Supporting Information for

Photochemical Generation of Highly Destabilized Vinyl Cations

The Effects of α- and β-Trifluoromethyl versus α- and β- Methyl Substituents

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(Z)- and (E)-2-bromo-1-phenylpropene (1Z and 1E) were synthesized in a 60:40 ratio from α-methylcinnamic acid and N-bromosuccinimide using a modified Hunsdiecker reaction. The E- and Z-isomer were separated using column chromatography (silica/petroleum ether 40-60) and obtained in >98% stereoisomeric and >99% overall purity.

1Z: $^1$H NMR δ 2.45 (s,3H), δ 6.96 (s,1H), δ 7.28 (m,5H). MS m/z (relative intensity) 198 196 (M⁺, 50, 45), 117 (M⁺-Br, 60), 115 (M⁺-H₂Br, 100). High resolution MS m/z 195.9879 (C₉H₉Br requires 195.9887). UV $\lambda_{max}$= 254 nm ($\epsilon$=1.6 $10^4$ l/mol.cm).

1E: $^1$H NMR δ 2.45 (s,3H), δ 6.69 (s,1H), δ 7.29 (m,3H), δ 7.53 (m,2H). MS m/z (relative intensity) 198 196 (M⁺, 40, 40), 117 (M⁺-Br, 45), 115 (M⁺-H₂Br, 100). High resolution MS m/z 195.9882 (C₉H₉Br requires 195.9887). UV $\lambda_{max}$= 249 nm ($\epsilon$=1.3 $10^4$ l/mol.cm).

(E)-1-Bromo-2-phenylpropene (2E). 20 mmol of 2-phenylpropene (8) (2.4 g) was dissolved in 30 ml CCl₄ at 0 °C and 24 mmol Br₂ (3.8 g) was added dropwise. After the addition was complete, the reaction was stirred at RT for 1 hour. The solvent was evaporated. The reaction mixture was dissolved in 100 ml t-BuOH together with 30 mmol t-BuOK (3.5 g) and refluxed for 1 hour. 100 ml of H₂O was added and the reaction mixture was extracted 3 times with 75 ml of diethyl ether. The combined ether layers were washed with H₂O, brine, and dried over MgSO₄. Evaporation and column chromatography using silica/pet. ether 40/60, afforded a colorless oil consisting of > 98% E-1-bromo-2-phenylpropene (2E) with an overall yield of 70%.

(Z)-1-Bromo-2-phenylpropene (2Z). 2Z was obtained from 2E via triplet-sensitized E/Z-isomerization by irradiating 2.5 mmol of 2E (0.5 g) with light of $\lambda_{exc}$=350nm in 150 ml acetone, followed by column chromatography (silica/pet ether 40-60).

2E: $^1$H-NMR δ 2.2 (s,3H), δ 6.4 (s,1H), δ 7.3 (m,5H). MS m/z (relative intensity) 198 196 (M⁺, 70, 65), 117 (M⁺-Br, 60), 115 (M⁺-H₂Br, 100). High resolution MS m/z 195.9881 (C₉H₉Br requires 195.9887). UV $\lambda_{max}$= 248 nm ($\epsilon$=1.6 $10^4$ l/mol.cm).

2Z: $^1$H-NMR δ 2.1 (s,3H), CH₃, δ 6.24 (s,1H), δ 7.3 (m,5H). MS m/z (relative intensity) 198 196 (M⁺, 70, 65), 117 (M⁺-Br, 60), 115 (M⁺-H₂Br, 100). High resolution MS m/z 195.9878 (C₉H₉Br requires 195.9887). UV $\lambda_{max}$= 254 nm ($\epsilon$=1.5 $10^4$ l/mol.cm).
(Z)-2-Chloro-3,3,3-trifluoro-1-phenylpropene (3Z) was synthesized from benzaldehyde and 1,1,1-trichloro-2,2,2-trifluoroethane, using zinc in DMF.\textsuperscript{3} A stereoisomeric mixture of 85:15 Z/E was obtained, which was used as such in the irradiations. \textsuperscript{19}F NMR δ 8.68 (s, 3F). \textsuperscript{1}H NMR δ 7.27 (s, 1H), δ 7.38 (m, 3H), δ7.72 (m, 2H). MS m/z (relative intensity) 208 206 (M\textsuperscript{+}, 35, 90), 171 (M\textsuperscript{+}-Cl, 58), 151 (M\textsuperscript{+}-HFCl, 100), 102 (M\textsuperscript{+}-CF\textsubscript{3}Cl, 35). High resolution MS m/z 206.0120 (C\textsubscript{9}H\textsubscript{6}F\textsubscript{3}Cl requires 206.0110). UV λ\textsubscript{max}= 257 nm (ε=1.9 10\textsuperscript{4} l/mol.cm).

