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Photochemistry of *N*-Acylimidazoles. III. Rates and Yields of N→C Acyl Migration and of C(α)–C(β) Cleavage of Acyl Side Chains

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Summary

Relative rates of the photoreactions of 1- (**1**), 2- (**2**) and 4(5)-valerylimidazole (**3**) as well as the yields of photo-fragmentation product **10** from 1- (**7**), 2- (**8**) and 4(5)-stearoylimidazole (**9**), respectively, were determined. A reaction path *via Norrish* Type II fragmentation involving the carbonyl group of 1-acylimidazoles was ruled out.

In preceding papers [2] [3] we have reported photochemical N→C acyl migration in *N*(1)-acylimidazoles as well as photo-fragmentation by a *Norrish* Type II process involving the acyl carbonyl group. This paper deals with a quantitative study of these photochemical processes.

Results. Tetrahydrofuran solutions of 1- (**1**), 2- (**2**) and 4(5)-valerylimidazole (**3**) were irradiated using a low pressure mercury lamp with quartz tubes (254 nm), a medium pressure mercury lamp with quartz tubes (> 235 nm) and a medium pressure lamp with pyrex tubes (> 280 nm). The relative consumption rate of each compound was determined by gas chromatography using valerophenone (**4**)[4]) as a comparison standard. The results are summarized in *Table 1*, which shows the wavelength dependence of relative reaction rates in each case. It should be noted that the values under conditions A (254 nm), B (> 235 nm) and C (> 280 nm) are not correlated to each other, but referred in each case, to the value of valevophenone at the same conditions.

The conversion rates of **2** and **3** become 3 and 1.5 times faster, respectively, than that of **4** in neutral solution, if hydrochloric acid is added to their irradiation solu-

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[4]) For the photochemical reactivity of this compound, see [4].

Scheme 1

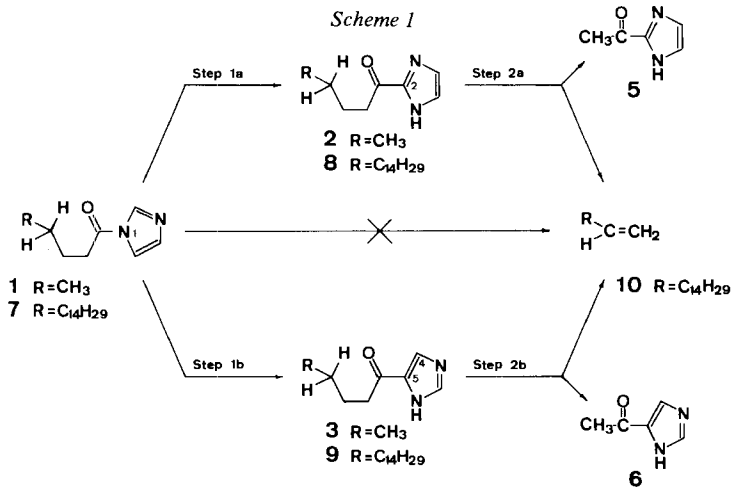


Table 1. *Rates of decrease of compounds* **1–3** *relative to that of valerophenone* (**4**)[a])[b])

Compound	Light			
	254 nm A	> 235 nm B	> 280 nm C	254 nm, H^+ D
1-Valerylimidazole (**1**)	0.75	0.36	–	–
2-Valerylimidazole (**2**)	0.21	0.49	0.26	2.94
4(5)-Valerylimidazole (**3**)	0.33	0.51	0.20	*ca.* 1.5
Valerophenone (**4**)	1.00	1.00[c])[d])	1.00	1.00[e])

[a]) The irradiation were made in tetrahydrofuran as the solvent.
[b]) Under each irradiation condition the relative value for valerophenone is given as 1.00.
[c]) The rate ratio in tetrahydrofuran/in benzene = 0.70.
[d]) Under the conditions used, half-life A/half-life B = 18.1.
[e]) Without addition of acid.

tions (condition D), whereas the rates of **2** and **3** under neutral conditions are much slower. This acceleration effect was also observed on adding acetic acid, sulfonic acids or boron trifluoride. On the other hand addition of alkali inhibited reaction almost completely.

The formation of intermediate products **2** and **3** on irradiation of **1** as well as their further photo-fragmentation to give 2- (**5**) and 4(5)-acetylimidazole (**6**) was followed by gas chromatography, and the results are summarized in *Table 2* and *4* (see exper. part for *Table 4*). These indicate that the maximum yields of **2** and **3** on irradiation with 254-nm-light in tetrahydrofuran were 22–24% at about 80% conversion of **1**, and that the maximum yield of **2** on irradiation with > 235-nm-light was about 6% at half conversion of **1**[5]).

