2,3-DIBROMO-3,4-DIHYDRO-4H-1,4-BENZOXAZINES AND THEIR NUCLEOPHILIC DISPLACEMENT REACTIONS : THE FIRST SYNTHESIS OF 4-ACETYL-4H-1,4-BENZOXAZINE-3-CARBONITRILE [1]

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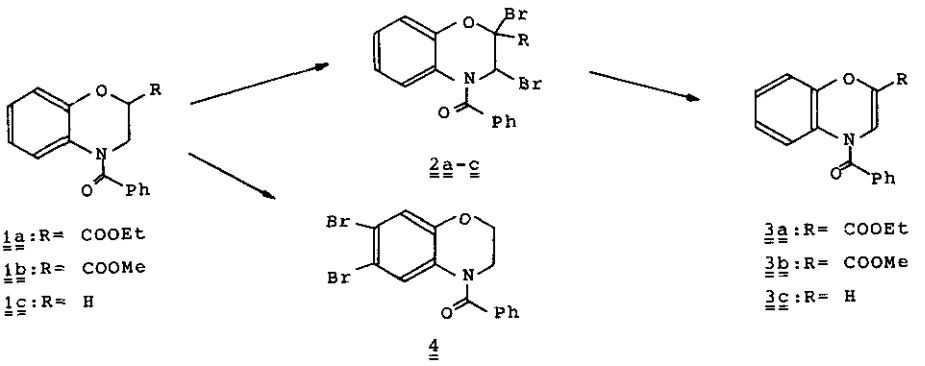
Abstract- The synthesis of 2,3-dibromo-3,4-dihydro-2H-1,4-benzoxazines is described. Their reaction with alcohols afforded the corresponding 2-bromo-3-alkoxy- and 2,3-dialkoxy derivatives,respectively, which were converted into various 1,4-benzoxazine-3-carbonitriles.

We recently reported two alternative pathways to functionalised 4H-1,4-benzoxazines: Electrophilic attack of isocyanates at the double bond of 4-acetyl-4H-1,4-benzoxazine[2] as well as modified Polonovski-reaction of 2-substituted 4-methyl-3,4-dihydro-1,4-benzoxazines[3] allows access exclusively to 4H-1,4-benzoxazine-2-carboxylic acid derivatives. However, the corresponding C-3 functionalised 1,4-benzoxazines have not yet been described and we assumed 2,3-dibromo-3,4-dihydro-2H-1,4-benzoxazines to be suitable synthons in the synthesis of these unknown benzoxazine derivatives.
Reportedly, treatment of dihydro-1,4-benzoxazines 1a,c with NBS/ABN gave the corresponding 2,3-dibromo derivatives 2a,c, which were converted with NaI into 4H-1,4-benzoxazines 3a,c[4] (Scheme 1). However, a reinvestigation of this reaction sequence led to partly different results and furthermore revealed a significant dependence of the radical bromination step on the N-substituent. An interesting difference in the reactivity of the bromines in 2,3-dibromobenzoxazine towards nucleophilic displacement provides the basis for their selective transformation into benzoxazine-3-carbonitriles.
Benzoxazine-2-carboxylic acid esters 1a,b could be brominated under radical conditions,[4,5] leading to 2a[4] and 2b, which underwent smooth debromination affording 3a[4] and 3b, respectively,(Scheme 1).

Scheme 1



1a:R= COOEt
1b:R= COOMe
1c:R= H

2a-c

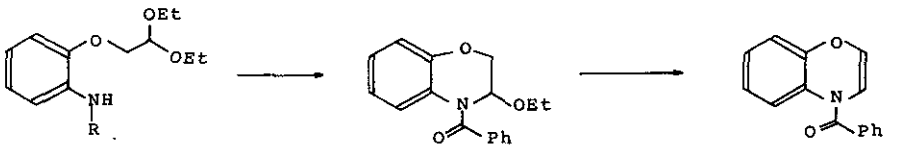
3a:R= COOEt
3b:R= COOMe
3c:R= H

4

However, the reported conversion of 1c into 3c[4] via 2c could not be repeated. Treatment of 1c with NBS under various conditions always resulted in bromination of the aromatic ring and the sole isolated product was identified as 4.

