Azabenzocycloheptenones. Part XVIII.[1] Amines and Amino-ketones of the Tetrahydro-3-benzazepin-1-one Series

By **Mary Lennon, Angus McLean, George R. Proctor,* and Ian W. Sinclair,** Department of Pure and Applied Chemistry, University of Strathclyde, Glasgow G1 1XL

2,3,4,5-Tetrahydro-3-benzazepin-1-one and its 3-benzyloxycarbonyl and 3-methyl derivatives have been synthesised from 2,3,4,5-tetrahydro-3-*p*-tolylsulphonyl-3-benzazepin-1-one. 2,3,4,5-Tetrahydro-7,8-dimethoxy-3-*p*-tolylsulphonyl-3-benzazepin-1-one was made by cyclisation of the corresponding glycine in polyphosphoric acid at 20° but all attempts to cyclise *N*-alkylglycines failed.

PREVIOUSLY 2,3,4,5-tetrahydro-3-*p*-tolylsulphonyl-3-benzazepin-1-ones (I; R^1 = tosyl) have been made [2,3] by cyclisation of appropriate *N*-tosylglycines with Lewis acids. The corresponding amino-ketones (I; R^1 = H or Me) have never been made: we now describe the synthesis of two of them and several other amines in the tetrahydro-3-benzazepine series.

One might expect that cyclisation of *N*-alkylglycines (II) would give the required compounds, especially since Rosenmund [4] and his co-workers have described a cyclisation of this type giving the indoloazepine (III). Accordingly we synthesised the esters (II; R^2 = Et, R^1 = Me or $CH_2 \cdot CO_2Et$), but neither they nor the acid

[1] Part XVII, M. Lennon, A. McLean, I. McWatt, and G. R. Proctor, *J.C.S. Perkin I*, 1974, 1828.

[2] M. A. Rehman and G. R. Proctor, *J. Chem. Soc.* (*C*), 1967, 58.

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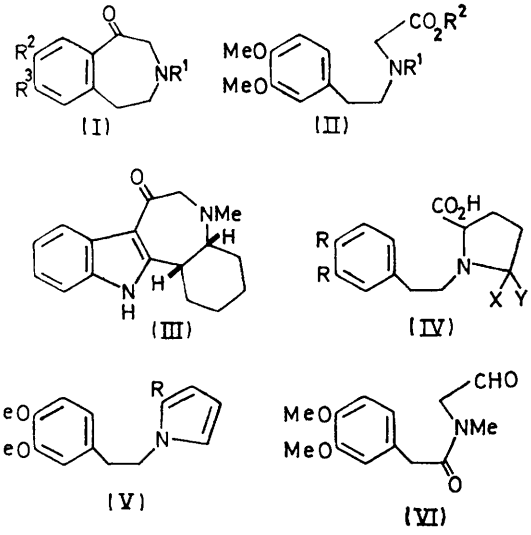
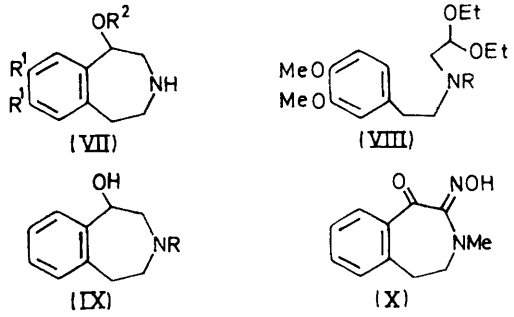
(II; R^1 = Me, R^2 = H) nor any derivatives thereof could be converted into useful products. We also made the acids (IV; R = H or OMe, X = Y = H) but neither of these could be cyclised (*cf.* refs. 5 and 6). During this work we discovered that the acid (II; R^1 = tosyl, R^2 = H) could be cyclised at 20—30° with polyphosphoric acid; * this suggested that glycines with non-basic nitrogen atoms could be cyclised. Accordingly we made the acids (II; R^1 = Ac, R^2 = H), (IV; R = OMe, XY = O), and (V; R = CO_2H) but none gave promising results under any of several sets of reaction conditions.

