tion of a common $\delta$-value for all bonds of the type C—X in formula (1) is an acceptable procedure in the sense that it leads to $\beta$-values in accordance with those calculated by eqn. (2).

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# Thiophene Analogues of Fluorene

## IV. An Unusual Behaviour of a Cyclopentadithiophenone in the Reaction with Dienophiles

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We have earlier demonstrated that 2,3,4,5-tetramethyl-7H-cyclopenta-[1,2-b:4,3-b']dithiophene-7-one (I) [1] reacts as a diene in the reaction with dimethyl acetylenedicarboxylate or maleic anhydride, the central formal cyclopentadienonic moiety of I functioning as the reacting dienic grouping.[1]

We have now also found that I reacts similarly with phenylacetylene to yield 1,2,7,8-tetramethyl-4-phenylbenzo[1,2-b:-4,3-b']dithiophene (II) in 39 % yield. The structure is based on a correct elementary analysis and on its spectral properties. Similarly, when the other "cyclopentadienonic" fluorenone analogue, 2,3,5,6-tetramethyl-4H-cyclopenta[2,1-b:3,4-b']dithiophen-4-one (III) [2] was reacted with dimethyl acetylenedicarboxylate and phenyl acetylene, 4,5-dicarbomethoxy-2,3,6,7-tetramethylbenzo[2,1-b:3,4-b']dithiophene (IV) and 2,3,6,7-tetramethyl-4-phenylbenzo[2,1-b:3,4-b']dithiophene (V) was obtained. The structure is based on correct elementary analyses and spectral properties. The NMR spectrum of V shows four methyl resonances, one of which appears at higher field than the other three. We ascribe this signal to the methyl group in the 3-position. The shift towards higher field is probably caused by the anisotropy effect of the neighbouring phenyl group.

Recently Wynberg [3] and coworkers and Loader and Timmons [4] prepared several thiophene and furan analogues of phenantrene by photochemically induced cyclization of thienyl ethenes. However, the synthesis of benzo[2,1-b:3,4-b']dithiophene by this method failed.[3]

The driving force for the easy decarbonylation in the reaction of I and III with acetylenes certainly is the formation of the aromatic analogues of phenantrene and similar decarbonylations have been observed with simple cyclopentadienones.[5]

However, the reaction of III with maleic anhydride and *N*-phenylmaleimide gave rise to unexpected products. In both cases evolution of hydrogen sulphide was noticed and the mass spectra of the isolated product showed molecular ions at 34 mass units lower than expected for the primary Diels-Alder adduct and analyzed correctly for such products. The IR spectra showed the presence of keto groups and anhydride and imide rings, respectively. Due to extremely low solubility, no NMR spectra could be obtained.

The product obtained from the reaction of III with maleic anhydride was converted into a dimethyl ester. Its NMR spectrum showed in addition to the $CO_2CH_3$ resonance at 6.10 $\tau$, three methyl bands with relative intensities of 3:3:6. On this basis we suggest this diester to be 7,8-dicarbomethoxy-2,3,5,6-tetramethyl-4H-indeno[1,2-b]thiophene-4-one (VI). The

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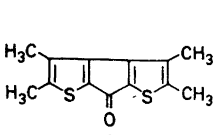
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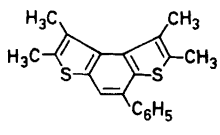
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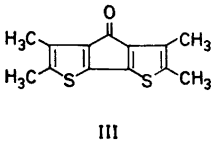
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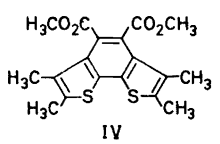
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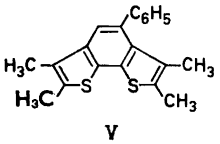
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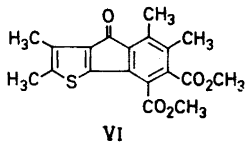
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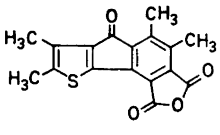
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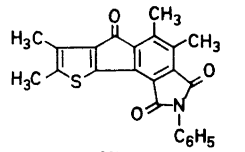
VIII

product isolated from the reaction of III with maleic anhydride and *N*-phenylmaleimide thus being the anhydride (VII) and the *N*-phenylimide VIII corresponding to VI.

