Synthesis and Circular Dichroism of Some Bicyclic Compounds Related to Camphor with Chirality due to Deuterium Substitution

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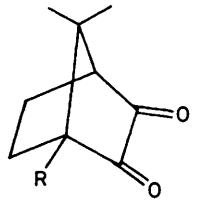
Deuteriated optically active fenchocamphorquinone (1a), apocamphoric anhydride (2a), apocamphorimide (3a), and *N*-nitrosoapocamphidine (4a) of known absolute configuration were prepared and their absorption and circular dichroism spectra were measured. The deuterium atom was introduced into the asymmetric 1-position by a method based on catalytic decarbonylation of the corresponding deuterio-aldehyde or, alternatively, by decarboxylation of deuterio-carboxylic acid. The contributions of the C–D and C–CH_3 bonds to the chiroptical activity were compared.

Considerable interest has recently been noted in the study of the chiroptical properties of compounds which owe their chirality to deuterium substitution.[1,2] Chiral isotopic perturbation being generally weak, these compounds usually show a very weak Cotton effect (CE). If, in addition, the CE is related to a electronic transition which is associated with strong absorption, then circular dichroism (c.d.) is difficult to measure. It is, therefore, understandable that previous studies have mainly been concerned with the CE associated with the ketone n ⟶ π* transition, and that most successes have been obtained in this area. However, the number of chromophores included in this kind of work has recently been increasing. The CE has been observed in the c.d. spectra of deuteriated thioketones,[3] sulphoxides,[4] alkenes,[2,5] aromatic compounds,[6] and carboxylic acids.[7] The structural rigidity of the models investigated makes it unnecessary to resort to conformational analysis which overshadows observation of the influence of deuterium perturbation on chiroptical activity. Particularly useful results have been obtained for (1*R*)-1-deuteriofenchocamphorquinone (1a).[8,9]

In this study a new method is presented for the synthesis of this attractive model and for some other bicyclic compounds derived from it such as (1*R*)-1-deuterioapocamphoric anhydride (2a), (1*R*)-1-deuterioapocamphorimide (3a), and (1*R*)-*N*-nitroso-1-deuterioapocamphidine (4a),[10] and their absorption and c.d. spectra are given. These compounds are new examples of chromophores whose optical activity is due to the presence of deuterium. It is worth stressing that imides and anhydrides belong to systems whose chiroptical properties have so far not been given much attention.[11,12] The presence of two n ⟶ π* transitions in the long-wavelength region of the spectrum is a feature common to α-diketones, anhydrides, and imides.



(1)

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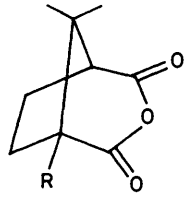
b; R = H
c; R = Me



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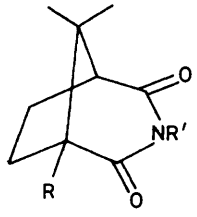
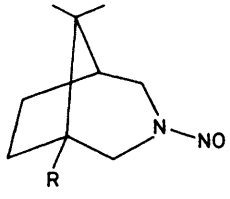


(3)

