REACTION OF CYCLIC SULFILIMINES

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Thermolysis of 2,2-dimethyl-1-(p-toluenesulfonylimino)thiochroman (I) afforded the dimerized product, N-[2-(3-methyl-3-butenyl)phenylthio]-N-(2'-methylthiochroman-2'-ylmethyl)-p-toluenesulfonamide (II), which decomposed to N,N-bis(2-methylthiochroman-2-ylmethyl)-p-toluenesulfonamide (III), 2-methyl-2-(p-toluenesulfonylaminomethyl)thiochroman (IV), 3-methyl-2,5-dihydro-1-benzothiepin (V) and 2,5-dihydro-1-benzothiepin-$\Delta^{3(4H)}$-methane (VI) when II was refluxed in xylene.

Reaction of I with acetic acid or acetic anhydride afforded IV and 2-acetoxymethyl-2-methylthiochroman (VII). Treatment of I in dimethyl sulfoxide also gave IV. These reactions are the first example of 1,3-abnormal Pummerer reaction of sulfilimine. The mechanism for the formation of 2-substituted thiochroman derivatives is considered to proceed via episulfonium intermediate.

Another interesting product of the reaction of I with sulfoxides is 2-formyl-2-methylthiochroman (VIII) formed by the oxidation of sulfoxides.

2-(3-Methyl-3-butenyl)phenyl phenyl disulfide (IX), N-benzyl-2-(3-methyl-3-butenyl)benzenesulfenamide (X) and 2-(3-methyl-3-butenyl)phenyl phenyl sulfide (XI) were formed, respectively, when I was treated with nucleophiles such as phenylmercaptan, benzylamine and phenylmagnesium bromide.