CYCLOADDITION REACTIONS OF 2,4-DIPHENYLTHIOPHENE AND 2,5-DIPHENYL-1,4-DITHIIN

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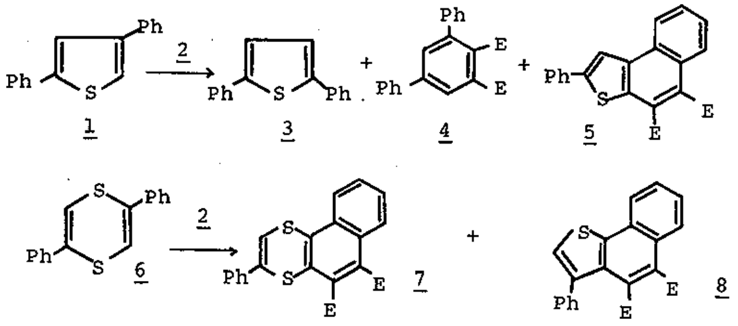
The reaction of 2,4-diphenylthiophene (1) with dimethyl acetylenedicarboxylate (2) in refluxing o-dichlorobenzene afforded 2,5-diphenylthiophene (3), the phthalate 4, and dimethyl 2-phenylnaphtho[2,1-b]thiophene-4,5-dicarboxylate (5) in 27, 12, and 6 % yields, respectively along with 36 % of recovered 1. The formation of 5 involves the unusual Diels-Alder addition of 2 to the diene comprised of one unsaturated bond of the thiophene system and one "Kekulé-bond" of a phenyl substituent.

The reaction of 2,5-diphenyl-1,4-dithiin (6) with 2 in o-dichlorobenzene at 130 °C for 30 hr led to the isolation of the naphthodithiin 7 (9%) and dimethyl 3-phenylnaphtho[1,2-b]thiophene-4,5-dicarboxylate (8) (8 %). The further conversion of 7 to 8 or 5 has not been effected. Thus extrusion of sulfur from an intermediate to 7 is assumed to proceed regioselectively to give 8, but not its isomer 5. When the reaction of 6 was carried out under the more vigorous conditions (in refluxing o-dichlorobenzene for 10 hr), 3 (6%), 4 (4%), and 5 (35%) were again isolated along with 1 (36%). Probably 3, 4, and 5 would be formed via 1 as a primary product from 6.

Treatment of 2,5-diphenyl-1,4-dithiin-1,1-dioxide (9) with 2 in o-dichlorobenzene at 180 °C gave 5-phenylthiophene-2,3-dicarboxylate (10) in 19 % yield. The mechanisms of the reaction are discussed in some detail.



E = COOCH$_3$