Thus a different route was chosen to obtain 3c (Scheme 2). The acetal 5b, readily

Scheme 2



5a:R= H
5b:R= COPh

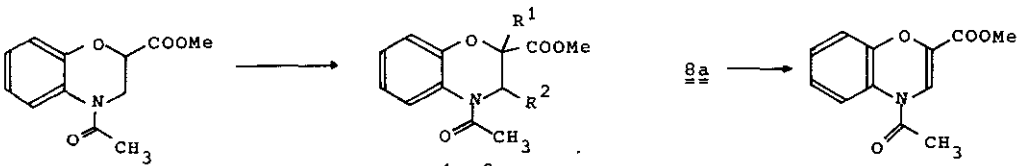
6

3c

available by treatment of 5a[6] with $(PhCO)_2O$/pyridine, was cyclised with TFA to 6. Refluxing 6 in benzene with p-TSA afforded 4-benzoyl-4H-1,4-benzoxazine (3c) almost quantitatively.

Bromination of the N-acetyl analogue 7 under various radical conditions gave only minor quantities of 8a, which underwent debromination under GC-conditions and hence was detected by MS as 10. However, the main product detected was always the monobromo derivative 8b (Scheme 3). The structure of the unstable bromination products were

Scheme 3



7

8a:R^1=R^2= Br
8b:R^1=Br; R^2= H
9a:R^1=Br; R^2= OCH_3
9b:R^1=OCH_3; R^2= H

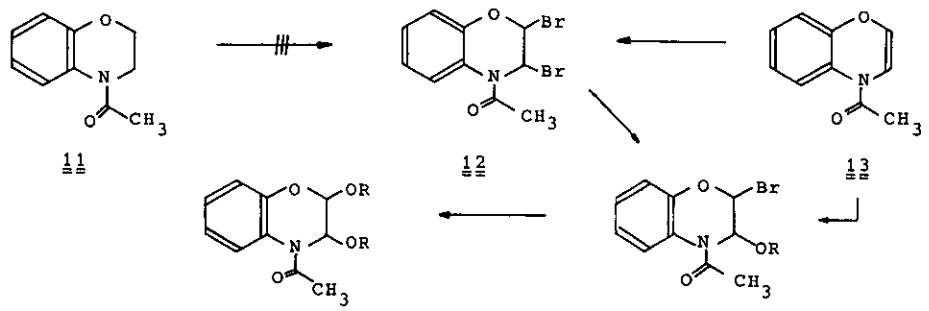
8a

10

unambiguously established by their conversion with methanol at 20°C into the monomethoxy derivatives 9a and 9b, respectively. Interestingly, the N-benzoyl analogues 2a,b remained unaffected in methanolic solution at 20°C and the different reactivity of the C-2 bromine is noteworthy.

The C-2 unsubstituted N-acetylbenzoxazine 11 was completely unreactive towards bromination under various radical conditions. However, the dibromo benzoxazine 12 was obtained quantitatively as an unstable oil through addition of bromine onto the double bond of 13[7] (Scheme 4). A coupling constant of $J_{H^2H^3}$=1.8Hz (C_6D_6) indicated trans-biaxial configuration of the bromine atoms in 12.

Scheme 4



Treatment of 12 with alcohols at room temperature resulted in stereospecific, selective displacement of the C-3 bromine furnishing 14a and 14b, respectively. The monobromo derivatives 14 are also directly attainable by addition of bromine in alcoholic solution to 13. Nucleophilic displacement of the second bromine in 14 required forcing conditions, the presence of pyridine and occurred with racemization at the chiral C-2, thus leading to two diastereomers of 15a and 15b, respectively.

