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SPIROHETEROCYCLES DERIVED FROM TETRALONE

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Abstract: New 2-heterospirotetrahydronaphthalenes with 3-, 4- and 5-membered rings have been prepared during the development of routes to tetralone derived spiroaziridines.

Spiroaziridines of the type (1) are unknown. Their synthesis presents problems because of potential benzylic cation mediated ring opening processes. It should be noted that the corresponding spiroepoxides are, not surprisingly, very reactive.[1] We report the outcome of a number of routes to (1) in which unexpected reactions emerged, and also a successful approach to the target molecules.

Carbene 1,2-cycloaddition reactions with tetralone imine (2)[2] represented an apparently obvious initial route. However, dichlorocarbene ($CHCl_3$, NaOH, ultrasound[3]) gave, in low yield, one product, with the molecular formula $C_{19}H_{19}NO$. Spectroscopic analysis showed structure (6), although its stereochemistry cannot rigorously be assigned on the basis of available data. Presumably, reaction occurs via the enamine (3), or the N-anion, which reacts with dichlorocarbene to give imine (4). Elimination of HCl from the imine to give the alkene (5) is followed by Michael addition of ethanol (from commercial $CHCl_3$) and thence (6). An alternative pathway involving an intermediate dichlorocyclopropane can also be envisaged. Interestingly, in ethanol-free chloroform no reaction occurs under similar conditions.

A wide range of other carbenes also failed to give the target spiroaziridine, although a reaction of ethyl diazoacetate produced unexpected results. Thus, irradiation of (2) with ethyldiazoacetate (low pressure Hg lamp) gave two crystalline products in moderate yield. Carbonyl bands at 1750 cm^{-1} and n.m.r. analysis excluded the desired aziridine structure. X-Ray crystallography, however, confirmed the β-lactam structures (7) and (8),[4] arising from rearrangement of the carbene by 1,2-migration to ethoxyketene,[5] followed by 2+2 cycloaddition to the imine.

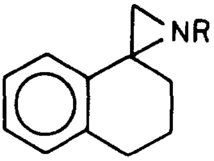
In an alternative approach to carbene cycloaddition, the reaction of dimethylsulphoxonium methylide with imine (2) was investigated. A preliminary study gave, in low yield, one isolable product of molecular formula $C_{26}H_{21}N$. A high element of symmetry was apparent from the n.m.r. spectra, and the possible structure 13-phenyl[a,i]dibenzo-5,6,7,8-tetrahydrocarbazole (9) was confirmed by X-ray crystallography.[6] This reaction necessitates an oxidation step, and if oxygen is rigorously excluded from the reaction and work-up, the compound is not formed. Conversely, if the imine is stirred with base (nBuLi or LDA) and then exposed to air, the yield was increased to 40%. A plausible reaction sequence involves addition of the imine anion to

(2), giving (10) which eliminates aniline, cyclizes and then is oxidized. Product (9) is a new dibenzocarbazole derivative in which the N-phenyl group assumes an orthogonal relationship with respect to the plane of the heterocycle.

A further synthetic approach to the target aziridines employed the vicinal aminoalcohols (11) and (12) as starting materials. Interestingly, these were not readily available from spiroepoxide (13), for example, by ring opening with benzylamine. Under standard conditions[7] the hydroxymethyldihydronaphthalene (14) was the sole product. Aminoalcohol (11) was prepared by the cyanohydrin route.[8] All attempts to cyclize (11) and (12) failed because of dehydration, giving, for example, (15). Yet another tactic involved preparing the oxazolidinone derivatives (16) and (17), followed by thermolysis. No aziridine (1) could be isolated.

The successful strategy utilized the methylidine (18) (obtained by Wittig reaction of α-tetralone) which was reacted with iodine monochloride and sodium azide in acetonitrile at -4°C, followed by immediate reduction of the unstable iodoazide (19) with lithium aluminium hydride[8] to give the aziridine (1, R=H). This unstable new compound was characterized as its N-methoxycarbonyl derivative (1, R=CO$_2$Me).

These explorations have thus produced new spiro 3-, 4- and 5-membered ring heterocycles, and have allowed definition of the reactivity parameters of a range of benzylically substituted tetrahydronaphthalenes. Further studies of the reactivity of aziridines (1) and synthetic applications will follow.



