ACTA CHEMICA SCANDINAVICA 15 (1961) 2047–2066

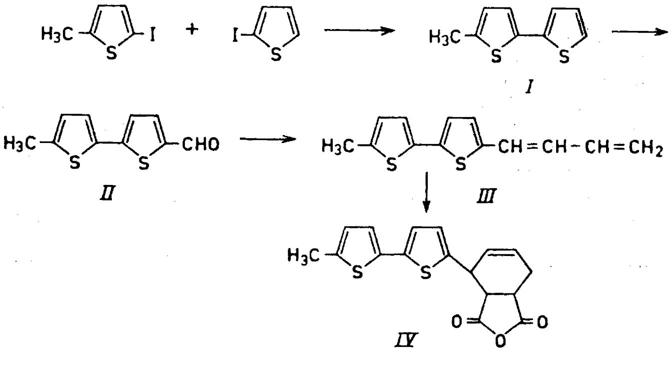
Short Communications

Studies Related to Naturally Occurring Acetylene Compounds XXX. The Synthesis of 5-Methyl-5'(buta-1,3-dienyl)-2,2'-bithienyl

LARS SKATTEBÖL*

Institutt for Organisk Kjemi, Norges Tekniske Högskole, Trondheim, Norway

In the preceding communication of this series Liaaen Jensen and Sörensen[1] described the isolation of a number of polyacetylenes and of a sulphur containing compound from plants of the genus *Bidens*. The latter was obtained as a crystalline compound, m.p. 42°, from *Bidens radiata* and assigned the structure 5-methyl-5'-(buta-1,3-dienyl)-2,2'-bithienyl (III). Because of the very small amount available and the low stability of the compound the structural assignment was based mainly on spectroscopic evidence. Hence, in order to confirm the proposed structure a synthesis of III was undertaken and this was achieved using the following sequence of reactions:



I

II

III

IV

5-Methyl-2,2'-bithienyl (I) was prepared according to Steinkopf, Leitsmann and Hofmann[2] from 2-iodothiophene and 2-iodo-5-methyl-thiophene with copper bronze. A Vilsmeier reaction on (I) using phosphorus oxychloride and N-methylformanilide gave the desired aldehyde (II) in a reasonable yield. This compound has recently been prepared by Lescot, Buu-Hoï and Xuong[3] in excellent yield using slightly different conditions. A Wittig reaction of this aldehyde with allyltriphenyl phosphonium bromide yielded III as pale yellow needles, m.p. 46–47°. The compound was extremely unstable and a satisfactory elementary analysis was not obtained. It was, however, characterized as the stable maleic anhydride adduct, m.p. 135°.

The infrared spectrum of III in carbon disulfide solution is shown in Fig. 1. A band at 992 cm^{-1} indicates that the double bond has the *trans* configuration.

At the time this synthesis was completed none of the naturally occurring substance was unfortunately available for a mixed melting point determination.

Experimental. All melting points are uncorrected. The ultraviolet absorption data were obtained using a Beckman, Model DK recording spectrophotometer. A Perkin Elmer Model 21 spectrophotometer was used for the infrared measurements. Elementary analysis was car-

---

* Present address: European Research Associates, s.a., 95, rue Gatti de Gamond, Brussels 18, Belgium.

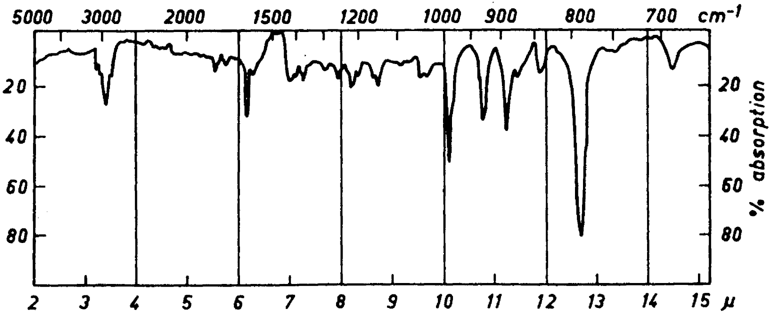


Fig. 1.

ried out by Dr. A. Elek, Los Angeles, Calif., U.S.A.

5-Methyl-2,2'-bithienyl (I) was prepared according to Steinkopf, Leitsmann and Hofmann [2]. I was separated from the reaction mixture by chromatography on alumina.

5-Formyl-5'-methyl-2,2'-bithienyl (II). I (2.2 g), phosphorus oxychloride (2.3 g) and N-methylformanilide (2.1 g) were mixed together and heated until hydrogen chloride was evolved. The mixture was then cooled in ice-water until the vigorous reaction had ceased and was finally heated at 100° for 20 min. The reaction mixture was poured into water and extracted with ether. The extract was washed with sodium bicarbonate and water until neutral and dried over sodium sulphate. Evaporation of the ether gave a crystalline residue which after recrystallization from ethanol gave pale yellow crystals (500 mg), m.p. 98—99° (Lescot, Buu-Hoï and Xuong [3] report m.p. 98°). Ultraviolet absorption (in *n*-hexane):

$\lambda_{\max}$ 3550 Å, $\varepsilon = 28\,000$.

5-Methyl-5'(buta-1,3-dienyl)-2,2'-bithienyl (III). Allyltriphenylphosphonium bromide (650 mg) was suspended in 10 ml of dry ether and methyllithium (6.5 ml; 0.23 M in ether) was added. After 2 h at room temperature the aldehyde (II, 30 mg), dissolved in dry ether-tetrahydrofuran (1:1; 5 ml), was added and the mixture shaken mechanically for some minutes. After 24 h at room temperature the mixture was heated under reflux for 15 min and filtered. The filtrate was subsequently washed with 2 N hydrochloric acid and water and dried over sodium sulphate. The solvents were evaporated under vacuum and the crystalline residue chromatographed on alumina (deactivated with ethyl acetate). A crystalline compound was eluted with petroleum ether 20—30 % benzene and recrystallization from hexane gave III as highly unstable, pale yellow crystals, m.p. 46—47° (evacuated tube). Ultra violet absorption (in *n*-hexane): $\lambda_{\max}$2215, 2568, 2608 and 3650 Å, $\varepsilon = 17\,500, 13\,700, 14\,000$ and 32 000, respectively.

Maleic anhydride adduct (IV). The bithienyl derivative (III, 30 mg) and maleic anhydride (100 mg) were dissolved in 2 ml of dry benzene and heated at 70° in a sealed tube for 4 h. The benzene was evaporated and the unreacted maleic anhydride sublimed in high vacuum (50°, 10^{-4} mm). The residue was recrystallized from acetone-petroleum ether to give slightly yellow needles (15 mg), m.p. 135° (Found: C 61.86; H 4.38. Calc. for $C_{17}H_{14}O_3S_2$; C 61.82; H 4.27). Ultraviolet absorption (in ethanol): $\lambda_{\max}$ 2450 and 3150 Å, $\varepsilon = 6\,800$ and 20 000 respectively.

1. Liaaen Jensen, S. and Sörensen, N. A. *Acta Chem. Scand.* **15** (1961) 1885.
2. Steinkopf, W., Leitsmann, R. and Hofmann, K. H. *Ann.* **546** (1941) 180.
3. Lescot jr., E., Buu-Hoï, Ng. Ph. and Xuong, N. D. *J. Chem. Soc.* **1959** 3234.

Received November 7, 1961.