The Synthesis of 1,4-Diketones via Fluoride-catalysed Michael Addition and Supported-permanganate-promoted Nef Transformation

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A versatile synthetic route for the preparation of 1,4-diketones from simple starting materials is described and applied to the preparation of a wide range of diketones. The two most important steps in the reaction are the fluoride ion-catalysed Michael addition of a nitroalkane to a vinyl ketone and the subsequent transformation of the nitro ketone to the diketone using supported permanganate as the oxidant. The interaction of F^- with nitroethane has been studied and a number of sources of F^- have been tested in the Michael addition reaction. Potassium fluoride supported on alumina and potassium permanganate supported on silica gel are remarkably efficient reagents for the Michael addition and Nef transformation stages, respectively, although it is important to determine the best reagent loadings and drying conditions for maximum reaction efficiency to be achieved.

Various synthetic methods for the preparation of 1,4-diketones have been developed [1] since these compounds are valuable intermediates in the preparation of natural products and related compounds containing furan or cyclopentenone ring systems. Certainly the most straightforward route is one which employs the 1,4-addition of an appropriate nucleophile to a suitable unsaturated acceptor.[2] The choice of the nucleophile presents difficulties, however, in that good Michael donors such as nitroalkanes lead to intermediates which may be difficult to transform to the required product.[3] Alternative routes to 1,4-diketones are usually more elaborate and none have matched the inherent simplicity, economy, and potential versatility of the 1,4-addition route.

We have developed a versatile and efficient synthetic route to 1,4-diketones (Scheme 1) involving the addition of a nitroalkane to an appropriate enone which may in some cases be generated in situ from a Mannich base (1).[4] The success of our route can be attributed to efficient Michael reaction and Nef transformation steps using fluoride ion [5] and silica-supported permanganate,[6] respectively. This paper describes the full scope of this synthetic route and presents our results and a discussion on the role of the inorganic reagents.

Results and Discussion

1,4-Diketones (3) and the intermediate nitro ketones (2) prepared by the method described here are listed in Tables 1 and 2 with their ^{13}C and ^{1}H n.m.r. chemical shifts. The product-controlling reactants are the enone (or the ketone and the aldehyde) and the nitroalkane and we have found that it is possible to vary any of these groups within the general reaction scheme thus providing excellent flexibility in product design. In our hands, the initial Mannich reaction was only successful for R^3 = H and Ph—other R groups failed to give satisfactory yields of the intermediate amine presumably due to aldol condensation competing significantly with the required Mannich reaction when R^3 contains a reactive α-CH atom. Attempts to replace the amine hydrochloride by other bases did little to improve the reaction although we did find that a dipolar aprotic solvent such as N,N-dimethylformamide (DMF) gave better yields than the more traditional alcoholic solvents.[7]

The usefulness of the general reaction scheme is further illustrated by the synthesis of dihydrojasmone (8) using 1-iodoheptane (4) as the starting material (Scheme 2). We also attempted to prepare the more important cis-jasmone by this
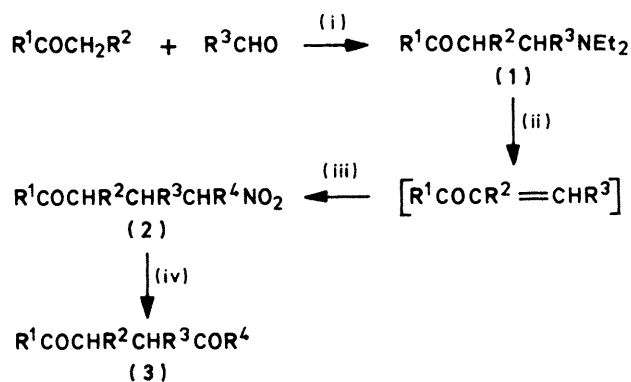
Scheme 1. Reagents: (i) Et_2NH_2 Cl^-; (ii) F^-; (iii) $R^4CH_2NO_2$, F^-; (iv) SiO_2–$KMnO_4$
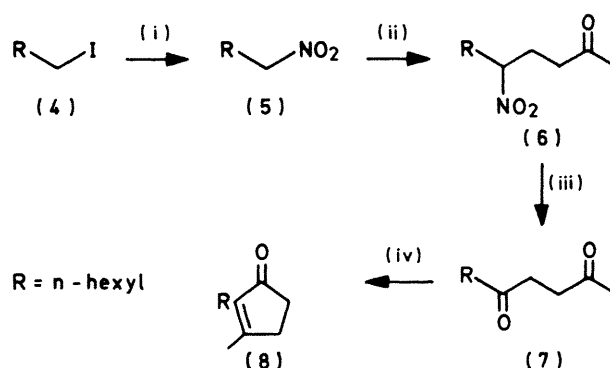
Scheme 2. Reagents: (i) $NaNO_2$–DMF; (ii) methyl vinyl ketone, F^-; (iii) SiO_2–$KMnO_4$; (iv) OH^-

