1,3,4,5-Tetrahydrobenz[*cd*]indoles and Related Compounds. Part III.[1]

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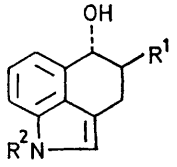
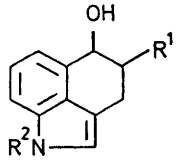
Syntheses of derivatives of the isomeric 4-amino-1,3,4,5-tetrahydrobenz[*cd*]indol-5-ols (1) and (6) and the structurally similar 4-amino-2a,3,4,5-tetrahydroacenaphthen-5-ols (22) and (28), and of certain *N*-alkyl and *NN*-dimethyl derivatives are described. Preparation of the tetrahydrobenz[*cd*]indole series was made possible by the use of the tosyl group for protection of the indole imino-group.

In continuation of our studies on the synthesis of 1,3,4,5-tetrahydrobenz[*cd*]indoles for biological testing, we report the preparation of derivatives of the isomeric 4-amino-1,3,4,5-tetrahydrobenz[*cd*]indol-5-ols (1) and (6) and the related tetrahydroacenaphthenes. Our interest in these substances stemmed from their structural relation to the naturally-occurring sympathomimetic amine, noradrenaline; in addition the structures (1) and (6) contain the tryptamine system.

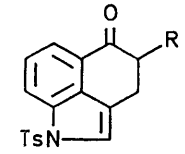


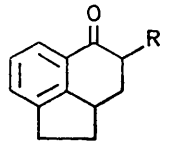


(1) $R^1 = NH_2$, $R^2 = H$
(2) $R^1 = NH_2$, $R^2 = Ts$
(3) $R^1 = NH{\cdot}CO_2Me$, $R^2 = Ts$
(4) $R^1 = NMe_2$, $R^2 = Ts$
(5) $R^1 = NMe_2$, $R^2 = H$

(6) $R^1 = NH_2$, $R^2 = H$
(7) $R^1 = NH_2$, $R^2 = Ts$
(8) $R^1 = N_3$, $R^2 = Ts$
(9) $R^1 = NH{\cdot}CO_2Me$, $R^2 = Ts$
(10) $R^1 = NMe_2$, $R^2 = H$
(11) $R^1 = NHMe$, $R^2 = H$

The bromo-ketone (12) does not give basic products on treatment with aliphatic bases,[1] but it does, however, react readily with sodium azide in dimethylformamide–acetic acid [2] to give high yields of the azido-ketone (13), which proved a key intermediate in the preparation of





(12) R = Br
(13) R = N_3
(14) R = NH_2,HCl
(15) R = $NH{\cdot}CO_2Me$

(16) R = H
(17) R = NH_2,HCl
(18) R = N_3
(19) R = NHBz
(20) R = NHAc
(21) R = CH_2NMe_2,HCl

Ts = p-$MeC_6H_4{\cdot}SO_2$

the isomeric amino-alcohols (5) and (10) and their derivatives. Hydrogenation of the azido-ketone (13) gave the amino-ketone hydrochloride (14), which was reduced with potassium borohydride to give a crystalline tosylamino-alcohol (2) (m.p. 166—168°) shown by its n.m.r.

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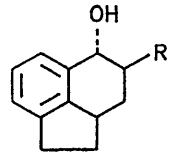
[1] Part II, R. E. Bowman, D. D. Evans, J. Guyett, H. Nagy, J. Weale, D. J. Weyell, and A. C. White, *J.C.S. Perkin I*, 1972, 1926.

[2] J. H. Boyer and D. Straw, *J. Amer. Chem. Soc.*, 1952, **74**, 4506.

