C—C Condensations with Silver Fluorodinitromethanide

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Two general methods for the synthesis of the fluorodinitromethyl moiety have been reviewed by Kamlet and Adolph[1]. These procedures include (1) fluorination of 1,1-dinitrocarbanion salts with perchloryl fluoride, and (2) the reaction of fluorotrinitromethane with certain nucleophiles. A third procedure is described by Grakauskas and Baum who report the synthesis of fluorodinitromethyl compounds by the reaction of 1,1-dinitrocarbanion salts with elemental fluorine[2]. We wish to report a fourth procedure for the synthesis of the fluorodinitromethyl compounds that involves the reaction of the salts of fluorodinitromethane with compounds containing a labile halogen atom.

Fluorodinitromethane (**1**) undergoes many reactions similar to those of nitroform (**2**).

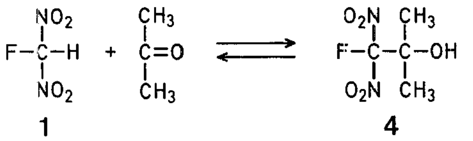
$HCF(NO_2)_2$ **1** $HC(NO_2)_3$ **2**

Compounds **1** and **2** both react with formaldehyde under acidic conditions to give substituted ethanols[1,3], and both undergo Michael additions with vinylcarbonyl compounds[4,5,6]. However, this parallel appears to fail in the case of the reactions between salts of **1** and **2** and active halogen compounds. Whereas some metallic salts of **2** readily react with alkyl halides to give trinitroalkanes[7], most salts of **1** decompose rapidly, and C—C coupling products have not been reported.

We report here a procedure for successful C—C coupling reactions involving the silver salt (**3**) of **1**. Silver fluorodinitromethanide (**3**) can be prepared by the reaction of silver oxide with **1** in many organic solvents.

$$\underset{}{Ag_2O} + \underset{\mathbf{1}}{2\ HCF(NO_2)_2} \longrightarrow \underset{\mathbf{3}}{2\ AgCF(NO_2)_2} + H_2O$$

In most organic solvents, **3** is unstable and readily decomposes. However, when acetone is used as a solvent for the preparation of **3**, decomposition is not evident, and the solution can subsequently be used for C—C coupling reactions. This lack of decomposition can be attributed to the fact that **1** and acetone form an adduct (**4**).

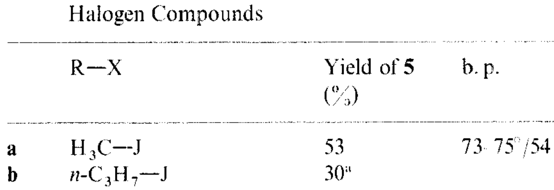


$$F-\overset{NO_2}{\underset{NO_2}{C}}-H + \overset{CH_3}{\underset{CH_3}{C}}=O \rightleftharpoons F-\overset{O_2N}{\underset{O_2N}{C}}-\overset{CH_3}{\underset{CH_3}{C}}-OH$$

1 **4**

Evidence for the formation of **4** has been noted by Adolph[8] and is analogous to stable adducts between **1** and aldehydes reported in the same paper. The equilibrium between **4** and its components lies in favor of **4** thereby keeping the concentration of **1** in the solution low. This equilibrium is slowly shifted to the left by the reaction of **1** with silver oxide. Since the resultant product (**3**) is unstable, an excess of an active halogen must be present in the reaction mixture to assure reaction with **3** before it decomposes. The mixture is stirred for ~20 hr to insure complete reaction.

Thus, mixtures of **1**, silver oxide, an active halogen compound (R—X), and acetone react slowly at ambient temperature to give the C—C coupling product (**5**) and silver halide.



$$\underset{\mathbf{3}}{AgCF(NO_2)_2} + R-X \longrightarrow R-\overset{NO_2}{\underset{NO_2}{C}}-F + AgX$$

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Table. Reaction of Silver Fluorodinitromethanide (**3**) with *C*-Halogen Compounds

	R—X	Yield of **5** (%)	b. p.
a	$H_3C—J$	53	73–75°/54 torr
b	n-$C_3H_7—J$	30[a]	
c	$C_6H_5—CH_2—Br$	20	68–75°/0.2 torr
d	$H_2C=CH—CH_2—Cl$	68	55–57°/40 torr

[a] In addition, dipropyl ether was isolated in 20% yield.

The nature of the alkyl halide is important to the success of this reaction. If the halide is too inert, as in the case of 1-chloropropane, no reaction occurs, and **3** decomposes as it is formed. If the halide is too reactive, it reacts preferentially with silver oxide to form a variety of products including olefins and ethers. For example, both *t*-butyl iodide and allyl iodide react rapidly with silver oxide to form a large variety of products. Allyl bromide, however does not react quickly with silver oxide and undergoes clean C—C condensation with **3** to give **5d**. Allyl chloride is too unreactive; thus, **3** decomposes before C—C condensation occurs. It was necessary to use methyl and propyl iodide for C—C coupling with **3**, since the bromo compounds were unreactive. Propyl iodide appeared to undergo limited reaction with silver oxide as shown by a 20% yield of dipropyl ether.

