

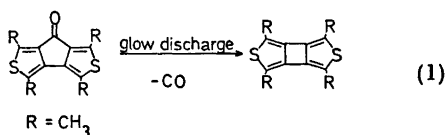
Reactions of Phenylthiophenes in Glow Discharges

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Naphthalene is the major product when phenylthiophenes are treated in the low-temperature plasma of glow discharges. The possibility of intervention of phenylcyclobutadiene is discussed.

The reactions of organic compounds in the low-temperature plasma of glow discharges have attracted much interest in recent years and the subject has been extensively reviewed.¹⁻³ Our interest in this field originated some time ago from an unsuccessful attempt to decarbonylate a thiophene analogue of fluorenone in a glow discharge [eqn. (1)]. The corresponding reaction with fluorenone is reported to give an excellent yield of biphenylene.⁴



However, in our case the reaction produced a complex mixture of material with high molecular weight which was not further characterised. We then decided to make a systematic study of the reactions of thiophenes in glow discharges and here report our results for the phenylthiophenes.

There were several reasons for our choice of substrates. First of all, phenylthiophenes have been extensively studied by mass spectrometry⁵⁻⁷ and also photochemically,⁸ both methods more or less related to plasma reactions.¹ Secondly, the benzene moiety has proved much more stable during electron impact than thiophenes, thereby increasing the possibility to isolate identifiable products. Finally, the glow

discharge reaction of thiophene itself has quite recently been reported from this Laboratory and the experimental details of the reactor are found in that report.⁹

RESULTS AND DISCUSSION

Only the ether-soluble products, amounting to nearly 80 % of the material passing the plasma zone, were analysed. The rest were polymeric deposits on the reactor walls, insoluble in both ether and chloroform, and gaseous products escaping the traps.

Table 1. Ether soluble products (excluding unchanged starting material) from reactions of phenylthiophenes in a glow discharge. The total yield of the sum of these products was in the range of 20–30 %.

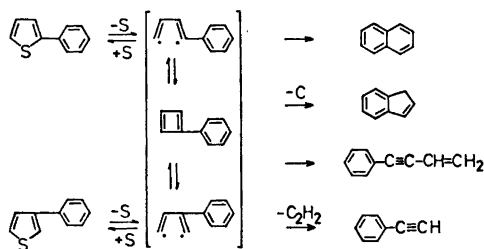
Products	Starting material		
	2-Phenylthiophene	3-Phenylthiophene	2-Phenylthiophene + acetylene ^a
2-Phenylthiophene	—	28 ± 5	—
3-Phenylthiophene	26 ± 5	—	—
Naphthalene	62 ± 10	44 ± 10	23 ± 5
Indene	5 ± 2	6 ± 2	15 ± 3
Biphenyl	0	0	Trace
1-Phenyl-3-buten-1-yne	2 ± 2	7 ± 3	15 ± 3
Phenylacetylene	5 ± 2	15 ± 3	23 ± 5
3 Comps. with M = 184	0	0	8 ± 2
Others	Trace	Trace	16 ± 3

^a Here the yields are calculated by excluding both unchanged and isomerised starting material.

Unchanged starting material constituted the major part (up to 60 %) of the ether-soluble products. The minor part had the composition shown in Table 1.

An immediate feature of these results is that 2-phenylthiophene isomerises to 3-phenylthiophene and *vice versa*. This reaction is probably not a mere fission/recombination of phenyl and thieryl radicals, but rather an *intra*-molecular rearrangement indicated by the absence of biphenyl, bithienyl, thiophene or benzene among the reaction products.

The major reaction product from both 2- and 3-phenylthiophene is naphthalene. Excluding starting material and isomerised starting material, the amount of naphthalene approaches 80–90 % of the ether soluble products. It is interesting that both isomers give naphthalene, indicating again a deep-seated rearrangement. Smaller amounts of indene, 1-phenyl-3-buten-1-yne and phenylacetylene were also produced. On the basis of this product distribution, the sequences shown in Scheme 1 are postulated.



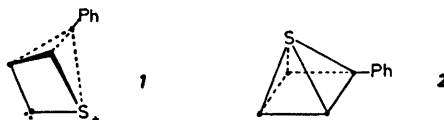
Scheme 1.

