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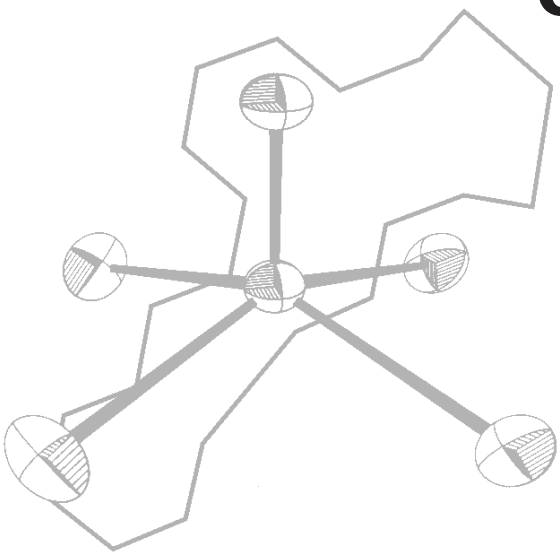

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The Preparation of Imidoyl Fluorides

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The first general synthesis of imidoyl fluorides is reported here. Irradiation of the initially formed *Z* isomers of *N*-methoxybenzenecarboximidoyl fluorides led to a photoequilibrium containing both the *E* and *Z* isomers. The pure *E* isomers were able to be isolated from these isomeric mixtures. The n.m.r. spectra of these isomers are discussed.

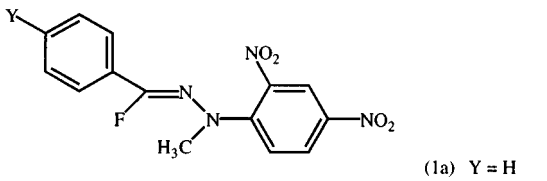
Introduction

A variety of methods have been reported for the synthesis of imidoyl chloride and bromide derivatives but only a very small number of the corresponding fluoro compounds have ever been reported. The chloro compounds have been prepared by reacting the corresponding amide derivative with phosphorus pentachloride[1] or triphenylphosphine and carbon tetrachloride,[2,3] while the most successful synthesis of the corresponding bromo compounds is by the reaction with triphenylphosphine and carbon tetrabromide.[3] Alternatively, the amidine can be reacted with sodium nitrite in the presence of either hydrochloric or hydrobromic acid.[4] None of these methods is readily applicable to the preparation of the corresponding fluoro compounds.

We[5,6] have prepared several hydrazonoyl fluorides (1) in fairly poor yields (*c.* 20–25%) by solvolysing the corresponding chloro or bromo derivative in aqueous dioxan (*c.* 70% dioxan) in the presence of a large excess of fluoride ion. The major product (>70%) is the corresponding hydrazide which can be readily removed from the product mixture by base extraction. This method does not have much general application and is a very wasteful synthesis. Compound (3) was prepared by the reaction of the hydrogen fluoride salt of the *N*-methoxy amide with DAST (Et_2NSF_3).[7] Several compounds (2) were isolated as part of the product mixture from the reaction of the corresponding Schiff base with elemental fluorine.[8] Bohme and Drechsler[9] have reported the preparation of several compounds (2; X = F) by the reaction of (2; X = Cl) with KF in 18-crown-6.

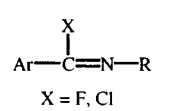
Calcium fluoride-supported alkali metal fluorides have been reported[10,11] to react to replace chlorine and bromine with fluorine in a variety of derivatives, by reaction in solvents such as sulfolane and acetonitrile. For example, benzoyl fluoride was prepared (80%) by reacting benzoyl chloride with KF–CaF_2 in acetonitrile.

