The Cleavage of a CC Double Bond after Chemical Ionization with NO^+—A Complex Rearrangement Process[1]

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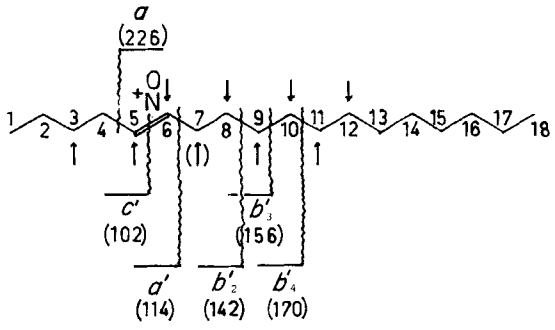
The fragmentation of alkenes after chemical ionization with NO^+, involving cleavage of the double bond, has been elucidated by deuterium labelling.

In an earlier publication[2] we showed that alkenes under chemical ionization (CI) conditions react in a specific way with NO^+: Electrophilic attack on the π system of the double bond leads to two isomeric molecular ions which give rise to two series of ions of the composition $C_nH_{2n}NO$ (ions *a*, *a'* and *b'* in Scheme 1) during the formation of which one hydrogen is transferred with high specificity from the hydrocarbon portion lost. In addition, an ion



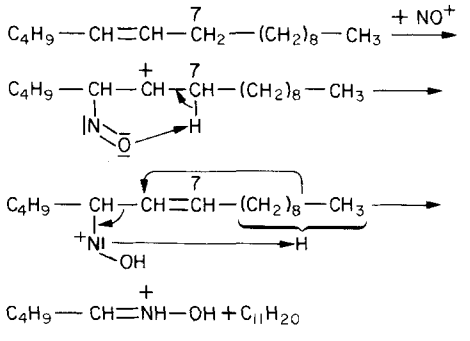
Scheme 1. Fragments formed by CI(NO) from *n*-octadecene-5. Arrows indicate the positions which have been labelled with D (C-7 see text).

$C_nH_{2n+2}NO^+$ is formed by cleavage of the double bond with loss of the larger chain accompanied by a transfer of 2 H to the ionized species (*c'*). In view of the importance of this ion for the localization of double bonds in alkenes carrying additional functional groups[3] and in consideration of the fact that relatively little is known about hydrogen rearrangements in CI(NO) spectra we decided to study this process in some detail.

From the labelling data mentioned in Ref. 2 it was evident (cf. Scheme 1) that, during the formation of *c'*, D atoms at C-3 and C-5‡ are retained and those of C-6 and C-12 are lost (hence not back-transfer from either of these positions). That the rearranged H atoms stem from a position farther away than C-12 in the case of a Δ^5-olefin seems unlikely if one assumes a specific transfer mechanism as ion *c'* is also observed in the CI(NO) spectrum of *n*-dodecene-5. For our labelling studies *n*-hexadecene-5 and *n*-octadecene-5 have been selected, since here formation of *c*-type ions occurs only by loss of the larger chain (*c'*). Likely loci for the origin of the migrating H atoms seemed to be either C-8/C-9 (since the transition states would then comprise 6- or 7-membered rings for an H transfer to one of the heteroatoms), or C-10/C-11 (in view of the rearrangement mechanism discussed for alkyl isocyanates and related compounds[4]).

The spectra of *n*-octadecenes-5 labelled at the positions C-8, C-9, C-10 and C-11 confirmed the specificity of the H transfers for the ion *a'* (C-8) and those of the *b'* series (C-10 for b_2', C-11 for b_3'), and showed the expected retention of two D (C-8, C-9, and C-10 for b_4', C-8 and C-9 for b_3', C-8 for b_2', and all positions labelled beyond C-4 for *a*). However, no transfer could be observed for *c'* from any of the labelled positions.