A recent study [7] of relative rates of electrophilic substitution suggests that, in at least one case, the rate of substitution of indoles may be *ca.* 10^6 times faster than that of anisole: this may explain Rosenmund's success [4] and our failures. In a recent cephalotaxine synthesis [6] an analogue of the amido-aldehyde (VI) was used for cyclisation to a dihydrobenzazepine derivative



but the unstable aldehyde (VI) itself did not yield isolable products. Amino-acetal reactions directed towards the benzazepine (VII; R^1 = OMe, R^2 = H) were unfruitful (*cf.* refs. 8 and 9).

The foregoing results made it clear that for our purposes we should study detosylation of the *N*-tosylbenzazepines (I; R^1 = tosyl, R^2 = R^3 = H or OMe). As in the case of tetrahydro-2-benzazepines,[10] attempted detosylation of the *N*-tosyl ketone caused decomposition, but when the *N*-tosyl alcohol (IX; R = tosyl) was treated with sodium in ammonia, smooth detosylation was observed and the amino-alcohol (VIII; R^1 = R^2 = H) was obtained as a stable solid. This was converted into the *N*-benzyloxycarbonyl compound (IX; R = $PhCH_2$·O·CO), which was oxidised with dipyridinechromium oxide in methylene chloride [to (I; R^2 = R^3 = H, R^1 = $PhCH_2$·O·CO)], and finally the protecting group was removed with hydrochloric acid yielding the hydrochloride of the amino-ketone (I; R^1 = R^2 = R^3 = H).



When the hydroxy-amine (VII; R^1 = R^2 = H) was reductively methylated, the expected *N*-methyl alcohol (IX; R = Me) was obtained, and oxidation with active manganese dioxide [11] gave the *N*-methyl ketone (I; R^2 = R^3 = H, R^1 = Me) as a gum. Elemental analysis and n.m.r. data indicate that this substance is correctly formulated although the mass spectrum did not show the molecular ion ($C_{10}H_{11}NO$ was the ion of highest mass). The amino-ketone (I; R^2 = R^3 = H, R^1 = Me) showed another deviation from expectation; it did not react with hydroxylamine except under forcing conditions; the product then appeared to be the hydroxyimino-ketone (X). The mass spectrum of the latter showed the molecular ion, $C_{11}H_{12}N_2O_2$, which demonstrates that the amino-ketone (I; R^1 = Me, R^2 = R^3 = H) did contain eleven carbon atoms. The *N*-tosyl ketone (I; R^1 = tosyl, R^2 = R^3 = H) behaved normally with hydroxylamine, forming an oxime which reacted as expected with *p*-methoxyphenyl isocyanate giving a carbamate.

EXPERIMENTAL

Ethyl N-[2-(3,4-*Dimethoxyphenyl*)*ethyl*]*glycinate* (II; R^1 = H, R^2 = Et).—2-(3,4-Dimethoxyphenyl)ethylamine (54 g), ethyl bromoacetate (12 g), freshly roasted potassium carbonate (60 g), and dry benzene were stirred for 12 h, then ethyl bromoacetate (12 g) was added. After a further 24 h, the product (51 g) was worked up as usual and distilled *in vacuo*; yield 14·3 g, b.p. 150° at 0·3 mmHg (Found: C, 63·5; H, 7·85; N, 5·7. $C_{14}H_{21}NO_4$ requires C, 63·0; H, 7·95; N, 5·25%); $\nu_{max.}$ (film) 3340 (NH) and 1735 cm^{-1} (ester); τ 3·24 (3H, s, aryl H), 5·85 (2H, q, CH_2·CH_3), 6·14 (3H, s, OMe), 6·17 (3H, s, OMe), 6·3—6·55 (2H, m, CH_2), 6·6 (2H, s, 2-H), 7·05 (1H, s, exch., NH), 7·1—7·45 (2H, m, CH_2), and 8·76 (3H, t, CH_3). The N-*acetate* had b.p. 120° at 0·03 mmHg (Found: N, 4·9. $C_{16}H_{23}NO_5$ requires N, 4·55%); τ 3·3 (3H, s, aryl H), 5·85 (2H, q, CH_2·CH_3), 6·16 (3H, s, OMe), 6·18 (3H, s, OMe), 6·45 (3H, s, Ac), 6·3—6·55 (2H, m, 1-H?), 6·95—7·4 (4H, m, 2- and 4-H?), and 8·75 (3H, t, CH_3·CH_2).

