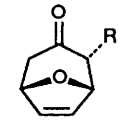
An Efficient Route to the Tropane Alkaloids

John Mann[a] **and Luiz-Claudio de Almeida Barbosa**[b]
[a] *Department of Chemistry, Reading University, Whiteknights, Reading RG6 2AD, UK*
[b] *Departamento de Quimica, Universidade Federal de Vicosa, 36570, Vicosa -MG, Brazil*

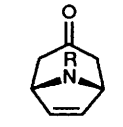
We describe the use of diethylzinc in conjunction with polybromo ketones for the production of oxyallyls, and the interception of these intermediates by furans and methyl pyrrole-*N*-carboxylate. This methodology allows the production of gramme quantities of tropane alkaloids, and 2-substituted 8-oxabicyclo[3.2.1]oct-6-en-3-ones that have been either difficult or impossible to prepare.

The use of oxyallyls for the production of a wide range of bicyclic products has been extensively reviewed.[1-3] None of the methods previously described allow access to simple 2-substituted-8-oxabicyclo[3.2.1]oct-6-en-3-ones **1**. In addition, 8-azabicyclo[3.2.1]oct-6-en-3-ones **2**, that are required for the synthesis of tropane alkaloids, can only be prepared[4] through the use of reactions involving an excess of 1,1,3,3-tetrabromoacetone and nonacarbonyldiiron. The former reagent is highly lachrymatory and the latter reagent is both expensive and toxic.

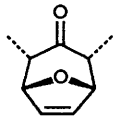
In this paper we describe new methodology that provides access to both classes of compounds on a multigramme scale.



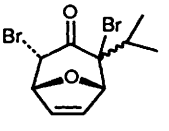
1 R = alkyl
5 R = H



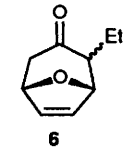
2 R = alkyl or CO_2alkyl



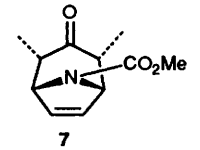
3



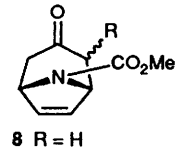
4



6

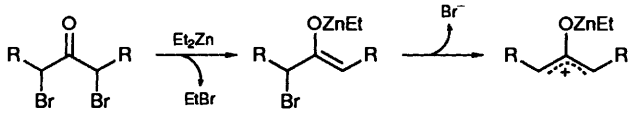


7



8 R = H
9 R = Et

Our rationale for this work was the proposal that diethylzinc would react with α,α'-dibromo ketones to produce oxyallyl carbocations *via* the mechanism shown in Scheme 1. In order to establish the validity of this proposal we treated 2,4-dibromopentan-3-one with diethylzinc and furan to produce 2,4-dimethyl-8-oxabicyclo[3.2.1]oct-6-en-3-one **3**. This reaction has hitherto been accomplished on the 0.1 mol dm^{-3} scale[5] using a mixture of copper and sodium iodide as reagents. The major product is always the diequatorial product (α,α), and this usually represents 80–90% of the isomer mixture. Using the new method (dibromopentanone, 1 equiv.; Et_2Zn, 1 equiv. of a 1 mol dm^{-3} solution in hexane; furan as solvent; 0 °C, 2 h, room temp., 25 h; 6 mmol scale) we obtained a 53% isolated yield of cycloadduct **3** (α,α:β,β 9:1). In addition, a considerable quantity of starting dibromo ketone was recovered and, allowing for this, the yield was in excess of 90%.