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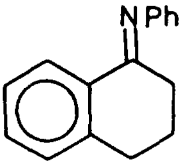

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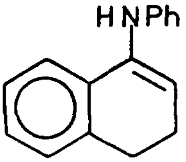

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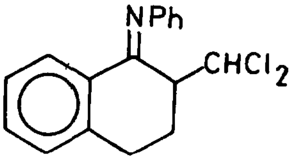

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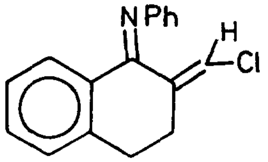

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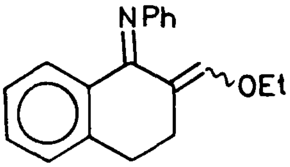

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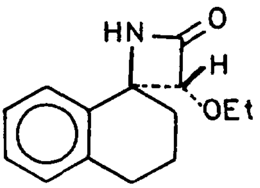

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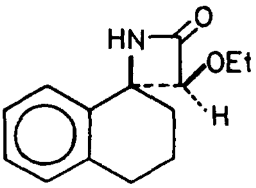

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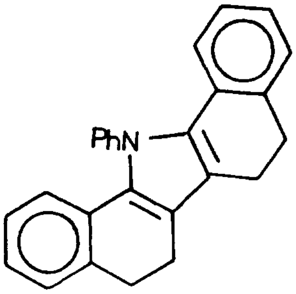

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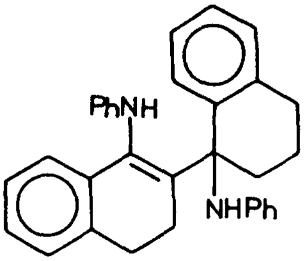

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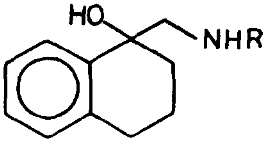
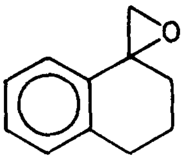


11 , R = Me
12 , R = C(Ph)$_3$



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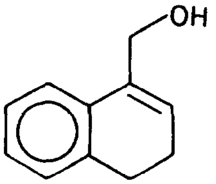

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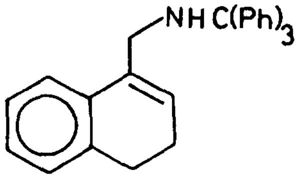

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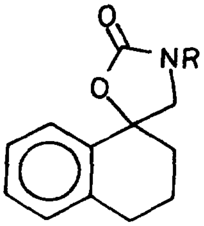
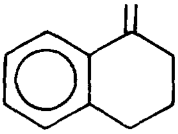


16, R=Me
17, R= C(Ph)$_3$



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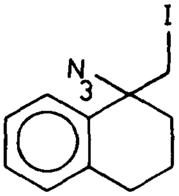

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Experimental

U.v. spectra were recorded as solutions in 98% ethanol. ^1H n.m.r. spectra were recorded at 100 and 400 MHz. Chemical ionisation mass spectrometric analyses were determined using isobutane as the ionizing medium.

2-Ethoxymethylene-3,4-dihydro-1(2H)-N-phenylnaphthylimine(6)

The imine (2) (0.44g) was added to a suspension of powdered sodium hydroxide (0.08g) in dry chloroform (20cm^3) and the reaction mixture, protected by an atmosphere of nitrogen, was placed in an ultrasonic bath.

After 4 days the solvent was removed and the residue chromatographed on silica, eluting with 30% diethyl ether in 60-80°C petrol. This gave the title compound as a colourless solid, m.p. 82-84°C, (0.05g, 10%); ν_{max}(Nujol) 1640, 1600, 1220cm^{-1}; δ_H($CDCl_3$), 7.2-6.8(9H,m, aromatics), 5.9(1H,t,J=Hz,CH-OEt), 4.45(2H,q,J=6Hz,$OC\underline{H}_2CH_3$), 2.60(2H,t,J=7Hz,$ArC\underline{H}_2$), 2.2-2.1(2H,m,$ArCH_2C\underline{H}_2$), 1.45(3H,t,J=6Hz,$OCH_2C\underline{H}_3$), [Found: C, 82.2; H,6.9; N,5.25 $C_{19}H_{19}NO$ requires: C,82.2; H.6.9; N,5.1%].