* Treatment of the acid chloride with aluminium chloride at −70° caused decomposition.

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By using twice the quantity of ethyl bromoacetate, *ethyl* N-*ethoxycarbonylmethyl*-N-[2-(3,4-*dimethoxyphenyl*)-*ethyl*]*glycinate* (II; $R^1 = CH_2{\cdot}CO_2Et$, $R^2 = Et$) was obtained, b.p. 180—190° at 0·3 mmHg; τ 3·24 (3H, s, aryl H), 5·85 (4H, q, $CH_2{\cdot}CH_3$), 6·15 (3H, s, OMe), 6·19 (3H, s, OMe), 6·95—7·4 (4H, m, CH_2), and 8·75 (6H, t, CH_3).

Ethyl N-*Methyl*-N-[2-(3,4-*dimethoxyphenyl*)*ethyl*]*glycinate* (II; $R^1 = Me$, $R^2 = Et$).—The foregoing ester (10 g), methanol (100 ml), and formalin (aqueous 40%; 50 ml) were stirred and left for 48 h at 20°. The mixture was hydrogenated over platinum oxide (100 mg), filtered, and evaporated. The residue was dissolved in benzene which was washed with water five times and dried. Evaporation left the *product* (9·3 g), b.p. 165° at 0·1 mmHg (Found: C, 64·3; H, 7·9; N, 5·2. $C_{15}H_{23}NO_4$ requires C, 64·1; H, 8·25; N, 5·0%); $\nu_{max.}$ (film) 1735 cm^{-1} (ester); τ 3·28 (3H, s, aryl H), 5·85 (2H, q, $CH_2{\cdot}CH_3$), 6·18 (3H, s, OMe), 6·2 (3H, s, OMe), 6·2—6·6 (2H, m, $CH_2{\cdot}CO_2R$), 6·72 (2H, s, $ArCH_2$), 7·28 (3H, s, NMe), 7·58 (2H, s, $ArCH_2{\cdot}CH_2{\cdot}N$), and 8·75 (3H, t, $CH_3{\cdot}CH_2$).

N-*Methyl*-N-[2-(3,4-*dimethoxyphenyl*)*ethyl*]*glycine* (II; $R^1 = Me$, $R^2 = H$).—The foregoing ester (1·2 g), ethanol (50 ml), and aqueous 2N-sodium hydroxide (2 ml) were refluxed for 3 h; the mixture was cooled and extracted with benzene, and the aqueous layer was neutralised and evaporated *in vacuo*. The *product* (550 mg) was obtained from the residue by crystallisation from absolute ethanol; m.p. 180° (decomp.) (Found: C, 61·3; H, 7·4; N, 5·45. $C_{13}H_{19}NO_4$ requires C, 61·7; H, 7·55; N, 5·55%); $\nu_{max.}$ (Nujol) 1605 cm^{-1} (C=O).

