

Thiophene Analogues of Fluorene

II. On the Reaction of Fluorenone Analogues with Dienophiles

ALLERT K. WIERSEMA and
SALO GRONOWITZ

Chemical Center, Division of Organic
Chemistry, University of Lund, P.O. Box 740,
S-220 07 Lund 7, Sweden

In connection with our interest in the effect of the mode of annelation on the reactivity and physical properties of thiophene analogues of fluorene,¹ we have reacted the ketones I to III and fluorenone IV with dimethyl acetylene dicarboxylate (V). When the ketones I–IV were refluxed with V in dimethylformamide only I yielded an adduct (VI) in 58 % yield, while in the other cases starting material was recovered.

NMR and mass spectra as well as elementary analyses clearly showed that the adduct VI formed is 4,5-dicarbomethoxy-1,2,7,8-tetramethylbenzo[1,2-b:4,3-b']-dithiophene, formed by decarbonylation of

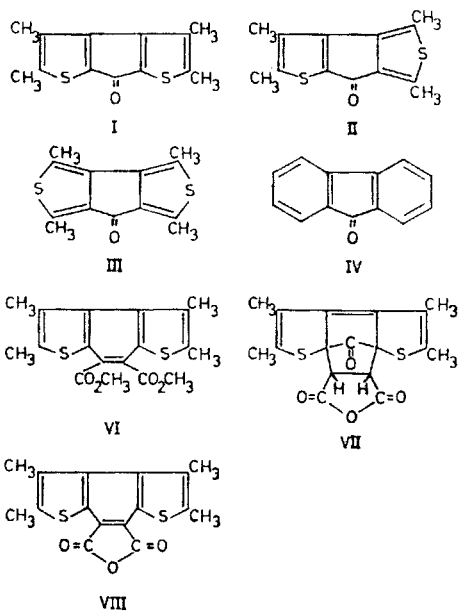
the primary Diels-Alder adduct. The parent benzo[1,2-b:4,3-b']dithiophene has recently been prepared by photochemically induced cyclisation of thienylethenes by Wynberg *et al.*² and by Loader and Timmons.³ When I was reacted with maleic anhydride in benzene, the adduct VII was obtained in low yield. The structure of VII follows from its IR spectrum which showed C=O stretchings at 1690 cm⁻¹ and 1790 cm⁻¹ and 1855 cm⁻¹ characteristic for the keto and the anhydride ring respectively.⁴ The mass spectrum is also in accordance with this structure. The stereochemistry of the adduct has not been determined. When I was reacted in refluxing *N,N*-dimethylformamide with maleic anhydride for 2 h a mixture of VII and the decarbonylated and dehydrogenated product VIII was obtained. Extending the reaction time to 8 h yielded only VIII in low yield. The structure of VIII is based on its IR and mass spectrum and on the similarity of its UV spectrum with that of VI. Chemical evidence for its structure was obtained from the transformation of VI into VIII, by means of basic hydrolysis and anhydridisation with acetic anhydride. The combined decarbonylation and aromatisation of Diels-Alder adducts from cyclopentadienones and maleic anhydride has been observed before.⁵

It is obvious from the above-mentioned reactions that in ketone I the cyclopentadienone character is more pronounced than in fluorenone and of course also more than in ketones II and III, which formally have cyclopentenone and cyclopentanone rings. These annelation effects have also been observed in a study of the kinetic acidities of the thiophene analogues of fluorene* corresponding to I–III.

The full synthesis of I–III will be published later.

Experimental. 4,5-Dicarbomethoxy-1,2,7,8-tetramethylbenzo[1,2-b:4,3-b']-dithiophene (VI). 0.50 g (2.0 mmole) of 2,3,4,5-tetramethyl-7H-cyclopenta[1,2-b:4,3-b']dithiophene-7-one (I) and 0.40 g (2.8 mmole) of dimethylacetylene dicarboxylate were boiled under reflux in 40 ml of dry *N,N*-dimethylformamide for 2 h. The reaction mixture was poured into water and the resulting solid material was taken up in ether. The ethereal solution was washed with water and dried over MgSO₄. After evaporation

* A preliminary report was given at the 13th Nordiske Kemikermøde, August 1968 in Copenhagen.



of the ether, the residue was crystallised from methanol, yielding 0.42 g (58 %) of 4,5-dicarboxymethoxy-1,2,7,8-tetramethylbenzo[1,2-b:4,3-b']dithiophene. Further crystallisation from methanol gave analytically pure product, m.p. 196.5–198°C. Mass spectrum: (*m/e*, %) 158, 5.8; 181, 11.0; 184, 5.2; 229, 9.0; 230, 5.5; 232, 5.5; 243, 6.0; 244, 21.7; 245, 11.4; 316, 13.4; 331, 36.2; 332, 7.9; 333, 5.2; 347, 9.7; 362, 100; 363, 22.2; 364, 12.8.

NMR (CDCl₃): $\tau_{\text{CO}_2\text{CH}_3}$ 6.03, τ_{CH_3} 7.53. UV (cyclohexane): λ_{max} $m\mu$ ($\epsilon \times 10^{-3}$) 220 (22.1); 262 (28.4); 274 (26.7); 349 (18.6). [Found: C 59.4; H 5.08; S 17.6. Calc. for C₁₈H₁₈O₄S₂ (362.5): C 59.65; H 5.01; S 17.69].