Spiro-[1,2,3,4-tetrahydronaphthalen-1,4'-(3'-ethoxy-1'-phenylazacyclobutan-2'-ones)] (7) and (8)

3,4-Dihydro-1(2$\underline{H}$)-N-phenyl-naphthylimine (0.5g) in benzene (500cm^3) containing ethyl diazoacetate (0.83g) was protected by a nitrogen atmosphere and irradiated with ultraviolet light generated from a Hanovia low pressure (16W) lamp. After 48 hr, the reaction was stopped and the solvent removed to yield a gum which, after chromatography on silica (diethylether - 60-80° petrol), afforded the title compounds. The α-isomer (7) has R_f 0.687, m.p. 104-105°C. Yield 0.18g (25%); ν_{max}(Nujol) 1750, 1360, 745cm^{-1}; δ_H($CDCl_3$), 7.20(8H,m), 7.0(1H,m), 3.85,3.65(2x1H,dq,J_1=8Hz,J_2=3Hz, $OC\underline{H}_2CH_3$), 2.90(2H,m H_2-4'), 2.42(1H,m,H-2'), 2.26(1H,dt,J=12Hz,J_2=3Hz, H-2^1), 2.00(2H,m,H_2-3'), 1.88(3H,t,J=8Hz,$OCH_3C\underline{H}_3$) [Found: C,77.8; H,6.9; N,4.65 $C_{20}H_{21}NO_2$ requires: C,78.1; H,6.9; N,4.6%].

The β-isomer (8) has R_f 0.5, m.p. 115-116°C, (yield 0.13g, 12%); ν_{max}(Nujol) 1770, 1510, 1390, 780, 760cm^{-1}; δ_H($CDCl_3$) 7.37(1H,dd,J_1=9Hz, J_2=1.5Hz), 7.3-7.15(7H,m), 7.05(1H,m), 3.32 and 3.00(2x1H,dq,J_1=14Hz, J_2=8Hz, $OC\underline{H}_2CH_3$),2.93(2H,m,H_2-4'), 2.56(1H,dt,J_1=14Hz, J_2=3Hz,, H-2'), 2.11(1H,m,H-2'),1.92(2H,m,H_2-3'), 1.89(3H,t,J=8Hz,$OCH_2C\underline{H}_3$) [Found: C,77.8; H,6.9; N,4.65, $C_{20}H_{21}NO_2$ requires: C,78.1; H,6.9; N,4.6%].

13-Phenyl[a,i]dibenzo-5,6,7,8-tetrahydrocabazole(9)

N-Butyllithium (17mMol) in dry tetrahydrofuran (10cm^3) was added slowly (15 min) to a suspension of trimethylsulphonium iodide (3.46g) in the same solvent (20cm^3) maintained at 0°C and protected by a nitrogen atmosphere. The imine (2) (2.5g) in tetrahydrofuran (10cm^3) was then introduced and the reaction mixture stirred overnight. At the end of this time air was admitted and, within a short period, a new spot appeared on tlc plates used to monitor the reaction. The intensity of this new spot gradually increased during the course of 48 hr. Water was added and then dichloromethane, the organic phase was removed and evaporated to afford an oil which was chromatographed on silica. Elution with 20% diethyl ether in 60-80°C petrol gave firstly unreacted imine (60%) and then the title compound (0.58g, 15%) as colourless prisms m.p. 197-198°C; $\lambda_{max}(\epsilon)$ 348(113,600), 364(114,232); ν_{max} 1600, 1490, 780, 710cm^{-1}; δ_H($CDCl_3$) 7.5(5H,m,$C_6\underline{H}_5$-), 7.18(2H,dd,J=8Hz, J_2=1Hz, H-1,H-2), 6.91(2x2H, 2xm, H-3, H-4, H-10, H-11), 6.25(2H,dd,J_1=8Hz, J_2=1Hz, H-4, H-9), 2.92(2x2H, 2xt, J=7Hz, H_2-6, H_2-7), 2.69(2x2H, 2xt, J=7Hz, H_2-5, H_2-8) δ_C($CDCl_3$), 140.3(s),136.6(s), 131.5(s), 130.3(s), 129.7(s), 129.0(d), 128.5(d), 128.2(d), 126.0(d), 124.6(d), 120.5(s), 30.8(t), 20.6(t) [Found: C,90.3; H,6.5; N,4.1 $C_{25}H_{21}N$ requires: C,89.5; H,6.3; N,4.2%].

