A. Hallberg and A. R. Martin (1)

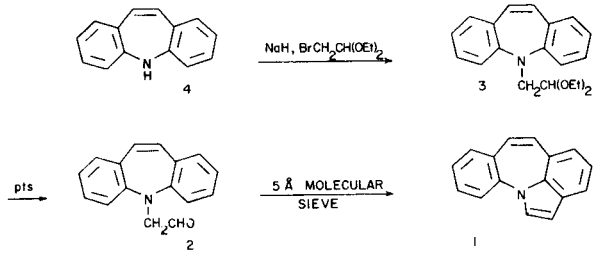
Department of Pharmaceutical Sciences, College of Pharmacy, The University of Arizona, Tucson, AZ 85721

Received April 16, 1981

The synthesis of indolo[1,7-*ab*][1]benzazepine was accomplished by cyclization of 5*H*-dibenz[*b,f*]azepine-5-acetaldehyde.

J. Heterocyclic Chem., **18**, 1255 (1981).

In connection with our efforts to synthesize dibenzazepine derivatives with conformationally restricted basic side chains as potential antidepressant agents, we were interested in preparing the previously unreported 18 π electron parent compound indolo[1,7-*ab*][1]benzazepine **1** as a key intermediate. There appeared to be a number of general approaches that could be employed toward the synthesis of **1**, for example: (I) Fischer cyclization from *N*-amino-derivative of **4** followed by decarboxylation; (II) ring closure of the *N*-halogenacetyl derivative to the corresponding oxindole and subsequent reduction; (III) introduction of a double bond in the previously reported (2) 6,7-dihydro-indolo[1,7-*a,b*][1]benzazepine; and finally (IV) cyclization via the aldehyde **2** as outlined in the scheme shown. The well known fact that iminostilbenes undergo acid catalyzed rearrangement reactions (3) persuaded us to consider the last synthetic approach as most attractive. Here we report the first successful synthesis of **1**, via this mild and convenient synthetic procedure.



The acetic **3** was obtained in 74% yield after alkylation of the sodium salt with 2-bromo-acetaldehyde diethylacetal in refluxing dioxane. After *p*-toluenesulfonic acid catalyzed hydrolysis of the acetal in aqueous acetone at room temperature the crude aldehyde **2** could be isolated in 48% yield. The conversion of the aldehyde to parent compound **1** occurred smoothly at room temperature using 5 Å Molecular sieve, Linde type, in toluene. The yield was 67% after chromatography. As the aldehyde darkened in air and decomposed according to tlc, we chose to prepare **1** directly from **3** without isolation of the intermediate aldehyde **2**, and achieved an improved over all yield (46%).

The nmr spectra of 1 shows two doublets (J = 3.7 Hz) on each side of the complex aromatic pattern, assigned to the 1-hydrogen (7.31 ppm) and the 2-hydrogen (6.40 ppm) by decoupling experiments. These signals appeared both at the same or slightly higher field than the corresponding signals obtained under the same conditions from pyrrolo-[3,2,1-*kl*]phenothiazine (4) (7.31 ppm and 6.40 ppm), 6,7-dihydroindolo[1,7-*ab*][1]benzazepine (2) (7.53 ppm and 6.70 ppm), and 1-phenylindole (5) (7.35 ppm and 6.67 ppm). A remarkable feature of the nmr spectrum is the large upfield shift observed for the signals of the 6- and 7-hydrogens (5.86 ppm and 7.75 ppm, J = 11.8 Hz), compared to the corresponding singlets from **2, 3** and **4**, (6.77 ppm, 6.70 ppm, 6.32 ppm, respectively) indicating that the vinylic function behaves like an isolated carbon-carbon double bond with little or no delocalization of its π bond electrons. This behavior apparently results from the rigidity conferred by the fused indole system in **1**, which cannot achieve coplanarity with the 6,7-carbon-carbon bond.

EXPERIMENTAL (6)

5*H*-Dibenz[*b,f*]azepine-5-acetaldehyde Diethylacetal (**3**).

To a solution of 4.80 g (100 mmoles) of sodium hydride (50% dispersion in oil) in 100 ml of dry dioxane, 9.65 g (50 mmoles) of 5*H*-dibenz[*b,f*]-azepine was added at room temperature. After reflux under nitrogen for 4 hours, 19.7 g (100 mmoles) 2-bromo-acetaldehyde diethylacetal was added dropwise to the black vigourously stirred mixture during a period of 1 hour. The mixture turned yellow under the addition. After additional reflux overnight the excess sodium hydride was destroyed by ethanol and the reaction was poured into toluene and water. The aqueous phase was extracted several times with toluene and the combined organic phases were washed with water, dried over magnesium sulfate and evaporated to give, after silica gel column chromatography using toluene as the eluent, 11.43 g (74%) of 5*H*-dibenz[*b,f*]azepine-5-acetaldehyde diethylacetal (**3**) as a yellow oil; nmr (deuterochloroform): δ 6.80-7.30 (8H, m, aryl), 6.70 (2H, s, CH=CH), 4.61 (1H, t, CH, J = 5.0 Hz), 3.89 (2H, d, CH_2N, J = 5.0 Hz), 3.48 (4H, q, CH_2O, J = 7.0 Hz), 1.11 (6H, t, CH_3, J = 7.0 Hz): ms: m/e (%) 309 (23), 206 (96), 103 (100).