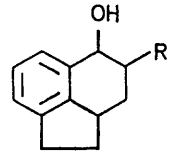
spectrum (J 6·5 Hz; diaxial protons) to be the *trans*-isomer (2), in which the hydroxy- and the amino-group take up equatorial conformations. On the other hand, reduction of the azido-ketone (13) with lithium aluminium hydride at room temperature gave a mixture of isomers from which a different stereoisomer (7) (m.p. 177—181°) could be isolated in low yield; if the amino-group takes up the preferred equatorial conformation as in the *trans*-isomer (2) then the conformation of the hydroxy-group in the *cis*-isomer (7) must be axial. A more satisfactory procedure for the preparation of the *cis*-amino-alcohol (7) in quantity involved reduction of the azido-ketone (13) with lithium borohydride to the azido-alcohol (8), which was reduced catalytically.

The isomeric tosyl-amino-alcohols (2) and (7) were converted into the corresponding indole *N*-methyl (11) and *NN*-dimethyl (5) and (10) analogues by standard procedures.

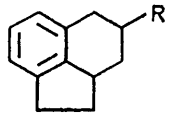
In the tetrahydroacenaphthene series 3,4-dihydroacenaphthen-5(2a*H*)-one (16) was converted into the amino-ketone hydrochloride (17) by three routes, *viz.* the Neber rearrangement,[3] oximation of the ketone (16) followed by hydrogenation of the α-hydroxyimino-ketone, and *via* the azido-ketone (18), in sharp contrast to the tetrahydrobenz[*cd*]indole series where only the azido-ketone route was successful.



(22) R = NH_2,HCl
(23) R = NHBz
(24) R = NHAc
(25) R = NMe_2,HCl
(26) R = NHMe,HCl
(27) R = CH_2NMe_2,HCl



(28) R = NH_2HCl
(29) R = NHBz
(30) R = NHMe,HCl
(31) R = NMe_2,HCl



(32) R = NH_2,HCl
(33) R = NHAc
(34) R = NHEt,HCl
(35) R = CH_2·NMe_2,HCl

Benzoylation of the amino-ketone hydrochloride (17) and reduction of the benzamido-ketone (19) with potassium borohydride gave the benzamido-alcohol (23), which was shown to be the *trans*-isomer (J 7 Hz, diaxial coupling, 4- and 5-H). Similarly prepared was the *trans*-acetamido-alcohol (24) (J 9 Hz). Reduction of the amino-ketone hydrochloride (17) with sodium borohydride also gave the *trans*-amino-alcohol which was isolated as its hydrochloride (22). Isomerisation and deacetylation of the *trans*-acetamido-alcohol (24) with refluxing 0·1N-hydrochloric acid yielded the *cis*-amino-alcohol hydrochloride (28), as shown by its conversion into the *cis*-benzamido-alcohol (29) (J 3·5 Hz, axial–equatorial coupled 4- and 5-H). A number of derivatives of the *cis*- and *trans*-amino-alcohols are described in the Experimental section together with details of their conversion into the *N*-methyl [(30) and (26)] and *NN*-dimethyl [(31) and (25)] analogues by standard procedures.

Again in contrast to the tetrahydrobenz[*cd*]indole series where hydrogenolysis of the 5-hydroxy-group was unsuccessful, the deoxy-analogue (32) was readily prepared by hydrogenolysis in the presence of 10% palladised charcoal under acidic conditions; certain of these acenaphthenamines were also converted into the corresponding *N*-alkyl analogues. The Mannich reaction was also carried out on the ketone (16); reduction of the resulting dimethylaminomethyl ketone (21) with potassium borohydride gave the dimethylaminomethyl alcohol (27), which yielded the deoxy-analogue (35) on hydrogenolysis.

