

SYNTHESIS OF CONDENSED THIOPHENES
BY THERMAL REACTIONS OF ARYL PROPARGYL SULFOXIDES

Yasuo Makisumi and Susumu Takada

Shionogi Research Laboratory, Shionogi & Co., Ltd.

Fukushima-ku, Osaka, 553

β -Naphthyl propargyl sulfoxide (Ia) was heated at 80°C in dimethylaniline to give 1-formyl-1,2-dihydronaphtho[2,1-b]-thiophene (IIa) in over 70 % yield. A possible mechanism was considered to involve a (2,3)-sigmatropic rearrangement to the sulfenate ester (A), and a (2,3)-sigmatropic rearrangement (Claisen rearrangement) followed by an intramolecular Michael addition of the resulting thiol (B). This mechanism was supported by trapping the intermediate IIIa (an equivalent of B) in CCl₄ or dioxane solution. The reactions of sulfoxides (Ia,b) in protic solvents gave mainly naphthothiophenes (IV) with incorporation of the solvent molecules as substituents. This is presumably caused by an S_N^{2'} displacement of the allylic hydroxyl group of III. Formation of the thiophene derivatives (IV) was more efficiently performed by a "one-flask" procedure in which the protic solvent and catalytic acid were added to III, obtained by heating a dioxane solution of I. These reactions were also applied to phenyl propargyl sulfoxides to give benzothiophene derivatives.