VII and VIII have been formed by 1,4-addition of maleic anhydride and *N*-phenylmaleimide to the formal diene system of a thiophene ring followed by aromatization through the subsequent loss of hydrogen sulphide. Thiophenes do not normally undergo the Diels-Alder reaction.[5] Exceptions are C-annelated systems like benzo[c]thiophenes (isothionaphthenes), where the formation of a complete benzene ring provides a strong driving force.[5,6] Some polycyclic aromatic systems containing thiophene rings also undergo the Diels-Alder reaction (for review, *cf.* Ref. 5). However, the fact that different "dienic" parts of III react with different dienophiles is very rare and as far as we could find has not been observed. Only the reaction of tetrachloro-*o*-benzoquinone with different olefins or acetylenes is somewhat reminiscent. Besides the "normal" dienic behaviour of the carbocyclic ring the 1,2-diketo grouping reacts in a pseudo Diels-Alder fashion with some olefins to give benzdioxanes.[7]

The reason for the different behaviour of I and III and especially the reaction pattern of III needs further study. Many factors which influence the Diels-Alder reaction can play a role (for discussion, *cf.* Ref. 8) and we believe that the ease with which aromatization of the primary adducts take place can play an important role in determining the product distribution.

As mentioned before non-cyclopentadienic tetramethyl substituted thiophene analogues of fluorenone did not undergo the Diels-Alder reaction[1] and recently Professor Wynberg[9] has informed us that this is also true for the non-methylated parent compounds of I and III. The activating effect of methyl groups on Diels-Alder reactions is evident from the reaction of naphthalene and 1,2,3,4-tetramethyl naphthalene with maleic anhydride.[10]

*Experimental. 4,5-Dicarbomethoxy-2,3,6,7-tetramethylbenzo[2,1-b:3,4-b']dithiophene (IV).* A solution of 0.30 g (1.2 mmole) of 2,3,5,6-tetramethyl-4H-cyclopenta[2,1-b:3,4-b']dithiophene-4-one[1] and 2.0 g of dimethyl acetylene dicarboxylate in 25 ml of dry DMF was boiled under reflux for 1.5 h. The solvent was removed *in vacuo*. The residue was recrystallised from methanol, yielding 200 mg (46 %) of the title compound as white leaflets. Further crystallization from methanol gave analytically pure product, m.p. 214.5–215.5°C. Mass spectrum: (*m/e*, %) 165, 15.0; 229, 5.6; 243, 9.6; 244, 12.4; 245, 5.1; 270, 20.4; 272, 9.3; 298, 88.2; 299 18.7; 300, 10.3; 315, 15.8; 316, 9.7; 330, 9.4; 331, 27.1; 332, 6.3; 362, 100; 363, 22.0; 364, 12.0. PMR ($CDCl_3$): $\tau_{CO_2CH_3}$ 6.06, $\tau_{CH_3}$ 7.56, 7.80. UV (cyclohexane): $\lambda_{max}$ m$\mu$ (log $\varepsilon$) 223 (4.31); 232 sh (4.29); 276 (4.58); 304 (3.99); 315 (3.97). [Found: C 59.2; H 4.97; S 17.7. Calc. for $C_{18}H_{18}O_4S_2$ (362.5): C 59.65; H 5.01; S 17.69].

*2,3,6,7-Tetramethyl-4-phenylbenzo[2,1-b:3,4-b']dithiophene (V).* A solution of 0.30 g (1.2 mmole) of 2,3,5,6-tetramethyl-4H-cyclopenta-[2,1-b:-3,4-b']dithiophene-4-one and 3.0 g of phenylacetylene in 25 ml of dry DMF was boiled under reflux for 3 days. The solvent was removed *in vacuo* and the residue was dissolved in benzene and eluted over alumina, with benzene as eluent. The first fraction gave upon evaporation a yellow oil, which was dissolved in a small amount of ethyl acetate. Addition of methanol gave solid material which was recrystallized from ethanol, yielding 70 mg

(18 %) of the title compound, m.p. 147–148°C. Mass spectrum: (*m/e*, %) 146, 7.4; 291, 5.3; 305, 5.6; 307, 18.8; 321, 11.8; 322, 100; 323, 25.8; 324, 12.6. PMR ($CDCl_3$): $\tau_{C_6H_5}$ 2.62, $\tau_H$ 2.67, $\tau_{CH_3}$ 7.50, 7.57, 7.71, and 8.31. UV (cyclohexane): $\lambda_{max}$ mμ (log ε) 220 (4.40); 238 sh (4.25); 270 (4.55); 300 (4.10); 312 sh (4.03); 333 (3.44). [Found: C 73.7; H 5.51. Calc. for $C_{20}H_{18}S_2$ (322.5): C 74.49; H 5.63].