[2-(3,4-*Dimethoxyphenyl*)*ethylamino*]*acetaldehyde Diethyl Acetal* (VIII; R = H).—2-(3,4-Dimethoxyphenyl)ethylamine (42 g), 2-bromoacetaldehyde diethyl acetal (8 g), benzene, and anhydrous potassium carbonate (50 g) were vigorously stirred at 100° for 18 h. More of the acetal (8 g) was added, and stirring and heating were continued for 20 h. Fractional distillation of the filtered mixture yielded the *product* (18·5 g), b.p. 142—148° at 0·3 mmHg (Found: N, 4·9. $C_{16}H_{27}NO_4$ requires N, 4·7%) (carbon figures were 1% high); τ 3·25 (3H, m, aryl H), 5·42 [1H, t, $CH(OEt)_2$], 6·16 (3H, s, OMe), 6·18 (3H, s, OMe), 6·45 (4H, m, $CH_2{\cdot}CH_3$), 7·05—7·3 (6H, m, CH_2), 8·02 (1H, s, exch., NH), and 8·82 (6H, t, CH_3).

The use of larger proportions of the acetal gave NN-*bis*-(2,2-*diethoxyethyl*)-2-(3,4-*dimethoxyphenyl*)*ethylamine* [VIII; $R = CH_2{\cdot}CH(OEt)_2$], b.p. 170° at 0·4 mmHg (Found: C, 64·4; H, 9·55; N, 3·6. $C_{22}H_{39}NO_6$ requires C, 64·0; H, 9·5; N, 3·4%), τ 3·25 (3H, m, aryl H), 5·47 [2H, t, $CH(OEt)_2$], 6·16 (3H, s, OMe), 6·18 (3H, s, OMe), 6·2—6·7 (8H, m, $CH_2{\cdot}CH_3$), 7·0—7·4 (8H, m, CH_2), and 8·8 (12H, t, CH_3).

N-[2-(3,4-*Dimethoxyphenyl*)*ethyl*]*proline* (IV; $R^1 = OMe$, X = Y = H).—L-Proline (11·5 g), 2-(3,4-dimethoxyphenyl)-ethyl chloride [12] (20·5 g), potassium carbonate (21 g), and methanol (200 ml) were refluxed and stirred for 7 days. 2-(3,4-Dimethoxyphenyl)ethyl chloride (5 g) was added on each of the first 4 days. The cooled mixture was filtered. Evaporation of the filtrate and chromatography of the residue on silica gel (elution with 35% methanol–chloroform) gave the *product* (6·1 g), m.p. 180° (from chloroform–toluene) (Found: C, 64·15; H, 5·3; N, 7·6. $C_{15}H_{21}NO_4$ requires C, 64·5; H, 5·2; N, 7·5%); τ (D_2O) 3·1—3·15 (3H, m, aryl H), 6·17 (3H, s, OMe), 6·19 (3H, s, OMe), 6·1—6·3 (1H, m, $CHCO_2D$), 6·5—7·2 (6H, m, CH_2), and 7·7—8·05 (4H, m, CH_2).

N-(2-*Phenylethyl*)*proline* (IV; $R^1 = X = Y = H$).—2-Phenylethyl bromide (18·5 g), L-proline (11·5 g), potassium carbonate (21 g), and methanol (200 ml) were stirred and refluxed for 7 days. Work-up as in the previous experiment gave the *product* (5·53 g), m.p. 186° (from toluene) (Found: C, 70·6; H, 7·5; N, 6·45. $C_{13}H_{17}NO_2$ requires C, 71·1; H, 7·8; N, 6·4%); $\nu_{max.}$ (Nujol) 1620 cm^{-1} (CO_2H).

N-[2-(3,4-*Dimethoxyphenyl*)*ethyl*]*pyrrole* (V; R = H).—2-(3,4-Dimethoxyphenyl)ethylamine (5·43 g), 2,5-dimethoxytetrahydrofuran (3·96 g), and acetic acid were refluxed for 1 h. Addition of water and the usual [13] work-up gave the *product* (5·5 g) as an oil, b.p. 150° at 0·1 mmHg (Found: C, 72·7; H, 7·65; N, 6·0. $C_{14}H_{17}NO_2$ requires C, 72·7; H, 7·4; N, 6·05%); τ 3·25—3·95 (7H, m, aryl H), 6·0 (2H, t, CH_2), 6·2 (3H, s, OMe), 6·28 (3H, s, OMe), and 7·1 (2H, t, CH_2).

