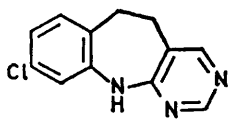
Azabenzocycloheptenones. Part 19.[1] Formation of Some Heterocyclic Annelated Compounds from 1,2,3,4-Tetrahydro-1-benzazepine Derivatives

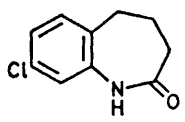
By **George R. Proctor** and **Brian M. L. Smith**, Department of Pure and Applied Chemistry, University of Strathclyde, Glasgow G1 1XL

Some 4-ethoxycarbonyl- and 4-formyl-1,2,3,4-tetrahydro-1-benzazepines have been converted into pyrimido[5,4-*d*][1]benzazepine, pyrazolo[4,3-*d*][1]benzazepine, and isoxazolo[4,5-*d*][1]benzazepine derivatives. Also made were isolated examples of thiadiazolo[5,4-*d*][1]benzazepine, quino[3,2-*d*][1]benzazepine, indolo[3,2-*c*][1]-benzazepine, and isoxazolo[4,3-*d*][1]benzazepine derivatives.

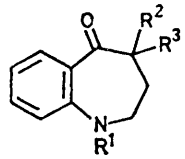
PREVIOUSLY [2] we have reported some substitution reactions in tetrahydro-1-benzazepin-5-ones; we have now studied reactions of readily available [3] tetrahydro-1-benzazepin-5-ones which would be expected to lead to annelation of a variety of heterocycles onto the 1-benzazepine skeleton.



(1)



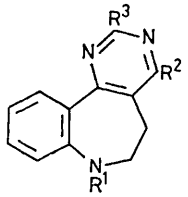
(2)



(3)

RESULTS AND DISCUSSION

Pyrimidines.—The only reported example [4] of a pyrimido[1]benzazepine (1) arose by treatment of the lactam (2) with phosphoryl chloride and dimethylformamide under pressure. We have examined the fusion of pyrimidine nuclei onto the 4,5-bond of the 1-benzazepine system by using the oxo-esters (3; R^1 = tosyl or Me, R^2 = CO_2Me or CO_2Et, R^3 = H). In spite of the frequency [5] with which the condensation of β-oxo-esters with urea and its derivatives has been reported, we found that this method was of rather limited applicability. Thus the *N*-tosyl β-oxo-ester [6] (3; R^1 = tosyl, R^2 = CO_2Et, R^3 = H) failed to react with urea, thiourea, and guanidine hydrochloride under a variety of conditions. Generally the β-oxo-ester was partly recovered and the only detectable reaction was decarboxylation, which gave (3; R^1 = tosyl, R^2 = R^3 = H). With the β-oxo-ester (3; R^1 = tosyl, R^2 = CO_2Et, R^3 = M), the only successful experiment involved lengthy reaction with guanidine carbonate [7-9] in ethanol which furnished a low yield of material formulated as (4; R^1 = tosyl, R^2 = OH, R^3 = NH_2) from analytical and spectroscopic data.



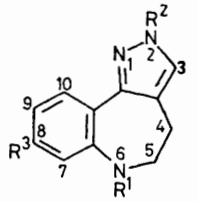
(4)

In attempting to rationalise the above comparative failures, we noted that aryl oxo-esters had been successfully employed in pyrimidine syntheses; [10] this drew attention to the steric–electronic role played by the *N*-tosyl group in obstructing nucleophilic attack by an

[1] Part 18, M. Lennon, A. McLean, G. R. Proctor, and I. W. Sinclair, *J.C.S. Perkin I*, 1975, 622.
[2] M. Lennon, A. McLean, I. McWatt, and G. R. Proctor, *J.C.S. Perkin I*, 1974, 1828.
[3] G. R. Proctor, W. I. Ross, and A. Tapia, *J.C.S. Perkin I*, 1972, 1803.
[4] S. Kobayashi, *Bull. Chem. Soc. Japan*, 1973, **46**, 2835.
[5] D. J. Brown, ' The Pyrimidines,' Supplement 1, in ' Chemistry of Heterocyclic Compounds,' ed. A. Weissberger and E. C. Taylor, Wiley–Interscience, New York, 1972, p. 22.
[6] I. McCall, G. R. Proctor, and L. Purdie, *J. Chem. Soc.* (*C*), 1970, 1126.
[7] T. Curatolo, *Annalen*, 1891, **262**, 365.
[8] E. A. Fallo, P. B. Russell, and G. H. Hutchings, *J. Amer. Chem. Soc.*, 1951, **73**, 3753.
[9] A. Rosowsky, L. P. Burrows, J. Huang, and E. J. Modest, *J. Heterocyclic Chem.*, 1972, **9**, 1239.
[10] R. M. Anker and A. H. Cook, *J. Chem. Soc.*, 1941, 323.

amino-group in the urea or guanidine molecules. *X*-Ray data [11] on the 8-chloro-analogue of (3; R^1 = tosyl, R^2 = CO_2Me, R^3 = H) revealed that this molecule was entirely enolic; while i.r. data on (3; R^1 = tosyl, R^2 = CO_2Et, R^3 = H) confirmed this finding ($\nu_{max.}$ 1 650 and 1 625 cm^{-1}), it appeared that the *N*-methyl oxo-ester (3; R^1 = Me, R^2 = CO_2Et, R^3 = H) which was not previously isolated [12] was much less enolic ($\nu_{max.}$ 1 745 and 1 655 cm^{-1}). Accordingly the *N*-methyl oxo-ester (3; R^1 = Me, R^2 = CO_2Et, R^3 = H) was treated with guanidine carbonate in ethanol and gave a 39% yield of the expected pyrimido[5,4-*d*][1]benzazepine (4; R^1 = Me, R^2 = OH, R^3 = NH_2). Treatment of the latter with phosphoryl chloride afforded the chloro-compound (4; R^1 = Me, R^2 = Cl, R^3 = NH_2) in moderate yield. None of the available β-oxo-esters could be made to react with either acetamidine [13,14] or benzamidine to yield pyrimidobenzazepine derivatives, nor did prevention of enolisation [*e.g.* by use of the 4-bromo- and 4-ethoxycarbonyl derivatives of (3; R^1 = tosyl, R^2 = CO_2Et, R^3 = H)] lead to any improvement. Of several reactions attemped [15,16] with the β-oxo-aldehyde * (3; R^1 = tosyl, R^2 = CHO, R^3 = H), only the one involving reflux in ethanol with guanidine hydrochloride was fruitful, though the product unexpectedly conformed to a structure having one more methyl group than we predicted. These facts are accommodated by structure (4; R^1 = tosyl, R^2 = NHMe), the unexpected methylation step being due to a simultaneous retro-aldol reaction on the starting material, which produces formaldehyde and the tosyl ketone (3; R^1 = tosyl, R^3 = R^3 = H) (readily identified [6]). Fused aminopyrimidines have been obtained by reaction of cyanoguanidine with cycloalkanones,[17,18] α-tetralone giving a far greater yield than 6,7,8,9-tetrahydrobenzocyclohepten-5-one.[19] The ketones (3; R^1 = Me or tosyl, R^2 = R^3 = H) failed to react with cyanoguanidine, a fact which may be due to ring size as much as anything else. Brown [20] has discussed this in terms of *I*-strain.

Pyrazoles.—Reaction of the α-hydroxymethylene ketone (3; R^1 = tosyl, R^2R^3 = CHOH,) or its 8-chloro-analogue with hydrazine under mild conditions [21] gave the expected pyrazolo[4,3-*d*][1]benzazepines (5; R^1 = tosyl, R^2 = H, R^3 = H or Cl). Acetylation gave products (5; R^2 = Ac) in which the n.m.r. signal of H-3 was shifted from 0.5 to 0.6 p.p.m. downfield, indicating the close proximity of the proton in question [22] to the *N*-acetyl group and confirming the structures as formulated rather than as the alternative 1*H* isomers. This is in accord with previous [16] work on similarly fused pyrazoles but there seems no way of establishing absolutely whether the products (5; R^2 = H) are as shown or



(5)

whether they have the alternative 1*H*-structures. The tosyl group could be removed from these compounds by sodium in liquid ammonia but a more fruitful route to the product (5; R^1 = R^2 = R^3 = H) commenced with the amino-ketone (3; R^1 = R_2 = R^3 = H), which reacted with ethyl formate to give (3; R^1 = CHO, R^2R^3 = CHOH), which in turn reacted with hydrazine yielding the pyrazolobenzazepine (5; R^1 = CHO, R^2 = R^3 = H); this was then deformylated with acid. The pyrazolobenzazepine (5; R^1 = R^2 = R^3 = H) gave a diacetate with acetic anhydride but with *NN*-dimethylcarbamoyl chloride in pyridine it gave a monosubstituted product judged to have structure (5; R^1 = R^3 = H, R^2 = $CONMe_2$) by comparison of the τ value (6.0) of the exchangeable proton in the n.m.r. spectrum with those of related compounds.

Phenylhydrazine reacted with the compounds (3; R^1 = tosyl or CHO, R^2R^3 = CHOH) giving complex mixtures and *p*-nitrophenylhydrazine reacted with them to give *p*-nitrophenylhydrazones whose mass spectra included a very strong $[M - H_2O]^+$ peak. Notwithstanding this, heating these substances under a variety of conditions failed to yield identifiable *p*-nitrophenylpyrazole derivatives.

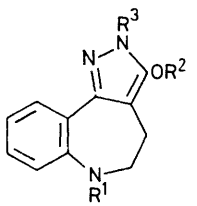
It might have been expected [23] that semicarbazide would react with the α-formyl ketones of this series to give 1-carbamoylpyrazolo[1]benzazepines, but we found that the products were the unsubstituted pyrazolo-1-benzazepines already discussed. While other workers have noted a similar ease of hydrolysis,[16,24] we found that it was not avoided even [25] by working at 0 °C. Thiosemicarbazide reactions were no more promising.

Application of the most fruitful pyrazolone synthesis [26]

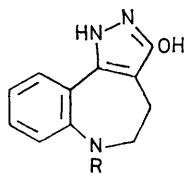
* This too is enolic, being best regarded as an α-hydroxymethylene ketone.