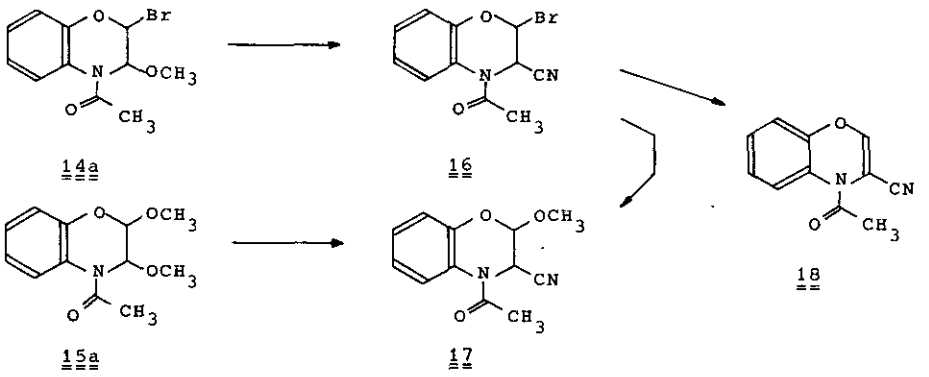
Table: Chemical shift of methine protons in 12,14 and 15 ($CDCl_3$)

Compound	C-2	C-3
12	6.83	6.83
14a	6.66	5.86
14b	6.72	5.96
15a (1)	5.03	5.91
15a (2)	5.15	5.60
15b (1)	5.10	5.96
15b (2)	5.26	5.71

The structures of 14a and 14b were conclusively proved by ^{1}H-nmr spectroscopy: As shown in the Table, displacement of bromine by an alkoxy group caused the expected diamagnetic shift of the methine protons, which is, however, significantly smaller for the C-3 proton, due to a deshielding effect of the carboxyl group. Thus, a doublet near 5.8 ppm unambiguously substantiated structure 14a and 14b.

The selective displacement of the methoxy group in 14a by cyanide with $(CH_3)_3SiCN/BF_3$[1] proceeded stereospecifically affording 2-bromo-3,4-dihydro-2H-1,4-benzoxazine-3-carbonitrile(16)(Scheme 5).

Scheme 5



Surprisingly, similar treatment of both diastereomers of 15a with $(CH_3)_3SiCN$ yielded the same racemate of benzoxazine-3-carbonitrile 17 and none of its other diastereomeres were detected. Apparantly this transformation occurs with both diastereomeres of 15a stereospecifically, once with retention and once with inversion of the configuration, thus indicating that two different mechanisms must be involved in this conversion.

By contrast, refluxing 16 with methanol in the presence of Et_3N resulted in partly racemisation at C-2; the main diastereomer of 17 isolated, was identical with the product obtained from the reaction of 15a. The other diastereomer of 17 could only be detected ^{1}H-nmr spectroscopically and was not obtained as analytically pure sample.

When a methanolic solution of 16 was refluxed in the presence of pyridine, dehydrobromination took place exclusively, furnishing the unsaturated 4H-1,4-benzoxazine-3-carbonitrile 18.

The mechanistic problems related to the conversion 15a into 17 and futher transformations of 18 are now under investigation.

EXPERIMENTAL

General Remarks: see Ref. 1

General Procedures for the Radical Bromination of 4-Acyl-3,4-dihydro-2H-1,4-benzoxazines.- Method A: A mixture of dihydro-1,4-benzoxazine (10 mmol), N-bromosuccinimide (7.12g, 40 mmol), calcium carbonate (1.5g) and 2,2'-azo-bis-isobutyronitrile (ABN) (0.1g) in dry tetrachloromethane (40ml) was refluxed for the indicated time. After cooling, the solid material was filtered off, the solution was evaporated and the residue recrystallised.

Method B: A solution of dihydro-1,4-benzoxazine (10 mmol), N-bromosuccinimide (22 mmol) and ABN (0.1g) in dry tetrachloromethane (40ml) was refluxed for the appropriate time. Work-up as in method A.

4-Benzoyl-2,3-dibromo-3,4-dihydro-2H-1,4-benzoxazine-2-carboxylic acid methyl ester (2b) Treatment of 1b (2.07g) according to method A or B gave after 3 h 2b (3.82g, 84%) as colourless crystals, mp 150-151°C (from ethyl acetate); ^{1}H-nmr ($CDCl_3$): δ 3.99 (s,3H, OCH_3), 6.89-7.03 (m,2H,aromat.), 7.12 (s,1H,NCH), 7.15-7.90 (m,7H,aromat.); MS m/e: 457,455,453 (M^+); Anal. Calcd. for $C_{17}H_{13}Br_2NO_4$: C, 44.87, H, 2.88, N, 3.08; Found: C, 45.07,H, 3.00, N, 2.99.