method starting with 7-chlorohept-3-yne but although the reaction went in high yield as far as the nitro ketone, attempted Nef reaction resulted in oxidation or cleavage of the alkyne bond as well as the desired reaction.

Michael Reactions Catalysed by Fluoride.—We have found the fluoride ion to be a particularly efficient catalyst for the addition of nitroalkanes to enones and since Michael reactions

Table 1. ^{13}C and ^{1}H n.m.r. δ-values of 1,4-diketones [a]

$$\overset{\text{a}}{R^1}CO\overset{\text{b}}{\underset{\text{c}}{CHR^2}}\overset{\text{e}}{\underset{\text{d}}{CHR^3}}\overset{\text{g}}{\underset{\text{h}}{COR^4}}$$

Structure	a (C)	a (H)	b	c (C)	c (H)	d (C)	d (H)	e (C)	e (H)	f (C)	f (H)	g	h (C)	h (H)
	29.9	2.20 (s)	202.3	36.9	2.70 (s)	—	—	36.9	2.70 (s)	—	—	207.3	29.9	2.20 (s)
	29.9	2.20 (s)	206.5	35.9	2.70 (s)	—	—	37.0	2.70 (s)	—	—	210.0	7.8, 35.7	1.10 (t), 2.45 (q)
	29.9	2.13 (s)	207.3	46.5	2.50 (c)	—	—	40.8	2.93 (dd)	16.8	1.10 (d)	214.0	7.7, 34.3	1.06 (t), 2.56 (q)
	29.9	2.16 (s)	206.8	46.6	2.50 (dd), 3.45 (dd)	—	—	53.0	4.20 (dd)	127.0—138.7	7.1—7.6 (c)	209.8	7.8, 30.4	0.96 (t), 2.45 (q)
	29.9	2.16 (s)	207.1	46.3	2.3—3.1 (c)	—	—	41.8	2.2—2.7 (c)	16.5	1.15 (d)	211.2	28.4	2.20 (s)
	127.2—139.1	7.2—8.0 (c)	198.8	48.7	5.10 (dd)	127.2—139.1	7.2—8.0 (c)	48.0	2.73 (dd), 3.60 (dd)	—	—	207.6	29.8	2.20 (s)
	128.0—137.0	7.2—8.0 (c)	203.2	36.2	3.90 (c)	17.8	1.23 (d)	46.8	2.46 (dd), 3.13 (dd)	—	—	207.0	30.0	2.15 (s)
	127.5—138.7	7.1—8.0 (c)	198.2	42.5	3.10 (dd), 3.93 (dd)	—	—	53.0	4.40 (dd)	127.5—138.7	7.1—8.0 (c)	209.9	7.9, 35.0	1.00 (t), 2.50 (q)
	7.8, 35.7	1.05 (t), 2.45 (q)	209.9	36.9	2.66 (s)	—	—	35.9	2.66 (s)	—	—	207.3	29.9	2.16 (s)
	128.1—136.7	7.2—8.0 (c)	198.5	37.1	2.7 (c)	—	—	32.5	3.30 (c)	—	—	207.3	30.1	2.20 (s)
	127.6—138.0	7.2—8.0 (c)	198.1	42.3	3.10 (dd), 3.96 (dd)	—	—	53.9	4.40 (c)	127.6—138.0	7.2—8.0 (c)	207.1	29.2	2.20 (c)

[a] c = Complex signal.