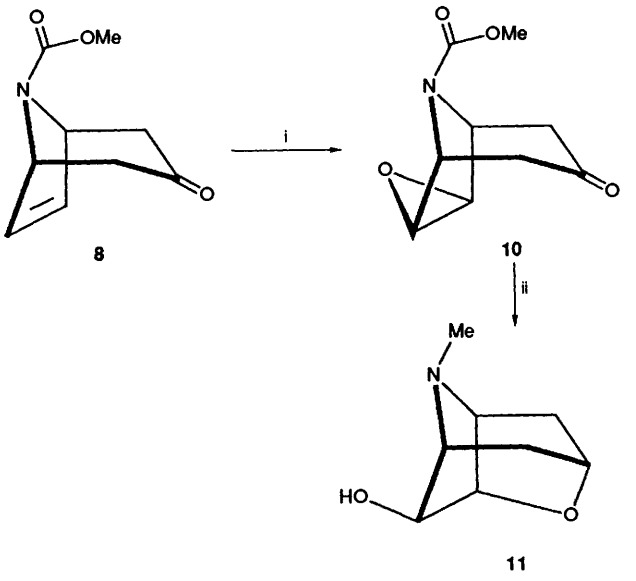


Scheme 1

Encouraged by this result, we used the same basic method with 1,1,3,3-tetrabromo-4-methylpentan-2-one (1 equiv.; Et_2Zn, 1 equiv.; furan, 20 equiv.; benzene, 0 °C–room temp., 6 h; 4 mmol scale) and obtained 2,4-dibromo-2-isopropyl-8-oxabicyclo-[3.2.1]oct-6-en-3-one **4** in an isolated yield of 52%. Since debromination is easily effected (Zn–Cu, MeOH, NH_4Cl),[6] this method allows easy access to oxabicycles of general structure **1**, which have hitherto only been available using Noyori's reaction protocol that involves nonacarbonyldiiron.[7] The parent oxabicycle **5** was produced on the multigramme scale (30 mmol scale) using the same methodology, in an isolated yield of 57%. This compares very favourably with other methods employing zinc–silver couple or nonacarbonyldiiron. In addition, around 9% of 2-ethyl-8-oxabicyclo[3.2.1]oct-6-en-3-one **6** was obtained as a mixture of stereoisomers. We believe that this is produced following formation of 1,1,3-tribromopentan-2-one by reaction of tetrabromoacetone and diethylzinc.

The reaction of 2,4-dibromopentan-3-one (1 equiv.), methyl pyrrole-*N*-carboxylate (1 equiv.), and diethylzinc (1 equiv.) in benzene (0 °C for 3 h, then room temp. for 17 h) provided a 55% isolated yield of the adduct methyl 2,4-dimethyl-3-oxo-8-azabicyclo[3.2.1]oct-6-ene-8-carboxylate **7**. Multigramme quantities of simple tropane alkaloid precursors could be prepared through the reaction of tetrabromoacetone (1 equiv.) and methyl pyrrole-*N*-carboxylate (1 equiv.) in the presence of Et_2Zn (1 equiv.) in benzene (0 °C–room temp., 22 h; 30 mmol scale), with subsequent debromination of the dibromocycloadduct to produce methyl 3-oxo-8-azabicyclo[3.2.1]oct-6-ene-8-carboxylate **8** in an isolated yield of 59%. This again compares extremely favourably with Noyori's work,[4] since although he obtained a similar yield of **8** (based upon the consumption of the pyrrole), a three-fold excess of both tetrabromoacetone and nonacarbonyldiiron had to be employed. Once again a small amount (around 7% yield) of the 2-ethyl analogue **9** was also produced.

Conversion of the adduct **8** into the tropane alkaloid scopoline[8] **11** was achieved *via* the route shown in Scheme 2. Formation of the epoxide **10** (83% isolated yield) was accomplished through reaction with *meta*-chloroperoxybenzoic acid, and this was reduced in a 'one-pot' process (excess DIBAL) to



Scheme 2 *Reagents, conditions and yields:* i, *m*CPBA, dichloromethane, room temp., 48 h, 83% yield; ii, DIBAH (10 equiv.), −78 °C 2 h, room temp. 22 h; 53% yield

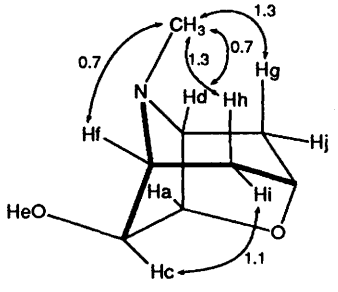


Fig. 1 Major NOE data for compound **11**

provide scopoline **11*** in 40–50% isolated yield on the multigramme scale. The scope of this interesting reaction, and of other more selective reductions, is being investigated.