a; R = D, R' = H
b; R = H, R' = H
c; R = Me, R' = H
d; R = Me, R' = Me



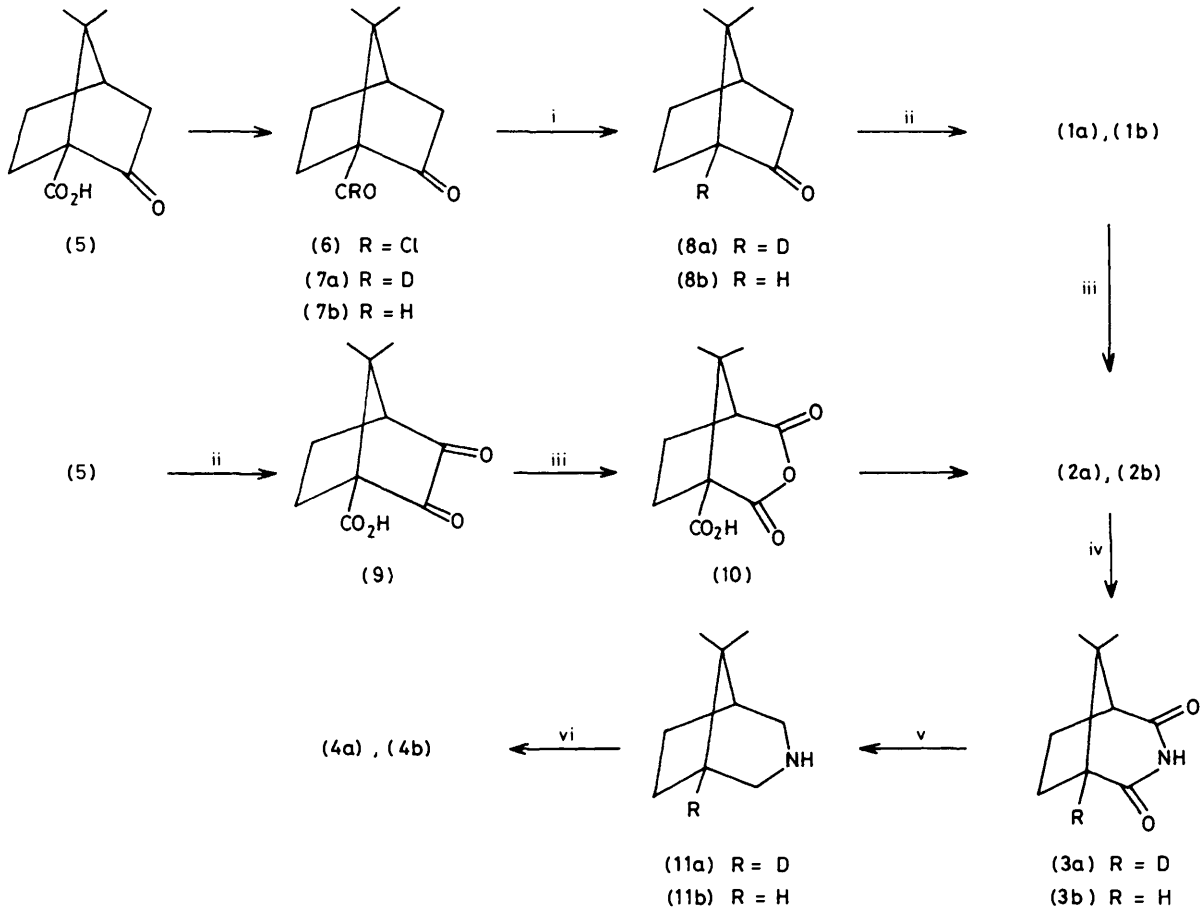
(4)

a; R = D
b; R = H
c; R = Me

Synthesis.—The optically active compounds (1a)—(4a) and for comparison, the symmetric compounds (1b)—(4b), were prepared from (+)-ketopinic acid (5), which because of its well-established derivation from (+)-camphor,[8,13] is recognized to have the absolute configuration indicated below (Scheme). Treatment of the acid (5) with thionyl chloride gave the corresponding acid chloride (6), which upon reduction with an excess of bis(triphenylphosphine)tetrahydroboratocopper(I) [$(Ph_3P)_2CuBH_4$] in acetone solution gave the aldehyde (7b). This procedure, recently proposed by Sorrell *et al.*[14] and Fleet *et al.*,[15] seems to be the most convenient and clean method for the selective reduction of acid chlorides to aldehydes. Analogously, from copper(I) chloride, triphenylphosphine, and sodium borodeuteride, bis(triphenylphosphine)-tetradeuterioboratocopper(I) [$(Ph_3P)_2CuBD_4$] was prepared and used for the reduction of the acid chloride (6) to give the deuterio-aldehyde (7a). By heating them without solvent, compounds (7a) and (7b) were decarbonylated with tris(triphenylphosphine)chlororhodium(I) [$(Ph_3P)_3RhCl$][16] to give the α-fenchocamphorones (8a) and (8b). This method of deuterium introduction into the bridgehead position overcomes the difficulties involved in the procedure reported by Kokke and Varkevisser,[8] which was based on bromine-atom substitution in (1*R*)-1-bromo-α-fenchocamphorone by heating for several days with a large excess of lithium aluminium deuteride in *N*-methylmorpholine.

