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The synthesis and characterization *N*-methyl-3-phenyl-norbornan-2-amine (Camfetamine™)

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***N*-Methyl-3-phenyl-norbornan-2-amine (*N*-methyl-3-phenylbicyclo[2.2.1]heptan-2-amine, Camfetamine™) is available from a number of online legal highs/research chemicals' vendors. Although it was developed as an analeptic by Merck in the early 1960s, it was never commercialized. However, the Association of Independent Research Chemical Retailers (AIRCR), an umbrella organization for a number of online vendors, has redeveloped it for use as a recreational drug. *N*-Methyl-3-phenyl-norbornan-2-amine is closely related to fencamfamine which has been widely used as a central nervous system (CNS) stimulant and appetite suppressant. In this paper we describe the synthesis of *N*-methyl-3-phenyl-norbornan-2-amine, its characterization and interpretations of its electron impact, and electrospray ionization mass spectra. Copyright © 2012 John Wiley & Sons, Ltd.**

Keywords: camfetamine; synthesis; mass spectrum

Introduction

N-methyl-3-phenyl-norbornan-2-amine (*N*-methyl-3-phenylbicyclo [2.2.1]heptan-2-amine, Camfetamine™) (Figure 1, (**5**)) is available from a number of online legal highs/research chemicals vendors, all of which are reportedly members of the Association of Independent Research Chemical Retailers (AIRCR).[1–3] The AIRCR website has recently become unavailable (November 2011) but when it was active, it listed N-methyl-3-phenyl-norbornan-2-amine as one of its custom projects.[4] The compound was patented in 1961 by E. Merck, Darmstadt, for use as a central nervous system (CNS) stimulant and its synthesis was also described by a group in Smith Kline and French Laboratories in 1961 when it was prepared as part of a study to elucidate the stereochemistry of 3-phenylnorbornan-2-amine.[5,6] Acetanilide derivatives of *N*-methyl-3-phenyl-norbornan-2-amine have also been reported to possess analgeic acitivity.[7] Apart from these reports, little is known about this compound.

However, the *N*-ethyl analogue of 3-phenyl-norbornan-2-amine, fencamfamine, is better known and has been sold under the trade name Reactivan™.[8] Fencamfamine has been shown to be a dopamine re-uptake inhibitor and also enhances dopamine release and was primarily used as an appetite suppressant. It is listed in Schedule IV of the UN Convention on Psychotropic Substances but the quantities being manufactured have reportedly been small recently.[9,10] However, *N*-methyl-3-phenyl-norbornan-2-amine is not listed.

Little is known about the pharmacology and toxicology of *N*-methyl-3-phenyl-norbornan-2-amine but it may be expected to have similar properties to fancamfamine. However one interesting point to note is that *N*-methyl-3-phenyl-norbornan-2-amine is potentially less lipophilic (calculated log D (pH 7.4) = −0.01 whereas the value fencamfamine is 0.31) and this may result in lower bioavailability across the blood brain barrier.[11] However, users discussing the effects of *N*-methyl-3-phenyl-norbornan-2-amine on popular drugs forums have reported that it produces euphoric effects.[12,13]

The appearance of a new recreational drug always poses the problem of obtaining an authentic reference standard for use in forensic analysis. It may be a case that *N*-methyl-3-phenyl-norbornan-2-amine is a standalone drug but if analogues were to be synthesized, they would most likely be substituted phenyl ring derivatives. Bearing this in mind, it was important to keep any methodologies for the syntheses of reference standards flexible enough to facilitate the preparation of potential analogues.

An examination of existing literature provided us with methodologies for the synthesis of *N*-methyl-3-phenyl-norbornan-2-amine and we have modified these procedures to (1) avoid processes such as distillation of small volumes of intermediates and (2) use milder conditions (Figure 1). However, one disadvantage of older published synthetic methods is that mass spectrometric data is absent. This was the case with *N*-methyl-3-phenyl-norbornan-2-amine for us, as we were aware of the potential for it to be encountered in drugs seizures but none of the published methods for its synthesis contained mass spectrometric data to facilitate an initial identification. In this paper, we describe the synthesis of *N*-methyl-3-phenyl-norbornan-2-amine, its characterization and an interpretation of its

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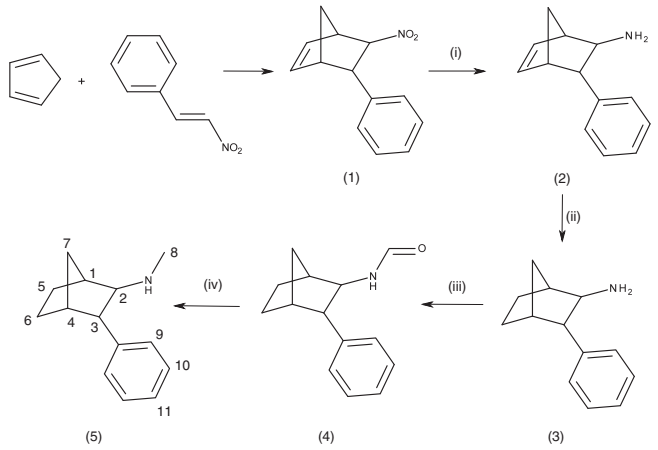

Figure 1. Synthetic scheme for the preparation of *N*-methyl-3-phenyl-norbornan-2-amine.

electron impact (EI) and electrospray (ES) ionization mass spectra. The use of various substituted nitrostyrene starting materials will facilitate the preparation of phenyl-substituted analogues.