Experimental

IR spectra were recorded with a Perkin-Elmer 881 double beam grating spectrophotometer. NMR spectra were recorded with a Perkin-Elmer R34 (220 MHz) instrument, a Bruker WH 400 spectrometer (400 MHz) at the University of Warwick or with a Varian T-60 (60 MHz) instrument, using tetramethylsilane as internal standard. *J* Values are given in Hz. Mass spectra were obtained at the University of Swansea using a VG ZAB-E high resolution spectrometer. Flash chromatography was performed using Crosfield Sorbil C60 (40–60 m). Solvents were purified according to Perrin, and light petroleum refers to the fraction with b.p. 40–60 °C, ether refers to diethyl ether.

2,4-*Dibromo*-2-*isopropyl*-8-*oxabicyclo*[3.2.1]*oct*-6-*en*-3-*one* **4**.—To an ice-cooled stirred solution of 1,1,3,3-tetrabromo-4-methylpentan-3-one (1.66 g, 4 mmol) and furan (5 cm^3, *ca.* 80 mmol) in dry benzene (80 cm^3) was added a 1 mol dm^{-3} solution of diethylzinc in hexane (4 cm^3, 4 mmol). The mixture was stirred at 0 °C for 3 h and at room temp. for a further 3 h. The reaction was quenched by addition of ethyl acetate (100 cm^3) and a saturated solution of Na_2EDTA (30 cm^3). The two layers were separated and the organic phase was washed with Na_2-EDTA solution (2 × 20 cm^3), brine (20 cm^3), dried ($MgSO_4$) and concentrated under reduced pressure to leave a brown residue. This residue was purified by flash chromatography (4:1 light petroleum–ether) to afford the required cycloadduct in a yield of 52.5% (680 mg, 2.1 mmol), as a mixture of two isomers (variable ratio). (It was observed that further reduction of this mixture using Zn–Cu couple yielded the α-isopropyl-8-oxabicyclo adduct as the sole product.) A pure sample of one of the isomers was obtained by fractional recrystallization of the mixture (ethyl acetate–light petroleum). TLC; R_f 0.4 (4:1, light petroleum–ether); 111–112 °C (white solid); $\nu_{max}(CHCl_3)/cm^{-1}$ 3021, 2972, 2880, 1731 (C=O), 1593 (C=C), 1469, 1390, 1128, 1104, 1050, 938 and 710; δ_H(250 MHz; $CDCl_3$) 1.03 (d, 3 H, *J* 6.5, CH_3), 1.23 (d, 3 H, *J* 6.5, CH_3), 1.95 [heptet, 1 H, *J* 6.5, $CH(CH_3)_2$], 5.06 (dd, 1 H, J_1 1.7, $J_{1,6}$ 0.4, 1-H), 5.14 (dd, 1 H, J_1 4.4, J_2 1.7, 5-H), 5.39 (d, 1 H, *J* 4.4, 4-H), 6.39 (dd, 1 H, J_1 6.1, J_2 1.7, 7-H) and 6.59 (d-br d, 1 H, J_1 6.1, J_2 1.7, 6-H); δ_C(62.5 MHz; $CDCl_3$) 17.90 (Me), 21.52 (Me), 32.29 (CH from isopropyl group), 53.47 (C-4), 77.96 (C-2), 82.64 (C-1), 84.64 (C-5), 132.48 (C-6), 134.30 (C-7) and 192.37 (C-3); *m/z* (%) 322/324/326 (M^+, 2%), 243/245 ([M − Br]$^+$, 55), 164 ([M − 2Br]$^+$, 100), 135(45) and 123(65); (Found: C, 37.25; H, 3.75; Br, 49.3. $C_{10}H_{12}Br_2O_2$ requires: C, 37.07; H, 3.73; Br, 49.32%).

