Some Substituted 2,2′-Bithiophenes

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OVER THE LAST ten years a number of investigators have reported the preparation of hydrocarbons, alcohols, ketones, mono- and dicarboxylic acids, and substituted acids by the desulfurization of selected derivatives of thiophene (*1, 2, 3, 4, 5, 8*).

While the preparation of some halogen (*6*), alkyl (*7*), and acetyl (*8*) derivatives of bithienyl has been reported, the desulfurization of these derivatives is very limited (*8*).

The use of bithienyl in place of thiophene in chain-extending reactions allows the introduction of four additional methylene groups into the final compound and thus can facilitate the preparation of long-chained compounds. This investigation was therefore undertaken to study the effect of the substitution of 2,2′-bithienyl for thiophene in chain-extending reactions.

The first phase of the work covered the preparation of hydrocarbons using thiophene as the chain extender in the synthesis of *n*-eicosane and *n*-octane, and bithienyl as the chain extender in the synthesis of *n*-tetracosane and *n*-dodecane. The basic conditions used for the necessary acylations and reductions were the same for both thiophene and bithienyl, affording the basis for a comparison of yields.

The acylation of thiophene, or bithienyl, by an acyl chloride (*5*) with anhydrous stannic chloride as catalyst was followed by reduction of the resulting ketone using hydrazine hydrate (*5*).

The resultant 2-*n*-alkylthiophene, or 5-*n*-alkyl-2,2′-bithienyl, was then acylated with the same acyl chloride as used in the first step, and the ketone thus formed was reduced, again with hydrazine hydrate. Reduction and desulfurization of the resultant 2,5-bis *n*-alkylthiophene, or 5,5′-bis *n*-alkyl-2,2′-bithienyl yielded the desired hydrocarbon.

The results of this phase of the work indicate that the overall yield of the hydrocarbon obtained by using bithienyl as a chain extender are similar to those obtained when thiophene is used, and that, therefore bithienyl can be substituted for thiophene as a chain extender in the preparation of hydrocarbons.

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Table I. Properties of Thiohydrocarbons

Yield	B.P., °C.	M.P., °C.	% C		% H		% S	
			Found	Calcd.	Found	Calcd.	Found	Calcd.
5-Octanoyl-2,2′-bithiophene								
79.0	...	82.5–83.0	65.83	65.71	6.78	6.89	22.18	21.92
5-*n*-Octyl-2,2′-bithiophene								
78.0	...	28.0–29.0	69.24	69.08	7.92	7.98	23.19	23.04
5-*n*-Octyl-5′-octanoyl-2,2′-bithiophene								
57.5	...	95.5–96.0	71.40	71.23	8.82	8.97	15.84	15.82
5,5′-Bis *n*-octyl-2,2′-bithiophene								
74.5		42.0–42.5	73.53	73.78	9.72	9.80	16.35	16.42
5-Ethyl-2,2′-bithiophene								
80.3	95–99(0.5mm)	...	60.89	61.81	5.44	5.19	32.67	32.96
5-Ethyl-5′-ethanoyl-2,2′-bithiophene								
65.2	...	106–107	61.20	60.98	4.97	5.12	27.26	27.98
5,5′-Bis ethyl-2,2′-bithiophene								
68.0	140–143(0.5mm)	...	64.59	64.80	6.20	6.35	28.65	28.84