Fluoride Ion as a Catalyst for Michael Additions to Nitro-Alkenes

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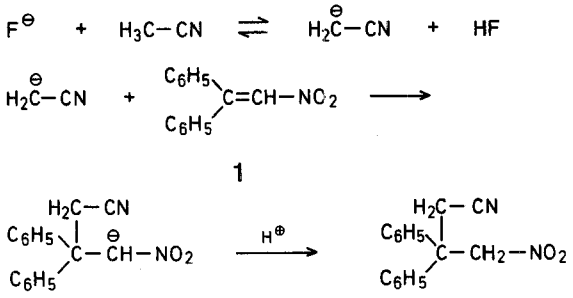
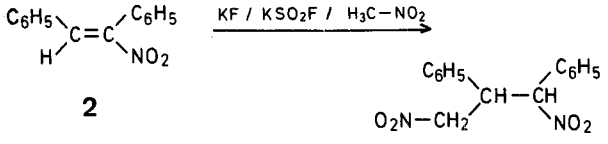
An attempt to prepare α-nitro-β-fluoroethanes by addition of fluoride ion to 1,1-diphenyl-2-nitroethene (**1**) in acetonitrile, and to *cis*-α-nitrostilbene (**2**) in nitromethane, resulted in a fluoride ion-catalyzed Michael addition of the solvent. While **1** was recovered unchanged from reaction with potassium fluoride in diglyme, reaction with tetraethylaminium fluoride[1] in acetonitrile gave 45% of 2,2-diphenyl-3-nitropropionitrile (**3**), identified by the two CH_2 singlets in deuterochloroform at $\delta = 5.26$ ppm (α to NO_2) and at $\delta = 3.53$ ppm (α to CN). The fluoride ion abstracts a proton from acetonitrile, and the cyanomethide ion formed adds to **1** (Scheme **A**).



Scheme **A**

Likewise, attempt to add fluoride ion from KF/KSO_2F[2] to the nitro-alkene **2** in nitromethane gave the solvent adduct, 1,3-dinitro-1,2-diphenylpropane **4** (Scheme **B**).



Scheme **B**

Recent work demonstrates that a fluoride ion in an aprotic solvent is a powerful base in elimination reactions[3]. The precedents known to us for a $F^{\ominus}$—catalyzed Michael reaction involve the rather acidic 1,2,3-triphenylcyclopentadiene[4] and several nitro-compounds[5], but proton abstraction from indene[6], fluorene[6], phenylacetylene[7], and acetonitrile[7], was demonstrated by condensation of the resulting anions with carbonyl compounds. The present examples suggest that while caution is required when trying to use fluoride anion as a carbon nucleophile, it can be used to advantage as a catalyst in Michael reactions involving weak carbon acids: special preparation of the strong base, which is frequently required for Michael additions of weak carbon acids, is not required, separation of the catalyst is easy, and reaction can be carried out when other strong bases are inert, i.e., **1** does not undergo addition of acetonitrile in the presence of triethylamine.

Reaction of 1,1-Diphenyl-2-nitroethene with Tetraethylaminium Fluoride in Acetonitrile:

A mixture of 1,1-diphenyl-2-nitroethene[8] (440 mg, 2 mmol) and tetraethylaminium fluoride[1] (2.8 g, 19 mmol) in acetonitrile (10 ml) was kept at room temperature for 2 h. The mixture was acidified (dilute hydrochloric acid), extracted with ether (25 ml), and the organic phase was washed with water, dried, and evaporated. The remaining oil was purified by a preparative thin layer chromatography on Kieselgur, using chloroform/carbon tetrachloride (1:1) as the eluent. Crystallization from petroleum ether (60–80°) gave 2,2-diphenyl-3-nitropropionitrile (**3**); yield: 240 mg (45%); m.p. 165°.

$C_{16}H_{14}N_2O_2$	calc.	C 72.18	H 5.30	N 10.53
(253.3)	found	71.98	5.08	10.27

I.R. (KBr): $\nu_{max} = 2240\ cm^{-1}$ (C≡N).

^{1}H-N.M.R. ($CDCl_3$): $\delta = 3.53$ (s, CH_2CN), 5.26 (s, CH_2NO_2), 7.20 ppm (m, C_6H_5).

Mass spectrum: $m/e = 266$ ($M^{\oplus}$, 35%), 226 ($M^{\oplus} - CH_2CN$, 18%), 220 ($M^{\oplus} - NO_2$, 28%), 180 ($M^{\oplus} - NO_2 - CH_2CN$, 100%).

Refluxing of **3** (1.6 g, 7.1 mmol) and potassium fluoride (7 g, 120 mmol) in dry diglyme for 7.5 h, gave back the starting material after work-up.

Reaction of *cis*-α-Nitrostilbene with Fluoride Ion in Nitromethane:

Cis-α-nitrostilbene[8] (1 g, 4,4 mmol) and a 1:1 mixture of potassium fluoride and potassium sulfinylfluoride (4.2 g, 23 mmol) were refluxed in nitromethane (12 ml) for 3 h. After cooling, the mixture was poured into ice/water (40 ml), extracted with chloroform (25 ml), the extract was washed with water, dried, and evaporated. The solid was crystallized from petroleum ether to give 1,3-dinitro-1,2-diphenylpropane; yield: 0.28 g (22%); m.p. 147°.

