Fluorocarbon Derivatives of Nitrogen. Part 17.[1] Oxidation of Unsymmetrical Polyfluorinated Diareno-1,2-diazepines. *X*-Ray Molecular Structures of 1,3,4-Trifluoro-7,9-dimethyl-11*H*-pyrido[4,3-*c*][1,2]benzodiazepine 5-Oxide and 5,6-Dioxide

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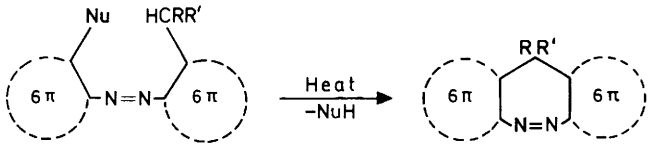
1,3,4-Trifluoro-7,9-dimethyl-11*H*-pyrido[4,3-*c*][1,2]benzodiazepine 5- and 6-oxide (**7**) and (**6**) and 5,6-dioxide (**8**) have been synthesized *via* oxidation of the parent diazepine (**1**) with 30% H_2O_2–AcOH and/or 85% H_2O_2–$(CF_3CO)_2O$–CH_2Cl_2. Use of chromic anhydride as the oxidant in boiling glacial acetic acid gave 1,3,4-trifluoro-7,9-dimethylpyrido[4,3-*c*][1,2]benzodiazepin-11-one, 1,3,4-trifluoro-7-methyl-11*H*-pyrido[4,3-*c*][1,2]benzodiazepine-9-carboxylic acid, and 1,3,4-trifluoro-7-methyl-11-oxopyrido[4,3-*c*][1,2]benzodiazepine-9-carboxylic acid. 1,3,4-Trifluoro-7,9-dimethyl-2-trifluoromethyl-11*H*-dibenzo[*c*,*f*][1,2]diazepine 5- and 6-oxide, 5,6-dioxide, and 1,3,4-trifluoro-7,9-dimethyl-2-(trifluoromethyl)dibenzo[*c*,*f*][1,2]diazepin-11-one plus 1,3,4-trifluoro-7-methyl-2-trifluoromethyl-11*H*-dibenzo[*c*,*f*][1,2]diazepine-9-carboxylic acid have been prepared similarly starting from 1,3,4-trifluoro-7,9-dimethyl-2-trifluoromethyl-11*H*-dibenzo[*c*,*f*][1,2]diazepine (**2**). Oxidation (30% H_2O_2–AcOH) of *trans*-tetrafluoro-4-(2,4,6-trimethylphenylazo)pyridine gave *trans*-2,3,5,6-tetrafluoro-4-(2,4,6-trimethylphenyl-*ONN*-azoxy)pyridine almost quantitatively. *X*-Ray crystallographic data for 1,3,4-trifluoro-7,9-dimethyl-11*H*-pyrido[4,3-*c*][1,2]benzodiazepine 5-oxide (**7**) and the corresponding 5,6-dioxide (**8**) are presented, as are details of n.m.r. analyses (^{13}C, ^1H, ^{19}F, and ^{15}N) carried out on the parent diazepines (**1**) and (**2**) and their various oxidation products.

Alty's serendipitous discovery[2a,b] of the ring-closure broadly defined in the Scheme has provided access to a range of unsymmetrical (in terms of substitution character or annulating systems) diareno-1,2-diazepines.[2a–f] Chemical, photochemical,

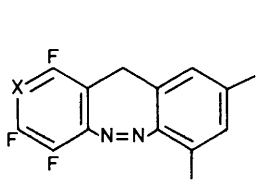


Nu = nucleofugal substituent (*e.g.* F, Br, NO_2) attached to a benzene,[2b,c] azine,[2b,c,e] diazine,[2a,b] or thiophene[2d] ring.
R,R' = H or alkyl

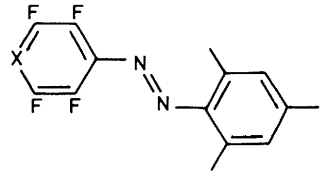
Scheme.

and thermochemical transformations of some of these tricyclic compounds are now being studied in an effort to enhance the value of this entry to the 1,2-diazepine domain. The present report concerns the oxidation of 1,3,4-trifluoro-7,9-dimethyl-11*H*-pyrido[4,3-*c*][1,2]benzodiazepine (**1**) and 1,3,4-trifluoro-7,9-dimethyl-2-trifluoromethyl-11*H*-dibenzo[*c*,*f*][1,2]diazepine (**2**), each of which can readily be procured in high yield by boiling a solution of the appropriate azo compound, (**3**) or (**4**), in mesitylene or *o*-dichlorobenzene.

Peracid Oxidations.—Having found[3] that peroxytrifluoroacetic acid [85% H_2O_2–$(CF_3CO)_2O$ in CH_2Cl_2] rapidly converts *trans*-tetrafluoro-4-(2,4,6-trimethylphenylazo)pyridine (**3**) into the corresponding *trans*-*ONN*-azoxy compound (**5**) in good yield (75%),† the same reagent was used initially[4] to



(**1**) X = N
(**2**) X = CCF_3

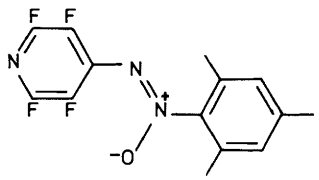


(**3**) X = N
(**4**) X = CCF_3

oxidise the analogous, and necessarily *cis*, diazepinic azo compound (**1**). This gave not only the precisely comparable monoxide, *i.e.* (**6**) rather than (**7**), in 47% yield, but also a dioxide (30%). The latter was shown by *X*-ray analysis to be the 5,6-dioxide (**8**) rather than the 2,5- or 2,6-dioxide [(**9**) or (**10**) respectively]. Similar oxidation of the trifluoromethyl substituted diazepine (**2**) provided products (**11**) and (**12**), corresponding to (**6**) and (**8**), in 26 and 25% yield respectively.

Experiments were next conducted with 30% hydrogen peroxide in glacial acetic acid, a milder reagent than peroxytrifluoroacetic acid and one which was used by Catala and Popp[5] to convert 3,8-difluoro-11*H*-dibenzo[*c*,*f*][1,2]diazepine (**13**; Z = F) to its mono-*N*-oxide in 82% yield. First, it was established that the reagent smoothly and efficiently (95% yield) effects the transformation (**3**) ⟶ (**5**) at elevated temperatures. Similar but incomplete (90%) conversion of the diazepinic analogue (**1**) of azo compound (**3**) gave only monoxide material (71% yield) which was found to be a *ca.* 1:2 mixture of the 5- and 6-oxides [(**7**) and (**6**) respectively]. With the trifluoromethylated diazepine (**2**) as substrate, the preference for formation of the 6-oxide (**11**) was less marked, the ratio of (**11**) to (**14**) being *ca.* 4.5:5; in this case the total yield was almost quantitative.

† Unless stated otherwise, yields refer to pure compounds.