Experimental

Chemicals

Dicyclopentadiene (cat. no. 454338), *trans*-β-nitrostyrene (99%, cat. no. N26806), triethylsilane (97%, 467448), anhydrous THF (cat. no. 401757), palladium on charcoal (cat. no. 75993), ethyl formate (97%, cat. no. 112682), granulated tin (99%, cat. no. 14507) and lithium aluminium hydride (95%, cat no.199877) were obtained from Sigma Aldrich (Arklow, Wicklow, Ireland). Acetonitrile (liquid chomatograph-mass spectrometry (LC-MS) grade), dichloromethane and methanol (both high performance liquid chromatography (HPLC) grade) were obtained from Fisher Scientific (Dublin, Ireland). Cyclopentadiene was prepared by heating dicyclopentadiene to approximately 200 °C (heating mantle) in a fractional distillation assembly. The distillate coming over at 40–50 °C was collected in a flask cooled in a ice bath and used immediately.

Instrumentation

^{1}H (600 MHz) and ^{13}C (150 MHz) spectra were recorded on a Bruker AV600 NMR spectrometer using a 5-mm TCI cryoprobe. High resolution electrospray mass spectra (HR-ESIMS) were recorded on by direct injection on an LTQ Orbitrap Discovery (Thermo Fisher, Bremen, Germany). Melting points are uncorrected.

GC-EIMS under the following conditions: Agilent 6890 gas chromatograph with a HP-ULTRA 1 capillary column (12 m x 0.2 mm x 0.33 μm). Helium (He) was used as the carrier gas at a flow rate of 1.0 ml/min. The injector port was set at 250 °C and the transfer line at 280 °C. The following temperature program was used: 100 °C for 1 min, 9 °C/min to 180 °C, 180 °C for 2 min, 25 °C/min to 295 °C and 295 °C for 2 min. The GC was coupled to an Agilent 5975 MSD (EI, 70 eV, TIC mode scanning *m/z* 40–450). Samples for gas chromatography–mass spectrometry (GC-MS) analysis were dissolved in methanol.

LC-ESIMS was performed on Agilent 1100 LC system (column – Allure PFP Propyl, 5 μm, 50 x 2.1 mm (Restek, Bellefonte, PA, USA); eluent A – acetonitrile containing 0.05% formic acid; eluent B – water containing 0.1% formic acid coupled to an Agilent LC-MSD (positive electrospray ionization mode, capillary voltage 3,000 V, drying gas (N_2) 12 l/min at 350 °C, nebulizer pressure 60 psig, *m/z* 50–500). Samples for LC-MS analysis were dissolved in acetonitrile/water (1/1, containing 0.1% formic acid) at a concentration of 5 μg/ml (2 μl injected). The following mobile phase was 12% A (0–5 min) followed by a linear gradient up to 35% A at 30 minutes at a flow rate of 1000 μl/min and column temperature of 30 °C. The fragmentor voltage was adjusted as required (70–130 V).

Raman spectroscopy was performed on a Horiba Jobin Yvon (Dilor Jobin Yvon Spex) spectrometer (laser line: 514 nm, argon ion laser; filter: 100%; hole: 900 μm; slit: 900 μm; spectrometer arbitrarily set at 3000 cm^{-1}; grating: 1800; objective: x20; exposure time: 15 s; accumulation number: 3 s). The infra-red spectrum (KBr disc) was recorded on a Nicolet 380 FTIR instrument.

3-Phenylbicyclo[2.2.1]hept-5-en-2-amine (2)

A mixture of cyclopentadiene (23 g) and β-nitrostryene (8 g, 13.4 mmol) was refluxed for 3 h, allowed to cool to room temperature, and left stirring overnight. The clear yellow solution was