N-[2-(3,4-*Dimethoxyphenyl*)*ethyl*]*pyrrole*-2-*carbaldehyde* (V; R = CHO).—The foregoing pyrrole (4·7 g) in dimethyl formamide (2·5 ml) was added to phosphoric trichloride (3·03 g) in dimethylformamide (1·5 ml) at 0° with stirring (*cf.* ref. 13). After 2 h at 0° the mixture was stirred overnight and poured onto ice. The usual work-up gave a tarry *product* (4·3 g), b.p. 140° at 0·05 mmHg (Found: C, 69·4; H, 6·65; N, 5·9. $C_{15}H_{17}NO_3$ requires C, 69·5; H, 6·55; N, 5·4%); $\nu_{max.}$ 1665br cm^{-1} (C=O); τ 0·46 (1H, s, CHO), 3·1—3·9 (6H, m, aryl H), 5·55 (2H, t, CH_2), 6·18 (3H, s, OMe), 6·23 (3H, s, OMe), and 7·08 (2H, t, CH_2).

N-[2-(3,4-*Dimethoxyphenyl*)*ethyl*]*pyrrole*-2-*carboxylic Acid* (V; $R = CO_2H$).—By adaptation of literature methods [13] the foregoing aldehyde (10·5 g) was converted *via* the oxime (8·8 g) into the nitrile (7·4 g), which was stirred at 170° with potassium hydroxide (12·3 g) and ethylene glycol (40 ml) for 3 h. Working up the acidic fraction gave the *product* (2·4 g), m.p. 112° (from toluene) (Found: C, 65·2; H, 6·6; N, 5·1. $C_{15}H_{17}NO_4$ requires C, 65·4; H, 6·2; N, 5·1%).

N-[2-(3,4-*Dimethoxyphenyl*)*ethyl*]-2-*oxopyrrolidine*-5-*carboxylic Acid* (IV; $R^1 = OMe$, XY = O).—2-(3,4-Dimethoxyphenyl)ethylamine (9 g), diethyl α-bromoglutarate,[14] and anhydrous sodium carbonate were stirred together at 100° for 24 h. After addition of methylene chloride and water, the layers were separated and the organic layer was washed with sodium hydrogen carbonate solution and dilute hydrochloric acid and dried. Evaporation yielded the crude ester (11·6 g), which was recovered unchanged after 1·5 h at 110° in polyphosphoric acid (excess). Refluxing with ethanol (150 ml) and aqueous 2N-sodium hydroxide (26 ml) for 4 h gave the desired *acid* (9·1 g) (from ethyl acetate), m.p. 109° (Found: C, 61·5; H, 6·65; N, 4·65. $C_{15}H_{19}NO_5$ requires C, 61·5; H, 6·55; N, 4·8%); $\nu_{max.}$ (Nujol) 1715—1690br cm^{-1} (CO_2H + CO); τ −0·3 (1H, s, exch., OH), 3·2—3·45 (3H, m, aryl H), 6·2 (6H, s, OMe), 5·95—6·25 (2H, m, 3-H), 6·75—7·0 (1H, m, 5-H), 7·15—7·35 (2H, m, CH_2), 7·4—7·68 (2H, m, CH_2), and 7·7—8·0 (2H, m, CH_2).

2-[N-*Methyl*-3,4-*dimethoxyphenylacetamido*]*ethanol*.—3,4-Dimethoxyphenylacetyl chloride (18 g), acetonitrile (100 ml), and anhydrous potassium carbonate (20 g) were stirred at −20° while 2-methylaminoethanol (7 g) was slowly added (10 min). After 3 h at −20°, the suspension was filtered, water was added to the filtrate, and the

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[13] G. Demartino, M. Scalzo, S. Massa, R. Giuliano, and M. Artico, *Farmaco Ed. Sci.*, 1972, **27**, 980, and earlier papers.