8-*Oxabicyclo*[3.2.1]*oct*-6-*en*-3-*one* **5**.—To an ice-cooled stirred solution of tetrabromacetone (11.22 g, 30 mmol) and furan (20 cm^3, *ca.* 720 mmol) in dry benzene (600 cm^3), was added a 1 mol dm^{-3} solution of diethylzinc in hexane (30 cm^3, 30 mmol). The resultant mixture was then stirred at 0 °C for 2.5 h and at room temp. for 14 h. The reaction was quenched by the addition of a saturated solution of Na_2EDTA (150 cm^3) and ethyl acetate (150 cm^3). The two layers were separated and the organic phase was washed with Na_2EDTA solution (50 cm^3), dried ($MgSO_4$), and concentrated under reduced pressure to leave a dark brown oil.

This oil was dissolved in a saturated methanolic solution of NH_4Cl (120 cm^3) and freshly prepared Zn–Cu couple (18 g, 0.25 mol) was added portionwise. The mixture was stirred at room temperature for 2.5 h and the solid was removed by filtration through a Celite pad. The filtrate was concentrated to remove some of the methanol, diluted with dichloromethane (200 cm^3) and washed with Na_2EDTA solution (2 × 50 cm^3). The combined organic phase was dried ($MgSO_4$) and concentrated under reduced pressure to leave the crude cycloadduct as a brown oil. This oil was purified by flash chromatography on silica gel (1:2 light petroleum–ether) to afford the required oxabicycle **5** in 57% yield (2.12 g, 17.1 mmol), and a small amount (430 mg, 2.8 mmol, 9.4%) of 2-ethyl-8-oxabicyclo-[3.2.1]oct-6-en-3-one **6**.

Oxabicycle **5**: TLC; R_f 0.37 (1:4, ether–light petroleum); m.p. 37–39 °C (white solid); $\nu_{max}(CHCl_3)/cm^{-1}$ 3080, 2960, 2905, 1710, 1340, 1180, 945 and 710; δ_H(60 MHz; $CDCl_3$) 2.30 (d, 2 H, *J* 17, 2*endo*-H and 4*endo*-H), 2.80 (dd, 2 H, J_1 17, J_2 5, 2*exo*-H and 4*exo*-H), 5.10 (d, 2 H, *J* 5, 1-H and 5-H) and 6.30 (s, 2 H, 6-H and 7-H); *m/z* (%) 124 (M^+, 80), 95(10), 82(90), 81(100), 68(10) and 54(0).

Oxabicycle **6**: TLC; R_f 0.55 (1:2, light petroleum–ether) (orange oil); ν_{max}(thin film)/cm^{-1} 3080, 2964, 2876, 1712, 1553, 1497, 1462, 1410, 1180, 1000, 960 and 710. δ_H(220 MHz; $CDCl_3$) (only peaks for major isomer are given) 1.10 (t, 3 H, *J* 8, CH_3), 1.90 (m, 2 H, CH_2), 2.20 (t, 1 H, *J* 8, 2-H), 2.3 (dt, 1 H, J_1 15, J_2 1, 4*endo*-H), 2.85 (dd, 1 H, J_1 15, J_2 5, 4*exo*-H), 4.90 (s, 1 H, 1-H), 5.06 (d, 1 H, *J* 5, 5-H) and 6.35 (s, 2 H, 6-H and 7-H); *m/z* (%)

* The microanalysis for our product was rather poor despite extensive purification, and our m.p. of 102–104 °C (from light petroleum) was somewhat lower than the one reported (108–109 °C) in the literature.[8] The compound is undoubtedly hygroscopic and this may account for the problems. There is very little spectroscopic data in the literature for scopoline, but our spectral data are fully consistent with the structure assigned. For major NOE data see Fig. 1.

153 ([M + 1]$^+$, 3), 137(3), 123(8), 109(8), 95(20), 81(100) and 55(40).

