THE REPLACEMENT OF VINYLIC HYDROGEN BY FLUORINE

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SUMMARY

In 3H,4H-tetrafluoro-3-thiolen and 1H,2H-octafluorocyclohexene, the
conversion of –CH=CH– into –CH=CF– by fluorination over KCoF$_4$ takes place
by saturation to –CHF–CHF– followed by dehydrofluorination, and not by
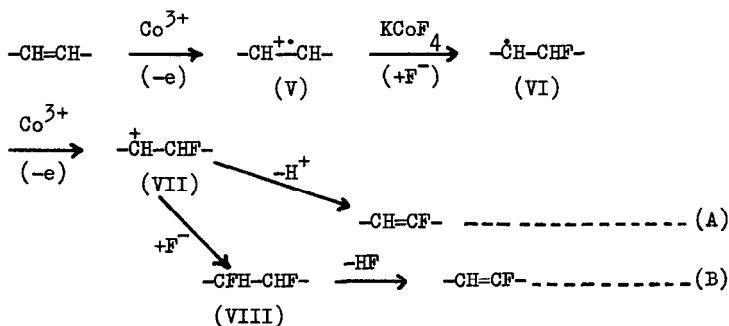direct replacement of a vinylic hydrogen.

INTRODUCTION

Potassium tetrafluorocobaltate is a milder fluorinating agent than
cobalt trifluoride [1,2,3] and relatively large quantities of unsaturated
fluorine-containing species are produced by its use. Benzene, for example,
affords, inter alia, I-IV [1] whereas with cobalt trifluoride the amount
of unsaturated material is very small [4].

I†   II   III   IV

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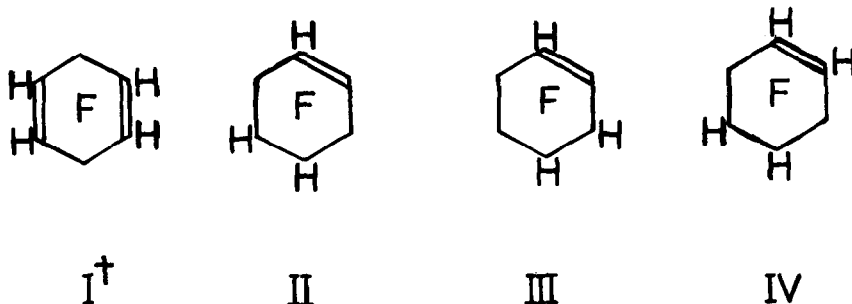
† 'F' in the centre of a ring indicates that all unmarked bonds are joined
to fluorine.

The major point to which we wish to address ourselves in this paper is the mechanism by which vinylic fluorine (as in II and III) arises in $KCoF_4$ fluorinations. Other examples of the significant occurrence of -CH=CF- units in the products of a high-valency metal fluoride fluorination include the reactions of pyridine [5] and thiophen [6] with $KCoF_4$ and of benzene with MnF_3 [4].

There are two obvious possibilities (Scheme 1) for the overall conversion of -CH=CH- into -CH=CF- (e.g. IV ⟶ III). Both pathways follow a common course to carbenium ion (VII) and then divide: in (A) a

$$-CH=CH- \quad \xrightarrow[(-e)]{Co^{3+}} \quad -CH\overset{+\cdot}{-}CH- \quad \xrightarrow[(+F^-)]{KCoF_4} \quad -\overset{\cdot}{C}H-CHF-$$
$$(V) \qquad\qquad (VI)$$

$$\xrightarrow[(-e)]{Co^{3+}} \quad -\overset{+}{C}H-CHF- \qquad \xrightarrow{-H^+}$$
$$(VII) \qquad\qquad\qquad -CH=CF- \ \text{--- ----------} (A)$$

$$\downarrow{+F^-}$$
$$-CFH-CHF- \quad \xrightarrow{-HF} \quad -CH=CF- \text{----------} (B)$$
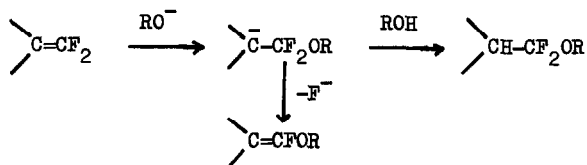$$(VIII)$$

Scheme 1

proton is lost, and in (B) the carbenium ion is quenched with fluoride ion and the saturated product (VIII) is subsequently dehydrofluorinated by fluoride ion. Dehydrofluorination by passage over heated sodium fluoride has been reported before [7].

The early stages of Scheme 1 (to VII) are based on the radical-cation theory of fluorination [3,8] although it is of little importance to the present paper precisely how the ion VII is reached; indeed some sort of bifurcation into (A) and (B) from radical VI would suffice equally.