Oxidation of compounds (8a) and (8b) with selenium dioxide gave the α-diketones (1a)† and (1b). These compounds were used as substrates in the synthesis of the models (2), (3),

† Although the deuterio-aldehyde (7a) (99% isotopic purity) was used as substrate, the compound (1a) was shown by mass spectroscopy to be 34% 1-^{2}H. Similarly, Kokke and Varkevisser[8] reported that (1a), prepared from the isotopically pure substrate, had 30.08% 1-^{2}H.



Scheme. *Reagents*: i, $(PPh_3)_3RhCl$; ii, SeO_2; iii, H_2O_2, AcOH; iv, NH_3; v, $LiAlH_4$; vi, HNO_2

and (4). The diketones (1a) and (1b) were oxidized with hydrogen peroxide in acetic acid to give the anhydrides (2a) and (2b), which were then treated as in the procedure of Toivonen *et al.*[17] An alternative, more efficient and very simple route was also proposed for the synthesis of the key intermediate (2a) (Scheme). This procedure is also based on (+)-ketopinic acid (5), which was transformed into the α-diketone (9) by the action of selenium dioxide in acetic acid. On oxidation with hydrogen peroxide, (9) gave the carboxy-anhydride (10). Deuterium exchange of the carboxylic proton in compound (10) was easily accomplished with deuterium oxide. Smooth decarboxylation of the acids (10) at 220 °C led to the anhydrides (2a) and (2b). This reaction shows that the Bredt rule [18] is not absolutely valid for compound (10).

The oxa-compounds (2a) and (2b) were converted into the imides (3a) and (3b) by the action of methanolic ammonia followed by heating at 180 °C. Derivatives (3a) and (3b) were reduced with lithium aluminium hydride, and the resulting apocamphidines (11a) and (11b) were nitrosated with nitrous acid in acetic acid to give the *N*-nitrosamines (3a) and (3b).

C.D. and U.V. Spectra.—In order to compare the contributions of the C–D and C–CH_3 groups to the chiroptical activity the c.d. and u.v. spectra of the deuteriated compounds (2a) and (3a) and their methyl analogues have been put together in Figures 1 and 2. The c.d. and u.v. spectra of (4a) and (4c) have already been reported in a preliminary communication.[10] The c.d. spectrum obtained for the α-diketone (1a) was identical with the one published by Kokke and Varkevisser.[8] The optical activities of compounds (2a), (3a), and (4a) are so low that it was very difficult to obtain c.d. spectra of them; however a fine spectrum was easily obtained for compound (1a), despite its considerably lower isotopic purity, because of lower absorption of the dione (1a) within the region investigated, than that of the other compounds, and thus because of the greater asymmetry coefficient (4R/D), compounds (1a), (2a), (3a), and (4a) are comparable despite the CE.

The c.d. measurements are much more reliable than the u.v. spectra alone in detecting the electronic transitions of the chromophores under investigation. The u.v. spectra for the anhydrides (2a) and (2c) show the presence of an absorption band at *ca.* 225 nm (Figure 1), while the c.d. spectrum of compound (2c) indicates the existence of two overlapping bands at *ca.* 225 and 245 nm. This, in turn, becomes still more evident in the c.d. spectrum of (2a), since the CE corresponding to these bands have opposite signs. In addition, the isoelectronic imide chromophore shows two absorption bands of moderate intensity near 250 and 230 nm, as well as a strong band near 210 nm in the u.v. spectrum (Figure 2). These bands are considerably easier to distinguish in the c.d. spectrum of camphorimide (3c) in which two bands with opposite signs can be observed in the 220—260 nm region. In the c.d. spectrum for compound (3a), however, the CE corresponding to the two bands are of the same sign.*

* Because of the poor quality of the c.d. spectrum for (3a), in Figure 2, the CE have been presented only for the longest wavelength band. It can however be stated, despite a high noise level, that the CE corresponding to the transition near 230 nm are also of positive sign.