[11] F. D. Sancilio and J. F. Blount, *Acta Cryst.*, 1976, **B72**, 2123.
[12] B. D. Astill and V. Boekelheide, *J. Amer. Chem. Soc.*, 1955, **77**, 4059.
[13] H. R. Snyder and H. M. Foster, *J. Amer. Chem. Soc.*, 1954, **76**, 118.
[14] M. G. Biressi, M. Carissimi, and F. Ravenna, *Gazzetta*, 1965, **95**, 1293.
[15] B. Lythgoe and L. S. Rayner, *J. Chem. Soc.*, 1951, 2323.
[16] A. Fravolini, G. Grandolini, and A. Martani, *Gazzetta*, 1973, **103**, 1063.
[17] E. J. Modest, S. Chatterjee, and H. K. Protopapa, *J. Org. Chem.*, 1965, **30**, 1837.
[18] E. J. Modest, S. K. Sengupta, S. Chatterjee, and H. K. Protopapa, *J. Org. Chem.*, 1972, **37**, 1323.
[19] A. Rosowsky, K. K. N. Chen, M. E. Nadel, P. St. Amand, and S. A. Yeager, *J. Heterocyclic Chem.*, 1971, **8**, 789.
[20] H. C. Brown, R. S. Fletcher, and R. B. Johanneson, *J. Amer. Chem. Soc.*, 1951, **73**, 212.
[21] C. Ainsworth, *Org. Synth.*, coll. vol. IV, 1963, p. 536.
[22] J. Elguero, A. Fruchier, and R. Jacquier, *Bull. Soc. chim. France*, 1966, 2075.
[23] K. Von Auwers and B. Otters, *Ber.*, 1925, **58**, 2072.
[24] R. E. Schaub, J. H. Van Den Hende, and M. J. Weiss, *J. Org. Chem.*, 1965, **30**, 2234.
[25] C. D. Hurd and C. D. Kelso, *J. Amer. Chem. Soc.*, 1940, **62**, 2184.
[26] R. H. Wiley and P. Wiley, ' Pyrazolones and Derivatives,' in ' The Chemistry of Heterocyclic Compounds,' ed. A. Weissberger, Interscience, 1964, p. 13.

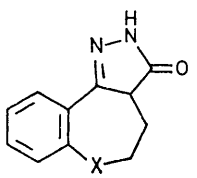
led to isolation of a ' hydroxypyrazole ' from the oxo-ester (3; R^1 = tosyl, R^2 = CO_2Et, R^3 = H). We prefer structure (6; R^1 = tosyl, R^2 = R^3 = H) for this product for the following reasons. There was no carbonyl peak in the i.r. spectrum although the corresponding tetrahydrobenzocycloheptenone ester gave [27] (7; X = CH_2), which showed ν(CO), and reaction of the 4-methyl derivative of (3; R^1 = tosyl, R^2 = CO_2-Et, R^3 = H) with hydrazine yielded (8; R = Me) having an i.r. absorption at 1 705 cm^{-1} and showing in the n.m.r. spectrum an exchangeable proton at τ −2.75 attributable to the pyrazole NH. The product in question [?(6; R^1 = tosyl, R^2 = R^3 = H)] formed a diacetate, although only one exchangeable proton peak (τ 6.75) was clearly visible in the n.m.r. spectrum. Several other compounds in this work exhibited this phenomenon. Reaction of this compound [?(6; R^1 = tosyl, R^2 = R^3 = H)] with *NN*-dimethylcarbamoyl chloride gave a monocarbamate (6; R^1 = tosyl, R^2 = $CONMe_2$, R^3 = H) in the n.m.r. spectrum of which the peak at τ 6.75 had disappeared. Compound (8; R = CO_2Et) proved inaccessible since reaction of the 4-ethoxycarbonyl derivative of (3; R^1 = tosyl, R^2 = CO_2Et, R^3 = H) yielded the same compound [?(6; R^1 = tosyl, R^2 = R^3 = H)] on reaction with hydrazine. Formula (7; X = *N*-tosyl) is thus excluded by the



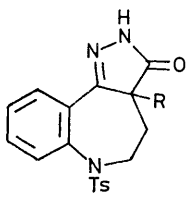
(6)



(6a)



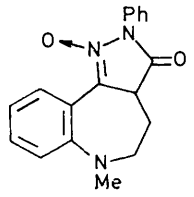
(7)



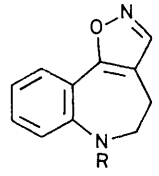
(8)

available evidence but there seems no absolutely certain way of excluding the 1*H*-lactim formulation (6a; R = tosyl); this finer point has been little discussed in the literature [26,28] insofar as it applies to enolic pyrazolones. The *N*-methyl oxo-ester (3; R^1 = Me, R^2 = CO_2Et, R^3 = H) and hydrazine gave a complex mixture from which, after acetylation, a diacetate [presumably from structure (6; R^1 = Me, R^2 = R^3 = H)] was isolated in low yield.

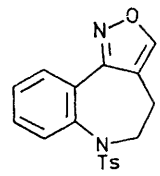
Reaction of phenyl hydrazine with oxo-esters (3; R^1 = tosyl and Me, R^2 = CO_2Et, R^3 = H) gave complex mixtures; in the latter case a compound $C_{18}H_{17}N_3O_2$ was isolated containing one more oxygen atom than expected. This compound had ν(CO) at 1 705 cm^{-1} (attributable to pyrazolone) and an exchangeable proton sharp signal at τ 8.5 in the n.m.r. spectrum: the mass spectrum revealed a large $[M - O]^+$ signal characteristic of *N*-oxides. The compound failed to form an acetate even under forcing conditions and was neither reduced by Sn–HCl nor gave a conclusive positive test for *N*-oxide.[29] Structure (9) is plausible but not beyond doubt.



(9)



(10)



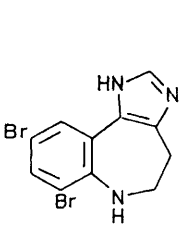
(11)

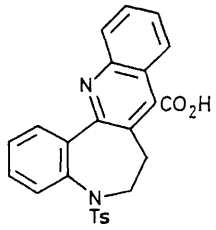
Isoxazoles.—The hydroxymethylene ketone (3; R^1 = tosyl, R^2R^3 = CHOH) reacted with hydroxylamine hydrochloride in acetic acid to give the isoxazolo[4,5-*d*][1]benzazepine (10; R = tosyl); the analogue (10; R = CHO) was similarly obtained. When compound (10; R = tosyl) was treated with sodium methoxide, the α-cyano-ketone (3; R^1 = tosyl, R^2 = CN, R^3 = H) was obtained,[30] though this product should be regarded as the enol form (see Experimental section), especially since ν(CO) was absent in the i.r. but conjugated C≡N and OH absorptions were present. Reaction of the hydroxymethylene ketone (3; R^1 = tosyl, R^2 = CHO, R^3 = H) with hydroxylamine hydrochloride in pyridine, on the other hand yielded the isomeric isoxazolo[4,3-*d*][1]benzazepine (11) which did not give the α-cyano-ketone (3; R^1 = tosyl, R^2 = CN, R = H) on treatment with sodium methoxide. Its mass-spectral cracking pattern (see Experimental section) was significantly different from that of the above isomer but there was no allylic coupling apparent in the n.m.r. signal for the isoxazole ring proton, a phenomenon that has been useful in some similar cases.[28]

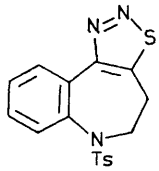
Miscellaneous.—A number of imidazole syntheses [31-34] were attempted using α-bromo-ketones that were available but all failed except that between the 7,9-dibromo-derivative of compound (3; R^1 = H, R^2 = R^3 = Br) and aqueous formaldehyde in ammonium hydroxide, which gave a poor yield of, presumably, the imidazo-[5,4-*d*][1]benzazepine [(12) or its tautomer]. The Pfitzinger reaction,[35] used previously in the 1-benzazepine

[27] H. J. Davies and B. G. Main, *J. Chem. Soc.* (*C*), 1970, 327.
[28] A. Fravolini, G. Grandolini, and A. Martani, *Gazzetta*, 1973, **103**, 1073.
[29] A. R. Katritzky and N. A. Coates, *J. Org. Chem.*, 1959, **24**, 1836.
[30] A. Fravolini, G. Grandolini, and A. Martani, *Gazzetta*, 1973, **103**, 755.
[31] H. Bredereck, R. Gompper, H. G. Schuh, and G. Theilig, ' Newer Methods of Preparative Organic Chemistry,' vol. 3, Academic Press, New York and London, 1964, p. 241.
[32] H. Schubert, *J. prakt. Chem.*, 1956, **3**, 146.
[33] J. W. Cornforth and H. T. Huang, *J. Chem. Soc.*, 1948, 1960.
[34] F. Knuckell, *Ber.*, 1901, **34**, 637.
[35] J. T. Braunholtz and F. G. Mann, *J. Chem. Soc.*, 1958, 3368.

series, gave compound (13), but attempts to decarboxylate or detosylate it were unsuccessful. A thiadiazolo-compound (14) was prepared by the action of thionyl

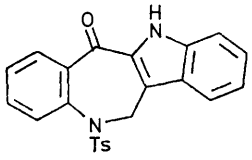

(12)

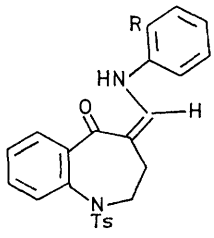

(13)


(14)

chloride [36] on the semicarbazone of the ketone (3; R^1 = tosyl, $R^2 = R^3 = H$).

The Japp–Klingemann reaction [37] on the hydroxymethylene ketone (3; R^1 = tosyl, R^2 = CHO, R^3 = H) gave the indolo[1]benzazepinone (15) which had an


(15)


(16)

abnormally low ν(CO) at 1 615 cm^{-1}; this is in accord with previous observations [38] for such hydrogen-bonded structures. Although the two hydroxy-α-imino-ketones (3; R^1 = tosyl or CH_3CO, R^2R^3 = NOH) could be made by conventional procedures,[39] only the *N*-acetyl one could be reduced to the unstable α-amino-ketone (3; R^1 = Ac, $R^2 = NH_2$, R^3 = H). The latter did not react productively with acetaldehyde oxime [40] or with hydroxylamine [41] thus preventing annelation reactions, although in the second case a very low yield of the α-dioxime was isolated.

