Nucleophilic Substitution in Octafluoro-9-fluorenone

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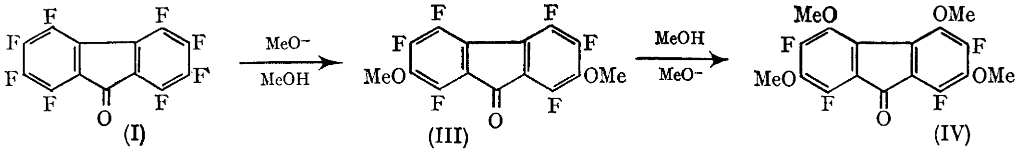
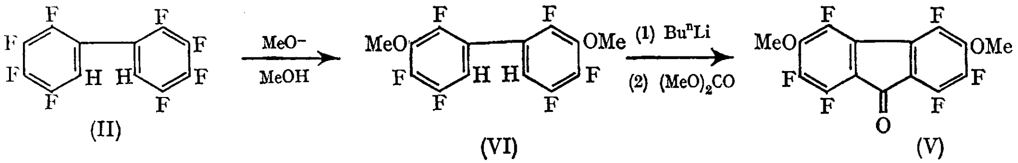
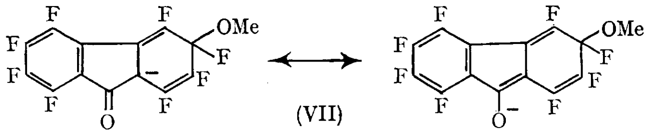
WE report the determination of the orientation of nucleophilic substitution in octafluoro-9-fluorenone (I). This compound has been prepared[1] by the reaction of octafluoro-2,2′-dilithiobiphenyl [prepared by lithiation of octafluoro-2,2′-dihydrobiphenyl (II)] with dimethyl carbonate. Nucleophilic substitution with sodium methoxide in methanol occurs first at the 2- and 7-positions to give hexafluoro-2,7-dimethoxy-9-fluorenone (III), and then at the 4- and 5-positions to give tetrafluoro-2,4,5,7-tetramethoxy-9-fluorenone (IV).



(I) (III) (IV)



(II) (VI) (V)



(VII)

These orientations were assigned by means of ^{19}F and ^{1}H n.m.r. spectroscopy.

Further confirmation of the above orientations was obtained by preparing hexafluoro-3,6-dimethoxy-9-fluorenone (V) by ring closure of the known[2] hexafluoro-2,2′-dihydro-5,5′-dimethoxybiphenyl (VI). Compound (V) had completely different spectroscopic properties (i.r., n.m.r.) from compound (III).

This orientation of substitution in (I) with the nucleophile substituting *meta* to the carbonyl group is not that expected on the basis of mesomeric effects, as these would require substitution to occur *para* to the carbonyl group for the greatest effect (VII). This type of orientation is in fact observed in decafluorobenzophenone which gives a 4-substitution product with methoxide in methanol.[3]

Thus, these results form an apparent exception to the generally accepted rule that a carbonyl group is best able to stabilise an adjacent carbanion when the geometry is planar.[4]

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[1] R. D. Chambers and D. J. Spring, to be published.
[2] R. D. Chambers, J. A. Cunningham, and D. J. Spring, *Tetrahedron*, 1968, **24**, 3997.
[3] R. D. Chambers and D. J. Spring, unpublished results.
[4] D. J. Cram, "Fundamentals of Carbanion Chemistry", Academic Press, New York, 1965, p. 53.