Four Isomers of Monobromo-2-stilbazole

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(Received November 30, 1965)

Monobromo-2-stilbazole, Ph–(CH=CBr)–Py-2, is expected to have four isomers: *cis*- and *trans*-2-(α-bromostyryl)-pyridine, Ph–CBr=CH–Py-2 and *cis*- and *trans*-2-(β-bromostyryl)-pyridine, Ph–CH=CBr–Py-2. However, only one species (m. p. 74—75°C) has been obtained by the dehydrobromination of 2-stilbazole dibromide,[1-3] its structure had not yet been established. The three other possible but unknown isomers have now been prepared in our laboratory, after which the structures and configurations of all the isomers have been established:

cis-2-(α-bromostyryl)-pyridine,
Ph–CBr=CH–Py-2 (I)

trans-2-(α-bromostyryl)-pyridine,
Ph–CBr=CH–Py-2 (II)

cis-2-(β-bromostyryl)-pyridine,
Ph–CH=CBr–Py-2 (III)

trans-2-(β-bromostyryl)-pyridine,
Ph–CH=CBr–Py-2 (IV)

I was prepared by the dehydrobromination of *threo*-2-stilbazole dibromide. Colorless prisms, m. p. 146.5—147.2°C (Found: Br, 31.08. Calcd. for $C_{13}H_{10}NBr$: Br, 30.73%). UV in heptane: 242 mμ (log ε, 3.90), 290 mμ (3.57). II was prepared either by the action of phosphorus pentabromide upon 2-phenacylpyridine, Ph–CO–CH_2–Py-2, or by hydrogen bromide addition to 2-tolazole, Ph–C≡C–Py-2. Liquid, b. p. 123°C/3 mmHg, n_D^{25} 1.6638. (Found: C, 59.93; H, 3.94; N, 5,50; Br, 30.55. Calcd. for $C_{13}H_{10}NBr$: C, 60.02; H, 3.87; N, 5.38; Br, 30.73%). UV: 220 mμ (4.05), 292 mμ(4.31). III was prepared by the dehydrobromination of *erythro*-2-stilbazole dibromide. Colorless prisms, m. p. 72.7—74.5°C. (Found: C, 60.06; H, 3.98; N, 5.57; Br, 30.69%). UV: 230 mμ (4.12), 286 mμ(3.89). IV was prepared by the action of phosphorus pentabromide upon 2-Pyridyl benzyl ketone, Ph–CH_2–CO–Py-2. Liquid, b. p. 127°C/3 mmHg, n_D^{25} 1.6710. (Found: C, 59.99, H, 4.06; N, 5.34; Br, 30.96%). UV: 223 mμ (4.17), 303 mμ(4.38).

The above-described structures of these isomers were established by the following experiments. (a) The process of preparing II and IV using pentabromide on the –CO–CH_2-group suggests that the bromine atom is combined with α-carbon in II and with β-carbon in IV respectively, and that they are both trans isomers. (b) III is the main product of the dehydrobromination of *erytho*-dibromide in an alcoholic potassium hydroxide solution and is supposed to be cis form as the result of trans elimination. (c) I and III are converted into II and IV respectively when heated at 200°C, while the reverse reactions from II and IV do not occur under the same conditions. (d) All isomers are converted into 2-tolazole by further dehydrobromination. The reactions of I and III are by far slower than those of II and IV. (e) By the reduction of bromine with zinc, II and IV are converted into *trans*-2-stilibazole, Ph–CH=CH–Py-2, almost quantitatively, while I and III are converted into *cis* 2-stilbazole. (f) The bathochromic shifts and remarkable increases in the absorption intensity occur as usual on passing from the cis isomers to the trans isomers.

A cis isomer usually melts at a much lower temperature than a trans isomer does, but in this case the cis isomers are crystal and the trans isomers are liquid. It is also interesting to note that the cis isomer I was the main product obtained from *threo*-dibromide, because the trans elimination of *threo*-dibromide generally gives the trans isomer.

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