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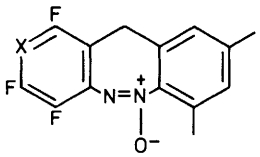
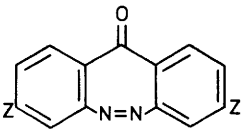


(6) X = N
(11) X = CCF_3



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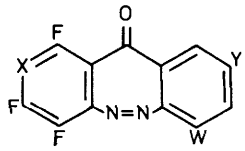
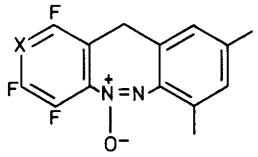
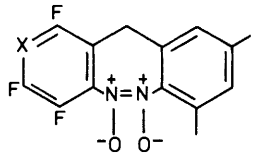


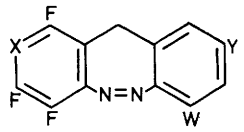
(17) X = N, W = Y = Me
(18) X = N, W = Me, Y = CO_2H
(20) X = N, W = CO_2H, Y = Me
(23) X = CCF_3, W = Y = Me



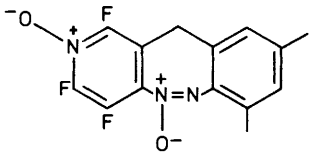
(7) X = N
(14) X = CCF_3



(8) X = N
(12) X = CCF_3



(19) X = N, W = Me, Y = CO_2H
(21) X = N, W = CO_2H, Y = Me
(22) X = CCF_3, W = Me, Y = CO_2H
(24) X = N, W = Me, Y = CH_2OAc



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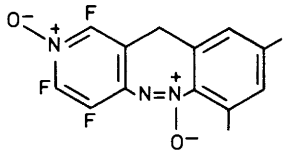

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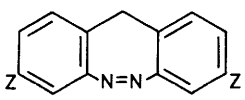

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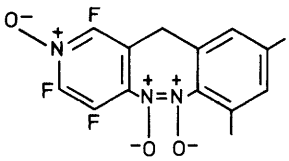

(15)

The structure of the 5-oxide (**7**) derived from the pyridodiazepine (**1**) was established by *X*-ray crystallography (see below); this enabled n.m.r. data to be rationalised (see below) and hence each individual monoxide derived from the trifluoromethylated dibenzodiazepine (**2**) to be assigned either structure (**11**) or (**14**) with confidence.

Attempts to prepare the trioxide (**15**) from a *ca.* 2:1 mixture of monoxides (**6**) and (**7**) were unsuccessful; thus 30% hydrogen peroxide in glacial acetic acid under reflux caused no change (by t.l.c. analysis), and 85% hydrogen peroxide–trifluoroacetic anhydride in dichloromethane converted the starting material into a complex mixture from which only the 6-oxide [(**6**); 9%] and the 5,6-dioxide [(**8**); 16%] could be isolated by dry-column flash chromatography.

Oxidation with Chromic Anhydride.—Catala and Popp[5] showed that symmetrical 3,8-dihalogeno-11*H*-dibenzo[*c*,*f*]-[1,2]diazepines (**13**; Z = F, Cl, Br, or I) can be converted into the corresponding dibenzodiazepin-11-ones (**16**) with chromic anhydride in boiling glacial acetic acid. Application of their methodology to compound (**1**) did give the desired diazepinone (**17**), but the yield was low (19%) owing to the formation of two diazepinic monocarboxylic acids. From the n.m.r. data (see below), these acids have been assigned the structures (**18**) (18% yield) and (**19**) (30%) rather than (**20**) and (**21**). Side-chain oxidation also occurred when the dibenzodiazepine (**2**) was heated with chromic anhydride in glacial acetic acid, giving a monocarboxylic acid (47%), which was judged from n.m.r. data to possess structure (**22**), and the expected diazepinone (**23**) (38%).

Crystallographic Analyses.—The *X*-ray molecular structures of the diazepine oxides (**7**) and (**8**) were determined as described in the Experimental section. The geometries of the respective molecules are displayed in Figures 1 and 2, and atomic coordinates and selected structural parameters are listed in Tables 1 and 2 respectively.

The monoxide (**7**) shares a common crystal packing system with the dioxide (**8**) comprising a tetrameric spiral cluster of molecules. The four members of each group are disposed so that π-interactions between the hydrocarbon ring of one molecule and the fluoropyridinic ring of another component are maximized. Within their e.s.d.'s, the interplanar angles between the annulating moieties in both oxides are identical [(**7**), 104.4(7)°; (**8**), 103.5(8)°; *cf.* (**1**),[2b] 117° and (**24**),[2f] 113.6(6)°].

Oxidation of the azo linkage in (**1**) also caused progressive lengthening of the N=N bond {(**1**),[2b] 1.26 [*cf.* (**24**),[2f] 1.263(4)]; (**7**), 1.274(2); (**8**), 1.340(3) Å} and increasing steric congestion [(**7**) O(5)···F(4) 2.765(4); (**8**), O(5)···F(4) 2.738(4) and O(6)···C(12) 2.907(6) Å]. N.m.r. analyses (see below) indicate that the non-bonding interactions are sufficient in the monoxide (**7**) to lock the conformation of the diazepine ring at ambient temperature; the extra lengthening of the N=N bond in the dioxide (**8**) allows inversion of the ring to occur, as in (**1**), despite the further increase in steric congestion.

N.m.r. Analyses.—The ^1H and ^{19}F n.m.r. spectral data for compounds, (**1**), (**2**), (**6**)—(**8**), (**11**), (**12**), (**14**), (**17**)—(**19**), (**22**), and (**23**) are summarised in Table 3. The two methyl groups produce a pair of singlets at δ = 2.3—2.8, coinciding in the oxides (**6**) and (**8**), but assignment of the individual bands specifically to the 7- or 9-methyl groups was not possible.