Methyl 2α,4α-Dimethyl-3-oxo-8-azabicyclo[3.2.1]*oct-6-ene-8-carboxylate* **7**.—To an ice-cooled solution of 2,4-dibromopentan-3-one (940 mg, 4 mmol) and methylpyrrole-*N*-carboxylate (500 mg, 4 mmol) in dry benzene (80 cm^3), was added a 1 mol dm^{-3} solution of diethylzinc in hexane (4 cm^3, 4 mmol). The resultant mixture was stirred at 0 °C for 3 h and at room temp. for 17 h, and then poured into an ice-cooled saturated solution of Na_2EDTA (50 cm^3). The product was extracted into ethyl acetate (3 × 50 cm^3), and the combined organic extracts were dried and concentrated under reduced pressure to leave the crude cycloadduct as a pale yellow oil. This oil was purified by flash chromatography on silica gel (ethyl acetate–light petroleum, 1:4) to afford the required product in a yield of 55% (460 mg, 2.2 mmol) and 10% recovery of the starting pyrrole. Compound **7**: TLC; R_f 0.32 (1:3, ethyl acetate–light petroleum); m.p. 60–61 °C (white solid); $\nu_{max}(CHCl_3)/cm^{-1}$ 3070, 2970, 2890, 1710, 1600, 1465 and 1115; δ_H(220 MHz; $CDCl_3$) 1.05 (d, 6 H, *J* 7, CH_3), 2.60–2.90 (br, 2 H, 2-H and 4-H), 3.80 (s, 3 H, OCH_3), 4.60–4.75 (br d, 2 H, *J* 8, 1-H and 5-H) and 6.30 (s, 2 H, 6-H and 7-H) (Found: C, 63.15; H, 7.2; N, 6.65. $C_{11}H_{15}NO_3$ requires C, 63.14; H, 7.23; N, 6.69%).

Methyl 3-Oxo-8-azabicyclo[3.2.1]*oct-6-ene-8-carboxylate* **8**.—A solution of tetrabromoacetone (11.22 g, 30 mmol) and methyl pyrrole-*N*-carboxylate (3.75 g, 30 mmol) in dry benzene (600 cm^3) was cooled to 0 °C, and to this was added a 1 mol dm^{-3} solution of diethylzinc in hexane (30 cm^3, 30 mmol) over a period of 1 h. The resultant mixture was stirred for a further 3 h at 0 °C and at room temp. for 19 h. The reaction was quenched by addition of ethyl acetate (200 cm^3) and a saturated solution of Na_2EDTA (150 cm^3). The two layers were separated and the organic phase washed with saturated Na_2EDTA (50 cm^3) and brine (50 cm^3) and dried ($MgSO_4$). After concentration under reduced pressure the crude cycloadduct was obtained as a brown oil (12 g).

This oil was dissolved in a saturated methanolic solution of NH_4Cl (120 cm^3) and freshly prepared Zn–Cu couple (18 g, 0.25 g.atm) was added portionwise. The mixture was stirred at room temp. for 2.5 h, and then the solid was removed by filtration through a Celite pad. The filtrate was concentrated under reduced pressure to remove some of the methanol, and subsequently diluted with dichloromethane (200 cm^3) and washed with Na_2EDTA solution (2 × 50 cm^3). The combined aqueous phases were extracted with dichloromethane (3 × 50 cm^3). The organic extract was then dried ($MgSO_4$) and concentrated under reduced pressure to leave the crude cycloadduct as a brown oil. This oil was purified by flash chromatography on silica gel using ethyl acetate–light petroleum (2:3) to afford the required cycloadduct **8** in 58.5% yield (3.17 g, 17.5 mmol) and a small amount (410 mg, 1.96 mmol) of the corresponding 2-ethylazabicyclo adduct **9** as an isomeric mixture, as shown by its 220 MHz ^{1}H NMR spectrum.

