

Research on the Mononitration of 2,2'-Bithienyl (1)

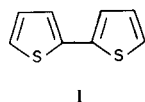
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Our interest in the behaviour of bithienyls toward electrophilic reagents led us to investigate the nitration reactions of these compounds in some detail (2).

The formylation (3), acetylation (4) and nitration (5) of 2,2'-bithienyl (1) has been investigated to some extent. In all cases the reactions furnished products substituted



exclusively in the 5 position with the exception of mononitration (5) which yielded a mixture of 5-nitro- and 3-nitro-2,2'-bithienyl in an undetermined 5-NO₂/3-NO₂ ratio.

Recently Taylor (6) pointed out that the 2-nitro/4-nitro ratios obtained in the biphenyl nitration are greatly influenced by the nitrating reagents employed and by temperature. With some reagents (nitric acid in acetic anhydride, nitrogen pentoxide, nitronium salts) the 2-substitution was dramatically enhanced at low temperatures.

In order to determine whether mononitration of 2,2'-bithienyl, in spite of greater reactivity of the 5 and 5' positions toward electrophilic reagents (7), yields 5-NO₂/3-NO₂ ratios analogously dependent upon nitrating reagents and temperature, we have studied the nitration behaviour of 1 with nitric acid in acetic acid and with nitric acid in acetic anhydride. Tables I and II report the 5-NO₂/3-NO₂ ratios (vpc determinations) obtained at different reaction temperatures.

TABLE I

5-NO₂/3-NO₂ Ratios Obtained in Mononitration of 2,2'-Bithienyl with Nitric Acid in Acetic Acid

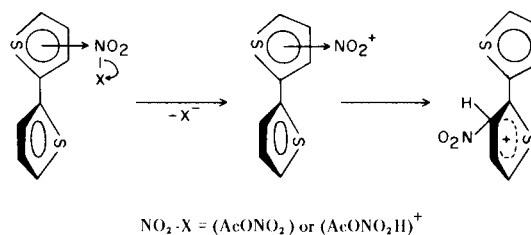
T° C	5/3 ratio
10°	3.25
20°	3.07

TABLE II

5-NO₂/3-NO₂ Ratios Obtained in Mononitration of 2,2'-Bithienyl with Nitric Acid in Acetic Anhydride

T° C	5/3 ratio
20°	1.46
0°	1.28
-10°	1.17
-20°	1.07
-40°	0.89

The behaviour observed for the reactions with nitric acid in acetic acid confirms the higher reactivity of the 5 position. With nitric acid in acetic anhydride, however, both lower 5-NO₂/3-NO₂ ratios and an enhanced 3-substitution with temperature decrease were observed. (At -40° prevalent 3-nitration was observed.) It is evident, therefore, that mononitration of 2,2'-bithienyl, as with biphenyl (6), gives lower 5-NO₂/3-NO₂ ratios as temperature decreases and the temperature dependence observed with nitric acid and acetic anhydride arises from an alternate mode of nitration. The π electrons of one of the thienyl rings causes nucleophilic displacement of X⁻ (or X) (see Scheme) from acetyl nitrate (or protonated acetyl nitrate) present in the reagent to give a π complex involving the nitronium ion. Subsequent rearrangement of the nitronium ion to the second ring gives, by virtue of the non-coplanarity of the thienyl rings (9), predominantly 3-substitution which is superimposed upon the normal substitution pattern produced by nitronium ions present in the reagent media.



The temperature dependence of the 5-nitro/3-nitro ratio can be attributed (6) to a lower activation energy of the nitration by acetyl nitrate (or protonated acetyl nitrate) than that involving preformation of nitronium ions followed by nitration. Moreover it is possible that the temperature decrease also favours the non-coplanarity of the bithienyl system to which an important role must be assigned in such a hypothesis.

EXPERIMENTAL

2,2'-Bithienyls (I), 5-nitro- and 3-nitro-2,2'-bithienyl were prepared according to the literature (5).

Nitration of I with Nitric Acid in Acetic Acid.

2,2'-Bithienyl (0.018 mole) was dissolved in acetic acid (12 ml.) and maintained at the appropriate temperature. Nitric acid ($d = 1.52$) (1.05 ml.) was then added dropwise. The reaction mixture was poured on ice and extracted with ether. The residue obtained after removal of the solvent was dissolved in a small amount of benzene and analysed by vpc. The analyses were performed with a 200 cm x 4.5 mm column packed with 5% silicon oil (SE 30) absorbed on Chromosorb W 80/100 at 200° using an Aerograph A-700 gas chromatograph: two well resolved peaks were obtained which were shown, by comparison with authentic compounds, to be 3-nitro- and 5-nitro-2,2'-bithienyl, respectively. Proportions of 5-NO₂/3-NO₂ isomers were calculated from the peak area. The dinitration was estimated at 1% of the overall nitro products. No 4-substitution was observed.

Nitration of I with Nitric Acid in Acetic Anhydride.

2,2'-Bithienyl (0.006 mole) was dissolved in acetic anhydride

(16 ml.) and maintained at the appropriate temperature. A mixture (7.8 ml.) of acetic anhydride (15 ml.) and nitric acid ($d = 1.52$, 0.6 ml.) was then added. Reaction times varied from 10 minutes at 20° to 4 hours at -40°. The reaction mixture was then worked-up and analysed as previously reported.

Acknowledgment.

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