β-Amino Alcohol Properfumes

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Amino-alcohol derivatives of fragrant, volatile aldehydes and ketones were synthesized in a one-pot procedure by sequential cyanohydrin formation with trimethylsilyl cyanide and reduction with lithium aluminium hydride, or by ammonolysis of epoxide precursors. The amino alcohols are nonvolatile, stable properfumes releasing fragrant carbonyls by oxidation with sodium periodate or sodium bismuthate. Examples include amino alcohol properfumes of citronellal, *Lilial*®, lauryl aldehyde, menthone, benzaldehyde, and anisaldehyde.

Introduction. – Over 3000 fragrance ingredients are available today for use in perfumery [1][2]. Factors such as chemical instability, reactivity, and evanescence, which are intrinsic to many fragrant compounds, however, strongly limit the choices for certain applications, in particular, when the active ingredients must be stored for some time before being released. Time-delayed fragrance-delivery systems have been developed, such as spray-dried and micro-encapsulated perfumes, and inclusion complexes with cyclodextrins [3]. Another approach consists in employing fragrance precursors or properfumes. This concept is the direct analog of the prodrug principle used in the pharmaceutical industry. Existing systems include the release of fragrant alcohols from esters by using either lipases or a photoisomerization-triggered lactonization of coumarate esters [4], and the release of aldehydes and ketones by a photochemical *Norrish-II* fragmentation of 2-oxo esters of the corresponding alcohols [5]. Herein, we report a novel properfume strategy, whereupon fragrant volatile aldehydes and ketones are released from stable nonvolatile β-amino-alcohol precursors by periodate oxidation in H_2O.

Results and Discussion. – $NaIO_4$ is a versatile oxidant best known for its ability to cleave the C−C bond of 1,2-diols to release two C=O groups [6]. Recently, we have shown that the reaction can also be used for fluorogenic and chromogenic enzyme assays [7]. Interestingly, 1,2-amino alcohols are oxidized even faster than 1,2-diols. We reasoned that the reaction might be used to release fragrant aldehydes and ketones, which are difficult to store due to their volatility and chemical instability, from β-amino alcohol precursors, themselves readily obtainable by cyanohydrin formation and reduction (*Scheme 1*). The advantage would be that both the periodate oxidant and the β-amino alcohol are nonvolatile and quite stable.

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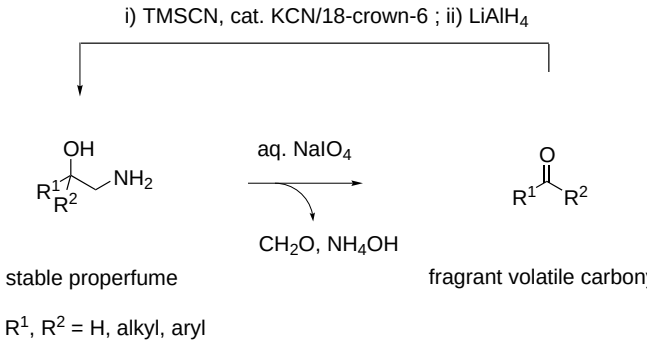
Scheme 1. *Preparation and Oxidative Activation of β-Amino Alcohol Properfumes*