EXPERIMENTAL

M.p.s were determined with a Kofler hot-stage apparatus. U.v. and i.r. spectra were determined for ethanolic solutions and Nujol mulls, respectively, unless otherwise specified. Potentiometric titrations were carried out for solutions in aqueous ethanol (1 : 1), and [$^2H_6$]dimethyl sulphoxide was used as solvent for n.m.r. spectra (Varian A60 spectrometer). All compounds gave satisfactory analytical figures. Analytical and spectral data are tabulated in Supplementary Publication No. SUP 20613 (8 pp).*

4-Azido-3,4-dihydro-1-(p-tolylsulphonyl)benz[cd]*indol-5*(1H)*-one* (13).—Sodium azide (2·5 g) in water (20 ml) was added to a solution of the tosyl-bromo-ketone (12) (6·95 g) in dimethylformamide (80 ml) and acetic acid (2·5 ml) at 0°. After a few minutes the yellow precipitate was filtered off, washed with ethanol and ether, and dried. This material was normally used without further purification. A sample crystallised by dissolving the solid in hot acetone–ethyl acetate, adding methanol, and allowing the solution to cool gave the *azido-ketone* (13), m.p. 176—178° (decomp. depending on rate of heating)

4-Amino-3,4-dihydro-1-(p-tolylsulphonyl)benz[cd]*indol-5*(1H)*-one Hydrochloride* (14).—The tosyl-azido-ketone (13) (1·57 g) was hydrogenated in ethanol (50 ml) in the presence of concentrated hydrochloric acid (1·57 ml) and 10% palladised charcoal (157 mg) for 5 h, the mixture was warmed and filtered, and the filtrate was evaporated *in vacuo* to give a yellow solid (1·38 g). Crystallisation from ethanol–ether gave the *hydrochloride* (14), m.p. 182—185° (decomp.); *methoxycarbonyl derivative* (15), m.p. 170—173° (from ethanol); *benzoyl derivative*, m.p. 114—118°.

trans-*4-Amino-1,3,4,5-tetrahydro-1-(p-tolylsulphonyl)benz*-[cd]*indol-5-ol* (2).—A suspension of the tosyl-amino-ketone hydrochloride (14) (5·9 g) in absolute ethanol (200 ml) was added in portions during 10 min to an ice-cooled stirred solution of sodium borohydride (1·2 g) in absolute ethanol

* For details of Supplementary Publications see Notice to Authors No. 7 in *J. Chem. Soc.* (*A*), 1970, Issue No. 20.

[3] C. O'Brien, *Chem. Rev.*, 1964, **64**, 81.

(100 ml) maintained at 5°. Stirring was continued for a further 1 h before the mixture was acidified with 2N-hydrochloric acid and the ethanol was evaporated off *in vacuo*. Isolation of the base in the usual way gave a solid (4·71 g, 87%), which crystallised from acetonitrile to give the trans-*tosyl-amino-alcohol* (2), m.p. 166—168°; *hydrochloride*, m.p. 235—237°; NO-*diacetyl derivative*, m.p. 183—185°; N-*benzoyl*, m.p. 278°; N-*acetyl*, m.p. 123—125°; NO-*diformyl*, m.p. 176·5—177·5°.

cis-4-*Amino*-1,3,4,5-*tetrahydro*-1-(p-*tolylsulphonyl*)*benz*[cd]*indol*-5-*ol* (7).—(*a*) A solution of the azido-ketone (13) (732 mg) in anhydrous tetrahydrofuran (45 ml) was added to a stirred suspension of lithium aluminium hydride (246 mg) in anhydrous tetrahydrofuran (30 ml) at 0—5°, and stirring was continued for 15 min before successive addition of water (0·25 ml), 4N-sodium hydroxide (0·25 ml), and water (0·75 ml). The mixture was filtered and evaporated to dryness *in vacuo*, and the basic product was extracted with aqueous citric acid in the usual way. Trituration of the product with ethyl acetate gave a solid (369 mg) m.p. 163—167°, which crystallised from acetonitrile to give the cis-*tosyl-amino-alcohol* (7), m.p. 177—181°.