Subsequently the yield of this product was increased to 40% by reacting the substrate (2) with one mol. equivalent of n-butyllithium at 0°C under an atmosphere of nitrogen and then allowing the reaction mixture to warm to room-temperature exposed to atmospheric oxygen. After a further 24 hr the solvent (THF) was removed and the product purified by chromatography (as before).

1-Aminomethyl-1,2,3,4-tetrahydronaphthalene-1-ol(11)[9]

α-Tetralone (4.5g, 0.03M) and trimethylsilylcyanide (5cm^3) containing a trace of anhydrous zinc iodide were sealed in a flask and stored at 0°C for several days under dry conditions. At the end of this time the reaction mixture was syringed into a suspension of lithium aluminium hydride (1.5g) in dry tetrahydrofuran (THF) (100cm^3) maintained at 0^{o}C. The cooling bath was then removed and the contents of the flask heated at reflux for 3 hr. Water (5cm^3) and then 30% sodium hydroxide (2cm^3) were introduced into the cooled medium and then more water (5cm^3). The tetrafuran layer was separated and the aqueous layer was extracted with diethyl ether (3x20cm^3). Finally the organic phases were combined, dried and evaporated to yield the title compound as a colourless oil (4.9g, 90%). ν_{max} 3380, 3330, 2940, 1490, 1450, 760, 750cm^{-1}; δ_H $CDCl_3$ 7-7.5(m,4H, aromatics), 2.8(m,4H, $C\underline{H}_2$-NH_2, C_4-$\underline{H}_2$), 2.2(bs,3H, exchanged with D_2O, $N\underline{H}_2$, $O\underline{H}$), 1.95-1.6(m,4H, C_2-$\underline{H}_2$, C_3-$\underline{H}_2$); $\underline{m}/\underline{z}$ 177.

1-[N-(Triphenylmethyl)aminomethyl]-1,2,3,4-tetrahydronaphthalene-1-ol(12)

Triphenylmethylchloride (1.1g, 0.04M) in Analar chloroform (10cm^3) was added to a solution of 1-aminomethyl-1,2,3,4-tetrahydronaphthalene-1-ol (11) (0.7g, 0.04M) in Analar chloroform (40cm^3) and anhydrous triethylamine (2cm^3) maintained at 0-5^{o}C. After the addition the reaction mixture was allowed to warm to room temperature during 24 hr. The solvent was then evaporated off and the residue chromatographed on neutral grade alumina, eluting with ethylacetate/60-80^{o}C petroleum ether (1:5), to give the title compound as a colourless crystalline solid, m.p. 158-159^{o}C (0.63g, 95%). ν_{max}($CHCl_3$) 3450, 3060, 1490, 1450cm^{-1}; δ_H($CDCl_3$), 7.6-7.0(m,19H, aromatics), 2.9(m,1H, exchanged with D_2O), 2.8-2.2(m.5H), 2.0-1.85(m,4H) [Found: C, 85.5; H, 7.1; N, 3.1 $C_{30}H_{29}NO$ requires: C, 85.9; H, 6.9; N, 3.3%].

1-[(N-Triphenylmethyl)aminomethyl]-3,4-dihydronaphthalene (15)

