respects with an authentic sample of 4-estrene-3,17-dione (4). The minor product was isolated in 5% yield and showed the following physical characteristics: mp 185–187 °C; ^{1}H NMR δ 0.93 (s, 3 H, C-18 Me), 5.99 (d, 1 H, J = 10 Hz, C-2 H), 7.08 (dd, 1 H, J = 10 Hz, J = 2 Hz, C-1 H). These data are essentially similar to those reported earlier[1] for 5β-estr-1-ene-3,17-dione (**5**).

Dehydrobromination of Compound 3 with $CaCO_3$/Dimethylacetamide. Compound **3** (50 mg) dissolved in dimethylacetamide (0.8 ml) was added portionwise to calcium carbonate (80 mg) in boiling dimethylacetamide (3 mL) during 3 min, and refluxing was continued for 15 min. Some of the solvent was distilled under vacuum; the residue was extracted with ether and washed with HCl and water. The ether was dried and evaporated and the residue streaked over silica gel plate as described above. Only one UV absorbing band was observed, which following elution gave 42 mg (84%) of pure product, which was found to be identical in all respects with 5β-estr-1-ene-3,17-dione (**5**).

Registry No. **1**, 5696-51-5; **3**, 102922-53-2; **4**, 734-32-7; **5**, 101469-27-6; **6**, 1229-12-5; **7**, 4588-83-4.

Effect of pH on the Regioselectivity of Pictet–Spengler Reactions of 3-Hydroxyphenethylamines with Formaldehyde and Acetaldehyde

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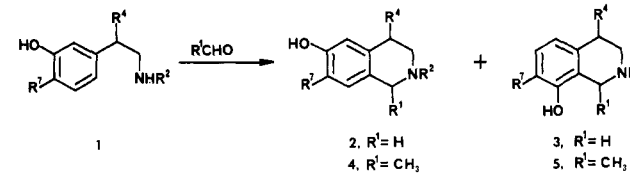
The Pictet–Spengler condensation of 3-alkoxyphenethylamines or 3-hydroxyphenethylamines **1** with aldehydes is widely utilized in the synthesis of tetrahydroisoquinolines[1] and also serves as the biosynthetic route to these alkaloids.[2] Cyclization has generally been reported to proceed para to the activating 3-alkoxy or 3-hydroxy group, thereby generating 6-alkoxy- or 6-hydroxytetrahydroisoquinolines (i.e. **2** or **4**), respectively.[1,3–5] With formaldehyde, cyclization ortho to the alkoxy or hydroxy group, forming 8-alkoxy- or 8-hydroxytetrahydroisoquinolines (i.e., **3**) has been reported to accompany para cyclization.[1,6–11] However very few instances of ortho cyclization with aldehydes other than formaldehyde have been reported.[8,9,12,13] and a systematic quantitative investigation of regioselectivity has not been performed.

We recently observed that condensation of norepinephrine (**1g**) and epinephrine (**1h**) with formaldehyde and acetaldehyde in neutral to mildly acidic aqueous solution affords 20–50% of the unexpected tetrahydro-4,7,8-isoquinolinetriols (**3g**, **3h**, **5g**, and **5h**) respectively, as well as the expected tetrahydro-4,6,7-isoquinolinetriols (**2g**, **2h**, **4g**, and **4h**).[8,9] We now report a systematic investigation of the regioselectivity of Pictet–Spengler condensations of a series of 3-hydroxyphenethylamines (**1**) with formaldehyde and acetaldehyde.

Results and Discussion

A series of 3-hydroxyphenethylamines **1** was treated with 8 equiv of aqueous formaldehyde or acetaldehyde at pH 2–8.5 at 20 °C. The reaction progress and product distribution were followed by thin-layer chromatography and liquid chromatography. In accord with Pictet–Spengler reactions of other 3-hydroxyphenethylamines,[1,5,8,9,13,14] the reaction rate was strongly influenced by pH. For example, the half-life for the reaction of **1d** with formaldehyde was 12 min at pH 2 and less than 1 min at pH 7. The half-life for the reaction of **1d** with acetaldehyde was 1.5 h at pH 2 and less than 1 min at pH 7. At pH 2, the yield of tetrahydroisoquinolines was nearly quantitative. At pH 7, the *N*-methyltetrahydroisoquinolines were obtained in high yields, while the yields of the N-unsubstituted tetrahydroisoquinolines were somewhat lower (60–80%) due to competing side reactions with excess aldehyde.[9]