The hydroxymethylene ketone (3; R^1 = tosyl, R^2 = CHO, R^3 = H) reacted with various amino-compounds (see Experimental section) but these could not be converted into heterocyclic compounds such as diazepines [42-44] or pyrroles. In the case of *o*-phenylenediamine the product (16; R = NH_2) was an enamine; the low τ value (— 1.35) for the NH proton is probably due to hydrogen bonding, and failure to cyclise further is not therefore due to the *trans*-geometry of the double bond as we first thought. Such failures have been noted previously.[16,44]

Finally, we note in summary that while α-hydroxymethylene ketones (3; R^1 = tosyl or CHO, R^2 = CHO, R^3 = H) undergo many of the reactions expected of them, both the β-oxo-esters (3; R^1 = tosyl or Me, $R^2 = CO_2Et$, R^3 = H) and the α-hydroxyimino-ketones (3; R^1 = tosyl and Ac, R^2R^3 = NOH) are abnormally unreactive in many cases, presumably for partly steric and partly electronic reasons since no clear pattern is discernible.

EXPERIMENTAL

Preparation of 2-Amino-6,7-dihydro-4-hydroxy-7-tosyl-5H-pyrimido[5,4-d][1]benzazepine (4; R^1 = tosyl, R^2 = OH, $R^3 = NH_2$).—The *N*-tosyl-β-oxo-ester (3; R^1 = tosyl, $R^2 = CO_2Et$, R^3 = H) (0.77 g, 2 mmol) and guanidine carbonate (0.185 g, 2.08 mmol) were refluxed for 48 h in ethanol (25 ml). At this point t.l.c. showed that decarboxylation was occurring but the ester was still present. Prolonged refluxing (7 days) followed by cooling afforded the *product* (0.185 g, 24%). Recrystallisation from ethanol gave needles, m.p. >270 °C (Found: C, 56.45; H, 5.15; N, 16.35%; *M*, 382.109 1. $C_{19}H_{18}N_4O_3S$ requires C, 56.7; H, 4.75; *N*, 14.65%; *M*, 382.109 9); $\nu_{max.}$ (KCl) 3 380 (N–H) and 1 655 cm^{-1} (C=O); τ(CD_3CO_2D) 2.5—3.1 (8 H, m, aromatic), 6.0 (2 H, br, 6-H), 7.2 (2 H, br, 5-H), and 7.7 (3 H, s, CH_3).

2-Amino-6,7-dihydro-4-hydroxy-7-methyl-5H-pyrimido-[5,4-d][1]benzazepine (4; R^1 = Me, R^2 = OH, $R^3 = NH_2$). —A mixture of 4-ethoxycarbonyl-1,2,3,4-tetrahydro-1-methyl-1-benzazepin-5-one (3; R^1 = Me, $R^2 = CO_2Et$, R^3 = H) (0.466 g, 2 mmol),[12] guanidine carbonate (0.185 g, 1.025 mmol), and absolute ethanol (20 ml) was stirred and refluxed for 48 h. Cooling gave a brown crystalline solid (0.18 g, 39%). Recrystallisation from ethanol gave the *product* as needles, m.p. 278—279 °C (Found: C, 62.3 H, 6.1; N, 21.7%; *M*, 242.114. $C_{13}H_{14}N_4O{\cdot}0.5H_2O$ requires C, 62.2; H, 6.0; N, 21.5%. $C_{13}H_{14}N_4O$ requires *M*, 242.117); $\nu_{max.}$ (KBr) 3 380, 3 100 (NH_2), and 1 650 cm^{-1} (C=O); τ(CD_3CO_2D) 2.55—2.85 (4 H, m, aromatic), 6.6 (2 H, t, 6-H), 7.2 (3 H, s, CH_3), and 7.5 (2 H, t, 5-H).

Action of Ethyl Chloroformate on 4-Ethoxycarbonyl-1,2,3,4-tetrahydro-1-tosyl-1-benzazepin-5-one (3; R^1 = tosyl, $R^2 = CO_2Et$, R^3 = H).—The *N*-tosyl-β-oxo-ester (3; R^1 = tosyl, $R^2 = CO_2Et$, R^3 = H) (7.5 g, 20 mmol) in dry dimethylformamide (75 ml) was treated with sodium hydride (80% dispersion; 1.5 g) at 70 °C for 3 h under nitrogen. Ethyl chloroformate (3.2 ml, 33.5 mmol) was added and heating continued at 70 °C for 2 h. Dilution with water and aqueous 8% hydrochloric acid, followed by extraction with chloroform, gave an oil on evaporation *in vacuo* of the dried extract. The oil was washed with light petroleum (b.p. 60—80 °C) and the product crystallised from ethanol as yellow crystals (3.6 g, 41%), m.p. 95—96 °C. The product was a mixture of 4,4-bis(ethoxycarbonyl)-1,2,3,4-tetrahydro-1-tosyl-1-benzazepin-5-one (3; R^1 = tosyl, $R^2 = R^3 = CO_2Et$) and 4-ethoxycarbonyl-1,2,3,4-tetrahydro-4-methoxycarbonyl-1-tosyl-1-benzazepin-5-one (3; R^1 = tosyl, $R^2 = CO_2Me$, $R^3 = CO_2Et$). In *ca.* 4 : 1 ratio (Found: C, 59.55; H, 5.3; N, 3.0%; *M*, 459.130 05,

[36] I. Lalezari, A. Shafiee, and S. Yazdany, *J. Pharm. Sci.*, 1974, **63**, 628.
[37] R. R. Phillips, *Org. Reactions*, 1959, **10**, 143.
[38] K. Fujimori and K. Yamane, *Bull. Chem. Soc. Japan*, 1974, **47**, 1951.
[39] R. D. Haworth, D. Caunt, W. D. Crow, and C. A. Vodoz, *J. Chem. Soc.*, 1950, 1631.
[40] J. B. Wright, *J. Org. Chem.*, 1964, **29**, 1620.
[41] L. H. Briggs, J. P. Bartley, and P. S. Rutledge, *J. Chem. Soc.* (*C*), 1971, 2115.
[42] G. Schwarzenbach and K. Lutz, *Helv. Chim. Acta*, 1940, **23**, 1139.
[43] R. H. McDougall and S. H. Malik, *J. Chem. Soc.* (*C*), 1969, 2044.
[44] W. A. Mosher and S. Piesch, *J. Org. Chem.*, 1970, **35**, 1026.

445.117 4. Calc. for $C_{22}H_{23}NO_7O$: C, 59.4; H, 5.2; N, 3.15%; *M*, 445.119 5. Calc. for $C_{23}H_{25}NO_7S$: C, 60.2; H, 5.5; N, 3.05%; *M*, 459.135 16); $\nu_{max.}$ (KBr) 1 760, 1 720, and 1 635 cm^{-1} (C=O); τ 2.4—2.9 (8 H, m, aromatic), 5.8 (m, 2-H and CH_2CH_3), 6.35 (s, CO_2CH_3), 7.55 (t, 3-H), 7.6 (s, CH_3), and 8.8 (m, CH_2CH_3).

Reaction of 1,2,3,4-*Tetrahydro*-4-*hydroxymethylene*-1-*tosyl*-1-*benzazepin*-5-*one* (3; R^1 = tosyl, R^2R^3 = CHOH) *with Guanidine Hydrochloride*.—Guanidine hydrochloride (0.375 g, 3.92 mmol) was added to a solution of sodium ethoxide [from sodium (0.235 g) in absolute ethanol (15 ml)]. The precipitated sodium chloride was filtered off and the hydroxymethylene ketone (3; R^1 = tosyl, R^2R^3 = CHOH) (0.525 g, 1.53 mmol) was added to the resultant solution of free guanidine. The mixture was refluxed for 48 h, after which a pale brown solid had been deposited. Addition of cold water afforded 6,7-*dihydro*-2-*methylamino*-7-*tosyl*-5H-*pyrimido*[5,4-d][1]*benzazepine* (4; R^1 = tosyl, R^2 = H, R^3 = NHMe) (0.29 g), m.p. 220 °C (Found: C, 62.7; H, 5.4; N, 14.7%; *M*, 380.130 3. $C_{20}H_{20}O_2S$ requires C, 63.1; H, 5.3; N, 14.75%; *M*, 380.130 7); $\nu_{max.}$ (KBr) 3 500, 3 380, 3 310, and 3 190 (NH), and 1 640 cm^{-1} (C=N); τ 2.6—3.3 (9 H, m, aromatic), 5.3 (1 H, s, NH, exchangeable), 5.95 (2 H, t, 6-H), 7.55 (2 H, t, 5-H), 7.7 (3 H, s, CH_3), and 7.8 (3 H, s, N-CH_3).

2-*Amino*-4-*chloro*-6,7-*dihydro*-7-*methyl*-5H-*pyrimido*[5,4-d][1]*benzazepine* (4; R^1 = Me, R^2 = Cl, R^3 = NH_2).—2-Amino-4-hydroxy-6,7-dihydro-7-methyl-5*H*-pyrimido-[5,4-*d*][1]benzazepine (4; R^1 = Me, R^2 = OH, R^3 = NH_2) (0.5 g) was added to stirred phosphoryl chloride (3 ml) and the mixture was heated at 100 °C for 8 h. The resultant gum was diluted with water and treated with sodium hydrogen carbonate (solid) to destroy the excess of phosphoryl chloride. Extraction with chloroform, gave the product (0.25 g, 47%), m.p. >270 °C (from ethanol). An analytically pure sample could not be obtained (Found: *M*, 260.081 6. Calc for $C_{13}H_{13}ClN_4$: *M*, 260.082 9); $\nu_{max.}$ (KBr) 3 380 cm^{-1} (NH); τ 2.6—3.15 (4 H, m, aromatic), 4.65 (2 H, s, NH, exchangeable), 6.7 (2 H, t, 6-H), and 7.15 (5 H, m, 5-H and CH_3).

2,4,5,6-*Tetrahydro*-6-*tosylpyrazolo*[4,3-d][1]*benzazepine* (5; R^1 = tosyl, R^2 = R^3 = H).—The *N*-tosylhydroxymethylene ketone (3; R^1 = tosyl, R^2R^3 = CHOH) (0.96 g) in methanol (75 ml) was treated with hydrazine hydrate (1.25 ml) and left at room temperature for 24 h. Evaporation and recrystallisation from ethanol afforded the *product* (0.9 g, 95%), m.p. 145 °C (Found: C, 63.5; H, 5.2; N, 12.4%; *M*, 339.103 5. $C_{18}H_{17}N_3O_2S$ requires C, 63.5; H, 5.0; N, 12.35%; *M*, 339.104 1); $\nu_{max.}$ (KBr) 3 360 (free NH) and 3 170 cm^{-1} (hydrogen-bonded NH); τ −0.75 (1 H, s, NH, exchangeable), 2.35—2.65 (2 H, m, aromatic), 2.8 (1 H, s, 3-H), 2.85—3.0 (4 H, m, aromatic), 3.15 (2 H, d, aromatic), 6.15 (2 H, t, $J_{4.5}$ 4 Hz, 5-H), 7.05 (2 H, t, $J_{4.5}$ 4 Hz, 4-H), and 7.9 (3 H, s, CH_2), $\lambda_{max.}$ 237 nm (ε 17 655).

