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A SIMPLE SYNTHESIS OF 2,2',5',2"-TERTHIENYL

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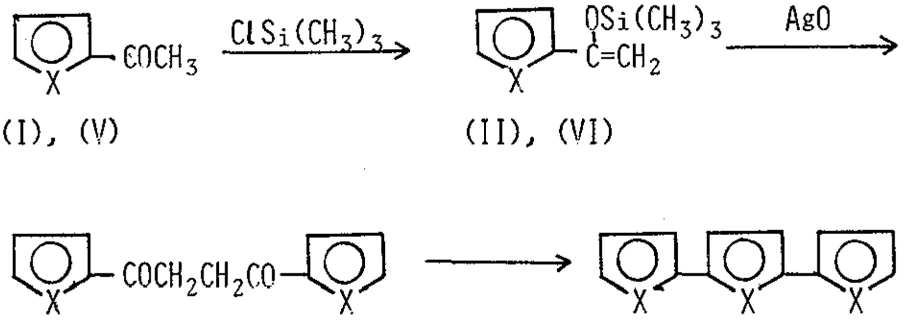
The synthesis of 2,2',5',2"-terthienyl (IV) is reported. A key intermediate in this synthesis was 1,4-di(2-thienyl)-1,4-butanedione (III), which was prepared from trimethylsilyl enol ether (II) of 2-acetylthiophene (I). Corresponding furyl derivatives were also synthesized by the similar procedure.

Since 2,2',5',2"-terthienyl (IV) was isolated from Tagestes plants[1], considerable attention have been given to synthesize it and some methods have been reported in literatures[2], because of its high nematicidal activity against nematodes such as *Ditylenchus dipsaci* and *Heterodea rostochiensis*[3].

However those methods are laborious and/or the yields are not satisfactory. In this paper, we wish to report a simple synthesis of IV from commercially available 2-acetylthiophen (I) in three steps.

Our synthetic scheme is based on preparation of 1,4-di-(2-thienyl)-1,4-butanedione (III) as a key intermediate derived from 2-acetylthiophene (I). Recently attention has been paid to the preparation of 1,4-butanedione derivatives[4], and as a new synthetic method, it was reported that trimethylsilyl enol ether of acetophenone gave 1,4-diphenyl-1,4-butanedione[5]. We prepared **III** by a modification of the method.



(I), (V)

(II), (VI)

(III), (VII)

(IV), (VIII)

(I), (II), (III)_ (IV): X = S

(V), (VI), (VII), (VIII): X = O

The reaction of **I** with trimethylchlorosilane (1.3 equiv) *and triethylamine (2.5 equiv) in dimethylformamide gave* trimethylsilyl enol ether (II) in an excellent yield (90%). The physical data of **II** are as follows: bp 73°/2 Torr: M^+ 198

($C_9H_{14}OSSi$): IR (liquid); no carbonyl, 1617 (shoulder) and 1595 cm^{-1}: nmr (CCl_4); δ 0.36 (s, 3H, Si-Me), 0.41 (s, 6H, Si-Me), 4.23 and 4.71 (d, each 1H, J=1.7, $=CH_2$), and 6.81-7.58 (m, 3H, ring H). Stirring of II with silveroxide (2 equiv) in dimethylformamide on a steam bath afforded pale yellow crystals of III in71% yield: mp 130° (130-131° in lit.[2(b)]): M^+ 250 ($C_{12}H_{10}O_2S_2$): nmr ($CDCl_3$); 3.32 (s, 4H, $COCH_2$), 7.04-7.82 (m, 6H, ring H): IR ($CHCl_3$); 1638 cm^{-1} (C=O). Treatment of III with hydrogen chloride and hydrogen sulfide in ethanol gave a greenish yellow substsnce (IV) in 66% yield: mp 92-93° (94-95.5° in lit.[1]). Its elemental analysis ($C_{12}H_8S_3$) and UV spectrum data confirm that the structure of IV is 2,2',5',2"-terthienyl[1].

Similarly, when 2-acetylfuran (V) was used as a starting material, trimethylsilyl enol ether (VI) and 1,4-di(2-furyl)-1,4-butanedione (VII) were obtained by the same procedure as above, and treatment of VII with acetic anhydride and hydrochloric acid gave pale yellow crystals of 2,2',5',2"-terfuryl (VIII) (overall yield 65%). These substances possess following properties. VI, bp 48-49°/3 Torr: IR (liquid); 3120, 2950, 1635 (shoulder) and 1618 cm^{-1}: M^+ 182 ($C_9H_{14}O_2Si$). VII, mp 128-130° (132 in lit.[6]): M^+ 218 ($C_{12}H_{10}O_4$). VIII, mp 62-63°: IR ($CHCl_3$); 3130, 1580, 1522, 1430 and 998 cm^{-1}: M^+ 200 ($C_{12}H_8O_3$): nmr ($CDCl_3$) δ 6.33-6.66 (m, 6H) and 7.33-7.48 (m, 2H).

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