4,5-Dicarboxylic acid anhydride-4a,5a,5a-tetrahydro-4a,5a-methano-1,2,7,8-tetramethylbenzo[1,2-b:4,3-b']dithiophene-9-one (VII). A solution of 0.30 g (1.2 mmole) of 2,3,4,5-tetramethyl-7H-cyclopenta[1,2-b:4,3-b']dithiophene-7-one (I) and 0.2 g (2.0 mmole) of maleic anhydride was refluxed for one week in 25 ml of dry benzene. The benzene was evaporated *in vacuo*, and the residue was treated with very little ethyl acetate. The undissolved crystals were filtered off by suction and recrystallised from ethyl acetate. This gave 15 mg (0.04 mmole) or 3.6 % of the adduct. From the filtrate 100 mg of starting material was obtained. Analytically pure material, which melted at 225–226°C, was obtained after further recrystallisation from ethyl acetate. Mass spectrum: (*m/e*, %) 26, 6.5; 44, 5.4; 54, 7.7; 59, 6.0; 98, 6.5; 124, 5.2; 171, 5.6; 18.7, 6.9; 204, 5.6; 205, 24.6; 219, 12.1; 242, 13.3; 246, 9.3; 247, 14.2; 248, 100; 249, 21.3; 250, 13.3; 298, 6.7; 299, 5.6; 346, 5.2. UV (dioxane): λ_{max} $m\mu$ ($\epsilon \times 10^{-3}$) 237 (11.6); 257 (s) (8.2); 220 (s) (6.7); 298 (s) (7.9); 304 (9.4); 323 (8.9); 336 (s) (7.7). [Found: C 58.9; H 4.15; S 18.3. Calc. for C₁₇H₁₄O₄S₂ (346.4): C 58.94; H 4.07; S 18.5].

4,5-Dicarboxylic acid anhydride-1,2,7,8-tetramethylbenzo[1,2-b:4,3-b']dithiophene (VIII). a. A solution of 0.25 g (1.0 mmole) of 2,3,4,5-tetramethyl-7H-cyclopenta[1,2-b:4,3-b']dithiophene-7-one (I) and 0.50 g (5.0 mmole) of maleic anhydride in 25 ml of dry *N,N*-dimethylformamide were refluxed for 8 h. The residue which remained after evaporating the solvent *in vacuo* was extracted with hot ethyl acetate. This solution was filtered and allowed to cool. The crystals that precipitated were recrystallised from ethyl acetate, yielding 25 mg (0.08 mmole) or 8 % of 4,5-dicarboxylic acid anhydride-1,2,7,8-tetramethylbenzo[1,2-b:4,3-b']dithiophene. Further work-up of the

ethyl acetate extract gave 50 mg of the starting material.

The anhydride thus obtained was recrystallised once more from ethyl acetate to give analytically pure product, m.p. 325–330° (decomp.). Mass spectrum: (*m/e*, %) 122, 6.2; 158, 6.1; 229, 10.7; 244, 44.5; 245, 9.0; 246, 5.4; 300, 11.0; 315, 100; 316, 21.2; 317, 14.0. UV (dioxane): λ_{max} $m\mu$ ($\epsilon \times 10^{-3}$) 242 (16.4); 271 (26.5); 292 (25.6); 393 (11.5). [Found: C 60.7; H 3.47; S 20.1. Calc. for C₁₈H₁₂O₃S₂ (316.4): C 60.74; H 3.82; S 20.27].

b. A mixture of 50 mg (0.14 mmole) of 4,5-dicarboxymethoxy-1,2,7,8-tetramethylbenzo[1,2-b:4,3-b']dithiophene, 5.0 g of potassium hydroxide, 20 ml of water and 30 ml of methanol was refluxed for 16 h, whereupon the reaction mixture was poured into water. After acidification with dilute hydrochloric acid, the precipitate was taken up in chloroform. The chloroform solution was washed with water and dried over MgSO₄. The residue obtained after evaporation of the chloroform *in vacuo* was dissolved in 10 ml of acetic anhydride under gentle heating. After heating for 5 min at about 100°C the solution was allowed to cool. Filtration gave 29 mg (0.09 mmole) or 65.5 % of 4,5-dicarboxylic acid anhydride-1,2,7,8-tetramethylbenzo[1,2-b:4,3-b']dithiophene. Its IR spectrum was identical with the IR spectrum of the anhydride obtained in the Diels-Alder reaction. M.p. 325–330°C (decomp.). Mixed m.p. 325–330°C (decomp.).

NMR spectra were obtained with a Varian A-60 high resolution spectrometer, and mass spectra with an LKB 900 mass spectrometer.

Acknowledgements. Grants from the Swedish Natural Science Research Council (to S.G.) are gratefully acknowledged.

1. Gronowitz, S., Skramstad, J. E. and Eriksson, B. *Arkiv Kemi* **28** (1967) 199.
2. Kellogg, R. M., Groen, M. B. and Wynberg, H. *J. Org. Chem.* **32** (1967) 3093.
3. Loader, C. E. and Timmons, C. J. *J. Chem. Soc. C* **1967** 1677.
4. Bellamy, L. J. *The Infrared Spectra of Complex Molecules*, Methuen 1954, pp. 90, 114.
5. Ogliaruso, M. A., Romanelli, M. G. and Becker, E. I. *Chem. Rev.* **65** (1965) 261.

Received October 1, 1969.