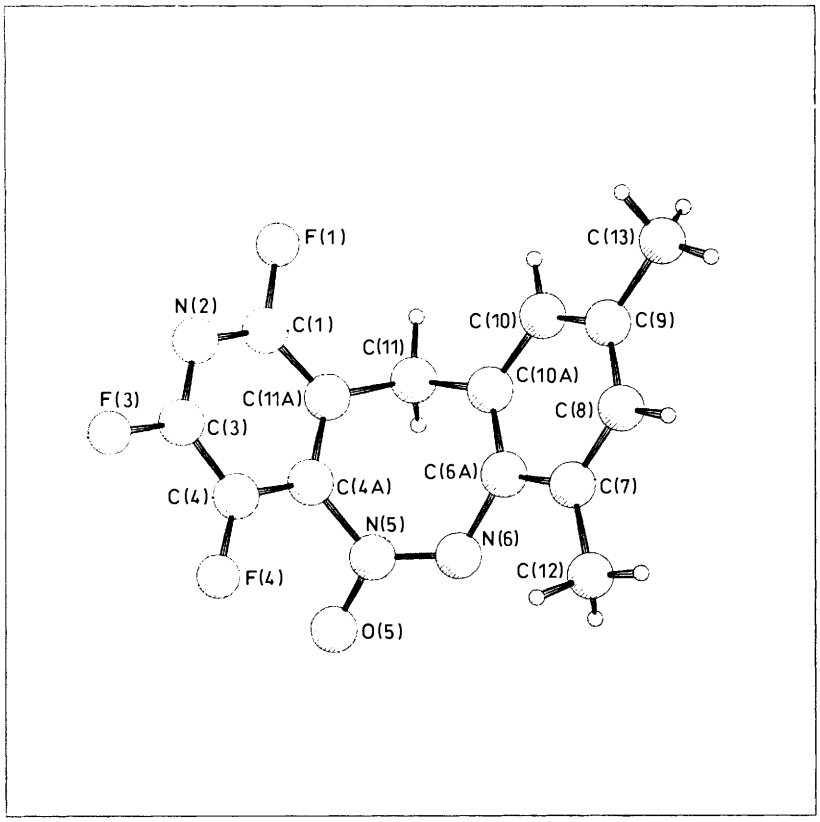

Figure 1. Molecule (**7**), including atomic labelling scheme

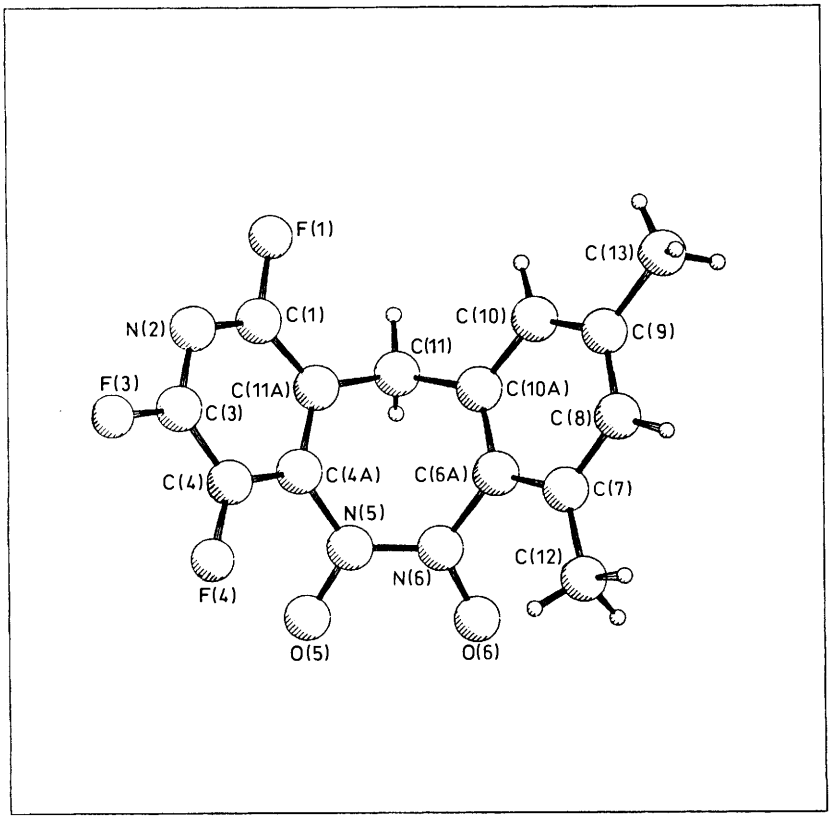

Figure 2. Molecule (**8**), including atomic labelling scheme

Table 1. Final atomic co-ordinates ($\times 10^4$) with their e.s.d.'s in parentheses

	x/a	*y/b*	*z/c*
Compound (**7**)			
C(1)	888(1)	1 766(1)	2 177(2)
N(2)	1 171(1)	2 317(1)	3 032(2)
C(3)	1 403(1)	2 134(1)	4 447(3)
C(4)	1 378(1)	1 408(1)	5 056(2)
C(4A)	1 087(1)	839(1)	4 100(2)
N(5)	1 072(1)	54(1)	4 671(2)
N(6)	1 374(1)	−514(1)	3 959(2)
C(6A)	1 685(1)	−443(1)	2 420(2)
C(7)	2 368(1)	−841(1)	2 154(3)
C(8)	2 680(1)	−815(1)	652(3)
C(9)	2 329(1)	−442(1)	−598(3)
C(10)	1 635(1)	−83(1)	−314(3)
C(10A)	1 309(1)	−71(1)	1 170(2)
C(11)	589(1)	376(1)	1 512(3)
C(11A)	821(1)	1 007(1)	2 599(2)
C(12)	2 764(2)	−1 266(2)	3 466(4)
C(13)	2 686(2)	−424(2)	−2 216(4)
F(1)	657(1)	1 977(1)	723(2)
F(3)	1 690(1)	2 699(1)	5 323(2)
F(4)	1 650(1)	1 268(1)	6 496(1)
O(5)	770(1)	−26(1)	6 010(2)
Compound (**8**)			
C(1)	874(1)	1 936(1)	7 189(3)
N(2)	1 194(1)	2 465(1)	7 984(2)
C(3)	1 425(1)	2 292(1)	9 402(3)
C(4)	1 359(1)	1 600(1)	10 054(3)
C(4A)	1 023(1)	1 056(1)	9 170(2)
N(5)	920(1)	344(1)	9 864(2)
N(6)	1 064(1)	−289(1)	9 100(2)
C(6A)	1 411(1)	−307(1)	7 548(3)
C(7)	2 042(1)	−737(1)	7 355(3)
C(8)	2 348(2)	−752(2)	5 852(3)
C(9)	2 037(2)	−378(2)	4 590(3)
C(10)	1 409(1)	40(1)	4 842(3)
C(10A)	1 083(1)	87(1)	6 315(2)
C(11)	455(1)	607(1)	6 646(3)
C(11A)	755(1)	1 215(1)	7 660(2)
C(12)	2 420(2)	−1 151(2)	8 674(4)
C(13)	2 392(3)	−409(4)	2 976(4)
F(1)	643(1)	2 134(1)	5 737(2)
F(3)	1 757(1)	2 829(1)	10 213(2)
F(4)	1 633(1)	1 470(1)	11 488(1)
O(5)	660(1)	311(1)	11 244(2)
O(6)	926(1)	−879(1)	9 820(2)

Similarly, the aromatic hydrogens give rise to slightly broadened singlets, but again assignment specifically to 8-H or 10-H was not possible. Oxidation of the 5- and/or 6-nitrogens has little effect on the positions of either the methyl or aryl hydrogen signals, but oxidation of the methylene group or of a methyl (shown below to be that at C-9) deshields the aryl hydrogens by 0.5—1.5 p.p.m.

The methylene group appears as a singlet at room temperature in the ^{1}H n.m.r. spectra of the parent compounds (**1**) and (**2**), the signal for the pyrido compound (**1**) appearing as an AB quartet (*J* 15 Hz) at −90 °C in [$^2H_6$]acetone with coalescence occurring at −43 °C.[2a] Evidently the puckered seven-membered rings in the four monoxides (**6**), (**7**), (**11**), and (**14**) are more rigid, since the methylene group signal appears as an AB pattern [^2J(HH) *ca.* 15 Hz] at room temperature. For compounds (**11**) and (**14**) the resonance at higher δ is also coupled weakly (*ca.* 2 Hz) to the fluorine at C-1. The spectrum of the 5,6-dioxide (**12**) also shows an AB pattern at room temperature, but the pyridine analogue (**8**) is more mobile, and shows only a singlet.

The ^{19}F resonances of the compounds were readily assigned by consideration of the chemical shifts and characteristic coupling constants. With the advantage of the *X*-ray structural determination it can be seen that oxidation of N-5 in both (**1**) and (**2**) causes more pronounced deshielding of F-4 and F-3 than does oxidation of N-6. Similarly, oxidation of 11-CH_2 results in deshielding of the adjacent F-1 and *para* F-3 by 5—10 p.p.m., while oxidation of the remote 9-Me group has but little effect on the ^{19}F absorption positions.

The ^{13}C n.m.r. spectra for several of the compounds are summarised in Table 4. Solubility of the compounds was such that although signal strength for the 'hydrocarbon part' of the molecules was adequate after overnight accumulation at 20 MHz with broad-band ^{1}H decoupling, the 'fluorocarbon part' required either broad-band ^{19}F decoupling or extended accumulation time (with ^{1}H decoupling) at 75 MHz. Assignment of the signals to the carbons of the pyridine nuclei of compounds (**1**), (**6**), (**7**), and (**18**) followed readily from comparison with shifts and coupling constants in known polyfluoropyridine derivatives,[6,7] and similar reasoning allowed the assignment of the signals of the trifluoro(trifluoromethyl)benzo entities of compounds (**2**), (**11**), (**12**), (**14**), (**22**), and (**23**). The signal for the methylene group at C-11 was well separated from those of the two methyls at C-7 and C-9 (one appeared consistently in the range δ 17.2—18.7 and the other within δ 20.7—21.6), and the absorptions of the hydrogen-carrying ring carbons (C-8 and C-10) were readily distinguished from those of the quaternary carbons (C-6a, C-7, C-9, and C-10a).

