NOVEL PENTAFLUOROPHENYL HYPERVALENT IODINE REAGENTS

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<u>Summary</u> The novel $C_6F_5I(0H)0Ts$ has been synthesized and shown to undergo ligand exchange with C_6H_5I , iodonium ylide formation with dimedone and iodonium salt formation with anisole.

Koser's reagent [hydroxy(tosyloxy)iodo]benzene,¹⁻³ C₆H₅I(OH)OTs, has been used widely for the synthesis of cis vic-bis(tosyloxy)alkanes, 4,5 tosyloxylactones, 6 and α tosyloxyketones.⁷ Also ligand transfer between $C_{6}H_{5}I(0H)0Ts$ and $RC_{6}H_{4}I$ to form new [hydroxy(tosy]oxy)iodo] arenes has been standardized.⁸ We now report the synthesis and reactions of the fluorinated analog of this valuable reagent. namely. [hydroxy(tosyloxy)iodo]pentafluorobenzene, $C_{\kappa}F_{\kappa}I(0H)0Ts$ (2). As shown in Scheme 1 reaction of [(bis-trifluoroacetoxy)iodo]pentafluorobenzene (1)⁹ with p-TsOH/CH₂CN yields 2, and the mesyloxy analog, 2a, can be made in a similar way (MsOH, CH₂CN, r.t).¹⁰

Three classes of reactions of <u>2</u> represented in <u>Scheme 1</u> are (<u>a</u>) ligand transfer $2 \div 3$, (<u>b</u>) pentafluorobenzene aryliodonium salt formation $2 \div 4$, and (<u>c</u>) iodonium ylide formation $2 \div 6$ via 5. The novel pentafluorophenyl iminoiodanes <u>7a</u> and <u>7b</u> were also made from 1.

Ligand exchange is an extremely important route for the synthesis of $[hydroxy(tosyloxy)iodo]arenes^8$ and we expect that the example 2 + 3 may be extended to other synthetically desirable systems. Formation of pentafluorophenyl(anisyl)iodonium p-toluenesulfonate $(4)^{11}$ is representative of a general route to unsymmetrical pentafluorophenyl iodonium salts which may be valuable substrates for aromatic nucleophilic displacement.¹² The novel class of pentafluorophenyliodonium ylides available by the route $2 + 5 + 6^{13}$ should enable a detailed study of the chemical behavior of iodonium ylides to be executed. Of particular interest is the mechanism of thermal decomposition¹⁴ as well as new synthetic reactions based on this decomposition.¹⁵

878



- iii) $C_6H_5OCH_3/CH_3COOH$, r.t.
- iv) dimedone/CHCl₃, r.t.
- v) aqueous K₂CO₃
- vi) RC₆H₄SO₂NH₂, KOH/MeOH, 0°C

Scheme 1

N-Tosyliminopentafluorobenzene iodinanes $(\underline{7a} \text{ and } \underline{7b})^{16}$ are of interest in connection with possible nitrene type reactions and in nitrogen atom transfer catalyzed by cytochrome P-450.¹⁷. Thermal decomposition of $\underline{7a}$ yielded o-toluenesulfonamide $(\underline{8})$ and none of the sultam <u>9</u> (Scheme 2). This result is similar to the course of thermal decomposition of N-tosyliminophenyliodinane to yield p-toluenesulfonamide.¹⁸



Work on further synthetic transformations using 2 is in progress and results will be communicated in the near future.

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- 10. p-TsOH (1.9 g, 10 mmol) in CH_3CN (25 ml) was added to a stirred solution of $C_6F_5I(0C0CF_3)_2$ (1)⁹ (2.6 g, 5 mmol) in CH_3CN (15 ml) at r.t. The resulting colorless solution changed to pale yellow and a white solid separated out of solution over a 15 min period. This solid was collected, washed with CH_3CN and then Et_20 to yield 2, 2.2 g (91%) m.p. 186-88°, NMR (CDCl₃ and DMS0·d₆) & 2.4 (s, 3H, CH_3) 7.27 and 7.67 ppm two doublets, 4H, aromatic protons. The mesyloxy analog, 2a had m.p. 124-126°C and CH_3 at & 2.6 ppm.