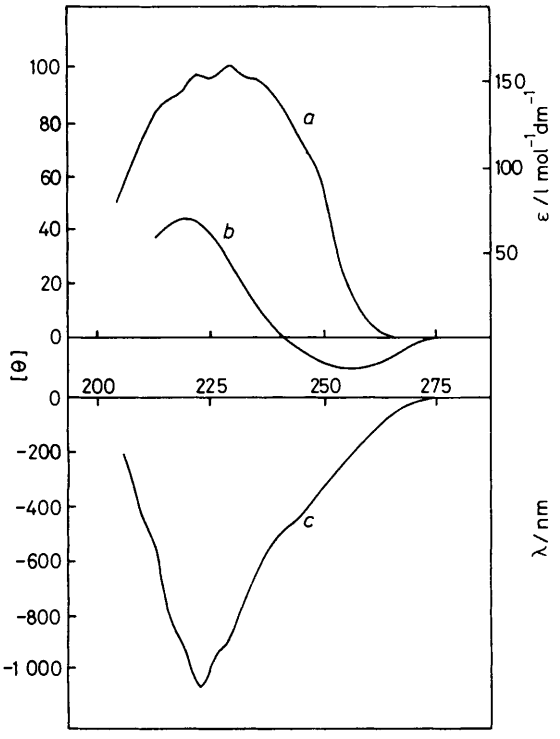


Figure 1. (*a*) U.v. and (*b*) c.d. spectra of (1*R*)-1-deuterioapocamphoric anhydride (2a), and (*c*) c.d. spectrum of (1*R*)-1-camphoric anhydride (2c) in dioxan

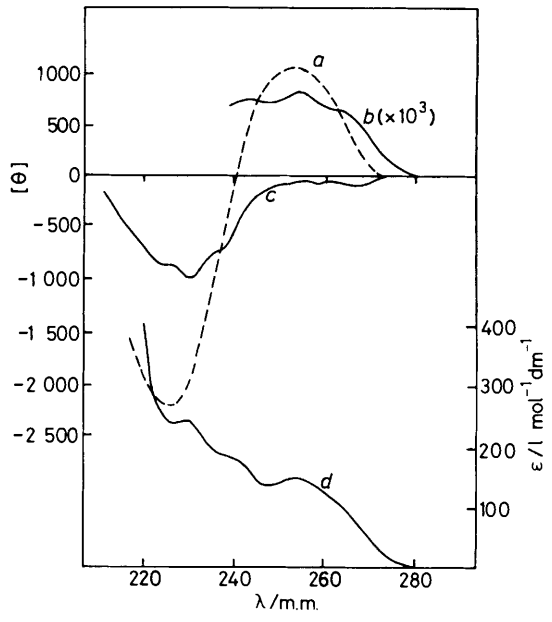


Figure 2. C.d. spectra of (1*R*)-camphorimide (3c) in (*a*) methanol and (*c*) cyclohexane; (*b*) c.d. and (*d*) u.v. spectra of (1*R*)-1-deuterioapocamphorimide (3a) in methanol