The existence of alternative pathways from an intermediate like VII is not without precedent. For example, the reaction of bromine with $Ar_2C=CH_2$ to give $Ar_2C=CHBr$ is believed [9] to proceed by proton loss from the intermediate ion ($Ar_2\overset{+}{C}-CH_2Br$), and this is analogous to path (A); the analogy to path (B) (as far as VIII) is, of course, normal bromine addition to an alkene. An extreme example of path (A)-type behaviour is electrophilic aromatic substitution, where species (VII) corresponds to a Wheland intermediate. A further example of dual pathways from a reactive intermediate, this time in carbanion chemistry, occurs in the reaction of

fluoro-alkenes with alkoxides [10]; in some cases the intermediate loses
F⁻ and in others it is quenched by protons:

$$\underset{/}{\overset{\backslash}{>}}C=CF_2 \quad \overset{RO^-}{\longrightarrow} \quad \underset{/}{\overset{\backslash}{>}}\overset{-}{C}-CF_2OR \quad \overset{ROH}{\longrightarrow} \quad \underset{/}{\overset{\backslash}{>}}CH-CF_2OR$$

$$\downarrow -F^-$$

$$\underset{/}{\overset{\backslash}{>}}C=CFOR$$

RESULTS AND DISCUSSION

We have sought to distinguish between routes (A) and (B) by carrying
out the fluorinations illustrated in Scheme 2 and investigating the
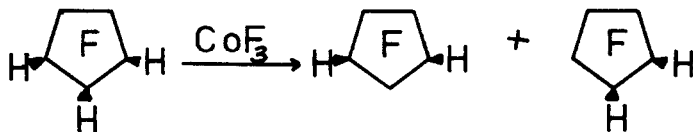products. In the thiolan/thiolen fluorinations, the ratio of the
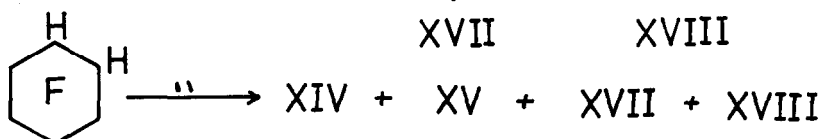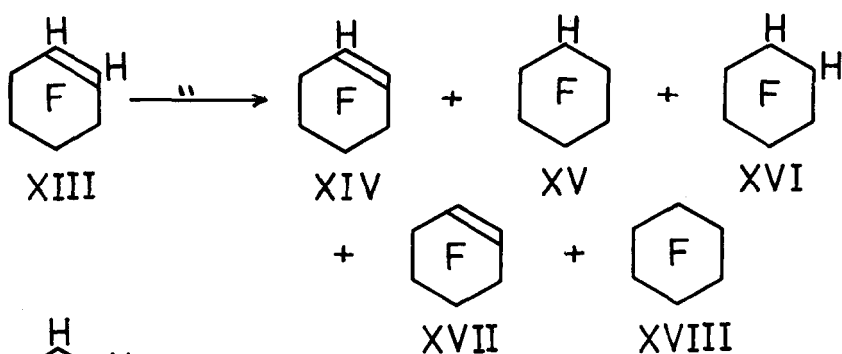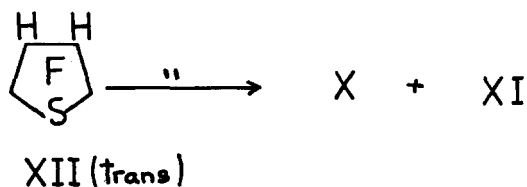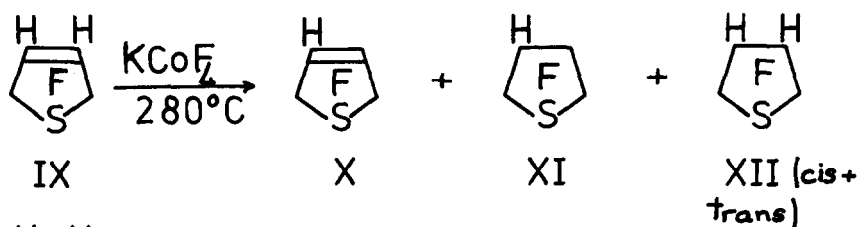
Scheme 2

vinylic substitution product (X) to the saturated compound (XI) was the same with both starting materials (IX and XII). A similar situation occurred with the 6-ring fluorinations: the same ratio of XIV to XV was obtained from the fluorination of XIII or XVI. The conclusion seems inescapable: vinylic replacement of hydrogen by fluorine takes place mainly or entirely via route (B) – saturation followed by dehydrofluorination. If it were not and route (A) were being followed, then coincidentally for each pair of substrates, the rates of formation of the vinylic products (X and XIV) relative to the rates of formation of the saturated products (XI and XV) would have to be the same even though the vinylic products at least were being formed in two different ways: vinylic substitution [route (A)] from IX and XIII and HF elimination [route (B)] from XII and XVI. This is surely unreasonable. It may be important to note that this preference for route (B) is now only established for heavily fluorinated substrates; it is conceivable, but experimentally difficult to test, that route (A) might occur with very lightly fluorinated compounds.

Three minor points also arise from this work. First, the cis-isomer of XII is a new compound and was not detected in the original fluorination of thiophen [6]. Its structure is quite straightforward from its ^{1}H and ^{19}F nmr specta.