- 11. Anisole (0.27 g, 2.5 mmol) was added with stirring to a solution of 2 (1.2 g, 2.5 mmol) in acetic acid (10 ml). The solution was stirred at room temperature for 30 min. Ether (25 ml) was added to the solution to yield a solid which was filtered and washed several times with ether to yield 4, 1.3 g (92%), m.p. 176-177°; NMR (DMSO-d₆) & 2.3 (s, 3H, CH₃), 3.7 (s, 3H, OCH₃), 6.7-8.1 (m, 8H, aromatic protons).
- For an excellent review of nucleophilic displacement upon diaryliodonium salts see
 G. F. Koser in "The Chemistry Functional Groups," Patai, S.; Editor, John Wiley 1983: Chap. 25, Halonium Ions, pages 1286-1310.
- 13. A solution of dimedone (0.35 g, 2.5 mmol) in chloroform (5 ml) was added with stirring to a mixture of 2 (1.2 g, 2.5 mmol) in chloroform (20 ml). The resulting yellow solution was stirred at room temperature for 15 min. During this time, a white solid precipitated out which was filtered and washed several times with chloroform to give 5, 1.4 g (90%), m.p. 149-151°; NMR (CDCl₃ & DMSO·d₆) δ 0.97 (<u>s</u>, 6H, <u>CH₃</u>'s), 2.35 (s, 3H, <u>CH₃</u>), 2.45 (<u>s</u>, 4H, <u>CH₂</u>'s), 7.26 & 7,57 (<u>dd</u>, 4H, aromatic protons).

Compound <u>5</u> (1.24 g, 2 mmol) was added to a saturated solution of aqueous potassium carbonate (20ml) and stirred at room temperature for 2 hrs. The solid was filtered washed several times with water, yielding <u>6</u>, 0.75 g (87%), m.p. 148-149°; NMR (DMSO-d₆) δ 0.95 (<u>s</u>, 6H, <u>CH</u>₃'s), 2.3 (<u>s</u>, 4H, CH₂'s).

- For a good discussion of the thermal, photochemical and Cu-catalysed decomposition of iodonium ylides especially with respect to carbene formation see: Y. Hayasi, T. Okada and M. Kawanisi, <u>Bull. Chem.</u> Soc. Japan, 43, 2506 (1970).
- 15. The thermal rearrangement of phenyldimedonyliodane to phenyl 2-iododimedonyl ether coupled with free radical cyclization of the vinyl iodine into the aromatic ring is a potentially useful synthetic reaction. For an example of this type of process see: T. Kappe, G. Korbuly and W. Stadlbaur, <u>Chem. Ber.</u>, <u>111</u>, 3857 (1978).
- 16. In a typical experiment, pentafluoroiodobenzene <u>bis</u>-trifluoroacetate (<u>1</u>) (5.20 g, 10 mmol) was added to a stirred mixture of <u>o</u>-toluenesulfonamide (1.71 g, 10 mmol), potassium hydroxide (1.40 g, 25 mmol) and methanol (30 ml) at 0°C. The reaction mixture was stirred at 0°C for 1 hr and then at room temperature for 2 hrs. The reaction mixture was poured into water (100 ml) and left at room temperature for 8 hrs. The yellow solid thus formed was filtered, washed with water, dried and crystallized from methanol to get 3.24 g (70%) of <u>7a</u>, m.p. 124-125°; NMR (DMS0d₆) δ 2.33 (<u>s</u>, 3H, <u>CH</u>₃), 7.03-7.93 (<u>m</u>, 4H, aromatic protons); <u>7b</u>; 78%, m.p. 129-131°; NMR (DMS0-d₆) δ 2.11 (<u>s</u>, 3H, <u>CH</u>₃), 7.15-7.93 (m, 4H, aromatic protons).
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