A mixture of 1-[(N-triphenylmethyl)aminomethyl]-1,2,3,4-tetrahydronaphthalene-1-ol (1g, 0.024M), triphenylphosphine (0.73g, 0.027M), carbon tetrachloride (0.4m^3), dry triethylamine (0.21g, 0.024M), and dry acetonitrile (50cm^3) was heated at 50^{o}C for 24 hr. The solvents were then removed *in vacuo* and the residue chromatographed on a column of silica using diethyl ether - 60-80^{o}C petroleum ether (1:1) as the eluant. This gave the title compound as a colourless crystalline solid (0.38g, 40%), m.p. 104-106^{o}C; $\lambda_{max}(\epsilon)$ 220(22,200)nm; ν_{max}($CHCl_3$) 1600, 1490, 1450cm^{-1}; δ_H($CDCl_3$), 7.0-7.6(19H,m, aromatics), 6.24(1H,t,$\underline{J}$=5Hz, C_2-$\underline{H}$), 3.08(2H,d,N-$C\underline{H}_2$) (when the ^{1}H n.m.r. sample was shaken with D_2O this signal collapsed to a singlet and that at δ1.67 disappeared), 2.68(2H,m,C_4-$\underline{H}_2$), 2.30(2H,m,C_3-$\underline{H}_2$), 1.67(1H,t,N$\underline{H}$). Elemental analyses results were variable. $\underline{m}/\underline{z}$ M^+ 401.2174; $C_{30}H_{27}N$ requires: 401.2205.

Spiro-[1,2,3,4-tetrahydronaphthalen-1,5'-(1',3'-oxazolidin-2'-one)] (16)

1-Aminomethyl-1,2,3,4-tetrahydronaphthalene-1-ol (2g, 0.011M) was added to a suspension of anhydrous potassium carbonate (1.6g) in dichloromethane (50cm^3) maintained at -60^{o}C. To this was added phosgene (14cm^3 of a 12% solution in toluene) and the mixture was allowed to warm to room temperature during 11/2 days. The solvent was then removed *in vacuo* and the residue chromatographed on alumina (neutral grade) using ethyl acetate/60-80^{o}C petroleum ether (1:1) as eluant to afford the title compound as a colourless oil (0.7g, 30%); m.p. 149-150^{o}C; $\lambda_{max}(\epsilon)$ 213(7,660)nm; ν_{max}3300, 1750, 1490, 1430 and 760cm^{-1}; δ_H($CDCl_3$) 7.5-7.0(m,4H, aromatics), 6.7(s,1H,N$\underline{H}$), 3.7(2xd,2H,$\underline{J}$=9Hz, $C\underline{H}_2$-N), $\underline{2}$.9(t,2H, $\underline{J}$=5.8Hz, C_4-$\underline{H}_2$), 2.5-1.8(m,4H,C_2-$\underline{H}_2$,C_3-$\underline{H}_2$); δ_C($CDCl_3$), 137.3(2xs, C-4a, C-8a), 129.0, 128.6, 126.9, 126.6(4xd, C-5, C-6, C-7, C-8), 82.2(s,C-1), 54.3(t,C-4'), 35.8(t,C-4), 29.1(t,C-2), 19.7(t,C-3); $\underline{m}/\underline{z}$ M^+203.0964, $C_{12}H_{13}NO_2$ requires: 203.0946.

Alternative preparation of spiro-[1,2,3,4-tetrahydronaphthalen-1,5'-(1',3'-oxazolidin-2'-one)](16)

The aminoalcohol (11) (3.0g, 0.017M) in dry tetrahydrofuran (20cm^3) was added slowly to a solution of 1,1'-carbonyldiimidazole (2.7g, 0.017M) in the same solvent (50cm^3). The reaction mixture was stirred for a day and the solvent then was evaporated off to leave a residue which was triturated several times with carbon tetrachloride. It was then dissolved in a small volume of ethyl acetate and chromatographed on neutral grade alumina eluting with ethylacetate/60-80°C (1:1) to yield the title compound (16) which had identical physical characteristics to those described previously. The yield was 1.1g, 36.6%.