Anal. Calcd. for $C_{20}H_{23}NO_2$: C, 77.64; H, 7.49; N, 4.52. Found: C, 76.79; H, 7.34; N, 4.10.

5*H*-Dibenz[*b,f*]azepine-5-acetaldehyde (**2**).

A solution of 3.09 g (10 mmoles) of 5*H*-dibenz[*b,f*]azepine-5-acetaldehyde diethylacetal (**3**), 0.19 g (1 mmole) of *p*-toluenesulfonic acid, 15.0 ml of acetone and 1.3 ml of water was stirred 16 hours at room temperature and was then poured into 300 ml toluene and 300 ml water. The aqueous phase was extracted several times with toluene and the combined organic phases were washed with sodium hydrogen carbonate and water, dried over magnesium sulfate and the solvent partly evaporated. The evaporation temperature was kept below 30°. The concentrated solution was put on a silica gel column and after eluation with toluene and subsequent evaporation 1.13 g (48%) of 5*H*-dibenz[*b,f*]azepine-5-acetaldehyde (**2**) was

0022-152X/81/061255-02$02.25

obtained; ir (film): ν 1725 cm^{-1} (C=O); deuteriochloroform): δ 5.98 (1H, t, CHO, J = 1.4 Hz), 6.85-7.40 (8H, m, aryl), 6.77 (2H, s, CH=CH), 4.40 (2H, d, CH_2N, J = 1.4 Hz); ms: m/e (%) 235 (12), 206 (100).

Indolo[1,7-*ab*][1]benzazepine (**1**).

I.

A solution of 1.18 g (5 mmoles) 5*H*-dibenz[*b*,*f*]azepine-5-acetaldehyde (**2**) in 100 ml of toluene was prepared and 5.0 g 5Å molecular sieve (Linde) was added. After stirring 16 hours at room temperature the molecular sieve was filtered and washed with toluene. The solution was evaporated and chromatographed (silica, hexane) to give 0.73 g (67%) of indolo[1,7-*ab*][1]benzazepine (**1**) as yellow crystals, mp 113-114°; uv (methanol): λ max 206 nm (32,300), 218 (34,640), 261 (24,580), 271 (28,930), 282 (19,530), 292 (21,210); λ min 209 (31,900), 243 (9,500), 265 (22,750), 277 (17,360), 287 (16,980); nmr (deuteriochloroform): δ 7.31 (1H, d, 1-H, J = 3.7 Hz), 6.40-7.20 (7H, m, aryl), 6.40 (1H, d, 2-H, J = 3.7 Hz), 5.86 (1H, d, CH=, J = 11.8 Hz), 5.75 (1H, d, CH=, J = 11.8 Hz); ms: m/e (%) 217 (100), 189 (30).

Anal. Calcd. for $C_{16}H_{11}N$: C, 88.43; H, 5.10; N, 6.45. Found: C, 88.64; H, 5.16; N, 6.35.

II.

A dried toluene extract containing **2** from hydrolysis of 3.09 g (10 mmoles) of **3** was concentrated to 150 ml and stirred, without further purification, with 10.0 g of 5Å Molecular sieve. The mixture was filtered, the residue washed with toluene, 4.0 g of fresh sieve was added and the mixture was stirred an additional 32 hours. Evaporation of the solvent and chromatography of the residue gave 0.99 g (46%) of **1**.

Acknowledgement.

We thank Mr. Brian Weck for obtaining the uv spectrum. This research was supported in part by National Institute of Health Grant #N514997.

REFERENCES AND NOTES

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(6) Infrared spectra were recorded on a Beckman Ir-33 spectrophotometer. Nmr spectra were recorded on a Varian EM360L spectrometer using tetramethylsilane as an internal standard and the mass spectra on a Varian MAT311A double focusing mass spectrometer. The melting point is uncorrected and was determined on a Thomas-Hoover capillary melting point apparatus. Microanalysis were performed by the University Analytical Center, Tucson, Arizona. Uv spectra were recorded on a Cary 14UV visible spectrophotometer.