(Z)-2-Chloro-3,3,3-trifluoro-1-phenyl-1-deuteropropene (3\textsubscript{d}Z) was synthesized via the same method as 3Z, using benzaldehyde-α-D instead of benzaldehyde. In a modification of the method in ref \textsuperscript{4} benzaldehyde-α-D was prepared by adding subsequently 11 ml concentrated H\textsubscript{2}SO\textsubscript{4}, 0.1 mol KCN (6.5 g) and 0.1 mol freshly distilled benzaldehyde (11 g) to 50 ml morpholine. This mixture was heated at 100 °C for 2 hrs and extracted with diethyl ether, dried over MgSO\textsubscript{4} and the diethyl ether evaporated. The white solid morpholino-nitrile product was dried overnight in a vacuum stove (yield 60%, 12.2 g). 10 g of this product was dissolved in 15 ml DMSO and 15 ml D\textsubscript{2}O and heated at 100°C for 5 hrs. The mixture is poured into cold H\textsubscript{2}O and the crystals are collected and dried. This procedure is repeated as often as necessary (normally two or three times) to obtain >99.5% deuterium incorporation. When this is achieved the deuterated morpholino-nitrile is hydrolyzed in a 2M HCl solution on a boiling water bath in 5 hrs, yielding 60 mmol benzaldehyde-α-D (6.4 g, 98% yield, overall yield 59%).
Identification of products

(E)-2-Chloro-3,3,3-trifluoro-1-phenylpropene (3E): $^1$H NMR δ 15.90 (s, 3F). MS m/z (relative intensity) 208 206 (M$^+$, 25, 85), 171 (M$^+$-Cl, 58), 151 (M$^+$-HFCI, 100), 102 (M$^+$-CF$_3$Cl, 35). High resolution MS m/z 206.0122 (C$_9$H$_6$F$_3$Cl requires 206.0110).

(Z)-1-Bromo-3,3,3-trifluoro-1-phenylpropene (4Z-Br): $^1$H NMR δ 7.36 (m, 6H). MS m/z (relative intensity) 252 250 (M$^+$,100, 90), 171 (M$^+$-Br, 40), 151 (M$^+$-HBrF, 50), 102 (M$^+$-CF$_3$Br, 60).

(Z)-1-Chloro-3,3,3-trifluoro-1-phenylpropene (4Z-Cl): $^1$H NMR δ 7.10 (s, 1H), δ 7.38 (m, 5H). MS m/z (relative intensity) 208 206 (M$^+$, 30, 100), 171 (M$^+$-Cl, 40), 151 (M$^+$-HFCI, 40), 102 (M$^+$-CF$_3$Cl, 80).

(Z)-1-Phenylpropene (5Z) was synthesized by irradiating 5E in acetone using light of $\lambda$=350 nm. MS m/z (relative intensity) 118 (M$^+$, 80), 117 (M$^+$-H, 100), 103 (M$^+$-CH$_3$, 10), 91 (M$^+$-C$_2$H$_3$, 30).

1-Phenylallene (6) was synthesized according to a literature procedure. $^7$ $^1$H NMR δ 5.13 (d (J$_{HH}$=6.9 Hz), 2H), δ 6.19 (t (J$_{HH}$=6.9), 1H), δ 7.23 (m,5H). MS m/z (relative intensity) 116 (M$^+$, 50), 115 (M$^+$-H, 100), 89 (M$^+$-C$_2$H$_3$, 40).

1-phenylpropyne (7) was synthesized according to a literature procedure. $^8$ $^1$H NMR δ 2.02 (s, 3H), δ 7.32 (m,5H). MS m/z (relative intensity) 116 (M$^+$, 60), 115 (M$^+$-H, 100), 89 (M$^+$-C$_2$H$_3$, 20).

(E)- and (Z)-1-Phenyl-3,3,3-trifluoropropene (14E and 14Z) were synthesized according to a literature procedure. $^9$ 14E: $^1$H NMR δ 6.18 (dq,1H), δ 7.13 (d,1H), 7.40 (m,5H). MS m/z (relative intensity) 172 (M$^+$, 100), 152 (M$^+$-HF, 30), 151 (M$^+$-H$_2$F, 50), 133 (M$^+$-C$_3$H$_3$, 30), 122 (M$^+$-CF$_2$, 35), 103 (M$^+$-CF$_3$, 45). High resolution MS m/z 172.0491 (C$_9$H$_7$F$_3$ required 172.0500). 14Z: $^1$H NMR δ 5.77 (dq,1H), δ 6.90 (d,1H), 7.40 (m,5H). MS m/z (relative intensity) 172 (M$^+$, 100), 152 (M$^+$-HF, 35), 151 (M$^+$-H$_2$F, 50), 133 (M$^+$-C$_3$H$_3$, 30), 122 (M$^+$-CF$_2$, 25), 103 (M$^+$-CF$_3$, 40). High resolution MS m/z 172.0541 (C$_9$H$_7$F$_3$ required 172.0500).

3,3,3-Trifluoro-1-phenylpropyne (15) was synthesized according to a literature procedure. $^{10}$ $^1$F NMR δ 27.63 (s). MS m/z (relative intensity) 170 (M$^+$, 100), 151 (M$^+$-
HF, 100), 120 (M⁺-CF₂, 25). High resolution MS m/z 170.0359 (C₉H₅F₃ requires 170.0344).

3-Chloro-3,3-difluoro-2-fluoro-1-phenylpropene (16) was synthesized according to a literature procedure.¹¹ ¹H NMR δ 6.32 (d (JHF=36 Hz), 1H), δ 7.40 (m, 5H). MS m/z (relative intensity) 208 206 (M⁺, 30, 90), 187 (M⁺-F, 25), 171 (M⁺-Cl, 55), 151 (M⁺-HFCI, 100), 102 (M⁺-CF₃Cl, 30).

3,3,3-Trifluoro-2-phenylpropene (18)⁶: ¹H NMR δ 5.74 (d, JHH=1.7Hz, 1H), δ 5.94 (d, JHH=1.7Hz, 1H), δ 7.37 (m, 5H). MS m/z (relative intensity) 172 (M⁺, 60), 103 (M⁺-CF₃, 100), 77 (M⁺-C₃H₂F₃, 50), 69 (M⁺-C₈H₆, 25).

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