Previous work[1,2,4–6] has yielded a variety of halo compounds and this paper reports their conversion into the corresponding fluoro compounds by reaction with KF or with KF–CaF_2. A more efficient synthesis of such fluoro compounds (1) and (5) was required for continuing mechanistic studies on nucleophilic substitution at the carbon–nitrogen double bond where the fluoro derivatives have shown promise as mechanistic probes.[5,12]

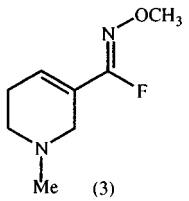


(Z)-(1)

(1a) Y = H
(1b) Y = OMe



X = F, Cl
(2) R = alkyl or aryl
(2a) R = Ar = Ph, X = F



(3)

Results and Discussion

The hydrazonoyl fluorides (1a,b) and imidoyl fluoride (2a)* were prepared in acceptable yields (50–65%) by reacting the corresponding chloro or bromo compounds

* (*Z*)-*N*-(2,4-Dinitrophenyl)-*N*-methylbenzenecarbohydrazonoyl fluoride (1a), (*Z*)-*N*-(2,4-dinitrophenyl)-4-methoxy-*N*-methylbenzenecarbohydrazonoyl fluoride (1b) and *N*-phenylbenzenecarboximidoyl fluoride (2a).

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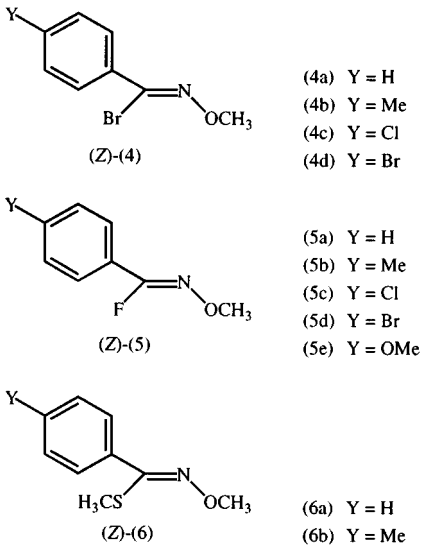
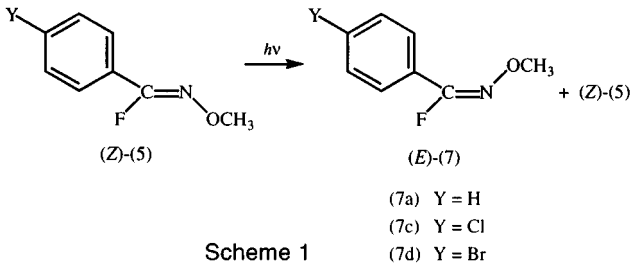
with an excess of CaF_2/KF in refluxing acetonitrile. Compounds (1a,b) had been prepared in poor yields previously. Compound (2a) was an unstable very readily hydrolysed liquid. The reaction leading to (1a) was also attempted with potassium fluoride alone, and gave almost no useful product under the same conditions. This result presumably reflects the much lower solubility of KF in acetonitrile compared to the CaF_2/KF reagent.



Reactions leading to compounds (5) required much more forcing conditions. Sulfolane had previously been used as a solvent for reactions with CaF_2/KF but even at 200° (*Z*)-*N*-methoxy-4-methylbenzenecarboximidoyl bromide (4b) did not lead to any fluoro product. However, in dimethyl sulfoxide at 150–170°, depending on the ring substituent, the desired products were observed. It was subsequently discovered that potassium fluoride alone under similar reaction conditions led to an almost identical product mixture. For these reactions in dimethyl sulfoxide, varying amounts of the corresponding methyl benzothiohydroximates (6) were also observed. These thio compounds had a much lower volatility than the corresponding fluoro compounds, and a lower R_F on silica, and could be removed by fractional distillation of the fluoro compounds or by chromatography. Finger *et al.*[13] have also reported the preparation of methylthio compounds during the preparation of fluoropyridines by the reaction of chloropyridines with KF in Me_2SO. The inadvertent synthesis of the previously unknown methylthio compounds could produce some useful compounds for our future mechanistic studies. Preliminary data indicate that irradiation of the *Z* methylthio isomers produced here leads to a photostationary equilibrium containing both the *Z* and *E* isomers.

