

The Homolytic Phenylation of Thiophen

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HOMOLYTIC aromatic substitution has been extensively investigated recently,¹ but relatively little attention has been directed to arylation of five-membered heterocycles. 2-Arylthiophenes² are the only reported products of Gomberg arylations of thiophen, although the formation of both 2- and 3-phenyl-thiophen (19:1 molar ratio) in the phenylation of thiophen with *N*-nitrosoacetanilide has been reported.³ No studies employing the thermal decomposition of dibenzoyl peroxide or phenylazotriphenylmethane or the photolysis of

Decomposition of a 0.01M-solution of dibenzoyl peroxide in thiophen at 80° led to the isolation of benzoic acid (1.15 mole/mole of peroxide), benzene, and a mixture of 2-phenylthiophen, 2,2'-bithienyl, and 2,3'-bithienyl (see Table). The unexpected formation of the bithienyls could result from the attack on solvent by thienyl radicals formed by the abstraction of hydrogen from thiophen by phenyl radicals (scheme 1). However, the analogous reaction between phenyl radicals and benzene has been shown to be of a low order of occurrence by Eliel⁵ and the thiophen system would be expected to possess similar energetics. The formation of "excess" of benzoic acid in the reaction of dibenzoyl peroxide and thiophen is indicative of an induced decomposition and suggests an oxidation process (2) and (3) leading to thienyl radicals and, ultimately, to the thienyls. The formation of radicals by a one-electron transfer process of this type was first postulated by Horner,⁶ from studies of the decomposition of dibenzoyl peroxide in tertiary anilines and the postulation has been supported by studies of the decomposition of dibenzoyl peroxide in the presence of sulphides.⁷ Pausacker has observed the formation of bipyridyls in the reaction of pyridine with dibenzoyl peroxide,⁸ a process which is probably analogous to (2)–(3). Radical-cations of type (I) derived from 2,3,4,5-tetra-arylthiophens have recently been

Biaryl fractions from homolytic phenylations of thiophen*

Product (mole-%)	Radical source			
	A†	B†	C†	D†
2-Phenylthiophen‡	.. 22.8	86.7	63.0	63.1
3-Phenylthiophen —	13.3	37.0	5.5
2,2'-Bithienyl 58.8	—	—	24.5
2,3'-Bithienyl 18.3	—	—	6.8

* Biaryl fractions analyzed by g.l.c.

† A, Dibenzoyl peroxide; B, phenylazotriphenylmethane in air; C, phenylazotriphenylmethane in nitrogen; D, iodobenzene.

‡ Yield of 2-phenylthiophen (based on radical source): A, 3.75%; B, 0.91%; C, 0.58%; D, 3.25%.

iodobenzene⁴ as sources of radicals for the phenylation of thiophen have been reported.

¹ G. H. Williams, "Homolytic Aromatic Substitution," Pergamon Press, New York, N.Y., 1960.

² M. Gomberg and W. E. Bachmann, *J. Amer. Chem. Soc.*, 1924, **46**, 2339; Ng. Ph. Buu-Hoi and Ng. Hoan, *Rec. Trav. chim.*, 1950, **69**, 1455; P. A. S. Smith and J. H. Boyer, *J. Amer. Chem. Soc.*, 1951, **73**, 2626.

³ J. Degani, M. Pallotti, and A. Tundo, *Ann. Chim. (Italy)*, 1961, **51**, 434.

⁴ W. Wolf and N. Kharasch, *J. Org. Chem.*, 1961, **26**, 283.

⁵ E. L. Eliel, M. Eberhardt, O. Sinamura, and S. Meyerson, *Tetrahedron Letters*, 1962, 749.

⁶ L. Horner, *J. Polymer Sci.*, 1955, **18**, 438.

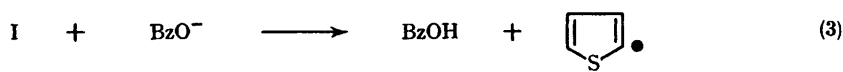
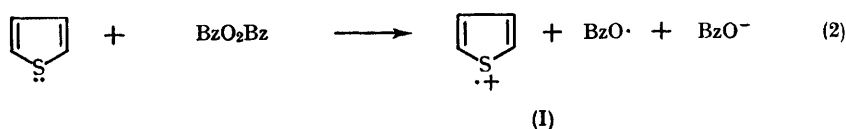
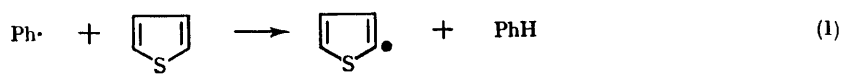
⁷ L. Horner and K. Scherf, *Annalen*, 1951, **573**, 35; L. Horner and E. Jürgens, *ibid.*, 1957, **602**, 135.

⁸ K. H. Pausacker, *Austral. J. Chem.*, 1958, **11**, 200.

detected by electron spin resonance spectroscopy.⁹

The formation of "excess" of benzoic acid and 2-phenylthiophen is in accord with the process (2)—(3). This process should not be observed with the employment of a radical source which cannot readily yield a stable nucleophile (*e.g.*, benzoate) as required in reaction (2)—(3). Thus the decomposition of phenylazotriphenylmethane,

it was shown that the bithienyls arising in this reaction were formed by the direct photolysis of thiophen. The only previous report of the irradiation of thiophen indicated the formation of hydrogen and hydrogen sulphide, but the non-gaseous products of the reaction were not investigated;¹⁰ the photolytic dimerization of benzothiophen has been demonstrated.¹¹



which yields phenyl and trityl radicals and nitrogen, would not be expected to yield the bithienyls. In accord with expectation, 2- and 3-phenylthiophens were the only biaryls isolated in the decomposition of a 0.01M-solution of phenylazotriphenylmethane in thiophen at 60° either in air or nitrogen.

The u.v. irradiation (96 hours) of a 0.01M-solution of iodobenzene in thiophen in the presence of metallic silver⁴ gave 2- and 3-phenylthiophen and 2,2'- and 2,3'-bithienyl. In a control experiment,

Thus it appears that for an oxidizable heterocycle (*e.g.*, thiophen), the process (2)—(3) leading to the radical-cation (I) is a plausible pathway.

The observed isomer ratios (2-/3-phenylthiophen) indicate a positional selectivity similar to that observed by Lynch and Chang¹² in the phenylation of 1-methyldiazoles and support the postulation that the site of free-radical attack can be predicted by resonance theory and free-valence numbers.^{12,13}

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⁹ U. Schmidt, K. Kabitzke, K. Markau, and A. Müller, *Annalen*, 1964, **672**, 78.

¹⁰ W. E. Haines, G. L. Cook, and J. S. Ball, *J. Amer. Chem. Soc.*, 1956, **78**, 5213.

¹¹ W. E. Haines, R. V. Helm, G. L. Cook, and J. S. Ball, *J. Phys. Chem.*, 1956, **60**, 549.

¹² B. M. Lynch and H. S. Chang, *Tetrahedron Letters*, 1964, 617.

¹³ F. L. Pilar and J. R. Morris, jun., *J. Chem. Phys.*, 1961, **34**, 389.