(*b*) The tosyl-azido-alcohol (8) (1·78 g) was hydrogenated in acetic acid (100 ml) over 10% palladised charcoal (450 mg). After 1·5 h, filtration, evaporation, and isolation of the basic product in the usual way gave a solid (958 mg) which crystallised from acetonitrile to give the *cis*-tosyl-amino-alcohol (7), m.p. and mixed m.p. 175—179°; *hydrochloride*, m.p. 248° (decomp.); NO-*diacetyl derivative*, m.p. 236—238; N-*acetyl*, m.p. 232—233°. Compound (2) depressed the m.p. of the sample from method (*b*).

cis-4-*Azido*-1,3,4,5-*tetrahydro*-1-(p-*tolylsulphonyl*)*benz*[cd]-*indol*-5-*ol* (8).—A solution of the azido-ketone (13) (4 g) in anhydrous tetrahydrofuran (200 ml) was added to an ice-cooled stirred solution of lithium borohydride (1 g) in tetrahydrofuran (40 ml) and stirring was continued for 1·5 h before the addition of 2N-hydrochloric acid. Most of the tetrahydrofuran was evaporated off *in vacuo*, and the product was extracted with ethyl acetate. Evaporation of the washed and dried extract gave an oil, which was triturated with ether to yield a solid (3·38 g). Crystallisation from methanol gave the cis-*azido-alcohol* (8), m.p. 163—166°.

Methyl trans-1,3,4,5-*Tetrahydro*-5-*hydroxy*-1-(p-*tolylsulphonyl*)*benz*[cd]*indole*-4-*carbamate* (3).—(*a*) A mixture of the tosyl-keto-urethane (15) (500 mg) and potassium borohydride (100 mg) in a mixture of tetrahydrofuran (5 ml) and methanol (10 ml) was stirred at room temperature for 2 h, then cooled in an ice-bath and acidified with 0·1N-hydrochloric acid. The organic solvents were evaporated off *in vacuo*, and the product was extracted with ethyl acetate. Evaporation of the washed and dried extract gave a white solid (480 mg). Crystallisation from ethanol gave the trans-*tosyl-hydroxy-urethane* (3), m.p. 189—191°.

(*b*) Reaction of the *trans*-tosyl-amino-alcohol (2) with methyl chloroformate in the usual way also gave the *trans*-tosyl-hydroxy-urethane (3), m.p. 190—191°; O-*acetyl derivative*, m.p. 158—160°.

Methyl cis-1,3,4,5-*Tetrahydro*-5-*hydroxy*-1-(p-*tolylsulphonyl*)*benz*[cd]*indole*-4-*carbamate* (9).—Reaction of the *cis*-tosyl-amino-alcohol (7) with methyl chloroformate as in the preceding experiment gave the cis-*hydroxy-urethane* (9), m.p. 183—184°; O-*acetyl derivative*, m.p. 237° (decomp.).

trans-4-*Dimethylamino*-1,3,4,5-*tetrahydrobenz*[cd]*indol*-5-*ol* (5).—(*a*) A mixture of the *trans*-tosyl-amino-alcohol (2) (342 mg), 90% formic acid (1 ml), and 36% (w/w) formaldehyde solution was refluxed for 5·5 h; water was added, followed by 2N-sodium hydroxide, and the basic product, isolated in the usual manner, gave an oil (325 mg). A solution of the oil in ethyl acetate (10 ml) was treated with acetic anhydride (1 ml) and set aside for 16 h. Isolation of the basic material in the usual manner gave a solid, which crystallised from propan-2-ol to yield the trans-*tosyl-acetoxy-dimethylamino-derivative* (243 mg), m.p. 162—164°. Hydrolysis of the latter with dilute sodium hydroxide gave the trans *tosyl-dimethylamino-alcohol* (4), m.p. 128—130°. Crystallisation from propan-2-ol did not raise the m.p. Hydrolysis with refluxing ethanolic 15% potassium hydroxide for 2·5 h gave the trans-*dimethylamino-alcohol* (5), m.p. 196—198°.

