SUBSTITUTED PYRIDINES. 2, 5-DIMETHYL-4-STYRYL- AND -4-PHENYLETHYNYLPYRIDINES

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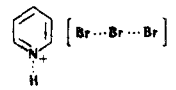
2, 5-Dimethyl-4-styrylpyridine and 2, 5-dimethyl-4-phenylethynylpyridine are prepared from 2, 5-dimethyl-4-β-phenylethylpyridine. Hydration of the second of these compounds gives ω-(2, 5-dimethylpyridyl-4)acetophenone.

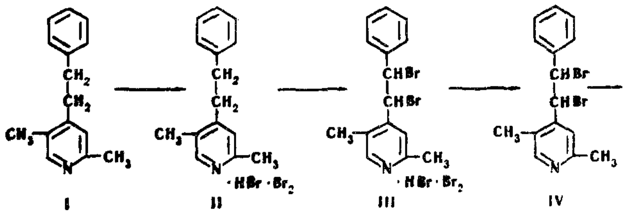
2, 5-Dimethyl-4-β-phenylethylpyridine I, previously described by us, is of interest as a starting compound for synthesizing pyridine bases of unsaturated character, with unsaturated substituents, and particularly for preparing substituted stilbazoles. It may also be of value for synthesizing condensed heterocyclic systems containing nitrogen.

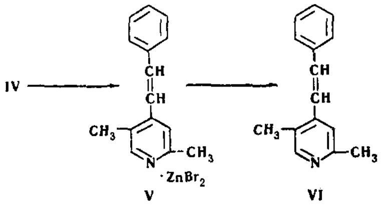
A study has been made of the bromination of 2, 5-dimethyl-4-β-phenylethylpyridine (I). The complex compound II, obtained by reaction of the hydrobromide of pyridine base I with bromine, was brominated. So far there are no explanations regarding structure and type of bond in such complexes, and basically only their compositions are known. Bromine is known to form comparatively stable complexes with pyridine bases, the stabilities of the complexes also depending on the structures of the pyridine bases. It is [2] assumed that these compounds are donor-acceptor complexes, which undergo charge-distributing absorption, and are formed from an organic cation and an inorganic anion.



The pyridine hydrobromide-bromine base is decomposed by heat and by UV light. It was also observed that recrystallization of II from chloroform led to its partial decomposition. The bromination was carried out in acetic acid with irradiation with UV light, at 85° C, to give a 25% yield of compound III, a complex between 1, 2-dibromo-1-phenyl-2-(2', 5'-dimethylpyridyl-4')ethane and bromine. The same compound III is obtained by treating pyridine base I with bromine in carbon tetrachloride while irradiating with UV light.

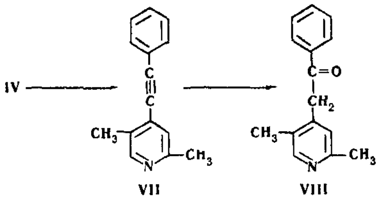
Decomposition of complex III with aqueous sodium carbonate solution gives 1, 2-dibromo-1-phenyl-2-(2', 5'-dimethylpyridyl-4')ethane (IV). Heating the latter with zinc dust in ethanol gave complex V, 2, 5-dimethyl-4-styrylpyridine-zinc bromide, decomposed by potassium hydroxide to 2, 5-dimethyl-4-styrylpyridine VI.





The UV spectrum of 2, 5-dimethyl-4-styrylpyridine VI resembles that of 4-styrylpyridine [3] (λ_{max} 305 nm).

Ethanolic potassium hydroxide didehydrobrominated 1, 2-dibromo-1-phenyl-2-(2', 5'dimethylpyridyl-4')-ethane (IV).



The resultant 2, 5-dimethyl-4-phenylethynylpyridine (VII) was then hydrated to ω-(2, 5-dimethylpyridyl-4)-acetophenone (VIII).

EXPERIMENTAL

1, 2-Dibromo-1-phenyl-2-(2', 5'-dimethylpyridyl-4')ethane (IV). 7.6 g (0.048 mole) Bromine was added to a stirred solution of 5 g (0.024 mole) 2, 5-dimethyl-4-β-phenylethylpyridine I in 200 ml CCl_4. The mixture was refluxed and illuminated with UV light for 3 hr. The precipitate formed was recrystallized from $CHCl_3$. Yield 3.4 g complex III, mp 187°–189° C (decomp). Found: Br 65.76; 65.66; N 2.45; 2.36%, calculated for $C_{15}H_{15}Br_2N \cdot HBr \cdot Br_2$: Br 65.54; N 2.29%.

