Tetrahedron Letters No. 10, pp. 619-621, 1963. Pergamon Press Ltd.
Printed in Great Britain.

MODEL COMPOUNDS RELATED TO "VITON A"[1]

By R.D. Chambers, J. Hutchinson, and W.K.R. Musgrave

The Chemistry Department, The University, South Road, Durham

(Received 17 January 1963)

The recent publications by Paciorek and co-workers[2,3,4] dealing with the mechanism of cross linking of fluorocarbon polymers, and the synthesis and study of the chemical reactivity of model compounds related to them, prompts us to communicate some of our results in this field.

We have synthesised model compounds related to "Viton A"[5] which is a co-polymer of hexafluoropropene and vinylidine fluoride where the predominating arrangement has been found to be $-CF_2-CF-(CF_3)\cdot CH_2\cdot CF_2\cdot CH_2\cdot CF_2-$.[6]

The new fluorocarbon iodide, heptafluoro-2-iodopropane[7] was used as the source of tertiary fluorine and this was added thermally to vinylidine fluoride. Heating together in a stainless steel rocking autoclave (150 ml.) equimoleoular amounts of heptafluoro-2-iodopropane and vinylidine fluoride to 185°C for 36 hours afforded the simple adduct (I) as the main product (80%) under these conditions.

---

[1] Registered trade mark of E.I. du Pont de Nemours & Co. Inc.

[2] Paciorek, K.L., Mitchell, L.C. and Lenk, C.T., J. Polymer Sci. 45, 405 (1960)

[3] Paciorek, K.L., Merkl, B.A. and Lenk, C.T., J. Org. Chem. 27, 266 (1962)

[4] Paciorek, K.L., Merkl, B.A. and Lenk, C.T., J. Org. Chem. 27, 1015 (1962)

[5] Dixon, S., Rexford, D.R. and Rugg, J.S., Ind. Eng. Chem. 49, 1687 (1957)

[6] Ferguson, R.C., J. Amer. Chem. Soc. 82, 2416 (1960)

[7] Chambers, R.D., Musgrave, W.K.R. and Savory, J., Proc. Chem. Soc. 113, (1961); J. Chem. Soc. 3779 (1961)

$$(CF_3)_2CFI + nCH_2CF_2 \longrightarrow (CF_3)_2CF\cdot(CH_2CF_2)_nI$$

This adduct was coupled by irradiating with ultra-violet light in the presence of mercury and gave 3,3,6,6-tetrahydroperfluoro-(2,7-dimethyloctane) (II) (>90%).

$$\underset{\text{I}}{(CF_3)_2CFCH_2CF_2I} \xrightarrow[\text{Hg}]{\text{ultraviolet light}} \underset{\text{II}}{[(CF_3)_2CF\cdot CH_2\cdot CF_2]_2}$$

which contains the essential structural elements of "Viton A". For comparison, similar models without tertiary fluorine have been synthesised using heptafluoro-1-iodopropane[8] and pentafluoroiodoethane as starting materials in the same reaction sequence to give $[n\text{-}C_3F_7\cdot CH_2\cdot CF_2]_2$ (III) and $[C_2F_5\cdot CH_2\cdot CF_2]_2$ (IV) respectively.

It has often been postulated that cross-linking agents (e.g. MgO, amines) used in the curing of commercial elastomers, act by causing the elimination of hydrogen halide as the first step. In the case of "Viton A", it is the tertiary fluorine atoms which are reputed to be the more easily eliminated.[2] Paciorek and co-workers[4] have shown that potassium hydroxide and amines both cause elimination of hydrogen fluoride (tertiary fluorine) from $CF_3\cdot CH_2\cdot CF(C_2F_5)\cdot CH = CF\cdot C_2F_5$. However, there is no illustration of the ease of elimination of hydrogen fluoride from saturated model compounds.

All of the model compounds II, III and IV showed considerable reluctance to react with solid or aqueous potassium hydroxide and, under conditions required to promote reaction, extensive decomposition occurred rather than simple elimination of hydrogen fluoride. However, amines eliminated hydrogen fluoride with comparative ease; primary amines with II and IV in dry ether gave a gel almost immediately at room temperature; secondary amines reacted similarly but tertiary amines under these conditions gave no precipitate. After heating II with tri-n-butylamine to

---

[8] Hauptschein, M., *J. Amer. Chem. Soc.* **80**, 846 (1958).

130°C for 3 hours in the absence of solvent the amine hydrofluoride was isolated together with an organic product which consisted mainly of one component. This main component was isolated by a preparative scale gas-liquid chromatography in 95% purity (estimated by analytical G.L.C.). The infra-red spectrum of this material had a strong main peak at 5·85 μ showing unsaturation. The fluorine magnetic resonance spectrum indicated that the ratio of $-CF_2$ to $>$C-F in the product was approximately 4:1. Since the corresponding ratio in II is 2:1, these results indicate preferential, but not necessarily exclusive, removal of tertiary fluorine. A similar reaction of IV with tri-n-butylamine gave a very much more complex mixture of products.

These results indicate the ease with which hydrogen fluoride may be removed from saturated sites in polymers with the structural units contained in these model compounds, and that elimination of tertiary fluorine is preferred, although it is not necessarily the only process which takes place.

A detailed investigation of the reaction of these model compounds is proceeding.

We wish to thank Yarsley Research Laboratories Ltd. for a maintenance grant to one of us (J.H.).