Bromination of 1a with Bromine in Acetic Acid. To a solution of 100 mg (0.42 mmol) of **1a** in 30 mL of acetic acid was added a solution of 160 mg (1.0 mmol) of bromine in 10 mL of acetic acid at rt. After the reaction mixture was stirred for 1 h, it was poured into water (10 mL). The organic layer was extracted with CH_2Cl_2. The extract was washed with 10% aqueous sodium thiosulfate, 10% aqueous sodium bicarbonate, and water (each 5 mL), dried (Na_2SO_4), and evaporated in vacuo to leave a residue, which was recrystallized from carbon tetrachloride to give 96 mg (58%) of **1c**: pale yellow prisms (carbon tetrachloride); mp >265 °C dec; IR (KBr) 3580 (OH) cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.52–2.96 (8 H, m), 3.70 (2 H, s, exchanged by D_2O), 7.16 (4 H, s); MS *m/e* 396, 398, 400 (M^+). Anal. Calcd for $C_{16}H_{14}O_2Br_2$: C, 48.27; H, 3.54. Found: C, 47.86; H, 3.51.

Protected β- and γ-Aspartic and -Glutamic Acid Fluorides

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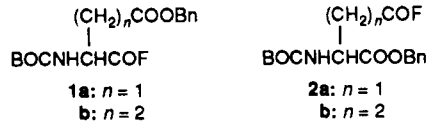
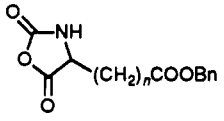
The preparation of synthetically useful FMOC-, BOC-, and Z-substituted α-amino acid fluorides, including those bearing a variety of protected side chains, has recently been described.[1,2] In the case of aspartic and glutamic acids the isomeric ω-acid fluorides could also prove to be of significant synthetic utility. The published collection of BOC-substituted α-amino amino acid fluorides included the β- and γ-benzyl ester, α-acid fluorides.[1b] More recently, in the pursuit of new routes to asparagine and glutamine derivatives, we had occasion to prepare the analogous β- and γ-acid fluorides and were surprised to find that the properties (mp, optical rotation) of these two compounds fit precisely the data previously recorded for the isomeric α-fluorides. Closer examination revealed that due to a labeling error the compounds listed earlier as **1a,b** are in fact the non-α-fluorides **2a,b**.



1a: *n* = 1 **b**: *n* = 2 **2a**: *n* = 1 **b**: *n* = 2

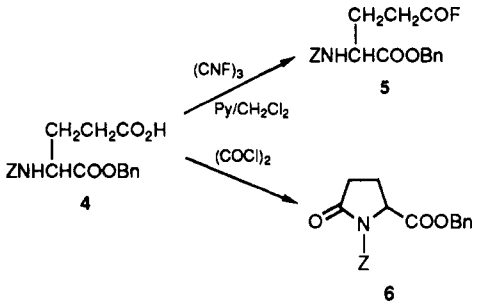
In the present note we describe the authentic α-acid fluorides **1a,b**. Both syntheses were accompanied by the formation of traces of the corresponding Leuch's anhydrides **3** (NCAs). Contamination by such NCAs is limited



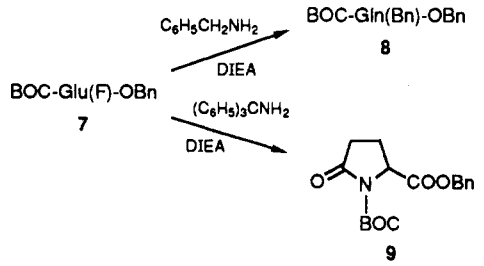
3a,b

to amino acids bearing α-BOC protection, no such reaction having yet been observed for the analogous FMOC- and Z-α-acid fluorides. Z-Amino acid chlorides differ from the fluorides in that the former are readily converted to NCAs on standing or heating.[3]

The FMOC- and Z-substituted β- and γ-acid fluorides are also described in the present note (Table I). In the case of α-FMOC-glutamic acid α-benzyl ester, γ-acid fluoride the reaction with cyanuric fluoride was carried out at room temperature as is normal for FMOC α-fluorides and a trace of the corresponding pyroglutamic acid ester accompanied the acid fluoride. No pyroglutamate was observed in the case of the α-BOC or α-Z analogs probably because these reactions were carried out at low temperatures (−30 to −20 °C) as is normal for the more acid-sensitive systems. Repetition of the FMOC synthesis at low temperature also avoided this side reaction. The preparations described here represent additional examples of the relative stability of amino acid fluorides vis-a-vis the corresponding chlorides. As in the NCA synthesis described earlier, an acid chloride intermediate is involved in some routes to pyroglutamates (e.g., **4** to **6**).[4,5]