1-[N-Methoxycarbonyl)methylamino-1,2,3,4-tetrahydronaphthalene-1-ol

Methyl chloroformate (1.6cm^3) was added in small portions to a solution of 1-methylamino-1,2,3,4-tetrahydronaphthalene-1-ol (11) (2.4g, 0.014M) in dry pyridine (30cm^3) (previously distilled from potassium hydroxide). The reaction mixture was stirred for 12 hr and water (15cm^3) and diethyl ether (100cm^3) were then added. The ether layer was collected and the aqueous phase was extracted several times with portions of diethyl ether. The ether layer and extracts were combined, washed with water, dried and evaporated to afford the title compound as a colourless solid m.p. 97°C(2.1g, 70%). ν_{max} 3420, 3340, 2940, 1700, 1540, 1250 and 760cm^{-1}; δ_H(CDCl$_3$), 7.45-7.05(m,5H, aromatics), 4.25(s,3H,$C\underline{H}_2$-N$\underline{H}$), 3.95(s,3H,OC$\underline{H}_3$), 2.85(t,2H, $\underline{J}$=2.5Hz, C_4-$\underline{H}_2$), 2.3-1.8(m,5H,C_2-$\underline{H}_2$, C_1-O$\underline{H}$); δC(CDCl$_3$) $\underline{1}$51.5(s,$\underline{C}O_2CH_3$), 137.6, 135.7(2xs, C-4a, C-8a), 129.9, 128.9, 127.0, 126.1, (4xd, C-5, C-6, C-7, C-8), 78.7(s,C-1), 56.6(q,$CO_2\underline{C}H_3$), 54.0(t,$\underline{C}H_2$NH), 35.5(t,C-4), 28.8(t,C-2), 19.5(t,C-3), [Found: C, 66.2; H, 7.5; N,6.0 $C_{13}H_{17}NO_3$ requires: C,66.4; H,7.2; N,6.0%].

1-(N-Methylmethylamino)-1,2,3,4-tetrahydronaphthalene-1-ol (11)

A suspension of lithium aluminium hydride (0.87g, 0.22M) in dry tetrahydrofuran (30cm^3) was maintained at 0°C in a vessel protected from atmospheric moisture. To this was added 1-[N-(methoxycarbonyl)methylamino]-1,2,3,4-tetrahydronaphthalene-1-ol (0.9g, 0.028M) in tetrahydrofuran (20cm^3). After the initial reaction had subsided, the temperature inside the flask was allowed to rise to room conditions during a period of 20 hr. Aqueous sodium hydroxide (20%) was added carefully drop by drop to the reaction mixture until all the excess reagent had been destroyed. The mixture was then diluted with more tetrahydrofuran (50cm^3) and filtered. Finally, the filtrate was collected and the solvent removed to give the title compound as a yellow oil (0.73g, 98%), ν_{max} 3400, 3320, 2940, 1450, 760 and 730cm^{-1}; δ(CDCl$_3$), 6.9-7.4(m,4H, aromatics), 2.8(bs, 2H, N-C$\underline{H}_2$), $\underline{2}$.50(s,3H,C$\underline{H}_3$N), 2.3(bs,1H,N$\underline{H}$), 1.7-2.2(m,7H,3xC$\underline{H}_2$ + O$\underline{H}$); $\underline{m/z}$ 191. Attempts to obtain a satisfactory elemental analysis for this compound failed.

Spiro-[1,2,3,4-tetrahydronaphthalen-1,5'-(3'-methyl-1',3'-oxazolidin -2'-one)] (16)

A mixture of anhydrous potassium carbonate (10.4g, 0.076M), dry dichloromethane (50cm^3) and 1-[N-methyl-aminomethyl]-1,2,3,4-tetrahydronaphthalene-1-ol (0.73g, 0.038M) was maintained at -60°C and treated with phosgene (4.7cm^3 of a 12% solution in toluene). After 2 hr, the reaction mixture was allowed to warm gradually to room temperature during 24 hr. The solvents were then removed in vacuo and the residue chromatographed on neutral grade alumina eluting with ethylacetate/60-80°C petroleum ether (1:1) to give the title compound as a colourless oil. ν_{max}3450, 2940, 1750, 765cm^{-1}; δ_H(CDCl$_3$) 7.4-7.05(m,4H, aromatics), 3.62(2xd, 2H, $\underline{J}$=8.5Hz, C_4-$\underline{H}_2$), 2.98(s,3H,N-C$\underline{H}_3$), 2.8(m,2H,C_4-H_2), 2.3-1.95(m,4H,C_2-H_2,C_3-H_2); δ_C(CDCl$_3$), 183.3(s,C-2'), 137.2(2xs, C-4a, C-8a), 128.9, 128.4, 126.8, 126.3(4xd, C-5, C-6, C-7, C-8), 78.1(s,C-1), 60.6(t,C-4'), 35.9(t,C-4), 31.0(q,N$\underline{C}H_3$), 29.0(t,C-2), 19.6(t,C-3); $\underline{m/z}$ M$^+$ 217.1103 $C_{13}H_{15}NO_2$ requires: 217.1096.

