

VILSMEIER-HAAK FORMYLATION OF 2,2'-BITHENYL

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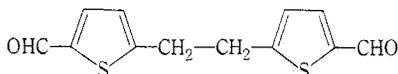
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Summary

The Vilsmeier-Haak formylation of 2,2'-bithenyl, using the complex prepared from phosphorus oxychloride and dimethylformamide, has been shown to give 5,5'-diformyl-2,2'-bithenyl and 1-[5-(5-formyl-2-thienyl)methyl-2-thienyl]-2,3-di(5-formyl-2-thienyl)propene. Two minor products, 5-formyl-2,2'-bithenyl and 1-(5-formyl-2-thienyl)-2-(2-thienyl)ethylene were isolated as the corresponding 2,4-dinitrophenylhydrazones. The structures of the formylation products were established by analysis, and by infrared and ultraviolet spectroscopy.

INTRODUCTION

During recent studies leading to the synthesis of [18]annulene trisulphide,¹ attention was given to the preparation of potentially useful intermediates, among which was 5,5'-diformyl-2,2'-bithenyl (I).

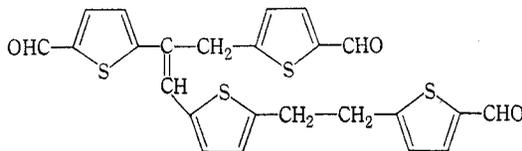


(I)

5,5'-Diformyl-2,2'-bithenyl had not been previously described and, as reactive heterocyclic rings were known to undergo ready formylation with Vilsmeier-Haak complexes,^{2,3} direct formylation of 2,2'-bithenyl appeared to be a convenient method of synthesis. The products of this reaction and methods of isolation are now described.

RESULTS AND DISCUSSION

The main products obtained, following formylation of 2,2'-bithenyl with a mixture of phosphorus oxychloride and dimethylformamide, were the required 5,5'-diformyl-2,2'-bithenyl (I) and 1-[5-(5-formyl-2-thienyl)methyl-2-thienyl]-2,3-di(5-formyl-2-thienyl)propene (II).



(II)

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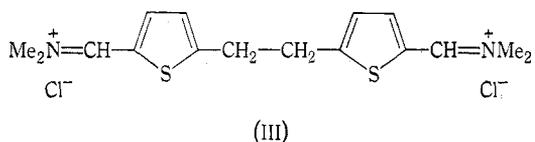
¹ Badger, G. M., Elix, J. A., and Lewis, G. E., *Proc. Chem. Soc.*, 1964, 82; *Aust. J. Chem.*, 1965, 18, 70.

² Minkin, V. I., and Dorofeenko, G. N., *Russ. Chem. Rev.*, 1960, 29, 599; *Usp. Khim.*, 1960, 29, 1301.

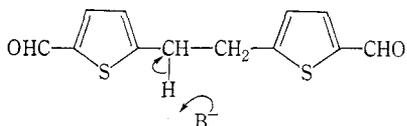
³ Normant, H., and Martin, G., *Bull. Soc. Chim. Fr.*, 1963, 1646.

The structure of 5,5'-diformyl-2,2'-bithenyl (I) was established by analysis, and by infrared and ultraviolet spectroscopy. As expected, the ultraviolet spectrum of (I) was practically identical with that of 5-methylthiophen-2-aldehyde. The structure of (II) was established in a similar manner. The ultraviolet spectrum of this compound displayed bathochromic shifts, relative to that of (I), and this was clearly due to extended conjugation. The infrared spectrum of (II) showed no absorption in the 960–980 cm^{-1} region characteristic of the *trans* CH=CH out-of-plane deformation band, but did exhibit absorption at 1580 and 830 cm^{-1} , which is characteristic of a >C=CH– group.⁴ Analysis of (II), and of the derived tri-2,4-dinitrophenylhydrazone, provided confirmation of the structure.

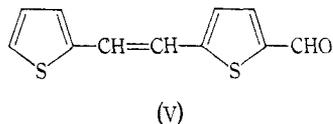
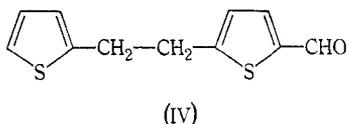
The formation of the trialdehyde (II) in all probability involves a base-catalysed self-condensation of 5,5'-diformyl-2,2'-bithenyl or its precursor (III).



Condensation could well be initiated by either the anion (OPOCl_2^-) present in the formylating mixture, or by the base (OH^-) used to hydrolyse the complex (III).



Minor quantities of 5-formyl-2,2'-bithenyl (IV) and 1-(5-formyl-2-thienyl)-2-(2-thienyl)ethylene (V) were also formed in this reaction.



These products were isolated as their 2,4-dinitrophenylhydrazones, and the structures were assigned on the basis of analytical data and infrared spectra.

EXPERIMENTAL

(i) Formylation of 2,2'-Bithenyl

A solution of 2,2'-bithenyl⁵ (4.85 g, 0.026 mole) in dimethylformamide (6.9 g, 0.095 mole) was cooled in ice-water while phosphorus oxychloride (8.8 ml, 0.093 mole) was added dropwise. The reaction mixture was protected from the atmosphere by CaCl_2 drying tubes. A vigorous exothermic reaction commenced when the reaction mixture was cautiously heated on a steam-bath, and this was controlled by cooling in ice. When evolution of hydrogen chloride had ceased, the reaction mixture was heated on a steam-bath (1 hr). The solution, obtained

⁴ Bellamy, L. J., "The Infrared Spectra of Complex Molecules." 2nd Edn. (John Wiley: New York 1959.)