Table 2. ^{13}C and ^{1}H n.m.r. δ-values of nitroketones

$$\overset{a}{R^1}CO\overset{c}{C}HR^2\overset{e}{C}HR^3\overset{g}{C}H(NO_2)\overset{h}{R^4}$$

Structure	a-C	a-H	b	c-C	c-H	d-C	d-H	e-C	e-H	f-C	f-H	g-C	g-H	h-C	h-H
	28.6	2.20 (s)	206.4	39.0	1.9—2.7 (c)	—	—	30.0	1.9—2.7 (c)	—	—	82.6	4.60 (c)	19.3	1.55 (d)
	19.3	2.20 (s)	210.0	36.7	2.45 (c)	—	—	36.1	1.7—2.2 (c)	—	—	82.6	4.40 (c)	7.8, 28.8	1.00 (t), 1.85
	30.5	2.16 (s)	206.5	46.5	2.45 (c)	—	—	32.2	2.3—2.7 (c)	15.0	1.03 (d)	94.4	4.40 (c)	10.6, 24.2	0.96 (t), 1.60 (c)
	30.6	2.10 (s)	205.6	46.3	2.86 (c)	—	—	44.6	3.7 (c)	127.8—143.4	7.1—7.3 (c)	94.3	4.60 (c)	10.4, 25.5	0.96 (t), 1.50 (c)
	30.4	2.20 (s)	206.5	46.2	2.50 (c)	—	—	33.2	2.3—2.7 (c)	16.1	1.00 (d)	86.7	4.50 (c)	15.0	1.55 (d)
	126.9—133.2	7.2—8.0 (c)	198.0	50.2	4.55 (dd)	126.9—133.2	7.2—8.0 (c)	39.3	2.1—3.0 (c)	—	—	80.9	4.60 (c)	20.2	1.55 (d)
	126.9—137.0	7.2—8.0 (c)	202.6	37.7	3.40 (c)	19.1	1.15 (d)	37.2	2.0—3.0 (c)	—	—	82.2	4.70 (c)	17.0	1.55 (d)
	127.7—138.7	7.2—8.0 (c)	197.1	41.5	3.40 (c)	—	—	44.8	3.83 (c)	127.7—138.7	7.2—8.0 (c)	94.5	4.75 (c)	10.5, 25.6	1.0 (t), 1.75 (c)
	7.7, 28.8	1.05 (t), 2.45 (q)	209.7	37.7	2.0—2.6 (c)	—	—	36.1	2.0—2.64 (c)	—	—	78.4	4.3—4.9 (c)	19.3	1.55 (d)
	128.0—136.4	7.2—8.0 (c)	198.0	34.2	2.35 (c)	—	—	29.1	3.0 (c)	—	—	82.8	4.65 (c)	19.5	1.55 (d)
	127.9—138.1 (c)	7.1—7.9 (c)	197.1	41.4	3.24 (c)	—	—	45.6	3.75 (c)	127.9—138.1	7.1—7.9 (c)	87.3	4.75 (c)	17.9	1.45 (d)

a c = Complex signal.

Table 3. Fluoride ion-catalysed Michael reaction of nitroethane with MVK [a]

Source of F[-]	t_{50} [b]/min
CsF–alumina [c]	1.0
CsF–alumina [d]	1.5
KF–alumina [c]	2.0
CsF–ethanol	3.0
CsF (wet) [e]	7.0
CsF (dried) [f]	12.0
Alumina (dried) [f]	30.0
KF–18-crown-6	50.0
KF (dried) [f]	1 000

[a] Acetonitrile solvent unless stated otherwise. See Experimental section for further details. [b] Time required for 50% reaction as measured by gas chromatography. [c] 2.5 Molecules nm^{-2} dried at 200 °C (1 mmHg) for 16 h. [d] 40 Molecules nm^{-2} dried at 200 °C (1 mmHg) for 16 h. [e] Finely ground material containing a trace of water. [f] Dried at 200 °C (1 mmHg) for 16 h.

are among the most important methods for forming carbon–carbon bonds, the choice and role of the fluoride are worthy of attention.

A number of Michael reactions catalysed by fluoride have already been reported in the literature.[5] A wide variety of fluorides have been employed including homogeneous metal fluoride–alcohol solutions,[8] heterogeneous metal fluoride–aprotic solvent systems,[9] KF–crown ethers,[10] and quaternary ammonium fluorides.[11] The commercial availability and ease of handling of the more reactive alkali metal fluorides such as KF and CsF make these materials the most attractive sources of fluoride and we have compared the efficiencies of various sources of these salts in catalysing a typical nitroalkane–enone addition reaction.