(*b*) A mixture of the *trans*-tosyl-amino-alcohol (2) (200 mg) and aqueous formaldehyde (36% w/w; 1·5 ml) in ethanol (30 ml) and propan-2-ol (10 ml) was hydrogenated over 10% palladised charcoal (200 mg) for 2·5 h. After filtration and evaporation, the basic product was isolated with aqueous citric acid and acetylated as in (*a*) to give the *trans*-tosyl-acetoxy-dimethylamino-derivative (80 mg), m.p. 162—165°, identical (i.r.) with the sample from (*a*).

cis-4-*Dimethylamino*-1,3,4,5-*tetrahydrobenz*[cd]*indol*-5-*ol* (10).—Reaction of the *cis*-tosyl-amino-alcohol (7) (342 mg) with 90% formic acid (1 ml) and 36% (w/w) aqueous formaldehyde as for the *trans*-isomer gave the cis-*tosyl-acetoxy-dimethylamino-derivative*, m.p. 182—184°. Hydrolysis with ethanolic 3N-potassium hydroxide for 2·25 h gave the cis-*dimethylamino-alcohol* (10), m.p. 155—157°.

cis-4,6,6a,9a-*Tetrahydro*-4-(p-*tolylsulphonyl*)*indolo*[3,4-fg]-*benzoxazol*-8(7H)-*one*.—Sodium hydrogen carbonate was added to an ice-cooled stirred mixture of the *cis*-tosyl-amino-alcohol (7) (342 mg), water (10 ml), 2N-hydrochloric acid (2 ml), and phosgene in toluene (12·5%; 3 ml) until the mixture was alkaline. Stirring was then continued for 1 h at ambient temperature, before ethyl acetate and a further 2 ml of the phosgene solution, followed by sodium hydrogen carbonate, were added. After a further 30 min water was added and the organic phase was separated, washed with water, dried, and evaporated to an oil (365 mg). Trituration with ether gave a solid (225 mg). Crystallisation from 96% ethanol gave the *oxazolone*, m.p. 233—235°, $\nu_{max.}$ 1755 and 3300 cm^{-1} (Found: C, 62·3; H, 4·6; N, 7·3. $C_{19}H_{16}N_2O_4S$ requires C, 61·9; H, 4·4; N, 7·6%).

cis-4,6,6a,9a-*Tetrahydro*-7-*methyl*-4-(p-*tolylsulphonyl*)-*indolo*[3,4-fg]*benzoxazol*-8(7H)-*one*.—A solution of the preceding oxazolone (600 mg) in anhydrous dimethylformamide (5 ml) was added slowly under nitrogen to an ice-cooled stirred solution of sodium hydride (50% dispersion in oil; 95 mg) and stirring was continued at room temperature for 0·5 h. The mixture was again cooled in ice, methyl iodide (2 ml) was added, and the mixture was stirred at room temperature for 0·5 h before evaporation. Water was added to the residue and the solid (640 mg) obtained was filtered off; crystallisation from benzene (charcoal) gave the *methyl-oxazolone*, m.p. 196—197·5, $\nu_{max.}$ 1740 cm^{-1} (Found: C, 63·5; H, 4·9; N, 7·6. $C_{20}H_{18}N_2O_4S$ requires C, 62·8; H, 4·75; N, 7·3%).

cis-1,3,4,5-*Tetrahydro*-4-*methylaminobenz*[cd]*indol*-5-*ol* (11).—(*a*) A stirred mixture of the *cis*-tosyl-hydroxy-urethane (9) (6·5 g) and lithium aluminium hydride (6·5 g) in anhydrous tetrahydrofuran (340 ml) was heated under reflux for 16·5 h. Work-up as before and isolation of the basic product with aqueous citric acid gave a solid (1·4 g)

which crystallised from ethanol to give the cis-*methylamino-alcohol* (11), m.p. 183—186°.

(*b*) The *cis*-tosyl-amino-alcohol (7) was converted with acetic formic anhydride into its NO-*diformyl derivative*, m.p. 98—100°, which was reduced with an equal weight of lithium aluminium hydride in tetrahydrofuran in 17 h to the *cis*-methylamino-alcohol (11), m.p. 185—188°.