Secondly, it is not clear from our work whether mono-H saturated compounds (XI and XV) arise by saturation of the corresponding olefins (X and XIV) with fluorine or by replacement of one hydrogen by fluorine in the di-H-compounds (XII and XVI), or by both routes. Whatever the answer to this point, our main conclusion is unaffected.

Thirdly, although fluoride-ion catalysed dehydrofluorination does occur in $KCoF_4$ fluorinations (i.e. XII $\longrightarrow$ X and XVI $\longrightarrow$ XIV), it cannot be prevalent in CoF_3 reactions. If it were then the many [4] fluorinations of saturated polyfluorohydrocarbons which have been carried out over CoF_3 at Birmingham would not have been stereospecific. For example, 1H,2H,3H/-heptafluorocyclopentane reacts thus [11]:

Neither of the other stereoisomers (1H/2H- or 1H/3H-octafluorocyclopentane) were detected (we have re-checked the original glc trace of this fluorination and there are no detectable peaks where the trans-isomers were known to appear). However, if fluorination had proceeded by initial dehydrofluorination, even in small part, then the following would have occurred:

Both the cis and trans 1H,2H-isomers would have formed, and similarly with the 1H,3H-pair. Since this did not occur, we conclude that although replacement of saturated hydrogen by fluorine over $KCoF_4$ takes place wholly or in part via dehydrofluorination, over CoF_3 it occurs wholly by a direct route; (C) and (D) are two obvious possibilities [8].

This remains to be explored more fully, as do comparable reactions with fluorinating agents of power between CoF_3 and $KCoF_4$, such as MnF_3.

EXPERIMENTAL

Fluorination of 3H,4H-Tetrafluoro-3-thiolen (IX)

The thiolen (2·8 g) [6] was added over a period of 30 minutes and in a stream of nitrogen (1 dm³/h) to a stirred and heated (230°C) bed of $KCoF_4$ (100 g) in a reactor of the type described before [4]. After the addition, the nitrogen stream (2 dm³/h) was continued for a further 2 h. The products (2·2 g) were collected in a trap cooled with liquid air, washed with water and separated by gas/liquid chromatography [Pye 104

instrument: column 2 m x 10 mm dia. packed with dinonyl phthalate on
Celite (1:2); temp. 100°C; N_2 flow-rate 5 dm^3/h] into: (a) a mixture
(0.35 g; 85:15 by ^{1}H nmr – vinyl-H compared to CHF) of 3H-heptafluoro-
thiolan (XI) and 3H-pentafluoro-3-thiolen (X) (i.r. acceptable); (b) 3H/
4H-hexafluorothiolan (0.65 g, i.r., XII); (c) trace, not identified;
(d) starting material (0.4 g, i.r.) [see ref. 6 for details of these
compounds]; (e) 3H,4H/-hexafluorothiolan nc (0.1 g, XII) [^{1}H nmr: δ =
5.1 p.p.m. (d, J∼50-55 Hz, with further complex coupling) due to CHF. [19]F
nmr: an AB pattern (δ_A = 72.3 p.p.m., δ_B = 82.9 p.p.m., J_{AB} = 208.7 Hz)
due to CF_2 adjacent to sulphur, and a signal of half the intensity at
212.2 p.p.m. (d, J∼50-55 Hz) due to CHF not adjacent to sulphur: these
assignments are based on analogy with the spectra of similar compounds –
see ref.[6].

Fluorination of 3H/4H-Hexafluorothiolan (XII)

The thiolan (2.8 g) [6] was fluorinated and the products separated
(at 85°C) as above to give: (a) a mixture (0.35 g; 85:15 by ^{1}H nmr of
3H-heptafluorothiolan (XI) and 3H-pentafluoro-3-thiolen (X); and (b)
starting material (0.8 g, i.r.).

Fluorination of 1H,2H-Octafluorocyclohex-1-ene (XIII)

This compound (2.7 g) [12] was fluorinated and the products (1.9 g)
separated (at 50°C) as above to give: (a) perfluorocyclohexane (0.25%,
identified by glc retention time only, XVIII); (b) decafluorocyclo-
hexene (7.2%, i.r., XVII); (c) undecafluorocyclohexane (0.5%, glc
retention time, XV); (d) 1H-nonafluorocyclohex-1-ene (11.5%, i.r., XIV);
(e) 1H/2H-decafluorocyclohexane (5.1%, i.r., XVI); (f) starting material
(75.5%, i.r.). [See ref. 4 for further details of these products.]

Fluorination of 1H,2H-Decafluorocyclohexane (XVI)

The compound (2.7 g) [13] was treated as above to give: (a) per-
fluorocyclohexane (1.9%, glc retention time, XVIII); (b) decafluorocyclo-
hexene (10%, i.r., XVII); (c) unknown (1.2%); (d) undecafluorocyclohexane
(1.9%, glc retention time, XV); (e) 1H-nonafluorocyclohex-1-ene (33%,
i.r., XIV); (f) starting material (45.6%, i.r.); (g) unknown (0.4%).

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