

Stereochemistry of Addition of Fluorine to Olefins by Cobalt Trifluoride

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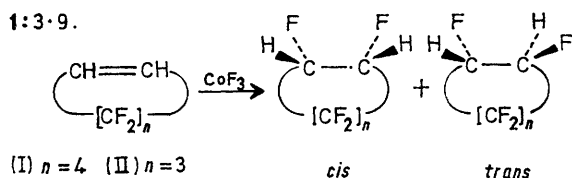
The addition of fluorine, by cobalt trifluoride, to the double bonds of 1*H*,2*H*-octafluorocyclohexene and 1*H*,2*H*-hexafluorocyclopentene is not highly stereoselective; *cis* : *trans* ratios of about 1 : 7 and 1 : 3.9, respectively, have been obtained.

ALTHOUGH it is well known¹ that cobalt trifluoride and some other high-valency metal fluorides can saturate carbon-carbon double bonds by addition of fluorine, there are no clear reports on the stereoselectivity of such additions.

We have now investigated the addition of fluorine to 1*H*,2*H*-octafluorocyclohexene (I) and 1*H*,2*H*-hexafluorocyclopentene (II), by cobalt trifluoride; in neither case

¹ M. Stacey and J. C. Tatlow, *Adv. Fluorine Chem.*, 1960, **1**, 166.

was the addition highly stereoselective. For the cyclohexene (I), the *cis* : *trans* ratio was about 1 : 1.7, and for the cyclopentene (II), about 1 : 3.9.



It was necessary to choose highly fluorinated substrates like (I) and (II) in order to avoid complications due to replacement of hydrogen on saturated carbon atoms by fluorine.¹ It was also necessary to choose fluorination conditions such that significant conversion of the initial *cis*- and *trans*-adducts into undecafluorocyclohexane and nonafluorocyclopentane did not occur; this meant that 75%, or more, of the crude fluorination mixture was unchanged starting material.

It has recently² been argued that fluorinations with cobalt trifluoride and similar reagents are basically oxidation reactions akin to those by better known reagents. It is therefore gratifying to note that the additions of two acetoxy-groups to olefins by both lead tetra-acetate^{3,4} and thallium triacetate⁴ are generally not highly stereoselective, *trans*-addition usually being favoured over *cis*- by only a small ratio. The mechanisms of these additions, or of our fluorinations, are not clear; metallation has been proposed⁴ as part of the sequence with the lead and thallium reagents, but this seems unlikely with a cobalt species.

² J. Burdon, I. W. Parsons and J. C. Tatlow, *Tetrahedron*, 1972, **28**, 43.

³ R. Criegee, *Annalen*, 1930, **481**, 263; *Angew. Chem.*, 1958, **70**, 173.

⁴ C. B. Anderson and S. Winstein, *J. Org. Chem.*, 1963, **28**, 605; H. J. Kabbe, *Annalen*, 1962, **656**, 204.

EXPERIMENTAL

Fluorination Reactor.—This was an electrically heated nickel tube (61 × 6 cm diam.) containing cobalt trifluoride (ca. 200 g) supported on iron gauzes (2.9 × 0.8 cm). It was equipped to allow the introduction of the starting material in a stream of nitrogen, and the collection of the product in a liquid-air-cooled trap.¹

Fluorination of 1H,2H-Octafluorocyclohexene.—The cyclohexene⁵ (2.0 g) was slowly (ca. 30 min) introduced in a stream of nitrogen (3.0 dm³ h⁻¹) into the fluorination reactor heated to 50 °C. The nitrogen stream was continued for a further 2 h. The products were washed with ice-water and analysed by g.l.c. (1.5 g). Separation of a sample (0.7 g) by g.l.c. gave (i) 1H/2H-decafluorocyclohexane (0.11 g); (ii) 1H,2H-octafluorocyclohexene (0.47 g); and (iii) 1H,2H-decafluorocyclohexane (0.05 g), all identified by comparison of their i.r. spectra with those of authentic specimens.⁶ There was also a minor peak attributable (retention time) to undecafluorocyclohexane, but this was present in too small an amount to be isolated.

Three such fluorinations gave (g.l.c. peak area ratios) 1.6 : 1, 1.7 : 1, and 1.8 : 1 for the ratio of 1H/2H- to 1H,2H/-decafluorocyclohexane.

Fluorination of 1H,2H-Hexafluorocyclopentene.—This⁷ (2.7 g) was fluorinated as above to give crude products (2.0 g), identified by i.r.⁸ as (i) 1H/2H-octafluorocyclopentane (0.16 g); (ii) starting material (1.6 g); and (iii) 1H,2H/-octafluorocyclopentane (0.08 g). Two such fluorinations gave 4.0 : 1 and 3.8 : 1 for the ratio of 1H/2H- to 1H,2H/-octafluorocyclopentane.

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⁵ D. E. M. Evans, W. J. Feast, R. Stephens, and J. C. Tatlow, *J. Chem. Soc.*, 1963, 4828.

⁶ R. P. Smith and J. C. Tatlow, *J. Chem. Soc.*, 1957, 2505.

⁷ W. J. Feast, D. R. A. Perry, and R. Stephens, *Tetrahedron*, 1966, **22**, 433.

⁸ R. J. Heitzman, C. R. Patrick, R. Stephens, and J. C. Tatlow, *J. Chem. Soc.*, 1963, 281.