Synthesis of 1-Bromo-2-ethoxycyclopent[*d*]azepine. A Route to Cyclopent[*d*]azepine[1]

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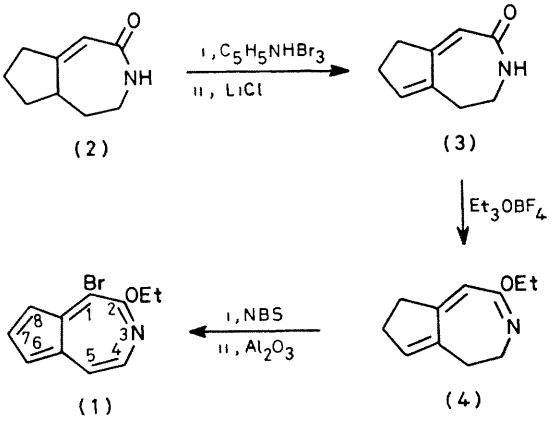
Summary The first derivative, 1-bromo-2-ethoxycyclopent[*d*]azepine, of the as yet unknown cyclopent[*d*]-azepine can be synthesized by dehydrogenation of 4,5,7,8-tetrahydro-2-ethoxycyclopent[*d*]azepine

THE similarities and differences in the behaviour of azulene and aza-azulenes are of interest[1,2] We now report the synthesis of the novel 1-bromo-2-ethoxycyclopent[*d*]-azepine (**1**)

The reaction sequence is outlined in the Scheme Compound (**2**) was prepared by the method of Duong *et al*[3] Bromination of (**2**) with 1 1 mol equiv of pyridinium bromide perbromide in acetic acid at 40 °C for 4 h, followed by dehydrobromination of the corresponding bromide (m p 105—106 °C) using LiCl in dimethylformamide (DMF) at 80 °C for 1 h, produced compound (**3**)† as colourless crystals in 50% yield, m p 112—114 °C (from light petroleum, i r (Nujol) 3180, 3040, 1640, and 1600 cm^{-1} ‡ *O*-Ethylation of (**3**) with Et_3OBF_4 led to the isolation of the ethoxy-compound (**4**) in 80% yield, as a pale brown oil, i r (Nujol) 2980, 2940, 2840 1645, and 1625 cm^{-1} †‡ Bromination of (**4**) with 1.1 mol equiv of *N*-bromosuccinimide (NBS) in $CHCl_3$ at 40 °C in the presence of a catalytic amount of benzoyl peroxide for 1 5 h,[4] followed by dehydrobromination of the corresponding bromide *in situ* on basic alumina, produced crude (**1**) in 4% yield It was purified by silica gel chromatography with CCl_4 as eluant to give the photo-sensitive sapphire blue (**1**), m p 45—47 °C (from CCl_4); M^+ (70 eV) *m/e* 250 9934 and 252·9888 ($C_{11}H_{10}$-



SCHEME

† The dehydrogenation of (**3**) and (**4**) with 2 3-dichloro 5 6 dicyanobenzoquinone produced complex, tarry mixtures The dehydrobromination of the bromide of (**3**), which was prepared by the bromination of (**3**) (1 1 equiv of NBS, benzoyl peroxide), with LiCl in DMF or potassium t-butoxide in tetrahydrofuran also produced uncharacterized products

‡ Satisfactory elemental analyses (C H, and N) were obtained for (**1**), (**3**), and (**4**)

BrNO requires *m/e* 250·9945 and 252·9925);‡ i.r.(Nujol) 1563, 1291, 1255, 1195, 1100, 1039, 875, 822, and 755 cm^{-1}.

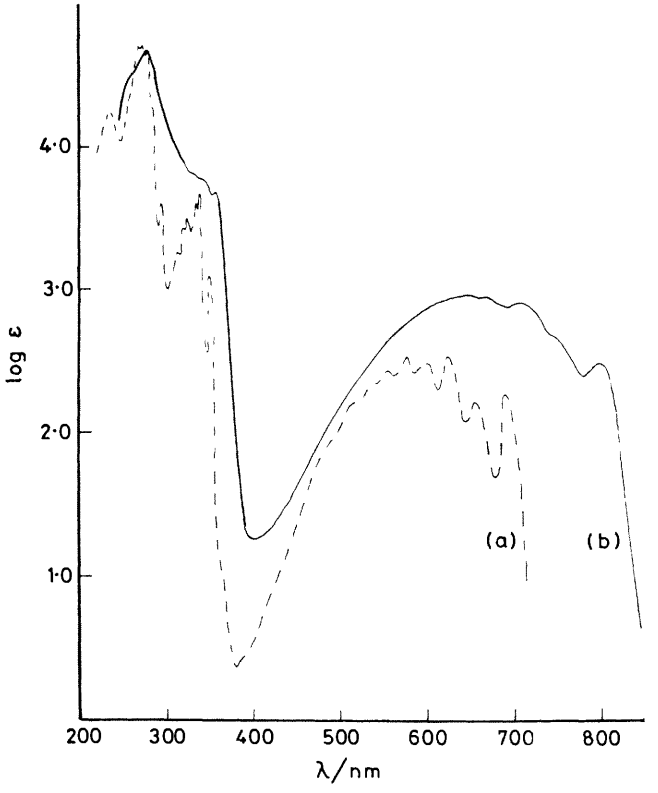


FIGURE. Electronic spectra: (a) azulene in heptane (ref. 6); (b) (**1**) in cyclohexane.

In the ^1H n.m.r. spectrum of (**1**) in CCl_4, the range of chemical shifts of the perimeter protons is almost the same as that of the protons in azulene.[5] This may well indicate the existence of a diamagnetic 10π electron ring current in (**1**). The three double doublets at δ 7·12 (q, $J_{6,7}$ 3·0, $J_{6,8}$ 1·5 Hz), 7·50 (q, $J_{7,8}$ 5·0, $J_{8,6}$ 1·5 Hz), and 7·92 (q, $J_{6,7}$ 3·0, $J_{7,8}$ 5·0 Hz) correspond in coupling pattern and chemical shift to the signals ascribed to H-8, H-6, and H-7, respectively. The H-4 and H-5 resonances were assigned from their coupling constants and coupling pattern expected from other aza-azulenes.[2] H-4 and H-5 resonate at δ 7·58 (d, $J_{4,5}$ 7·0 Hz) and 7·81 (d, $J_{5,4}$ 7·0 Hz), respectively, and the resonances at δ 1·47 (t, *J* 7·4 Hz) and 4·38 (q, *J* 7·4 Hz) correspond to the 2-ethoxy group. The lack of a resonance which can reasonably be ascribed to H-1 indicates that this position is substituted by bromine, and this is supported by the *peri* deshielding effect on H-8 due to the bromine atom at C-1.

The electronic spectrum of (**1**) in cyclohexane (Figure) resembles that of azulene.[6] The nitrogen atom, ethoxy-group, and bromine atom cause a bathochromic shift of 100 nm of the absorption maxima in the visible region compared with azulene, while in the u.v. region the shifts are small. A theoretical calculation predicts that replacement of the appropriate CH of azulene by nitrogen should effect a bathochromic shift of the longest wavelength absorption in cyclopent[*d*]azepine.[1,7] The electronic spectrum of (**1**) agrees reasonably with this tendency.

We are indebted to Professor S. Morosawa for encouragement.

(*Received*, 23*rd June* 1980; *Com.* 678.)

§ The high-resolution mass spectrum of (**1**) was measured on a JEOL JMS-D300 mass spectrometer on-line with JMA-2000 mass data system.

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