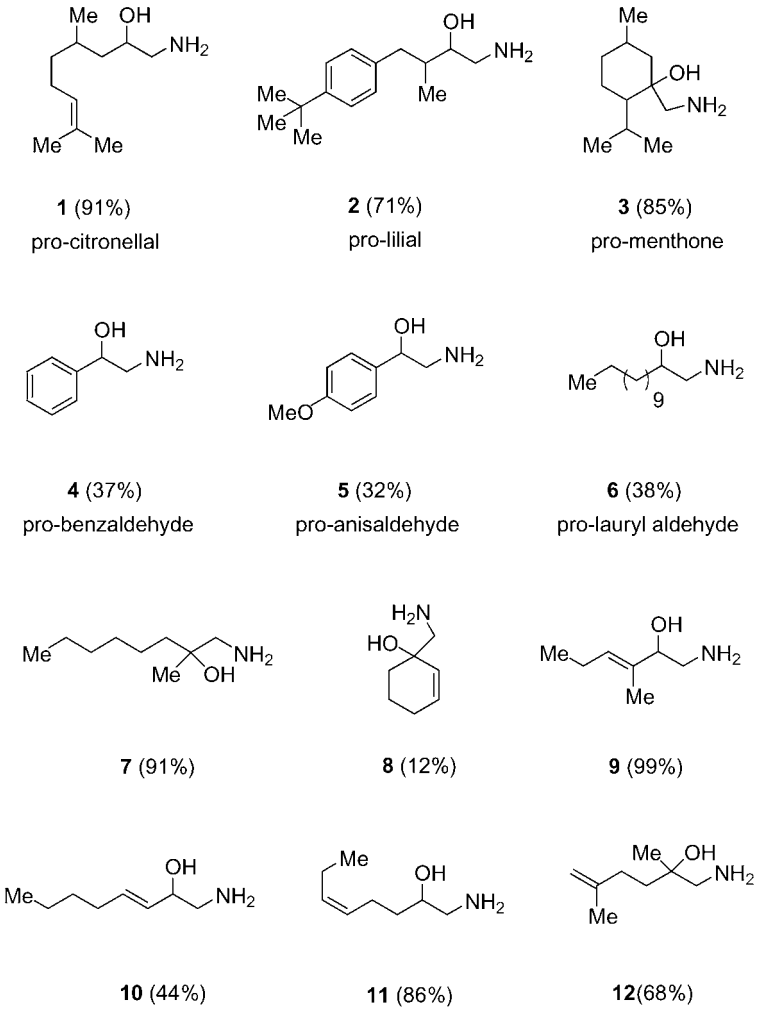


We prepared a series of β-amino alcohols, **1**–**12**, from volatile carbonyl fragrances, including citronellal, used in soaps and detergents, *Lilial*® (= 3-[4-(*tert*-butyl)phenyl]-2-methylpropanal), which serves as a base component in many perfumes, and lauryl aldehyde, a fatty-orange note used in '*Chanel N°5*' [1]. β-Amino alcohol derivatives were obtained in excellent purity and good yields by a one-pot procedure involving reaction with Me_3SiCN (TMSCN) under anionic catalysis by KCN/18-crown-6, followed by reduction with $LiAlH_4$ [8] and an aqueous extractive workup, which avoided the use of chromatographic purification. All β-amino alcohols were racemic, or, in the case of citronellal, menthone, and *Lilial*®, mixtures of stereoisomers (*Scheme 2*).

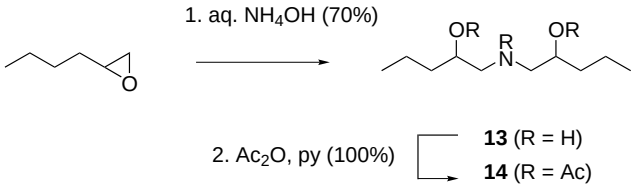
Amino alcohols are also easily prepared from epoxides by ammonolysis. We looked into that possibility to prepare a precursor for the volatile butanal, which is an important odor component for butter. Interestingly, reaction of 2-butyloxirane with aqueous NH_3 gave a crystalline product, which was identified as the yet unreported secondary amine **13** (*Scheme 3*), resulting from double substitution of ammonia with the epoxide by reaction at the terminal epoxide C-atom. The structure was established by mass spectrometry as well as by NMR analysis of the acetylated derivative **14**. Although there was only one set of NMR signals, the formation of a single diastereoisomer seems improbable, and we assume that both possible diastereoisomers have identical ^{1}H- and ^{13}C-NMR signatures.

All the amino alcohols prepared were nonvolatile, completely odorless products. Properfume activation by periodate oxidation was carried out under three different formulations. In the first case, anhydrous Na_2SO_4 was ground with 1%-weight of the amino alcohol and solid $NaIO_4$. The resulting colorless powder was completely odorless, but slowly released its active component when left exposed to air, due to the slow uptake of humidity, which solubilized the component sufficiently for the reaction to take place. A distinct odor was perceptible even after several weeks in these preparations. By comparison, anhydrous Na_2SO_4 ground with 1%-weight of the volatile carbonyl compounds themselves initially released a very strong fragrance, but any odor had disappeared within 12 h of exposure to air. Similar results were obtained with MgO, or mixtures of Na_2SO_4 and MgO as the inorganic support for the properfumes.

Scheme 2. *Structures of β-Amino Alcohol Properfumes.* Yields obtained with the one-pot cyanohydrin formation/reduction procedure are given in parentheses.



Scheme 3. *Reaction of 2-Butyloxirane with Ammonia*



In the second formulation, acidic salts of the amino alcohols were prepared by reaction with 1 equiv. of either HCl, AcOH, or PhCOOH in MeOH, and evaporation. Aqueous solutions of these salts were prepared at a concentration of 50 mM. While these solutions were completely odorless, the immediate, strong fragrance was released when adding an equal volume of an aqueous 50 mM solution of $NaIO_4$, or by adding solid $NaIO_4$. The aqueous solutions of β-amino alcohol salts were stable and odorless over weeks at room temperature, and released their fragrance upon treatment with periodate independent of the length of the storage period. Organic solvent extracts (AcOEt) of the properfume aqueous solution were free of any detectable product under analysis by GC/MS, and showed the expected volatile carbonyl as the only detectable product after treatment with $NaIO_4$, showing that the oxidation reaction produced only the expected product (*Fig.*).