In order to determine the yields of the *Norrish* Type II fragmentation reaction of acylimidazoles possessing secondary γ-hydrogen atoms, 1- (**7**)[6]), 2- (**8**)[6]) and

[5]) No reliable data about the yields of **3** and **6** could be obtained under these gas chromatographic conditions.
[6]) See [3].

Table 2. *Yield of photo-rearrangement products* **2** *and* **3** *and photo-fragmentation products* **5** *and* **6** *(254-nm-light, in THF)*

Conversion of 1-valeryl-imidazole (**1**) [%]	Yield (%) of photo-products[a])			
	2-Valeryl-imidazole (**2**)	2-Acetyl-imidazole (**5**)	4(5)-Valeryl-imidazole (**3**)	4(5)-Acetyl-imidazole (**6**)
0	0	0	0	0
10	4.5	–	4	–
20	8	–	8	–
30	11	2	10	–
40	14	3	13	–
60	20	6	22	4
80	22	7	24	5
90	21	5	22	–

[a]) Accuracy ± 1%.

Table 3. *Yields* [%][a]) *of 1-hexadecene* (**10**) *from stearoylimidazoles* **7–9**

Starting material	THF		EtOH	EtOH, H^+
	254 nm	> 235 nm	> 235 nm	> 235 nm
1-Stearoylimidazole (**7**)	33	38	–	–
2-Stearoylimidazole (**8**)	43	46	56	49
4(5)-Stearoylimidazole (**9**)	41	46	50	66

[a]) Accuracy ± 1%.

4(5)-stearoylimidazole (**9**)[6]) were irradiated with 254-nm- and > 235-nm-light. The yields of the fragmentation product 1-hexadecene (**10**) as determined by gas chromatography are shown in *Table 3*. Irradiation of **8** and **9** in ethanol gave higher yields of **10** than in tetrahydrofuran, but ethanol is unsuitable for the irradiation of **7** because normally 1-acylimidazoles are susceptible to alcoholysis.

When compound **8** was irradiated in tetrahydrofuran with > 235-nm-light there were obtained, in addition to **10**, 2-(1′-hydroxy-octadecyl)imidazole (**11**; 6%), 2-(1′-hydroxy-2′-tetradecylcyclobutyl)imidazole (**12**; 8%) and the diastereomers of 2-[1′-hydroxy-1′-(2″-tetrahydrofuryl)octadenyl]imidazole (**13a** and **13b**; 5 and 7%, respectively). Under the same irradiation condition **9** afforded 4(5)-(1′-hydroxy-octadecyl)imidazole (**14**; 5%) and 2-(1′-hydroxy-2′-tetradecylcyclobutyl)imidazole (**15**; 6%). The stereoisomeric solvent addition products (**16a** and **16b**) could not be isolated in pure form.

Structures of Photoproducts. The suggested structures of valerylimidazoles **2** and **3** are based on their IR. spectra, as discussed previously [2]. Structures of compounds **11–16** are likewise in accord with their spectral data (see exper. part), and in addition those of **11** and of **14** were confirmed by oxidation to the known 2- and 4(5)-stearoylimidazoles (**8** and **9**), respectively [3]. The structural assignment of compound **12** rests upon its conversion into 2-(tetradecyl)cyclobutanone (**17**) by quaternisation with methyl iodide followed by cleavage in hot aqueous sodium hydroxide (this reaction will be discussed in a subsequent paper [5]); **17** shows the expected

Scheme 2

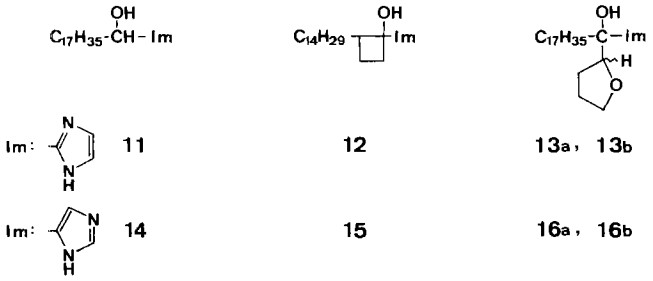


Table 4. *Yields of* **2** *and* **5** *(> 235-nm-light, in THF)*

Conversion of 1-valerylimidazole (**1**) [%]	2-Valerylimidazole (**2**) [%]	2-Acetylimidazole (**5**) [%]
0	0	0
11.7	2.5	0.8
23.0	5.1	3.0
37.8	5.5	2.4
46.8	6.2	3.0
55.9	6.2	4.0
71.6	6.2	5.0
83.3	3.8	4.4