Treatment of 3.4 g complex III with Na_2CO_3 solution, followed by extraction with ether, gave 2.6 g IV, colorless crystals, mp 131°–133° C (ex heptane). Found: Br 42.99; 43.09; N 3.65; 3.57%, calculated for $C_{15}H_{15}Br_2N$: Br 43.32; N 3.79%.

The complex 2, 5-dimethyl-4-β-phenylethylpyridine-hydrobromide-bromine was prepared for comparison. HBr gas was led into a solution of 2.3 g (0.011 mole) I in 70 ml ether, to give 2.7 g hydrobromide of pyridine base I, forming colorless crystals, mp 159°–162° C (ex EtOAc-MeOH). Found: N 4.79; 4.80%, calculated for $C_{15}H_{17}N \cdot HBr$: N 4.79%.

A solution of 4.4 g (0.028 mole) bromine in 10 ml AcOH was poured into a solution of 8 g (0.027 mole) 2, 5-Dimethyl-4-β-phenylethylpyridine I in 50 ml glacial AcOH. Recrystallization of the resultant precipitate from $CHCl_3$ gave 10.4 g complex II, as yellow crystals mp 122.5°–124° C (decomp). Recrystallization of the complex was found to lead to decomposition.

2, 5-Dimethyl-4-styrylpyridine (VI). 1 g (1.6 mM) Complex III and 1.1 g (0.017 g at) Zn dust in 30 ml absolute EtOH were refluxed together for 6 hr. The EtOH was distilled off, and the residue washed with hot $CHCl_3$. Removal of the $CHCl_3$ by distillation gave 0.45 g complex V, 2, 5-dimethyl-4-styrylpyridine-$ZnBr_2$, as colorless crystals mp 247°–250° C. Found: N 3.25; 2.90%, calculated for $C_{15}H_{15}N \cdot ZnBr_2$: N 3.22%.

0.45 g (1 mM) Complex V was boiled with 15% aqueous KOH, then the organic bases extracted with ether. The ether extracts gave 0.13 g VI, as colorless crystals, mp 86°–88° C (ex heptane). Found: C 85.79; 86.19; H 7.51; 7.03; N 6.36; 6.43%, calculated for $C_{15}H_{15}N$: C 86.12; H 7.17; N 6.69%.

The UV spectra of 2, 5-dimethyl-4-β-phenylethylpyridine (I) and 2, 5-dimethyl-4-styrylpyridine (VI) showed absorption bands at 268 and 305 nm respectively. Displacement of an absorption band towards the longer wavelength region with VI compared with I, is due to conjugation of an ethylenic double bond with aromatic radicals [4].

2, 5-Dimethyl-4-phenylethynylpyridine (VII). 6.7 g (0.023 mole) IV and 10 g (0.18 mole) KOH in 100 ml MeOH were refluxed together for 4 hr. After distilling off the MeOH, 30 ml water was added, and the reaction products extracted with ether. The ether extracts gave 5.15 g VII as colorless crystals, mp 90°–92° C (ex petrol ether). Found: C 86.55; 87.43; H 6.31; 6.39; N 6.68; 6.54%, calculated for $C_{15}H_{13}N$: C 86.95; H 6.28; N 6.76%.

The IR spectrum of VII had a weak band at 2220 cm^{-1}, characteristic of the structural type Ar—C≡C—Ar [5].

ω-(2, 5-Dimethylpyridyl-4)acetophenone (VIII). 2.6 g (0.013 mole) VII, 48 ml 52% H_2SO_4, and 0.4 g basic mercuric sulfate were stirred and heated together for 6 hr on a steam bath. The products were first treated with 50 ml 10% Na_2CO_3 solution, then saturated with crystalline Na_2CO_3. The organic bases were extracted with ether. After removing the ether from the extracts, the residue (2.6 g) was recrystallized from heptane, and gave VIII, mp 108°–110° C. Found: C 80.16; 80.12; H 6.51; 6.61; N 5.91; 5.81%, calculated for $C_{15}H_{15}NO$: C 80.00; H 6.66; N 6.22%.

The IR spectrum of VIII showed an intense band at 1681 cm^{-1}, due to valence vibrations of the C≡O group conjugated with the aromatic radical [5].

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