2-*Acetyl*-2,4,5,6-*tetrahydro*-6-*tosylpyrazolo*[4,3-d][1]*benzazepine* (5; R^1 = tosyl, R^2 = Ac, R^3 = H).—The foregoing pyrazole (0.25 g) was stirred for 2 days in pyridine (9 ml) and acetic anhydride (12 ml) at 20 °C. Addition of water yielded the *product* as a white solid, which was washed with water, and recrystallised from benzene–light petroleum (b.p. 60—80 °C) as prisms (0.15 g, 53%), m.p. 110 °C (Found: C, 63.05; H, 5.0; N, 11.3. $C_{20}H_{19}N_3O_3S$ requires C, 63.05; H, 5.0; N, 11.0%); $\nu_{max.}$ (KBr) 1 730 cm^{-1} (C=O); τ 2.0 (1 H, m, aromatic), 2.2 (1 H, s, 3-H), 2.4 (1 H, m, aromatic), 2.55—2.75 (4 H, m, aromatic), 3.05 (2 H, d, aromatic), 5.95 (2 H, t, 5-H), 7.05 (2 H, t, 4-H), 7.35 (3 H, s, $COCH_3$), and 7.75 (3 H, s, CH_3).

8-*Chloro*-1,2,3,4-*tetrahydro*-4-*hydroxymethylene*-1-*tosyl*-1-*benzazepin*-5-*one* [8-*Chloro*-(3; R^1 = tosyl, R^2R^3 = CHOH)].—A solution of the chloro-ketone 8-chloro-(3; R^1 = tosyl, R^2R^3 = H) (4.85 g) in ethyl formate (4.5 ml, 4.125 g) and dry toluene (150 ml) was cooled to 0 °C and added to a suspension of sodium ethoxide [from sodium (5.45 g)] in dry toluene (80 ml) at 0 °C. The mixture was shaken and left at room temperature for 24 h. Water was then added and the toluene layer extracted with cold aqueous 8% sodium hydroxide. The combined aqueous extracts were acidified with ice-cooling and extracted with chloroform; the extracts were dried and evaporated *in vacuo* to leave an oil which slowly solidified. Recrystallisation from toluene gave the *product* (4.7 g, 91%) as pale brown crystals, m.p. 148 °C (Found: C, 57.4; H, 4.5; N, 3.5. $C_{18}H_{16}ClNO_4S$ requires C, 57.3; H, 4.3; N, 3.7%); $\nu_{max.}$ (KBr) 1 630 cm^{-1} (C=O, chelated); τ −3.95 (1 H, s, OH, exchangeable), 2.3—2.85 (8 H, m, aromatic and 3-H), 6.0 (2 H, t, $J_{2.3}$ 4 Hz, 2-H), 7.6 (3 H, s, CH_3), and 7.8 (2 H, t, $J_{2.3}$ 4 Hz, 3-H).

8-*Chloro*-2,4,5,6-*tetrahydro*-6-*tosylpyrazolo*[4,3-d][1]-*benzazepine* (5; R^1 = tosyl, R^2 = H, R^3 = Cl). To the foregoing chlorohydroxymethylene ketone (0.8 g) in methanol (80 ml) and benzene (2 ml) was added hydrazine hydrate (0.15 ml). After 24 h at room temperature, the solution was evaporated *in vacuo* to half its volume. A yellow solid was deposited, which on recrystallisation from methanol gave the *product* (0.765 g, 98%) as yellow cubes, m.p. 142 °C (Found: C, 57.8; H, 4.45; N, 11.6. $C_{18}H_{16}ClN_3O_2S$ requires C, 57.95; H, 4.3; N, 11.25%); $\nu_{max.}$ (KBr) 3 350 (free NH) and 3 160 cm^{-1} (hydrogen-bonded NH); τ 0.2 (1 H, s, NH, exchangeable), 2.4—2.6 (2 H, m, aromatic), 2.75 (1 H, s, 3-H), 2.85—3.1 (3 H, m, aromatic), 3.2 (2 H, d, aromatic), 6.2 (2 H, t, 5-H), 7.05 (2 H, t, 4-H), and 7.9 (3 H, s, CH_3).

2-*Acetyl*-8-*chloro*-2,4,5,6-*tetrahydro*-7-*tosylpyrazolo*[4,3-d][1]*benzazepine* (5; R^1 = tosyl, R^2 = Ac, R^3 = Cl).—The foregoing pyrazole (0.23 g) was heated at 100—110 °C for 10 h in acetic anhydride (10 ml). The usual work-up afforded the *product* (0.185 g, 73%) from ethanol as crystals, m.p. 152 °C (Found: C, 57.8; H, 4.3; N, 10.0%; *M*, 417.070 4. $C_{20}H_{18}ClN_3O_3S$ requires C, 57.5; H, 4.5; N, 10.1%; *M*, 417.072 8); $\nu_{max.}$ (KBr) 1 730 cm^{-1} (C=O); τ 2.1 (1 H, s, 3-H), 2.2—2.9 (5 H, m, aromatic), 3.1 (2 H, d, aromatic), 6.1 (2 H, t, $J_{4.5}$ 4 Hz, 5-H), 7.05 (2 H, t, $J_{4.5}$ 4 Hz, 4-H), 7.4 (3 H, s, $COCH_3$), and 7.8 (3 H, s, CH_3).

1-*Formyl*-1,2,3,4-*tetrahydro*-4-*hydroxymethylene*-1-*benzazepin*-5-*one* (3; R^1 = CHO, R^2R^3 = CHOH).—A solution of the amino-ketone (3; R^1 = R^2R^3 = H) (4.95 g) [2] in ethyl formate (10 ml, 9.17 g) and dry toluene (150 ml) was cooled to 0 °C and added to a slurry of sodium ethoxide [from sodium (6 g)] in dry toluene (80 ml) at 0 °C. The mixture was shaken and left at 20 °C for 36 h, then diluted with water; the toluene layer was washed with cold 8% aqueous sodium hydroxide. The combined aqueous washings were acidified with ice-cooling and extracted with chloroform; the extracts were dried and evaporated *in vacuo* to give a solid. Recrystallisation from toluene gave the *product* (4.85 g, 83%) as crystals, m.p. 131 °C (Found: C, 66.45; H, 5.2; N, 6.45%; *M*, 217.073 2. $C_{12}H_{11}NO_3$ requires C, 66.75; H, 5.2; N, 6.4%; *M*, 217.073 9); $\nu_{max.}$ (KBr) 1 675 (amide) and 1 635 cm^{-1} (C=O chelated), τ −4.7 (1 H, s, OH, exchangeable), 1.8 (1 H, s, CHO), 2.2—2.9

(5 H, m, aromatic olefinic), 6.05 (2 H, t, 2-H), and 7.25 (2 H, t, 3-H).

6-Formyl-2,4,5,6-tetrahydropyrazolo[4,3-d][1]*benzazepine* (5; R^1 = CHO, R^2 = R^3 = H).—1-Formyl-1,2,3,4-tetrahydro-4-hydroxymethylene-1-benzazepin-5-one (3; R^1 = CHO, R^2R^3 = CHOH) (2 g) in methanol (100 ml) was treated with hydrazine hydrate (0.35 ml) and left at 20 °C overnight. Evaporation *in vacuo* left a yellow solid, which crystallised from ethanol (yield 1.76 g, 89%); m.p. 178 °C (Found: C, 67.55; H, 5.5; N, 19.6%; *M*, 213.089 7. $C_{12}H_{11}N_3O$ requires C, 67.7; H, 5.2; N, 19.7%; *M*, 213.090 2); $\nu_{max.}$ (KBr) 3 460 (free NH), 3 210 (hydrogen-bonded NH), and 1 670 cm^{-1} (C=O); τ 1.35 1 H, s, NH, exchangeable), 1.8 (1 H, s, CHO), 2.05 (1 H, m, aromatic), 2.7 (1 H, s, 3-H), 2.8—3.1 (3 H, m, aromatic), 6.2 (2 H, t, 5-H), and 7.0 (2 H, t, 4-H).

2-Acetyl-6-formyl-2,4,5,6-tetrahydropyrazolo[4,3-d][1]*benzazepine* (5; R^1 = CHO, R^2 = Ac, R^3 = H).—The foregoing pyrazole (0.4 g) was added to a stirred mixture of acetic anhydride (3 ml) and pyridine (6 ml) and left overnight at room temperature. The usual work-up gave the *product* (0.45 g, 94%) as a cream solid, m.p. 119—121 °C (EtOH) (Found: C, 66.05; H, 5.2; N, 16.7. $C_{14}H_{13}N_3O_2$ requires C, 65.9; H, 5.1; N, 16.5%); $\nu_{max.}$ (KBr) 1 730 ($COCH_3$) and 1 670 cm^{-1} (CHO); τ 1.7—1.8 (1 H, m, aromatic), 1.8 (1 H, s, CHO), 2.1 (1 H, s, 3-H), 2.75—3.1 (3 H, m, aromatic), 6.2 (2 H, t, 5-H), 7.05 (2 H, t, 4-H), and 7.35 (3 H, s, CH_3).

