SYNTHESIS OF NITROFURAN DERIVATIVES
(REACTION OF 5-NITROFURFURAL WITH TOLUIC ACID)

Ichiro Hirao, Fumihiro Tone, and Hideki Morishima
Department of Industrial Chemistry, Kyushu Institute of Technology
Tobata-ku, Kitakyushu, Japan

The reaction of 5-nitrofurfural with toluic acid was studied to produce the compounds having C=C double bond by the condensation of aldehyde compounds with ring compounds having active methyl group.

The direct dehydration condensation of 5-nitrofurfural with toluic acid, the Perkin type condensation reaction of 5-nitrofurfural with 4-carboxyphenylacetic acid and the Wittig reaction of 5-nitrofurfural with 4-methoxycarbonylbenzyltriphenylphosphonium bromide were investigated to synthesize 5-nitro-2-(4-carboxystyryl)furan. In these reactions, the Wittig reaction was favorable one to produce 5-nitro-2-(4-carboxystyryl)furan in a good yield and conveniently.

Then, the authors investigated the reaction of 5-nitrofurfural with the related compounds of toluic acid (o,m,p-nitro-toluic acid, 2,3-cresotic acid, 2,4-cresotic acid, 2,5-cresotic acid) through the Wittig reaction.

5-Nitro-2-(4-nitro-2-carboxystyryl)furan, 5-nitro-2-(4-nitro-3-methoxycarbonylstyryl)furan and 5-nitro-2-(2-nitro-4-carboxystyryl)furan were synthesized through the Wittig reaction of 5-nitrofurfural with the corresponding phosphonium salts prepared from 5-nitro-2-bromomethylbenzoic acid, methyl 2-nitro-5-bromomethylbenzoate and 3-nitro-4-bromomethylbenzoic acid with triphenylphosphine respectively.

Also, 5-nitro-2-(3-hydroxy-4-carboxystyryl)furan, 5-nitro-2-(4-hydroxy-5-carboxystyryl)furan and 5-nitro-2-(2-hydroxy-3-carboxystyryl)furan were prepared through the Wittig reaction of 5-nitrofurfural with 3-hydroxy-4-methoxycarbonylbenzyltriphenylphosphonium bromide, 4-hydroxy-5-methoxycarbonylbenzyltriphenylphosphonium bromide and 2-hydroxy-3-methoxycarbonylbenzyltriphenylphosphonium bromide respectively. 5-Nitro-2-(3-hydroxy-4-carboxystyryl)furan was prepared in a good yield, but the other compounds were in a few % yield. Therefore hydroxy-group of methyl cresotate was acetylated to protect against base. Consequently, the yield of 5-nitro-2-(4-hydroxy-5-carboxystyryl)-furan and 5-nitro-2-(2-hydroxy-3-carboxystyryl)furan were elevated from a few% to 10-20 %.

Then the ester and carbamoyl derivatives were prepared by the reaction of 5-nitro-2-(4-nitro-2-carboxystyryl)furan, 5-nitro-2-(2-nitro-4-carboxystyryl)furan and 5-nitro-2-(3-hydroxy-4-carboxystyryl)furan with alcohols and amines respectively.