Table 1. ^{1}H NMR data *N*–methyl–3–phenyl–norbornan–2–amine

	Hydrochloride salt (d_6 DMSO)				Free base ($CDCl_3$)			
Position	^{1}H(ppm)	No. H	Multiplicity	J (Hz)	^{1}H(ppm)	No. H	Multiplicity	J (Hz)
1	2.14–2.17	1	m	–	2.46	1	m	–
2	3.64–3.68	1	dd	5, 5	3.07	1	ddd	5, 5, 2
3	2.77	1	dd	5, 2	2.18	1	dd	5, 2
4	2.64–2.69	1	m	–	2.30	1	m	–
5	1.60–1.67	2	m	–	1.71–1.83 (m, 2 H, one H from H–6 and H–7b), 1.59–1.70			
6	1.49–1.57 and 1.78–1.85	each 1	2 x m	–	(m, 1H, one H from H–5) and 1.41–1.51 (m, 2 H, one H each from H–5 and H–6)			
7a	1.33	1	d	9	1.37	1	dddd	10, 2, 2, 2
7b	1.73	1	d	9	See above			
8	–	–	–	–	–	–	–	–
9	7.33–7.38	4	m	–	7.28–7.36	4	m	–
10								
11	7.22–7.27	1	m	–	7.19.7.24	1	m	–
12	2.41	3	s	–	2.36	3	s	–

Table 2. ^{13}C NMR data *N*-methyl-3-phenyl-norbornan-2-amine

Position	Hydrochloride salt (d_6 DMSO) ^{13}C (ppm)	Free base ($CDCl_3$) ^{13}C (ppm)
1	38.73	39.29
2	65.80	70.24
3	51.07	55.92
4	45.70	44.12
5	30.03	31.96
6	21.01	20.21
7	35.72	36.29
8	143.62	146.20
9	128.86	128.38
10	127.57	127.05
11	126.79	125.84
12	32.35	35.27

then added to a mixture of glacial acetic acid (60 ml) and granulated tin (15 g), and refluxed for 1 h. The cooled supernatant was added to water (400 ml), made basic with aqueous 5 M sodium hydroxide, and extracted with dichloromethane. The combined dichloromethane extracts were washed with aqueous hydrochloric acid. The hydrochloric acid extract was then washed with dichloromethane, made basic with aqueous 5 M sodium hydroxide and extracted with dichloromethane. Drying ($MgSO_4$) and removal of the solvent afforded a yellow oil (4.18 g, 22.7 mmol, 42%): ^{1}H NMR ($CDCl_3$) δ 7.37-7.31 (m; 4 H; Ar-H), 7.24-7.19 (m; 1 H; Ar-H), 6.59 (dd; J = 6, 3 Hz; 1 H; H-5), 6.27 (dd; J = 6, 3 Hz; 1 H; H-6), 3.48 (dd, J = 5, 5 Hz; 1 H; H-2), 2.96-2.93 (m; 1 H; H-4), 2.93-2.90 (m; 1 H; H-1), 2.19 (m; 1 H; H-3), 1.85 (d; J = 9 Hz; 1 H, one H from H-7) and 1.63 (d; J = 9 Hz; 1 H, one H from H-7); ^{13}C NMR ($CDCl_3$) δ 144.33 (C-8), 140.49 (C-5), 133.21 (C-6), 128.31 (C-9), 127.06 (C-10), 125.77 (C-11), 60.71 (C-2), 55.77 (C-3), 49.11 (C-1), 48.83 (C-4) and 46.80 (C-7); EIMS m/z (%) 167 (1), 152 (2), 128 (2), 119 (100), 104 (3), 91 (14) and 77 (5); HR-ESIMS found 186.1273 (theor. for M + H, $C_{13}H_{16}N$, 186.1277).

3-Phenylbicyclo[2.2.1]heptan-2-amine (3)

A mixture of the amine **(2)** (1.50 g, 8.1 mmol), methanol (10 ml), triethylsilane (10 ml) and Pd-C (250 mg 10% Pd, Aldrich product no. 75993) was stirred under nitrogen at room temperature overnight. The mixture was then filtered through Celite and evaporated to dryness. The residue was dissolved in dichloromethane and extracted with aqueous hydrochloric acid. The hydrochloric acid extract was made basic with aqueous 5 M sodium hydroxide and extracted with dichloromethane. Drying ($MgSO_4$) and removal of the solvent afforded a colourless oil (981 mg, 5.2 mmol, 64%): ^{1}H NMR ($CDCl_3$) δ 7.36-7.28 (m; 4 H; Ar-H), 7.24-7.19 (m; 1 H; Ar-H), 3.28 (dd, J = 5, 5 Hz; H-2), 2.42-2.37 (m; 1 H; H-3), 2.29-2.25 (m; 1 H; H-4), 2.14-2.11 (m; 1 H; H-1), 1.89-1.83 (m; 1 H; one H from H-6), 1.81 (d; J = 9 Hz; one H from H-7), 1.74-1.66 (m; 1 H, one H from