4-Benzoyl-6,7-dibromo-3,4-dihydro-2H-1,4-benzoxazine (4)- Treatment of 1c (2,39g) by methods A/B gave 4 (2.6g, 65%) as colourless crystals, mp 152°C (from methanol); ^{1}H-nmr ($CDCl_3$): δ 3.81-3.96 (m,2H,OCH_2), 4.22-4.39 (m,2H,NCH_2), 7.22 (s,1H,aromat.,H-8), 7.50 (s,5H,aromat.), 7.55 (s,1H,aromat.,H-5); MS m/e: 399,397,395 (M^+); Anal. Calcd. for $C_{15}H_{11}Br_2NO_2$: C, 45.37, H, 2.79, N, 3.53; Found: C, 45.77, H, 2.92, N, 3.52.

4-Acetyl-2-bromo-3,4-dihydro-2H-1,4-benzoxazine-2-carboxylic acid methyl ester (8b) and 4-Acetyl-4H-1,4-benzoxazine-2-carboxylic acid methyl ester (10)- Reflux of 7 (2.35g) according to method A or B for 4 h furnished after work-up an orange oil, which was subjected to GC-MS analysis (20m, SE 30, 0.3µm, 2.5ml He/min., 150-320°C, 10°C/min.): 7: MS m/e: 235 (M^+,5%), 193 (M^+-ketene,30%); 10: MS m/e: 233 (M^+,17%), 181 (M^+-ketene,100%); 8b: MS m/e: 315 (M^+,13%), 313 (M^+,12%), 273,271 (M^+-ketene,24%).

4-Acetyl-2-bromo-3-methoxy-3,4-dihydro-2H-1,4-benzoxazine-2-carboxylic acid methyl ester (9a) and 4-Acetyl-2-methoxy-3,4-dihydro-2H-1,4-benzoxazine-2-carboxylic acid methyl ester (9b)- The oily residue, obtained in the bromination of 7 as described above, was stirred with methanol (30ml) at room temperature. Removal of the solvent afforded an oily mixture, which was separated by chromatography (silica gel, toluene/ethyl acetate 6:4): 9a (0.5g, 14%) as colourless crystals, mp 161°C (from methanol);

^{1}H-nmr ($CDCl_3$):δ 2.50 (s,3H,CH_3), 3.41 (s,3H,OCH_3), 4.00 (s,3H,OCH_3), 6.23 (s,1H,NCH), 7.10-7.63 (m,4H,aromat.); MS m/e: 345,343 (M^+), 303,301 (M^+-ketene); Anal.Calcd. for $C_{13}H_{14}BrNO_5$: C, 45.37, H, 4.10, N, 4.07; Found: C,45.42, H, 4.12, N, 4.03; and 9b (1.27g,48%) as light yellow oil, $bp_{0.03}$ 120°C; ^{1}H-nmr ($CDCl_3$): δ 2.26 (s,3H,CH_3), 3.41 (s,3H,OCH_3), 3.68 and 4.31 (AB-system,2H,NCH_2,J_{AB}=13.5Hz),3.85 (s,3H,OCH_3), 6.86-7.23 (m,4H,aromat.); MS m/e: 265 (M^+), 223 (M^+-ketene); Anal. Calcd. for $C_{13}H_{15}NO_5$: C, 58.86, H, 5.70, N, 5.28; Found: C, 58.57, H, 5.72, N, 5.22 .

4-Benzoyl-4H-1,4-benzoxazine-2-carboxylic acid methyl ester (3b) - A solution of 2b (4.55g, 10 mmol in dry acetone (80ml) was stirred at room temperature with sodium iodide (3.0g, 20 mmol) for 1 h. The solvent was removed, the residue was taken up with ether and water, and the organic layer was washed with sodium thiosulphate and sodium hydrogene carbonate. The organic layer was evaporated to afford 3b (2.8g, 95%) as colourless crystals after recrystallisation from methanol; mp 110°C; ^{1}H-nmr ($CDCl_3$):δ 3.78 (s,3H,OCH_3), 6.80-7.12 (m,2H,aromat.), 7.35 (s,1H,CH), 7.45-7.74 (m,7H,aromat.); MS m/e: 295 (M^+); Anal.Calcd. for $C_{17}H_{13}NO_4$: C, 69.14, H, 4.45, N, 4.74; Found: C, 68.96, H, 4.56, N, 4.66 .