In the CI(NO) spectrum of [7,7-$^2H_2$]-hexadecene-5, however, a complete shift of the ion *c'* to *m/z* 103 was observed,§ hence one of the transferred hydrogens stems from the allylic position. As it seems improbable that the second one migrates exclusively from a position beyond C-12 (cf. above), it is more likely that it comes non-specifically from various places of the carbon chain yielding a protonated oxime, possibly with concomitant formation of cycloalkenes of varying ring size (Scheme 2). That no shifts of ion *c'* could be



c', *m/z* 102

Scheme 2. Formation of ion *c'*.

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‡ That only one of the olefinic deuterium atoms is retained has been confirmed[2] for [4,5-$^2H_2$]-octadecene-4.

§ Ions *a*, b_2', b_3' and b_4' are shifted by 2 units (cf. Scheme 1 and the discussion of the *n*-octadecenes-5).

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observed in the spectra of the various labelled octadecenes-5 is understandable if one considers the low intensity of this ion (about 5% rel. int.) and the fact that a strong isotope effect discriminating against deuterium should be expected.[5]

SYNTHESES

The labelled analogues of *n*-octadecene-5 and [7,7-$^2H_2$]-*n*-hexadecene-5 were synthesized as indicated below:

(1) 7,7-d_2: n-$C_9H_{19}COOC_2H_5 \xrightarrow{LAD} n$-$C_9H_{19}CD_2OH \xrightarrow{PBr_3}$

n-$C_9H_{19}CD_2Br \xrightarrow{n\text{-}C_4H_9C\equiv CLi} n$-$C_9H_{19}CD_2{-}C{\equiv}C{-}C_4H_9 \xrightarrow{H_2}$

n-$C_9H_{19}CD_2{-}CH{=}CH{-}C_4H_9$

(2) 8,8-d_2: n-$C_{10}H_{21}COOC_2H_5 \xrightarrow{LAD} n$-$C_{10}H_{21}CD_2OH \xrightarrow{PBr_3}$

n-$C_{10}H_{21}CD_2Br \xrightarrow[(ii)\ ethylene\ oxide\ (iii)\ H^+, H_2O]{(i)\ Mg} n$-$C_{10}H_{21}CD_2(CH_2)_2OH \xrightarrow[Py]{CrO_3}$

n-$C_{10}H_{21}CD_2CH_2CHO \xrightarrow{Wittig} n$-$C_{10}H_{21}CD_2CH_2CH{=}CH\text{-}C_4H_9$

(3) 9,9-d_2: n-$C_9H_{19}COOC_2H_5 \xrightarrow{cf(2)} \longrightarrow \longrightarrow n$-$C_9H_{19}CD_2(CH_2)_2OH \xrightarrow{PBr_3}$

n-$C_9H_{19}CD_2(CH_2)_2Br \xrightarrow[(ii)\ HC(OC_2H_5)_3\ (iii)\ H^+, H_2O]{(i)\ Mg} n$-$C_9H_{19}CD_2(CH_2)_2CHO$

$\xrightarrow{Wittig} n$-$C_9H_{19}CD_2(CH_2)_2CH{=}CH\text{-}C_4H_9$

(4) 10,10-d_2: n-$C_8H_{17}Br \xrightarrow[(ii)\ \delta\text{-valerolactone}\ (iii)\ H_2O, H^+]{(i)\ Li} n$-$C_8H_{17}CO(CH_2)_4OH$

$\xrightarrow[(ii)\ LiAlD_4\ (iii)\ D_2O]{(i)\ p\text{-}CH_3C_6H_4SO_2NHNH_2} n$-$C_8H_{17}CD_2(CH_2)_4OH \xrightarrow[Py]{CrO_3}$

n-$C_8H_{17}CD_2(CH_2)_3CHO \xrightarrow{Wittig} n$-$C_8H_{17}CD_2(CH_2)_3CH{=}CH{-}C_4H_9$

(5) 11,11-d_2: n—$C_7H_{15}Br \xrightarrow[(\varepsilon\text{-caprolactone})]{cf.\ (4)} \longrightarrow \longrightarrow$

n-$C_7H_{15}CD_2(CH_2)_4CH{=}CH\text{-}C_4H_9$

EXPERIMENTAL

Spectroscopy and chromatography

Mass spectra. Finnigan 3200. CI(NO): GC; source temp. 60–80 °C, 80 eV, emission 0.4 mA. EI: GC or direct; 70 eV.