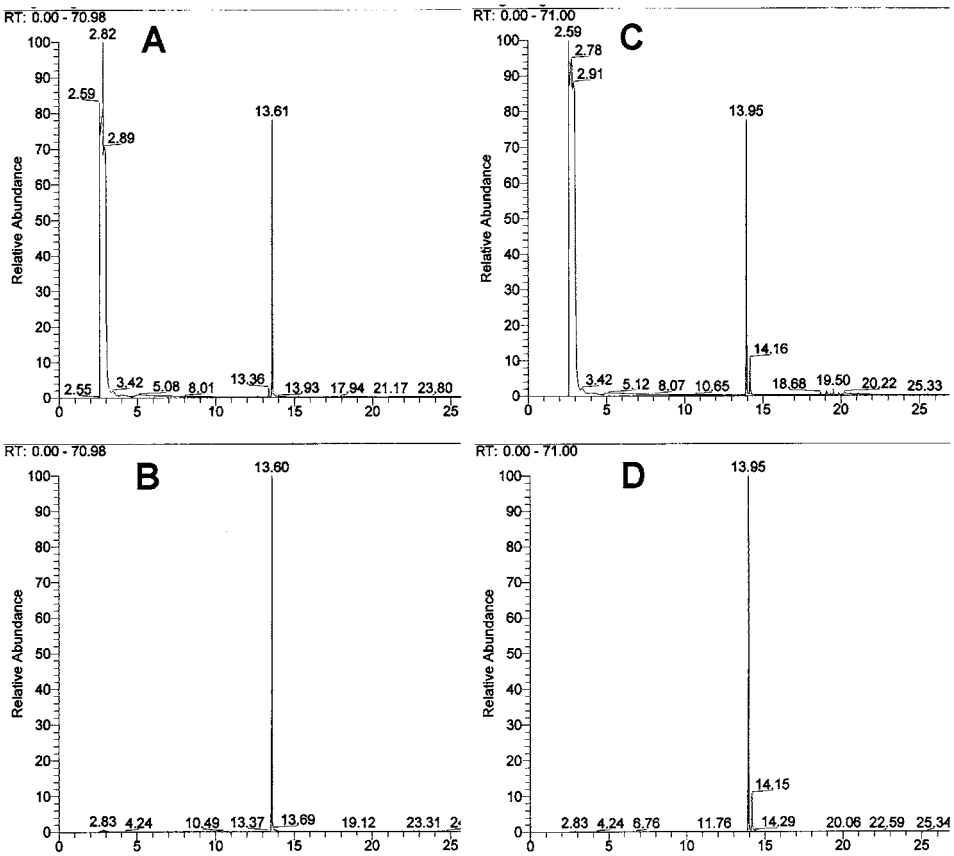


Figure. *GC/MS Analysis of organic extracts of properfume solutions. A*) FID Total-ion-current trace for acetate salt of pro-citronellal (**1**) after treatment with $NaIO_4$, *B*) signal at *m/z* 154; *C*) FID-total-ion-current trace for hydrochloride salt of pro-menthone (**3**) after treatment with $NaIO_4$, *D*) signals at *m/z* 154. There were no detectable signals in the GC traces of the organic phase under the same conditions before treatment with $NaIO_4$.

In the third formulation, we made use of the higher reactivity of β-amino alcohols towards periodate oxidation in comparison to 1,2-diols. A simple release system was build with two superimposed sheets of filter paper, one of which had been impregnated with a β-amino alcohol solution and dried. The sheets were held together by a piece of scotch-tape, with a small amount of solid $NaIO_4$ added on the glue-face in contact with the nonimpregnated filter paper. Addition of a few drops of H_2O to the filter-paper device immediately released the fragrances, indicating that both the amino alcohol and the β-amino alcohol dissolved rapidly in H_2O, and that the oxidative properfume release took place faster than the reaction of periodate with 1,2-diols present in the cellulose of the paper (*Table*).

Table. *Properfume Properties upon Release from Filter Paper*[a])

Properfume	Amount [mg]	Fragrance	Description	Persistance[b])
1	0.26	Citronellal	Citronella, strong	30 min
2	0.47	*Lilial*®	Fresh lila, weak	> 30 min
3	0.37	Menthone	Mint, strong	10 min
4	0.27	Benzaldehyde	Almond, strong	10 min
5	0.33	Anisaldehyde	Cinnamon, middle	20 min
6	0.40	Lauryl aldehyde	Fatty orange, middle	> 30 min

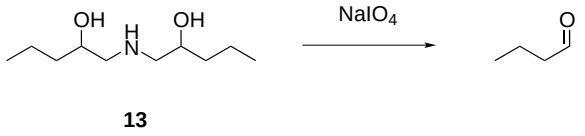
[a]) 0.02 ml of a 0.1M ethanolic solution of β-amino alcohol was adsorbed on a filter paper and dried. $NaIO_4$ Treatment was carried out by addition of H_2O as described in the text and judged qualitatively. [b])Time after which the fragrance was not detectable any more. Compounds **7**–**12** were similarly tested. The released carbonyls had stingy (**9**–**11**), sweet (**7** and **12**), or only weak (**8**) fragrances.