Compound **8**: TLC; R_f 0.35 (2:3, ethyl acetate–light petroleum); m.p. (hexane) 68–69 °C; $\nu_{max}(CHCl_3)/cm^{-1}$ 3080, 2960, 2890, 1710 (C=O and NCO_2Me), 1600 (C=C), 1460, 1400, 1310, 1120 and 900; δ_H(60 MHz; $CDCl_3$) 2.30 (dd, 2 H, J_1 16.5, J_2 1.5, 2*endo*-H and 4*endo*-H), 2.77 (dd, 2 H, J_1 16.5, J_2 4, 2*exo*-H and 4*exo*-H), 3.73 (s, 3 H, OMe), 4.80 (br d, 2 H, *J* 4, 1-H and 5-H) and 6.13 (t-like, 2 H, 6-H and 7-H); δ_C(220 MHz; $CDCl_3$) 42.14, 42.23, 51.85, 52.18, 52.46, 52.70, 52.80, 156.57 and 204.60; (Found: C, 59.65; H, 6.1; N, 7.75. $C_9H_{11}NO_3$ requires C, 59.66; H, 6.12; N, 7.73%).

Methyl 2-ethyl-3-oxo-8-azabicyclo[3.2.1]oct-6-ene-8-carboxylate: TLC; R_f 0.24 (2:3, ethyl acetate–light petroleum) (orange oil); ν_{max}(thin film)/cm^{-1} 3080, 2960, 2880, 1705, 1450, 1390, 1200, 1110 and 980; δ_H(220 MHz; $CDCl_3$) 1.08 (t, 3 H, *J* 7, CH_3), 1.40–2.40 (m, 5 H, 2-H, 4*exo*-H, 4*endo*-H and CH_2-side chain), 3.77 and 3.78 (2s, 3 H overall, ratio 4:1, OMe from the two isomers), 4.80–4.90 and 4.90–4.95 (continuous broad band, 2 H, 1-H and 5-H) and 6.25 (br s, 2 H, 6-H and 7-H); *m/z* (%) 209 (M$^+$, 30), 176(15), 138(100), 94(40) and 80(40).

Methyl exo-6,7-*Epoxy-3-oxo-8-azabicyclo*[3.2.1]*octane-8-carboxylate* **10**.—*m*-Chloroperbenzoic acid (55–60% purity, 4.29 g, *ca.* 12.5 mmol) was added to a solution of methyl 3-oxo-8-azabicyclo[3.2.1]oct-6-ene-8-carboxylate (1.5 g, 8.29 mmol) in dry dichloromethane (35 cm^3) at room temp. After the mixture had been stirred at room temp. for 48 h, it was diluted with dichloromethane (100 cm^3) and washed with saturated aqueous $NaHCO_3$ (3 × 30 cm^3), Na_2SO_3 (10% aqueous solution, 10 cm^3), and brine (30 cm^3). The resultant organic phase was dried ($MgSO_4$) and concentrated under reduced pressure to leave the crude product as pale yellow oil. This oil was then submitted to flash chromatography (1:1 ethyl acetate–light petroleum) to afford the required epoxide as a colourless oil in 82.7% yield (1.4 g, 7.11 mmol). The product was triturated with ether to yield a white solid; TLC; R_f 0.2 (1:1, ethyl acetate–light petroleum); m.p. 76–77 °C; $\nu_{max}(CHCl_3)/cm^{-1}$ 3022, 2958, 2917, 1709, 1452, 1330, 1298, 1115, 1037, 871 and 701; δ_H(220 MHz; $CDCl_3$) 2.40 and 2.46 (2d, 2 H, *J* 18, 2*endo*-H and 4*endo*-H), 2.68 and 2.74 (2dd, 2 H, J_1 18, J_2 5, 2*exo*-H and 4*exo*-H), 3.54 (sh m, 2 H, 6-H and 7-H), 3.78 (s, 3 H, OMe) and 4.62 and 4.72 (2d, 2 H, *J* 5, 1-H and 5-H); *m/z* (%) 197.0688 (M$^+$, $C_9H_{11}NO_4$ requires *M*, 197.0688, 100%), 182(5), 168(18), 154(48), 96(55), 82(88), 68(25) and 59(35) (Found: C, 54.8; H, 5.65; N, 7.05. $C_9H_{11}NO_4$ requires C, 54.82; H, 5.62; N, 7.10%).