Ultraviolet irradiation of benzene solutions of (*Z*)-(5) gave a photostationary mixture of the *E* and *Z* isomers with a *c.* 1:1 mixture of the two isomers. The *E* isomer was separated from the *Z* isomer by preparative gas chromatography, or, in the case of 4-bromo-*N*-methoxybenzenecarboximidoyl fluoride (7d), by separation of the isomers on a preparative silica plate. The corresponding chloro compounds have been reported previously by Johnson[1] (the stereochemistries reported in ref. 1 should be reversed) and the bromo compounds by Kikugawa.[14] In the preparation of the *E* bromo compounds, unless great care was taken with the photolytic conditions, the major product was found to be the corresponding nitrile. Indeed, Kikugawa has reported this reaction as a possible synthetic route to nitriles.[15] Gas chromatographic analysis of the reaction mixture after irradiating (*Z*)-*N*-methoxybenzenecarboximidoyl fluoride (5a) for 5 h indicated 49% *E* hydroximoyl fluoride (7a) (see Scheme 1), 47% of the *Z* isomer (5a) and 4% benzonitrile. The *E* fluorides once isolated seem to be thermally stable, with an n.m.r. solution [in (^{2}H)chloroform] kept at room temperature for more than a month showing no sign of any *Z* isomer. Irradiation of a benzene solution of (1a), under similar conditions to the preparation of (7d), led to rapid decomposition [70% of (1a) had reacted after 30 min] with the appearance of an *N*-Me resonance at 4·10 ppm but without any trace of an *N*-Me resonance for the corresponding *E* isomer (expected at *c.* 2·90 ppm—see below).



Scheme 1

N.m.r. studies indicate that, as for all other halo compounds in these series that have been investigated, the thermodynamically more stable isomer has the *Z* configuration. The *O*-methyl group resonates at a very slightly higher field in the *E* (7) than in the *Z* isomer (5) (3·94 versus 3·96 ppm where R = H). For other halo compounds these assignments based on n.m.r. data have been confirmed by X-ray crystal structure analysis.[16–18] The *E* isomers of the halo compounds (1) have never been isolated,[2] but the position of the *N*-methyl group at *c.* 3·6 ppm for (1) is consistent with other *Z* isomers and is quite different from the position at *c.* 2·9 ppm for other similar *E* isomers reported in the literature.[2,5] The ^{13}C spectra are characterized by very large $^1J_{C-F}$ coupling constants of 320–340 Hz in the *Z* isomers, and around 230 Hz for the *E* isomers of the *N*-methoxybenzenecarboximidoyl fluorides. This significant difference in the coupling constants could be a useful way of distinguishing between these isomers. Bohme and Drechsler reported $^1J_{C-F}$ coupling

constants of 333–348 Hz for their compounds (2).[9] Smaller couplings to the *ipso* carbon (20–30 Hz) and to the *ortho* carbon (3–5 Hz) were also observed. The compounds (*Z*)-(5) showed no or very small coupling between the fluorine and the *O*-methyl protons, suggesting these compounds adopt the s-*trans* configuration preferentially (shown), while for compounds (1) there was coupling between the fluorine and the *N*-methyl group in both the ^{13}C (*c.* 5 Hz) and the ^{1}H (3 Hz) spectra. For these compounds, the preferred conformation must have the *N*-methyl group in fairly close proximity to the fluorine, as shown, with the bulky dinitrophenyl group pointing outwards. Two of the *E* isomers of the *N*-methoxybenzenecarboximidoyl fluorides (7a) (Y = H) and (7c) (Y = Cl) did show a very small coupling between the fluorine and the *O*-methyl group in the proton spectrum, and, in the case of the 4-chloro compound, also in the carbon spectrum.