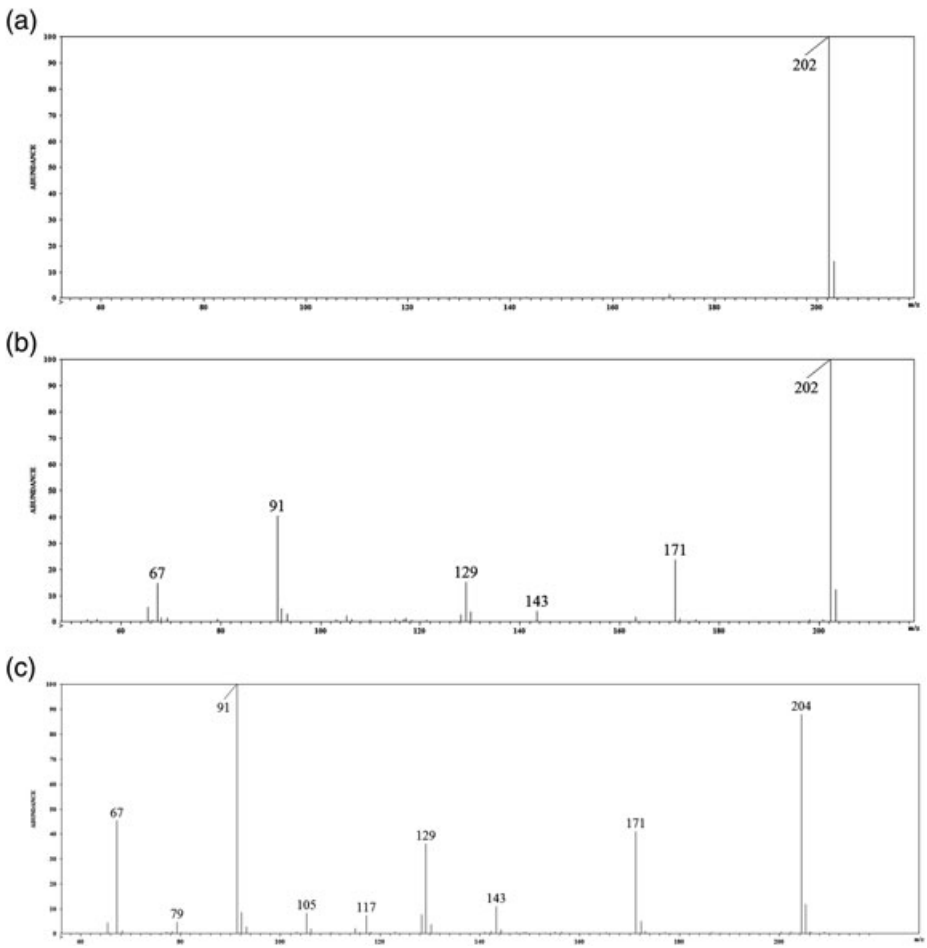

Figure 2. Electrospray ionization mass spectra for *N*-methyl-3-phenyl-norbornan-2-amine (a). 70 V, (b). 130 V, (c). 130 V using deuterated solvents.

