Tetrahedron Letters No.58, pp. 5041-5044, 1970. Pergamon Press. Printed in Great Britain.

REARRANGEMENTS IN COBALTIC FLUORIDE FLUORINATIONS OF BRIDGED RING HYDROCARBONS

By J. Battersby, R. Stephens and J. C. Tatlow

(Department of Chemistry, The University, P.O. Box 363, Birmingham. B15 2TT)

(Received in UK 21 October 1970; accepted for publication 13 November 1970)

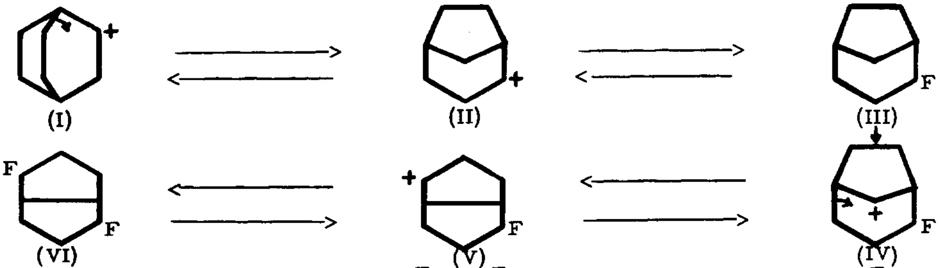
The cobaltic fluoride fluorination of hydrocarbons has been studied extensively as a method of producing fluorocarbons in good yield (1). The predominant by-products (other than fluorohydrocarbons) have been considered to arise from carbon chain breakdown but not from rearrangement. Examples are reported here of major skeletal rearrangements in the fluorination of bicyclo-(2.2.2)- and -(3.2.1)-octane of a type which should be common to all fluorinations of bridged ring hydrocarbons.

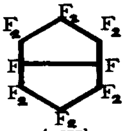
Bicyclo(2.2.2)octane was passed over cobaltic fluoride at 320° and the product subjected twice more to the same procedure over fresh cobaltic fluoride. The ultimate highly fluorinated product was a mixture of a clean mobile liquid and a white crystalline solid, in the ratio of 3:2. Analytical g.l.c. of the liquid (9.2 m. col. of ucon oil/chromosorb P, 1:4; 22°) indicated the presence of 3 compounds shown to be tetradecafluorobicyclo-(3.3.0)-, -(3.2.1)- and -(2.2.2)-octane (VII)-(IX), in the ratio of 63:29:8, respectively, together with a number of smaller peaks (presumably derived from ring opening reactions). The solid product was dissolved in the minimum volume of perfluoromethylcyclohexane and shown by g.l.c. to contain similar proportions of the same isomeric tetradecafluorobicyclo octanes (VII)-(IX). Semi-preparative g.l.c. (9 m. col of ucon oil/chromosorb P, 1:4) separation at room temperature gave pure specimens of the three isomeric fluorocarbons; tetradecafluorobicyclo-(3.3.0)- (2) and -(2.2.2)- (3) octanes were identified by a comparison with authentic specimens which had correct elemental analyses and consistent IR-,NMR- and mass-spectra. Tetradecafluorobicyclo(3.2.1)octane was identified by the same techniques.

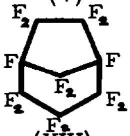
When subjected to an identical fluorination procedure, bicyclo(3. 2. 1)octane, prepared from cisbicyclo(3. 3. 0)octane (4), gave a similar product which was shown by g. l. c. (25°) to contain tetradecafluorobicyclo-(3. 3. 0)-, -(3. 2. 1)- and -(2. 2. 2)-octane in the ratio of 51:41:8, respectively, and a small amount of other products presumably derived from ring opening reactions.

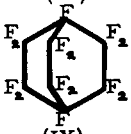
However, bicyclo(3. 3. 0)octane, prepared from cyclo octane (5), under similar fluorination conditions gave a liquid product which was shown by g. l. c. (22°) to contain mainly tetradecafluorobicyclo(3. 3. 0)octane together with a number of smaller peaks (presumably breakdown products), but none of the isomeric bicyclo-(3. 2. 1)- and -(2. 2. 2)-fluorocarbons.

