

Later work, however, in this laboratory⁸ has shown that the triazine obtained by De's method, which has the structure given to (D) above, has a melting point of 200°–201° C.

We have extended the above observation to quinone-monoximes, *o*-nitrosophenols and 1,2-monooximino-dicarbonyl compounds. The preparation of the oxy-triazines, and the oxyoso- and the oso-triazoles from these materials, is being undertaken.

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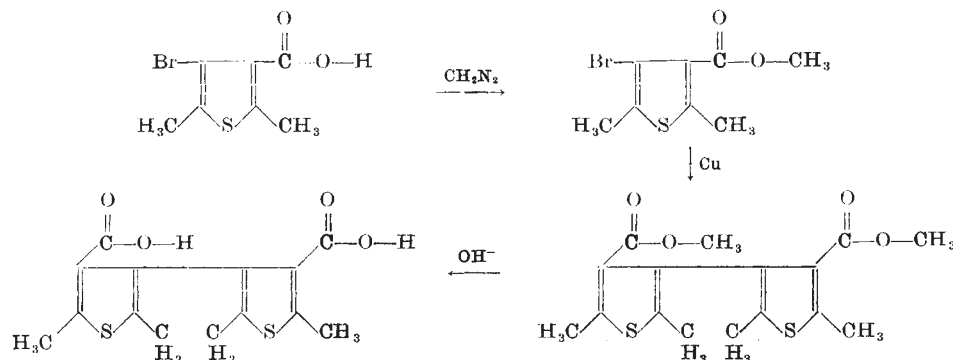
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Symmetrical Bi-Aromatics

PREVIOUSLY reported work¹ from this laboratory indicated the feasibility of condensing 2-halo-3-thenoic acids to form symmetrically substituted 2,2'-bithienyls. This provided the experimental basis



for the continuation of our studies in the field of mixed bi-aromatics, wherein it was shown² that an unsymmetrically substituted α -phenylthiophene actually exists in two stereoisomeric forms due to restricted rotation. In view of this fact, the above method was applied to 3-halo-*o*-substituted thenoic acids in order to study the possible existence of optical activity in the corresponding β -phenylthiophenes. Accordingly, the synthesis of a symmetrically substituted 3,3'-bithienyl was undertaken. Although some investigations have already been reported in this field^{3,4}, no work has been published concerning symmetrical 3,3'-dithienyl-dicarboxylic acids.

The readily available 2,5-dimethyl-4-bromo-3-thenoic acid⁵ was selected as the starting material in the series of reactions indicated above.

The 2,5-dimethyl-4-bromo-3-thenoic acid was dissolved in methyl alcohol and esterified with diazo-

methane *via* nitrosomethylurea. After removal of the solvent, the residue was taken up in ether and washed with 10 per cent sodium carbonate solution to remove unchanged acid. The ether layer was then washed with water and dried over anhydrous potassium carbonate. After filtering and removal of the solvent, the residual liquid was fractionally distilled to yield methyl 2,5-dimethyl-4-bromo-3-thenoate (b.p. 138–139°/8 mm.; n_D^{25} – 1.5591; calc. for $C_8H_9O_2SBr$: C, 38.55; H, 3.61; found: C, 38.83; H, 3.67 per cent).

This mono-ester was then condensed in the manner of the Ullmann reaction⁶, using an excess of Baker's precipitated copper as the condensing reagent. While keeping the temperature of the reaction mixture at 250–255°, the copper was added in small portions during the course of one hour; after the final addition, the temperature was raised to 280° for 15 min. Upon cooling, the mixture was extracted with ether and filtered. The ether and unchanged mono-ester were removed by distillation *in vacuo*, the residual material taken up in ethyl alcohol in the presence of 'Norit-a', and allowed to crystallize. The product consisted of yellow plates (m.p. 48–48.5°) and proved to be the dimethyl ester of 2,5,2',5'-tetramethyl-3,3'-dithienyl-4,4'-dicarboxylic acid (calc. for $C_{16}H_{18}O_4S_2$: C, 56.76; H, 5.33; found: C, 57.05; H, 5.29 per cent).

The corresponding dibasic acid was obtained by refluxing the above di-ester with an excess of 10 per cent aqueous potassium hydroxide. Acidification yielded the 2,5,2',5'-tetramethyl-3,3'-dithienyl-4,4'-dicarboxylic acid, which, after sublimation *in vacuo*, gave white crystals melting with decomposition at

295–305° (calc. for $C_{14}H_{14}O_4S_2$: C, 54.19; H, 4.52; found: C, 54.45; H, 4.54 per cent).

This investigation is being carried out under the auspices of the Office of Naval Research.

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