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UNSYMMETRICAL COUPLING OF 2-ARYLTHIOPHENES BY CATION EXCHANGE RESIN

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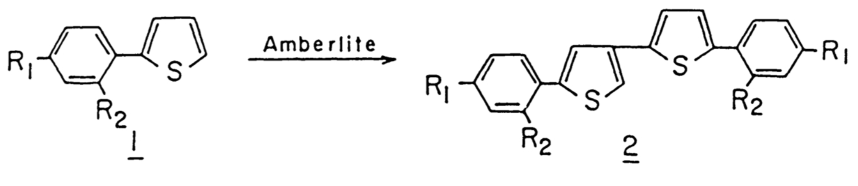
2-Arylthiophenes coupled through the 4,5'-positions of the two thiophene rings by the action of cation exchange resin to afford unsymmetrical 5,5'-diaryl-2,3'-bithienyls as principal products.

Interest is increasing in the preparation of oligothienylenes and those containing aromatic ring(s) in connection with their potential biological activity1) and electroconducting polymer.2)

Polymerization of certain thiophene derivatives by the action of acidic materials has been well known;3) in most cases resinous materials possessing complicated structures are formed. In contrast, we have recently found that cation exchange resin produces the simple oligomers of 2-methyl-4a) and 2-chlorothiophenes.4b) The structures of the oligomers depend markedly upon the substituent; in the former case a mixture of the cis and trans isomers of 2,4-bis(5-methyl-2-thienyl)-2-methyltetrahydrothiophene is formed, while in the latter the dimer type products containing a tetrahydro-2-thiophenone moiety are formed. We now wish to report the acid-catalyzed reaction of 2-arylthiophenes (1) with cation exchange resin yielding the coupling products, unsymmetrical 5,5'-diaryl-2,3'-bithienyls (2), as principal products. The coupling through the 2,3'-positions of two thiophene rings appears to be unique,6) and 2 constitute a new class of oligothienylene analogues.



a: R_1=R_2=H b: R_1=CH_3, R_2=H c: R_1=R_2=CH_3
d: R_1=Br, R_2=H e: R_1=OCH_3, R_2=H

A typical procedure is as follows. A mixture of 2-phenylthiophene (1a, 6.4 g) and half its own weight of Amberlite CG-120 (H^+ form) was stirred for 30 hr at 130-135°C. The reaction mixture was extracted with chloroform in a Soxhlet extractor. Ether was added to the cooled extract to precipitate yellow crystals of 5,5'-diphenyl-2,3'-bithienyl (2a), which were collected by filtration and dried (1.2 g, mp 168-170°C). The solvents were evaporated from the filtrate and the residual mass was chromatographed (silica gel/hexane-chloroform (4:1)) to give an additional amount of 2a (0.4 g) together with unchanged 1a (2.2 g) and other minor products.8)

The structure of 2a was determined by spectroscopic method as well as by independent synthesis. Thus, the structure containing 2,3'-bithienylene unit was suggested by its UV spectrum (Table 1), which was distinguished from those of the symmetrical isomers.9) The authentic sample was synthesized by the reaction of 2-phenyl-4-oxotetrahydrothiophene with 5-phenyl-2-thienyllithium, followed by acidification, dehydration, and then dehydrogenation of the resulting dihydro compound by DDQ.

Similarly, the reaction of some 2-arylthiophenes (1b-1e) with the Amberlite leads to the formation of corresponding 5,5'-diaryl-2,3'-bithienyls (2b-2e), which would otherwise be accessible only by multi-step synthesis, in 38-51% yields (~65% conversion) with the exception of 2c (Table 1).