Experimental

General Methods

Calcium fluoride was 325 mesh 99·9% from Aldrich Chemical Company. Potassium fluoride was either BDH analyical reagent grade or the spray-dried reagent from Aldrich. Photochemical isomerization reactions were carried out in quartz tubes placed in a Rayonet reactor, RPR-100 (The Southern New England Ultraviolet Company), fitted with 15 low-pressure lamps (253·7 nm). The ^{1}H n.m.r. spectra were acquired at 300·13 MHz, and the ^{13}C spectra at 75·47 MHz, on either a Bruker AM 300 spectrometer or a Varian Mercury 300 MHz spectrometer in (^{2}H)chloroform. Low-resolution mass spectra were obtained on a Varian Saturn 3 ion-trap gas chromatograph–mass spectrometer. New compounds gave a single spot by t.l.c. analysis or a single peak in the g.c./m.s., and showed the required numbers of carbons in the ^{13}C n.m.r. spectrum. Most compounds were further characterized from their high-resolution mass spectra. Elementary analysis of some compounds described in this work was carried out by Midwest Microlab, Indianapolis, Inc. Exact masses were obtained by the Central Science Laboratory at the University of Tasmania.

Preparation of CaF_2/KF Reagent

Calcium fluoride (5·0 g, 0·064 mol) was added to a solution of potassium fluoride (1·2 g, 0·021 mol) in methanol (20 ml) and the resulting slurry evaporated slowly to dryness in a vacuum oven at 80° over 5 h. The resulting solid was ground to a fine powder (5·7 g) and stored in a desiccator until required.

(Z)-N-*(2,4-Dinitrophenyl)*-N-*methylbenzenecarbohydrazonoyl Fluoride (1a)*

CaF_2/KF (0·5 g) and *N*-(2,4-dinitrophenyl)-*N*-methylbenzenecarbohydrazonoyl bromide (0·16 g, 0·42 mmol) in dry acetonitrile (5 ml), under an atmosphere of nitrogen, were heated under reflux and stirred for 24 h. On cooling, dichloromethane (20 ml) was added and the resulting slurry filtered to remove the inorganic salts. The organic solution was washed with 2% sodium hydroxide solution (to remove any hydrazide formed), dried, and the solvent removed by evaporation. The product was purified by dry column chromatography on silica with dichloromethane/hexane (3 : 1) as the eluting solvent, followed by recrystallization from dichloromethane/hexane, yielding a yellow/brown crystalline solid (0·085 g, 65%), m.p. 131–133° (lit.[6] 131–133°). ^{1}H n.m.r. δ 3·59, d, $J_{H,F}$ 3·0 Hz, 3H, NCH_3; 7·46, m, 4H, ArH; 7·74, d, *J* 7·8 Hz, 2H, ArH; 8·28, dd, J_{ortho} 9·4 Hz, J_{meta} 2·6 Hz, 1H, ArH; 8·56, d, J_{meta} 2·6 Hz, 1H, ArH. ^{13}C n.m.r. δ 42·6, d, *J* 5·6 Hz; 117·2; 122·4; 126·7, d, J_{CCCF} 4·4 Hz; 127·0, d, J_{CCF} 34·4 Hz; 127·0; 128·8; 132·0; 138·9; 139·5; 146·9; 147·9, d, J_{CF} 333·6 Hz.

(Z)-N-*(2,4-Dinitrophenyl)-4-methoxy*-N-*methylbenzenecarbohydrazonoyl Fluoride (1b)*

This compound was prepared by a similar procedure to the hydrazonoyl fluoride (1a) except that a reaction time of 7 h was used leading to the desired product in 65%, m.p. 148–149° (lit.[5] 145–147°). ^{1}H n.m.r. δ 3·57, d, $J_{H,F}$ 2·7 Hz, 3H, NCH_3; 3·87, s, 3H, OMe; 6·95, d, *J* 8·8 Hz, 2H, ArH; 7·37, d, *J* 9·4 Hz, 1H, ArH; 7·72, d, *J* 8·8 Hz, 2H, ArH; 8·29, dd, J_{ortho} 9·4 Hz, J_{meta} 2·6 Hz, 1H, ArH; 8·57, d, J_{meta} 2·6 Hz, 1H, ArH. ^{13}C n.m.r. δ 42·6, d, *J* 4·7 Hz; 55·4; 114·3; 116·5; 118·9, d, J_{CCF} 35·2 Hz; 122·5; 127·0; 128·7; 138·6; 139·0; 146·6; 149·9, d, J_{CF} 333·6 Hz; 162·9.