Table 3 summarises the catalytic efficiencies of KF and CsF in the reaction of nitroethane with methyl vinyl ketone (MVK). For ordinary CsF it is clear that traces of water can assist the reaction. This may be due to activation of surface water by $F^- \cdots HOH$ hydrogen bonding.[12] Similarly, well dried alumina containing only traces of physisorbed water is quite reactive. The high reactivity of CsF–ethanol is perhaps surprising in view of the known reduction of F^- nucleophilic reactivity on hydrogen bonding to protic solvent molecules. The best analogy for this observation is the known reaction behaviour of fluoride–carboxylic acid systems which behave as poor sources of F^- but excellent sources of carboxylate anions.[12] Thus F^- probably enhances the nucleophilicity of the alcohol oxygen through strong $F^- \cdots HOC_2H_5$ hydrogen bonding.

The most reactive catalysts for the Michael reaction that we studied are KF or CsF supported on alumina. We have found that a loading of fluoride corresponding to ca. 2.5 molecules of fluoride nm^{-2} of surface gives excellent results. The reagent should be well dried to ensure optimum efficiency. These observations are in line with our previous experience of supported reagents [6] and with thermogravimetric and other studies on supported fluorides, details of which will be published elsewhere. The results of these studies suggest that reactions involving supported fluorides occur largely at the surface of the alumina involving fluoride ions physisorbed to the surface hydroxy groups. The efficient dispersion of the fluoride over the large surface area of the support will result in enhanced reagent reactivity. Supported fluoride reagents containing excess of fluoride or those that are inefficiently dried probably contain partially solvated ions trapped within the pores as well as at the surface.

$$CH_3CH_2NO_2 + F^-$$

$$CH_3CH=NO_2H \ldots F^-$$

(i)

$$CH_3\dot{C}HNO_2 + HF_2^- \longrightarrow CH_3CH(NO_2)CH(NO_2)CH_3$$

further oxidation products
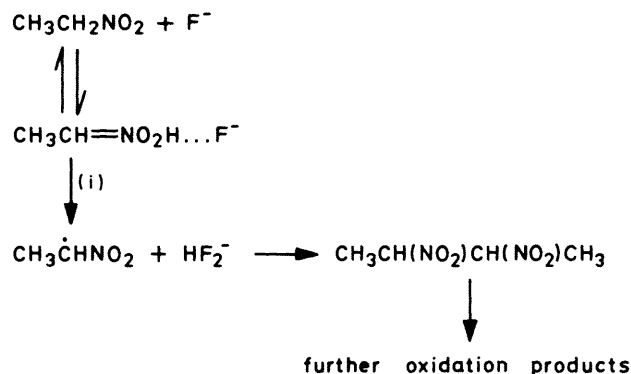
Scheme 3. Reagent: (i) O_2

Nitroalkane–Fluoride Interactions.—It has been reported that fluoride can assist the tautomerism of 2-nitropropane to produce the *aci*-form which is stabilised by strong hydrogen bonding.[11] It is known that *aci*-anions of nitroalkanes can undergo oxidation reactions.[13] We have investigated the interaction of nitroethane with fluoride by ^{1}H and [13]C n.m.r. and i.r. spectroscopy. Spectra of mixtures resulting from prolonged stirring of nitroethane with CsF can be complex but clearly reveal the presence of 2,3-dinitrobutane as the major product, along with carbonyl-containing products. An equimolar ratio of bifluoride $CsHF_2$ to nitroethane is also formed during the reaction. The formation of 2,3-dinitrobutane is considerably reduced by running the reaction under nitrogen whereas an oxygen atmosphere increases the yield. These observations are consistent with mechanism shown in Scheme 3. It is therefore important to realise that if a fluoride-catalysed Michael reaction is to be carried out, air should be excluded from the system in order to minimise side-products.

Supported-permanganate-promoted Nef Transformation.— The use of supported permanganate as an oxidant was first reported in 1977.[14] Subsequent to this we have shown that, with the aid of i.r. spectroscopy and thermogravimetric analysis, it is possible to determine the best drying conditions and reagent loading for achieving optimum reactivity and selectivity of the permanganate.[6]

The optimum loading is dependent on the surface area and pore diameter of the silica-gel support. For the fairly small pore BDH silica gel used here, a loading of ca. 0.2 mmol g^{-1} appears to give the maximum reaction efficiency. Loadings up to 1.0 mmol g^{-1} were used but only ca. 0.2 mmol g^{-1} of these reagents was effective under the conditions used. Presumably, excess of permanganate above the 0.2 mmol g^{-1} level is not dispersed over the surface and remains an unreactive ion clusters. Removal of the product dicarbonyl compounds from the surface of the silica gel was not straightforward and required multiple washings with diethyl ether, presumably due to surface hydroxyl–carbonyl hydrogen bonding. Ironically, it was usually easier to remove products from reagents containing excess of permanganate.