⁵ Blicke, F. F., and Burkhalter, J. H., *J. Am. Chem. Soc.*, 1942, **64**, 477.

after the reaction mixture had been poured onto crushed ice (200 g), was made weakly alkaline by addition of sodium hydroxide. The deposited gum was then extracted with chloroform, and the chloroform solution thereafter washed several times with water, dried (Na_2SO_4), and finally concentrated.

(ii) *Isolation of the Main Products*

The semi-solid residue, obtained by the above procedure, was diluted with a little chloroform (10 ml). A yellow crystalline product (0.57 g) was deposited, and this was collected and washed with chloroform. After recrystallization from dimethylformamide (charcoal) 1-[5-(5-formyl-2-thienyl)methyl-2-thienyl]-2,3-di(5-formyl-2-thienyl)propene (II) was obtained as fine yellow needles, m.p. 290–292°, yield 9.4% (Found: C, 59.75; H, 3.3. $\text{C}_{24}\text{H}_{18}\text{O}_3\text{S}_4$ requires C, 59.7; H, 3.8%). The ultraviolet spectrum (95% ethanol) showed maxima at 245, 273, 316, and 361 μ . The infrared spectrum (Nujol) showed peaks at 1670, 1580, and 830 cm^{-1} .

The tri-2,4-dinitrophenylhydrazone of the trialdehyde (II) crystallized from dimethylformamide as a deep red solid, which did not melt (Found: C, 49.6; H, 3.3. $\text{C}_{42}\text{H}_{30}\text{N}_{12}\text{O}_{12}\text{S}_4$ requires C, 49.3; H, 3.0%).

After concentration of the chloroform washings another solid product was isolated. This was washed with a little cold benzene (5 ml), and then recrystallized from benzene (charcoal). 5,5'-Diformyl-2,2'-bithenyl (I) was thereby obtained as pale yellow prisms (1.0 g, 16.7%), m.p. 136–5–138° (Found: C, 57.9; H, 4.1; S, 25.95. $\text{C}_{12}\text{H}_{10}\text{O}_2\text{S}_2$ requires C, 57.6; H, 4.0; S, 25.6%). The ultraviolet spectrum (95% ethanol) showed maxima at 268 and 303 μ and the infrared spectrum (CHCl_3) showed peaks at 1670 and 1450 cm^{-1} .

5,5'-Diformyl-2,2'-bithenyl bis-2,4-dinitrophenylhydrazone crystallized from methanol/dimethylformamide as red-brown needles, m.p. 296–298° (Found: C, 47.5; H, 3.2; S, 10.4. $\text{C}_{24}\text{H}_{18}\text{N}_8\text{O}_8\text{S}_2$ requires C, 47.2; H, 3.0; S, 10.5%).

(iii) *Chromatographic Separation of Dinitrophenylhydrazones*

Evaporation of the mother liquor remaining after removal of 5,5'-diformyl-2,2'-bithenyl, yielded an oily residue which was dissolved in methanol and treated with a slight excess of 2,4-dinitrophenylhydrazine (in a 1:10 mixture of concentrated hydrochloric acid and methanol). The solid product was collected (4.0 g) and chromatographed on a column of alumina (60 by 4 cm), using chloroform for elution. Collection of fractions was commenced as soon as the eluate became coloured.

The initial fraction (400 ml) yielded 1-(5-formyl-2-thienyl)-2-(2-thienyl)ethylene 2,4-dinitrophenylhydrazone as a bright red solid (68 mg, 0.5%), which crystallized from chloroform in scarlet needles, m.p. 255–257°, ν_{max} (Nujol) 3300, 1615, 1595, 1580, and 860 cm^{-1} (Found: C, 51.3; H, 2.7. $\text{C}_{17}\text{H}_{12}\text{N}_4\text{O}_4\text{S}_2$ requires C, 51.0; H, 3.0%). The next fraction (400 ml) contained no dissolved product, but the following fraction (1 l.) yielded 5-formyl-2,2'-bithenyl 2,4-dinitrophenylhydrazone (0.6 g, 4.6%) as an orange-pink solid. This crystallized from chloroform as orange-pink needles, m.p. 241–243° (Found: C, 50.6; H, 3.6; S, 16.0. $\text{C}_{17}\text{H}_{14}\text{N}_4\text{O}_4\text{S}_2$ requires C, 50.8; H, 3.5; S, 15.9%), ν_{max} (Nujol) 3300, 1615, 1595 cm^{-1} .

The remaining strongly adsorbed material was extracted with chloroform in a Soxhlet extractor. 5,5'-Diformyl-2,2'-bithenyl bis-2,4-dinitrophenylhydrazone (0.96 g, 5%) was obtained on concentration of the chloroform solution, and after recrystallization from methanol/dimethylformamide formed red-brown needles, m.p. 296–298°, alone or admixed with the authentic sample described above.

ACKNOWLEDGMENTS

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