(*c*) Reduction of the preceding tosyl-oxazolidone with an equal weight of lithium aluminium hydride for 17 h gave the *cis*-methylamino-alcohol (11), m.p. 180—184°.

(*d*) Hydrolysis of the preceding tosyl-*N*-methyl-oxazolidone with ethanolic 15% potassium hydroxide under nitrogen for 2·5 h gave the *cis*-methylamino-alcohol (11), m.p. 185—188°.

Samples from (*a*), (*b*), (*c*), and (*d*) were identical (mixed m.p.).

3,4-*Dihydroacenaphthen*-5(2aH)-*one* O-p-*Tolylsulphonyloxime*.—A mixture of 3,4-dihydroacenaphthen-5(2a*H*)-one oxime (935 mg) and toluene-*p*-sulphonyl chloride (1·05 g) in pyridine (5 ml) was heated on a steam-bath for 1 h; the mixture was poured into water and the solid was filtered off, washed, and dried. Crystallisation from ethyl acetate gave the *ester*, m.p. 165—166°.

4-*Acetamido*-3,4-*dihydroacenaphthen*-5(2aH)-*one* (20).—A solution of trimethylphenylammonium tribromide (1·88 g) in tetrahydrofuran (10 ml) was added dropwise to a stirred solution of 3,4-dihydroacenaphthen-5(2a*H*)-one (16) (860 mg) in tetrahydrofuran (10 ml) at 5°. After 10 min the mixture was filtered and the filtrate was evaporated to dryness *in vacuo* to give an oil (2·1 g), which was dissolved in ether. Evaporation of the washed and dried ethereal solution gave an oil (1·64 g). A stirred solution of the oil in dimethylformamide (10 ml) and acetic acid (0·5 ml) was treated with sodium azide (1 g) in water (2 ml), and the mixture was stirred for 1 h before being diluted with water. Isolation of the product by extraction with ether gave an oil (1·5 g), $\nu_{max.}$ 2100 cm^{-1} (azide). Hydrogenation of the latter in acetic acid (10 ml) over 10% palladised charcoal (100 mg) for 4 h and subsequent acetylation gave the *acetamido-ketone* (20), m.p. 167—170° (from 1 : 1 aqueous methanol).

4-*Amino*-3,4-*dihydroacenaphthen*-5(2aH)-*one Hydrochloride* (17).—(*a*) Solutions of 3,4-dihydroacenaphthen-5(2a*H*)-one (16) (3·45 g) in anhydrous ether (20 ml) and pentyl nitrite (2·8 ml; 0·02 mol) in t-butyl alcohol (10 ml) were added successively to a stirred solution of potassium t-butoxide [from potassium (800 mg, 0·02 mol)] in t-butyl alcohol (40 ml) under nitrogen, and the mixture was heated under reflux for 3 h. The residue obtained on evaporation to dryness was partitioned between ether and water; the aqueous phase was separated, and acidified with 2N-hydrochloric acid. The oily product, isolated by extraction with ether, was triturated with ether to give the crude α-hydroxyimino-ketone (1·4 g), m.p. 185° (decomp.). A portion (620 mg) of the latter was hydrogenated in acetic acid (15 ml) over 10% palladised charcoal to give the amino-ketone, which was isolated as the *hydrochloride* (17) (600 mg), m.p. 202—205°; acetyl derivative (20), m.p. 166—169°. The same acetyl derivative was obtained by hydrogenation of the α-hydroxyimino-ketone in acetic acid–acetic anhydride; *benzoyl* derivative (19), m.p. 181—183°; *methoxycarbonyl*, m.p. 146—148°; p-*tolylsulphonyl*, m.p. 165—166°.