[14] E. Schwenk and D. Papa, *J. Amer. Chem. Soc.*, 1948, **70**, 3626.

product was extracted with chloroform. Crystallisation from toluene gave *material* (15·7 g) of m.p. 93—95° (Found: C, 62·05; H, 5·4; N, 7·6. $C_{13}H_{19}NO_4$ requires C, 61·7; H, 5·55; N, 7·55%); $\nu_{max.}$ (Nujol) 3270 (OH) and 1610 cm^{-1} (C=O).

Treatment of this alcohol with either active manganese dioxide [11] or dimethyl sulphoxide–dicyclohexylcarbodiimide [6] gave an unstable product [presumably (VI)] whose i.r. spectrum showed little hydroxy-absorption but had a peak at 1705 cm^{-1}.

2,3,4,5-*Tetrahydro*-N-p-*tolylsulphonyl*-3-*benzazepin*-1-*one* (I; R^1 = tosyl, R^2 = R^3 = H).—The original method [2,15] was adapted as follows. The acid chloride (from 34·5 g of acid) in methylene chloride was vigorously stirred at −40° while anhydrous aluminium chloride (50 g) was added. The temperature was raised to −15° in 2 h and kept for 3·5 h at −10 to −15°: then the mixture was added to ice. The product (27·7 g, 85%), crystallised once from methanol, had m.p. 152—154° (lit.,[2] 156—157°). The *oxime* had m.p. 174—175° (Found: C, 61·5; H, 5·35; N, 8·4. $C_{17}H_{18}N_2O_3S$ requires C, 61·85; H, 5·5; N, 8·5%); τ 1·6br (1H, exch., OH), 2·5—3·05 (8H, m, aryl H), 5·5 (2H, s, 2-H), 6·5 (2H, t, 4-H), 7·2 (2H, t, 5-H), and 7·65 (3H, s, Me).

Treatment of the oxime with *p*-methoxyphenyl isocyanate yielded a *carbamate*, m.p. 88—90° (from benzene) (Found: C, 63·0; H, 5·2; N, 8·45. $C_{25}H_{25}N_3O_5S$ requires C, 62·7; H, 5·25; N, 8·75%); $\nu_{max.}$ (Nujol) 3270 (NH) and 1725 cm^{-1} (C=O), τ 1·9 (1H, s, NH), 2·5—3·2 (12H, m, aryl H), 5·4 (2H, s, 2-H), 6·24 (3H, s, OMe), 6·5 (2H, t, 4-H), 7·18 (2H, t, 5-H), and 7·65 (3H, s, CH_3).

1,2-*Dihydro*-5-(p-*methoxyphenyl*)-N-p-*tolylsulphonyl*-3-*benzazepine*.—*p*-Methoxyphenylmagnesium bromide (excess) reacted with 2,3,4,5-tetrahydro-*N*-*p*-tolylsulphonyl-3-benzazepin-1-one (5 g) in tetrahydrofuran to give, in the usual way, the *product* (4·75 g), m.p. 135° (from ethanol) (Found: C, 71·3; H, 5·7; N, 3·55. $C_{24}H_{23}NSO_3$ requires C, 71·15; H, 5·7; N, 3·45%); $\nu_{max.}$ (Nujol) 1610 cm^{-1} (C=C), τ 2·35 (1H, d, 6-H), 2·7—3·25 (12H, m, aryl H + 4-H), 6·07—6·2 (2H, t, 2-H), 6·2 (3H, s, OMe), 7·06—7·22 (2H, t, 1-H), and 7·63 (3H, s, CH_3).

2,3,4,5-*Tetrahydro*-1H-3-*benzazepin*-1-*ol* (IX; R = H).—Sodium (2·04 g) was added in small pieces over 45 min to the acetal [2] (VIII; R = tosyl) (12 g) stirred in tetrahydrofuran (100 ml) and ammonia (700 ml). After addition of ammonium chloride (5 g) and evaporation of ammonia, the basic material was extracted with hydrochloric acid (5N) and crystallised from ethanol at −20° giving *prisms*, m.p. 131—132° (Found: C, 73·4; H, 8·1; N, 8·85. $C_{10}H_{13}NO$ requires C, 73·6; H, 8·0; N, 8·55%), $\nu_{max.}$ (Nujol) 3300 cm^{-1} (OH and NH), τ 1·3—2·8 (4H, m, aryl H), 5·0 (1H, q, *J* 7 and 3 Hz, 1-H), and 6·6—7·4 [8H, m, 2-, 4-, and 5-H and NH and OH (exch.)].