1-(2-Benzoylaminophenoxy)-2,2-diethoxyethane (5b) - A mixture of 5a[6] (4.50g, 20 mmol) and benzoic acid anhydride (4.97g, 22 mmol) in dry pyridine (20 ml) was stirred for 24h at room temperature. After removal of pyridine, the residue was taken up in ether, washed with 2N-HCl, aqueous sodium carbonate and water. The organic layer was evaporated and the oily residue gave after destillation 5b (6.5g,98%) as colourless crystals; $bp_{0.005}$ 170°C, mp 37-39°C; ^{1}H-nmr ($CDCl_3$): δ 1.20 (t,6H,CH_3,J=7Hz), 3.53-3.83 (m,4H,OCH_2), 4.13 (d,2H,OCH_2,J=7Hz), 4.86 (d,1H,OCHO,J=7Hz), 7.03-8.20 (m,8H, aromat.), 8.52-8.67 (m,1H,aromat.,H-3), 8.71-8.90 (m,1H,NH); MS m/e: 329 (M^+); Anal. Calcd. for $C_{19}H_{23}NO_4$: C, 69.28, H, 7.04, N, 4.25; Found: C,69.54, H, 7.05, N, 4.14 .

4-Benzoyl-3-ethoxy-3,4-dihydro-2H-1,4-benzoxazine (6) - A solution of 5b (3.29g, 10 mmol) in trifluoroacetic acid (4ml) was left at room temperature for 2h. After removal of TFA the remaining residue was solved in ether and washed with aqueous sodium carbonate and water. Evaporation of the solvent yielded after recrystallisation from pentane 6 (2.68g, 95%) as colourless crystals; mp 128-131°C; ^{1}H-nmr ($CDCl_3$): δ 1.16 (t,3H,CH_3,J=7Hz), 3.66 (dq,2H,OCH_2,J=7Hz), 4.33 and 4.55 (AB-part of an ABX-system,2H, OCH_2, J_{AX}=J_{BX}=1.5Hz, J_{AB}=10.5Hz), 5.96 (X-part,1H,NCH), 5.56-6.66 (m,2H,aromat), 6.90-7.00 (m,2H,aromat.), 7.22-7.60 (m,5H,aromat.); MS m/e: 283 (M^+); Anal.Calcd. for $C_{17}H_{17}NO_3$: C, 72.07, H, 6.05, N, 4.94; Found: C, 72.11, H, 6.07, N, 4.96 .

4-Benzoyl-4H-1,4-benzoxazine (3c) - A solution of 6 (1.41g, 5mmol) in dry benzene (100ml) was refluxed with catalytic amounts of p-toluenesulphonic acid for 10 h. The cooled solution was extracted with aqueous sodium hydrogen carbonate and the organic solvent was evaporated. The remaining oil was crystallised with petrol ether to afford 3c (1.15g,98%) as colourless needles; mp 85-86°C; ^{1}H-nmr ($CDCl_3$):δ6.05 and 7.05 (AB-system,2H,CHCH,J_{AB}=5Hz), 6.86-7.05 (m,4H,aromat.), 7.36-7.66 (m,5H,aromat.); MS m/e: 237 (M^+); Anal. Calcd. for $C_{15}H_{11}NO_2$: C, 75.94, H, 4.67, N, 5.90; Found: C, 75.90, H, 4.83, N, 5.90 .

4-Acetyl-2,3-dibromo-3,4-dihydro-2H-1,4-benzoxazine (12) - To a solution of 13[7] (1.75g, 10mmol) in dry tetrachloromethane (50ml) was slowly added a solution of bromine (1.60g, 10mmol) in tetrachloromethane (10ml) at 20°C. Removal of the solvent gave 12 in quantitative yield as an unstable oil. ^{1}H-nmr (C_6D_6): δ 1.85 (s,3H,CH_3), 6.20 (d, 1H,OCH,J=1.8Hz), 6.46 (d,1H,NCH,J=1.8Hz), 6.6-6.8 (m,3H,aromat.), 7.3-7.5(m,1H,aromat.)

