

Received: September 2, 1990; accepted: November 19, 1990

PRELIMINARY NOTE

Photochemical Selective Fluorination of Organic Molecules Using Mercury (II) Fluoride

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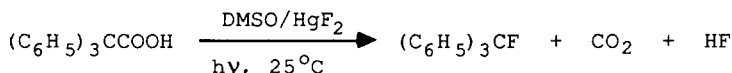
SUMMARY

Organic compounds, such as triphenylacetic acid, triphenyl ethylene, and triethyl phosphite can be selectively fluorinated in dimethylsulfoxide/ HgF_2 solutions under UV-visible illumination. Product yields, determined by ^{19}F -NMR, are essentially quantitative for the compounds studied, and in some cases only a single fluorinated product is formed.

Progress in organofluorine chemistry has always depended on the discovery of alternatives to elemental fluorine as a reagent. There are still relatively few methods available for selective fluorination in which fluorine [1,2], or other fluorine-containing reagents [3-8] are used. Recently, we reported a photochemical method which allows one to introduce fluorine selectively into organic molecules by means of relatively mild fluorine sources such as AgF coupled to a semiconductor photocatalyst [3]. An equally viable approach to photochemically driven fluorination might involve light-sensitive metal fluorides which are poor fluorinating agents in the dark, but which might be considerably more reactive under illumination. In this note, we wish to report the selective photochemical fluorination of organic molecules using HgF_2 . Relatively little work has been reported on thermal reactions using mercury(II)fluoride as fluorinating agent [9-10]. In preliminary experiments, we have found

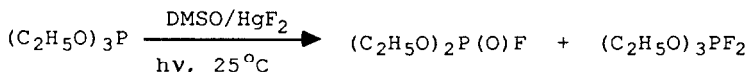
that this reagent can be activated photochemically, affording selectively fluorinated products in essentially quantitative yield.

Photo-Kolbe reaction

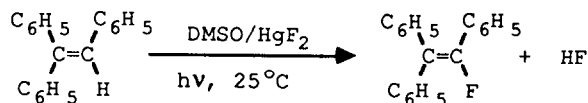


In a typical procedure, a mixture of triphenylacetic acid (144 mg, 0.50 mmol), mercury(II)fluoride (239 mg, 1.00 mmol), cesium fluoride (76 mg, 0.50 mmol to absorb HF generated in the reaction), and dry dimethyl sulfoxide (2.0 mL) were loaded into a 10-mm diameter borosilicate NMR tube. The mixture was deaerated with argon, and then stirred and illuminated at ambient temperature using a 500 watt mercury-xenon lamp for 24 h. During the reaction a black product was formed, presumably elemental mercury adsorbed onto the surface of the solid $\text{CsF} \cdot x\text{HF}$. The latter was separated by filtration and the product in the solution was identified by ^{19}F NMR and GC-mass spectral analysis as triphenylfluoromethane (yield $\geq 95\%$). All yields reported are based on NMR (they are not isolated yields), using C_6F_6 as the internal standard. ^{19}F NMR: -126.4 (s), upfield from CFCl_3 , using C_6F_6 as an internal standard. This assignment is consistent with the literature value for the chemical shift [11]. MS: 262 m/z.

Arbuzov rearrangement



This reaction followed a similar procedure to that described above: triethyl phosphite (83 mg, 0.50 mmol), mercury(II)fluoride (239 mg, 1.00 mmol), and 2.0 mL dry dimethyl sulfoxide were stirred and illuminated for 30 h. After filtration, the products in the solution were identified by ^{19}F NMR and GC-MS as $(\text{C}_2\text{H}_5\text{O})_2\text{P}(\text{O})\text{F}$ (NMR yield 53%) and $(\text{C}_2\text{H}_5\text{O})_3\text{PF}_2$ (NMR yield 47%). ^{19}F NMR: -81.5 (d, $J_{\text{PF}} = 960$ Hz) upfield from CFCl_3 ; MS: 156 m/z for $(\text{C}_2\text{H}_5\text{O})_2\text{P}(\text{O})\text{F}$, and ^{19}F NMR: -68.1 (d, $J_{\text{PF}} = 750$ Hz); MS: 204 m/z for $(\text{C}_2\text{H}_5\text{O})_3\text{PF}_2$, consistent with literature values [11]. (Caution: compounds of this type, R_3PF_2 and $\text{R}_2\text{P}(\text{O})\text{F}$ (R = alkyl, alkoxy), can be highly toxic).

Oxidative substitution of olefins

This reaction was done in the same manner, using triphenylethylene (128 mg, 0.50 mmol), mercury(II)fluoride (239 mg, 1.00 mmol), cesium fluoride (76 mg, 0.50 mmol), and 2.0 mL dry dimethyl sulfoxide. The suspension was stirred and illuminated for 48 h. After filtration, the product in solution was identified as triphenylfluoroethylene (NMR yield $\geq 95\%$) by fluorine NMR and GC-MS. ^{19}F NMR: -163.1 (s), upfield from CFCl_3 , MS: 274 m/z for triphenylfluoroethylene, consistent with literature values [11].

Control experiments have established that these reactions are photochemically driven; for example, in the photo-Kolbe reaction of triphenylacetic acid, the yield of triphenylfluoromethane is only about 5% without illumination. As in the TiO_2 -photocatalyzed fluorination reactions previously reported [3], organic substrates which are not easily oxidized do not appear to be reactive. For example, no fluorinated products are formed from either 2,2-diphenylpropane or benzoic acid and HgF_2 under UV-visible illumination. It is therefore unlikely that free radicals such as $\text{F}\cdot$ are produced in the reaction (although fluorine atoms are generated when HgF_2 is photolyzed in the gas phase at 157 nm [12]). The detailed mechanism and scope of photochemical fluorination reactions involving HgF_2 are currently under investigation in our laboratory.

This work was supported by grants from the Texas Advanced Research Program and the National Science Foundation (PYI Award CHE-8657729). TEM also thanks the Camille and Henry Dreyfus Foundation for support in the form of a Teacher-Scholar Award.

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