The position of the carboxy group and of the remaining methyl in the monocarboxylic acid obtained from diazepine (**2**) were established by use of a fully coupled ^{13}C spectrum. The carboxy resonance showed a 4 Hz triplet splitting (3-bond coupling to 8-H and 10-H) and the methyl signal at δ 17.2 showed a 3-bond doublet (coupling to 8-H), consistent only[8] with oxidation of the 9-methyl to give derivative (**22**). The methyl signal at *ca.* δ 18 in the other compounds is thus assigned to the 7-methyl, and that at *ca.* δ 21 to the 9-methyl. The assignment to C-6a of the benzene ring carbon resonance at highest frequency, initially made on the grounds of expected chemical shifts, was confirmed by the observation of a 2.8 Hz quartet (3-bond coupling to the 7-methyl) in the fully coupled spectrum of (**22**). The quaternary carbon signal at δ 137.0 was firmly assigned to C-7, since it also showed a quartet (*J* 4 Hz), and that at 133.1 to C-9, since it showed no coupling. Similarly, the strong band at δ 131.7, which in addition to one-bond coupling showed a 6 Hz doublet (to the hydrogen at C-10) of 4 Hz quartets (to the methyl at C-7), could be assigned to C-8, leaving the other strong signal in the decoupled spectrum (at δ 127.0) for C-10.

The ^{15}N n.m.r. spectra were measured to help determine the position of oxidation in the monoxides. Because of the low solubility no spectra could be obtained for the dioxides, and the pyridine nitrogen peak was seldom observed (in overnight spectra) because of the triplet splitting.[9,10] The ^{15}N results and tentative assignments are given in Table 4. The shifts for the trifluoromethylated compound (**2**) (δ 107.5 and δ 164.6) are in the region expected from reported shifts for $C_6F_5N{=}NC_6F_5$ (δ 147.7),[11] PhN=NPh (*trans* δ 129, *cis* δ 146.5)[12] and related diazenes.[13] However, higher shielding was observed for the pyridino analogue (**1**), with signals at δ 33.9 (doublet, *J* 2.2 Hz) and δ 98.7. This was in contrast to the chemical shifts of δ 113.7 and δ 195.9 (triplet, *J* 6.5 Hz, for the nitrogen β to the perfluoroaryl group) observed for the diazene (**3**), and δ 162.2 for (C_5F_4N-4)N=N(C_5F_4N-4).[11] Turning to the diazepine monoxides, the shielding in the trifluoromethyl derivatives (**11**) and (**14**) is comparable to that in the diazene monoxides

Table 2. Selected bond lengths (Å) and angles (°) with e.s.d.'s in parentheses

Compound (**7**)			
C(1)–N(2)	1.302(3)	C(1)–C(11A)	1.378(3)
C(1)–F(1)	1.347(2)	N(2)–C(3)	1.304(3)
C(3)–C(4)	1.371(3)	C(3)–F(3)	1.332(3)
C(4)–C(4A)	1.378(3)	C(4)–F(4)	1.330(2)
C(4A)–N(5)	1.455(3)	C(4A)–C(11A)	1.384(3)
N(5)–N(6)	1.274(2)	N(5)–O(5)	1.258(2)
N(6)–C(6A)	1.417(3)	C(6A)–C(7)	1.400(3)
C(6A)–C(10A)	1.404(3)	C(7)–C(8)	1.384(3)
C(7)–C(12)	1.505(4)	C(8)–C(9)	1.385(3)
C(9)–C(10)	1.388(3)	C(9)–C(13)	1.504(3)
C(10)–C(10A)	1.378(3)	C(10A)–C(11)	1.508(3)
C(11)–C(11A)	1.492(3)		
C(11A)–C(1)–N(2)	126.9(2)	F(1)–C(1)–N(2)	114.8(2)
F(1)–C(1)–C(11A)	118.3(2)	C(3)–N(2)–C(1)	116.6(2)
C(4)–C(3)–N(2)	124.2(2)	F(3)–C(3)–N(2)	116.6(2)
F(3)–C(3)–C(4)	119.2(2)	C(4A)–C(4)–C(3)	117.3(2)
F(4)–C(4)–C(3)	120.2(2)	F(4)–C(4)–C(4A)	122.5(2)
N(5)–C(4A)–C(4)	119.4(2)	C(11A)–C(4A)–C(4)	120.7(2)
C(11A)–C(4A)–N(5)	119.9(2)	N(6)–N(5)–C(4A)	124.8(2)
O(5)–N(5)–C(4A)	114.3(2)	O(5)–N(5)–N(6)	120.8(2)
C(6A)–N(6)–N(5)	121.7(2)	C(7)–C(6A)–N(6)	115.5(2)
C(10A)–C(6A)–N(6)	123.7(2)	C(10A)–C(6A)–C(7)	120.5(2)
C(8)–C(7)–C(6A)	117.9(2)	C(12)–C(7)–C(6A)	121.3(2)
C(12)–C(7)–C(8)	120.8(2)	C(9)–C(8)–C(7)	122.9(2)
C(10)–C(9)–C(8)	117.9(2)	C(13)–C(9)–C(8)	121.5(2)
C(13)–C(9)–C(10)	120.7(2)	C(10A)–C(10)–C(9)	121.7(2)
C(10)–C(10A)–C(6A)	119.1(2)	C(11)–C(10A)–C(6A)	119.0(2)
C(11)–C(10A)–C(10)	121.8(2)	C(11A)–C(11)–C(10A)	105.9(2)
C(4A)–C(11A)–C(1)	114.3(2)	C(11)–C(11A)–C(1)	125.1(2)
C(11)–C(11A)–C(4A)	120.1(2)		
Compound (**8**)			
C(1)–N(2)	1.304(3)	C(1)–C(11A)	1.377(3)
C(1)–F(1)	1.350(2)	N(2)–C(3)	1.312(3)
C(3)–C(4)	1.371(3)	C(3)–F(3)	1.331(3)
C(4)–C(4A)	1.377(3)	C(4)–F(4)	1.336(3)
C(4A)–N(5)	1.425(3)	C(4A)–C(11A)	1.402(3)
N(5)–N(6)	1.340(3)	N(5)–O(5)	1.264(2)
N(6)–C(6A)	1.460(3)	N(6)–O(6)	1.252(2)
C(6A)–C(7)	1.385(3)	C(6A)–C(10A)	1.398(3)
C(7)–C(8)	1.392(3)	C(7)–C(12)	1.510(4)
C(8)–C(9)	1.385(4)	C(9)–C(10)	1.378(4)
C(9)–C(13)	1.514(4)	C(10)–C(10A)	1.384(3)
C(10A)–C(11)	1.499(3)	C(11)–C(11A)	1.496(3)
C(11A)–C(1)–N(2)	127.6(2)	F(1)–C(1)–N(2)	114.6(2)
F(1)–C(1)–C(11A)	117.8(2)	C(3)–N(2)–C(1)	116.2(2)
C(4)–C(3)–N(2)	124.1(2)	F(3)–C(3)–N(2)	116.4(2)
F(3)–C(3)–C(4)	119.5(2)	C(4A)–C(4)–C(3)	117.9(2)
F(4)–C(4)–C(3)	119.8(2)	F(4)–C(4)–C(4A)	122.3(2)
N(5)–C(4A)–C(4)	118.3(2)	C(11A)–C(4A)–C(4)	120.3(2)
C(11A)–C(4A)–N(5)	121.3(2)	N(6)–N(5)–C(4A)	122.9(2)
O(5)–N(5)–C(4A)	118.3(2)	O(5)–N(5)–N(6)	118.7(2)
C(6A)–N(6)–N(5)	122.7(2)	O(6)–N(6)–N(5)	116.7(2)
O(6)–N(6)–C(6A)	120.5(2)	C(7)–C(6A)–N(6)	118.1(2)
C(10A)–C(6A)–N(6)	118.9(2)	C(10A)–C(6A)–C(7)	122.9(2)
C(8)–C(7)–C(6A)	116.5(2)	C(12)–C(7)–C(6A)	124.1(3)
C(12)–C(7)–C(8)	119.4(3)	C(9)–C(8)–C(7)	122.6(3)
C(10)–C(9)–C(8)	118.6(2)	C(13)–C(9)–C(8)	120.8(3)
C(13)–C(9)–C(10)	120.6(3)	C(10A)–C(10)–C(9)	121.5(2)
C(10)–C(10A)–C(6A)	117.8(2)	C(11)–C(10A)–C(6A)	119.9(2)
C(11)–C(10A)–C(10)	121.9(2)	C(11A)–C(11)–C(10A)	107.1(2)
C(4A)–C(11A)–C(1)	113.9(2)	C(11)–C(11A)–C(1)	125.6(2)
C(11)–C(11A)–C(4A)	120.1(2)		

$C_6F_5N{=}N^+(O^-)C_6F_5$ (δ −52 and −68 respectively),[14] and *trans*- or *cis*- $PhN{=}N^+(O^-)Ph$ (δ −47, −54 and −20, −36 respectively).[15] Higher shielding was observed in the pyrido derivatives (**6**) and (**7**).