NMR. Varian EM 309, $CDCl_3$, TMS, δ ppm.

IR. Perkin–Elmer 283, film.

Column chromatography. Silica gel 60 (Macherey & Nagel) or Kieselgel 60 (Merck) for purification (if not indicated otherwise).

Syntheses

Standard procedures will not be described *in extenso*. For compounds prepared in analogy to literature data only reference will be given to the latter. Isotopic purities have been determined for the labelled olefins. Those of the precursors have to be at least as high as those of the former.

[1,1-$^2H_2$]-*n*-Decan-1-ol. From *n*-decanoic acid ethyl ester with $LiAlD_4$. Yield: 95%. Mass spectrum: *m/z* 142 ($[M-H_2O]^{+\cdot}$).

[1,1-$^2H_2$]-1-Bromo-*n*-decane. From [1,1-$^2H_2$]-*n*-decan-1-ol and PBr_3 (cf. Ref. 6). Purification by distillation. Yield: 58%. B.p.: 115 °C (12 Torr). Mass spectrum: *m/z* 222/24 (0.4%, $[M]^+$), 151/53 (5%), 137/39 (35%). NMR: 1.86 (br.t, 7.5 Hz, 2 H), 1.33 (br.s, 14 H), 0.89 (t, 7 Hz, 3 H).

[7,7-$^2H_2$]-*n*-Hexadecyne-5. From [1,1-$^2H_2$]-1-bromo-*n*-decane with 1-hexynyl-Li (cf. Ref. 7). Yield: 45%. Mass spectrum: *m/z* 224 ($[M]^+$). NMR: 2.16 (t, 6 Hz, 2 H), 1.2–1.9 (m, 20 H), 0.89 (2 t, 6 H). IR: 2926, 2853, 2186 and 2096 (C—D), 1462, 721 cm^{-1}.

[7,7-$^2H_2$]-*n*-Hexadecene-5. From [7,7-$^2H_2$]-*n*-hexadecyne-5 by Lindlar hydrogenation (cf. Ref. 8). Yield: 91%. Isotopic purity: 98%. Mass spectrum: *m/z* 226

($[M]^+$). NMR: 5.37 (br.t, part of an ABX_2 system, 2 H), 2.03 (m, 4 H), 1.27 (br.s, 18 H), 0.87 (2 t, 6 H). IR: 3004, 2950, 2921, 2853, 2189, and 2096 (C—D), 1463, 720 cm^{-1}.

[1,1-$^2H_2$]-*n*-Undecan-1-ol. From *n*-undecanoic acid ethyl ester with $LiAlD_4$. Yield: 98%. Mass spectrum: *m/z* 156 ($[M-H_2O]^{+\cdot}$). IR: 3332, 2925, 2856, 2196 and 2092 (C—D), 1466, 1134, 1098, 969.

[1,1-$^2H_2$]-1-Bromo-*n*-undecane. From [1,1-$^2H_2$]-*n*-undecan-1-ol and PBr_3 (cf. Ref. 6). Purification by distillation. Yield: 56%. B.p.: 130 °C (13 Torr). Mass spectrum: *m/z* 236/38 (0.3%, $[M]^+$), 165/67 (0.5%), 151/53 (7%), 137/39 (46%).

[3,3-$^2H_2$]-*n*-Tridecan-1-ol. From [1,1-$^2H_2$]-1-bromo-*n*-undecane by a Grignard reaction with ethylene oxide (cf. Refs 9, 10). Yield: 44%. M.p.: 32 °C. Mass spectrum: *m/z* 184 ($[M-H_2O]^{+\cdot}$).

