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SYNTHESIS OF PERFLUOROBICYCLIC ETHERS

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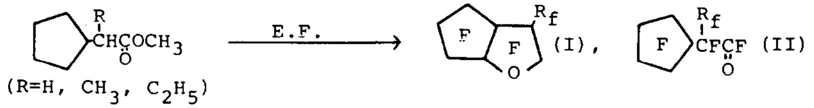
The electrochemical fluorination of cycloalkyl-substituted acetic and propionic acids were conducted to obtain several kinds of perfluorobicyclic ethers [reaction conditions: Anodic current density: 3.5 A/dm^2, Volt: 5∼8V, Temp: 5∼6 °C]. For example, from cyclopentyl-substituted acetic acids, perfluoro(4-alkyl-2-oxabicyclo[3.3.0]octane)s (I) were formed as the cyclization products in yields of 10∼19% together with the corresponding perfluoroalkanoyl fluorides (II) (Y=3∼13%).



While, perfluorospiro-ethers were obtained from the fluorination of 3-cycloalkyl-substituted propionic acids. The characterization of these perfluorobicyclic ethers which consists of the reaction with anhydrous aluminum chloride will be reported also.

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ON THE MECHANISM OF ELECTROFLUORINATION OF ORGANIC COMPOUNDS

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After a short review of the current mechanisms, the Authors describe the electrofluorination process of organic compounds in anhydrous HF. Several electrofluorination experiments carried out for some years with a particular attention to their industrial applications are reconsidered in view of the fluorination mechanism.

These experiments carried out either with organic acids (butirric, isobutirric, benzensulfonic and toluensulfonic), either with tertiary amines (tripropylamine, tributylamine, N-ethylpiperidine and N-methylmorpholine), bring new support to the mechanism suggesting an initial anodic oxidation of the organic molecule adsorbed on the anode thus forming a radical-cation, which originates the corresponding cation whose stabilisation is effected by addition of a fluoride anion.