Formation of Thiophyne at High Temperatures

By ELLIS K. FIELDS
(*Research and Development Department, Amoco Chemicals Corporation, Whiting, Indiana*)
and SEYMOUR MEYERSON
(*Research and Development Department, American Oil Company, Whiting, Indiana*)

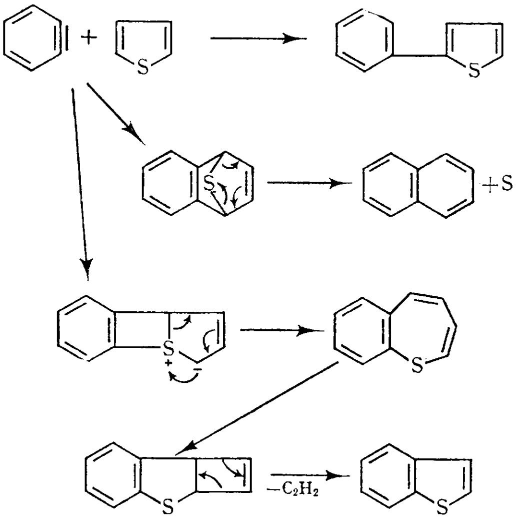
IN a continuing study of the formation and reactions of arynes at high temperatures,[1] we pyrolyzed a solution of phthalic anhydride (0·02 mole, freshly sublimed) in thiophen (0·4 mole, 99·8% purity) at 690°. The pyrolysis was run in a Vycor tube filled with Vycor beads, under pure, dry nitrogen flowing at the rate of 0·1 cu. ft./hr. The contact time was 15 sec. The condensed pyrolysate was distilled to recover the material boiling below 120°; the residue and distillate were analyzed by mass spectrometry and gas chromatography.

The products (2·5 g.) contained as major components:

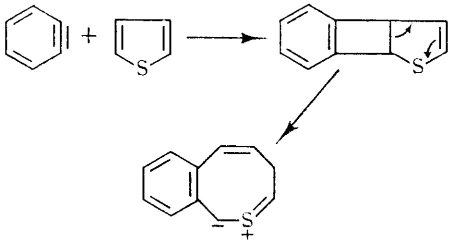
Product	Relative Intensity[a]
Naphthalene	160
Benzothiophen	18·1
Phenylthiophen	133
Bithienyl	100

[a] The numbers are the relative intensities of parent peaks in the low voltage mass spectrum. The intensities are all relative to a value of 100 assigned to bithienyl.

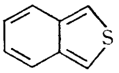
Bithienyls are formed by the pyrolysis of thiophen alone. The other products can be accounted for by 1,2- and 1,4-addition and insertion of benzyne from phthalic anhydride into thiophen:



The relatively large amount of naphthalene produced indicates the strong tendency of benzyne to act as a dienophile and to add 1,4 rather than 1,2 to thiophen. (Some contribution to the yield of naphthalene might have come from a 1,2-adduct of benzyne with thiophen at the 2- and 3-positions:

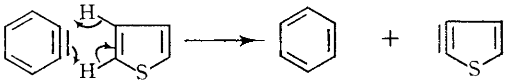


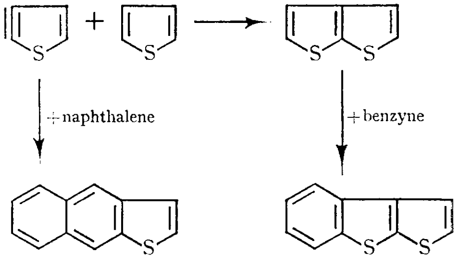
Elimination of sulphur from this adduct to give naphthalene would be more difficult than from the 1,4-adduct: elimination of acetylene would yield benzo[*c*]thiophen.



This may indeed have formed, but is so unstable[2] it would not be expected to survive the pyrolysis temperature.) The approximately 9 : 1 preference for 1,4-addition so inferred is somewhat greater than was observed in the reactions with dichlorobenzenes[1c] and pyridine,[1f] 7 : 1 in both cases. However, the difference, if real, may simply reflect a greater reactivity of benzothiophen compared to naphthalene, leading to more extensive loss by subsequent reactions.

