

one of these acids has been elucidated through a study of its degradation products.

2. 3-Ethoxycinchoninic acids and 3-ethoxyquinolines resist reduction by means of concd. hydriodic acid and red phosphorus, but the

ether linkage is cleaved by this treatment.

3. Both 3-ethoxy-4-quinolinecarboxylic acid and 3-hydroxyquinaldine on phthalonation yield the same phthalone.

AUSTIN, TEXAS

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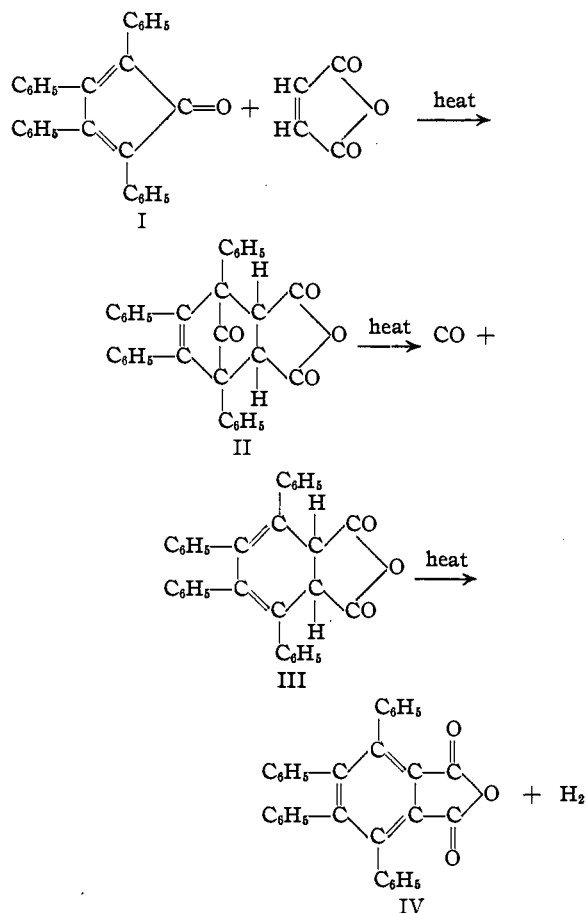
The Reaction of a Thiophene Derivative with Maleic Anhydride

By DANIEL B. CLAPP¹

It has been shown by Dilthey and his collaborators² that diene syntheses may be carried out readily between various highly arylated cyclopentadienones and maleic anhydride or other ethylenic or acetylenic derivatives. A typical example is the reaction of 2,3,4,5-tetraphenylcyclopentadienone (tetracyclone) (I) with maleic anhydride.^{2a} The initial product of this reaction is 3,6-endocarbonyl-3,4,5,6-tetraphenyl-1,2-dihydrophthalic anhydride (II) which on heating successively loses carbon monoxide and hydrogen yielding tetraphenylphthalic anhydride (IV).

In the hope that the same product might be obtained in starting with the sulfur analog of tetracyclone, an attempt was made to bring about a reaction between tetraphenylthiophene (thionessal) and maleic anhydride. By analogy, if an adduct were formed, it might be expected to lose hydrogen sulfide. However, several attempts to carry out this reaction gave completely negative results.

Since it is well known that furan and many of its derivatives will take part readily in diene syntheses, undoubtedly attempts have been made to carry out such syntheses with corresponding thiophene derivatives. However, in a recent review of the Diels-Alder reaction³ it is stated that no case of a thiophene derivative undergoing this reaction has been recorded. It is evident that the 1,4-conjugate system in thiophene compounds is less active than that present in furan derivatives, the former class being more aromatic in character and resembling benzene derivatives, none of which have been shown to undergo a Diels-Alder reaction. It may be noted that



Schomaker and Pauling⁴ recently have shown that electron diffraction results, resonance energies, and other considerations indicate a greater degree of resonance stabilization for thiophene than for furan.

It is possible that the introduction of certain substituents into the thiophene nucleus might so activate the 1,4-system that a diene synthesis could occur. In the case of hydrindene, fixation

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(2) (a) *Ber.*, **66**, 1627 (1933); (b) *ibid.*, **67**, 495, 1959, 2004 (1934); (c) *ibid.*, **68**, 1159 (1935); (d) *ibid.*, **71**, 974 (1938).

(3) Delaby, *Bull. soc. chim.*, [5] **4**, 765 (1937).

(4) Schomaker and Pauling, *THIS JOURNAL*, **61**, 1769 (1939).

