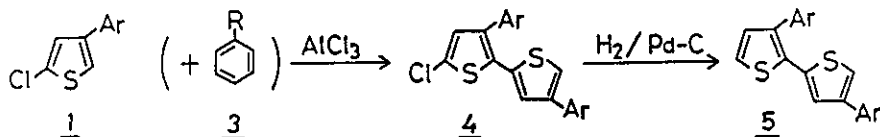


ALUMINUM CHLORIDE-CATALYZED REACTIONS OF 4-ARYL-2-CHLORO- AND
3-ARYL-2-CHLOROTHIOPHENES WITH SOME AROMATIC COMPOUNDS

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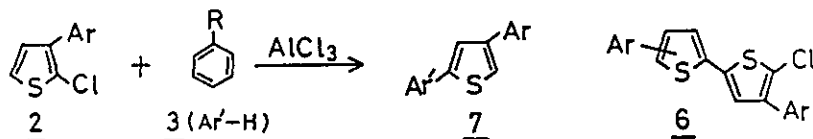
Recently we have found that, in the presence of aluminum chloride, 2-chlorothiophene and 2,5-dichlorothiophene react with some aromatic compounds to form the corresponding 2-arylthiophenes and 4-aryl-2-chlorothiophenes, respectively. As an extension of the study, the aluminum chloride-catalyzed reactions of 4-aryl-2-chloro- (1) and 3-aryl-2-chlorothiophenes (2) with some aromatic compounds (3) has been investigated. The reaction of 1 (1:3:AlCl₃ = 1:0-3:1) took place easily under mild conditions yielding the self-condensation products, 5-chloro-3,4'-diaryl-2,2'-bithienyls (4), as the major products. The catalytic dechlorination of 4 gave the parent diaryl-2,2'-bithienyls (5) in good yields.



a: Ar=C₆H₅; b: Ar=p-CH₃C₆H₄; c: Ar=p-C₂H₅C₆H₄
d: Ar=p-CH₃OC₆H₄; e: Ar=2-naphthyl

The reaction of 2a with benzene or toluene also gave the self-condensation product (6a) of 2a but in low yield. On the other hand, the reaction of 2a-c with more reactive aromatic compounds such as anisole and 1-methoxynaphthalene unexpectedly led to 2,4-diarylthiophenes (7d-g) in 41-66% yields.

These reactions provide a new route to certain 3,4'-diaryl-2,2'-bithienyls (5) and 2,4'-diarylthiophenes (7).



a: Ar=C₆H₅; b: Ar=p-CH₃OC₆H₄; c: Ar=5-chloro-2-thienyl; d: Ar=C₆H₅,
Ar'=p-CH₃OC₆H₄; e: Ar=Ar'=p-CH₃OC₆H₄; f: Ar=C₆H₅, Ar'=1-methoxy-
4-naphthyl; g: Ar=5-chloro-2-thienyl, Ar'=p-CH₃OC₆H₄