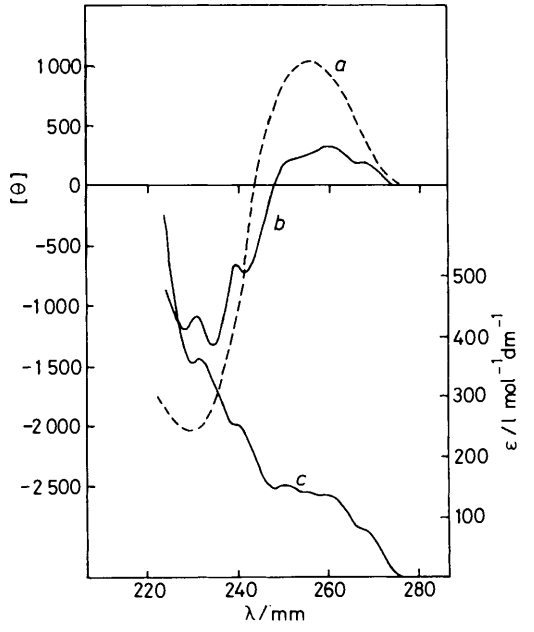


Figure 3. C.d. spectra of (1*R*)-*N*-methylcamphorimide (3d) in (*a*) methanol and (*b*) cyclohexane and (*c*) u.v. spectrum of (3d) in cyclohexane

The nature of the transitions observed in acid anhydrides and imides is rather complex, as indicated by CNDO/2-CI calculations.[19] The two low-energy transitions have n ⟶ π* character, as confirmed by their relatively low intensity, while the strong intensity transition near 210 nm for imides has π ⟶ π* character, where the two ' non-bonding ' orbitals n and π* are delocalized over the whole chromophore. These facts point to a certain similarity of these chromophores to the α-dicarbonyl system,[20] even though energetic separation of the n orbitals is considerably greater in the latter.

Comparison of the CE for the deuteriated compounds and their methyl analogues calls for some explanation. In the cases of compounds (2a) and (3a), the CE for the long-wavelength transition n ⟶ π* are of the same sign as in compounds (2c) and (3c), whereas the shorter wavelength n ⟶ π* transitions give CE of opposite sign for either of the two groups. The reverse occurs in the case of α-diketones, where the CE for the deuteriated derivative (1a) has the opposite sign to that for (1*R*)-camphorquinone (1c), whereas the CE for the higher energy transition n ⟶ π* are of the same sign for both these compounds.*

These data point to an anomaly, *e.g.* in relation to ketones where the CE for the deuteriated compounds are of the opposite sign to those of their methyl analogues.[1] However, interpretation of the c.d. sign for the systems investigated calls for some caution, because here the solvation and association effects seem to play a considerable role, as indicated by the strong influence of solvents on the c.d. of the imide (3c) (Figure 2). Even though this molecule is sterically rigid, the transition from a methanol solution to one in cyclohexane causes considerable changes in the shape of the c.d. curve, and the sign of the CE near 250 nm is reversed. The fact that this is brought about by association of the molecules (3c) is confirmed by the c.d. spectra of the *N*-methyl analogue (3d), where a considerably weaker influence of solvents is observed (Figure 3). A further reason for this anomaly may be the fact that the dissymmetric perturber in the compounds investigated is close to the nodal plane of the chromophore; it is from this that the low optical activity and the strong influence of the environment on the c.d. of the systems under investigation results. Still to be discussed remains the least compli-

* (1*R*)-Camphorquinone (1c) shows $\lambda_{max.}$ (Δε) 484 (0.45) and 293 (0.29).[21]

cated example of *N*-nitrosoamines (4a) and (4c). These compounds show a CE near 370 nm corresponding to a n ⟶ π* transition.[22,23] Comparison of the c.d. spectra of compounds (4a) and (4c) [10] shows that the contributions of the groups C–D and C–CH_3 in position 1 of the apocamphidine skeleton to the optical activity of that transition are dissignate,[24] according to the general trend observed for other chromophores.[1] The reason for this is the lower polarizability of the deuterium atom in comparison with that of hydrogen, as well as the fact that the C–D bond is shorter than the C–H bond, or, according to Lightner's conception,[25] the fact that the sign of the CE is determined by a comparably more consignate contribution of the C–H bond than is that of the C–D bond which is situated on the other side of the mirror plane which bisects the molecule.