(*b*) A solution of sodium ethoxide (0·01 mol) [from sodium (260 mg) and ethanol (10 ml)] was added to a stirred solution of 3,4-dihydroacenaphthen-5(2a*H*)-one *O*-*p*-tolylsulphonyloxime (3·41 g) in benzene (60 ml) and stirring was continued for 23 h. The mixture was filtered through supercel and the filtrate was extracted with 2N-hydrochloric acid. Evaporation of the extract gave a solid, which was extracted with absolute ethanol, and the insoluble material was filtered off. The filtrate, evaporated to dryness *in vacuo*, gave a residue which was triturated with acetone–ether to yield the crude hydrochloride (17) (1·42 g). The acetyl derivative (20), m.p. 161—164°, was identical (mixed m.p.) with a sample from (*a*).

trans-4-*Acetamido*-2a,3,4,5-*tetrahydroacenaphthen*-5-*ol* (24).—Sodium borohydride (100 mg) was added to a stirred solution of the acetamido-ketone (20) (500 mg) in methanol (10 ml). After 10 min a solid was precipitated; after stirring for a further 50 min water was added and the solid (382 mg) was filtered off. Crystallisation from ethanol–propan-2-ol (1 : 1; 5 ml) gave the trans-*acetamido-alcohol* (24), m.p. 214—216°. Similarly prepared was the corresponding *trans*-hydroxy-urethane, m.p. 159—161°; trans-*benzamido-alcohol* (23), m.p. 224—227°.

trans-4-*Amino*-2a,3,4,5-*tetrahydroacenaphthen*-5-*ol Hydrochloride* (22).—A suspension of the amino-ketone hydrochloride (17) (1·0 g) in absolute ethanol (30 ml) was added during 10 min to an ice-cooled solution of sodium borohydride (200 mg) in absolute ethanol (10 ml). Stirring was continued for 1 h, the mixture was poured into 2N-hydrochloric acid (50 ml), and the ethanol was evaporated off *in vacuo*. The residual aqueous phase was washed with ether, and basified with 2N-sodium hydroxide; the product was extracted with ether, and isolated as the *hydrochloride* (717 mg) which melted (decomp.) from 275°; NO-*dibenzoyl derivative*, m.p. 182—184°; N-*methoxycarbonyl*, m.p. 159—160°; N-p-*tolylsulphonyl*, m.p. 169·5—171°.

cis-4-*Amino*-2a,3,4,5-*tetrahydroacenaphthen*-5-*ol Hydrochloride* (28).—A stirred suspension of the *trans*-acetamido-alcohol (24) (4·3 g) in 0·1N-hydrochloric acid was heated under reflux for 2 h; within 1 h the suspended solid had dissolved. The solution was decolourised with charcoal, filtered, concentrated to *ca.* 20 ml, and left for 1 h. The solid which separated was the cis-*amino-alcohol hydrochloride* (1·96 g), m.p. 255—262°, which furnished (94%, yield) the *N*-benzoyl derivative (29), m.p. 217—219°; *diformyl derivative*, m.p. 197—202°.

cis- *and* trans-4-*Dimethylamino*-2a,3,4,5-*tetrahydroacenaphthen*-5-*ol Hydrochlorides*.—A mixture of the *trans*-amino-alcohol hydrochloride (22) (2·26 g), sodium formate (680 mg), 36% (w/w) aqueous formaldehyde (10 ml), and 90% formic acid (20 ml) was heated under reflux for 4·5 h, cooled, and poured into water. The mixture was washed with ether and the aqueous acidic phase was basified with ice-cold 5N-sodium hydroxide; the product was extracted with ether and isolated as the trans-*hydrochloride* (25), m.p. 259—261° (from 2N-hydrochloric acid).