2,4,5,6-Tetrahydro-1H-pyrazolo[4,3-d][1]*benzazepine* (5; R^1 = R^2 = R^3 = H).—(*a*) 6-Formyl-2,4,5,6-tetrahydropyrazolo[4,3-*d*][1]benzazepine (5; R^1 = CHO, R^2 = R^3 = H) and 8% hydrochloric acid (10 ml) were refluxed for 4 h. The mixture was cooled and diluted with ice-water, and basified with 8% sodium hydroxide with ice-cooling. The alkaline solution was extracted with chloroform, and the extracts were dried and evaporated *in vacuo* to give the crude *product* as a dark green powder. Recrystallisation from ethanol afforded the *product* (1.5 g, 75%) as prisms, m.p. 148—150 °C (Found: C, 71.55; H, 6.15; H, 22.95. $C_{11}H_{11}N$ requires C, 71.4; H, 6.0; N, 22.7%); $\nu_{max.}$ (KBr) 3 410 (free NH) and 3 200 cm^{-1} (hydrogen-bonded NH), τ 2.2 (1 H, d, aromatic), 2.55 (1 H, s, 3-H), 2.75—3.35 (4 H, m, 3 aromatic + =N–NH exchangeable), 6.65 (2 H, t, 5-H), and 7.1 (2 H, t, 4-H). (*b*) The *N*-tosylpyrazole (5; R^1 = tosyl, R^2 = R^3 = H) (0.66 g, 1.82 mmol) and liquid ammonia (40 ml) were stirred while small pieces of sodium (0.17 g, 7.4 mmol) were added over 15 min, causing a colour change from yellow to green–blue. This colour was discharged by addition of an excess of ammonium chloride. The ammonia was allowed to evaporate from the resultant grey suspension, and aqueous sodium chloride (10%; 60 ml) was added to the residue and the mixture was shaken. The alkaline solution was extracted with chloroform, and the extracts were dried and evaporated *in vacuo* to give a yellow gum (0.36 g). Crystallisation afforded the product (0.31 g, 91%), identical to that obtained in (*a*).

2,6-Diacetyl-2,4,5,6-tetrahydropyrazolo[4,3-d][1]*benzazepine* (5; R^1 = R^2 = Ac, R^3 = H).—The aminopyrazole (5; R^1 = R^2 = R^3 = H) (0.2 g) was heated for 48 h at 100 °C with pyridine (9 ml) and acetic anhydride (3.5 ml). The usual work-up gave the *product* (0.17 g, 58%) as pale brown crystals, m.p. 156—157 °C (EtOH) (Found: C, 66.9; H, 4.8; N, 15.6%; *M*, 269.114 1. $C_{15}H_{15}N_3O_2$ requires C, 67.0; H, 4.6; N, 15.6%; *M*, 269.116 4); $\nu_{max.}$ (KBr) 1 730 (2-$COCH_3$) and 1 665 cm^{-1} (6-$COCH_3$); τ 1.85 (1 H, m, aromatic), 2.05 (1 H, s, 3-H), 2.7—3.0 (3 H, m, aromatic), 5.3 (2 H, m, 5-H), 7.0 (2 H, m, 4-H), 7.3 (3 H, s, 2-$COCH_3$), and 8.1 (3 H, s, 6-$COCH_3$).

2,4,5,6-Tetrahydro-2-(dimethylcarbamoyl)pyrazolo[4,3-d][1]*benzazepine* (5; R^1 = R^3 = H, R^2 = $CONMe_2$).—The aminopyrazole (5; R^1 = R^2 = R^3 = H) (0.55 g, 3 mmol) and dimethylcarbamoyl chloride (0.33 g, 3.05 mmol) were heated at 60 °C for 4 h in pyridine (6 ml). The usual work-up gave an oil which was extracted with hot light petroleum (b.p. 60—80 °C); on cooling, the extract afforded the *product* (0.415 g, 54%) as yellow prisms, m.p. 97 °C (Found: C, 65.6; H, 6.1; N, 21.65. $C_{14}H_{16}N_4O$ requires C, 65.7; H, 6.3; N, 21.9%); $\nu_{max.}$ (KBr) 3 360 (NH) and 1 670 cm^{-1} (C=O); τ 2.05 (1 H, s, 3-H), 2.8—3.25 (4 H, m, aromatic), 6.0 (1 H, br, NH, exchangeable), 6.7 (2 H, t, 5-H), 6.75 (6 H, s, NMe), and 7.15 (2 H, t, 4-H).

2,4,5,6-Tetrahydro-2-methyl-6-tosylpyrazolo[4,3-d][1]*benzazepine* (5; R^1 = tosyl, R^2 = Me, R^3 = H) *Methiodide*.—The *N*-tosylpyrazole (5; R^1 = tosyl, R^2 = R^3 = H) (0.2 g), potassium carbonate (0.25 g), and methyl iodide (1.0 ml) in acetone (25 ml) were refluxed for 15 h. The filtered solution was evaporated *in vacuo* to leave a gum, which crystallised from ethanol to give the *product* (0.185 g, 80%) as pale brown crystals, m.p. 190 °C (Found: C, 48.15; H, 4.55; N, 8.55%; *M*, 353.118 3. $C_{20}H_{22}IN_3O_2S$ requires C, 48.55; H, 4.5; N, 8.5%. $C_{19}H_{19}N_3O_2S$ requires *M*, 353.119 8); $\nu_{max.}$ (KBr) 1 600 cm^{-1} (C=C); τ[$(CD_3)_2SO$] 1.85 (1 H, s, 3-H), 2.0 (1 H, s, aromatic), 2.5 (3 H, m, aromatic), 2.85 (4 H, m, aromatic), 6.2 (2 H, t, 5-H), 6.75 (8 H, br, 2 NCH_3 + 4-H), and 7.75 (3 H, s, CH_3).

Reaction of 1,2,3,4-Tetrahydro-4-hydroxymethylene-1-tosyl-1-benzazepin-5-one (3; R^1 = tosyl, R^2R^3 = CHOH) *with p-Nitrophenylhydrazine*.—*p*-Nitrophenylhydrazine (0.105 g, 0.69 mmol) was added to a stirred solution of the hydroxymethylene ketone (0.23 g, 0.68 mmol) in methanol (15 ml) and left overnight at room temperature. Filtration gave an orange solid (0.23 g, 74%), which crystallised from ethanol as an orange powder, m.p. 180—182 °C, shown to be *1,2,3,4-tetrahydro-4-(p-nitrophenylhydrazinomethylene)-1-tosylbenzazepin-5-one* (3; R^1 = tosyl, R^2R^3 = *p*-$NO_2C_6H_4$-NHNHCH=) (Found: C, 58.3; H, 4.75; N, 11.05%; *m/e*, 460.120 3. $C_{24}H_{22}N_4O_5S$ requires C, 58.1; H, 4.9; N, 11.3%; *M*, 478.131 11; $[M - H_2O]^+$, 460.120 5); $\nu_{max.}$ (KBr) 3 270 (NH) and 1 630 cm^{-1} (C=O, chelated); τ(C_5D_5N) — 1.55 (1 H, s, =CH–N*H*–, exchangeable), 1.8–3.15 (9 H, m, aromatic + olefinic), 5.95 (2 H, t, 2-H), 7.6 (2 H, br, 3-H), and 7.85 (3 H, s, CH_3).

In similar fashion was obtained *1-formyl-1,2,3,4-tetrahydro-4-(p-nitrophenylhydrazinomethylene)-1-benzazepin-5-one* (3; R^1 = CHO, R^2R^3 = *p*-$NO_2C_6H_4NHNHCH$=), m.p. 190—210 °C (Found: C, 60.9; H, 4.65; N, 15.8%; *M*, 352.115 8. $C_{18}H_{16}N_4O_4$ requires C, 60.6; H, 4.3; N, 15.95%; *M*, 352.117 1); $\nu_{max.}$ (KBr) 3 240 (NH) and 1 655 cm^{-1} (chelated C=O); τ(C_5D_5N) —1.65 (1 H, s, =CH–N*H*– exchangeable), 1.5 (1 H, s, CHO), 1.6—3.1 (9 H, m, aromatic + olefinic), 5.9 (2 H, br, 2-H), 6.4 (1 H, br, ArN*H*– exchangeable), and 7.4 (2 H, t, 3-H); *m/e* ([*M* — H_2O]) 334.106 5 ($C_{18}H_{14}N_6O_3$ requires 334.106 6).

Reaction of 1-Formyl-1,2,3,4-tetrahydro-4-hydroxymethylene-1-benzazepin-5-one (3; R^1 = CHO, R^2R^3 = CHOH) *with Semicarbazide Hydrochloride*.—Semicarbazide hydrochloride (0.05 g) in water (1.5 ml) was added to a stirred solution of the *N*-formylhydroxymethylene ketone (0.10 g) in ethanol (4 ml) and the mixture was left at room temperature for 2 days. The resultant solid (0.025 g) was filtered off and

recrystallised from ethanol to give, as a solid, m.p. 178 °C, 1-formyl-2,4,5,6-tetrahydropyrazolo[4,3-*d*][1]benzazepine (5; R^1 = CHO, R^2 = R^3 = H) (mixed m.p. 178 °C, i.r.).

1,2,3,4-*Tetrahydro*-1-*tosyl*-4-(*semicarbazidomethylene*)-1-*benzazepin*-5-*one* (3; R^1 = tosyl, R^2R^3 = NH_2CONHN-HCH=).—Semicarbazide hydrochloride (0.16 g, 1.43 mmol) in water (2 ml) was added to a stirred solution of the *N*-tosylhydroxymethylene ketone (3; R^1 = tosyl, R^2R^3 = CHOH) (0.46 g, 1.33 mmol) in ethanol (20 ml). This caused immediate crystallisation, and after 1 h the *product* was filtered off and recrystallised from methanol to give yellow prisms (0.46 g, 88%), m.p. 207 °C (Found: C, 56.85; H, 5.1; N, 13.8%; *M*, 400.122 4. $C_{19}H_{20}N_4O_4S$ requires C, 57.05; H, 5.05; N, 14.0%; *M*, 400.120 5); $\nu_{max.}$ (KBr) 3 450, 3 380, 3 280, 3 215 (NH), 1 700 (amide), and 1 645 cm^{-1} (C=O); τ[$(CD_3)_2SO$] 0.5 (1 H, d, chelated NH, exchangeable), 2.5—2.8 (9 H, m, aromatic + olefinic), 3.9 (1 H, s, NH, exchangeable), 6.15 (2 H, t, 2-H), 6.7 (2 H, s, NH_2 exchangeable), 7.65 (3 H, s, CH_3), 7.75 (2 H, t, 3-H).

2,4,5,6-*Tetrahydro*-3-*hydroxy*-6-*tosylpyrazolo*[4,3-d][1]-*benzazepine* (6; R^1 = tosyl R^2 = R^3 = H).—The *N*-tosyl-β-oxo-ester (3; R^1 = tosyl, R^2 = CO_2Et, R^3 = H) (2.615 g) and hydrazine hydrate (2 ml) were left at room temperature in methanol (120 ml) for 48 h. Evaporation of two-thirds of the solvent furnished a white solid (1.565 g, 65%), and recrystallisation from ethanol afforded the *product*, m.p. 230 °C (decomp.) (Found: C, 60.45; H, 4.85; N, 11.95%; *M*, 355.098 8. $C_{18}H_{17}N_3O_3S$ requires C, 60.9; H, 4.85; N, 11.85%; *M*, 355.099 1); $\nu_{max.}$ (KBr) 3 370 cm^{-1} (OH, NH); τ[$(CD_3)_2SO$] 2.4—3.0 (8 H, m, aromatic), 6.3 (2 H, br, 5-H), 6.75 (1 H, s, OH exchangeable), 7.3 (2 H, t, 4-H), and 7.75 (3 H, s, CH_3).

