INTERACTION OF POLYFLUORINATED BENZO-CYCLOALKENES WITH LEWIS ACIDS. SKELETON REARRANGEMENTS IN THESE REACTIONS

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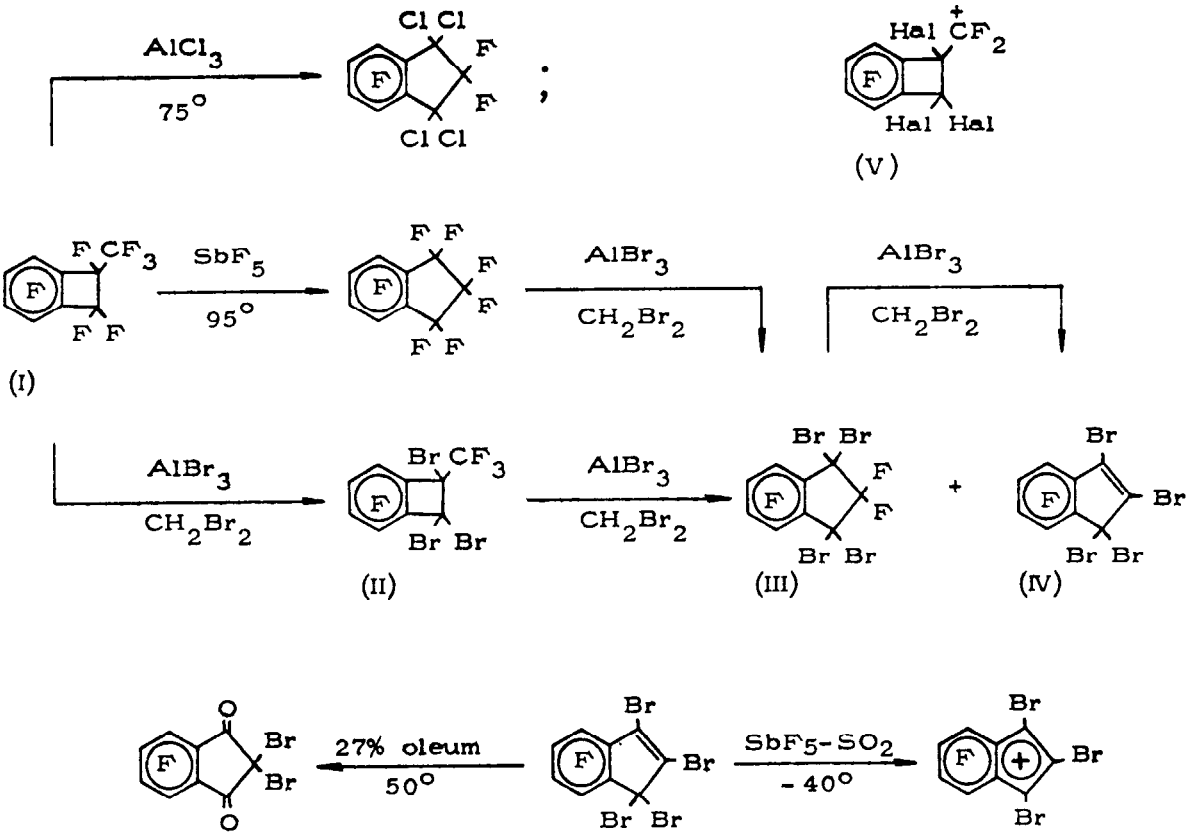
Interaction of polyfluorinated benzocycloalkenes containing four-, five- and six-membered cycles with a number of Lewis acids (SbF_5, $AlCl_3$, $AlBr_3$) have been investigated.

An unknown ring expansion of halogenated benzocycloalkenes has been found when perfluoro-1-methylbenzocyclobutene (I) was reacted with Lewis acids. Perfluoroindane was formed under heating of compound (I) with SbF_5. The interaction of compound (I) with $AlBr_3$ (25-30°C) depends on the amounts of $AlBr_3$ and gives compounds (II) or (IV), or a mixture of compounds (II), (III) and (IV). Some of the investigated transformations are shown on the scheme. The ring expansion in these reactions perhaps proceeds via intermediate cation (V) (or crypto-ion).

Some reactions of compound (IV) and other compounds have been investigated. The reaction pathways of the titled transformations will be discussed.


AlCl3
75°
Cl Cl
F
F
Cl Cl
;
Hal CF2
Hal Hal
(V)
F CF3
F F
SbF5
95°
F F
F
F
F F
AlBr3
CH2Br2
AlBr3
CH2Br2
(I)
AlBr3
CH2Br2
Br CF3
Br Br
(II)
AlBr3
CH2Br2
Br Br
F
F
Br Br
(III)
+
Br
Br
Br Br
(IV)
O
Br
Br
O
27% oleum
50°
Br
Br
Br Br
SbF5-SO2
-40°
Br
Br
Br