$C_{15}H_{14}N_2O_4$	calc.	C 62.91	H 4.93	N 9.79
(286.3)	found	63.10	4.88	9.54

^{1}H-N.M.R. ($CDCl_3$): $\delta = 4.40$ (m, 3H, $-C\underline{H}_2-$ and $C_6H_5-C\underline{H}$), 5.88 (d, 1H, $C_6H_5-C\underline{H}(NO_2)-$), and 7.40 ppm (m, 10H, C_6H_5-).

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J. Hayami, N. Uno, A. Kaji, *Tetrahedron Lett.* **1968**, 1385.
[2] B. Green, D. B. Sowerby, *J. Chem. Soc.* [A] **1970**, 987.
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N. Uno, *Bull. Chem. Soc. Japan* **44**, 1369 (1970).
F. Naso, L. Rozini, *J. C. S. Perkin Trans.* II **1974**, 340.
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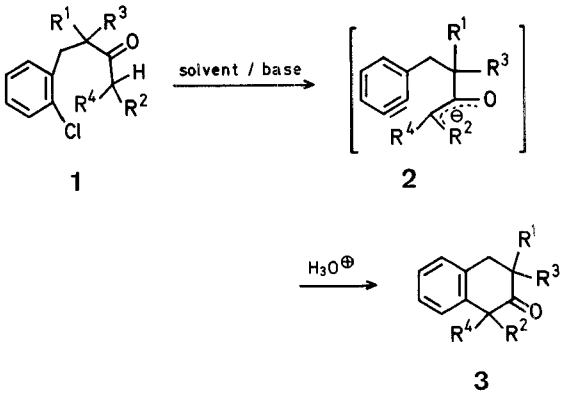
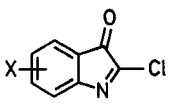
Errata

B. Loubinoux, P. Caubere, *Synthesis* **1974**, 201–203;
The formula scheme (p. 201) should be:



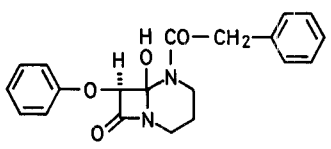
1 2 3

J. Grimshaw, W. J. Begley, *Synthesis* **1974**, 496–498;
The formula **2** in Table 1 (p. 497) should be:



2

A. K. Bose, J. C. Kapur, M. S. Manhas, *Synthesis* **1974**, 891–894;
The formula for compound **18** (p. 891) should be:

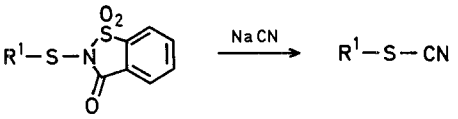


18

H. R. Kricheldorf, E. Leppert, *Synthesis* **1975**, 49–50;
The last entry in the first column of the Table (p. 50) should be:
N-phenyl-*N*-methylimido.

S. Kasina, J. Mematollahi, *Synthesis* **1975**, 162–163;
The name of compound **2** should be:
5,10-dioxo-5*H*,10*H*-diimidazo[3,4-*a*; 3′,4-*d*]pyrazine.

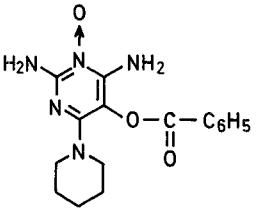
M. Furukawa, T. Suda, A. Tsukamoto, S. Hayashi, *Synthesis* **1975**, 165–167;
The reaction scheme **1**→**4** (p. 166) should be:



1 4

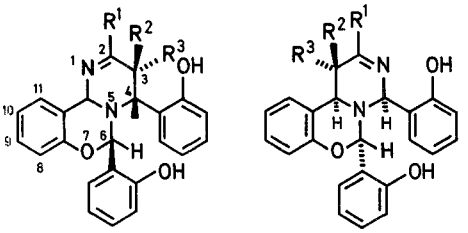
H. Singh, S. Sharma, R. N. Fyer, *Synthesis* **1975**, 325–326;
The name of the title compounds **2** should be:
5-oxobenzimidazo[2,1-*b*][1,3]benzoxazines.

J. M. McCall, R. E. TenBrink, *Synthesis* **1975**, 443–444;
The formula for compound **4** should be:



4

S. Kambe, T. Takajo, K. Saito, T. Hayashi, A. Sakurai, H. Midorikawa, *Synthesis* **1975**, 802–804;



6 7

The names for compounds **6** should be:
6a: 4,6-Bis[2-hydroxyphenyl]-3,3-dimethyl-3,4-dihydro-11b*H*-pyrimido[1,2-*c*][1,3]benzoxazine
6b: 4,6-Bis[2-hydroxyphenyl]-2,3,3-trimethyl-3,4-dihydro-11b*H*-pyrimido[1,2-*c*][1.3]benzoxazine
6c: 4,6-Bis[2-hydroxyphenyl]-2-methyl-3-phenyl-3,4-dihydro-11b*H*-pyrimido[1,2-*c*][1,3]benzoxazine

The names for compounds **7** should be:
7b: 4,6-Bis[2-hydroxyphenyl]-1,1,2-trimethyl-1,4-dihydro-11b*H*-pyrimido[3,4-*c*][1,3]benzoxazine
7c: 4,6-Bis[2-hydroxyphenyl]-1-methyl-2-phenyl-1,4-dihydro-11b*H*-pyrimido[3,4-*c*][1,3]benzoxazine