*2,3,5,6-Tetramethyl-4H-indeno[1,2-b]thiophene-4-one-7,8-dicarboxylic acid anhydride (VII).* A solution of 0.3 g (1.2 mmole) of 2,3,5,6-tetramethyl-4H-cyclopenta[2,1-b:3,4-b']dithiophene-4-one and 2.0 g of maleic anhydride in 25 ml of dry DMF were boiled under reflux for 1 h. The smell of hydrogen sulphide was detected. After removal of the solvent *in vacuo*, the residue was treated with 10 ml of ethyl acetate. The undissolved solid was filtered off and recrystallised from dioxane, giving 150 mg (40 %) of the orange-red title compound, m.p. 279–280°C. Mass spectrum: *m/e* 312. IR (KBr): 1840, 1775, 1705, and 1640 $cm^{-1}$. UV (dioxane): $\lambda_{max}$ mμ (log ε) 248 (4.42); 267 sh (4.24); 299 sh (4.05); 308 (4.07); 336 sh (3.82); 380 sh (3.76); 393 (3.78); 450 (2.94). [Found: C 64.9; H 3.87; S 10.4. Calc. for $C_{17}H_{12}O_4S$ (312.3): C 65.37; H 3.87; S 10.27].

*7,8-Dicarbomethoxy-2,3,5,6-tetramethyl-4H-indeno[1,2-b]thiophene-4-one (VI).* 160 mg (0.5 mmole) of VII were refluxed over night with 50 ml of dioxane, 50 ml of water and 5 g of sodium hydroxide. The solution was poured into water and acidified. The crude acid was filtered by suction and esterified with an excess of diazomethane, yielding 180 mg (98 %) of the title compound, m.p. 174–175°C after recrystallization from chloroform-hexane. IR (KBr): 1725, 1700 $cm^{-1}$. PMR ($CDCl_3$): $\tau_{CO_2CH_3}$ 6.10, $\tau_{CH_3}$ 7.50, 7.77, 7.87. [Found: C 63.8; H 5.15; S 8.87. Calc. for $C_{19}H_{18}O_5S$ (358.4): C 63.67; H 5.06; S 8.95].

*The Diels-Alder reaction of II with N-phenylmaleimide (VIII).* A solution of 0.3 g (1.2 mmole) of 2,3,5,6-tetramethyl-4H-cyclopenta[2,1-b:3,4-b']dithiophene-4-one and 0.3 g of *N*-phenylmaleimide in 25 ml of dry DMF were boiled under reflux for 24 h. Evaporation of the DMF *in vacuo* left a residue which was extracted with ethyl acetate, leaving an orange coloured substance. Recrystallization from chloroform-hexane yielded 50 mg (13 %) of VIII, m.p. 330–331°C. Mass spectrum: *m/e* 387. IR (KBr): 1715, 1700, 1615 $cm^{-1}$. [Found: C 69.4; H 4.57; N 3.72. Calc. for $C_{23}H_{17}NO_3S$ (387.5): C 71.30; H 4.42; N 3.62].

*1,2,7,8-Tetramethyl-4-phenylbenzo[1,2-b:4,3-b']dithiophene (II).* In a similar way as described for V, 150 mg (39 %) of the title compound was obtained from 0.2 g of 2,3,4,5-tetramethyl-7H-cyclopenta[1,2-b:4,3-b']dithiophene-7-one.[1] M.p. after sublimation and recrystallization from ethanol 153.5–155°C. Mass spectrum: (*m/e*, %) 145, 5.2; 146, 5.7; 161, 8.5; 307, 19.7; 321, 7.9; 322, 100; 323, 24.4; 324, 11.4. PMR ($CDCl_3$): $\tau_{arom}$ 2.44, $\tau_{CH_3}$ 7.46, 7.52, 757. UV (cyclohexane): $\lambda_{max}$ mμ (log ε) 257 (4.40); 275 sh (4.13); 285 (4.16); 320 (4.35). [Found: C 74.4; H 5.72. Calc. for $C_{20}H_{18}S_2$ (322.5): C 74.49; H 5.63; S 19.89].

PMR spectra were obtained with a Varian A60 high resolution spectrometer, mass spectra with an LKB 900 mass spectrometer and UV spectra with a Unicam SP 800 spectrophotometer.

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