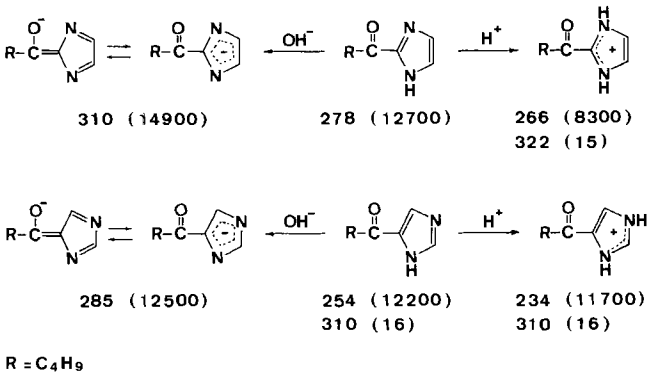
infrared carbonyl band at 1773 cm^{-1}. Stereoisomers **13a** and **13b** were correlated by being both converted into the known compound **8** on oxidation with lead tetraacetate.

As for compound **15**, its mass spectrum and elemental analysis indicated that it is an isomer of **9**. Its IR. spectrum showed no carbonyl band but instead OH and NH bands (3600–3000 cm^{-1}, broad), and in the NMR. spectrum no signals due to vinylic or *H*–C–OH type protons appeared. These facts together with a consideration of the reaction mechanism suggest a structure with a cyclobutanol moiety. The fragmentation patterns in the mass spectrum of **15** and the signal pattern of its NMR. spectrum in the region of 3.0–0.8 ppm are indeed similar to those of **12**.

Discussion. The observed relative rates of the decreases of compounds **1–3** shown in *Table 1* are in agreement with the finding that irradiation of **1** using 254-nm-light allowed for temporal accumulation of acyl migration products **2** and **3** *(Table 2)*, while on irradiation with >235-nm-light these were found only in small amounts *(Table 4)*[5]); this is in accord with results reported previously [3]. The results listed in *Table 2* indicate that the yields of **2** and **3** (step 1a and 1b in *Scheme 1*) are almost the same, and that true yields of acyl migration products are found to be at least 40% each. These values were obtained at an early stage of conversion of **1** (20%), where further transformation of **2** and **3** is minimized.

The theoretical extent of C(2′)–C(3′) cleavage in the photolysis of *N*-acylimidazoles possessing secondary hydrogen atoms in γ-position to the carbonyl group was thus calculated from the yields of steps 1 and 2 *(Table 3)* according to *Scheme 1*. The calculated value in the case of irradiation with 254-nm-light in tetrahydrofuran

Scheme 3



is 33.6% which coincides almost exactly with the observed yield of **10** from **7** under the same irradiation condition (33%; s. *Table 3*). Similarly the calculated yield of **10** on irradiation with >235-nm-light was found to be 36.6% assuming that the yields of step 1 are identical with those obtained with 254-nm-light. This value is also in good agreement with the observed yield of **10** (38%) obtained on irradiation of **7** under these conditions. These findings thus exclude a direct fragmentation path from *N*-acylimidazoles.

It is conceivable that photoproducts **11**–**16** could also be formed through hydrogen abstraction by the excited carbonyl group, either (or both) in an intramolecular (cyclobutanol formation) or intermolecular way (reduction, addition of solvent). If so, a judicious choice of irradiation solvent might improve the yield of Type II elimination products. However, tetrahydrofuran remained the solvent of choice, dictated by its transparency to all wavelengths of irradiation used, its lack of reaction with substrates, and its excellent solvent properties.

The pronounced influences of both acid and base on the photoreactivities of 2- and 4(5)-acylimidazoles appeared to be related to their significant effects on the UV. absorptions of acylimidazoles. The UV. absorption spectra of 2- (**2**) and 4(5)-valerylimidazole (**3**) in ethanol showed on addition of 1.5 equivalent of hydrochloric acid a hypsochromic shift of the π,π^* absorption band by 12–20 nm, but no shift of the n,π^* transitions which are responsible for the hydrogen abstraction reactions. On the other hand the addition of 1.5 equivalent of aqueous sodium hydroxide caused a large bathochromic shift (31–32 nm) of the π,π^* bands, and no n,π^* band was discernible. Protonated and deprotonated structures as depicted in *Scheme 3* could explain their photochemical behavior; the photoreactivity of the former might be interpreted as the result of an inductive effect on the electrophilic character of hydrogen abstraction by the n,π^* transition of the carbonyl groups, and lack of reactivity of the latter could be due to the inversion of the orders of their lowest n,π^* and π,π^* triplet states as demonstrated in the photoreactivities of substituted phenyl alkyl ketones [4] or could be due to the predominant enolate forms.