It should be mentioned that we did not detect the odor of either formaldehyde or ammonia, which are by-products of the periodate oxidation reaction, in any of the properfume formulations. These components, which do not have a very strong intrinsic odor per unit of weight when compared to most fragrances, are also sufficiently H_2O-soluble to not show significant vapor pressure at the concentrations used. We also did not detect any significant fatty acid smells that could result from overoxidation during or after the reaction, even when using an excess of periodate. The fragrances released, which are relatively hydrophobic, are most likely immediately removed from the aqueous phase used for the oxidation of the amino alcohol with periodate.

Secondary amines behaved similarly to the other amino alcohols with respect to $NaIO_4$ oxidation, thus representing further interesting low-volatility precursors for volatile carbonyl compounds. For example, secondary amine **13** released butanal upon treatment with $NaIO_4$. Similarly, ephedrine (**15**), also bearing a secondary amine, reacted with $NaIO_4$ to give PhCHO, also obtained from amino alcohol **4**, confirming the suitability of secondary amines for the oxidation chemistry (*Scheme 4*). The rate of oxidation of **4** and ephedrine (**15**) was almost identical, as shown by the fact that both amino alcohols were consumed to the same extent by treatment of an equimolar solution of these with 1 equiv. of $NaIO_4$. Ephedrine (**15**) was, however, not completely equivalent to **4** as a properfume. Indeed, it was possible to detect the acrid smell of MeCHO as one of the by-products of **15**. Amino alcohols of tertiary amines did not react with periodate. This was shown by the fact that pretreatment of $NaIO_4$ (10 mM in

H_2O) with excess triethanolamine (=2,2′,2″-nitrilotris[ethanol]; 20 mM) for 30 min at 20° did not reduce its oxidizing power towards amino alcohols.

Scheme 4. *Amino Alcohols with Secondary Amines as Properfumes*



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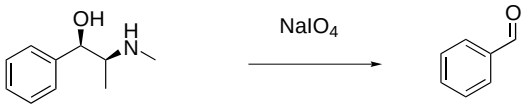

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Since $NaIO_4$ is potentially problematic for applications due to its reported toxicity, we looked for alternative oxidants to perform the oxidative cleavage of amino-alcohol properfumes. There was no measurable reaction with H_2O_2 or $NaMnO_4$. However, we found that $NaBiO_3$, which is reportedly nontoxic (for example, bismuth salicylate is prescribed in large amounts against stomach pain), slowly reacted with the amino alcohols to release the perfumes over weeks. Thus, a slurry of $NaBiO_3$ and procitronellal (**1**) could be left open at air for several weeks and kept releasing a fresh citrus smell.

Conclusions. – The above experiments show that β-amino alcohols are stable, nonvolatile, and odorless precursors of fragrant aldehydes and ketones, which can be released by reaction with $NaIO_4$ or $NaBiO_3$. These properfumes are readily prepared from the parent carbonyl compounds in an efficient one-pot procedure involving cyanohydrin formation and reduction, and obtained pure by simple extractive workup. Alternatively, amino alcohols are readily prepared from epoxides, with both primary and secondary amines, to give oxidizable properfumes, a strategy that allows to formulate completely nonvolatile precursors of volatile carbonyls. This simple process represents an attractive properfume strategy for a variety of applications, including experimental demonstrations for students. The oxidative chemistry of β-amino alcohols should also be of general value to release any active but sensitive carbonyl component from more-stable precursors, in particular, in the area of prodrug formulations.

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Experimental Part

General. All reagents were purchased from either *Aldrich* or *Fluka*. Et_2O was dried over Na. M.p. *Büchi 510* apparatus; uncorrected. IR Spectra: *Perkin-Elmer Spectrum One* series. ^{1}H- and ^{13}C-NMR spectra: *Bruker AC-300* spectrometer. Mass spectra were provided by Dr. *Thomas Schneeberger* (University of Bern).

