itsumaro Kumadaki

Tokyo College of Pharmacy, 1432-1, Horinouchi, Hachioji, Tokyo 192-03, Japan

Photoreaction of tetrakis(trifluoromethyl)thiophene gave a "Dewar" thiophene. This isolation of the highly strained compound is believed to be due to the stabilizing effect of the trifluoromethyl groups. This effect is called as "perfluoroalkyl effect", but it is not clear what factor of trifluoromethyl groups control the stability of the strained compounds. To make this point clear, we planned the photoisomerization of bis- or tris(trifluoromethyl)thiophenes; namely, the numbers and the positions of trifluoromethyl groups which make the Dewar isomer stable enough for isolation would be useful for understanding the "perfluoroalkyl effect".

Syntheses of bis- and tris(trifluoroalkyl)thiophenes (A, B, C, and D) are summarized in the following scheme.



Photolysis of A in gas phase gave a mixture of two Dewar isomers and 2,3,5-tris(trifluoromethyl)thiophene. Addition of furan to the mixture gave only one adduct. This fact shows that an equilibrium is present between two isomers of Dewar type and that one isomer is more reactive than the other. Photoreaction of B gave a mixture of two Dewar isomers and 2,5-bis(trifluoromethyl)thiophene. The Dewar isomers reacted with furan to give two adducts, but the ratio of the adducts was different from that of the Dewar isomers. Photoreaction of C did not give the Dewar isomer.

