# Tetrafluorothiophen

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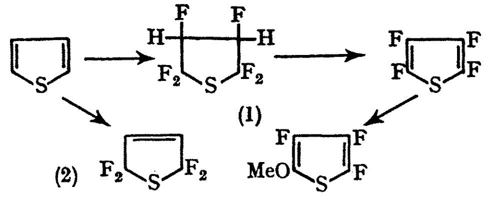
ALTHOUGH tetrafluorothiophen has been reported in a patent,[1] its chemical properties have not been described. We have now made this compound by a new route, further characterised it, and examined its nucleophilic replacement reaction with sodium methoxide.

| Compound | Chemical shifts[a] | | | | | Courling constants (Hz) | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | F(2) | F(3) | F(4) | F(5) | OMe | $J_{2,3}$ | $J_{2,4}$ | $J_{2,5}$ | $J_{3,4}$ | $J_{3,5}$ | $J_{4,5}$ | $J_{\mathrm{OMe-F}}$ |
| Tetrafluorothiophen[b] .. .. | 164·9 | 155·6 | 155·6 | 164·9 | | 7 | 17 | 31 | 7 | 17 | 7 | |
| 2,3,4-Trifluoro-5-methoxythiophen | 164·0 | 156·1 | 154·6 | | 6·24 | 5·4 | 17·8 | | 10·0 | | | 0·6 |
| 2,3,5-Trifluoro-4-methoxythiophen | 166·8 | 153·1 | | 164·9 | 6·05 | 5·4 | | 30·6 | | 15·4 | | 2·1[c], *ca.* 0·2[d] |

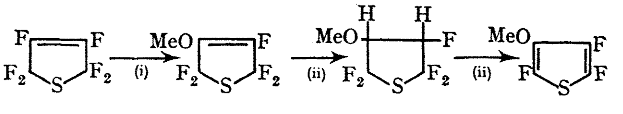
[a] $^{19}F$ Shifts in p.p.m. upfield from internal $CFCl_3$; $^1H$ Shifts on $\tau$ scale. [b] $J$ Values ±2 Hz. As the central lines of the $A_2X_2$ spectrum were incompletely resolved. [c] To F(4). [d] To F(5). [e] To F(3).

Thiophen was fluorinated with the supposed potassium tetrafluorocobaltate(III) [prepared[2] from potassium trifluorocobaltate(II) and fluorine] to give (1) and (2) as major products.



The structures of these compounds were determined by n.m.r. spectroscopy. Fluorination of thiophen with cobalt trifluoride gave mainly polyfluorobutanes and only a very low yield of (1).

When compound (1) was bubbled through molten potassium hydroxide at *ca.* 250°, tetrafluorothiophen, a liquid, b.p. 60° (lit.,[1] 68°), was formed in low yield. It showed a typical $A_2X_2$ pattern in its $^{19}F$ n.m.r. spectrum (Table), $\nu_{max}$ at 1670 and 1450 cm.$^{-1}$, strong end-absorption in the u.v. ($\epsilon$ 5800 at 220 nm.), and the molecular ion as the base peak in its mass spectrum. It did not polymerise at room temperature nor did it add bromine, in contrast to tetrafluorofuran[3] which polymerises rapidly and which easily forms a dibromo-adduct. Tetrafluorothiophen reacted slowly with sodium methoxide in methanol to give trifluoro-5-methoxythiophen; this was distinguished from the other possible isomer, trifluoro-4-methoxythiophen, which was unambiguously synthesised as follows:



Reagents: (i) NaOMe; (ii) $H_2$–Pd; (iii) KOH.

The starting material, the known[1,4] hexafluoro-3-thiolen, was a minor product in the thiophen–$KCoF_4$ reaction. Both methoxy-thiophens were liquids which polymerised to brown resins in less than 1 hr. at room temperature.

The $^{19}F$. n.m.r. spectra (Table) of the fluoro-thiophens was surprising since the most consistent way of analysing them placed the α-fluorines to high field of the β; the simple electronegativity argument predicts the opposite result, and further work[5] on polyfluorofurans is in agreement with this: the α-fluorines in the furans resonate at lower field than the β. The large four-bond coupling ($J_{2,5}$) in our thiophens is also noteworthy.

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[1] E. M. Ilgenfritz and R. P. Ruh, U.S.P. 2,932,651/1960 (*Chem. Abs.*, 1960, **54**, 18549i).

[2] P. L. Coe, R. G. Plevey, and J. C. Tatlow, *J. Chem. Soc.* (*A*), to be published.

[3] J. Burdon, D. F. Thomas, and J. C. Tatlow, *Chem. Comm.*, 1966, 48.

[4] C. G. Krespan, U.S.P. 3,069,431/1962 (*Chem. Abs.*, 1963, **58**, 10173h).

[5] J. Burdon, G. C. Chivers, and J. C. Tatlow, unpublished work.