The β- and γ-acid fluorides described in this note were initially examined as intermediates for the synthesis of the *N*-trityl derivatives of Asn and Gln. Although simple amines reacted readily, e.g., **7** on treatment with benzyl amine to give **8**, the highly hindered[6] tritylamine gave none



of the glutamine derivative. Instead only the pyroglutamic acid ester **9** was obtained. In the meantime simple routes to the *N*-trityl derivatives of both Asn and Glu have been reported.[7] Both of these compounds have now been converted to the corresponding FMOC-protected α-acid fluorides which proved to be soluble, highly reactive, stable acylating agents for solution and solid-phase peptide synthesis.

Once all four isomers of the fluorides of BOC-substituted aspartic acid and glutamic acid esters became available it could be seen by comparison of their ^1H NMR spectra that the α-acid fluorides can be distinguished from their β- and γ-isomers by virture of differences in the methylene protons α to the acid fluoride and ester carbonyl functions. Thus for **1b** the methylene group α to the carbonyl ester function appears as a clean triplet whereas for **2b** this

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Table I. ^{1}H NMR Data for α-, β-, and γ-Aspartic and -Glutamic Acid Fluorides [ppm ($CDCl_3$)][a]

compound	$C(CH_3)_3$	$-(CH_2)_x-$ or $-CH_2O-$	α-CH	CH_2Ar or OCH_2CH	-NH-	aromatic protons
BOC-Asp(F)-OBn[b]	1.46 (s, 9)	3.15 (m, 2, β-CH_2)	4.65 (m, 1)	5.23 (s, 2)	5.50 (d, 1)	7.38 (s, 5)
BOC-Glu(F)-OBn[b]	1.46 (s, 9)	2.0 and 2.25 (2 m, 2, β-CH_2) 2.55 (m, 2, γ-CH_2)	4.45 (m, 1)	5.23 (s, 2)	5.18 (d, 1)	7.38 (s, 5)
Z-Asp(F)-OBn[c,d]		3.15 (m, 2, β-CH_2)	4.70 (m, 1)	5.17 (s, 2) 5.20 (s, 2)	5.79 (d, 1)	7.38 (s, 10)
Z-Glu(F)-OBn[c,e]		1.98 and 2.25 (2 m, 2, β-CH_2) 2.55 (m, 2, γ-CH_2)	4.55 (m, 1)	5.13 (s, 2) 5.20 (s, 2)	5.55 (d, 1)	7.37 (s, 10)
Fmoc-Asp(O-*t*-Bu)-F	1.45 (s, 9)	2.90 (dq, 2, β-CH_2)	4.85 (m, 1)	4.25 (t, 1, OCH_2CH) 4.42 (m, 2, CH_2O)	5.85 (d, 1)	7.25–7.8 (m, 8)
Fmoc-Glu(O-*t*-Bu)-F	1.45 (s, 9)	2.1 and 2.25 (2 m, 2, β-CH_2) 2.4 (m, 2, γ-CH_2)		4.2 (t, 1, OCH_2CH) 4.45 (m, 3, CH_2O, α-CH)	5.7 (d, 1)	7.25–7.82 (m, 8)
Fmoc-Asp(F)-O-*t*-Bu[c,f]	1.51 (s, 9)	3.15 (m, 2, β-CH_2)	4.55 (m, 1)	4.24 (t, 1, OCH_2CH) 4.42 (d, 2, CH_2O)	5.80 (d, 1)	7.25–7.82 (m, 8)

[a] For compounds not listed here see the Experimental Section. [b] For yield data and physical constants see ref 1b. [c] Prepared as described for FMOC-Glu(F)-O-*t*-Bu in the Experimental Section at −30 to −20 °C for the Z derivatives and at room temperature for the FMOC derivative. [d] Yield 88.8%; mp 83–4 °C (CH_2Cl_2/hexane); $[\alpha]^{28}_D$ −12.8 (*c* 1, EtOAc). Anal. Calcd for $C_{19}H_{18}FNO_5$: C, 63.51; H, 5.05; N, 3.90. Found: C, 63.52; H, 5.00; N, 3.83. [e] Yield 70.0%; mp 55–7 °C (Et_2O/hexane); $[\alpha]^{28}_D$ −10.8 (*c* 1, EtOAc). Anal. Calcd for $C_{20}H_{20}FNO_5$: C, 64.34; H, 5.40; N, 3.75. Found: C, 64.29; H, 5.36; N, 3.69. [f] Yield 73.2%; mp 74–5 °C (Et_2O/hexane); $[\alpha]^{28}_D$ −11.0 (*c* 1, EtOAc). Anal. Calcd for $C_{23}H_{24}FNO_5$: C, 66.82; H, 5.85; N, 3.39. Found: C, 66.95; H, 5.96; N, 3.38.