General Procedures for the Preparation of 14 - Method A: A solution of 12 (1mmol) in the appropriate alcohol was left at room temperature for 0.5h. The solvent was removed and the remaining residue was recrystallised. - Method B: To a solution of 13 (1mmol) in tetrachloromethane (10ml) was slowly added a solution of bromine (1mmol) in the appropriate alcohol at 20°C. Work-up as in method A.

4-Acetyl-2-bromo-3-methoxy-3,4-dihydro-2H-1,4-benzoxazine (14a)- Both methods afforded 14a quantitatively; mp 123°C (from methanol); ^{1}H-nmr ($CDCl_3$): δ 2.46 (s,3H,CH_3), 3.40 (s,3H,OCH_3), 5.86 (d,1H,NCH,J=1.9Hz), 6.66 (d,1H,OCH,J=1.9Hz),7.03-7.20 (m,4H,aromat.); MS m/e: 287,285 (M^+); Anal.Calcd. for $C_{11}H_{12}BrNO_3$: C, 46.17, H, 4.22, N, 4.89; Found: C, 46.04, H, 4.34, N, 4.72 .

4-Acetyl-2-bromo-3-ethoxy-3,4-dihydro-2H-1,4-benzoxazine (14b) - Both methods gave 14b as colourless oil in quantitative yields. ^{1}H-nmr ($CDCl_3$): δ 1.13 (t,3H,CH_3,J=7Hz), 2.43 (s,3H,CH_3), 3.63 (q,2H,CH_2), 5.96 (d,1H,NCH,J=1.9Hz), 6.72 (d,1H,OCH,J=1.9Hz), 6.97-7.36 (m,4H,aromat.); MS m/e: 301,299 (M^+), 259,257 (M^+-ketene); Anal.Calcd. for $C_{12}H_{14}BrNO_3$: C, 48.01, H, 4.66, N, 4.66; Found: C, 47.72, H, 4.59, N, 4.63 .

4-Acetyl-2,3-dimethoxy-3,4-dihydro-2H-1,4-benzoxazine (15a) - A methanolic solution of 14a (1.43g, 5mmol) was refluxed with pyridine (0.5ml) for 2.5h . Removal of the solvent gave the crude mixture of diastereomers, which were separated by column chromatography (silica gel, benzene/ethyl acetate 8:2). 1. Diastereomer: yield: 0.75g (65%), mp 151°C (from methanol); ^{1}H-nmr ($CDCl_3$): δ 2.33 (s,3H,CH_3), 3.33 (s,3H,OCH_3), 3.70 (s, 3H,OCH_3), 5.03 (d,1H,OCH,J=1.8Hz), 5.91 (d,1H,NCH,J=1.8Hz), 6.95-7.23 (m,4H,aromat.);

MS m/e: 237 (M^+); Anal.Calcd. for $C_{12}H_{15}NO_4$: C, 60.75, H, 6.37, N, 5.90; Found: C, 60.62, H, 6.31, N, 5.81; 2. Diastereomer: oil, yield: 0.16g (15%); ^{1}H-nmr ($CDCl_3$): δ 2.33 (s,3H,CH_3), 3.33 (s,3H,OCH_3), 3.46 (s,3H,OCH_3), 5.15 (d,1H,OCH, J=1.8Hz), 5.60 (d,1H,NCH,J=1.8Hz), 6.90-7.23 (m,4H,aromat.); Anal.Calc. for $C_{12}H_{15}NO_4$: C, 60.75, H, 6.37, N, 5.90; Found: C, 60.39, H, 6.21, N, 5.60 .

