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SHORT COMMUNICATION

Highly Fluorinated Heterocycles. Part X. [1]

The Fluorination of 3-Methyl Thiophen over Potassium Tetrafluorocobaltate (III).

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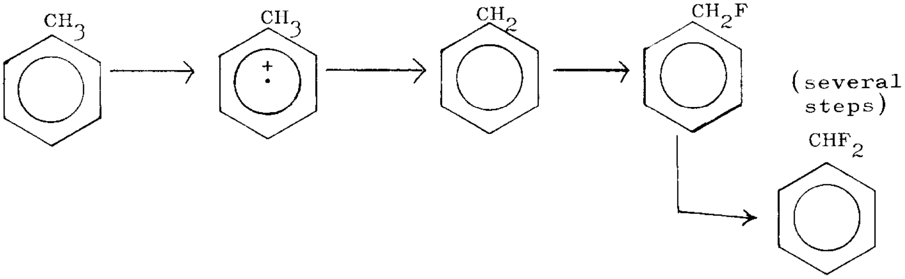
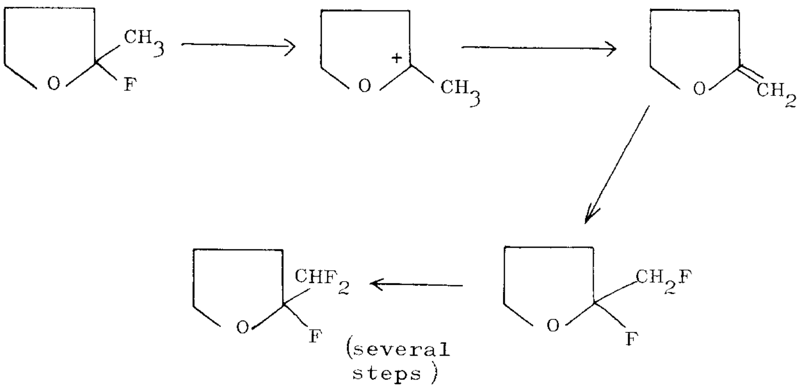
Previous work [2] has shown that when aromatics with methyl side chains are fluorinated over potassium tetrafluorocobaltate (III) ($KCoF_4$), the major products contain difluoromethyl groups. The fluorination products of 2-methyl- and 2,5-dimethyl-tetrahydrofuran [1] also contain $-CHF_2$ groups.

In the former case, the difluoromethyl groupings have been supposed [2] to arise via cation radical routes [3] followed by stages depicted in Scheme 1. In the latter case, rapid elimination of methyl hydrogens has been assumed to follow initial introduction of F at the 2-position, the positive charge being stabilized by the neighbouring oxygen [1] (scheme 2). The reluctance of the difluoromethyl group to react further is explained by analogy with the known [4] lack of acidity of the hydrogen in a CHF_2 grouping.

SCHEME 1



SCHEME 2 (essential features only shown)



In the fluorination of 3-methyl thiophen, therefore, if the aromaticity is destroyed rapidly, e.g. by 2,5 addition, the methyl group could be little fluorinated, whereas if aromaticity persists a difluoromethyl group may well be expected.

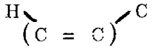
Fluorination of 3-methyl thiophen using $KCoF_4$ at 200° gave 3-difluoromethyl-2,2,5,5-tetrafluoro-3-thiolen as almost the sole product in ca. 87% yield, its identity being established by analysis and spectroscopy.

This implies that the aromaticity is not rapidly destroyed although it is of course impossible to say whether substitution of fluorine into the ring occurs before, during, or after the conversion of the $-CH_3$ group to $-CF_2H$.

This result suggests that the major difference in the fluorination products from thiopen [5] and tetrahydrofuran [6] (which almost certainly oxidises to furan in the reactor) - i.e. that the major product from the fluorination of tetrahydrofuran retains a hydrogen in the 2 position [6] whereas in the case of thiophen [5] both 2,5 hydrogens are removed - is due to the greater aromaticity of thiophen rather than to any superior liganding power [7] of the sulphur to the transition metal.

EXPERIMENTAL

3-Methyl thiophen (84.6g) was fluorinated in the usual [8] way over $KCoF_4$ (2Kg) at 200°. The product was washed with water to give 161.8g of crude product. Analytical glc (di-*iso*-decylphthalate on Chromosorb P, 1:3 130°) showed a single major peak (97% of the product). A sample (25.0g) of this product was purified in a single run by preparative glc (dinonyl-phthalate on Chromosorb P, 1:5, 100°, N_2 flow rate 50 cm^3/hr : tube dimensions 75mm x 4.8m) to give an 87% recovery of 3-difluoromethyl-2,2,5,5-tetrafluoro-3-thiolen (nc) b.p. 91° (Found: C, 28.9; H, 1.3; F, 54.7; S, 15.5 $C_5H_2F_6S$ requires C, 28.8; H, 1.0; F, 54.8; S, 15.4%). ^{19}F nmr showed three bands at 71.1 and 72.9 ϕ (broad singlets) ($-C\underline{F}_2-S$) and 120.1 ϕ (J_d = 53.5Hz) ($-C\underline{F}_2H$), in the ratios of 1:1:1. ^1H nmr showed a singlet at 6.33δ, and a triplet (J_T = 53.7Hz) centred at 6.11δ, in the ratio 1:1. Ir spectroscopy showed bands at 3100cm^{-1} (olefinic C – H), 2980cm^{-1} (saturated C – H), and 1700 cm^{-1}



$\overset{H\searrow}{(C} = \overset{\nearrow C}{C)}$

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