[3,3-$^2H_2$]-*n*-Tridecanal. From [1,1-$^2H_2$]-*n*-tridecan-1-ol by oxidation with CrO_3 and pyridine in CH_2Cl_2 (cf. Ref. 11). Yield: 77%. Mass spectrum: *m/z* 200 ($[M]^+$). NMR: 9.87 (t, 3 Hz, 1 H), 2.42 (br.d., 2 H), 1.28 (br.s, 18 H), 0.89 (t, 6 Hz, 3 H). IR: 2929, 2858, 2725, 2190 and 2067 (C—D), 1720, 1469, 758 cm^{-1}.

[8,8-$^2H_2$]-*n*-Octadecene-5. From [3,3-$^2H_2$]-*n*-tridecanal with a Wittig reagent prepared from *n*-$C_5H_{11}Br$ (cf. Ref. 12). Yield: 40%. Isotopic purity: 100%. Mass spectrum: *m/z* 254 ($[M]^+$). NMR: 5.38 (m, 2 H), 2.03 (br.s, 4 H), 1.23 (br.s, 22 H), 0.9 (2 t, 6 H). IR: 3008, 2957, 2925, 2853, 2183 and 2103 (C—D), 1467, 720 cm^{-1}.

[3,3$^2H_2$]-*n*-Dodecan-1-ol. From [1,1-$^2H_2$]-1-bromo-*n*-decane by a Grignard reaction with ethylene oxide (cf. Refs 9, 10). Yield: 45%. M.p. 26 °C. Mass spectrum *m/z* 170 ($[M-H_2O]^{+\cdot}$).

[3,3-$^2H_2$]-1-Bromo-*n*-dodecane. From [3,3-$^2H_2$]-*n*-dodecan-1-ol and PBr_3 (cf. Ref. 6). Purification by distillation. Yield: 44%. B.p.: 141 (11 Torr). Mass spectrum: *m/z* 250/52 (0.2%, $[M]^+$), 151/53 (5%), 137/39 (36%). NMR: 3.40 (t, 7.5 Hz, 2 H), 1.87 (br.t, 7.5 Hz, 2 H), 1.23 (br.s, 16 H), 0.88 (t, 2 Hz, 3 H).

[4,4-$^2H_2$]-*n*-Tridecanal. From [3,3-$^2H_2$]-1-bromo-*n*-dodecane by a Grignard reaction with HC $(OC_2H_5)_3$ (cf. Ref. 13). Yield: 43%. Mass spectrum: *m/z* 200 (0.4%, $[M]^+$), *m/z* 45 (47%, McLafferty rearrangement with D transfer). NMR: 9.83 (t, 3 Hz, 1 H), 2.43 (dt, 3 Hz, 7.5 Hz, 2 H), 1.63 (br.t, 7.5 Hz, 2 H), 1.23 (br.s, 16 H), 0.87 (t, 6 Hz, 3 H). IR: 2925, 2852, 2716, 2173 and 2100 (C—D), 1728, 1467, 758.

[9,9-$^2H_2$]-*n*-Octadecene-5. From [4,4-$^2H_2$]-*n*-tridecanal with a Wittig reagent prepared from *n*-$C_5H_{11}Br$ (cf. Ref. 12). Isotopic purity: 100%. Mass spectrum: *m/z* 254 ($[M]^+$). IR: 3007, 2957, 2926, 2854, 2177 and 2100 (C—D), 1467, 720.

5-Keto-*n*-tridecan-1-ol. By reaction of *n*-octyllithium (from 1-bromo-*n*-octane[14]) with δ-valerolactone (cf. Refs 15, 16). Yield: 71%. M.p. 42–46 °C. Mass spectrum: *m/z* 214 ($[M]^+$). NMR: 3.63 (t, 6 Hz, 2 H), 2.4 (2 t, 4 H), 1.2–1.85 (m, 17 H), 0.89 (t, 6 Hz, 3 H). IR: 3442, 2925, 2855, 1709, 1455, 1410, 1375, 1059, 721.