4-Acetyl-2,3-diethoxy-3,4-dihydro-2H-1,4-benzoxazine (15b) - Treatment of 14b (1.5g, 5mmol) with ethanol as described in the synthesis of 15a gave after similar work-up two diastereomers of 15b. 1. Diastereomer: yield: 0.8g (61%), mp 73-74°C (from ethanol); ^{1}H-nmr ($CDCl_3$): δ 1.06 (t,3H,CH_3,J=7Hz), 1.30 (t,3H,CH_3,J=7Hz), 2.33 (s, 3H,CH_3), 3.58 (q,2H,CH_2,J=7Hz), 3.93 (cm,2H,CH_2), 5.10 (d,1H,OCH,J=1.8Hz), 5.96 (d, 1H,NCH,J=1.8Hz), 6.86-7.23 (m,4H,aroamt.); MS m/e: 265 (M^+); Anal.Calcd. for $C_{14}H_{19}NO_4$: C, 63.39, H, 7.17, N, 5.29; Found: C, 63.29, H, 7.08, N, 5.23; 2. Diastereomer: oil, yield: 0.2g (15%); ^{1}H-nmr ($CDCl_3$): δ 1.08 (t,3H,CH_3,J=7Hz), 1.15 (t, 3H,CH_3,J=7Hz), 2.33 (s,3H,CH_3), 3.60 (q,2H,CH_2,J=7Hz), 3,78 (cm,2H,CH_2), 5.26 (d,1H, OCH,J=1.8Hz), 5.71 (d,1H,NCH,J=1.8Hz), 6.86-7.20 (m,4H,aromat.); MS m/e: 265 (M^+); Anal.Calcd. for $C_{14}H_{19}NO_4$: C, 63.39, H, 7.17, N, 5.29; Found: C, 63.07, H, 7.15, N, 5.02 .

General Procedure for the Reaction of 14a and 15a with $(CH_3)_3SiCN/BF_3$ - A solution of benzoxazines 14a or 15a (1mmol) in dry diethyl ether (5-10ml) was stirred with $(CH_3)_3SiCN$ (0.2g,2mmol) in the presence of catalytic amounts of BF_3-etherate for 5h at room temperature. The organic layer was separated and the oily residue was extracted exhaustively with diethyl ether. The solvent was removed and the remaining solid recrystallised.

4-Acetyl-2-bromo-3,4-dihydro-2H-1,4-benzoxazine-3-carbonitrile (16) - Compound 14a (0.28g) gave by general procedure 16 (0.21g,75%) as colourless crystals, mp 155°C (from methanol); ^{1}H-nmr ($CDCl_3$): δ 2.46 (s,3H,CH_3), 6.2-6.3 (broad,1H,NCH), 6.88 (d,1H,OCH, J=2Hz), 7.10-7.40 (m,4H,aromat.); MS m/e 282,280 (M^+), 240,238 (M^+-ketene); Anal. Calcd. for $C_{11}H_9BrN_2O_2$: C, 46.99, H, 3.23, N, 9.97; Found: C, 47.04, H, 3.25, N, 9.75 .

4-Acetyl-2-methoxy-3,4-dihydro-2H-1,4-benzoxazine -3-carbonitrile (17) -

(i) - Separate treatment of the diastereomeres of 15a (o.24g) as described above yielded 17 (0.17g,71%) as colourless crystals, mp 115-120°C (from benzene/pentane); ^{1}H-nmr ($CDCl_3$): δ 2.38 (s,3H,CH_3), 3.54 (s,3H,OCH_3), 5.41 (d,1H,OCH,J=2.1Hz), 6.0-6.2 (broad,1H, NCH), 7.00-7.40 (m,4H,aromat.); MS m/e: 232 (M^+), 190 (M^+-ketene); Anal. Calcd. for $C_{12}H_{12}N_2O_3$: C, 62.06, H, 5.21, N, 12.06; Found: C, 62.44, H, 5.43, N, 11.77 .

(ii) - Refluxing a methanolic solution of 16 (0.28g, 1mmol) with Et_3N (0.1ml) for 3h gave after usual work-up 17 (0.1g,45%), mp 115-120°C.

4-Acetyl-4H-1,4-benzoxazine-3-carbonitrile (18) - A solution of 16 (0.28g, 1mmol) in methanol (5ml) was refluxed in the presence of pydridine (0.5ml) for 3h. After removal of the solvent, the residue was taken up in diethyl ether, extracted with 2N-hydrochloric acid and washed with water. Evaporation of the solvent afforded 18 as a colourless oil quantitatively. ^{1}H-nmr ($CDCl_3$): δ 2.38 (s,3H,CH_3), 7.21 (s,1H, OCH), 7.0-7.50 (m,4H,aromat.); MS m/e : 200.058 ($C_{11}H_8N_2O_2$ requires 200.058,M^+).

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Received, 16th July, 1984