N-*Phenylbenzenecarboximidoyl Fluoride (2a)*

CaF_2/KF (0·9 g) and *N*-phenylbenzenecarboximidoyl chloride (0·3 g, 0·14 mmol) in dry acetonitrile (5 ml), under an atmosphere of nitrogen, were heated under reflux and stirred for 18 h. The acetonitrile was removed by evaporation and the resulting solid triturated with hexane (4×5 ml) and the hexane removed by evaporation to leave an *oil* (50%) (Found: $M^{+\bullet}$, 199·0795. $C_{13}H_{10}FN$ requires $M^{+\bullet}$, 199·0797). ^{13}C n.m.r. δ 123·3; 125·3; 128·5; 128·8; 132·2; 143·0, d, J_{CNCF} 12·5 Hz; 148·4, d, J_{CF} 340·7 Hz.

(Z)-N-*Methoxy-4-methylbenzenecarboximidoyl Bromide (4b)*

Sodium nitrite (1·6 g, 23 mmol) in water (10 ml) was added dropwise to a stirred ice-cold solution of *N*-methoxy-4-methylbenzenecarboximidamide[1,19] (1·5 g, 9·1 mmol) in 50% HBr (14 ml). The resulting solution was stirred and cooled in an ice bath for 1 h and at room temperature for an additional 1 h. The organic product was extracted in dichloromethane (2×15 ml). Removal of the solvent gave the desired *bromo compound* (40%) (Found: $M^{+\bullet}$, 226·9944. $C_9H_{10}BrNO$ requires $M^{+\bullet}$, 226·9946). ^{1}H n.m.r. δ 2·37, s, 3H, $ArCH_3$; 4·12, s, 3H, OCH_3; 7·18, d, *J* 8·0 Hz, 2H, ArH; 7·72, d, *J* 8·0 Hz, 2H, ArH. ^{13}C n.m.r. δ 21·3, 62·9, 128·2, 129·1, 130·3, 131·2, 140·8.

(Z)-*4-Bromo*-N-*methoxybenzenecarboximidoyl Bromide (4d)*

This compound was prepared by a similar procedure as a *solid* (56%), m.p. 36–37° (Found: $M^{+\bullet}$, 290·8898. $C_8H_7Br_2NO$ requires $M^{+\bullet}$, 290·8894). ^{13}C n.m.r. δ 63·1, 125·0, 129·1, 129·6, 131·5, 132·8.

(Z)-*4-Chloro*-N-*methoxybenzenecarboximidoyl Bromide (4c)*

Phosphorus pentabromide was added to 4-chloro-*N*-methoxybenzamide[1] (17·99 g, 0·0970 mol) in a 100 ml three-neck round-bottomed flask fitted with condenser, drying tube, and J-Kem temperature probe. The mixture was heated to 80°C with stirring and held there for $2\frac{1}{2}$ h. The mixture was cooled to room temperature and poured into ice-cold water (200 ml). The resulting mixture was extracted with ether (3×150 ml). The combined ether extracts were washed with saturated sodium hydroxide solution (6×50 ml) and dried. The ether was removed by evaporation to yield an amber-coloured oil (13·87 g). Vacuum distillation of this oil gave a light yellow *oil* (13·00 g, 54 %) which solidified upon cooling (Found: $M^{+\bullet}$, 246·9410. $C_8H_7BrClNO$ requires $M^{+\bullet}$, 246·9400). ^{1}H n.m.r. δ 4·13, s, 3H, OCH_3; 7·35, d, *J* 9·0 Hz, 2H, ArH; 7·77, d, *J* 9·0 Hz, 2H, ArH. ^{13}C n.m.r. δ 63·1, 128·4, 128·8, 129·2, 132·1, 136·4. G.c./m.s.: *m/z* 251 (M, 11%), 249 (60), 247 (44), 170 (33), 168 (100), 155 (32), 153 (99), 139 (35), 137 (98), 102 (42).