Experimental

N.m.r. spectra were taken with a Tesla BS-487 80 MHz spectrometer with tetramethylsilane as internal standard. I.r. spectra were obtained on a Zeiss IR-10 spectrophotometer. U.v. measurements were performed on a Beckman 3600 spectrophotometer. Mass spectra were determined on a Varian MAT-711 mass spectrometer, applying electron impact ionization. C.d. spectra were recorded on JASCO J-20 and J-500 spectropolarimeters with DP-500 N data processor. The accumulation technique (32-fold accumulation) for compounds (2a), (3a) and (4a) was applied to improve the S/N ratio for deuteriated compounds. M.p.s are uncorrected. Ether refers to diethyl ether throughout. Bis(triphenylphosphine)tetradeuterioboratocopper(I) which was prepared according to the Sorrell [14] procedure had the same features as its tetrahydro-analogue $(Ph_3P)_2CuBH_4$. Compounds (3c), (3d), and (4c) were obtained according to literature methods.[23,26]

(1R)-7,7-*Dimethyl*-2-*oxobicyclo*[2.2.1]*heptane*-1-*carbaldehyde* (7b).—A solution of (+)-ketopinic acid (5) [9,14] (2.0 g, 11 mmol) was refluxed for 1 h in 10 ml of thionyl chloride and then evaporated to dryness. The residue was evaporated with two portions (50 ml) of CCl_4 to remove the rest of the thionyl chloride. The resulting acid chloride (6) was dissolved in acetone (50 ml), and triphenylphosphine (6.03 g, 23 mmol) and bis(triphenylphosphine)tetrahydroboratocopper(I) (9.65 g, 16 mmol) were added; the mixture was refluxed for 30 min. The solution was filtered and the filter was washed with ether. The combined filtrates were evaporated to dryness. The residue was dissolved in ether (20 ml), refrigerated for 1 h, filtered and evaporated. The residue was sublimed at reduced pressure and crystallized from hexane to give the product (1.55 g, 84%), m.p. 202—204 °C (lit.,[27] m.p. 204—205 °C); $[\alpha]_D^{20}$ +77° (*c* 2 in EtOH) {lit.,[28] $[\alpha]_D^{25}$ +75° (*c* 2 in EtOH)}; δ(CCl_4) 9.73 (s, 1 H, CHO), 1.07 (s, 3H, CH_3), and 0.95 (s, 3 H, CH_3); $\nu_{max.}$ (KBr) 2 750 (CHO), 1 745, and 1 720 cm^{-1}; *m/e* 166 (*M*).

(1R)-7,7-*Dimethyl*-2-*oxobicyclo*[2.2.1]*heptane*-1-[^{2}H]-*carbaldehyde* (7a).—The deuterioaldehyde (7a) was prepared from the acid (5) and bis(triphenylphosphine)tetradeuterioboratocopper(I) by the same procedure as for its analogue (7b), m.p. 202—204 °C, $\nu_{max.}$ (KBr) 2 105 (CDO), 1 745 and 1 720 cm^{-1}; *m/e* 167 (*M*) (98% ^{2}H).

7,7-*Dimethylbicyclo*[2.2.1]*heptane*-2,3-*dione* (1b).—The aldehyde (7b) (1.0 g, 6 mmol) and tris(triphenylphosphine)-chlororhodium(I) (5.55 g, 6 mmol) were mixed and heated under a reflux condenser at 180 °C until the dark red melt turned yellow (*ca.* 2 h). The resultant semicrystalline solid was triturated with pentane. After evaporation, the colourless semisolid (8b) (0.52 g) was dissolved in acetic acid (5 ml), and selenium dioxide (0.45 g, 0.4 mmol) was added. The mixture was refluxed for 1 h, filtered and evaporated. The residue was dissolved in ether, washed with saturated aqueous $NaHCO_3$, dried (Na_2SO_4), and evaporated. The residue was sublimed under reduced pressure and crystallized from hexane to give the dione (1b) (0.30 g) as yellow crystals, m.p. 136 °C (lit.,[8] m.p. 138.5—139.5 °C); δ($CDCl_3$) 2.50 (t, 2 H, CH), 1.0 (s, 3 H, CH_3), and 0.98 (s, 3 H, CH_3); *m/e*: 152 (*M*).

