The hydrochloride obtained from the aqueous and ether portions of two such runs was decomposed with 20 g. of 50% potassium hydroxide solution and the free amine boiled at 125–145°, mainly at 138°. Only 0.4 g. was obtained.

Titration. Subs., 0.1910: 26.7 cc. of $N/14$ HCl. Calcd. for $C_6H_{11}N$, neutral equivalent: 97.1; found, 100. The physical constants on this sample were: n_D^{20}, 1.4807; d_4^{20}, 0.9342; M_D, calcd., 31.00; found, 29.85.

β-Vinyl Piperidine.—Using a procedure identical with that described above, 12.4 g. of 2-β-piperidylethanol-1 was dehydrated. The hydrochloride came down as a gummy mass. The yield of free base, b. p. 152–155°, was 1.4 g. (13% of the theoretical amount).

Titration. Subs., 0.0824: 6.41 cc. of 0.1138 N HCl. Calcd. for $C_7H_{13}N$: neutral equivalent, 111.1; found, 113.2.

β-Vinyl piperidine of this purity has the following physical constants: $n_D^{25} = 1.4731$; $d_4^{25} = 0.9274$; M_D, calcd., 35.62; found: 33.61.

The chloroplatinate separated as a gummy solid from water but crystallized from 70% alcohol. The product darkened at 220° and melted with decomposition at 223–224°.

Anal. Subs., 0.1535, 0.0502: Pt, 0.0452, 0.0147. Calcd. for $(C_7H_{13}N)_2.H_2PtCl_6.2H_2O$: Pt, 29.27. Found: Pt, 29.5.

Summary

β-Vinyl piperidine has been prepared from β-piperidyl carbinol and most of the intermediate products have been isolated and characterized.

URBANA, ILLINOIS

[CONTRIBUTION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF THE STATE UNIVERSITY OF IOWA]

FURTHER OBSERVATIONS CONCERNING THE MIGRATION OF ACYL FROM NITROGEN TO OXYGEN

BY L. CHAS. RAIFORD AND F. C. MORTENSEN

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Studies published from this Laboratory[1] have shown that, in general, but one acetyl-benzoyl derivative of an ortho-aminophenol can be obtained, regardless of the order in which the radicals are introduced.[2] When one of the reacting groups (amino and hydroxyl) is on a side chain, as in *o*-hydroxybenzylamine and its isomeride, *o*-aminobenzyl alcohol, isomeric mixed diacyl derivatives were obtained and no rearrangement was observed.[3] This behavior, as well as the results reported by Auwers and co-workers[4] to the effect that they observed a rearrangement in which acyl wandered from oxygen to nitrogen when oxygen was attached to the ring and nitrogen was on a side chain, raised the question of the extent to which this migration is influenced by the cyclic radical of the starting

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[1] Raiford and Lankelma, THIS JOURNAL, **47**, 1111 (1925).

[2] For exceptions, see Raiford and Couture, *ibid.*, **46**, 2307 (1924).

[3] Raiford and Clark, *ibid.*, **45**, 1738 (1923).

[4] Auwers and others, *Ber.*, **33**, 1923 (1900).

material. That the particular structure of the latter cannot be the sole cause of the migration seems probable, for it has been observed in naphthalene[5] as well as in benzene derivatives. Thus Armstrong[6] was able to obtain but one acetyl-benzoyl derivative from 1-amino-2-naphthol and its halogenated substitution products, while Raiford and Clark[7] found that acetylation of 8-benzoylamino-1-naphthol and benzoylation of 8-acetylamino-1-naphthol gave but one product, and that this had the benzoyl radical attached to nitrogen.

In the experiments recorded below, one of the bases used was *o*-aminocyclohexanol,[8] which differs from *o*-aminophenol to the extent that it is a cycloparaffin instead of a benzene derivative. The second was α-aminobenzyl-2-naphthol, m. p. 125°,[9] in which the amino radical was attached to a side chain. Though the acyl radicals were introduced in both possible orders in each instance, no rearrangement was observed.

Experimental Part

A. Derivatives of *o*-Aminocyclohexanol

2-Benzoylaminocyclohexanol.—This was prepared in 97% yield by treatment of *o*-aminocyclohexanol in caustic alkali solution with 1.5 molecular proportions of benzoyl chloride in the usual way. Crystallization from benzene gave nearly colorless, short needles, m. p. 168–169°.