(Z)-N-*Methoxy-4-methylbenzenecarboximidoyl Fluoride (5b)*

KF (0·7 g, 12 mmol) and *N*-methoxy-4-methylbenzenecarboximidoyl bromide (4b) (0·54 g, 1·4 mmol), in dry dimethyl sulfoxide (8 ml), under an atmosphere of dry nitrogen, were heated and stirred at 158° for 22 h. On cooling the organic products were extracted into pentane (5×8 ml). The pentane layer was washed with water, dried and the solvent removed by evaporation. The n.m.r. of the crude product indicated a mixture of the desired fluoro compound (5b) and methyl (*Z*)-*O*,4-dimethylbenzothiohydroximate (6b) (*c.* 3 : 1 by n.m.r.). The products were separated by dry column chromatography on silica with dichloromethane/pentane (1 : 1) as the eluting solvent yielding the desired product (5b) as an *oil* (0·18 g, 46%) (Found: $M^{+\bullet}$, 167·0756. $C_9H_{10}FNO$ requires $M^{+\bullet}$, 167·0746). ^{1}H n.m.r. δ 2·37, s, 3H, $ArCH_3$; 3·94, s, 3H, OCH_3; 7·19, d, *J* 8·0 Hz, 2H, ArH; 7·61, d, *J* 8·0 Hz, 2H, ArH. ^{13}C n.m.r. δ 21·4; 63·1; 123·7, d, J_{CCF} 30·6 Hz; 125·7, d, J_{CCCF} 4·0 Hz; 129·2; 141·3; 150·6, d, J_{CF} 320·6 Hz.

Methyl (*Z*)-*O*,4-dimethylbenzothiohydroximate (6b) (0·072 g, 16%) was obtained as an *oil* (Found: $M^{+\bullet}$, 195·0724. $C_{10}H_{13}NOS$ requires $M^{+\bullet}$, 195·0718). ^{1}H n.m.r. δ 2·03, s, 3H, SCH_3; 2·36, s, 3H, $ArCH_3$; 4·02, s, 3H, OCH_3; 7·20, d, *J* 8·0 Hz, 2H, ArH; 7·29, d, *J* 8·0 Hz, 2H, ArH. ^{13}C n.m.r. δ 14·9, 21·3, 62·4, 128·7, 129·2, 132·0, 139·5, 155·7.

(Z)-*4-Bromo*-N-*methoxybenzenecarboximidoyl Fluoride (5d)*

This compound was prepared by a similar procedure as a waxy *solid* (90%), m.p. 35–36° (Found: $M^{+\bullet}$, 230·9695. C_8H_7BrFNO requires $M^{+\bullet}$, 230·9695). ^{1}H n.m.r. δ 3·94, s, 3H, OCH_3; 7·48, d, *J* 8·7 Hz, 2H, ArH; 7·55, d, *J* 8·7 Hz, ArH, 2H. ^{13}C n.m.r. δ 63·2; 125·4; 125·5, d, J_{CCF} 31·6 Hz; 127·0, d, J_{CCCF} 3·4 Hz; 131·7; 149·5, d, J_{CF} 321·3 Hz.

(Z)-N,*4-Dimethoxybenzenecarboximidoyl Fluoride (5e)*

This compound was obtained as an *oil* by a similar procedure except that the temperature was maintained at 152° (yield 40%) (Found: $M^{+\bullet}$, 183·0694. $C_9H_{10}FNO_2$ requires $M^{+\bullet}$, 183·0696). ^{1}H n.m.r. δ 3·81, s, 3H, OCH_3; 3·92, s, 3H, OCH_3; 6·88, d, *J* 8·8 Hz, 2H, ArH; 7·65, d, *J* 8·8 Hz, 2H, ArH. ^{13}C n.m.r. δ 55·4; 63·0; 114·0; 118·9, d, J_{CCF} 30·5 Hz; 127·4, d, J_{CCCF} 4·7 Hz; 150·5, d, J_{CF} 319·3 Hz; 161·8.

