SYNTHESIS OF PHOSPHONATES FROM HETEROAROMATIC CATIONS AND THEIR USE IN WITTIG REACTION

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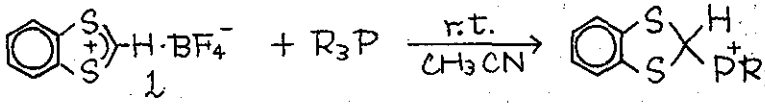
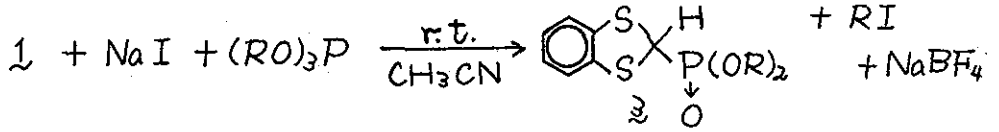
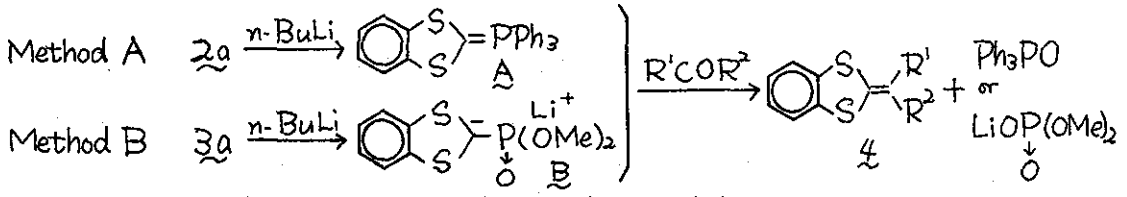
1,3-Benzodithiolylium tetrafluoroborate (1) reacted with phosphines in acetonitrile at room temperature to give the corresponding phosphonium salts (2) in high yields [2a: R=Ph, 87%, mp 211.5–212.5 °C (dec.); 2b: R=n-Bu, 90%, mp 166.5–168.0 °C].



Also, 1 reacted with trialkyl phosphites in the presence of an equimolar amount of sodium iodide to give dialkyl 1,3-benzodithiolylphosphonates (3) [3a: R=Me, 93%, mp 121.5–122.5 °C; 3b: R=Et, 90%, mp 115.0–116.0 °C].



Both 2 and 3 were deprotonated with n-butyllithium in THF at -78 °C and the resulting anions (A and B) reacted with carbonyl compounds to give 1,4-benzodithiafulvenes (4) in good yields (74–98%). Moreover, B reacted with fluorenone, tetracyclone, xanthone, thioxanthone, N-methylacridone, and so on to give 1,4-benzodithiafulvalenes which are iso-π-electronic with sesquifulvalenes or heptafulvalenes.



Heteroaromatic cations such as 1,3-dithiolylium, acridinium, xanthylium, thioxanthylium, and thiochromenium ions also reacted with trimethyl phosphite in dry acetonitrile to give the corresponding phosphonates in high yields (76 - 92%). These phosphonates were submitted to Wittig-Horner reaction to give the expected products in good yields (~80%).