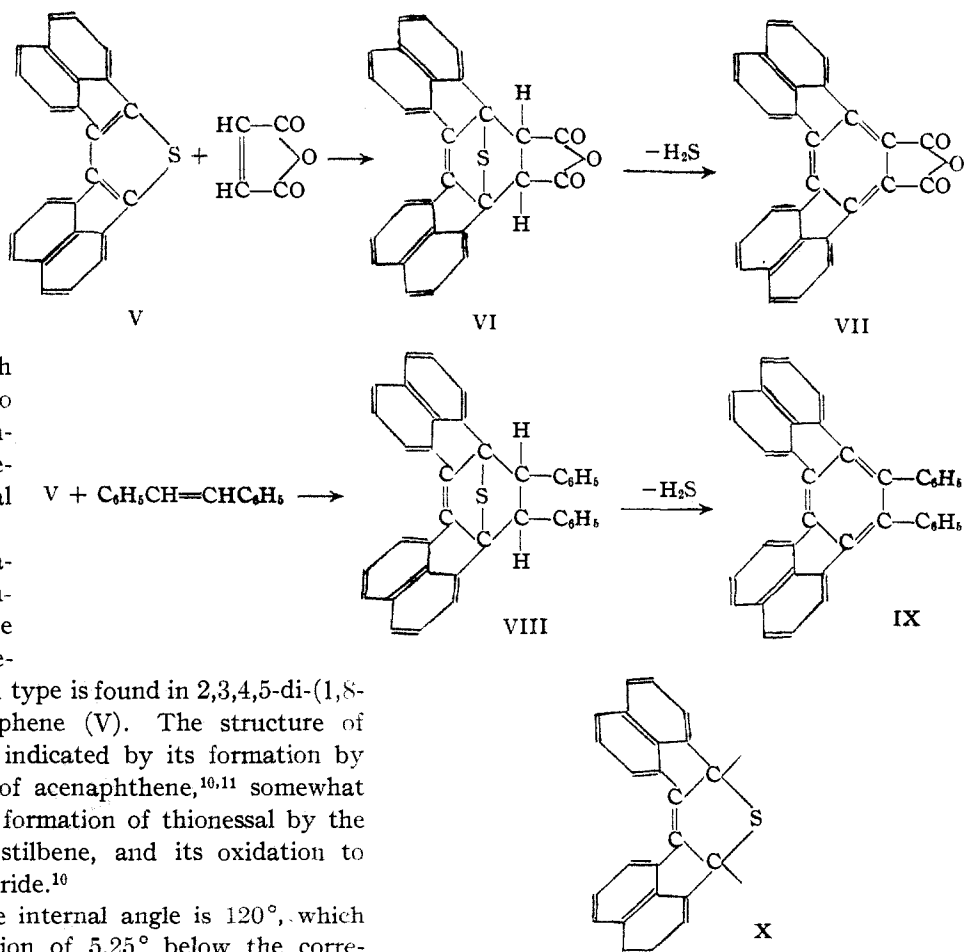
of the double bonds in the benzene ring, so as to leave a single bond common to the two rings, has been suggested.⁵⁻⁷ Hence, it might be supposed that the presence of fused five-membered rings in the 2,3- and 4,5-positions of thiophene would increase the activity of the conjugate system, on account of the strain in such a molecule.

Since the resonance energy in hydrindene has been shown to be practically the same as in benzene,⁸ the idea of the fixation of double bonds, at least in hydrindene, is untenable. It has been pointed out⁹ that great differences in chemical reactivity may arise from quite small differences in electron distribution. However, the fixation hypothesis is certainly useful for the prediction of reactions and "reaction-structures," even though such structures do not represent completely the molecule in the physical sense.

For the application of this hypothesis to thiophene derivatives, a molecule of the desired type is found in 2,3,4,5-di-(1,8-naphthylene)-thiophene (V). The structure of this substance is indicated by its formation by the sulfur fusion of acenaphthene,^{10,11} somewhat analogous to the formation of thionessal by the sulfur fusion of stilbene, and its oxidation to naphthalic anhydride.¹⁰

In benzene, the internal angle is 120° , which requires a reduction of 5.25° below the corresponding angle in open-chain structures; this necessitates increases in each of the two external angles.⁵ Since the internal angles involved in thiophene, if the values calculated by Schomaker and Pauling⁴ are assumed, are about 112° , in this

case the external angles are increased still more. If it is assumed that these angles are increased proportionally, there will be a greater difference between the β -angle and the α -angle than in the case of benzene. In hydrindene, that structure in which the two greater angles, the β -angles, are included in the 5-ring, will be under the greater strain, since the normal internal angle of this 5-ring (108°) is more nearly equal to the α -angle. In dinaphthylenethiophene, an even greater distortion of the β -angles is required, particularly if the involved internal angles of the 5-ring are



- (5) Mills and Nixon, *J. Chem. Soc.*, 2510 (1930).
 (6) Sidgwick and Springall, *ibid.*, 1532 (1936).
 (7) Fieser and Lothrop, *THIS JOURNAL*, **58**, 2050 (1936).
 (8) *Ann. Reports*, **34**, 219 (1937).
 (9) Sutton and Pauling, *Trans. Faraday Soc.*, **31**, 939 (1935).
 (10) Dzewonski, *Ber.*, **36**, 966 (1903).
 (11) Rehlander, *ibid.*, **36**, 1586 (1903).

assumed to be those in acenaphthene; these latter, according to Banerjee and Sinha,¹² are 97° .