Anal. Subs., 0.1372, 0.2011: CO_2, 0.3583; H_2O, 0.0923; 9.20 cc. of 0.1 *N* acid. Calcd. for $C_{13}H_{17}O_2N$: C, 71.23; H, 7.76; N, 6.39. Found: 71.20, 7.40, 6.40.

2-Benzoylaminocyclohexyl Benzoate.—Six g. of the above-described product was dissolved in 25 cc. of pyridine and treated with 1.5 molecular proportions of benzoyl chloride as directed by Einhorn and Hollandt.[10] A yield of 93% was obtained. Portions crystallized from benzene and alcohol, respectively, separated in colorless needles, m. p. 204–205°.

Anal. Subs., 0.3211, 0.5002: CO_2, 0.8637; H_2O, 0.1897; 15.64 cc. of 0.1 *N* acid. Calcd. for $C_{20}H_{21}O_3N$: C, 74.30; H, 6.50; N, 4.33. Found: 73.34, 6.56, 4.37.

Hydrolysis of the Dibenzoyl Derivative.—When 3.5 g. was warmed with 16 cc. of alcoholic potassium hydroxide containing 1.5 molecular proportions of the alkali, all was dissolved. After thirty minutes the liquid was neutralized with concentrated hydrochloric acid, the potassium chloride filtered off, the filtrate concentrated and allowed to

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[5] It is well known that many naphthalene derivatives show a behavior similar to that of an aliphatic rather than that of a true benzene compound [Graebe, *Ber.*, **13**, 1849 (1880); Liebermann and Hagen, *Ber.*, **15**, 1427 (1882)].

[6] Armstrong, unpublished report.

[7] Raiford and Clark, THIS JOURNAL, **48**, 483 (1926).

[8] This product, m. p. 65°, corresponds to that first prepared by Brunel [*Compt. rend.*, **137**, 198 (1903)] and recorded by Richter as the *cis* form. Senderens and Aboulenc [*ibid.*, **177**, 160 (1923)] obtained by reduction of *o*-aminophenol, in presence of nickel, what they regarded as a mixture of the *cis* and *trans* forms. No record of the pure *trans* form was found.

[9] Betti [*Gazz. chim. ital.*, **36**, II, 392 (1906)] recorded 124° for the racemic form.

[10] Einhorn and Hollandt, *Ann.*, **301**, 101 (1898).

stand overnight. The solid deposited represented a yield of 90%. Crystallization from benzene gave needles, melting at 168–169°, which were identified by mixed melting point as 2-benzoylaminocyclohexanol.

2-Benzoylaminocyclohexyl Acetate.—Ten g. of the *N*-benzoyl derivative was acetylated by Liebermann and Hörmann's[11] method. A yield of 84% was obtained. Crystallization from 50% alcohol gave nearly colorless plates, m. p. 143–144°.

Anal. Subs., 0.3192, 0.2008: CO_2, 0.8045; H_2O, 0.2087; 7.6 cc. of 0.1 *N* acid. Calcd. for $C_{15}H_{19}O_3N$: C, 68.96; H, 7.28; N, 5.36. Found: 68.73, 7.26, 5.29.

Hydrolysis of the above-described product caused the loss of the acetyl radical. The *N*-benzoyl derivative, m. p. 168–169°, was recovered to the extent of 87%.

2-Acetylaminocyclohexyl Acetate.—This product was obtained by heating a mixture of equal weights of the free base and anhydrous sodium acetate with an excess of acetic anhydride for a few minutes. The crystalline mass that formed on cooling was dissolved in water, extracted with ether, the extract dried with anhydrous sodium sulfate and the ether distilled off. The residue was purified by treatment of its benzene solution with ligroin (b. p. 70–80°) which gave irregularly shaped crystalline masses, m. p. 117–118°.

Anal. Sub., 0.1941, 0.1999: CO_2, 0.4290; H_2O, 0.1480; 10.09 cc. of 0.1 *N* acid. Calcd. for $C_{10}H_{17}O_3N$: C, 60.30; H, 8.54; N, 7.03. Found: 60.27, 8.47, 7.06.

The diacetyl derivative was hydrolyzed with alcoholic potassium hydroxide, as indicated above. After neutralization by hydrochloric acid and removal of potassium chloride, the filtrate was concentrated to one-third its volume and allowed to stand. A yield of 81% of the *N*-acetyl derivative separated. Crystallization from benzene gave needles that melted at 314–315° and which were identical with the mono-acetyl compound prepared directly from the free base by Lumière and Barbier's[12] method.

