CROTYLATION OF 2-SODIOOXYPYRIDINE

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2-Sodiooxypyridine reacts with crotyl bromide in ethanol or benzene to form 1-crotylpyrid-2-one.

In the reaction of metal derivatives of 2-hydroxypyridine with alkyl halides, N- and O-alkylation take place simultaneously [1]. The simultaneous formation of lactim and lactam derivatives is also observed in the allylation of 2-sodiooxypyridine with allyl chloride and bromide [2]. By analogy with this, the reaction of 2-sodiooxypyridine with crotyl bromide might be expected to give 2-crotyloxypyridine and N-crotylpyrid-2-one.

2-Sodiooxypyridine reacts with crotyl bromide in ethanolic solution with the migration of the reaction center to form only 1-crotylpyrid-2-one. The expected 2-crotyloxypyridine was not detected. The crotylation of 2-sodiooxypyridine in a nonpolar solvent, benzene, also gives only 1-crotylpyrid-2-one.

For identification, the 1-crotylpyrid-2-one was hydrogenated. The hydrogenation product had constants similar to those of the 1-butylpyrid-2-one synthesized by the reaction of 2-sodiooxypyridine with butyl bromide and differed markedly from the 2-butoxypyridine obtained by the reaction of 2-bromopyridine with sodium butoxide.

In addition, the structure of the 1-crotylpyrid-2-one obtained was confirmed by its IR spectrum, which had a strong band at 1660 cm^{-1} (C=O).

EXPERIMENTAL

1-Crotylpyrid-2-one. 15 g (0.13 mole) of 2-sodiooxypyridine, 35 ml of absolute ethanol, and 20 g (0.15 mole) of freshly distilled crotyl bromide (bp 104–107° C, d_4^{20} 1.3344; n_D^{20} 1.4820) [3,4] were mixed. After the end of the vigorous reaction, the mixture was boiled for another 3.5 hr. After cooling, the precipitate of sodium bromide was filtered off and the ethanol and the excess of crotyl bromide was distilled off from the filtrate. The residue was treated with conc NaOH solution and a small amount of water. The upper layer was separated off and the lower layer was twice extracted with benzene. The benzene extract and the upper layer were combined and dried with potassium carbonate. After the benzene had been driven off distillation of the residue in vacuum yielded 8.1 g (43%) of 1-crotylpyrid-2-one in the form of a light yellow oil. Bp 114–115° C (1.5 mm); d_4^{20} 1.0575; n_D^{20} 1.5560. Found, %: N 9.25, 9.36; mol. wt . 147.0, 145.0; MR_D 45.04. Calculated for $C_9H_{11}NO$, %: N 9.39; mol. wt. 149.2; MR_D 44.11. Picrate – mp 107.5–108.5° C (from ethanol). 1-Crotylpyrid-2-one is soluble in ethanol, benzene, and water.

The crotylation of 2-sodiooxypyridine in dry benzene was carried out similarly. The reaction mixture was boiled for 4.5 hr. The yield of 1-crotylpyrid-2-one was 49%. No 2-crotyloxypyridine was detected in the reaction products.

1-Butylpyrid-2-one. A) 1-Crotylpyrid-2-one was hydrogenated in the presence of Raney nickel catalyst in ethanolic solution at normal pressure and room temperature. The catalyst was filtered off and the ethanol was evaporated off, after which vacuum distillation yielded 1-butylpyrid-2-one. Yield 72%. Bp 106–107° C (1 mm); d_4^{20} 1.0252; n_D^{20} 1.5320. Found, %: N 9.20, 9.03; mol. wt. 157.4, 158.2; MR_D 45.70. Calculated for $C_9H_{13}NO$, %: N 9.27; mol.wt. 151.2; MR_D 44.58. Picrate–mp 105–106° C (from ethanol).

B) A mixture of 15 g (0.13 mole) of 2-sodiooxypyridine, 19.25 g (0.14 mole) of butyl bromide, and 25 ml of absolute ethanol was boiled for 2.5 hr. After cooling, the precipitate of sodium bromide was filtered off and the ethanol was evaporated off. The residue was distilled in vacuum, giving two fractions. The first consisted of 2-butoxypyridine in the form of a colorless mobile liquid insoluble in water. Yield 1.98 g (10.2%). Bp 48.5–51° C (1.5 mm); d_4^{20} 0.9702; n_D^{20} 1.4899. Found, %: N 9.17, 9.06%; mol. wt. 149.5; 147.9; MR_D 45.06. Calculated for $C_9H_{13}NO$, %: N 9.27; mol. wt. 151.2; MR_D 45.74. It did not form a picrate. The second fraction consisted of 1-butylpyrid-2-one in the form of a colorless oily liquid. Yield 11.8 g (60.9%). Bp 106–107° C (1 mm); d_4^{20} 1.0259; n_D^{20} 1.5320. Picrate, mp 104.5–106° C (from ethanol).

2-Butoxypyridine. 3.2 g (0.14 g-at) of sodium was dissolved in 25 g (0.33 mole) of butanol, and then 15 g (0.1 mole) of 2-bromopyridine (bp 192–194° C [5]) was added. The reaction mixture was heated until Beilstein's halogen test was negative. After cooling, the sodium bromide was filtered off and the butanol was distilled off. The vacuum distillation of the residue yielded 2-butoxypyridine in the form of a colorless mobile liquid. Yield 6.68 g (46.5%). Bp 39–40.5° C (0.5 mm); d_4^{20} 0.9704; n_D^{20} 1.4900. Found, %: N 9.20, 9.12; mol. wt. 150.3, 149.1; MR_D 45.05. Calculated for $C_9H_{13}NO$, %: N 9.27%; mol. wt. 151.2; MR_D 45.74. It did not form a picrate. The 2-butoxypyridine obtained was identical with the substance isolated in the butylation of 2-sodiooxypyridine.

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