It has been found that dinaphthylenethiophene reacts smoothly with maleic anhydride. If a mixture of these two substances is heated at about 225° , evolution of hydrogen sulfide occurs, and the reaction product, which is obtained in good yield, is undoubtedly 3,4,5,6-di-(1,8-naphthylene)-phthalic anhydride (VII). Confirmation

- (12) Banerjee and Sinha, *Indian J. Phys.*, **11**, 21 (1937).

of its structure is desirable, and this problem is being attempted. It may be noted that the substance resembles in its appearance and properties certain of the highly arylated phthalic anhydrides prepared by Dilthey.² In spite of numerous essays, isolation of the intermediate addition product (VI) has not been accomplished, but this is not surprising in view of the temperature necessary to initiate the reaction.

By the reaction of V with stilbene, 1,2-diphenyl-3,4,5,6-di-(1,8-naphthylene)-benzene (IX) is obtained. A similar reaction appears to take place with cinnamic acid, hydrogen sulfide being evolved steadily, but as yet no pure substance has been isolated from the reaction product.

The reactivity and unsaturated character of dinaphthylenethiophene is indicated by preliminary experiments on the formation of dissociable addition products with chlorine and bromine, details of which will be reported later. These experiments together with the intense red color of dinaphthylenethiophene are, in some degree, suggestive of a diradical structure (X) for the substance.

The work is being extended, and the reactions of other thiophene derivatives with various ethylenic and acetylenic compounds are being studied.

Experimental

2,3,4,5-Di-(1,8-naphthylene)-thiophene.—This substance was obtained by fusion of acenaphthene and sulfur according to the directions of Dziejowski¹⁰ and Rehlander.¹¹ It was purified by vacuum sublimation at 2.5 mm. and a bath temperature of 260°, followed by recrystallization from xylene; red needles, m. p. 285.5–286° (corr.).

3,4,5,6-Di-(1,8-naphthylene)-phthalic Anhydride.—An intimate mixture of dinaphthylenethiophene (0.12 g.) and maleic anhydride (0.4 g.) was introduced into a test-tube fitted with a long air-condenser. The mixture was heated in a bath, maintained at 225°, for fifteen minutes. The reaction mixture was cooled, broken up, and heated with water; the undissolved solid was then filtered off, dried, finely ground, and boiled with 10 cc. of potassium hydroxide solution (5%). The phthalic anhydride, which was largely unattacked by this treatment, was filtered off, dried, and twice recrystallized from phenyl ether; yield 0.08 g. (60%); yellow needles, decomposing without melting about 385°; almost insoluble in common solvents and aqueous alkali; slightly soluble in alcoholic alkali.

Anal. Calcd. for C₂₈H₁₂O₃: C, 84.83; H, 3.06. Found: C, 84.45, 84.72; H, 3.00, 2.97.

1,2-Diphenyl-3,4,5,6-di-(1,8-naphthylene)-benzene.—Dinaphthylenethiophene (0.5 g.) and maleic anhydride (0.5 g.) were heated at a bath temperature of 310–320° for nine hours, at the end of which time evolution of hydrogen sulfide was complete. The reaction mixture was dissolved in benzene, and a crude product was precipitated by the addition of methyl alcohol. On sublimation at 3 mm. and a bath temperature of 255–260°, 0.25 g. of yellow material was obtained, which was recrystallized three times from benzene–methyl alcohol; yield 0.11 g. (14%); greenish yellow crystals, with pronounced yellow-green fluorescence in ultraviolet light; m. p. 290–291° (corr.).

Anal. Calcd. for C₃₈H₂₂: C, 95.36; H, 4.64; mol. wt., 478.5. Found: C, 95.21; H, 4.72; mol. wt. (Rast), 473.

Summary

3,4,5,6-Di-(1,8-naphthylene)-phthalic anhydride and 1,2-diphenyl-3,4,5,6-di-(1,8-naphthylene)-benzene have been obtained from 2,3,4,5-di-(1,8-naphthylene)-thiophene by reaction with maleic anhydride and stilbene, respectively.

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