Spiro-[1,2,3,4-tetrahydronaphthalen-1,2'-oxacyclopropane] (13)

Dimethylsulphoxonium iodide (30g, 0.14M) was added rapidly to a well stirred suspension of sodium hydride (3.3g, 0.14M) in anhydrous dimethylsulphoxide (50cm^3) protected by an atmosphere of nitrogen and maintained at 0°C. After the addition, stirring was continued for a further 15 min and 1-tetralone (10g, 0.07M) was then introduced. The reaction mixture was allowed to warm to room temperature and it was then heated to reflux for 1 hr and finally set aside to cool overnight. The next day water (100cm^3) was added and the product extracted into diethyl ether (2x100cm^3). Evaporation of the combined, dried extracts afforded the oxirane (13) as an oil (11g, 98%); ν_{max} 3140, 2940, 1490, 1450, 760cm^{-1}; δ_H(CDCl$_3$) 7.55-6.85(4H,m, aromatics), 2.90(2H,s, C$\underline{H}_2$O), 2.89-1.59(6H,m,C_2-$\underline{H}_2$,C_3-$\underline{H}_2$,C_4-$\underline{H}_2$); $\underline{m}/\underline{z}$ 160 [Found: C, 82.3; H, 7.1 calculated for $C_{11}H_{12}O$: C, 82.5; H, 7.5%].

1-Hydroxymethyl-3,4-dihydronaphthalene (14)[10]

The epoxide (205) (1.5g, 0.009M) in dimethylformamide (40cm^3) containing benzylamine (1g, 0.009M) was saturated with hydrogen chloride during 3 hr. Water was then added and sufficient sodium carbonate to render the mixture neutral to litmus. This was then extracted with diethyl ether (3x20cm^3) and the combined extracts, dried and evaporated to yield a gum. Chromatography on neutral grade alumina using diethyl ether and 60-80°C petroleum ether (1:1) gave the alcohol (207) (0.4g, 30%) as an oil. Early fractions containing unreacted starting material (0.9g, 60%); ν_{max} 3400, 2940, 1480, 1450, 750, 730cm^{-1}; δ_H(CDCl$_3$) 7.3-7.0(4H,m, aromatics), 6.0(1H,t, $\underline{J}$=4Hz, C_2-$\underline{H}$), 4,5(2H,s,C$\underline{H}_2$OH), 3.0-2.7(2H,m, C_4-$\underline{H}_2$), 2.5-2.2(2H,m,C_3-$\underline{H}_2$), 1.9(1H,bs, exchanged with D_2O, -O$\underline{H}$); $\underline{m}/\underline{z}$ M^+ 160.0888; $C_{11}H_{12}O$ requires: 160.0867.

Alternative preparation of 1-hydroxymethyl-3,4-dihydronaphthalene (14)

The epoxide (13) (0.8g, 0.0005M) in dry tetrahydrofuran (50cm^3) containing zinc iodide (1.75g) was stirred for 15 min and benzylamine (0.5g, 0.005M) was then added. The reaction mixture was allowed to stand for 12 hr, the solvent was then removed and the residue chromatographed on neutral grade alumina using diethyl ether/60-80°C petroleum ether (1:1) as eluant. This gave the alcohol (14) as a colourless oil (0.3g, 50%). All spectroscopic data for this compound agreed with those obtained for the product from the previous experiment.

3,4-Dihydro-1(2H)-methylenenaphthalene (18)[11]

n-Butyllithium in dry diethylether (95cm^3, 0.14M solution) was added slowly to a mixture of triphenylphosphonium iodide (58.6g, 0.14M) in dry diethyl ether (250cm^3). After 20 min, tetralone (12cm^3, 0.9M) was introduced into the reaction mixture which was stirred at room temperature for a day and then heated at reflux for 1 hr.