2,3-*Diacetyl*-4,5-*dihydro*-6-*tosylpyrazolo*[4,3-d][1]*benzazepine* (6; R^1 = tosyl, R^2 = R^3 = Ac).—The foregoing hydroxy-pyrazole (0.145 g), acetic anhydride (3 ml), and pyridine (4 ml) were left overnight at 20 °C. Addition of water gave a solid, which was recrystallised from ethanol to give the white *product* (0.08 g, 45%), m.p. 132 °C (decomp.) (Found: C, 60.5; H, 4.95; N, 9.25%; *M*, 439.118 7. $C_{22}H_{21}N_3O_5S$ requires C, 60.2; H, 4.8; N, 9.6%; *M*, 439.120 2); $\nu_{max.}$ (KBr) 1 790 ($OCOCH_3$) and 1 740 cm^{-1} ($NCOCH_3$); τ(C_5D_5N) 2.05—3.0 (8 H, m, aromatic), 6.05 (2 H, br, 5-H), 7.1 (2 H, t, 4-H), 7.3 (3 H, s, $NCOCH_3$), and 8.05 (6 H, s, CH_3 and $OCOCH_3$).

3-(*Dimethylcarbamoyl*)-2,4,5,6-*tetrahydro*-6-*tosylpyrazolo*-[4,3-d][1]*benzazepine* (6; R = tosyl, R^2 = Me_2NCO, R^3 = H).—The *N*-tosylhydroxypyrazole (6; R^1 = tosyl, R^2 = R^3 = H) (0.162 g, 0.45 mmol), dimethylcarbamoyl chloride (0.06 g, 0.55 mmol), and pyridine (4 ml) were stirred at room temperature for 2 h. The usual work-up gave from light petroleum (b.p. 60—80 °C) the *product* (0.15 g, 77%) as a white solid, m.p. 185 °C (Found: C, 59.1; H, 5.3; N, 13.0. $C_{21}H_{23}N_4O_4S$ requires C, 59.2; H, 5.2; N, 13.15%); $\nu_{max.}$ (KBr) 3 360 (NH) and 1 730 cm^{-1} (C=O); τ 2.5—3.0 (6 H, m, aromatic), 3.15—3.25 (2 H, d, aromatic), 6.25 (2 H, br, 5-H), 7.0 (3 H, s, N-CH_3) 7.10 (3 H, s, N-CH_3), 7.2 (2 H, t, 4-H), and 7.8 (3 H, s, CH_3); $\lambda_{max.}$ 240 and 265infl nm (ε 19 980 and 13 400).

2,3-*Diacetyl*-2,4,5,6-*tetrahydro*-6-*methylpyrazolo*[4,3-d][1]-*benzazepine* (6; R^1 = Me, R^2 = R^3 = Ac).—The *N*-methyl-β-oxo-ester (3; R^1 = Me, R^2 = CO_2Et, R^3 = H) (0.5 g) and hydrazine hydrate (0.4 ml) in methanol (5 ml) were left at room temperature for 6 days. The solvent was removed *in vacuo* and the resultant gum treated with pyridine (5 ml) and acetic anhydride (3 ml) at room temperature for 3 days. Addition of water gave an amorphous solid, which crystallised from ethanol to give the *product* (0.24 g, 38%) as a white powder, m.p. 138 °C (Found: C, 64.3; H, 5.8; N, 14.15%; *M*, 299.126 7. $C_{16}H_{17}N_3O_3$ requires C, 64.3; H, 5.75; N, 14.05%; *M*, 299.127 0); $\nu_{max.}$ (KBr) 1 790 ($OCOCH_3$) and 1 730 cm^{-1} ($NCOCH_3$); τ 1.85 (1 H, d, aromatic), 2.9 (1 H, m, aromatic), 3.2 (2 H, m, aromatic), 6.8 (2 H, t, 5-H), 7.05 (3 H, s, CH_3), 7.35 (5 H, s + overlapping t, 4-H + $NCOCH_3$), and 7.65 (3 H, s, $OCOCH_3$).

3a,4,5,6-*Tetrahydro*-3a-*methyl*-6-*tosylpyrazolo*[4,3-d][1]-*benzazepin*-3(2H)-*one* (8; R = Me).—4-Ethoxycarbonyl-1,2,3,4-tetrahydro-4-methyl-1-tosyl-1-benzazepin-5-one (3; R^1 = tosyl, R^2 = CO_2Et, R^3 = Me) (0.205 g) and hydrazine hydrate (0.5 ml) in methanol (10 ml) were left at room temperature for 8 h. Evaporation *in vacuo* gave the *product*, which crystallised from ethanol as white needles (0.170 g, 90%), m.p. 254—255 °C (Found: C, 62.1; H, 5.25; N, 11.35%; *M*, 369.114 7. $C_{19}H_{19}N_3O_3S$ requires C, 61.85; H, 5.2; N, 11.4%; *M*, 369.110 8); $\nu_{max.}$ (KBr) 3 180, 3 160, 3 080 (NH), and 1 705 cm^{-1} (C=O); τ(C_5D_5N) — 2.75 (1 H, s, NH exchangeable), 2.4—3.05 (8 H, m, aromatic), 6.35 (2 H, t, 5-H), 7.7 (2 H, t, 4-H), 7.95 (3 H, s, CH_3), and 8.82 (3 H, s, 3a-CH_3); $\lambda_{max.}$ 244 and 275 nm (ε 12 750 and 8 395).

Reaction of 4-*Ethoxycarbonyl*-1,2,3,4-*tetrahydro*-1-*methyl*-1-*benzazepin*-5-*one* (3; R^1 = Me, R^2 = CO_2Et, R^3 = H) *with Phenylhydrazine*.—A mixture of the β-oxo-ester (0.95 g, 4 mmol), phenylhydrazine (0.45 g, 4.15 mmol), and glacial acetic acid (0.15 ml) was heated for 6 h at 100 °C. T.l.c. showed the resultant red-brown gum to consist of many compounds. The gum was taken up in the minimum volume of hot ethanol, and cooling afforded a yellow solid (0.357 g), m.p. 170 °C, believed to be 3a,4,5,6-*tetrahydro*-6-*methyl*-2-*phenylpyrazolo*[4,3-d][1]*benzazapin*-3(2H)-*one* 1-*oxide* (9) (Found: C, 71.7; H, 5.6; N, 13.8%; *M*, 307.132 2. $C_{13}H_{17}N_3O_2$ requires C, 70.7; H, 5.6; N, 13.7%; *M*, 307.132 1); $\nu_{max.}$ (KBr) 1 700 cm^{-1} (C=O); τ 2.4—4.0 (9 H, m, aromatic), 6.0—7.3 (3 H, m, 3a- and 5-H), 7.02 (3 H, s, N-Me), and 7.87 (2 H, br, d, 4-H).

5,6-*Dihydro*-6-*tosyl*-4H-*isoxazolo*[4,5-d][1]*benzazepine* (10; R = tosyl).—1,2,3,4-Tetrahydro-4-hydroxymethylene-1-tosyl-1-benzazepin-5-one (3; R^1 = tosyl, R^2R^3 = CHOH) (0.12 g, 0.35 mmol) and hydroxylamine hydrochloride (0.025 g, 0.355 mmol) were refluxed in acetic acid (10 ml) for 10 h. Addition of water afforded the *product* as a white powder, which was crystallised from ethanol as plates, m.p. 143 °C (0.09 g, 74%) (Found: C, 63.6; H, 4.7; N, 8.0%; *M*, 340.087 0. $C_{18}H_{16}N_2O_3S$ requires C, 63.6; H, 4.7; N, 8.25%; *M*, 340.088 2); τ 2.05—2.15 (1 H, m, aromatic) 2.1 (1 H, s, 3-H), 2.25—2.35 (1 H, m, aromatic), 2.55—2.8 (4 H, m, aromatic), 3.05 (2 H, d, aromatic), 6.1 (2 H, s, 5-H), 7.15 (2 H, t, 4-H), and 7.8 (3 H, s, CH_3); *m/e* 276.125 6 ($C_{18}H_{16}N_2O$ requires 276.126 3), 185.071 5 ($C_{11}H_9N_2O$ requires 185.071 5), and 158.044 8 ($C_9H_6N_2O$ requires 158.048 0).

4-*Cyano*-1,2,3,4-*tetrahydro*-1-*tosyl*-1-*benzazepin*-5-*one* (3; R^1 = tosyl, R^2 = CN, R^3 = H).—Sodium methoxide [from sodium (0.5 g)] in methanol (20 ml) was added dropwise to a stirred solution of the foregoing isoxazole (2.49 g) in dry benzene (45 ml) and methanol (6 ml), and the mixture was left at room temperature overnight. The solvent was removed *in vacuo* and 8% hydrochloric acid was added to the residue. The aqueous layer was extracted with chloroform; the resultant extract was dried and evaporated *in vacuo* to give a brown oil which slowly crystallised. Recrystallis-

ation from ethanol afforded the *product* as prisms, m.p. 152—154 °C (Found: C, 63.1; H, 4.8; N, 8.1%; *M*, 340.086 3. $C_{18}H_{16}N_2O_3S$ requires C, 63.6; H, 4.75; N, 8.25%; *M*, 340.088 2); $\nu_{max.}$ (KCl) 3 100 (OH) and 2 220 cm^{-1} (CN); τ[$(CD_3)_2CO$] 2.3—2.8 (8 H, m, aromatic), 6.0 (2 H, t, 2-H), 7.15 (1 H, br s), 7.6 (3 H, s, CH_3), and 7.85 (2 H, t, 3-H).