Several products were formed in the reaction of phthalic anhydride with thiophen in addition to those listed. These include thiophthen, benzothiophthen, and naphthothiophen. These can all be accounted for by intermolecular transfer of hydrogen from thiophen to benzyne and the formation of thiophyne:





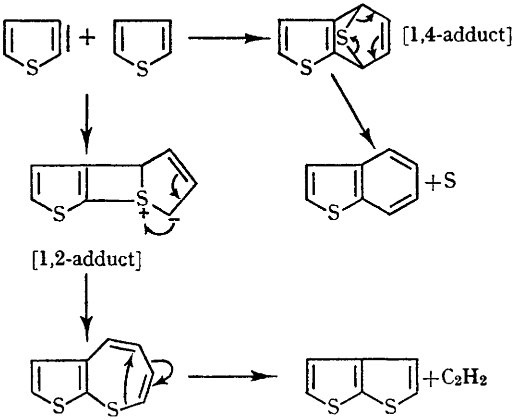
Thiophyne formation in this way would require that benzene be formed; benzene was found among the pyrolysis products from phthalic anhydride and thiophene, neither of which originally contained any benzene.[3]

The questions raised by these products led to a study of the pyrolysis products of thiophen itself. Thiophen (0·4 mole) pyrolyzed alone under the identical conditions as with phthalic anhydride, gave 0·76 g. of product (thiophen-free) that analyzed:

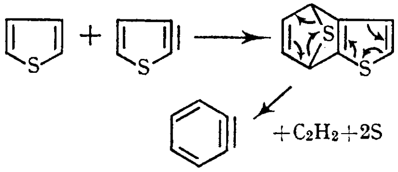
Benzothiophen	7·2
Thiophthen	1·8
Phenylthiophen	5·4
Bithienyl	100

Wynberg and Bantjes[4] pyrolyzed thiophen at 800—850° for unspecified lengths of time and found these same products in different ratios. They explained the formation of benzothiophen and phenylthiophen by Diels–Alder addition of thiophen to itself; thiophthen was presumed to arise as a known product from the reaction of acetylene and sulphur.[5]

We suggest rather that thiophyne is formed by intramolecular dehydrogenation, and that the minor pyrolysis products of thiophen arise from the reaction of thiophyne with thiophen:



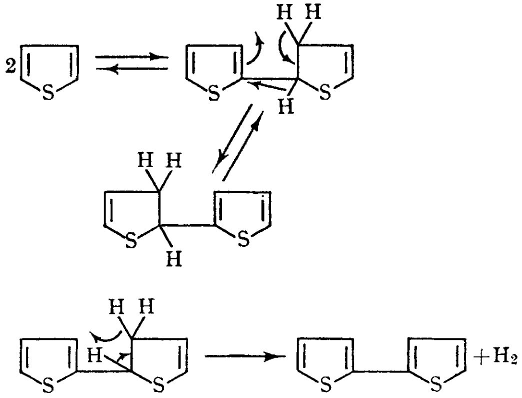
Phenylthiophen is a major product from benzyne and thiophen, and would therefore strongly suggest the formation of benzyne from thiophen and thiophyne. This may be visualized as:



Such a scheme parallels the behaviour of benzene, which at 690° gives a small but definite amount of naphthalene. Presumably this arises from intramolecular dehydrogenation to benzyne[1d]:

and the known reaction of benzyne with benzene to give naphthalene and biphenyl.

The formation of bithienyls can perhaps best be explained by invoking a thienyldihydrothiophen:



Thienyldihydrothiophen is the thiophen analogue of the phenylcyclohexadiene intermediate deduced from scrambling of protium and deuterium in the pyrolysis of deuterated benzene.[1d] Both intermediates account for the formation of dimeric species without formation of highly energetic free hydrogen atoms.

The reactions of thiophen with other arynes from aromatic anhydrides and dianhydrides and the formation of thiophynes in these reactions are being investigated.

(*Received, August* 18*th*, 1966; *Com.* 610.)

---

[1] (a) E. K. Fields and S. Meyerson, *Chem. Comm.*, 1965, 474; (b) S. Meyerson and E. K. Fields, *ibid.*, 1966, 275; (c) S. Meyerson and E. K. Fields, *Chem. and Ind.*, 1966, 1230; (d) E. K. Fields and S. Meyerson, *J. Amer. Chem. Soc.*, 1966, **88**, 21; (e) E. K. Fields and S. Meyerson, *ibid.*, p. 3388; (f) E. K. Fields and S. Meyerson, *Amer. Chem. Soc., Petrol. Preprints*, 1966, **11**, No. 3, 225; (g) E. K. Fields and S. Meyerson, *J. Org. Chem.*, in the press.

[2] R. Mayer, H. Kleinert, S. Richter, and K. Gewald, *Angew. Chem. Internat. Edn.*, 1962, **1**, 115.

[3] In the reaction of benzyne with pyridine at 690°, we have found minor products that are most easily rationalized by the formation and reactions of pyridyne. Hydrogen abstraction by perinaphthalyne from cyclohexene has been observed by C. W. Rees and R. C. Starr, *Chem. Comm.*, 1965, 193.

[4] H. Wynberg and A. Bantjes, *J. Org. Chem.*, 1959, **24**, 1421.

[5] H. D. Hartough, "Thiophene and Its Derivatives," Interscience, New York, 1952, p. 49.