2-Acetylaminocyclohexyl Benzoate.—One g. of the *N*-acetylaminohexanol dissolved in 10 cc. of water containing 0.4 g. of sodium hydroxide was mixed with 1.5 molecular proportions of benzoyl chloride, the mixture shaken for thirty minutes and allowed to stand for twelve hours; yield, 81%. After recrystallization from benzene, the product melted at 198–199°.

Anal. Subs., 0.3180, 0.2004: CO_2, 0.8022: H_2O, 0.2074; 7.70 cc. of 0.1 *N* acid. Calcd. for $C_{15}H_{19}O_3N$: C, 68.96; H, 7.27; N, 5.36. Found: 68.79, 7.24, 5.38.

This diacyl derivative was hydrolyzed with alcoholic potassium hydroxide as described above and the filtrate left after removal of potassium chloride was evaporated until crystals appeared. Recrystallization from benzene gave needles that melted at 313–315° and which were identified as 2-acetylaminocyclohexanol.

B. Derivatives of α-Aminobenzyl-2-naphthol

α-Acetylaminobenzyl-2-naphthyl Benzoate.—One g. of α-acetylaminobenzyl-2-naphthol,[13] m. p. 240–241°, dissolved in pyridine, was treated with excess of benzoyl chloride as directed by Einhorn and Hollandt.[14] A yield of 75% was obtained. Crystallization from alcohol gave nearly colorless needles, m. p. 176–177°.

Anal. Subs., 0.1010: 2.57 cc. of 0.1 *N* acid. Calcd. for $C_{26}H_{21}O_3N$: N, 3.54. Found: 3.56.

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[11] Liebermann and Hörmann, *Ber.*, **11**, 1619 (1878).

[12] Lumière and Barbier, *Bull. soc. chim.*, **33**, 784 (1905).

[13] This material was obtained by following the series of preparations described by Betti, *Gazz. chim. ital.*, **33**, I, 7 (1903), who recorded 236–237° as the melting point.

[14] Einhorn and Hollandt, *Ann.*, **301**, 95 (1898). The Schotten-Baumann method was not successful in this case.

Hydrolysis of the above product gave the *N*-acetyl naphthol from which the diacyl derivative was prepared.

α-Benzoylaminobenzyl-2-naphthyl Benzoate.—This product was obtained in 96% yield from the corresponding aminonaphthol by the Schotten-Baumann method when an excess (4 molecular proportions) of benzoyl chloride was used. Crystallization from benzene gave fawn-colored nodules, m. p. 118–119°.

Anal. Subs., 0.2012: 4.42 cc. of 0.1 *N* acid. Calcd. for $C_{31}H_{23}O_3N$: N, 3.06. Found: 3.07.

Hydrolysis of the dibenzoyl derivative gave an almost quantitative yield of a phenolic product which, after crystallization from alcohol, melted at 240–241°.[15] The same product was obtained in the present work by benzoylation of the hydrochloride of the corresponding aminonaphthol with 2 molecular proportions of benzoyl chloride. Analysis indicated a monobenzoyl derivative.

Anal. Subs., 0.2005: 5.72 cc. of 0.1 *N* acid. Calcd. for $C_{24}H_{19}O_2N$: N, 3.96. Found: 3.99.

α-Benzoylaminobenzyl-2-naphthyl Acetate.—Ten g. of the corresponding *N*-benzoylaminonaphthol and an equal weight of anhydrous sodium acetate were warmed for ten minutes with 25 cc. of acetic anhydride. Water was added to the cold mixture and the solution extracted with ether. The residue after distillation of the ether was purified by pouring its alcoholic solution into water with rapid stirring. Nearly colorless needles separated; yield, 90%; m. p. 118–119°.

Anal. Subs., 0.5027: 12.47 cc. of 0.1 *N* acid. Calcd. for $C_{26}H_{21}O_3N$: N, 3.54. Found: 3.47.

Hydrolysis of this product gave the benzoylaminonaphthol from which the diacyl derivative was obtained.

Summary

1. The acetyl-benzoyl derivatives of *o*-aminocyclohexanol were obtained in isomeric forms that showed no tendency to rearrange.

2. The observations made with mixed diacyl derivatives of α-aminobenzyl-2-naphthol indicate that the migration characteristic of ortho-aminophenols does not occur when one of the reacting groups is attached to a side chain. This confirms the conclusions previously reached.

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[15] Betti (ref. 13) recorded 224° for a compound obtained by action of benzoyl chloride on the benzylaminonaphthol, and which analyzed for a monobenzoyl derivative. A mixture of our product and α-acetylaminobenzyl-2-naphthol, m. p. 240–241°, melted at 218–223°.