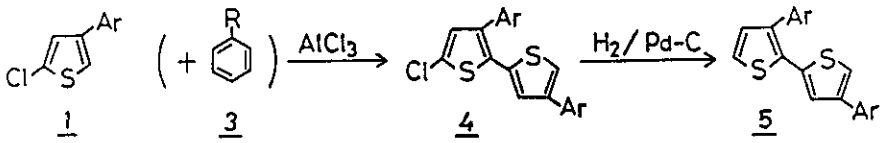
# ALUMINUM CHLORIDE-CATALYZED REACTIONS OF 4-ARYL-2-CHLORO- AND 3-ARYL-2-CHLOROTHIOPHENES WITH SOME AROMATIC COMPOUNDS

T. Sone, K. Sato, and Y. Umetsu

Department of Applied Chemistry, Faculty of Engineering, Yamagata University, Yonezawa 992, Japan

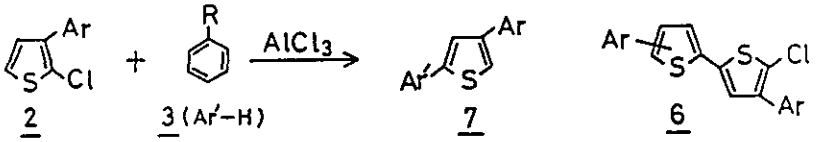
Recently we have found that, in the presence of aluminum chloride, 2-chlorothiophene and 2,5-dichlorothiophene react with some aromatic compounds to form the corresponding 2-arylthiophenes and 4-aryl-2-chlorothiophenes, respectively. As an extension of the study, the aluminum chloride-catalyzed reactions 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:$AlCl_3$= 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.




1 3 4 5

a: Ar=$C_6H_5$; b: Ar=p-$CH_3C_6H_4$; c: Ar=p-$C_2H_5C_6H_4$
d: Ar=p-$CH_3OC_6H_4$; 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).




2 3 (Ar'-H) 7 6

a: Ar=$C_6H_5$; b: Ar=p-$CH_3OC_6H_4$; c: Ar=5-chloro-2-thienyl; d: Ar=$C_6H_5$, Ar'=p-$CH_3OC_6H_4$; e: Ar=Ar'=p-$CH_3OC_6H_4$; f: Ar=$C_6H_5$, Ar'=1-methoxy-4-naphthyl; g: Ar=5-chloro-2-thienyl, Ar'=p-$CH_3OC_6H_4$