The N-*acetate* (IX; R = Ac) had m.p. 100—101° (from ethanol) (Found: C, 69·8; H, 7·25; N, 6·95. $C_{12}H_{15}NO_2$ requires C, 70·3; H, 7·4; N, 6·85%), τ 2·6—3·0 (4H, m, aryl H), 5·22 (1H, t, 1-H), 5·6—7·3 [7H, m, 2-, 4-, and 5-H and OH (exch.)], and 7·72 and 7·80 (3H, 2 s, CH_3 two conformers [10]). The N-*benzyl derivative* had m.p. 71° (Found: N, 5·65. $C_{17}H_{19}NO$ requires N, 5·55%); τ 2·65—3·05 (9H, m, aryl H), 5·4 (1H, d, 1-H), 6·3 (2H, s, CH_2Ph), and 6·7—7·7 [7H, m, 2-, 4-, and 5-H and OH (exch.)].

3-*Benzyloxycarbonyl*-2,3,4,5-*tetrahydro*-1H-3-*benzazepin*-1-*ol* (IX; R = $CO{\cdot}O{\cdot}CH_2Ph$).—Benzyloxyformyl chloride (0·54 g), the foregoing amino-alcohol (0·47 g), sodium carbonate (0·54 g), tetrahydrofuran (5 ml), and water (5 ml) were stirred for 0·5 h. After addition of chloroform and water, the product was obtained in the usual way from the organic layer as a buff solid (0·77 g, 90%); $\nu_{max.}$ (Nujol) 3450 and 1680 cm^{-1} ($N{\cdot}CO{\cdot}O{\cdot}CH_2Ph$), which was used without further purification.

3-*Benzyloxycarbonyl*-2,3,4,5-*tetrahydro*-3-*benzazepin*-1-*one* (I; R^1 = $CO{\cdot}O{\cdot}CH_2Ph$, R^2 = R^3 = H).—Dipyridinechromium(VI) oxide (4·02 g) was stirred with the foregoing product (0·77 g) in methylene chloride (90 ml) for 5 min; the mixture was then set aside for 0·5 h, filtered, and evaporated. The residue was extracted with toluene; the extract was filtered and evaporated to leave the product (0·63 g, 82%) which crystallised from methanol as *plates*, m.p. 90—91° (Found: C, 73·3; H, 5·8; N, 4·55. $C_{18}H_{17}NO_3$ requires C, 73·2; H, 5·8; N, 4·75%); $\nu_{max.}$ (Nujol) 1680 cm^{-1} (both C=O); τ 2—3·1 (9H, m, aryl H), 5·1 (2H, s, $CO_2{\cdot}CH_2Ph$), 5·77 (2H, m, 2-H), 6·3 (2H, m, 4-H), and 7·0 (2H, m, 5-H).

2,3,4,5-*Tetrahydro*-3-*benzazepin*-1-*one* (I; R^1 = R^2 = R^3 = H) *Hydrochloride*.—The foregoing ketone (0·3 g) in ethanol (15 ml) was saturated with hydrogen chloride gas and left for 10 days. The excess of hydrogen chloride was removed by a stream of nitrogen and the remaining solution was evaporated *in vacuo*, yielding the product (0·15 g, 74%), which was washed with chloroform and recrystallised from methanol–acetone (1 : 1) to give *prisms*, m.p. 150° (decomp.) (Found: C, 61·05; H, 6·15; N, 6·9. $C_{10}H_{12}ClNO$ requires C, 60·75; H, 6·05; N, 7·1%), $\nu_{max.}$ (Nujol) 2300—2700 ($R_2\overset{+}{N}H_2$) and 1680 (C=O) cm^{-1}; τ ($CF_3{\cdot}CO_2H$) 1·4—2·7 (6H, m, 4 aryl + NH_2^+), 5·4 (2H, m, 2-H), 6·1 (2H, m, 4-H), and 6·6 (2H, m, 5-H); τ (D_2O) 2·2—2·6 (4H, m, aryl H), 5·7 (2H, s, 2-H), 6·4 (2H, m, 4-H), and 6·7 (2H, m, 5-H).