1-Amino-4,8-dimethylnon-7-en-2-ol (**1**). A soln. of 18-crown-6 (132 mg, 0.5 mmol) and KCN (32.5 mg, 0.5 mmol) in 10 ml of MeOH was stirred at 25° for 10 min. The solvent was evaporated, and the residue was redissolved in 10 ml of CH_2Cl_2, and treated with citronellal (620 mg, 4 mmol) and Me_3SiCN (397 mg, 4 mmol). After completion of the reaction (TLC, 14 h), the solvent was evaporated, and the residue was redissolved in dry Et_2O (10 ml) and treated with $LiAlH_4$ (400 mg, 12 mmol). After completion of the reaction (7 h at 25°), the mixture was cooled to 0°, and the reaction was quenched by dropwise addition of aq. 2N HCl (30 ml). The aq. phase was washed with Et_2O (3 × 30 ml), basified with 15% aq. NaOH (70 ml), and extracted with Et_2O (3 × 30 ml). The org. phase was washed with brine (2 × 30 ml), dried (Na_2SO_4), and evaporated to dryness to give **1** (680 mg, 3.67 mmol, 91%). Colorless liquid. IR ($CHCl_3$): 3437, 2967, 2925, 1635, 1489, 1094, 1057. ^{1}H-NMR (300 MHz, $CDCl_3$): 5.10 (br. *t*, *J* = 6, 1 H); 3.61 (*m*, 1 H); 2.81 (*ddd*, *J* = 12.5, 5.5, 3.3, 1 H); 2.50 (*dt*, *J* = 12.5, 8.0, 1 H); 2.0 (br. *s*, 3 H); 1.65 (*s*, 3 H); 1.58 (*s*, 3 H); 1.48 – 1.02 (*m*, 4 H); 0.94, 0.92 (2*d*, *J* = 6.6, 3 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 132.0; 125.5; 70.9 (70.5); 48.9 (48.4); 43.0 (42.9); 38.7 (37.6); 30.1 (29.7); 26.5; 20.7; 19.9; 18.5. EI-MS (pos.): 186 ($[M+H]^+$), 135. HR-MS: 185.177900 ($C_{11}H_{23}NO^+$; calc. 185.177965).

*1-Amino-4-[(*tert*-butyl)phenyl]-3-methylbutan-2-ol* (**2**). Application of the procedure for **1** starting with 3-[4-(*tert*-butyl)phenyl]-2-methylpropanal (160 mg, 0.78 mmol; reaction times: 10 h with Me_3SiCN and 10 h with $LiAlH_4$) gave **2** (130 mg, 0.55 mmol, 71%). Colorless oil. IR ($CHCl_3$): 3398, 2965, 1641, 1570, 1514, 1463, 1364, 1270, 1110, 1075, 1020, 807, 758, 711. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.28 (*d*, *J* = 8.1, 2 H); 7.09 (*d*, *J* = 8.1, 2 H); 3.51 – 3.30 (*m*, 1 H); 2.92 (*m*, 1 H); 2.75 (*m*, 1 H); 2.56 (*m*, 1 H); 2.31 (*m*, 1 H); 2.0 – 1.5 (br. *m*, 3 H); 1.30 (*s*, 9 H); 0.89, 0.81 (2*d*, *J* = 7.0, 3 H). ^{13}C-NMR (75 Hz, $CDCl_3$): 129.9 (129.7); 126.1 (126.0); 76.3 (75.3); 46.2 (45.4); 40.2 (40.1); 39.5 (39.4); 32.3; 16.0 (14.9). EI-MS (pos.): 235, 236 ($[M+H]^+$), 204, 205, 189, 174, 147, 148, 131, 132, 117, 91, 60, 57, 41. HR-MS: 235.193700 ($C_{15}H_{25}NO^+$; calc. 235.193615).

1-(Aminomethyl)-5-methyl-2-(1-methylethyl)cyclohexanol (**3**). Application of the procedure for **1** starting with menthone (mixture of isomers; 620 mg, 4 mmol, reaction times: 14 h with Me_3SiCN and 7 h with $LiAlH_4$) gave **3** (630 mg, 3.40 mmol, 85.0%). Pale yellow liquid. IR ($CHCl_3$): 3429, 2955, 2927, 2871, 1644, 1578, 1457, 1388, 1295, 1168, 1105, 1030, 938, 706. ^{1}H-NMR (300 MHz, $CDCl_3$): 2.88 – 2.46 (*m*, 2 H); 2.17 – 1.91 (*m*, 1 H); 1.84 (*m*, 1 H); 1.79 – 1.63 (*m*, 2 H); 1.63 – 1.26 (*m*, 5 H); 1.17 – 1.05 (*m*, 1 H); 1.03, 0.94 (2*d*, *J* = 7.0, 3 H); 0.92 – 0.84 (*m*, 5 H); 0.77(*d*, *J* = 7, 3 H). ^{13}C-NMR (75 MHz, $CDCl_3$; mixture of three diastereoisomers) 74.9 (74.7, 74.4); 52.3 (48.4, 46.7); 46.5 (50.5, 50.1); 43.3 (46.3, 42.1); 35.8 (35.9, 31.5); 30.7 (29.5, 28.5); 26.9 (26.7, 26.0); 25.4 (25.3, 24.4); 24.2 (23.5, 21.5); 23.1 (23.2, 22.9); 20.2 (21.6, 18.8). EI-MS (pos.): 185 ($[M+H]^+$), 155, 137, 112, 95, 81, 69, 55, 43, 41, 39.