6-*Formyl*-5,6-*dihydro*-4H-*isoxazolo*[4,5-d][1]*benzazepine* (10; R = CHO).—1-Formyl-1,2,3,4-tetrahydro-4-hydroxymethylene-1-benzazepin-5-one (3; R^1 = CHO, R^2R^3 = CHOH) (0.48 g, 2.2 mmol) and hydroxylamine hydrochloride (0.17 g, 2.45 mmol) were refluxed in acetic acid (40 ml) for 36 h. Work-up as above gave the *product* (0.30 g, 62%) as brown needles, m.p. 141—142 °C (EtOH) (Found: C, 66.9; H, 4.75; N, 13.1. $C_{12}H_{10}N_2O_2$ requires C, 67.3; H, 4.7; N, 13.1%); $\nu_{max.}$ (KBr) 1 663 cm^{-1} (amide); τ 1.75 (1 H, s, CHO), 1.95—2.1 (1 H, m, aromatic), 2.0 (1 H, s, 3-H), 2.65 3.0 (3 H, m, aromatic), 6.2 (2 H, t, 5-H), and 7.1 (2 H, t, 4-H).

5,6-*Dihydro*-6-*tosyl*-4H-*isoxazolo*[4,3-d][1]*benzazepine* (11).—A solution of hydroxylamine hydrochloride (0.525 g) in water (1 ml) was added to 1,2,3,4-tetrahydro-4-hydroxymethylene-1-tosyl-1-benzazepin-5-one (3; R^1 = tosyl, R^2R^3 = CHOH (1.075 g) in pyridine (8 ml) and the mixture was refluxed for 6 h. Addition of cold water afforded a solid (0.88 g), and extraction of the aqueous filtrate with chloroform gave further material (0.11 g). Recrystallisation from ethanol yielded the *product* (0.93 g, 79%) as prisms, m.p. 109—110 °C (Found: C, 63.75; H, 4.65; N, 8.15%; *M*, 340.087 5. $C_{18}H_{16}N_2O_3S$ requires C, 63.6; H, 4.75; N, 8.25%; *M*, 340.088 2); τ 2.05—2.15 (1 H, m, aromatic), 2.15 (1 H, s, 3-H), 2.4—2.6 (1 H, m, aromatic), 2.65—2.95 (4 H, m, aromatic), 3.15 (2 H, d, aromatic), 6.1 (2 H, t, 5-H), 7.1 (2 H, t, 4-H), and 7.8 (3 H, s, CH_3); *m/e* 312.092 6 ($C_{17}H_{16}N_2O_2S$ requires 312.093 2), 247.123 6 ($C_{17}H_{15}N$ requires 247.123 6), and 185.070 6 ($C_{11}H_9N_2O$ requires 185.071 5).

1,2,3,4-*Tetrahydro*-4-*hydroxyimino*-1-*tosyl*-1-*benzazepin*-5-*one* (3; R^1 = tosyl, R^2R^3 = NOH).—Isopentyl nitrate (0.9 ml, 1.245 g, 10.65 mmol) was added to a stirred solution of the tosyl ketone (3; R^1 = tosyl, R^2 = R^3 = H) (1.8 g, 5.7 mmol) in dry methanol (120 ml) at −15 °C, and dry hydrogen chloride gas was passed through the solution for 4.5 h. After 16 h at room temperature the solvent was removed *in vacuo* to leave the *product*, which crystallised from ethanol as cream needles (1.6 g, 82%), m.p. 171—172 °C (Found: C, 59.15; H, 4.75; N, 7.9. $C_{17}H_{18}N_2O_4S$ requires C, 59.35; H, 4.65; N, 8.15%); $\nu_{max.}$ (KBr) 3 300 (OH) and 1 690 cm^{-1} (C=O), τ(CD_3CN) 0.3 (1 H, br, OH exchangeable), 2.4—2.95 (8 H, m, aromatic), 6.2 (2 H, t, H-2), 7.3 (2 H, t, H-3), and 7.65 (3 H, s, CH_3). The *acetate* (pyridine–acetic anhydride) formed crystals, m.p. 183 °C (Found: C, 58.8; H, 4.85; N, 7.15%; *M*, 386.089 9. $C_{19}H_{18}N_2O_5S$ requires C, 59.1; H, 4.95; N, 7.25%; *M*, 386.093 6), $\nu_{max.}$ (KBr) 1 775 ($COCH_3$) and 1 695 cm^{-1} (ArC=O), τ(C_5D_5N) 2.4—3.0 (8 H, m, aromatic), 5.95 (2 H, t, 2-H), 7.05 (2 H, t, 3-H), 7.85 (3 H, s, CH_3), and 7.87 (3 H, s, $COCH_3$).

1,2,3,4-*Tetrahydro*-1-*tosyl*-1-*benzazepin*-5-*one* (3; R^1 = tosyl, R^2 = R^3 = H) *O-Tosyloxime*.—The 1,2,3,4-tetrahydro-1-tosyl-1-benzazepin-5-one oxime [oxime of (3; R^1 = tosyl, R^2 = R^3 = H)] (0.33 g, 1 mmol) in acetone (50 ml) and 8% sodium hydroxide (1.3 ml) were cooled to 0 °C. Tosyl chloride (0.35 g, 1.8 mmol) was added, and the mixture was stirred for 1 h at 0 °C and for 1 h at room temperature. It was then evaporated *in vacuo*, acidified with 8% hydrochloric acid, and extracted with benzene. The benzene extract was dried and evaporated *in vacuo*, and the residue was recrystallised from benzene to give the *product* (0.3 g, 62%) as white crystals, m.p. 126 °C (Found: C, 59.4; H, 5.05; N, 5.8. $C_{24}H_{24}N_2S_2O_5$ requires C, 59.55; H, 5.0; N, 5.8%); $\nu_{max.}$ (KBr) 1 600 (C=N); τ 2.1 (2 H, d, aromatic), 2.4—2.9 (10 H, m, aromatic), 6.4 (2 H, t, 2-H), 7.56 (3 H, s, CH_3), 7.6 (3 H, s, CH_3), 7.7 (2 H, t, 3-H), and 8.4 (2 H, m. 4-H).

1-*Acetyl*-1,2,3,4-*tetrahydro*-4-*hydroxyimino*-1-*benzazepin*-5-*one* (3; R^1 = Ac, R^2 = R^3 = NOH).—A solution of the *N*-acetyl ketone (3; R^1 = Ac, R^2 = R^3 = H) (0.8 g, 3.95 mmol) [2] in methanol (60 ml) was cooled to between 0 and −20 °C and dry hydrogen chloride gas was passed through the solution for 2 h. Isopentyl nitrite (0.52 g, 4.4 mmol) was added and the solution stirred for 4 h at between 0 and −20 °C. After a further 4 h at room temperature, the solvent was removed and the crude product (0.69 g, 75%) was recrystallised from ethanol to give white *crystals*, m.p. 189 °C (Found: C, 61.7; H, 5.2; N, 11.45%; *M*, 232.084 5. $C_{12}H_{12}N_2O_3$ requires C, 62.1; H, 5.2; N, 11.1%; *M*, 232.084 8); $\nu_{max.}$ (KCl) 3 300 (OH), 1 680 (CH_3CO), and 1 675 cm^{-1} (ArC=O); τ(C_5D_5N) −4.9 (1 H, br, OH exchangeable), 2.05—2.2 (1 H, m, aromatic + 6-H), 2.5—3.0 (3 H, m, aromatic), 5.9 (2 H, br, 2-H), 7.0 (2 H, br, 3-H), and 8.3 (3 H, s, CH_3).

1-*Acetyl*-4-*amino*-1,2,3,4-*tetrahydro*-1-*benzazepin*-5-*one* (3; R^1 = Ac, R^2 = NH_2, R^3 = H) *Hydrochloride*.—The foregoing hydroxyimino-ketone (1.3 g) in ethanolic hydrogen chloride (50 ml) containing Adams catalyst (PtO_2; 0.15 g) was hydrogenated at 50 lb in^{-2} until absorption ceased. Filtration, and evaporation *in vacuo* gave a brown oil, which crystallised from ethanol to afford the *product*. Further recrystallisation from ethanol gave a cream solid, m.p. 191 °C (35%) (Found: C, 56.1; H, 6.0; N, 10.6%; *M*, 217.098 1. $C_{12}H_{14}ClN_2O_2$ requires C, 56.5; H, 5.95; N, 11.0%. $C_{12}H_{13}N_2O_2$ requires *M*, 217.097 7); $\nu_{max.}$ (KBr) 3 400, 2 800 (NH), and 1 685 cm^{-1} (C=O), τ(D_2O) 2.0—2.7 (4 H, m, aromatic), 6.4 (2 H, br, 2-H), 7.0—7.6 (3 H, br, H-3 and -4), and 7.95 (3 H, s, CH_3).

Reaction of 1,2,3,4-*Tetrahydro*-4-*hydroxyimino*-1-*tosyl*-1-*benzazepin*-5-*one* (3; R^1 = tosyl, R^2R^3 = NOH) *with Hydroxylamine Hydrochloride*.—The hydroxyimino-ketone (0.69 g, 2 mmol) and hydroxylamine hydrochloride (0.17 g, 3 mmol) in pyridine (8 ml) and methanol (20 ml) were refluxed for 24 h. Evaporation *in vacuo* gave a gum, which was taken up in the minimum volume of hot ethanol. Cooling afforded a solid (0.145 g, 20%) which was recrystallised from ethanol to give 2,3,4,5-*tetrahydro*-4,5-*bishydroxyimino*-1-*tosyl*-1H-1-*benzazepine* as prisms, m.p. 200 °C (Found: C, 56.8; H, 4.9; N, 11.3%; *M*, 359.093 9. $C_{17}H_{17}N_3O_4S$ requires C, 56.85; H, 4.75; H, 11.7%; *M*, 359.094 0); $\nu_{max.}$ (KBr) 3 350 (OH) and 1 630 cm^{-1} (CN); τ(C_5D_5N) −3.8 (2 H, br, OH exchangeable), 2.3—3.1 (8 H, m, aromatic), 5.95 (2 H, t, 2-H), 7.05 (2 H, t, 3-H), and 8.0 (3 H, s, CH_3).