These results can be rationalised on the basis of cobaltic fluoride, acting either as a strong Lewis acid (6), or as an oxidising species, generating from the starting hydrocarbon or a very lightly fluorinated derivative, a carbonium ion which then rearranges as in a sequence such as (I)⟶(VI)




(VII)


(VIII)


(IX)

The relative equilibrium concentrations of the hydrocarbon bicyclo octanes in the presence of aluminium bromide have been established (7) as (3. 3. 0) > (3. 2. 1) > (2. 2. 2) above 105° and the absence of rearrangement in the fluorination of bicyclo(3. 3. 0)octane is consistent with equilibrium concentrations extrapolated to the range 300-320°.

The issue is complicated, however, by the fact that at some intermediate point in the fluorination process the opportunity for carbonium ion rearrangements ceases. It has been established that cobaltic fluoride fluorination of carbomethoxy heptafluorobicyclo(2. 2. 2)oct-5-ene (3), 2*H*, 2*H*, 3*H*, 3*H*-octafluorobicyclo(2. 2. 2)oct-5-ene (8), 1*H*, 2*H*, 2*H*, 3*H*, 3*H*-heptafluorobicyclo(2. 2. 2)oct-5-ene (8) and 2, 2, 3, 3, 5, 6-hexafluorobicyclo(2. 2. 2)oct-5-ene (8) all give tetradecafluorobicyclo(2. 2. 2)octane as the only detectable bicyclo octane fluorocarbon. Presumably in all four systems a free carbonium ion is markedly destabilised by the fluorine substituents.

It is pertinent to note that although detectable isomerisation products are not obtained in the fluorination of norbornadiene, since rearrangement retains the (2. 2. 1)-skeleton, a clear indication that rearrangements can occur in the system is available. Thus, fluorination of endo-perfluorotricyclo[5. 2. 1. $0^{2,6}$]deca-3, 8-diene (9), the thermal dimer of hexafluorocyclopentadiene (10), gave a highly crystalline perfluorodecane (endo-) whereas the analogous hydrocarbon endo-deca-3, 8-diene gave a liquid perfluorodecane (exo-endo mixture) (11). Clearly the perfluoro-diene should not favour the production of carbonium ions and hence will not rearrange to give the exo-system whereas the analogous hydrocarbon endo-diene should give both the exo- and endo-perfluorodecanes.

Acknowledgments: We thank the British Petroleum Company for a maintenance award (to J. Battersby) and for a sample of bicyclo(2. 2. 2)octane.

REFERENCES

1. M. Stacey and J. C. Tatlow in "Advances in Fluorine Chemistry", Butterworths, London, 1960, 176.

2. J. A. Oliver, R. Stephens and J. C. Tatlow, unpublished work.

3. W. B. Hollyhead, R. Stephens, J. C. Tatlow and W. T. Westwood, *Tetrahedron*, 1969, *25*, 1777.

4. J. W. Barrett and R. P. Linstead, *J. Chem. Soc.*, 1936, 611.

5. B. A. Kazanskii, E. A. Shokova, S. I. Khromov, V. T. Aleksanyan and K. E. Sterin, Dokl. Akad. Nank. S.S.S.R., 1960, **133**, 1090.

6. R. G. Pearson, J. Amer. Chem. Soc., 1963, **85**, 3533.

7. P. vR. Schleyer, K. R. Blanchard and C. D. Woody, J. Amer. Chem. Soc., 1963, **85**, 1358.

8. J. Battersby, R. Stephens and J. C. Tatlow, unpublished work.

9. J. Burdon, T. M. Hodgins, D. R. A. Perry, R. Stephens and J. C. Tatlow, J. Chem. Soc., 1965, 808.

10. R. Fields, M. Green and A. Jones, J. Chem. Soc., 1967, 270.

11. R. J. Heitzman, C. R. Patrick, R. Stephens and J. C. Tatlow, J. Chem. Soc., 1963, 281.