CHEMISTRY LETTERS, pp. 121-122, 1980.

A NEW ROUTE TO PERFLUOROBICYCLIC ETHERS. AN UNUSUAL FLUORINATION PRODUCT FROM CYCLOHEXEN-2-YL-SUBSTITUTED CARBOXYLIC ACID ESTERS

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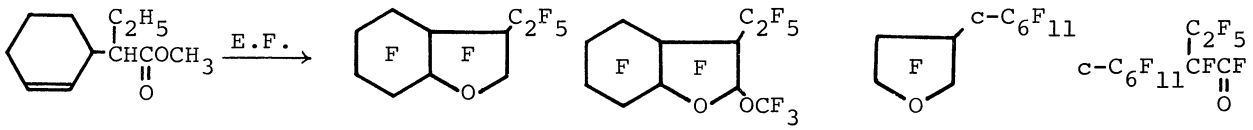
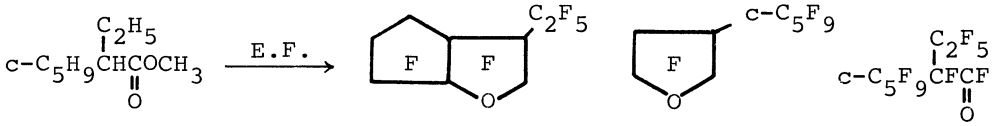
The electrochemical fluorination of methyl cyclohexen-2-ylbutyrate (1) afforded perfluoro(8-methoxy-9-ethyl-7-oxabicyclo[4.3.0]nonane) (1b) together with perfluoro(9-ethyl-7-oxabicyclo[4.3.0]nonane) (1a) as the cyclization product in a fair yield. The compound 1b having an acetal structure was confirmed by its spectral data and also by examining the chlorination products which were obtained by the reaction of 1b with anhydrous aluminum chloride.

In conjunction with our interest in developing the utility of cyclization of the carboxylic acids during electrochemical fluorination for projected synthesis of the perfluorobicyclic ethers, we have investigated the fluorination of such esters of cyclohexenyl-substituted carboxylic acids as methyl cyclohexen-2-yl-butyrate (1). In this communication, we wish to report the formation of the compound having an acetal structure by the fluorination of 1.

From 1, the following two kinds of products (1a and 1c) were expected to be formed as cyclization products analogously to the fluorination[1] of methyl 2-cyclopentylbutyrate (2).



1 1a 1b 1c 1d

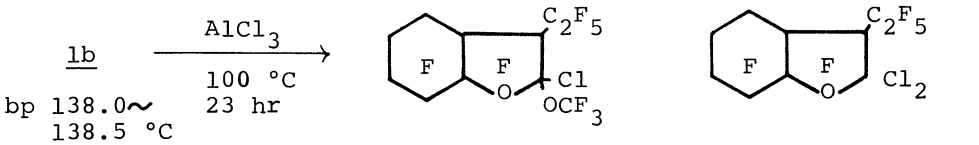


2 2a (Y=14.7%) 2b (Y=5.0%) 2c (Y=8.1%)

Compound 1 (31.6 g, 0.174 mol) was fluorinated in a manner described previously[2] using a 1 l electrolytic cell under the following conditions; Anodic current density 3.5 A/dm^2, Cell voltage 5.2~8.4 V, Cell temp 5~6°C, 220 Ahr. GLC analysis [Column: 30% 1,6-bis(1,1,12-trihydroperfluorododecyloxy)hexane on Chromosorb PAW, Carrier: He] of the product (57.1 g) showed the formation of perfluoro(9-ethyl-7-oxabicyclo[4.3.0]nonane) (1a) and the compound found to be perfluoro(8-methoxy-9-ethyl-7-oxabicyclo[4.3.0]nonane) (1b) in yields of 22.9% and

10.1% respectively, together with degradation products. These were characterized in the usual manner (^{19}F nmr, mass, IR and elemental analysis). Neither 1c nor 1d was detected in the product. The formation of 1b which retained the original ester linkage [-C(C=O)-O- ⟶ -C(-C-O-)-O-] was quite unexpected. Because, it has been known that ester is apt to be converted into acid fluoride and alcohol due to the solvolysis which takes place easily in anhydrous hydrogen fluoride during fluorination[3].

Furthermore, the structure of 1b was confirmed by examining the chlorination products which were obtained by treating 1b with anhydrous aluminium chloride.



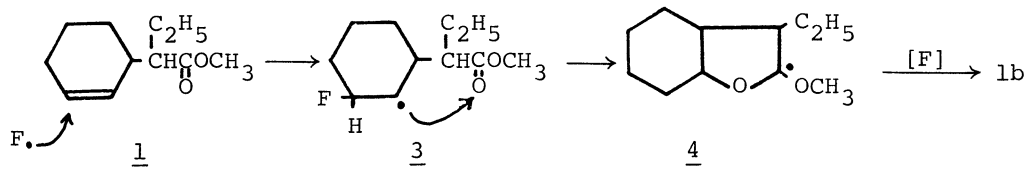
Y=32.1%
bp 147.0~147.7 °C

Y=19.6%
bp 183.0~183.5 °C

In their ^{19}F nmr spectra, the signals of the methine fluorine at the C-9 position of these mono- and di-chlorosubstituted compounds shift to a low field from ϕ 172.4 ppm of that of 1b, to ϕ 154.3 ppm and ϕ 143.9 ppm, respectively.

We have also found that the introduction of a double bond into the cyclohexane framework either at 1 or 2 position of the starting methyl cyclohexylacetate improved considerably the yields of perfluorobicyclic ethers obtained. Thus, fluorinations of methyl cyclohexen-2-ylacetate and methyl cyclohexen-1-ylacetate afforded perfluoro(7-oxabicyclo[4.3.0]nonane) and perfluoro(8-methoxy-7-oxabicyclo[4.3.0]nonane) in yields of 19.3% and 8.8%, and 13.1% and 5.6%, respectively. From methyl cyclohexylacetate, the former compound was obtained in a yield of 11.8% together with the latter (Y=4.3%).

Based on these results, it is considered that the cyclization of 1 may proceed through initial formation of an intermediate 3, which will create the resonance stabilized radical 4 by the immediate intramolecular attack toward carbonyl oxygen.



The study on the synthesis of several kinds of the 8-perfluoroalkoxy-substituted perfluoro(7-oxabicyclo[4.3.0]nonane) is in progress.

References

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2) T. Abe, K. Kodaira, H. Baba, and S. Nagase, J. Fluorine Chem., 12, 1 (1978).
3) R. Kojima and S. Nagase, Bull. Chem. Soc. Jpn., 34, 1468 (1961).

(Received October 16, 1979)