4-(2-*Aminoanilinomethylene*)-1,2,3,4-*tetrahydro*-1-*tosyl*-1-*benzazepin*-5-*one* (16; R = NH_2).—A hot (*ca.* 70 °C) solution of *o*-phenylenediamine (0.20 g, 2 mmol) in xylene (11 ml) was mixed with a hot solution of the *N*-tosylhydroxymethylene ketone (3; R^1 = tosyl, R^2R^3 = CHOH) (0.69 g, 2 mmol) in xylene (8 ml) and left to cool. Filtration gave the *product* as bright yellow crystals. Recrystallisation from benzene–ether gave a yellow powder (80%), m.p. 200 °C (Found: C, 67.1; H, 5.15; N, 9.75%;

M, 433.145 2. $C_{24}H_{23}N_3O_3S$ requires C, 66.9; H, 4.85; N, 9.75%; *M*, 433.146 0); $\nu_{max.}$ (KBr) 3 405, 3 315 (NH), and 1 640 cm^{-1} (C=O); τ −1.35 (1 H, d, NH exchangeable), 2.5—3.0 (7 H, m, aromatic and olefinic), 3.0—3.45 (6 H, m, aromatic), 6.1 (2 H, t, 2-H), 6.75 (2 H, br, NH_2 exchangeable), 7.75 (2 H, t, 3-H), and 8.05 (3 H, s, CH_3).

4-(*Anilinomethylene*)-1,2,3,4-*tetrahydro*-1-*tosyl*-1-*benzazepin*-5-*one* (16; R = H).—A hot solution of the *N*-tosylhydroxymethylene ketone (3; R^1 = tosyl, R^2R^3 = CHOH) (0.34 g, 1 mmol) in benzene (3 ml) was added to a solution of aniline (0.10 g, 1 mmol) in benzene (1 ml). The solvent volume was reduced *in vacuo* by 50%, and the solution was left overnight at room temperature. This produced the *product* (0.34 g, 85%) as large yellow prisms which were recrystallised from toluene; m.p. 196 °C (Found: C, 68.8; H, 5.45; N, 6.6. $C_{24}H_{22}N_2O_3S$ requires C, 68.9; H, 5.3; N, 6.7%); $\nu_{max.}$ (KBr) 3 370 (NH) and 1 640 cm^{-1} (C=O); τ −1.5 (1 H, d, NH exchangeable), 2.45—3.15 (14 H, m, aromatic and olefinic), 6.1 (2 H, t, 2-H), 7.75 (2 H, t, 3-H), and 7.95 (3 H, s, CH_3).

4-(2-*Aminoethylaminomethylene*)-1,2,3,4-*tetrahydro*-1-*tosyl*-1-*benzazepin*-5-*one*.—Ethylenediamine (0.3 g) was added to a warm solution of the *N*-tosylhydroxymethylene ketone (3; R^1 = tosyl, R^2R^3 = CHOH) (0.25 g) to cause an exothermic reaction. Evaporation left a red oil, which crystallised from ethanol to give the crude *product* (0.098 g, 29%). A further recrystallisation from ethanol afforded pale brown *crystals*, m.p. 150 °C (Found: C, 62.6; H, 5.5; N, 10.65%; *M*, 385.146 8. $C_{20}H_{23}N_3O_3S$ requires C, 62.4; H, 5.5; N, 10.9%; *M*, 385.146 0); $\nu_{max.}$ (KBr) 3 360, 3 280 (NH), and 1 640 cm^{-1} (chelated C=O), τ 2.6—3.1 (8 H, m, aromatic), 3.55 (1 H, d, olefinic), 6.25 (2 H, t, 2-H), 6.85 (4 H, m, $CH_2CH_2NH_2$), 7.7 (3 H, s, CH_3), and 7.95 (2 H, t, 3-H).

6,7-*Dihydro*-5-*tosyl*-5H-*quino*[3,2-d][1]*benzazepine*-8-*carboxylic Acid* (13).—Isatin (0.605 g, 4 mmol) was added to a refluxing solution of the tosyl ketone (3; R^1 = tosyl, R^2 = R^3 = H) (1.38 g, 4 mmol) and potassium hydroxide (7.17 g) in water (12 ml) and ethanol (25 ml). After 4.5 h, the mixture was poured into 10% acetic acid (250 ml), and the resultant cream precipitate filtered off and dried to give the *product* (1.91 g, 88%) as a white solid. This formed crystals, m.p. >320 °C (from ethanol) (Found: C, 66.2; H, 4.65; N, 5.9%; *M*, 444.112 3. $C_{25}H_{20}N_2O_4S$ requires C, 67.5; H, 4.6; N, 5.8%; *M*, 444.113 8); $\nu_{max.}$ (KBr) 3 400 (OH) and 1 700 cm^{-1} (C=O), τ(C_5D_5N) −1.4 (1 H, br, OH exchangeable), 1.6—2.7 (10 H, m, aromatic), 3.4 (2 H, d, aromatic), 5.4 (2 H, br), 7.0 (2 H, br, 6-H), and 8.35 (3 H, s, CH_3).

1,2,3,4-*Tetrahydro*-1-*tosyl*-1-*benzazepin*-5-*one* (3; R^1 = tosyl, R^2 = R^3 = H) *Semicarbazone*.—The tosyl ketone (0.63 g), semicarbazide hydrochloride (0.27 g), and sodium acetate (0.27 g) in water (2 ml) were refluxed in ethanol (20 ml) for 3 h. Cooling gave a solid, and recrystallisation from ethanol afforded the *product*, m.p. 234 °C (70%) (Found: C, 57.95; H, 5.55; N, 14.6. $C_{18}H_{20}N_4O_3S$ requires C, 58.2; H, 5.4; N, 15.0%); $\nu_{max.}$ (KBr) 3 450, 3 210 (NH), and 1 700 cm^{-1} (C=O), τ[$(CD_3)_2SO$] 1.05 (1 H, s, NH exchangeable), 2.5—2.85 (8 H, m, aromatic), 3.7 (2 H, s, NH_2 exchangeable), 6.35 (2 H, t, 2-H), 6.7 (3 H, s, CH_3), 7.9 (2 H, m, 3-H), and 8.4 (2 H, t, 4-H).

5,6-*Dihydro*-6-*tosyl*-4H-*thiadiazolo*[5,4-d][1]*benzazepine* (14).—The foregoing semicarbazone (0.35 g) was added in portions over 40 min to stirred thionyl chloride [36] (2 ml) at 0 °C. The solution became pink and eventually solidified. More thionyl chloride (0.5 ml) was added and the mixture was stirred for a further 2 h at 0 °C, and overnight at room temperature. Chloroform was added, followed by a cooled concentrated solution of sodium carbonate, and the chloroform layer was separated. This was dried, and evaporated *in vacuo* to give a solid, which was recrystallised from ethanol to give the *product* (0.19 g, 57%) as cubes, m.p. 120—122 °C (Found: C, 56.9; H, 4.35; N, 12.05%; *M*, 357.058 6. $C_{17}H_{15}N_3O_2S$ requires C, 57.2; H, 4.25; N, 11.75%; *M*, 357.060 6); $\nu_{max.}$ (KBr) 1 595 cm^{-1} (C=C); τ 1.75 (1 H, m, aromatic), 2.45—3.0 (5 H, m, aromatic), 3.15 (2 H, d, aromatic), 6.05 (2 H, t, 2-H), 6.65 (2 H, t, 3-H), and 7.85 (3 H, s, CH_3).

2,3-*Dihydro*-1-*tosyl*-1-*benzazepine*-4,5-*dione* 4-*Phenylhydrazone* (3; R^1 = tosyl, R^2R^3 = PhNHN=).—A solution of sodium acetate (2.2 g) in water (7.5 ml) was added to a stirred solution of the *N*-tosylhydroxymethylene ketone (3; R^1 = tosyl, R^2R^3 = CHOH) (3.43 g) in methanol (50 ml) and benzene (15 ml) at 0 °C. To this was then added a solution of benzenediazonium chloride [from aniline (0.93 g)], dropwise, over 20 min; this immediately caused precipitation of an orange solid. The suspension was stirred for 20 min, and the solid filtered off and recrystallised from ethanol give the *product* (3.155 g, 75%), m.p. 189 °C (Found: C, 66.25; H, 5.0; N, 10.35%; *M*, 419.128 5. $C_{23}H_{21}N_3O_3S$ requires C, 65.95; H, 5.05; N, 10.05%; *M*, 419.130 3); $\nu_{max.}$ (KCl) 3 270 (NH) and 1 665 cm^{-1} (C=O); τ −3.35 (1 H, s, NH, exchangeable), 2.65—3.3 (13 H, m, aromatic), 6.05 (2 H, t, 2-H), 7.75 (2 H, t, 3-H), and 8.0 (3 H, s, CH_3).

5,12-*Dihydro*-11-*tosylindolo*[3,2-c][1]*benzazepin*-6(11H)-*one* (15).—The foregoing phenylhydrazone (0.25 g) was heated (100—110 °C) in glacial acetic acid (2 ml) and concentrated hydrochloric acid (0.3 ml) overnight. The purple acid solution was poured onto crushed ice and extracted with chloroform. The extract was dried, and evaporated *in vacuo* to give a brown oil (0.23 g), which crystallised from ethanol as buff crystals. Further recrystallisation from ethanol afforded the *product* as cubes, m.p. 228—230 °C (Found: C, 68.65; H, 4.7; N, 6.95%; *M*, 402.100 3. $C_{23}H_{18}N_2O_3S$ requires C, 68.7; H, 4.5; N, 6.95%; *M*, 402.103 8); $\nu_{max.}$ (KBr) 3 310 (NH) and 1 615 cm^{-1} (C=O); τ 1.1 (1 H, s, NH exchangeable), 2.05 (1 H, m, aromatic), 2.35—2.9 (9 H, m, aromatic and 6-H), 3.3—3.4 (4 H, q, aromatic), and 7.9 (3 H, s, CH_3).

7,9-*Dibromo*-1,4,5,6-*tetrahydroimidazo*[4,5-d][1]*benzazepine* (12).—4,4,7,9-Tetrabromo-1,2,3,4-tetrahydro-1-benzazepin-5-one [7,9-dibromo-(3; R^1 = H, R^2 = R^3 = Br)] (3.2 g), ammonia (specific gravity 0.88; 25 ml), ethanol (150 ml), and aqueous formaldehyde (40%; 10 ml) were refluxed for 24 h. After removal of solvent, chromatography on silica with elution by 5% ethanol–$CHCl_3$ gave the *product* (500 mg), m.p. 230—232 °C (decomp.) (Found: C, 38.75; H, 2.75; N, 11.95%; *M*, 344.912 2/342.912 6/340.912 5. $C_{11}H_9Br_2N_3$ requires C, 38.5; H, 2.65; N, 12.25%; *M*, 344.912 5/342.914 5/340.916 4).

We thank Bristol Laboratories (Syracuse, New York) for a studentship.

[7/1594 *Received*, 7th *September*, 1977]