2-Amino-1-phenylethanol (**4**). Application of the procedure for **1** starting with PhCHO (423 mg, 4 mmol; reaction times: 18 h with Me_3SiCN and 5 h with $LiAlH_4$) gave **4** (203 mg, 1.48 mmol, 37%). Colorless oil. IR ($CHCl_3$): 3366, 3030, 2925, 2872, 1579, 1478, 1453, 1331, 1204, 1064, 749, 699. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.31 – 7.17 (*m*, 5 H); 4.52 (*dd*, *J* = 7.7, 4.0, 1 H); 2.80 (*dd*, *J* = 12.9, 4.0, 1 H); 2.67 (*dd*, *J* = 12.9, 7.7, 1 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 143.3; 129.0; 128.1; 126.5; 74.9; 49.9. EI-MS (pos.): 137 ($[M+H]^+$), 118, 107, 91, 79, 77, 65, 51, 41, 39.

2-Amino-1-(4-methoxyphenyl)ethanol (**5**). Application of the procedure for **1** starting with anisaldehyde (545 mg, 4 mmol; reaction times: 12 h with Me_3SiCN and 4 h with $LiAlH_4$) gave **5** (210 mg, 1.26 mmol, 32%). Colorless oil. IR ($CHCl_3$): 3417, 1645, 1514, 1467, 1250, 1178, 1029, 831, 815. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.23 (*d*, *J* = 8.4, 2 H); 6.85 (*d*, *J* = 8.4, 2 H); 4.53 (*dd*, *J* = 7.7, 4.0, 1 H); 3.79 (*s*, 3 H); 2.87 (*dd*, *J* = 12.5, 4.0, 1 H); 2.73 (*dd*, *J* = 12.5, 8.1, 1 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 159.4; 135.1; 127.5; 114.1; 74.4; 55.6; 49.7. EI-MS (pos.): 167 ($[M+H]^+$), 149, 137, 121, 109, 94, 77, 66, 59, 51, 39.

1-Aminotridecan-2-ol (**6**). Application of the procedure for **1** starting with laurinaldehyde (737 mg, 4 mmol; reaction time: 4 h with Me_3SiCN and 4 h with $LiAlH_4$) gave **6** (326 mg, 1.51 mmol, 38%). Colorless liquid. IR (KBr): 3368, 2957, 2918, 2851, 1596, 1491, 1471, 1380, 1133, 1085, 719. ^{1}H-NMR (300 MHz, $CDCl_3$): 3.45 – 3.52 (*m*, 1 H); 2.80 (*dd*, *J* = 12.51, 3.33, 1 H); 2.45 (*dd*, *J* = 12.51, 8.46, 1 H); 1.37 – 1.42 (*m*, 4 H); 1.34 (*s*, 20 H); 0.84 (*t*, *J* = 6.99, 3 H). ^{13}C-NMR (75 Hz, $CDCl_3$): 72.8; 48.1; 35.5; 32.6; 30.5; 30.4; 30.4; 30.3; 30.1; 26.4; 23.4; 14.8. EI-MS (pos.): 215 ($[M+H]^+$), 205, 198, 197, 180, 168, 97, 83, 70, 60, 56, 43, 41, 39.

1-Amino-2-methyloctan-2-ol (**7**). Application of the procedure for **1** starting with octan-2-one (513 mg, 4 mmol; reaction times: 5 h with Me_3SiCN and 12 h with $LiAlH_4$) gave **7** (580 mg, 3.64 mmol, 91.0%). Pale yellow liquid. IR ($CHCl_3$): 3368, 2958, 2933, 2861, 1575, 1489, 1469, 1378, 1329, 1163, 1105, 947, 823, 725. ^{1}H-NMR (300 MHz, $CDCl_3$): 2.60 (*d*, *J* = 12.8, 1 H); 2.53 (*d*, *J* = 12.8, 1 H); 1.8 – 1.6 (br. *s*, 2 H); 1.43 – 1.26 (*m*, 11 H); 1.08 (*s*, 3 H); 0.84 (*m*, 3 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 72.2; 51.5; 40.4; 32.5; 30.6; 24.8; 24.5; 23.3; 14.7. EI-MS (pos.): 160 ($[M+H]^+$), 144, 129, 111, 85, 74, 69, 55, 43, 41, 39.

1-(Aminomethyl)cyclohex-2-en-1-ol (**8**). Application of the procedure for **1** starting with cyclohexen-2-one (390 mg, 4 mmol; reaction times: 12 h with Me_3SiCN and 3 h with $LiAlH_4$) gave **8** (60 mg, 0.47 mmol, 12%).