[5,5-$^2H_2$]-*n*-Tridecan-1-ol. From 5-keto-*n*-tridecan-1-ol by reduction (cf. Ref. 17) of the tosyl hydrazone (cf. Ref. 18) with $LiAlD_4/D_2O$. Yield: 29%. Mass spectrum: *m/z* 183/184 ($[M-HDO/H_2O]^{+\cdot}$).[19] IR: 3349, 2927, 2856, 2176 and 2100 (C—D), 1463, 1059 cm^{-1}.

[5,5-$^2H_2$]-*n*-Tridecanal. From [5,5-$^2H_2$]-*n*-tridecan-1-ol by oxidation with CrO_3 and pyridine in CH_2Cl_2 (cf. Ref. 11). Yield: 76%. Mass spectrum: *m/z* 200 ($[M]^+$). NMR: 9.8 (t, 3 Hz, 1 H), 2.43 (dt, 3 and 7.5 Hz, 2 H), 1.2–1.85 (m, 18 H), 0.87 (t, 6 Hz, 3 H). IR: 2920, 2854, 2714, 2173 and 2095 (C—D), 1725, 1461, 756 cm^{-1}.

[10,10-$^2H_2$]-*n*-Octadec-5-ene. From [5,5-$^2H_2$]-*n*-tridecanal with a Wittig reagent prepared from *n*-$C_5H_{11}Br$ (cf. Ref. 12). Yield: 46%. Isotopic purity: 88% d_2, 12% d_1. Mass spectrum: *m/z* 254 ($[M]^+$). NMR: 5.38 (m, 2 H), 2.03 (m, 4 H), 1.26 (br.s, 22 H), 0.88 (2 t, 6 H). IR: 3003, 2919, 2851, 2173 and 2904 (C—D), 1460, 718 cm^{-1}.

6-Keto-*n*-tridecan-1-ol. By reaction of *n*-heptyllithium with ε-caprolactone (cf. Refs 15, 16). Yield: 83%. M.p.: 33–36 °C. Mass spectrum: *m/z* 214 ($[M]^+$). NMR: 3.63 (t, 6 Hz, 2 H), 2.38 (2 t, 4 H), 1.2–1.8 (m, 17 H), 0.87 (t, 6 Hz, 3 H). IR: 3373, 2935, 2858, 1724, 1463, 1057 cm^{-1}.

[6,6-$^2H_2$]-*n*-Tridecan-1-ol. From 6-keto-*n*-tridecan-1-ol by reduction (cf. Ref. 17) of the tosyl hydrazone (cf. Ref. 18) with $LiAlD_4/D_2O$. Yield 27:%. Mass spectrum: *m/z* 184 ($[M-H_2O]^{+\cdot}$). IR: 3444, 2925, 2853, 2173 and 2095 (C—D), 1463, 1052 cm^{-1}.

[6,6-$^2H_2$]-*n*-Tridecanal. From [6,6-$^2H_2$]-*n*-tridecan-1-ol by oxidation with CrO_3 and pyridine in CH_2Cl_2 (cf. Ref. 11). Yield: 77%. Mass spectrum: *m/z* 200 ($[M]^+$). NMR: 9.87 (t, 3 Hz, 1 H), 2.43 (dt, 3 and 7.5 Hz, 2 H), 1.2–1.8 (m, 18 H), 0.88 (t, 6 Hz, 3 H), IR: 2921, 2854, 2714, 2174 and 2095 (C—D), 1726, 1461 cm^{-1}.

[11,11-$^2H_2$]-*n*-Octadecene. From [6,6-$^2H_2$]-*n*-tridecanal with a Wittig reagent prepared from *n*-$C_5H_{11}Br$ (cf. Ref. 12). Yield: 36%. Isotopic purity: 91% d_2, 9% d_1. Mass spectrum: *m/z* 254 ($[M]^+$). NMR: 5.37 (m, 2 H), 2.03 (m, 4 H), 1.25 (br.s, 22 H), 0.9 (2 t, 6 H). IR: 3004, 2919, 2851, 2172 and 2095 (C—D), 1460, 720.

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