The nitrogen shielding in the diazepines is largely determined by the n(N)→π* excitation energies,[16] the n(N) levels being n_+ and n_- combinations of the non-bonding (lone pair) orbitals on the adjacent nitrogens. The n_+–n_- splitting is small in *trans*-

Table 3. ^{1}H and ^{19}F n.m.r. parameters

	Chemical shifts (δ/p.p.m.)							Coupling constants (*J*/Hz)			
Compd.	7,9-CH_3	11-CH_2	8-, 10-H	F-1	F-3	F-4	CF_3	1,3	1,4	3,4	1,CF_3
(**1**)	2.35, 2.58	3.40	6.92, 7.15	−2.4	−12.0	−78.3	—	13.5	28.8	22.0	—
(**6**)	2.36	3.78[a]	6.97, 7.10	−1.7	−10.7	−74.5	—	14.0	26.5	20.7	—
(**7**)	2.30, 2.39	3.78[b]	6.98, 7.80	1.0	−6.0	−69.2	—	13.0	29.5	21.4	—
(**8**)	2.30	3.9	6.9, 7.0	1.3	−5.8	−66.4	—	13.0	28.2	20.9	—
(**17**)	2.50, 2.80	—	7.49, 7.60	8.3	−2.0	−74.2	—	11.8	28.7	21.0	—
(**18**)	2.70	—	8.05, 8.28	6.0	−4.4	−74.0	—	10.2	28.5	23.1	—
(**19**)	2.63	3.54	7.80, 7.98	−1.5	−12.1	−76.5	—	13.9	29.3	23.7	—
(**2**)	2.30, 2.52	3.40	6.86, 7.10	−46.1	−58.8	−70.1	22.0	3.7	16.0	21.1	22.8
(**11**)	2.34, 2.36	3.81[b,c]	6.99, 7.12	−46.0[c]	−58.1	−67.2	22.3	3.0	14.0	20.0	22.4
(**12**)	2.32, 2.37	4.0[b]	7.00, 7.09	−43.5	−53.6	−60.5	29.0	*ca.* 3	14.5	19.5	22.4
(**14**)	2.30, 2.38	3.82[b,d]	6.93, 7.04	−44.1[d]	−54.7	−64.1	22.1	3.0	16.1	20.3	23.7
(**22**)	2.04	3.13	7.32, 7.42	−47.1	−61.6	−73.0	21.0	*ca.* 4	15.0	19.6	22.4
(**23**)	2.44, 2.72	—	7.40, 7.52	−40.7	−49.7	−65.8	21.8	—	16.1	20.3	23.0

[a] AB quartet, J_{AB} 14.7 Hz, with high frequency band split into 2 Hz doublets, but no extra coupling observable in ^{19}F spectrum. [b] AB quartet, J_{AB} 15 Hz. [c] *J*[H(11a)–F(1)] 2 Hz. [d] *J*[H(11a)–F(1)] 2.5 Hz.

Table 4. ^{13}C and ^{15}N Chemical shifts (δ/p.p.m.) for diazepine derivatives

Carbon/Compound	(**1**)	(**6**)	(**7**)	(**18**)	(**2**)	(**11**)	(**12**)	(**14**)	(**22**)	(**23**)
1	149.4	150.1	149.1	151.1	149.1	150.0	149.6	148.9	149.2	150.6
2	—	—	—	—	108.9	107.0	111.2	111.1	108.7	110.9
3	147.2	147.1	147.7	150.9	146.7	146.8	147.4	147.0	147.0	150.0
4	137.5	135.1	136.1	n.o.	142.7	140.3	141.4	141.1	143.1	144.0
4a	146.2	143.1	142.2	145.0	139.2	135.5	137.0	135.5	139.9	137.7
6a	147.2	143.2	135.7[a]	147.5	146.9	143.0[a]	142.5	139.8[a]	150.8	144.6[a]
7	137.8[a]	136.5[a]	137.9[a]	134.0[a]	137.5[a]	136.6[a]	137.2[a]	135.2[a]	137.1	140.7[a]
8	131.3	132.0	131.4	136.7	131.4	132.3	132.5	131.2	131.7	136.9
9	143.2[a]	142.6[a]	140.3[a]	140.9[a]	142.9[a]	142.6[a]	136.9[a]	137.9[a]	133.1	143.7[a]
10	125.5	124.9	126.5	136.4	125.5	124.8	125.5	126.2	127.0	124.4
10a	131.2	133.4	131.4	131.8	131.3	133.6	135.7	131.7	132.8	132.6
11	26.8	27.2	27.8	181.3	26.4	27.0	27.6	27.5	26.0	182.7
11a	114.5	114.4	118.8	n.o.[c]	120.2	120.3	120.7	124.5	120.8	118.9
7-Me	17.9	18.3	18.2	17.9	17.9	18.6	18.6	18.0	17.2	18.7
9-Me	21.0	20.7	20.9	(164.8)[b]	21.1	20.9	21.0	20.8	(165.8)[b]	21.5
2-CF_3	—	—	—	—	121.0	121.0	120.5	120.5	121.6	120.4
Nitrogen[d]										
2	206.6[e]	n.o.[c]	n.o.[c]		—	—		—		
5	33.9[f]	−98.1[a]	−136.9		107.5[g]	−44.3[a]		−63.1		
6	98.7	−86.0[a]	−86.0		164.6	−35.5[a]		−14.9		

[a] These assignments may be interchanged. [b] 9-CO_2H. [c] Not observed. [d] Reference = $MeNO_2$. [e] 51 Hz triplet. [f] 2.2 Hz doublet. [g] 7 Hz doublet.

diazenes, because of the low overlap of the adjacent n(N) orbitals, and larger in *cis*-diazenes, which have better overlap. The *cis*-diazenes thus tend to have red-shifted n(N)→π* bands and lower nitrogen shielding compared to the corresponding *trans*-diazenes, *cf.* δ 129 and 146.5 for *trans*- and *cis*-PhN=NPh respectively. In the diazepines, therefore, the nitrogen shifts are very sensitive to the local geometry, since it determines the overlap and energies not only of the adjacent n(N) orbitals but also of the π-systems.