(Z)-N-*Methoxybenzenecarboximidoyl Fluoride (5a)*

(*Z*)-*N*-Methoxybenzenecarboximidoyl bromide[4] (4a) (15·02 g, 0·0702 mol) was placed in a three-neck 250 ml round-bottomed flask fitted with water-cooled condenser, nitrogen gas inlet, and J-Kem temperature probe. Potassium fluoride (16·38 g, 0·28 mol) in dimethyl sulfoxide (240 ml) was added to the flask with stirring. The mixture was heated to 150°C with stirring for 14 h. The reaction mixture was cooled to room temperature and then combined with 150 ml of saturated sodium chloride solution. This mixture was extracted with ether (4×150 ml). The combined ether extracts were dried and the ether was removed by evaporation to give an amber-coloured oil (9·04 g). Fractional distillation under vacuum gave (5a) as a colourless *oil* (5·45 g, 51%), b.p. *c.* 45°C/5 mmHg (Found: C, 62·6; H, 5·2; F, 12·4; N, 9·1. C_8H_8FNO requires C, 62·7; H, 5·3; F, 12·4; N, 9·2%). ^{1}H n.m.r. δ 3·96, s, 3H, OCH_3; 7·44, m, 3H, ArH; 7·74, d, *J* 7·6 Hz, 2H, ArH. ^{13}C n.m.r. δ 63·2; 125·7, d, J_{CCCF} 3·7 Hz; 126·6, d, J_{CCF} 30·6 Hz; 128·5; 130·9; 150·3, d, J_{CF} 321·3 Hz. G.c./m.s.: *m/z* 153 (M, 100%), 122 (14), 108 (37), 103 (9), 77 (65).

Further fractional distillation gave *methyl* O-*methylbenzothiohydroximate* (6a) (1·83 g, 14%) (Found: $M^{+\bullet}$, 181·0566. $C_9H_{11}NOS$ requires $M^{+\bullet}$, 181·0561). ^{1}H n.m.r. δ 2·02, s, 3H, SCH_3; 4·02, s, 3H, OCH_3; 7·39, s, 5H, ArH. ^{13}C n.m.r. δ 14·9, 62·5, 128·6, 128·8, 129·4, 132·6, 155·6. G.c./m.s.: *m/z* 181 (M, 54%), 180 (46), 150 (19), 134 (26), 119 (100), 104 (37), 103 (36), 91 (23), 77 (42).

(Z)-*4-Chloro*-N-*methoxybenzenecarboximidoyl Fluoride (5c)*

The procedure described above was used when (*Z*)-4-chloro-*N*-methoxybenzenecarboximidoyl bromide (4c) (13·25 g, 0·0534 mol) and potassium fluoride (12·41 g, 0·21 mol) in dimethyl sulfoxide (240 ml) were heated at 150°C with stirring for 19 h. Fractional distillation of the crude product under vacuum gave a colourless *oil* (2·29 g, 23%), b.p. *c.* 55°C/1·2 mmHg (Found: $M^{+\bullet}$, 187·0199. C_8H_7ClFNO requires $M^{+\bullet}$, 187·0200). ^{1}H n.m.r. δ 3·96, d, $J_{H,F}$ 1·2 Hz, 3H, OCH_3; 7·38, d, *J* 8·4 Hz, 2H, ArH; 7·68, d, *J* 8·4 Hz, 2H, ArH. ^{13}C n.m.r. δ 63·6; 125·3, d, J_{CCF} 30·9 Hz; 127·2; 129·1, d, J_{CCCF} 2·3 Hz; 137·3; 149·7, d, J_{CF} 321·1 Hz. G.c./m.s.: *m/z* 189 (M, 34%), 187 (100), 158 (10), 156 (32), 144 (8), 142 (15), 137 (23), 113 (16), 111 (45).