The advantage of this synthesis over those reviewed by Kamlet and Adolph[1] and Grakauskas and Baum[2] are mainly in the synthesis of certain compounds that contain groups sensitive to fluorination. Unsaturated derivatives of **3**, such as 4-fluoro-4,4-dinitro-1-butene (**5d**) and 2-fluoro-2,2-dinitro-1-phenylethane (**5c**), and their precursors are not stable under fluorination conditions with elemental fluorine, although fluorinations of this type have not been reported using perchloryl fluoride. The procedure described above circumvents this problem by having the fluorination step occur in the preparation of a precursor, namely **3**.

The fluorodinitromethyl compounds discussed in this paper are *explosives* of moderate to considerable sensitivity to initiation by impact, friction, shock, or other means. In addition, many fluorodinitro compounds may cause painful *burns* or *loss of sensitivity* when brought in contact with the skin. Consequently, they should be *handled with care*.

Fluorodinitromethane was prepared according to the procedure described by Grakauskas and Baum[2].

1-Fluoro-1,1-dinitroethane (5a):

A solution of fluorodinitromethane (**1**; 2.00 g, 16.1 mmol) in dry acetone (5 ml) was added dropwise with stirring over a 20 min period to a mixture of silver oxide (1.87 g, 8.07 mmol), methyl iodide (9.16 g, 64.7 mmol), and dry acetone (15 ml) at −5° to 0°. The reaction mixture was allowed to warm to room temperature and stirring was continued for 18 hr. Silver iodide was removed by filtration and the solvent evaporated leaving 1.52 g of a pale yellow liquid. Distillation under reduced pressure afforded a colorless liquid; yield: 1.17 g (53%); b.p. 73–75°/54 torr. The product was identified as **5a** by its ^{1}H-N.M.R. spectrum and comparison of its I.R. spectrum with that reported previously[2].

4-Fluoro-4,4-dinitro-1-butene (5d):

A solution of fluorodinitromethane (**1**; 5.00 g, 41 mmol) in dry acetone (10 ml) was added dropwise with stirring over a 15 min period to a mixture of allyl bromide (22.4 g, 202 mmol), silver oxide (10.2 g, 44 mmol), and dry acetone (50 ml) at 5°. After the addition was complete, the mixture was allowed to warm to room temperature and stirring was continued for 24 hr. The mixture was then filtered to remove 16.3 g of a light brown solid (silver oxide, silver bromide), and the solvent and excess allyl bromide were removed in vacuo to leave a pale yellow liquid; yield: 6.17 g. G.L.C. analysis of this liquid showed that it consisted of 80% of **5d**; major impurities were acetone, allyl bromide, fluorodinitromethane, and 1-fluoro-2-hydroxy-2-methyl-1,1-dinitropropane. The product mixture was subjected to short-path distillation at reduced pressure; yield of major product: 3.61 g; b.p. 55–57°/40 torr. G.L.C. analysis of this product showed that it consisted of 94% **5d** and 6% fluorodinitromethane. A small sample was purified by G.L.C.

$C_4H_5FN_2O_4$	calc.	C 29.27	H 3.07	N 17.07
(164.1)	found	29.25	3.02	17.36

I.R. (neat): ν_{max} = 3000 (w, C—H), 1600 (s, C—NO$_2$), 1350 cm^{-1} (m, C—F).

^{1}H-N.M.R. ($CDCl_3$): $\delta=4.56$ (m, 3H, $\underline{H}_2C{=}C\underline{H}{-}$), 6.54 ppm (d of d, 2H, $J_{HF}=19$ Hz, $J_{HH}=5$ Hz, $-CH_2-$).

1-Fluoro-1,1-dinitrobutane (5b):

The synthesis of **5b** was similar to that described for **5d**. 1-Iodopropane was used as the starting alkyl halide. The reaction product was shown to consist of 60% **5b** and 40% dipropyl ether by G.L.C. analysis (5 ft × $^1/_8$ in. aluminum column packed with 4% QF-1 on Chromosorb G ®). Both products were isolated by preparative G.L.C.; yield of **5b**: 30%.

$C_4H_9FN_2O_4$	calc.	C 28.92	H 4.25	N 16.86
(168.1)	found	28.83	4.31	17.01

^{1}H-N.M.R. ($CDCl_3$): $\delta=0.92$ (t, 3H, CH_3), 1.68 (sextuplet, 2H, $H_3C{-}C\underline{H}_2{-}$), 4.04 ppm (t, 2H, $H_3C{-}CH_2{-}C\underline{H}_2{-}$).

1-Fluoro-1,1-dinitro-2-phenylethane (5c):

The synthesis of **5c** was similar to that described for **5d**. Benzyl bromide was used as the starting alkyl halide. The reaction product was distilled in vacuo; yield: ~20%; b.p. 68–75°/0.2 torr. Benzyl alcohol was present in the crude reaction mixture.

$C_8H_7FN_2O_4$	calc.	C 44.87	H 3.29	N 13.08
(214.2)	found	45.16	3.19	13.07

^{1}H-N.M.R. ($CDCl_3$): $\delta=7.1$–7.4 (m, 5H_{arom}), 3.98 ppm (d, 2H, $J_{HF}=20.6$ Hz, $-CH_2-$).

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