The optimised supported permanganate is a very efficient reagent for the transformation of nitro groups to carbonyls as described here. Previous applications of permanganate to such reactions have been hindered by the harsh conditions of temperature and/or pH required and have often proceeded in low yield. Our reagent operates at close to neutral conditions and although we routinely ran the transformations at 70 °C, some reactions seemed to occur at room temperature in the absence of solvent.

Experimental

¹H N.m.r. spectra were recorded with a Varian EM360A (60 MHz) spectrometer. The ¹³C n.m.r. spectra were recorded with a Jeol FX90Q (22.63 MHz) spectrometer using broad-band decoupling. Mass spectra were obtained with an A.E.I. MS-3076 spectrometer. I.r. spectra were recorded on a Perkin-Elmer 683 ratio-recording spectrophotometer interfaced to a 64K data station for spectral processing. Gas chromato-graphs were obtained on a Pye-Unicam 104 using a Carbowax 20M column.

Alumina-supported KF and CsF were prepared by eva-porating an aqueous solution containing a calculated amount of pure fluoride onto a mesoporous neutral alumina (*e.g.* BDH reagent for chromatography). Conditions employed in the subsequent drying of the reagents are given in Table 3. Silica-gel-supported $KMnO_4$ was prepared as previously described[6] using 60—120 mesh BDH silica gel. Fluorides were usually dried at *ca.* 200 °C and stored in a desiccator before use unless stated otherwise (see Table 3). Acetonitrile was dried over 4 Å molecular sieves before use. 18-Crown-6 was dried by dissolving a sample in an excess of acetonitrile, removing the bulk of the solvent on a rotary evaporator, and final drying the resulting solid at *ca.* 1 mmHg for several hours at room temperature. Most of the other chemicals used were untreated BDH reagents.

Experimental details for a representative Mannich reaction, a Michael addition using KF–18-crown-6, and a Nef trans-formation are given below along with the full experimental details for the preparation of dihydrojasmone. All products gave mass spectra and ¹³C and ¹H n.m.r. spectra consistent with their structures (see Tables 1 and 2).

3-Diethylamino-1,2-diphenylpropan-1-one (1; $R^1 = R^2 =$ Ph, $R^3 = H$).—The Mannich base of deoxybenzoin was obtained by mixing equimolar amounts of diethylamine hydrochloride, deoxybenzoin, and paraformaldehyde (0.05 mol) in DMF (30 cm³) containing concentrated hydrochloric acid (0.2 cm³). The mixture was heated at 80 °C for 14 h, cooled, and then made alkaline with aqueous sodium hydr-oxide. Water (50 cm³) was added, the resulting mixture was extracted with diethyl ether (3 × 50 cm³), and the extracts were washed with water (3 × 50 cm³) to remove DMF. The combined extracts were then dried ($MgSO_4$) and evaporated to give the title compound (85%).

When the same reaction was carried out in methanol, a much lower yield (31%) of the product was obtained.

5-Nitrohexan-2-one (2; $R^1 = R^4 = Me$, $R^2 = R^3 = H$).—MVK (25 mmol) and nitroethane (0.5 mol) were added to dry acetonitrile (60 cm³) followed by oven-dried KF (5 mmol) and 18-crown-6 (1.5 mmol). The mixture was stirred at reflux temperatures for 2 h. The solvent was removed by evapor-ation, dichloromethane was added to the residue, and the solution was washed with 2M HCl. Removal of the dichloro-methane and excess of nitroethane by evaporation left the required nitro ketone in 98% yield. No further purification was required.

When a Mannich base was used to liberate the enone *in situ*, the reaction was usually allowed to proceed for somewhat longer (typically 5—7 h).

As indicated below, it is not usually necessary to use reflux temperatures for the Michael reaction especially when a supported fluoride is used as the catalyst. The use of reflux temperatures did, generally seem to guarantee very high yields of spectroscopically pure material.