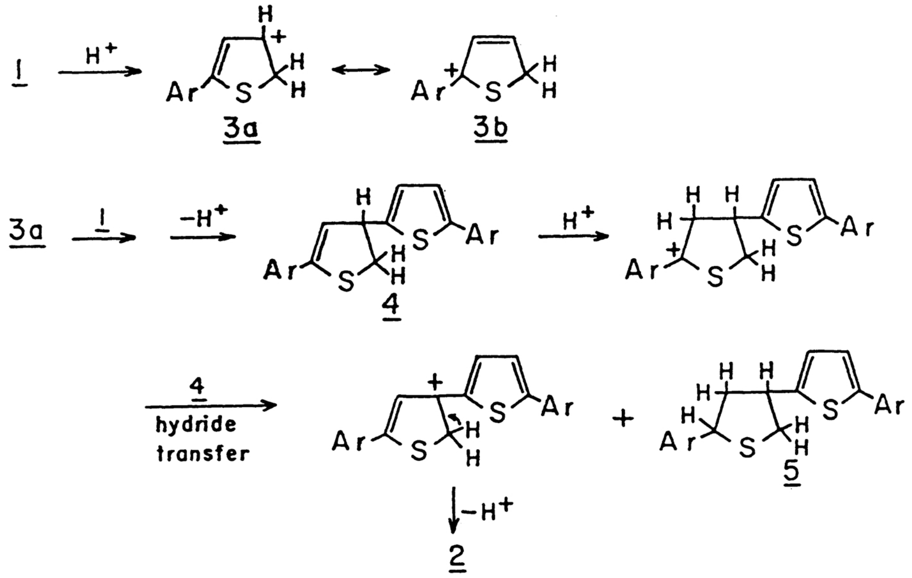
Table 1. Yields and physical properties of 5,5'-diaryl-2,3'-bithienyls[a]

Compd.		Mp (°C)	MS m/e(M^+)	UV $\lambda_{max}^{benzene}$ nm (log ε)	Yield[b] (%)
2a	$R_1=R_2=H$	168-169	318	303 (4.49), 325 (4.49)	38
2b	$R_1=CH_3$, $R_2=H$	189-190	346	305 (4.46), 326 (4.43)	44
2c	$R_1=R_2=CH_3$	64-65	374	294-302 (4.32)	19
2d	$R_1=Br$, $R_2=H$	208-210	474	311 (4.43), 333 (4.46)	50
2e	$R_1=OCH_3$, $R_2=H$	240-242	378	311 (4.43)	51

a) Satisfactory analyses were obtained for all new compounds.

b) Isolated yield based on 1 consumed.

A probable reaction pathway for the formation of the coupling products (2) is shown in Scheme 1. The low yield of 2c indicates the importance of the conjugation effect of aryl group in the arylthiophene molecules for the coupling reaction. The protonated intermediate 3b (Ar=H and CH_3 in the cases of thiophene and 2-methylthiophene), which is considered to play an important role in the acid-catalyzed reactions of thiophene⁵⁾ and 2-methylthiophene⁴ᵃ⁾ leading to the so-called thiophene trimers, does not make significant contributions, at least, to the coupling reaction.



Scheme 1

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4) a) T. Sone and M. Kubo, presented at the Tohoku District Meeting of the Chemical Society of Japan, Yonezawa, October, 1972. To be published elsewhere. Recently, Ishigaki et al. also reported the structure of the 2-methylthiophene trimer which was obtained by the method of Meisel et al.;5a) A. Ishigaki and T. Shono, Bull. Chem. Soc. Jpn., 48, 2977 (1975).
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6) Incidentally, an attempted oxidative coupling of 1 with an aluminum chloride-cupric chloride system, which had been successfully used for the coupling of aromatic nuclei by Kovacic et al.,7) afforded symmetrical 5,5'-diaryl-2,2'-bithienyls as the major products; T. Sone and S. Kohno, unpublished results.

7) L.-S. Wen, R. C. Zawalski, and P. Kovacic, J. Org. Chem., 43, 2435 (1978), and the preceding papers.

8) Oily compound (m/e 322) corresponding to the tetrahydrothiophene derivative 5 and 2,7-diphenylbenzo[b]thiophene (mp 92-93°C) were isolated as the by-products.

9) The symmetrical isomers were prepared by the reactions of 5-phenyl-2-thienyllithium and 2-phenyl-4-thienyllithium with cupric chloride, respectively. 5,5'-Diphenyl-2,2'-bithienyl (mp 246-247°C), λmax (benzene) 372 (4.50); 5,5'-diphenyl-3,3'-bithienyl (mp 168-169°C), UV (benzene) featureless beyond 280 nm.

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