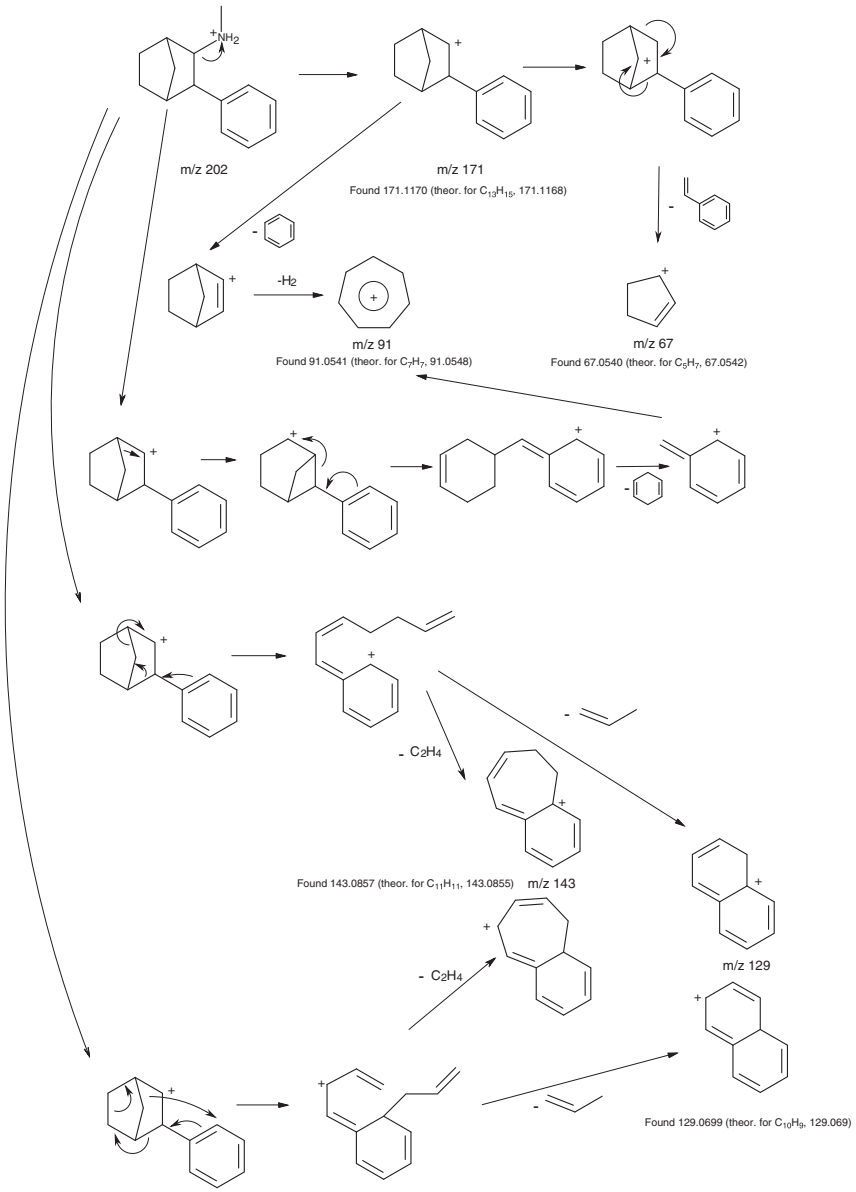

Figure 3. Possible electrospray ionization (130 V) fragmentation pathways for *N*-methyl-3-phenyl-norbornan-2-amine.

H-5), 1.55-1.50 (m; 1 H; one H from H-6), 1.50-1.44 (m; 1 H; one H from H-5) and 1.40 (d; J = 9 Hz; one H from H-7); ^{13}C NMR ($CDCl_3$) δ 145.78 (C-8), 128.28 (C-9), 126.59 (C-10), 125.99 (C-11), 62.64 (C-2), 57.65 (C-1), 43.57 (C-3), 43.08 (C-4), 36.82 (C-7), 31.27 (C-5), and 19.91 (C-6); EIMS m/z (%) 187 (100, $M^{+\cdot}$), 170 (21), 158 (46), 142 (19), 129 (19), 118 (20), 115 (32), 96 (27), 91 (52), 82 (21) and 77 (18); HR-ESIMS found 188.1433 (theor. for M + H, $C_{13}H_{18}N$,188.1434).

N-Methyl-3-phenylbicyclo[2.2.1]heptan-2-amine hydrochloride (5)

A mixture of 3-phenylbicyclo[2.2.1]heptan-2-amine **(3)** (0.98 g, 5.2 mmol) and ethyl formate (4.5 ml) was refluxed for 6 h and then left stirring overnight at room temperature. The mixture was then evaporated to dryness, the residue dissolved in dichloromethane and washed with aqueous hydrochloric acid (1 M) followed by aqueous sodium hydroxide (1 M). Drying ($MgSO_4$) and removal of the solvent afforded a colourless oil (700 mg). This was dissolved in THF (5 ml) and slowly added to a suspension of lithium aluminium hydride (250 mg) in THF (10 ml) at room temperature. The mixture was then refluxed for 2 h. The mixture was allowed to cool to room temperature, quenched with water and the THF was removed under vacuum. The residue was partitioned between dichloromethane and water. The dichloromethane layer was then extracted with hydrochloric acid (1 M). The aqueous layer was then made basic and extracted into dichloromethane. Drying ($MgSO_4$) and removal of the solvent afforded a colourless oil which was converted to the hydrochloride salt with ethereal hydrogen chloride (2 M) to afford a colourless solid (331 mg, 1.4 mmol, 42%): m. pt. 191-3 °C (lit. 198 °C[3]) ^{1}H NMR (Table 1); ^{13}C NMR (Table 2); EIMS *m/z* (%); HR-ESIMS found 202.1587 (theor. for M + H, $C_{14}H_{20}N$, 202.1590).

Results and discussion

N-methyl-3-phenyl-norbornan-2-amine was synthesized as shown in Figure 1. Cyclopentadiene was prepared by a retro-Diels Alder