methylene group, being α to the carbonyl fluoride unit, is subject to additional H/F coupling. For the aspartic acid pair a similar situation holds for **1a** which shows the methylene group adjacent to the benzyl ester carbonyl at δ 3.0 as two AB quartets whereas **2a** shows this methylene at δ 4.2 as a highly complex multiplet. Remaining absorptions are difficult to distinguish in the two isomeric pairs. Similar characteristic differences are exhibited by the α-Z and to a lesser extent the α-FMOC acid fluoride, ester pairs.

Experimental Section

BOC-Asp(OBn)-F. To a stirred solution of BOC-Asp(OBn)-OH (0.646 g, 2 mmol) in a mixture of dry CH_2Cl_2 and CH_3CN[8] (8 mL, 1:1) and pyridine (2 mmol, 162 μL) kept under a N_2 atmosphere was added cyanuric fluoride (6 mmol, 540 μL) at −30 to −20 °C. The reaction was followed by TLC using CH_2Cl_2/acetone/HOAc (8/2/0.1) or $CHCl_3$/MeOH/HOAc (9/1/0.1) by spotting the reaction mixture directly until no residual free acid was observed (45–60 min). After the reaction mixture was stirred for 1 h, crushed ice was added along with 15 mL of additional CH_2Cl_2. The organic layer was separated and the aqueous layer extracted with 5 mL of CH_2Cl_2. The combined organic layers were extracted with 10 mL of ice-cold water and dried ($MgSO_4$), and the solvent was removed with a rotary evaporator at room temperature. Upon recrystallization from CH_2Cl_2–hexane with cooling and scratching, the first material which separated (0.1 g) was identified as the corresponding Leuch's anhydride, mp 121–3 °C (lit.[9] mp 120–1 °C). Concentration of the filtrate followed by cooling gave 0.45 g (69.8%) of the acid fluoride as white crystals: mp 46–8 °C; $[\alpha]^{26}_D$ = −7.4 (*c* 1, EtOAc); IR (KBr) 1841 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.48 (s, 9, *t*-Bu), 3.05 (dq, 2, β-CH_2), 4.85 (m, 1, α-CH), 5.18 (s, 2, CH_2O), 5.55 (d, 1, NH), 7.38 (s, 5, aryl).

Anal. Calcd for $C_{16}H_{20}FNO_5$: C, 59.07; H, 6.20; N, 4.31. Found: C, 58.68; H, 5.88; N, 4.59.

BOC-Glu(OBn)-F. BOC-Glu(OBn)-OH (0.665 g) was treated as described for the aspartic acid analog except that 8 mL of CH_2Cl_2 was used as solvent in accordance with previously described general techniques. Again the first crop of crystals (0.05 g) proved to be the corresponding Leuch's anhydride, mp 73–75 °C or 79–81 °C (different runs) (lit.[10] mp 96–97 °C). Concentration of the filtrate gave 0.5 g (73.7%) of the acid fluoride as a white solid: mp 83–85 °C; $[\alpha]^{26}_D$ = −15.5 (*c* 1, EtOAc); IR (KBr) 1841 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.48 (s, 9, *t*-Bu), 2.1 and 2.25 (2 m, 2, β-CH_2), 2.51 (t, 2, γ-CH_2), 4.5 (m, 1, α-CH), 5.19 (s, 2, CH_2O), 5.25 (m, 1, NH), 7.38 (s, 5, aryl).

Anal. Calcd for $C_{17}H_{22}FNO_5$: C, 60.17; H, 6.53; N, 4.13. Found: C, 59.94; H, 6.17; N, 4.23.