The regioselectivities of the Pictet–Spengler cyclization of **1** (including those investigated previously[8,9]), determined by analytical liquid chromatography, are summarized in Table I as percentage of ortho cyclization. The regioselectivity is influenced only subtly by the aldehyde or the substituents on **1**. At pH 2, cyclization occurs exclusively or primarily para to the activating aromatic hydroxy group, affording **2** and **4**. At pH 5, significant cyclization ortho



1 2, R¹ = H; 4, R¹ = CH₃ 3, R¹ = H; 5, R¹ = CH₃

to the activating hydroxy group occurs, affording **3** and **5** as well as **2** and **4**. The amount of ortho cyclization is greatest at pH 7, and generally somewhat less at pH 8.5. Since the ratio of isomeric products does not vary significantly during the course of the reaction, selective destruction of one isomer apparently does not occur.

All of the tetrahydroisoquinoline products except **4b** and **5d** were previously known (see references in Table I) and were chromatographically and spectrally identical with

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0022-3263/86/1951-3061$01.50/0

Table I. Percentage of Ortho Pictet–Spengler Cyclization of 1 as a Function of pH

starting material 1	R^2	R^4	R^7	% ortho cyclization[b] pH 2	5	7	8.5	ref[a]
				$R^1CHO = CH_2O$				
a	H	H	H	13	39	50	20	18,19
b	Me	H	H	3	41	40	32	10,18,19,20
c	H	H	OH	0	7	20	7	18,21,22
d	Me	H	OH	0	20	20	5	22,23
e	H	OH	H	10	40	44	25	7,11
f	Me	OH	H	8	35	42	15	10
g	H	OH	OH		12	20		9,24
h	Me	OH	OH	5		50		8,24
				$R^1CHO = CH_3CHO$				
a	H	H	H	0	15	25	5	25
b	Me	H	H	5	40	40	30	20
c	H	H	OH	0	20	50	18	5,13
d	Me	H	OH	0	22	31	10	5
g	H	OH	OH			28		9,24
h	Me	OH	OH	15	50	26	34	8,24

[a] Literature references to authentic tetrahydroisoquinoline products. [b] $100 \times [3]/[2 + 3]$ or $100 \times [5]/[4 + 5]$.

authentic samples. Partial ortho cyclization had previously been reported for the Pictet–Spengler reactions of **1e** and **1f** with formaldehyde[7,10] and **1c** with acetaldehyde.[13] The Pictet–Spengler reaction of **1d** with acetaldehyde, however, had previously been reported to afford only **4d**.[5]

The high selectivity observed for cyclization para to the 3-hydroxy group of **1** at low pH is consistent with the high regioselectivity of the well-studied Pictet–Spengler reactions of 3-*alkoxy*phenethylamines which are generally conducted under acidic conditions.[1] Presumably in acidic solution a late transition state in the intramolecular electrophilic aromatic substitution by the iminium ion leads to highly regioselective ring closure at the less sterically demanding position, para to the activating hydroxy group. While it is conceivable that the product distribution under acidic conditions could be under thermodynamic control, this is not the case. Although the Pictet–Spengler reaction could, in principle, be reversible[15] no isomerization of **3** or **5** to **2** or **4** was observed under the reaction conditions, or even in the 6 M HCl solution used to prepare authentic **3** and **5**.

Under mildly acidic to mildly alkaline conditions, 3-hydroxyphenethylamines are able to cyclize by a different mechanism involving attack on the iminium ion (or an equivalent precursor) by the carbon ortho or para to the deprotonated 3-hydroxy substituent. The rate of this process increases with increasing deprotonation, reaching a maximum that is several orders of magnitude faster than the rate under acidic conditions.[8] The lack of regioselectivity observed in neutral solution may be ascribed to an early transition state caused by the high electron density of the deprotonated phenol.[1] Ortho cyclization may also be favored by dipolar attraction between the iminium cation and phenolate anion. This could explain the decrease in ortho cyclization above pH 7. Ortho cyclization is also observed in the analogous intermolecular Mannich condensations of phenols under neutral conditions[16] and in intramolecular as well as intermolecular alkylations of phenols.[17]

Many 8-hydroxytetrahydroisoquinolines and 8-methoxytetrahydroisoquinolines derived therefrom arise biosynthetically from enzyme-catalyzed ortho Pictet–Spengler reactions of 3-hydroxyphenethylamines. Our results demonstrate that these enzyme-catalyzed Pictet–Spengler cyclizations mimic nonenzymatic ortho Pictet–Spengler reactions under neutral conditions.