2,3,4,5-*Tetrahydro*-3-*methyl*-1H-3-*benzazepin*-1-*ol* (IX; R = Me).—2,3,4,5-Tetrahydro-1*H*-3-benzazepin-1-ol (0·4 g), methanol (10 ml), formaldehyde (aqueous 40%; 2 ml), and Adams catalyst (0·065 g) were hydrogenated for 16 h. The mixture was filtered and the *product* distilled; b.p. 180° at 0·3 mmHg (Found: C, 74·2; H, 8·1. $C_{11}H_{15}NO$ requires C, 74·5; H, 8·45%); $\nu_{max.}$ (film) 3350 cm^{-1} (OH); τ 2·7—3·0 (4H, m, aryl H), 5·35br (1H, d, *J* 8 Hz, 1-H), 6·6—7·6 (6H, m, 2-, 4-, and 5-H), and 7·6 (3H, s, CH_3). The *methiodide* crystallised from ethanol as prisms, m.p. 183—184° (Found: C, 45·15; H, 5·55; N, 4·55. $C_{12}H_{18}INO$ requires C, 45·1; H, 5·7; N, 4·4%).

2,3,4,5-*Tetrahydro*-3-*methyl*-3-*benzazepin*-1-*one* (I; R^1 = Me, R^2 = R^3 = H).—The foregoing *N*-methyl alcohol (0·39 g), dry methylene chloride (30 ml), and active manganese dioxide [11] (2·1 g) were stirred for 4 h. Filtration through silica gel and distillation gave the *product* (115 mg), b.p. 126° at 0·3 mmHg (Found: C, 76·1; H, 7·6; N, 7·75. $C_{11}H_{13}NO$ requires C, 75·5; H, 7·5; N, 8·0%); $\nu_{max.}$ (film) 1645 cm^{-1} (C=O); τ 2·0—3·0 (4H, m, aryl H), 6·3—6·6 (2H, m, 5-H), 6·9 (3H, s, NMe), 7·1—7·26 (2H, m, 4-H), and 7·6 (2H, s, 2-H).

The 2-*oxime* (X), obtained by refluxing the foregoing ketone (320 mg) with hydroxylamine hydrochloride (400 mg) in pyridine (20 ml) for 6 h, had m.p. 250° (decomp.) (Found: N, 13·35; M^+, 204·0899. $C_{11}H_{12}N_2O_2$ requires N, 13·7%; *M*, 204·0899); $\nu_{max.}$ (Nujol) 3170 (OH) and 1625 cm^{-1} (C=O).

[15] I. McDonald and G. R. Proctor, *J. Chem. Soc.* (*C*), 1969, 2151

2,3,4,5-*Tetrahydro*-7,8-*dimethoxy*-N-p-*tolylsulphonyl*-3-*benzazepin*-1-*one* (I; R^1 = tosyl, R^2 = R^3 = OMe).—The acid [16] (II; R^1 = tosyl, R^2 = H) (26·25 g) and polyphosphoric acid (1·4 kg) were stirred for 24 h at 18—25° and then left for 24 h. Working up the neutral fraction gave the product (16·68 g, 67%), m.p. 210° [from acetone–ethanol (3 : 2)] (lit.,[3] 211°).

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[16] G. R. Proctor and R. H. Thomson, *J. Chem. Soc.*, 1957, 2302.

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