FMOC-Glu(F)-O-t-Bu. Treatment of 0.425 g (1 mmol) of the acid with cyanuric fluoride and pyridine in CH_2Cl_2 under the normal conditions at room temperature for 2 h gave a mixture of the corresponding FMOC pyroglutamic acid *tert*-butyl ester [mp 163–5 °C; IR (KBr) 1762, 1735, 1715 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.46 (s, 9, CMe_3), 2-2.8 (m, 4, CH_2CH_2), 4.30–4.65 (m, 4, OCH_2CH, α-CH), 7.25–7.80 (m, 8, aryl)] and the acid fluoride. Repetition of the reaction at −30 to −20 °C gave an oil which after evacuation under high vacuum for 3 h and recrystallization from ether–hexane gave the acid fluoride as a solvent-swollen white solid. Alternatively the acid fluoride could be purified by column chromatography over ordinary silica without hydrolysis using ethyl acetate–hexane (7/3) as eluent. Evacuation under high vacuum overnight expelled the solvent to give 0.28 g (65.6%) of the pure fluoride as a dry white solid: mp 40–42 °C; $[\alpha]^{24}_D$ = 11.4 (*c* 1, EtOAc); IR (KBr) 1844 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.47 (s, 9, CMe_3), 1.95 and 2.35 (2 m, 2, β-CH_2), 2.55 (m, 2, γ-CH_2), 4.20 (t, 1, OCH_2CH), 4.4 (m, 3, CH_2O, α-CH), 5.45 (d, 1, NH), 7.25–7.80 (m, 8, aryl).

Anal. Calcd for $C_{24}H_{26}FNO_5$: C, 67.43; H, 6.13; N, 3.28. Found: C, 67.61; H, 6.40; N, 3.16.

BOC-Gln(Bn)-OBn. To a stirred solution of 0.107 g of benzylamine (1 mmol) and 0.129 g (1 mmol) of DIEA in 3 mL of dry CH_2CL_2 was added 0.373 g (1.1 mmol) of BOC-Glu(F)-OBn at room temperature. After 5 min additional CH_2Cl_2 (5–10 mL) was added, the layers were separated, and the organic phase was washed three times each with 10% $KHSO_4$, 10% $NaHCO_3$, and H_2O. Evaporation of the dried ($MgSO_4$) solution gave an oil which was recrystallized from CH_2Cl_2–hexane to give 0.3 g (70.4%) of the pure amide ester: mp 90–91 °C; $[\alpha]^{24}_D$ = −9.8 (*c* 1, EtOAc); IR (KBr) 1739 (ester), 1690 (urethane), 1645 (amide) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.45 (s, 9, CMe_3), 1.98 (m, 2, β-CH_2), 2.25 (t, 2, γ-CH_2), 4.35 (m, 1, α-CH), 4.42 (d, 2, $NHCH_2C_6H_5$), 5.18 (q, 2, $OCH_2C_6H_5$), 5.36 (d, 1, CONH), 6.28 (bs, 1, $NHCH_2$), 7.28 (m, 5, aryl), 7.38 (s, 5, aryl).

Anal. Calcd for $C_{24}H_{30}N_2O_5$: C, 67.59; H, 7.09; N, 6.57. Found: C, 67.33; H, 7.44; N, 6.39.

BOC-*p*-Glu-OBn. Substitution of tritylamine for benzylamine in the reaction described directly above gave only the corresponding pyroglutamic acid ester, yield 75%. After recrystallization from ethyl acetate–hexane the ester was obtained as a white solid: mp 72–73 °C; IR (KBr) 1783, 1740, 1703 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.42 (s, 9, CMe_3), 2–2.6 (m, 4, CH_2CH_2), 4.6 (m, 1, α-CH), 5.22 (s, 2, CH_2O), 7.4 (s, 5, aryl).

Anal. Calcd for $C_{17}H_{21}NO_5$: C, 63.94; H, 6.63; N, 4.39. Found: C, 63.96; H, 6.71; N, 4.39.

FMOC-Asn(Trt)-F. This compound was prepared by the general method described previously.[1] Recrystallization of the crude acid fluoride from CH_2Cl_2–hexane gave in 83.3% yield the

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pure fluoride: mp 116–118 °C; $[\alpha]^{28}_D$ = +3.0 (c 1, EtOAc); IR (KBr) 1846 cm^{-1} (COF); ^{1}H NMR ($CDCl_3$) δ 2.95 (dq, 2, β-CH_2), 4.20 (t, 1, OCH_2CH), 4.40 (m, 2, CH_2O), 4.79 (m, 1, α-CH), 5.95 (d, 1, NH), 6.75 (s, 1, NH), 7.05–7.80 (m, 23, aryl).

Anal. Calcd for $C_{38}H_{31}FN_2O_4$: C, 76.24; H, 5.22; N, 4.68. Found: C, 76.15; H, 5.43; N, 4.52.