(1R)-7,7-*Dimethyl*[1-^{2}H]*bicyclo*[2.2.1]*heptane*-2,3-*dione* (1a).—The deuterio-α-diketone (1a) was obtained from the deuterio-aldehyde (7a) in the same manner as for its analogue (1b), m.p. 136 °C (lit.,[8] m.p. 137.5—139 °C) *m/e* 153 (*M*) (34% ^{2}H); λ([θ])(cyclohexane) 487 (69), 465 (55), 447 (28), 432 (17), 420 (9), 330 (9), 315 (31), 330 (55), 286 (60), 274 (44), 263 (18), and 253 nm (5).

(1S)-7,7-*Dimethyl*-2,3-*dioxobicyclo*[2.2.1]*heptane*-1-*carboxylic Acid* (9).—(+)-Ketopinic acid (5) (9.1 g, 50 mmol) and selenium dioxide (7.77 g, 70 mmol) were refluxed in acetic acid (50 ml) for 18 h. After cooling, the reaction mixture was filtered and evaporated to dryness. The residue was dissolved in ethyl acetate and washed with water, dried (Na_2SO_4), and evaporated. Crystallization from ethyl acetate–hexane gave the product (8.2 g, 83%), m.p. 239 °C; $[\alpha]_D^{20}$ −204° (*c* 0.5 in $CHCl_3$) (Found: C, 61.1; H, 6.2. $C_{10}H_{12}O_4$ requires C, 61.2; H, 6.2%).

(1S)-8,8-*Dimethyl*-2,4-*dioxo*-3-*oxabicyclo*[3.2.1]*octane*-1-*carboxylic Acid* (10).—To the acid (9) (5.88 g, 30 mmol) in glacial acetic acid (8 ml) was added 20 ml of 30% hydrogen peroxide in two portions at room temperature. After a vigorous reaction the colourless reaction mixture was cooled to precipitate the bicyclo-octane (10) as white needles. The crystals were filtered off, washed with water, dried and crystallized from ethyl acetate–hexane to give the *product* (5.5 g, 86%), m.p. 201—202 °C (decomp.); $[\alpha]_D^{20}$ −1.5° (*c* 5 in AcOEt); δ($CDCl_3$) 9.86 (s, 1 H), 2.70 (t, 1 H), 2.7—1.7 (m, 4 H), 1.23 (s, 3 H), and 0.95 (s, 3 H) (Found: C, 56.4; H, 5.9. $C_{10}H_{12}O_5$ requires C, 56.6; H, 5.7%).

8,8-*Dimethyl*-3-*oxabicyclo*[3.2.1]*octane*-2,4-*dione* (2b).—*Method A.* To the α-diketone (1b) (0.30 g, 2 mmol) in glacial acetic acid (2 ml), 4 ml of 30% hydrogen peroxide was added at room temperature. After cooling, the precipitated product was filtered off, washed with water and dried. Crystallization from ethyl acetate–hexane gave the dione (2b) (0.23 g, 69%), m.p. 175 °C (lit.,[29] m.p. 175—175.5 °C); δ($CDCl_3$) 2.65 (t, 4 H), 2.3—1.5 (m, 4 H), 1.08 (s, 3 H), and 0.97 (s, 3 H); $\nu_{max.}$ (KBr) 1 800 and 1 770 cm^{-1}; *m/e* 169 (*M* + 1).

Method B. Decarboxylation of the acid (10) (2.12 g, 10 mmol) was carried out by heating it at 200 °C until CO_2 evolution had ceased (*ca.* 3 h). After cooling, the product was crystallized to yield the dione (2b) (1.43 g, 85%), m.p. 175 °C.