The tentative assignments in Table 4 are based on the π-fluoro effects on n.m.r. shifts,[17] analogous to those used in photoelectron and electronic spectroscopy to distinguish σ from π orbitals. Perfluorination stabilises the σ framework, which includes the n(N) orbitals, relative to the π manifold, which is destabilised by conjugative effects of the n(F) electrons. The resulting increase in n(N)→π* energies increases the nitrogen shielding, as observed in azabenzenes[9] and aryl azides,[10] and also for Nα in aryldiazonium compounds and *cis*-diazene monoxides (the Nβ shielding increases rather less, or may decrease).[11,14] Further, there are the known effects of *N*-oxidation. In pyridazine (1,2-diazabenzene), mono-oxidation increases the shielding of the *ipso* nitrogen by 75 p.p.m. and that of the adjacent nitrogen by 53.6 p.p.m.,[18] *cf.* the increase in shielding by *ca.* 180 p.p.m. on mono-oxidation of diphenyldiazene.[15]

The ^{15}N n.m.r. spectroscopy does, therefore, distinguish the position of oxidation in the monoxides. With diazepine (**1**) as starting material, it was found that the monoxide eluted first from the chromatography column used to separate them had closely spaced signals, and that eluted second, widely spaced signals. *X*-Ray diffraction results show clearly that the compound with widely separated signals is the 5-oxide (**7**) and the one with the small separation the 6-oxide (**6**), and this agrees with the criteria described above for assignment of the signals. The signals are closely spaced in the 6-oxide because the N-5 shielding is increased by perfluorination of the ring to which it is attached, while the N-6 shielding is increased by *N*-oxidation. In the 5-oxides, both of these influences increase the shielding of N-5 relative to N-6. A similar pattern of early elution and close ^{15}N signals, and late elution and widely spaced signals, was observed for the monoxides obtained from the trifluoromethylated compound (**2**), and these were assigned structures (**11**)

and (**14**) respectively. It is hoped to confirm the detailed assignments and to resolve remaining ambiguities by the use of ^{15}N-enriched compounds in future work.

Experimental

X-*Ray Crystallography*.—(*a*) 1,3,4-*Trifluoro*-7,9-*dimethyl*-11H-*pyrido*[4,3-c][1,2]*benzodiazepine* 5-*oxide* (**7**). (*i*) *Crystal data*. $C_{14}H_{10}F_3N_3O$, M_r 293.25, T = 293 K, tetragonal, a = b = 17.474(4), c = 8.462(2) Å, V = 2 583(1) Å^3 (by least squares refinement on setting angles of 25 reflections, 12.7 < θ < 15.7°), Mo-K_α radiation (λ = 0.710 69 Å, μ = 0.085 mm^{-1}), space group $P4_2/n$ (origin choice 2), Z = 8, D_x = 1.51 Mg m^{-3}, F(000) = 1 200; crystal: yellow, *ca.* 0.3 × 0.3 × 0.4 mm.

(*ii*) *Data collection and processing*. An Enraf Nonius CAD4 diffractometer was used in ω/2θ scan mode, with ω scan width of 0.60 + 0.35 tan θ and scan speed ranging from 0.3 to 5 ° min^{-1}, depending on the intensity measured in a pre-scan [graphite monochromatized Mo-K_α radiation; 2 132 reflections measured (I > 0; 0 < θ < 25°, 0 < h < 20, 0 < k < 20, 0 < l < 10) yielding 1 630 unique $F > 3\sigma(F)$; R_{int} = 0.016]. Negligible drift in intensity standards (11 −3 −2; −7 −8 1; 10 1 2) measured at intervals of 2.5 hours. L_p Corrections were applied but absorption ignored.

(*iii*) *Structure solution and refinement*. Solved by direct methods, heavier atoms from Fourier map, hydrogens from difference Fourier. Full matrix least-squares with non-hydrogen atoms anisotropic and hydrogen isotropic. Final R = 0.039 {R_w = 0.044, $w = 1.494/[\sigma^2(F_o) + 0.0005F_o^2]$; $\sigma^2(F_o)$ from counting statistics}. Maximum shift/e.s.d. in final cycle 0.06 [y, H(132)]. Fluctuations in the final difference Fourier map ranged from −0.20 to 0.19 e Å^{-3}.

(*b*) 1,3,5-*Trifluoro*-7,9-*dimethyl*-11H-*pyrido*[4,3-c][1,2]*benzodiazepine* 5,6-*Dioxide* (**8**).—(i) *Crystal data*. $C_{14}H_{10}F_3N_3O_2$, M_r 309.25, T = 293 K, tetragonal (yellow crystal, 0.4 × 0.4 × 0.2 mm), a = b = 18.040(1), c = 8.495 1(9) Å, V = 2 765(1) Å^3 (by least-squares refinement on setting angles of 25 reflections, 7.4 < θ < 11.7°), Mo-K_α radiation (μ = 0.086 mm^{-1}, λ = 0.710 69 Å), space group $P4_2/n$ (origin choice 2), Z = 8, D_x = 1.49 Mg m^{-3}.

(*ii*) *Data collection and processing*. As for compound (**7**) but with ω scan width of 1.00 + 0.35 tanθ; 4 275 reflections were measured (0 < I, 0 < θ < 25°, −21 < h < 21, 0 < k < 21, 0 < l < 10), yielding 1 814 $F > 3\sigma(F)$, R_{int} = 0.012. Negligible drift occurred in intensity standards (measured at intervals of 3 h; 4 8 0; 10 −2 0; 2 1 4). L_p Corrections were applied, absorption ignored.

(*iii*) *Structure solution and refinement*. As above for compound (**7**), with a final R of 0.045 {R_w = 0.041, $w = 1.8037/[\sigma^2(F_o) + 0.000\,05F_o^2]$}. The maximum shift/e.s.d. was 0.10 [x, H(112)]. Fluctuations in the final difference Fourier map ranged from −0.22 to 0.23 e Å.

(*c*) *Computational Details for Compounds* (**7**) *and* (**8**).[19]—MULTAN 80 was used for direct methods and SHELX 76 for least-squares refinement. All computations were carried out on the joint CDC 7600/Amdahl 470 system of the University of Manchester Regional Computing Centre. Neutral-atom scattering factors were used throughout. The Cambridge Crystallographic Database was surveyed using the Crystal Structure Search and Retrieval interactive system accessed *via* the UMIST link to the VAX at Daresbury.

Final atomic co-ordinates are listed in Table 1, and selected details of molecular geometry appear in Table 2. Stereoformulae (see Figures 1 and 2) were drawn using PLUTO. Tables of additional molecular geometry (including torsion angles), non-hydrogen atom anisotropic vibrational parameters, normalised least-squares planes and isotropic thermal parameters are available on request from the Cambridge Crystallographic Data Centre.*

Spectroscopic Analyses.—The instruments used to record spectra have been named previously.[1] N.m.r. chemical shifts were measured relative to Me_4Si (^{13}C, ^{1}H), CF_3CO_2H (^{19}F), or $MeNO_2$ (^{15}N), positive values being assigned to absorptions appearing downfield from reference signals.

Starting Materials.—(*a*) 1,3,4-*Trifluoro*-7,9-*dimethyl*-11H-*pyrido*[4,3-c][1,2]*benzodiazepine* (**1**) (*with A. C. Alty*). A solution of 2,3,5,6-tetrafluoro-4-(2,4,6-trimethylphenylazo)pyridine (**3**)[1] (2.0 g, 6.7 mmol) in mesitylene (20 cm^3) was heated under reflux for 8 h. After evaporation of the solvent (Rotavapor), the product was worked up using dry-column flash chromatography (d.c.f.c.; silica). Elution with light petroleum (b.p. 40—60 °C) gave unchanged starting material (**3**) (0.12 g, 0.40 mmol, 6% recovery), and subsequent elution with dichloromethane–light petroleum (b.p. 40—60 °C) (1:1, v/v) gave (**1**) [1.47 g, 5.31 mmol, 84% based on (**3**) converted], which recrystallized from aqueous ethanol as bright orange *needles*, m.p. 137—138 °C (Found: C, 60.7; H, 3.8; F, 20.4; N, 15.0. $C_{14}H_{10}F_3N_3$ requires C, 60.6; H, 3.6; F, 20.7; N, 15.2%); m/z 277 (M^+).

On a larger scale, a solution of the azo compound (**3**) (7.52 g) in mesitylene (65 cm^3) was boiled for 14 h to provide the diazepine (**1**) (5.00 g, 72%) and unchanged starting material (1.10 g, 15%).