The intermediates are formulated as two phenylbutadiene diradicals in rapid equilibrium through phenylcyclobutadiene, a hypothesis that is supported by recent work of Suhr and Roskamp.¹⁰ They studied the reaction of phenylacetylene with acetylene in a low-temperature plasma and reported naphthalene as the major product and styrene, indene, benzene and toluene as the other liquid products. The formation of naphthalene was rationalised by postulating phenylcyclobutadiene to be the primary product which subsequently ring-opened to 1-phenylbutadiene diradical and cyclised to naphthalene. Also the formation of 1-phenyl-3-buten-1-yne through phenylcyclo-

butadiene finds support in this work, where the analogous vinylacetylene is reported to be formed from cyclobutadiene *via* the corresponding diradical.

It is also interesting to note that Bowie *et al.*⁵ postulated the phenylcyclobutadiene structure for the ion with $m/e = 128$ produced by loss of sulfur from the molecular ion of 2-phenylthiophene during electron impact in the mass spectrometer. In the opinion of the present authors the m/e 128 ion could, however, as well be attributed to a naphthalene structure.

The isomerisation of 2-phenylthiophene and 3-phenylthiophene is also explained by this reaction scheme. It is pertinent that 2-phenylthiophene has been found to undergo an irreversible photo-isomerisation to 3-phenylthiophene, also without breaking the aryl-aryl bond.⁸ The current hypothesis is that this isomerisation proceeds through the excited intermediate/transition state 1 which is stabilised by Möbius-like overlap.⁸



Although 1 would also explain the plasma induced isomerisations, it does seem neither necessary nor probable in explaining the formation of naphthalene or 1-phenyl-3-buten-1-yne.

In order to explain the fragmentation of ¹³C-labelled phenylthiophenes during electron impact in the mass spectrometer, Weringa *et al.*⁷ postulated the intermediate Ladenburg structure 2. It is very difficult to rule out such a possibility for the plasma isomerisation reactions, but again it is certainly not necessary for the naphthalene formation.

With the intention of checking whether phenylcyclobutadiene is an intermediate or merely a transition state, the plasma reaction of 2-phenylthiophene was performed also in the presence of acetylene (Table 1). One important result of this experiment is that biphenyl was detected in trace amounts only. Considering the high Diels-Alder reactivity of cyclobutadienes,¹¹ it is reasonable to regard phenylcyclobutadiene as nothing more than a transient species in these reactions. It is also worth mentioning

that the three isomeric products with molecular weight 184 (Table 1) correspond to starting material substituted by one ethynyl group. This indicates the existence of ethynyl radicals capable of attacking the thienyl and/or the phenyl ring.

The results presented provide an explanation for the failure to produce a thiophene analogue of biphenylene by a glow discharge reaction as mentioned initially (eqn. 1). The apparent reason being that sulfur is lost from the ketone before decarbonylation (or from the decarbonylated product) and that no simple route to stable products is open with the consequent formation of a very complex mixture of products.

EXPERIMENTAL

The substrates 2- and 3-phenylthiophene, were prepared according to literature procedures.¹²⁻¹⁴ The glow discharge reactor* was operated at an input effect of 30–50 W (as measured by the wattmeter between the transmitter and the generator plates). The rate of distillation per applied energy units was in the range of 10–60 g/kWh (0.1–0.3 mol/kWh) and was regulated by changing the temperature of the distillation flask.

The ether soluble products, accounting for 70–80 % of the material passing the plasma zone, were collected in the cooling trap at –78 °C and were analysed by GLC, performed on a Hewlett-Packard 5700 A with 10 % OV 17 or 10 % PEG 4000 columns (*l* 2.5 m, i.d. 0.02 m) using a flame ionisation detector. The identity of the products was also established by GLC/MS with the use of a Perkin Elmer 990 gas chromatograph coupled with a Hitachi-Perkin Elmer RMU-GL mass spectrometer. The preparative separation of naphthalene was performed on a Varian Aerograph 200 gas chromatograph. The NMR analyses were run on Varian HA-60A and HA-100.

All recorded products (Table 1) were identified by comparison with authentic samples. 1-Phenyl-3-buten-1-yne was prepared by treatment of 1-phenyl-3-tosyloxy-1-butyne with *t*-BuOK in THF. The tosylate was kindly supplied by Dr. J. L. Derocque, University of Saarland, to whom we extend our acknowledgements.

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