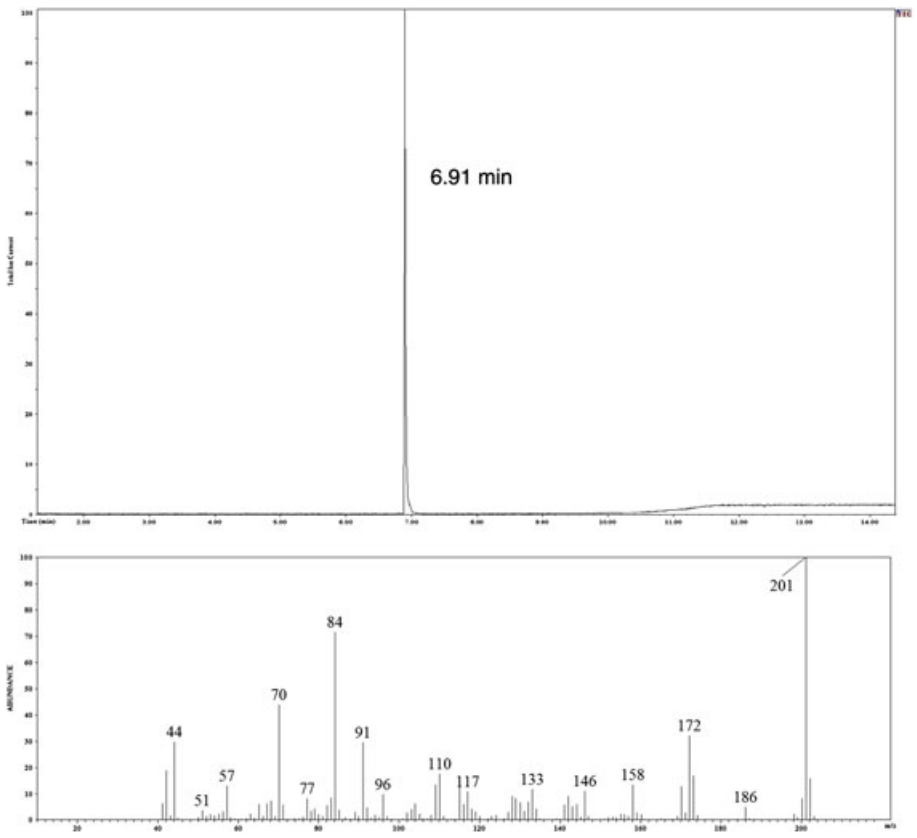

Figure 4. TIC and electron impact mass spectrum for *N*-methyl-3-phenyl-norbornan-2-amine.

reaction from dicyclopentadiene and was used immediately as it quickly reverts back to the dimer on standing. The Diels Alder adduct formed by reacting *trans*-β-nitrostyrene with cyclopentadiene was not isolated but carried through to a reduction to with granulated tin and acetic acid to afford 3-phenylbicyclo[2.2.1]hept-5-en-2-amine **(2)** as a yellow oil in 42% yield.[6] Reduction with triethylsilane and palladium on charcoal proceeded smoothly, affording 3-phenylbicyclo[2.2.1]heptan-2-amine **(3)** as a colourless oil in 64% yield.[14] The use of this Catalytic Transfer Hydrogenation (CTH) protocol eliminated the need for the potentially more dangerous hydrogen gas.

It was found difficult to achieve mono *N*-methylation in a single step but a combination of formylation with ethyl formate and subsequent reduction with lithium aluminium hydride proved to be successful giving N-methyl-3-phenyl-norbornan-2-amine (N-methyl-3-phenylbicyclo[2.2.1]heptan-2-amine) hydrochloride as a colourless solid in 7% overall yield from *trans*-β-nitrostyrene.[6]

Analysis by ^{1}H and ^{13}C NMR (Tables 1 and 2) indicated that the ratio of 2-*endo*-(methylamino)-3-*exo*-phenyl: 2-*exo*-(methylamino)-3-*endo*-phenyl isomers in the final product was 7:1 based on the integration signals from the H-3 hydrogens in both isomers. This is as expected as the *endo*-nitro-*exo*-phenyl isomer has been reported to be major Diels Alder adduct formed by reacting β-nitrostyrene with cyclopentadiene and subsequent synthetic steps would not be expected to alter this stereochemistry.[6,15,16]

In the ^{1}H NMR spectrum (free base in $CDCl_3$), the hydrogens on the 2 and 3 positions for the 2-*endo*-(methylamino)-3-*exo*-phenyl isomer are observed as a double double doublet (3.07 ppm, $J_{H\text{-}2,\ H\text{-}1} = 5$ Hz, $J_{H\text{-}2,\ H\text{-}3} = 5$ Hz and $J_{H\text{-}2,\ H\text{-}6a} = 2$ Hz) and double doublet (2.18 ppm, $J_{H\text{-}3,\ H\text{-}2} = 5$ Hz and $J_{H\text{-}3,\ H\text{-}7a} = 2$ Hz), respectively. This is consistent in terms of δ values and coupling constants with previously reported data for the 2-*endo*-3-*exo* isomer of fencamfamine (H-2, 3.15 ppm, $J_{H\text{-}2,\ H\text{-}1} = 5$ Hz, $J_{H\text{-}2,\ H\text{-}3} = 5$ Hz and $J_{H\text{-}2,\ H\text{-}6a} = 2$ Hz and H-3, 2.15 ppm, $J_{H\text{-}3,\ H\text{-}2} = 5$ Hz and $J_{H\text{-}3,\ H\text{-}7a} = 2$ Hz).[14] The H-2 and H-3 hydrogens in the 3-exo-2-endo isomer are at markedly different resonances and have been reported to be both double doublets at 2.75 and 2.85 ppm. In the ^{1}H NMR spectrum of the *N*-methyl-3-phenyl-norbornan-2-amine synthesized as above, these hydrogens were observed as a multiplet at 2.78–2.85 ppm.