(*b*) 1,3,4-*Trifluoro*-7,9-*dimethyl*-2-*trifluoromethyl*-11H-*dibenzo*[c,f][1,2]*diazepine* (**2**) (*with A. C. Alty*). A solution of 2,3,5,6-tetrafluoro-2′,4′,6′-trimethyl-4-(trifluoromethyl)azobenzene (**4**) (2.95 g, 8.10 mmol) in glacial acetic acid (100 cm^3) was heated under reflux for 1 h. Evaporation of the solvent followed by chromatography (d.c.f.c.; silica eluted with light petroleum–dichloromethane mixtures) gave unchanged starting material (1.96 g, 66%) and the diazepine (**2**) (0.49 g, 1.42 mmol, 52% based on (**4**) converted) as orange *needles*, m.p. 112—113 °C (Found: C, 55.8; H, 2.6; F, 33.3; N, 8.4. $C_{16}H_{10}F_6N_2$ requires C, 55.8; H, 2.9; F, 33.1; N, 8.1%); m/z 344 (M^+).

Better yields and conversions were achieved using 1,2-dichlorobenzene or mesitylene as solvent. Thus, (**4**) (1.21 g) underwent 89% conversion into the diazepine (97%) in boiling *o*-dichlorobenzene (10 cm^3) over 6 h; in boiling 1,3,5-trimethylbenzene (65 cm^3), (**4**) (7.52 g) underwent 86% conversion into the diazepine (84%) over 14 h.

Oxidation of trans-2,3,5,6-*Tetrafluoro*-4-(2,4,6-*trimethylphenylazo*)*pyridine* (**3**).—The red colour of a solution of the azo compound (**3**) (3.0 g, 10.1 mmol) in glacial acetic acid (45 cm^3) changed immediately to yellow when aqueous hydrogen peroxide (30% w/v; 9.0 g, 78 mmol) was added. After the mixture had been boiled for 2 h (the progress of the oxidation was followed by t.l.c.), it was poured onto ice. The precipitate was purified chromatographically (d.c.f.c.) then recrystallized twice from ethanol to provide *trans*-2,3,5,6-tetrafluoro-4-(2,4,6-trimethylphenyl-*ONN*-azoxy)pyridine (**5**) (3.0 g, 9.6 mmol. 95%), m.p. 116—118 °C (lit.,[3] 118—119 °C) (Found: C, 53.6; H, 3.3; F, 24.2; N, 13.4. Calc. for $C_{14}H_{11}F_3N_3$: C, 53.7; H, 3.5; F, 24.3; N, 13.4%). Spectroscopic properties (i.r. ^{19}F n.m.r., and mass) were identical with those found previously.[3]

Oxidation of 1,3,4-*Trifluoro*-7,9-*dimethyl*-11H-*pyrido*[4,3-c]-[1,2]*benzodiazepine* (**1**).—(*a*) *With hydrogen peroxide–acetic*

* See Instructions for Authors (1989) *J. Chem. Soc., Perkin Trans. 1*, 1989, issue 1.

acid. Aqueous hydrogen peroxide (30% w/v; 18.0 g, 160 mmol) was added dropwise to a solution of the diazepine (**1**) (7.64 g, 27.58 mmol) in glacial acetic acid (90 cm^3) and the mixture was boiled for 2 h. It was then poured onto ice and the yellowish-brown precipitate was stored *in vacuo* over phosphorus pentaoxide overnight. Chromatographic separation (d.c.f.c.) gave unchanged starting material (**1**) [0.80 g, 2.89 mmol, 10% recovery; eluted with light petroleum (b.p. 40—60 °C)] and a mixture [*5.15 g, 17.58* mmol. 71% based on (**1**) converted; eluted with light petroleum (40—60 °C)–dichloromethane (95:5 v/v)] of the two monoxides (**6**) and (**7**) described below (the mixture was analysed by h.p.l.c. and ^{19}F n.m.r. techniques). A sample (0.50 g) of the mixture was separated chromatographically [semi-prep. h.p.l.c. Partisil (20 μm) eluted with hexane–dichloromethane (1:1 v/v) to give yellow 1,3,4-*trifluoro*-7,9-*dimethyl*-11H-*pyrido*[4,3-c][1,2]*benzodiazepine* 6-*oxide* (**6**) (0.30 g), m.p. 135—137 °C [Found: C, 58.0; H, 3.1; N, 14.1%; *M* (mass spec.), 293. $C_{14}H_{10}F_3N_3O$ requires C, 57.3; H, 3.4; N, 14.3%; *M*, 293], and 1,3,4-*trifluoro*-7,9-*dimethyl*-11H-*pyrido*[4,3-c]-[1,2]*benzodiazepine* 5-*oxide* (**7**) (0.15 g) as glistening yellow crystals, m.p. 216—218 °C. [Found: C, 57.6; H, 3.3; F, 21.5; N, 14.3%, *M*; (mass spec.), 293. $C_{14}H_{10}F_3N_3O$ requires C, 57.3; H, 3.4; F, 19.5; N, 14.3%; *M*, 293]. The structure of (**7**) was established by *X*-ray crystallography (see Figure 1).

(*b*) *With hydrogen peroxide–trifluoroacetic anhydride.* 'High-test' aqueous hydrogen peroxide (85% w/v; 23 cm^3) and trifluoroacetic anhydride (50 cm^3) were added simultaneously but separately to a cold (0 °C) solution of the diazepine (**1**) (3.0 g, 10.8 mmol) in dichloromethane (100 cm^3) sited behind a blast screen. The mixture was boiled for 30 min and then cooled and quenched with water (1 l). The organic material was extracted with diethyl ether (4 × 100 ml) and the combined extracts were dried ($MgSO_4$) and evaporated (Rotavapor). Chromatography of the residue (d.c.f.c.) yielded 1,3,4-trifluoro-7,9-dimethyl-11*H*-pyrido[4,3-*c*][1,2]benzodiazepine 6-oxide (**6**) (1.5 g, 5.2 mmol, 47%), m.p. 135—137 °C, with correct spectroscopic properties (^{19}F n.m.r.), and 1,3,4-*trifluoro*-7,9-*dimethyl*-11H-*pyrido*[4,3-c]-[1,2]*benzodiazepine* 5,6-*dioxide* (**8**) (1.0 g, 3.2 mmol, 30%) as shiny yellow crystals, m.p. 158—160 °C (Found: C, 54.2; H, 3.2; F, 18.3; N, 13.4. $C_{14}H_{10}F_3N_3O_2$ requires C, 54.4; H, 3.2; F, 18.4; N, 13.6%); *m/z* 293 (top-mass peak; $C_{14}H_{10}F_3N_3O^+$, 98%). The structure of (**8**) was established by *X*-ray crystallography (see Figure 2).