Hexane-2,5-dione (3; $R^1 = R^4 = Me$, $R^2 = R^3 = H$).—5-Nitrohexan-2-one (4.5 mmol) and silica-gel-supported potas-sium permanganate (15 g; 0.2 mmol g⁻¹ or 1 mmol g⁻¹) were vigorously stirred together in benzene (30 cm³) at reflux temperatures for 3.5 h at which time ¹H n.m.r. spectroscopy showed complete transformation into the dione had occurred. The mixture was filtered and the solid residue was washed several times with diethyl ether. Water was then added to the solid residue and the mixture was washed with diethyl ether. The combined benzene mother-liquor and ethereal extracts were then evaporated to dryness to give the title diketone (55%) which was shown to be *ca.* 90% pure by ¹H n.m.r. spectroscopy.

Dihydrojasmone (8).—1-Iodoheptane (4) (0.1 mol) and sodium nitrite (0.2 mol) were added to DMF (250 cm³) and the mixture was stirred at room temperature for 6 h. After addition of cold water (250 cm³) the mixture was extracted with diethyl ether and the combined extracts were washed in turn with 10% aqueous $Na_2S_2O_3$ and water. The ether was removed from the dried ($MgSO_4$) solution to give a mixture of 1-nitroheptane (5) and heptyl nitrite. Vacuum distillation of this mixture gave a 70% yield of 1-nitroheptane (b.p. 63 °C at 3 mmHg).

A solution of 1-nitroheptane (20 mmol) and MVK (20 mmol) in ethanol (20 cm³) was stirred at room temperature with CsF–alumina for 1 h. The solvent was removed by evaporation, dichloromethane was added to the residue, and the solution was washed with 2M HCl before being dried over $MgSO_4$. Removal of the solvent gave 5-nitroundecan-2-one (6) (85%).

A solution of 5-nitroundecan-2-one (4.5 mmol) in benzene (30 cm³) was added to $KMnO_4$–silica gel (15 g) and the mix-ture was stirred at reflux temperatures for 10 h. Recovery by the method described above gave impure undecane-2,5-dione (7) (50%) which was purified by passage through a short column of neutral alumina with diethyl ether–acetone as eluant to give a 40% yield of *ca.* 90% pure material (by ¹H n.m.r.).

Cyclisation of the diketone to dihydrojasmone (8) could be carried out with ethanolic sodium hydroxide solution as described previously although in our hands this gave a low yield of the product.[15]

Michael Reaction using Different Fluoride Ion Sources.—A solution containing excess of nitroethane (0.25 mol) and MVK (12.5 mmol) in dry acetonitrile (30 cm³) was stirred with the source of fluoride (2.5 mmol equiv. F⁻) at room temper-ature. Samples (0.5 cm³) were removed at intervals, rapidly quenched in a mixture of diethyl ether (5 cm³) and dichloro-methane (5 cm³), and then immediately injected into the gas chromatograph. The progress of the reaction was monitored by measuring the peak area ratio of the nitro ketone adduct to the excess of nitroalkane. Reactions were allowed to run until no further change in this ratio was observed. Typical solutions were checked by ¹H n.m.r. spectroscopy to confirm completion of the reaction. The method described gave results reproducible to better than ±20%.

Reaction of Nitroethane with Fluoride.—In a typical experi-ment, caesium fluoride (10 mmol) and nitroethane (0.5 mol) were stirred together at room temperature for 24 h while a steady stream of oxygen gas was bubbled through the mixture. Filtration of the mixture followed by evaporation to remove the nitroethane left a viscous yellow oil. The major peaks in the ¹H and ¹³C n.m.r. spectra were due to 2,3-dinitrobutane [δ_H 1.32 (ddd, CH_3) and *ca.* 4.3 (m, CH); δ_C 16.1 (CH_3), 19.3 (CH_3), 87.0 (CH), and 89.0 p.p.m. (CH)]. The i.r. spectrum of the filtered solid showed bands consistent with the presence of HF_2^- (2 040, 1 830, and 1 230 cm⁻¹) and

titration of the solid with standard base revealed the presence of an equivalent amount (with respect to 2,3-dinitrobutane) of bifluoride (*ca.* 2 mmol). Running the reaction in air reduced the rate of reaction whereas if nitrogen were bubbled through the mixture no changes in the ^{1}H n.m.r. spectrum were apparent.

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