FLUOROSULFATION OF THE DOUBLE BOND: A NEW DIRECTION IN THE REACTIONS OF CESIUM FLUOROXYSULFATE WITH OLEFINS

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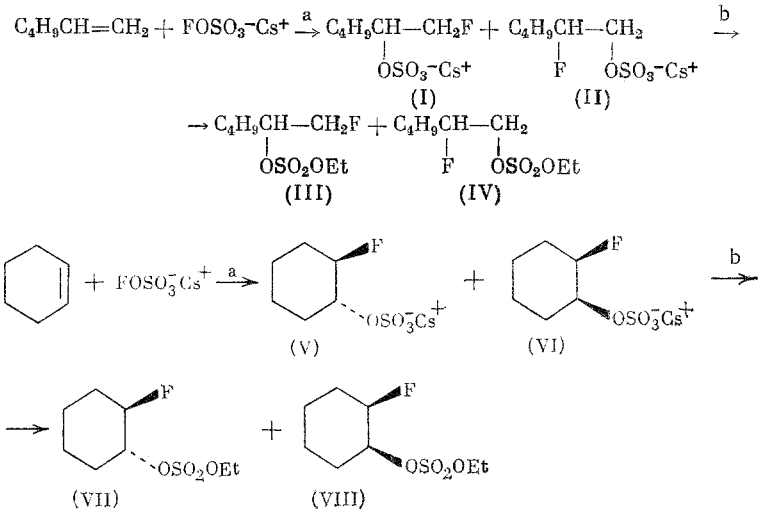
UDC 542.91:546.36'226'161-36:547.313

In contrast to the reactions of olefins with halosulfates [1-4] which proceed by the usual 1,2-addition at the double bond, the reaction of cesium fluoroxysulfate (CFOS) with unsaturated compounds leads either to vinyl fluorides or products of concerted fluorination involving external nucleophiles [1, 2]. We have found a previously unreported direction for the reactions of CFOS with olefins entailing 1,2-addition at the double bond and formation of the cesium salts of fluoroalkyl sulfates (I), (II), (V), and (VI).



AcOEt, 20°, 5 h (a); $Et_3O^+BF_4^-$, AcOEt, 20°, 1 h (b).

For identification, these salts were converted to ethyl sulfates (III), (IV), (VII), and (VIII) by the action of triethyloxonium tetrafluoroboride. The reaction with 1-hexene gives a 1:1 mixture of regioisomers (III) and (IV) in 50% yield. A 2:1 mixture of stereoisomers (VII) and (VIII) was formed in 40% yield in the case of cyclohexene. The structures and compositions of (III), (IV), (VII), and (VIII) were established by ^1H and ^{19}F NMR spectroscopy, mass spectrometry, and elemental analysis.

Thus, we have found the first example of the addition of cesium fluoroxysulfate to olefins with the formation of 1,2-fluoroalkyl sulfates. This reaction is still the only case of the simultaneous introduction of a fluorine atom and nucleofugic sulfate group into an organic molecule.

LITERATURE CITED

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M. V. Lomonosov Moscow State University. N. D. Zelinskii Institute of Organic Chemistry, Academy of Sciences of the USSR, Moscow. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 11, pp. 2636-2637, November, 1987. Original article submitted July 2, 1987.

0568-5230/87/3611-2451$12.50