Water was then added to dissolve the salts which had formed and the organic layer was dried and evaporated to give an oil. This material was chromatographed on alumina using 60-80°C petrol to elute the title compound (6.5g, 50%) as a colourless oil; ν_{max} 1640cm^{-1} δ_H(CDCl$_3$), 7.2-7.0(4H,m, aromatics), 5.5 and 4.9(2x1H, 2xd $\underline{J}$=0.7Hz, C=C$\underline{H}_2$), 2.8(2H,t,$\underline{J}$=4Hz, C_4-$\underline{H}_2$), 2.6(2H,bt, $\underline{J}$=4.5Hz, C_2-H_2), 1.9(2H,t, $\underline{J}_1$=4.5Hz, J_2=4Hz, C_3-$\underline{H}_2$); δ_C(CDCl$_3$), 143.5, 137.3(2xs, C-4a, C-8a), 129.2, 127.6, 125.9, 124.2(4xd, C-5, C-6, C-7, C-8), 107.8(t, exocyclic carbon), 33.3(C-4), 30.5(C-2), 23.8(C-3), the resonance position of C-1 could not be assigned. $\underline{m}/\underline{z}$ 144.

1-Azido-1-iodomethyl-1,2,3,4-tetrahydronaphthalene (19)

Sodium azide (2.3g, 0.035M) and anhydrous acetonitrile (40cm^3) were cooled to -15°C and treated with iodine monochloride (2.6g, 0.02M) in anhydrous acetonitrile (4cm^3). The addition took place over a period of 15 min and the reaction mixture was stirred for a further 10 min before 3,4-dihydro-1(2H)-methylenenaphthalene (2g, 0.014M) was introduced. The reaction mixture was then allowed to stir and warm to room temperature overnight.

Water ($30cm^3$) was then added and the product extracted into diethyl ether ($2x20cm^3$). The combined dried extracts were evaporated to afford a yellow oil (4.2g, 95%); ν_{max}2960, 2120, 1500, 1450, 1260, 770, $740cm^{-1}$; $\delta_H(CDCl_3)$ 7.5–7.0(4H,m, aromatics), 3.45(2H,s,$C\underline{H}_2I$), 2.78(2H,t, *J*=4Hz, C_4-$\underline{H}_2$), 2.4–1.6(4H,m, C_2-$\underline{H}_2$, C_3-$\underline{H}_2$); $\delta_C(CDCl_3)$, 137.4, 134.5(2xs, C-4a, C-8a), 129.6, 128.5, 126.7(3xd, C-5, C-6, C-7, C-8), 63.8(s,C-1), 34.4(t,C-4), 29.4(t,C-3), 19.5(t,C-2), 16.6(t,$C\underline{H}_2I$); *m/z* 313.

Spiro-[1,2,3,4-tetrahydronaphthalen-1,2'-(1H-azacyclopropane)(1,R=H)

1-Azido-1-iodomethyl-1,2,3,4-tetrahydronaphthalene (1.6g, 0.01M), in dry diethyl ether ($15cm^3$) was added slowly to a suspension of lithium aluminium hydride (1.2g) in the same solvent ($10cm^3$) maintained at 0°C. After the addition the reaction mixture was allowed to warm to room temperature overnight. Excess reagent was then destroyed by the addition of 20% aqueous sodium potassium tartarate solution and the ether layer decanted off. The residue was washed twice with diethyl ether ($100cm^3$) and the combined organic phases were then dried and avaporated to yield the aziridine (1,R=H) as a very unstable colourless oil (0.1g, 60%); ν_{max}3300, 2940, 1500, 1460, $760cm^{-1}$; $\delta_H(CDCl_3)$7.25–6.80(4H,m, aromatics), 2.90(2H,bt,*J*=4Hz, C_4-$\underline{H}_2$), 2.12(1H,s,$N\underline{H}$, exchanged with D_2O), 2.05–1.78 (6H,m,$C\underline{H}_2N$, C_2-$\underline{H}_2$, C_3-$\underline{H}_2$); *m/z* 159.

The N-methoxycarbonyl derivative (1,R=CO_2Me) of this compound was made by reaction with methyl chloroformate and triethylamine. It is also an oil; pν_{max} 1700, 1440, $760cm^{-1}$; *m/z* 217.1119 $C_{13}H_{15}NO_2$ requires: *m/z* 217.1103.

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