Similarly, from the *cis*-methylamino-alcohol hydrochloride (30), was prepared the cis-*dimethylamino-alcohol hydrochloride* (31), m.p. 220—230°.

cis- *and* trans-4-*Methylamino*-2a,3,4,5-*tetrahydroacenaphthen*-5-*ol Hydrochlorides*.—The *trans*-amino-alcohol hydrochloride (22) was converted with acetic formic anhydride and sodium formate into its NO-*diformyl derivative*, m.p. 187—188°. A stirred mixture of this derivative (7·58 g) and lithium aluminium hydride (3·8 g) in tetrahydrofuran (175 ml) was heated under reflux in nitrogen for 18·5 h. Work-up in the usual manner with potassium sodium tartrate

solution and extraction of the basic product with 2N-hydrochloric acid gave the trans-*hydrochloride* (26), m.p. 252° (from dilute hydrochloric acid).

Similarly prepared was the cis-*methylamino-alcohol hydrochloride* (30), m.p. 200—210°.

trans-4-*Ethylamino*-2a,3,4,5-*tetrahydroacenaphthen*-5-*ol Hydrochloride*.—The *trans*-amino-alcohol hydrochloride (22) was converted with acetic anhydride in pyridine into the trans-NO-*diacetyl derivative*, m.p. 176—177°; this was converted with lithium aluminium hydride, as described for the *trans-NO*-diformyl derivative, into the *title compound*, m.p. 241—242° (from 2N-hydrochloric acid).

2a,3,4,5-*Tetrahydroacenaphthen*-4-*amine Hydrochloride* (32).—The *trans*-amino-alcohol hydrochloride (22) (2·27 g) was hydrogenated in acetic acid (50 ml) in the presence of concentrated sulphuric acid (2·5 ml) and 10% palladised charcoal (500 mg) to give the deoxy-amine, which was isolated as the *hydrochloride* (32), m.p. *ca.* 325° (decomp.); *acetyl derivative* (33), m.p. 175—177°.

Similarly prepared was the N-*methyl hydrochloride*, m.p. 255—257°.

N-*Ethyl*-2a,3,4,5-*tetrahydroacenaphthen*-4-*amine Hydrochloride* (34).—A stirred mixture of the acetamido-derivative (33) (1·5 g) and lithium aluminium hydride (750 mg) in tetrahydrofuran (100 ml) was heated under reflux for 18 h, and worked up in the usual manner with aqueous potassium sodium tartrate. Extraction of the basic product with ethyl acetate gave an oil, which was converted into the *hydrochloride* (920 mg), m.p. 251—253°.

4-*Dimethylaminomethyl*-3,4-*dihydroacenaphthen*-5(2aH)-*one Hydrochloride* (21).—A mixture of 3,4-dihydroacenaphthen-5(2a*H*)-one (16) (3·45 g), dimethylamine hydrochloride (2·02 g), paraformaldehyde (1·8 g), and concentrated hydrochloric acid (5 drops) in 96% ethanol (25 ml) was heated under reflux for 1·5 h. Work-up in the usual manner gave an oil (1·6 g) which was converted into the *hydrochloride* (21), m.p. 192—193°.

4-*Dimethylaminomethyl*-2a,3,4,5-*tetrahydro*-5-*acenaphthenol Hydrochloride* (27).—Reduction of the ketone hydrochloride (21) (1·0 g) with sodium borohydride (250 mg) in absolute ethanol (35 ml) for 1 h gave the *hydrochloride* (27), m.p. 222—223° (from ethanol–ether).

2a,3,4,5-*Tetrahydro*-NN-*dimethylacenaphthene*-4-*methylamine Hydrochloride* (35).—A mixture of the preceding hydrochloride (27) (2·0 g) and 10% palladised charcoal (0·5 g) in acetic acid (50 ml) and concentrated sulphuric acid (2 ml) was stirred in hydrogen; absorption ceased after 35 min and the catalyst was filtered off. The basic product was isolated as an oil which was converted into the *hydrochloride* (35), m.p. 259—260° (from ethanol).

We thank Mr. R. B. Scott for determining ^{1}H n.m.r. spectra, Miss E. M. Tanner for other physico-chemical determinations, and Mr. F. H. Oliver for microanalyses.

[2/1437 *Received*, 20*th June*, 1972]