# The Pyrolysis of 2,3,4,5-Tetraphenylthiophen 1,1-Dioxide

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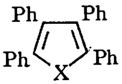
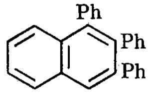


(I)



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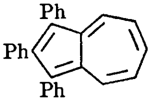

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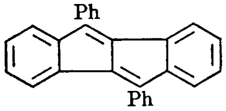

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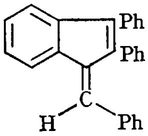
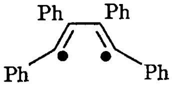


(V)



(VI)

THE pyrolysis of 2,3,4,5-tetraphenylthiophen 1,1-dioxide (I; X=$SO_2$), both alone and in the presence of metal halides, has been studied as a possible method of obtaining tetraphenylcyclobutadiene or a metal complex thereof.

When the thiophen dioxide was heated under reflux in boiling di-n-butyl phthalate (b.p. 340°) for 1 hr. it gave 1,2,3-triphenylnaphthalene (II), m.p. 153—154°, and 1,2,3-triphenylazulene (III), m.p. 214—215°, together with unchanged material (85%). Pyrolysis of the molten thiophen dioxide at 500—550° gave none of the naphthalene or the azulene but yielded tetraphenylthiophen (I; X=S), m.p. 184—185°, and the corresponding furan (I; X=O), m.p. 167—168°, in 10 and 17% yields, respectively, the main product being a brown amorphous solid which resisted purification.

A mixture of the thiophen dioxide and nickel bromide trihydrate at temperatures between 300° and 400° gave the naphthalene (II), tetraphenylthiophen, 3,6-diphenyl-1,2-3,4-dibenzopentalene (IV), m.p. 260—261°, and a small amount of a white solid, $C_{28}H_{20-22}$, m.p. 241—242°.

Diphenylacetylene might be formed during the pyrolyses and then be converted into the observed products. To test this possibility it was heated with nickel bromide trihydrate at 350°. This reaction gave 2,3,8-triphenylbenzofulvene (V), m.p. 182—183° and a trace of a white solid, m.p. >400°. It thus appears that diphenylacetylene is not an intermediate in the above pyrolyses. However, the benzofulvene (V), together with the compounds (I; X=S), (II), (III), and (IV) were obtained when the thiophen dioxide was heated with cuprous) bromide at 350°.

Irradiation of diphenylacetylene with ultraviolet light has been reported[1] to give low yields of 1,2,3-triphenyl-naphthalene and -azulene, together with minute traces of hexaphenylbenzene, m.p. 437—439°, and octaphenylcyclo-octatetraene (formerly[2] thought to be "octaphenylcubane"), m.p.

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[1] G. Büchi, C. W. Perry, and E. W. Robb, *J. Org. Chem.*, **1962**, **27**, 4106.

[2] G. S. Pawley, W. N. Lipscomb, and H. H. Freedman, *J. Amer. Chem. Soc.*, **1964**, **86**, 4725; H. P. Throndsen, P. J. Wheatley, and H. Zeiss, *Proc. Chem. Soc.*, **1964**, 357.

427—429°. Tetraphenylthiophen dioxide is unaffected by irradiation with ultraviolet light in Pyrex-glass apparatus (the reaction is now being studied in quartz apparatus, cf. ref. 3). It is probable that the same intermediate diradical (VI) (or possibly tetraphenylcyclobutadiene, which would be expected to behave as a diradical[4]), is produced in both the pyrolysis and the irradiation experiments but that the ways in which the diradical undergoes cyclisation are modified in the presence of nickel and copper.

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[3] M. P. Cava, R. H. Schlessinger, and J. P. van Meter, *J. Amer. Chem. Soc.*, 1964, **86**, 3173.

[4] H. H. Freedman, *J. Amer. Chem. Soc.*, 1961, **83**, 2195.