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ELECTROCHEMICAL FLUORINATION OF 3-ALKYLIDENES

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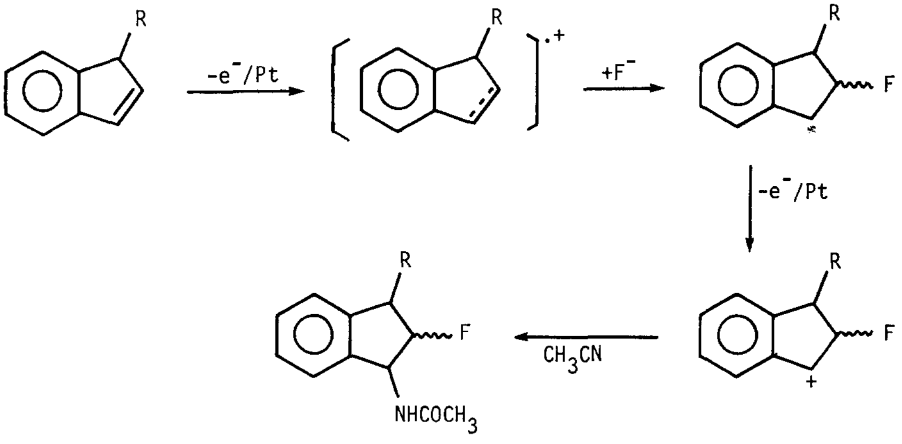
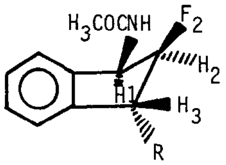
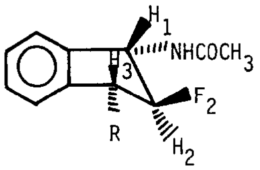
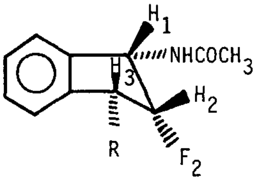
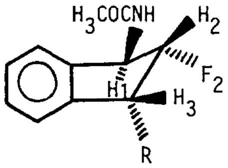
A series of 3-alkylindenes (alkyl = ethyl, isopropyl, t-butyl) has been subjected to anodic oxidation in acetonitrile/Et_3N,3HF solution. The reaction leads predominantly to the formation of fluoroacetamides with an excellent diastereoselectivity.



The configuration of each stereoisomer is assigned according to $^3J_{H_2H_1}$, $^3J_{H_2H_3}$ and $^3J_{C_4F_2}$ values (C_4 is the carbon atom of R directly linked to the indane skeleton). R and F_2 pseudoaxial positions agree with $^3J_{H_2H_3}$=0 and $^3J_{C_4F_2}$ about 9 Hz. R and $NHCOCH_3$ pseudoequatorial positions agree with $^3J_{H_2H_3}$= $^3J_{H_2H_1}$=4 to 6 Hz. In this case $^3J_{C_4F_2}$ is less than 3 Hz for a pseudo-equatorial fluorine and about 8 Hz for a pseudoaxial position.

R = tBu	IsoPr	Et	
87	81	72	
13	19	10	
0	0	12	
0	0	6	

In the reaction mixture the isomers with acetamido and F_2 *cis* to one another predominate (> 80 %). Moreover an exclusive *trans* F_2/R relationship for R = t-butyl or isopropyl is observed and only a preferential one for R = Et (18 % of the products have a *cis* F_2/R arrangement).

This result suggests an addition between F^-, CH_3CN and a cation-radical (and cation) adsorbed on the electrode.