Experimental Section

General Procedures. ^1H NMR were recorded at 80 MHz, and ^{13}C NMR were recorded at 20 MHz on a Varian CFT-20 spectrometer. DSS (δ 0.0) and dioxane (δ 67.39) respectively were utilized as ^1H and ^{13}C NMR internal standards. Analytical liquid chromatography was performed on a C_{18} Porasil colum as previously described.[8,9] Analytical silica gel 60 TLC plates were eluted with ether–methanol–ammonium hydroxide mixtures (75:20:5 and 80:10:10). Other procedures have been previously described.[8,9]

3-(2-Aminoethyl)phenol hydrochloride (1a) was prepared by hydrogenolysis[26] of the diacetate of norphenylephrine (**1e**) or more conveniently by direct hydrogenolysis of **1e** as follows: norphenylephrine (**1e**) (2.0 g, 10.5 mmol) dissolved in 6 M HCl (40 mL) was hydrogenated over 10% Pd–C (2.5 g) for 30 h at 15–35 psi on a Parr shaker. Removal of the catalyst and evaporation of the solvent afforded crude product (1.8 g, mp 133–140 °C), which was recrystallized from absolute ethanol (0.91 g, 50% yield): mp 139–140 °C (lit. mp 142 °C[27]); ^1H NMR (D_2O) δ 3.00 (2 H, d), 3.24 (2 H, d), 6.8 (3 H, m), 7.25 (1 H, m).

3-[2-(Methylamino)ethyl]phenol hydrochloride (1b) was prepared by hydrogenolysis of the diacetate of phenylephrine (**1f**) as previously described:[26] ^1H NMR (D_2O) δ 2.68 (3 H, s), 2.96 (2 H, d), 3.12 (2 H, d), 6.75 (3 H, m), 7.15 (1 H, m).

4-[2-(Methylamino)ethyl]-1,2-benzenediol hydrobromide (1d) was prepared from **1c** as previously described:[28] ^1H NMR (D_2O) δ 2.62 (3 H, s), 2.87 (2 H, d), 3.12 (2 H, d), 6.8 (3 H, m).

Pictet–Spengler condensations of **1** with aqueous formaldehyde or acetaldehyde (800 mol%) were conducted at pH 2 to 8.5 at 20 °C as previously described.[8,9] Reaction progress, yields, and isomer distributions (Table I) were determined by liquid chromatography.[8,9] The isomeric mixtures of tetrahydroiso-

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quinolines were separable by column chromatography on silica gel eluted with 2-butanol–14 M formic acid[8,9] or by fractional recrystallization from ethanol, ethanol–ether, or 2-propanol. The tetrahydroisoquinoline products **2–5** were identified by comparison with authentic samples synthesized by known methods or by the procedures described below. All tetrahydroisoquinolines except **4b** and **5d** were previously known (see references in Table I).

Authentic tetrahydroisoquinolines 2 and 4 which were difficult to obtain by literature procedures were synthesized by Pictet–Spengler reactions under strongly acidic conditions as follows: A formaldehyde solution (8.5 mmol, 120 mol %) was added to a solution of the phenethylamine **1** (7.0 mmol) dissolved in water (2–5 mL) at pH 0.5. When the reaction was essentially complete according to chromatography (5–20 days at 20 °C), 1 M $NaHCO_3$ was added to pH 2, the water was evaporated in vacuo, and the residue was sequentially triturated with 95% then 100% ethanol to afford crude product (80–100% yield). Recrystallization from ethanol, ethanol–ether, or 2-propanol afforded the pure product as the hydrochloride salt.

1,2,3,4-Tetrahydro-1,2-dimethyl-6-isoquinolinol hydrochloride (4b): mp 207–209 °C; ^1H NMR (D_2O) δ 1.70 (3 H, d), 3.00 (3 H, s), 3.12 (2 H, t), 3.60 (2 H, t), 4.60 (1 H, q), 6.8–7.2 (3 H, m); MS, *m/e* (relative intensity) 177.1159 (2, M^+, calcd 177.1154), 163 (19), 162 (100), 44 (33).