Pale yellow liquid. IR ($CHCl_3$): 3418, 2932, 2862, 1651, 1572, 1449, 1339, 1155, 1066, 916, 754. ^{1}H-NMR (300 MHz, $CDCl_3$): 5.88–5.82 (*m*, 1 H); 5.55 (*d*, *J* = 9.9, 1 H); 2.60 (*m*, 2 H); 2.09–1.49 (*m*, 9 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 131.8; 131.3; 69.8; 54.2 (51.9); 34.3; 26.1; 19.7. EI-MS (pos.): 128, 129 ($[M+H]^+$), 110, 97, 91, 79, 70, 55, 41, 39.

1-Amino-3-methylhex-3-en-2-ol (**9**). Application of the procedure for **1** starting with 2-methylpent-2-enal (393 mg, 4 mmol; reaction times: 2 h with Me_3SiCN and 7 h with $LiAlH_4$) gave **9** (510 mg, 3.95 mmol, 99%). Orange, waxy solid. IR ($CHCl_3$): 3374, 2964, 2935, 2876, 1569, 1488, 1463, 1380, 1332, 1069, 865, 755. ^{1}H-NMR (300 MHz, $CDCl_3$): 5.39 (br. *t*, *J* = 7, 1 H); 3.86 (*dd*, *J* = 7.4, 4.8, 1 H); 2.76 (*dd*, *J* = 12.8, 4.4, 1 H); 2.64 (*dd*, *J* = 12.8, 7.7, 1 H); 2.02 (*quint*, *J* = 7, 2 H); 1.88 (br. *s*, 2 H); 1.56 (*s*, 3 H); 0.91 (*t*, *J* = 7, 3 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 135.1; 129.1; 78.0; 46.3; 21.4; 14.7; 12.7. EI-MS (pos.): 129 ($[M+H]^+$), 112, 100, 99, 81, 71, 55, 43. HR-MS: 129.115390 ($C_7H_{15}NO^+$; calc. 29.115364).

*(*E*)-1-Aminooct-3-en-2-ol* (**10**). Application of the procedure for **1** starting with (*E*)-hept-2-enal (449 mg, 4 mmol; reaction times: 3 h with Me_3SiCN and 3 h with $LiAlH_4$) gave **10** (250 mg, 1.75 mmol, 44%). Milky rime. M.p. 49–51°. IR ($CHCl_3$): 3333, 2958, 2927, 2859, 1572, 1467, 1378, 1330, 1063, 969, 822. ^{1}H-NMR (300 MHz, $CDCl_3$): 5.77–5.67 (*m*, 1 H); 5.38 (*dd*, *J* = 15.4, 6.6, 1 H); 4.03–3.96 (*m*, 1 H); 2.78 (*dd*, *J* = 12.9, 4.4, 1 H); 2.59 (*dd*, *J* = 12.9, 8.6, 1 H); 2.01 (*m*, 2 H); 1.90–1.55 (br. *s*, 3 H); 1.43–1.24 (*m*, 4 H); 0.86 (*t*, *J* = 7, 3 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 133.9; 130.9; 73.8; 48.1; 32.6; 31.9; 22.9; 14.6. EI-MS (pos.): 143, 144 ($[M+H]^+$), 126, 113, 99, 95, 82, 69, 57, 55, 43, 41, 39. HR-MS: 143.131010 ($C_8H_{17}NO^+$; calc. 143.131014).

*(*Z*)-1-Aminooct-5-en-2-ol* (**11**). Application of the procedure for **1** starting with (*Z*)-hept-4-enal (449 mg, 4 mmol; reaction times: 3 h with Me_3SiCN and 3 h with $LiAlH_4$) gave **11** (490 mg, 3.42 mmol, 86%). Colorless liquid. IR ($CHCl_3$): 3438, 2965, 2935, 1635, 1572, 1489, 1337, 1069, 724. ^{1}H-NMR (300 MHz, $CDCl_3$): 5.42–5.27 (*m*, 2 H); 3.55–3.47 (*m*, 1 H); 2.78 (*dd*, *J* = 12.5, 3.3, 1 H); 2.48 (*dd*, *J* = 12.5, 8.4, 1 H); 2.21–1.99 (*m*, 7 H); 1.49–1.40 (*m*, 2 H); 0.92 (*t*, *J* = 7.3, 3 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 132.6; 128.9; 72.1; 47.8; 35.1; 23.8; 20.9; 14.7. EI-MS (pos.): 143, 144 ($[M+H]^+$), 128, 65, 84, 72, 69, 43, 41, 39. HR-MS: 143.131560 ($C_8H_{17}NO^+$; calc. 143.131014).