(*c*) *With chromic anhydride.* A mixture of the diazepine (**1**) (3.0 g, 10.8 mmol), glacial acetic acid (100 cm^3) and chromic anhydride (9.0 g, 90.0 mmol) was boiled for 2 h (no starting material remained by t.l.c.). The greenish solution was added to water (1 l) and the aqueous mixture was extracted with diethyl ether (4 × 150 cm^3), and the dried ($MgSO_4$) extract evaporated (Rotavapor). The sticky residue was chromatographed (d.c.f.c.; silica) to give (i) 1,3,4-*trifluoro*-7,9-*dimethylpyrido*[4,3-c][1,2]-*benzodiazepin*-11-*one* (**17**) (0.6 g, 2.1 mmol, 19%) eluted with hexane–dichloromethane (1:1 v/v), as red needles, m.p. 171—173 °C (Found: C, 58.5; H, 3.0; F, 19.6; N, 13.7. $C_{14}H_8F_3N_3O$ requires C, 57.7; H, 2.7; F, 19.6; N, 14.4%); *m/z* 291 (M^+, 66.8%), 263 [M^+ − CO (or N_2), 21.3], 235 (M^+ − CO − N_2, 18.6), and 220 ($C_{12}H_5F_3N^+$, 100); $\nu_{max.}$ (soln. in CCl_4) 1 690 cm^{-1} (C=O), (ii) yellow 1,3,4-*trifluoro*-7-*methyl*-11H-*pyrido*[4,3-c]-[1,2]*benzodiazepine*-9-*carboxylic acid* (**19**) (1.0 g, 3.3 mmol, 30%), eluted with dichloromethane, m.p. 199—200 °C, $\nu_{max.}$ (mull) 3 200—2 300 (vbr., OH) and 1 660 cm^{-1} (br, C=O); *m/z* 307 (M^+, 41.2%), 279 (M^+ − N_2, 3.3), 262 (M^+ − COOH, 2.3), 234 (M^+ − CO_2H − N_2, 54.8), and 220 ($C_{12}H_5F_3N^+$, 100), and (iii) red 1,3,4-*trifluoro*-7-*methylpyrido*[4,3-c][1,2]-*benzodiazepin*-11-*one*-9-*carboxylic acid* (**18**) (0.6 g, 1.9 mmol, 18%), eluted with dichloromethane, m.p. > 320 °C (Found: C, 51.9; H, 2.0; F, 17.6; N, 12.7. $C_{14}H_6F_3N_3O_3$ requires C, 52.3; H, 1.9; F, 17.75; N, 13.0%); $\nu_{max.}$(mull) 3 200—2 300 (vbr, O–H) and 1 680 cm^{-1} (br, C=O); *m/z* 321 (M^+, 52.8%), 293 [M^+ − N_2 (or CO), 6.6%], 276 (M^+ − CO_2H, 5.3), and 220 ($C_{12}H_5F_3N^+$, 100).

In a similar experiment [(**1**), 10 mmol; CrO_3, 80 mmol; AcOH, 100 cm^3] with a shorter reaction period (1 h), work-up as above gave the red diazepinone (**17**) (1.7 mmol, 17%), m.p. 172—174 °C, this time possessing acceptable C, N values (Found: C, 57.8; H, 2.6; N, 14.6%). The other products were not examined.

Oxidation of 1,3,4-*Trifluoro*-7,9-*dimethyl*-2-*trifluoromethyl*-11H-*dibenzo*[c,f][1,2]*diazepine* (**2**).—(a) *With hydrogen peroxide–acetic acid.* A mixture of the diazepine (**2**) (1.00 g, 2.90 mmol), glacial acetic acid (15 cm^3), and 30% hydrogen peroxide (3 cm^3) was heated under reflux for 1 h then poured onto ice. The resulting solid was dried *in vacuo* (over P_2O_5) and then separated chromatographically (d.c.f.c.; silica) to yield yellow 1,3,4-*trifluoro*-7,9-*dimethyl*-2-*trifluoromethyl*-11H-*dibenzo*[c,f]-[1,2]*diazepine* 6-*oxide* (**11**) (0.52 g, 1.44 mmol, 50%), eluted with light petroleum (b.p. 40—60 °C), m.p. 179—180 °C (Found: C, 53.3; H, 2.7; F, 31.3; N, 7.6. $C_{16}H_{10}F_6N_2O$ requires C, 53.3; H, 2.8; F, 31.7; N, 7.8%); *m/z* 360 (M^+, 100%) and 344 (M^+ − O, 20.3), and yellow 1,3,4-*trifluoro*-7,9-*dimethyl*-2-*trifluoromethyl*-11H-*dibenzo*[c,f][1,2]*diazepine* 5-*oxide* (**14**) (0.46 g, 1.27 mmol, 44%) eluted with light petroleum–dichloromethane (9:1 v/v), m.p. 179—181 °C (Found: C, 53.6; H, 2.8; F, 31.4; N, 7.8. $C_{16}H_{10}F_6N_2O$ requires C, 53.3; H, 2.8; F, 31.7; N, 7.8%); *m/z* 360 (M^+, 100%) and 344 (M^+ − O, 9.3).

(*b*) *With hydrogen peroxide–trifluoroacetic anhydride.* Hydrogen peroxide (85% w/v; 23 cm^3) and trifluoroacetic anhydride (50 cm^3) were added simultaneously but separately to a solution of the diazepine (**2**) (3.7 g, 10.8 mmol) in dichloromethane (100 cm^3) cooled to 0 °C. The stirred mixture was allowed to warm to room temperature and then boiled for 35 min, cooled to 20 °C, and shaken with water (1 l). The organic material was extracted with diethyl ether and the dried ($MgSO_4$) extract was evaporated, leaving a yellow residue which was chromatographed [d.c.f.c.; silica eluted with light petroleum (40—60 °C)–dichloromethane (1:1 v/v)] to provide 1,3,4-trifluoro-7,9-dimethyl-2-trifluoromethyl-11*H*-dibenzo[*c*,*f*][1,2]diazepine 6-oxide (**14**) (1.0 g, 2.8 mmol, 26%), m.p. 179—180 °C, with correct spectroscopic properties (^1H, ^{19}F n.m.r.) and pale cream 1,3,4-*trifluoro*-7,9-*dimethyl*-2-*trifluoromethyl*-11H-*dibenzo*[c,f][1,2]-*diazepine* 5,6-*dioxide* (**12**) (1.0 g, 2.7 mmol, 25%), m.p. 161—162 °C. (Found: C, 51.2; H, 2.6; F, 30.6; N, 7.3. $C_{16}H_{10}F_6N_2O_2$ requires C, 51.1; H, 2.7; F, 30.3; N, 7.4%); *m/z* 376 (M^+, 16.1%), 360 (M^+ − O, 100%), and 344 (M^+ − 2O, 29.1).

(*c*) *With chromic anhydride.* The oxidising agent (4.0 g, 40 mmol) was added to a magnetically stirred solution of the diazepine (**2**) (2.0 g, 5.8 mmol) in glacial acetic acid (50 cm^3). After being heated under reflux for 2 h, the mixture was stored at room temperature overnight and then shaken with water (1 l). The organic product was isolated by ether extraction (4 × 150 cm^3) and then worked up by standard methods, culminating in d.c.f.c. (silica), to provide (i) an orange solid, eluted with light petroleum (40—60 °C)–dichloromethane (1:1 v/v), which was purified by semi-preparative h.p.l.c. (20 μm Partisil eluted with 1:3 v/v dichloromethane–hexane) to give 1,3,4-*trifluoro*-7,9-*dimethyl*-2-(*trifluoromethyl*)*dibenzo*[c,f][1,2]*diazepin*-11-*one* (**23**) (0.8 g, 2.2 mmol, 38%), m.p. 156—158 °C (Found: 53.9; H, 2.5; F, 31.6; N, 7.5. $C_{16}H_8F_6N_2O$ requires C, 53.6; H, 2.2; F, 31.8; N, 7.8%); *m/z* 358 (M^+, 81.8%), 330 [M^+ − CO (or N_2), 41.8), 302 (M^+ − CO − N_2, 14.5) and 287 ($C_{14}H_5F_6^+$, 100), and (ii) 1,3,4-*trifluoro*-7-*methyl*-2-*trifluoromethyl*-11H-*dibenzo*[c,f]-[1,2]*diazepine*-9-*carboxylic acid* (**22**) (1.0 g, 2.7 mmol, 47%) eluted with dichloromethane, as yellow crystals, m.p. 230—232 °C (Found: C, 51.2; H, 2.2; F, 30.1; N, 7.1. $C_{16}H_8F_6N_2O_2$ requires C, 51.3; H, 2.2; F, 30.1; N, 7.5%); $\nu_{max.}$(mull) 3 300—

2 300 (vbr, O–H) and 1 700 (br, C=O); *m/z* 374 (M^+, 100%), 355 ($M^+ - F$, 28.9), 329 ($M^+ - CO_2H$, 2.5), and 301 ($M^+ - CO_2H - N_2$, 81.3).

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