(1R)-8,8-*Dimethyl*-[1-^{2}H]-3-*oxabicyclo*[3.2.1]*octane*-2,4-*dione* (2a).—The acid (10 (6.36 g, 6 mmol) was dissolved in a mixture of ethyl acetate (30 ml) and benzene (30 ml) and shaken with deuterium oxide (15 ml; 99.9%). This procedure was repeated 10 times. The organic layer was separated, dried (Na_2SO_4) and evaporated to dryness. The residue was decarboxylated according to method B. After crystallization the deuterio-dione (2a) (3.8 g) was obtained, m.p. 175 °C; $\nu_{max.}$ (KBr) 1 800 and 1 770 cm^{-1}; *m/e* 170 (*M* + 1) (78% ^{2}H).

8,8-*Dimethyl*-3-*azabicyclo*[3.2.1]*octane*-2,4-*dione* (3b).—The anhydride (2b) (1.3 g, 0.77 mol) was dissolved in saturated methanolic ammonia (15 ml) and, after 30 min, evaporated to dryness. The residue was heated at 180 °C for 10 h. The result-

ing product was sublimed under reduced pressure and crystallized from ethyl acetate–hexane to give the *aza-compound* (3b) (0.88 g, 75%), m.p. 192 °C; δ($CDCl_3$) 8.67 (br, 1 H, NH), 2.43 (t, 2 H, CH), 1.06 (s, 3 H), and 0.90 (s, 3 H); $\nu_{max.}$ (KBr) 3 220 (br), 3 095, 1 720, and 1 690 cm^{-1}; *m/e* 167 (*M*) (Found: C, 64.6; H, 7.9; N, 8.3. $C_9H_{13}O_2N$ requires C, 64.7; H, 7.8; N, 8.4%).

(1R)-8,8-*Dimethyl*-[1-^{2}H]-3-*azabicyclo*[3.2.1]*octane*-2,4-*dione* (3a).—The deuterio-imide (3a) was obtained from the oxo-analogue (2a) by the same procedure as for compound (3b), m.p. 190—191 °C; $\nu_{max.}$ (KBr) 3 220 (br), 3 095, 1 720, and 1 690 cm^{-1}; *m/e* 168 (*M*) (76% ^{2}H).

8,8-*Dimethyl*-3-*azabicyclo*[3.2.1]*octane* (11b).—The amine (11b) was obtained by $LiAlH_4$ reduction of the dione (3b) in THF; hydrobromide, m.p. 275—277 °C (Found: C, 48.87; H, 8.4; N, 6.3. $C_9H_{18}BrN$ requires C, 49.1; H, 8.2; N, 6.4%).

(1R)-8,8-*Dimethyl*-[1-^{2}H]-3-*azabicyclo*[3.2.1]*octane* (11a).—The deuterio-amine (11a) was obtained by $LiAlH_4$ reduction of the deuterio-dione (3a); hydrobromide, m.p. 276—278 °C.

8,8-*Dimethyl*-3-*nitroso*-3-*azabicyclo*[3.2.1]*octane* (4b).—The hydrobromide of the amine (11b) (0.22 g, 1 mmol) was dissolved in 20% acetic acid (6 ml) and sodium nitrite (0.5 g) was added. The reaction mixture was left overnight, then neutralized with $NaHCO_3$ and extracted with pentane. The organic layer was dried (Na_2SO_4), evaporated and crystallized by freezing from hexane to give the product (0.15 g, 89%), m.p. 114 °C; *m/e* 168 (*M*) (Found: C, 64.1; H, 9.6; N, 16.5. $C_9H_{16}N_2O$ requires C, 64.3; H, 9.6; N, 16.7%).

(1R)-8,8-*Dimethyl*-3-*nitroso*-[1-^{2}H]-3-*azabicyclo*[3.2.1]-*octane* (4a).—The nitrosoamine (4a) was obtained by nitrosation of the amine (11a) in the same manner as for its analogue (4b), m.p. 114 °C; *m/e* 169 (*M*) (76% ^{2}H).

Acknowledgements

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