1-Amino-2,5-dimethylhept-5-en-2-ol (**12**). Application of the procedure for **1** starting with 5-methylhex-5-en-2-one (449 mg, 4 mmol; reaction times: 3 h with Me_3SiCN and 3 h with $LiAlH_4$) gave **12** (390 mg, 2.72 mmol, 68%) as a pale yellow liquid. IR ($CHCl_3$): 3431, 2973, 2939, 1647, 1570, 1490, 1376, 1330, 1135, 887. ^{1}H-NMR (300 MHz, $CDCl_3$): 4.69 (*d*, *J* = 0.7, 2 H); 2.55 (*dd*, *J* = 22.8, 12.9, 2 H); 2.03 (*m*, 2 H); 1.73 (*s*, 3 H); 1.60–1.45 (*m*, 2 H); 1.12 (*s*, 3 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 146.9; 110.2; 72.1; 51.5; 38.3; 32.6; 24.8; 23.4. EI-MS (pos.): 144 ($[M+H]^+$), 128, 126, 113, 112, 95, 86, 74, 69, 55, 43, 41, 39. HR-MS: 144.1394 ($C_8H_{18}NO$, $[M+H]^+$; calc. 144.1388).

1-[(2-hydroxypentyl)amino]pentan-2-ol (**13**). A solution of 2-pentyloxirane (860 mg, 10 mmol) in 25% aq. NH_4OH was stirred at r.t. for 24 h, then the soln. was filtered and dried to give **13** (700 mg, 68%). Colorless solid. M.p. 101–103°. IR ($CHCl_3$): 3326, 3299, 2956, 2926, 2903, 2874, 2834, 1463, 1451, 1337, 1126, 1026, 905, 890, 846. ^{1}H-NMR (300 MHz, $CDCl_3$): 3.68–3.60 (*m*, 1 H); 2.66 (*dd*, *J* = 12.2, 3.3, 1 H); 2.47 (*dd*, *J* = 12.2, 8.8, 1 H); 1.52–1.30 (*m*, 4 H); 0.90 (*t*, *J* = 7.35, 3 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 70.2; 55.7; 37.6; 19.2; 14.5. EI-MS (pos.): (M^+), 189, 146, 116, 98, 69, 42. HR-MS: 189.172870 ($C_{10}H_{23}NO_2^+$; calc. 89.172879).

N,N-*Bis(2-acetoxypentyl)acetamide* (**14**). Acetylation of **13** (100 mg) in Ac_2O (1 ml) and pyridine (1 ml) for 24 h at 20°, followed by evaporation with toluene, gave **14** quantitatively. Pale yellow oil. ^{1}H-NMR (300 MHz, $CDCl_3$): 5.05 (*ddd*, *J* = 10.7, 8.8, 4.05, 2 H); 3.76 (*dd*, *J* = 14.3, 8.8, 1 H); 3.49–3.32 (*m*, 2 H); 3.19 (*d*, *J* = 14.7, 1 H); 1.47–1.41 (*m*, 4 H); 1.39–1.31 (*m*, 4 H); 2.08 (*s*, 3 H); 2.08 (*s*, 3 H); 2.00 (*s*, 3 H); 1.47–1.41 (*m*, 4 H); 1.39–1.31 (*m*, 4 H); 0.94–0.86 (*m*, 6 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 171.8; 171.5; 170.9; 72.2; 71.4; 52.2; 48.8; 34.9; 34.7; 22.2; 21.8; 21.6; 19.2; 19.1; 14.49; 14.48.

Preparation of Acidic Salts. Acidic salts of the amino alcohols were prepared by adding either 2 equiv. of 1M aq. HCl or 1 equiv. of AcOH or PhCOOH to a soln. of amino alcohol (100 mg) in 10 ml of EtOH. The soln. were briefly heated at 40° and evaporated to dryness. The salts showed NMR, MS, and IR data in accordance with the expected products.

Preparation of Amino Alcohol-Impregnated Supports. Na_2SO_4 or MgO (1 g) were mixed with the amino alcohol (10 mg) and $NaIO_4$ (10 mg), and thoroughly ground. Alternatively, a filter-paper disk (10-cm diameter) was impregnated with 60 µl of a 0.1M soln. of amino alcohol in EtOH and dried. The impregnated filter-paper disk was put on top of a second, non-impregnated filter-paper disk. Solid $NaIO_4$ (50 mg) in grains was attached to the other side of this second filter paper with scotch tape. Both the powder formulation and the filter-paper-device formulation could be stored under anh. conditions at r.t. Fragrance released could be triggered at will by addition of a few drops of H_2O, even after several months of storage. When left in moist air, the devices slowly released the fragrant carbonyl.

GC/MS Experiments. An aq. soln. of the AcOH salt of amino alcohol **1** (pro-citronellal; 0.07 ml, 0.1M) was stirred with 1 ml of AcOEt. GC/MS Analysis of the org. phase showed no detectable peak. $NaIO_4$ (0.1M in H_2O, 0.07 ml) was then added. After 10 min, the org. phase was separated and analyzed by GC/MS, showing the presence of citronellal. The experiment with the hydrochloride salt of promenthone **3** gave identical results.

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