(E)-N-*Methoxybenzenecarboximidoyl Fluoride (7a)*

A solution of the *Z* imidoyl fluoride (5a) (1·16 g) in benzene (20 ml) was irradiated for 5 h. The mixture was immediately extracted with saturated sodium bicarbonate solution (3×20 ml). The benzene extract was dried and the benzene removed by evaporation. G.c./m.s. analysis of the resulting oil revealed that it contained a mixture of approximately 50 : 50 of the *E* and *Z* isomers. The geometric isomers were separated by preparative gas chromatography. This yielded the *E* imidoyl fluoride (7a) as a clear *oil* (0·066 g, 5·7%) (Found: C, 62·5; H, 5·3; F, 12·2; N, 9·2. C_8H_8FNO requires C, 62·7; H, 5·3; F, 12·4; N, 9·2%). ^{1}H n.m.r. δ 3·94, d, $J_{H,F}$ 0·8 Hz, 3H, OCH_3; 7·48, m, 3H, ArH; 8·00, 7·97, dd, *J* 8·1, 1·8 Hz, 2H, ArH. ^{13}C n.m.r. δ 63·3; 124·9, d, J_{CCF} 35·5 Hz; 128·2; 128·4, d, J_{CCCF} 6·9 Hz; 131·5; 156·0, d, J_{CF} 232·0 Hz. G.c./m.s.: *m/z* 153 (M, 100%), 122 (14), 108 (33), 103 (12), 77 (62).

(E)-*4-Chloro*-N-*methoxybenzenecarboximidoyl Fluoride (7c)*

The procedure described above was used to obtain a mixture (50 : 50 by g.c./m.s.) of the *E* and *Z* isomers. The geometric isomers were separated by preparative gas chromatography. The *E* imidoyl fluoride (7c) was obtained as a clear *oil* (Found: C, 51·4; H, 3·6; Cl, 18·9; F, 9·8; N, 7·4. C_8H_7ClFNO requires C, 51·2; H, 3·8; Cl, 18·9; F, 10·1; N, 7·5%). ^{1}H n.m.r. δ 3·94, d, $J_{H,F}$ 0·9 Hz, 3H, OCH_3; 7·44, d, *J* 9·0 Hz, 2H, ArH; 7·94, d, *J* 9·0 Hz, 2H, ArH. ^{13}C n.m.r. δ 63·5, d, J_{CONCF} 2·3 Hz; 123·2, d, J_{CCF} 35·5 Hz; 128·6, d, J_{CCCCF} 2·3 Hz; 129·8, d, J_{CCCF} 6·8; 137·6; 155·0, d, J_{CF} 230·4 Hz. G.c./m.s.: *m/z* 189 (M, 33%), 187 (100), 158 (10), 156 (31), 144 (9), 142 (17), 137 (24), 113 (17), 111 (50).

(E)-*4-Bromo*-N-*methoxybenzenecarboximidoyl Fluoride (7d)*

A solution of the *Z* imidoyl fluoride (5d) in pentane/ether (3 : 1) was irradiated with a single 150 Watt mercury lamp for 4 h. The mixture of isomers was separated on a preparative silica plate kept in the dark; hexane/dichloromethane (2 : 1) was used as the eluting solvent. The *E* imidoyl fluoride (7d) was the lower R_F compound and was obtained as an *oil* which solidified on cooling (Found: $M^{+\bullet}$, 230·9706. C_8H_7BrFNO requires $M^{+\bullet}$, 230·9695). ^{1}H n.m.r. δ 3·92, s, 3H, OCH_3; 7·55, d, *J* 8·6 Hz, 2H, ArH; 7·81, d, *J* 8·6 Hz, 2H, ArH. ^{13}C n.m.r. δ 63·5; 123·9, d, J_{CCF} 36·0 Hz; 126·3; 130·1, d, J_{CCCF} 6·6 Hz; 131·7; 155·4, d, J_{CF} 230·0 Hz.

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