SYNTHESIS OF CONDENSED THIOPHENES BY THERMAL REACTIONS OF ARYL PROPARGYL SULFOXIDES

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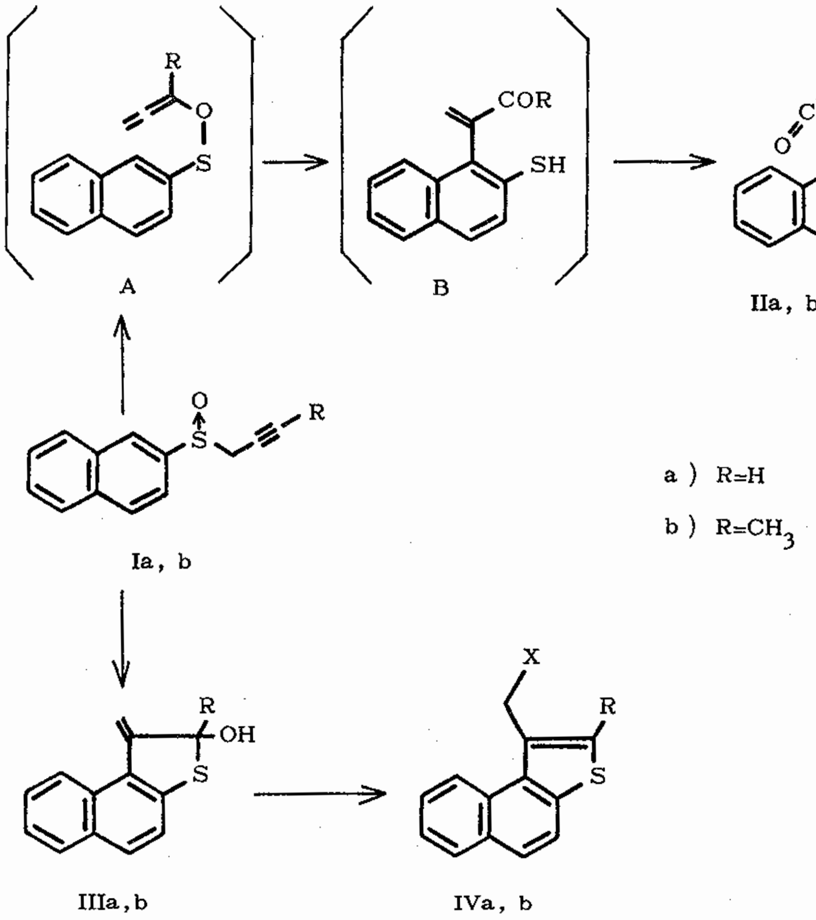
β-Naphthyl propargyl sulfoxide (Ia) was heated at 80°C in dimethylaniline to give 1-formyl-1,2-dihydronaphtho[2,1-b]-thiophene (IIa) in over 70 % yield. A possible mechanism was considered to involve a [2,3]-sigmatropic rearrangement to the sulfenate ester (A), and a [2,3]-sigmatropic rearrangement (Claisen 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 CCl_4 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_N2' 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.


A
B
IIa, b
Ia, b
IIIa,b
IVa, b
R
O
S
COR
SH
C
OH
X
a) R=H
b) R=CH3