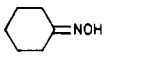
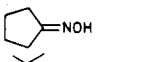
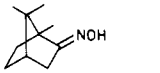
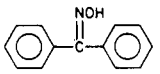
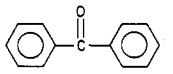
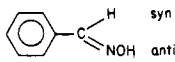
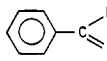
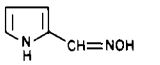
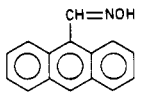
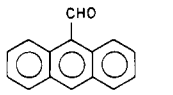
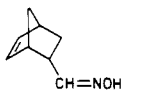
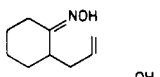
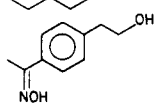
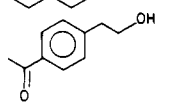
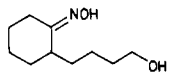
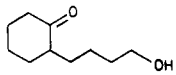
Authentic tetrahydroisoquinolines 3 and 5 which were difficult to obtain by literature procedures were synthesized by catalytic hydrogenolysis of the known 4-hydroxytetrahydroisoquinolines (see Table I) under the conditions described for synthesis of **1a**.

1,2,3,4-Tetrahydro-1,2-dimethyl-7,8-isoquinolinediol hydrochloride (5d): mp 157–160 °C; ^1H NMR (D_2O) δ 1.58 (3 H, d), 2.88 (3 H, s), 3.0 (2 H, m), 3.4 (2 H, m), 4.36 (1 H, q), 6.65 (2 H, s); ^{13}C NMR (D_2O, pH 5) δ 16.73, 22.86, 40.50, 45.32, 56.59, 116.75, 121.38, 121.94, 122.29, 141.97, 143.60; MS, *m/e* (relative intensity) 193.1106 (2, M^+, calcd 193.1103), 192 (4), 179 (18), 178 (100).

Acknowledgment. This investigation was supported in part by the U.S. Public Health Service, Grant AA05472, and Biomedical Research Support Grant 5 SO7 RR07067.

Registry No. **1a**·HCl, 3458-98-8; **1b**·HCl, 33543-61-2; **1c**, 51-61-6; **1d**·Br, 18191-22-5; **1e**, 536-21-0; **1f**, 532-38-7; **1g**, 586-17-4; **1h**, 6912-68-1; **2a**, 14446-24-3; **2b**, 14097-39-3; **2c**, 34827-33-3; **2d**, 37491-98-8; **2e**, 93202-93-8; **2f**, 23824-24-0; **2g**, 50988-14-2; **2h**, 82563-75-5; **3a**, 32999-37-4; **3b**, 14788-32-0; **3c**, 102830-09-1; **3d**, 102830-10-4; **3e**, 102830-11-5; **3f**, 23824-25-1; **3g**, 102830-12-6; **3h**, 82334-24-5; **4a**, 61562-93-4; **4b**, 102830-13-7; **4c**, 525-72-4; **4d**, 102830-14-8; **4e**, 102830-15-9; **4f**, 102830-16-0; **4g**, 33698-46-3; **4h**, 35589-37-8; **5a**, 102830-17-1; **5b**, 32999-47-6; **5c**, 102917-28-2; **5d**, 102830-18-2; **5e**, 102830-19-3; **5f**, 102830-20-6; **5g**, 102830-21-7; **5h**, 102830-22-8; CH_2O, 50-00-0; MeCHO, 75-07-0.

Table I. Oxidative Cleavage of Oximes with CTAP

entry	oxime	condtn: time, min	carbonyl comp[a]	% yield[b]
1		15		98
2		60		94
3		20		89
4		40		95
5		20 35		90
6		15		88
7		15		96
8		15		92
9		20		90
10		30		86
11		30		88

derivatives apart from exchange reactions with pyruvic acid[2] or levulinic acid,[3] ozonolysis at low temperature[4] and treatment with titanous ion[5] are the commonly employed methods of deprotection. Although these methods are generally useful they have limited applicability when extended to complex molecules having multifunctional groups which are prone to oxidation under the reaction conditions. Thus a need exists for the development of an oxidizing agent which is mild and selective and is capable of effecting the oxidative cleavage of the carbon–nitrogen double bond in the presence of other functional groups.

Recently, we reported on the usefulness in organic synthesis of an oxidizing agent—cetyltrimethylammonium permanganate (CTAP) for cis-hydroxylation of olefins[6] and for selective oxidation of benzylic alcohols.[7] In the course of our studies to explore the usefulness of this reagent in

A Mild and Highly Selective Method for the Regeneration of Carbonyl Compounds from Oximes and (2,4-Dinitrophenyl)hydrazones

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Regeneration of carbonyl compounds from its derivatives under mild conditions is an important process in synthetic organic chemistry. Readily prepared and highly stable ketoximes are particularly useful both as protective groups and selective activating groups. Several oxidative methods are available for deoximation.[1] In the case of 2,4-DNP

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