In the ^{13}C NMR spectrum, carbons C-5 and C-6 were observed at 31.96 and 20.21 ppm which is again consistent with the major isomer being 2-*endo*-3-*exo*. It has been previously reported that C-5 and C-6 resonances occur at 31.38 and 20.24 ppm for the 2-*endo*-3-*exo* isomer of fencamfamine whereas as the values for 2-*exo*-3-*endo* isomer are 22.21 and 27.37 ppm, respectively.[17] An attempt to separate the isomers by thin layer chromatography proved unsuccessful and it was not possible to obtain complete NMR data for the minor 2-*exo*-methylamino-3-*endo*-phenyl isomer.

Also, it was not possible to separate the 2-*endo*-methylamino-3-*exo*-phenyl and 2-*exo*-methylamino-3-*endo*-phenyl isomers by GC or LC. However, analysis by LC-MS revealed that the final mixed isomer product was approximately 97% pure. The electrospray ionization mass spectrum showed the expected M + H peak at *m/z* 202. Increasing the fragmentor voltage from 70 V to 130 V lead to the formation of fragment ions m/z 171, 143, 129, 91 and 67 (Figure 2). The mass ion 171 arises from loss of methylamine whereas *m/z* 143, 129, and 67 may be dihydrobenzoannulenylium, dihydronaphthalenylium and cyclopentenylium ions, respectively (Figure 3). Formula assignment for each fragment was made by means of accurate mass measurement. The sample was run using

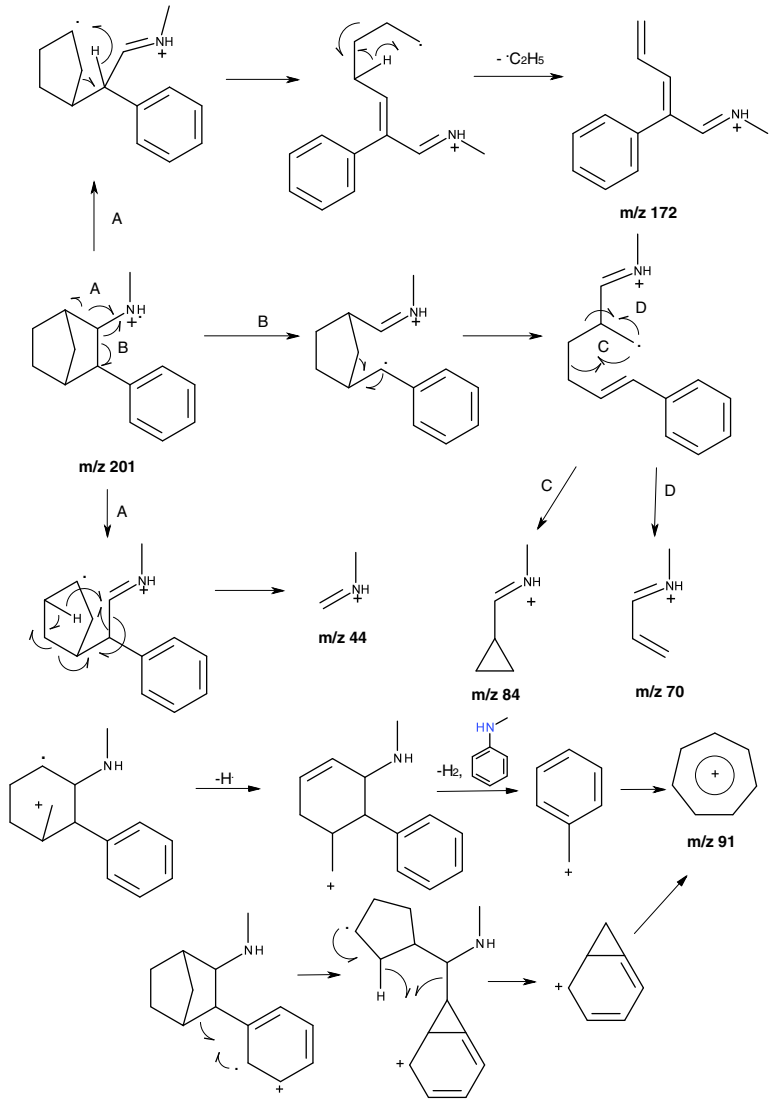

Figure 5. Possible electron impact ionization fragmentation pathways for *N*-methyl-3-phenyl-norbornan-2-amine.