(±)-*Scopoline* **11**.—A solution of methyl *exo*-6,7-epoxy-3-oxo-8-azabicyclo[3.2.1]octane-8-carboxylate (250 mg, 1.27 mmol) in dry toluene (5 cm^3) was cooled to −78 °C and to this a 1 mol dm^{-3} solution of DIBAH in toluene (13 cm^3, 13 mmol) was added. The mixture was stirred at the same temperature for 2 h and at room temp. for 22 h. The resultant mixture was quenched by addition of water (*ca.* 2 cm^3) and stirred for 12 h. The resultant gel was extracted repeatedly with ethyl acetate (8 × 30 cm^3) and the combined organic extracts were dried, and concentrated to leave the crude product as a pale yellow oil. This oil was purified by flash chromatography (ether–NH_4OH, 95:5) on silica gel to afford 104 mg (0.67 mmol, 53%, variable yield) of the required product as a pale yellow oil; TLC; R_f 0.1 (ether–NH_4, 95:5) (pale yellow oil, solidifies on storage in a refrigerator); ν_{max}(thin film)/cm^{-1} 3480 (OH), 2937, 2851, 1461, 1438, 1400, 1352, 1247, 1152, 1072, 1054, 1040, 978, 893 and 771; δ_H(400 MHz; $CDCl_3$)* 1.19–1.25 (m, 1 H, H_j); 1.40 (dddd, 1 H, J_{ih} 13.7, J_{ib} 3.9, J_{ij}, J_{if} 2, H_i), 1.87 (dd, 1 H, J_{hi} 13.7, J_{hf} 3.7, H_h), 2.33 (d, 1 H, J_{gj} 12, H_g), 2.55 (s, 3 H, CH_3), 2.93–2.94 (br, 1 H, H_f), 3.10–3.30 (br, 1 H, OH), 3.64 (br dd, 1 H, $J_{da} \cong J_{dj}$ 4.3, H_d), 3.85 (s, 1 H, H_c), 4.22 (br t, 1 H, $J_{bi} \cong J_{bj} \cong$ 3.9, H_b) and 4.47 (br dd, 1 H, J_{ad} 4.3, J_{af} 1.5, H_a); %NOE (Fig. 1): da 1.8, dg 1.4, dj 2.1, ci 1.1, dMe 0.7, gMe 1.3, hMe 1.3 and fMe 0.7; δ_C(100.53 MHz; $CDCl_3$) 27.55, 30.25, 33.69, 61.32, 63.97, 74.23, 75.27 and 83.48; *m/z* (%) 156.1025 ([M + 1]$^+$, $C_8H_{14}NO_2$ requires *M*, 156.1025, 100%), 138(38), 126(20), 110(12), 96(62) and 81(18); (Found: C, 61.7; H, 8.55; N, 8.6. $C_8H_{13}O_2$ requires C, 61.90; H, 8.46; N, 9.02%).

Acknowledgements

We thank the CNPq, Brazil for a scholarship for L.-C. de A. B., and Dr. O. Howarth for extensive NMR investigations.

* See Fig. 1 for NOE assignment for compound **11**.

References

1 H. M. R. Hoffmann, *Angew. Chem.*. 1984, **23**, 1.
2 R. Noyori and Y. Hayakawa, *Org. React.*, 1983, **29**, 163.
3 J. Mann, *Tetrahedron*, 1986, **42**, 4611.
4 Y. Hayakawa, Y. Baba, S. Makino and R. Noyori, *J. Am. Chem. Soc.*, 1978, **100**, 1786.
5 M. R. Ashcroft and H. M. R. Hoffmann, *Org. Synth., 1978*, **58**, 17.
6 R. Noyori, S. Makino, T. Okita and Y. Hayakawa, *J. Org. Chem.*, 1975, **40**, 806.
7 H. Takay, Y. Hayakawa, S. Makino and R. Noyori, *J. Am. Chem. Soc.*, 1978, **100**, 1778.
8 K. Zeile and A. Heusner, *Chem. Ber.*, 1956, **90**, 2800, 2809.

Paper 1/05899A
Received 20*th November* 1991
Accepted 22*nd January* 1992