FMOC-Gln(Trt)-F. Obtained as described above for the Asn analog in 81.7% yield: mp 132–134 °C; $[\alpha]^{28}_D$ = −7.2 (c 1, EtOAc); IR (KBr) 1847 cm^{-1} (COF); ^{1}H NMR ($CDCl_3$) δ 2.10 and 2.20 (2 m, 2, β-CH_2), 2.38 (t, 2, γ-CH_2), 4.20 (t, 1, OCH_2CH), 4.35 (m, 2, CH_2O). 4.55 (m, 1, α-CH), 5.65 (d, 1, NH), 6.68 (s, 1, NH), 7.1–7.75 (m, 23, aryl).

Anal. Calcd for $C_{39}H_{33}FN_2O_4$: C, 76.45; H, 5.43; N, 4.57. Found: C, 76.62; H, 5.49; N, 4.32.

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Evidence for a Hydrogen Atom Transfer Mechanism or a Proton/Fast Electron Transfer Mechanism for Monoamine Oxidase

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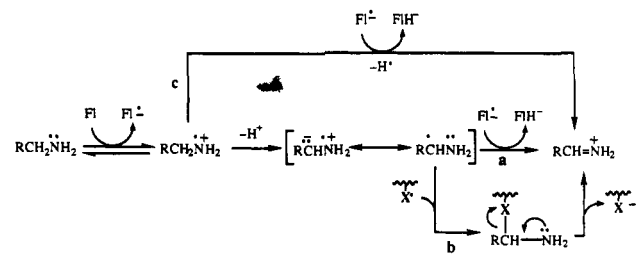
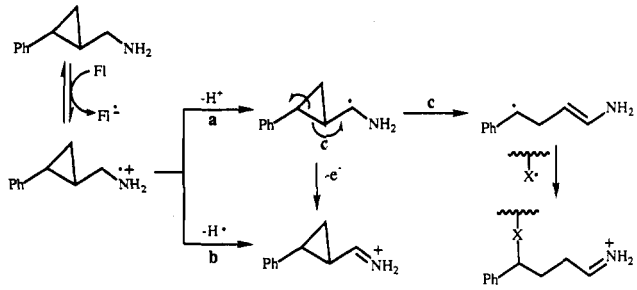
Monoamine oxidase (EC 1.4.3.4, MAO) has been known for over 60 years,[1] yet its mechanism for amine oxidation is still unclear. On the basis of investigations with mechanism-based enzyme inactivators[2] the most reasonable family of mechanisms for this enzyme is shown in Scheme I. Studies with cyclopropylamines[3–13] and cyclobutylamines[14,15] are consistent with an initial one-electron transfer mechanism from the amine to the flavin to give the amine radical cation. The next step in the mechanism, either proton/electron transfer (Scheme I, pathway a or b) or hydrogen atom transfer (pathway c), is debatable. Nelson and Ippoliti[16] have indicated that

Scheme I



Scheme II



α-deprotonation of an amine radical cation is not as favorable a pathway as hydrogen atom abstraction on the basis of a thermodynamic acidity measurement. However, Dinnocenzo and Banach[17] argued that the thermodynamic acidity is irrelevant and that the true pK_a for amine radical cations, determined by direct measurement, is no more than about 10; consequently, they suggest that α-deprotonation is a favorable pathway. Das and von Sonntag[18] determined the pK_a of trimethylamine radical cation to be 8. On the basis of photochemical amine oxidation reactions Hasegawa et al.[19] also have evidence that the α-deprotonation/electron-transfer pathway is favorable. We were interested in obtaining evidence for one of these pathways as it relates to monoamine oxidase-catalyzed reactions.

Results and Discussion

The approach that we took to differentiate the second step in the MAO oxidation mechanism was based on the cyclopropylcarbinyl radical rearrangement to the 3-butenyl radical, which is well known to occur at an exceedingly rapid rate estimated to be approximately 10^8 s^{-1}.[20] This rate increases when the cyclopropyl ring is substituted with radical-stabilizing groups. For example, the 2-phenylcyclopropylcarbinyl radical opens to the 1-phenyl-3-butenyl radical at a rate of approximately 10^{11} s^{-1}.[21] This is the sort of rate that could be competitive with electron-transfer mechanisms. Consequently, we synthesized *trans*-1-(aminomethyl)-2-phenylcyclopropane hydrochloride (1) to be used in a test for the α-deprotonation/electron transfer mechanism (pathway a) or hydrogen atom transfer mechanism (pathway b) catalyzed by monoamine oxidase (Scheme II). Monoamine oxidase-catalyzed cyclopropyl ring cleavage of 1, which could lead to inactivation of the enzyme as depicted in pathway c (Scheme II), would be evidence in favor of an α-deprotonation pathway leading to the α-carbon radical (2). If no cyclopropyl ring cleavage occurred, it would indicate

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