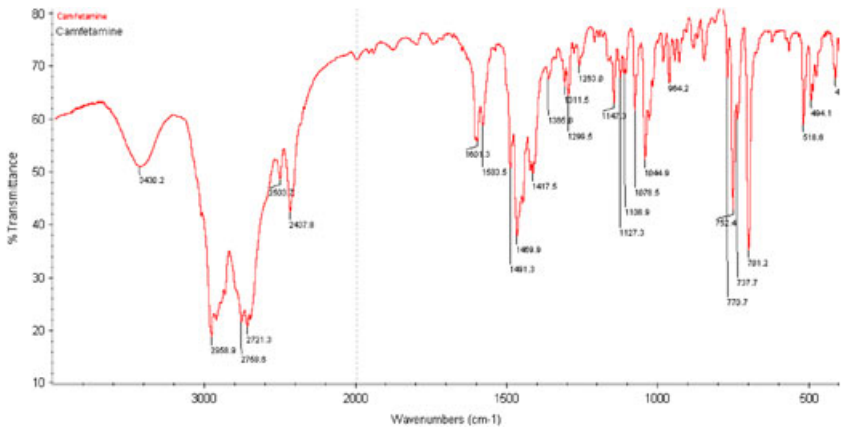

Figure 6. Infra-red spectrum of *N*-methyl-3-phenyl-norbornan-2-amine hydrochloride.

deuteriated solvents which resulted in an expected $[M+D]^+$ of 204 Daltons as the labile amine hydrogens undergo D-H substitution.

The EI mass spectrum of N-methyl-3-phenyl-norbornan-2-amine is shown in Figure 4. The compound produces a reasonably strong molecular ion and *m/z* 172 arises through loss of an ethyl radical (Figure 5). Three characteristic imminim ions, cyclopropyl-N-methylmethaniminium (*m/z* 84, base peak), N-methylprop-2-en-1-iminium (*m/z* 70) and N-methylmethaniminium (*m/z* 44) are also

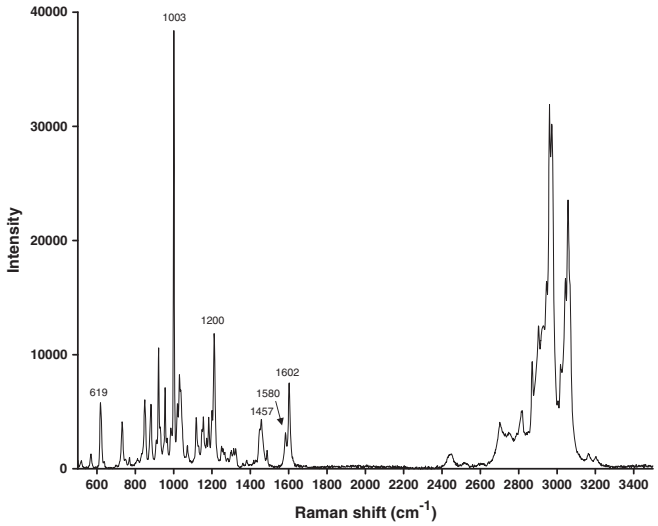

Figure 7. Raman spectrum of *N*-methyl-3-phenyl-norbornan-2-amine hydrochloride.

observed. Overall the EI mass spectrum is quite characteristic with the bicyclic hydrocarbon structure contributing significantly to the fragmentation, a feature that has been noted with similar compounds.[18,19] In the absence of a reference standard, *N*-methyl-3-phenyl-norbornan-2-amine should be readily identifiable from its mass spectrum.

The IR spectrum is shown in Figure 6. An aliphatic stretching band is observed at 2959 cm^{-1}. The bands at 2510 and 2437 cm^{-1} may be due to NH_2^+ symmetric and asymmetric stretching as the product is a hydrochloride salt.[20] The bands at 1607 and 1471 cm^{-1} can be assigned to aromatic ring vibrations. Aromatic bending bands, characteristic of a mono-substituted benzene ring are seen at 752 and 700 cm^{-1}. The Raman spectrum (Figure 7) displays a very characteristic strong band at 1003 cm^{-1} arising from aromatic ring breathing. Bands at 1602 and 1580 cm^{-1} are characteristic of aromatic ring quadrant stretching and one at 619 cm^{-1} can be assigned to an aromatic ring in-pane deformation. Bands at 1457 and 1200 cm^{-1} may arise from CH_2 deformations within the norbornane structure and an Ar-C vibration, respectively.[21,22]

Conclusion

We have synthesized *N*-methyl-3-phenyl-norbornan-2-amine hydrochloride as a colourless solid in 7% overall yield from *trans*-β-nitrostyrene. Analysis by ^1H and ^{13}C NMR indicated the ratio of 2-*endo*-(methylamino)-3-*exo*-phenyl: 2-*exo*-(methylamino)-3-*endo*-phenyl isomers in the final product was 7:1. Possible fragmentation pathways for both the electron impact and electrospray ionization mass spectra are presented.

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