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Experimental Part

General. – *Melting points* (M.p.) were taken using a *Büchi* apparatus (type Dr. *Tottoli*) and are not corrected. – *UV. spectra* were measured on a *Perkin-Elmer* apparatus (model 402), the maxima are given in nm (extinction ε). – *IR. spectra* were measured on a *Perkin-Elmer*-spectrophotometer (model 297) and recorded in cm^{-1}; intensity: *w* = weak, *m* = medium, *s* = strong. – *Mass spectra* were measured on a *Hitachi-Perkin-Elmer* RMU-6M instrument and reported in *m/e* (relative intensity). – *^{1}H-NMR. spectra* were measured on a *Varian* H-100 or XL-100 instrument (100 MHz); the chemical shift is (in δ) given in ppm relative to TMS (= 0 ppm) as internal standard; *s* = singlet, *d* = doublet, *t* = triplet, *qa* = quadruplet, *m* = multiplet, br. = broad, coupling constant *J* in Hz, $w_{1/2}$ = half width in Hz).

Thin layer chromatography was carried out on *Merck* «DC.-Fertigplatten», Kieselgel 60 F-254, and *column chromatography* on silicagel *Merck* (0.063–0.200 mm). – *Gas chromatography* (GLC.) was performed on a *Varian* apparatus model 90-P. Columns used were 11% QF-1 on *Chromosorb* W (60/80 AW/DMCS) and 10% *Apiezon* L (60/100 AW/DMCS) at 172° and 245°, respectively.

For irradiation a low pressure mercury lamp (TMN 15132, *Quarzlampen GmbH*, Hanau; lamp A) or a 125 W medium pressure mercury lamp (QM 125, *Meda-Licht AG*, Basel; lamp B) through a quartz immersion well were used.

Preparation of valerylimidazoles. – *1-Valerylimidazole* (**1**) was prepared by treatment of valeryl chloride with two mol-equiv. of imidazole in benzene, b.p. 120°/7 Torr. – UV. (THF): 245 (3300). – IR. (CCl_4): 3165*w*, 3140*w*, 2960*s*, 2935*s*, 2875*m*, 1743*s*, 1620*w*, 1472*s*, 1460*s*, 1385*s*, 1270*s*, 1222*s*, 1095*s*, 1072*s*, 1038*m*, 945*m*. – ^{1}H-NMR. ($CDCl_3$): 8.07 (br. *s*, H–C(2)); 7.39 (*d*×*d*, *J* = 1.0, H–C(5)); 7.01 (*d*×*d*, *J* = 1.0, H–C(4)); 2.81 (*t*, *J* = 6.0, CH_2–CON(1)); 2.5–1.1 (*m*, 4 H); 0.90 (*t*, *J* = 7.0, terminal CH_3). – MS.: 152 (M^+, 16), 124 (8), 123 (8), 95 (12), 85 (53), 69 (80), 68 (29), 57 (*100*), 55 (29).

$C_8H_{12}N_2O$ (152.18) Calc. C 63.13 H 7.95 N 18.41% Found C 63.31 H 7.90 N 18.32%

4 g of **1** in 400 ml of THF was irradiated (lamp A) for 24 h, and the resulting mixture, after evaporation of the solvent, was separated by repeated silicagel chromatography to give 1.0 g of crude *2-valerylimidazole* (**2**) and 920 mg of *4(5)-valerylimidazole* (**3**). The former was recrystallized from benzene to give needles, m.p. 102.5–104°. – UV. (EtOH): 278 (12700). UV. (EtOH + 1.5 equiv. of HCl): 266 (8300), 322 (15). UV. (EtOH + 1.5 equiv. of aq. NaOH-solution): 310 (14900). – IR. ($CHCl_3$): 3440*m*, 3270*m*, 2960*m*, 2935*m*, 2870*w*, 1670*s*, 1415*s*, 1125*m*, 1080*m*, 1030*m*, 940*m*. – ^{1}H-NMR. ($CDCl_3$): 7.4–7.2 (*m*, H–C(4) and H–C(5)); 3.14 (*t*, *J* = 7.0, CH_2–COC(2)); 1.94–1.24 (*m*, 4 H); 0.94 (*t*, *J* = 7.0, terminal H_3C). – MS.: 152 (M^+, 70), 137 (10), 123 (37), 110 (93), 95 (87), 82 (52), 68 (*100*), 57 (17), 55 (10), 41 (33).

$C_8H_{12}N_2O$ (152.18) Calc. C 63.13 H 7.95 N 18.41% Found C 63.18 H 7.92 N 18.32%

3 was recrystallized from benzene to give needles, m.p. 115–117°. – UV. (EtOH): 254 (12200), 310 (16): UV. (EtOH + 1.5 equiv. of HCl): 234 (11700), 310 (16). UV. (EtOH + 1.5 equiv. of aq. NaOH solution). 285 (12500). – IR. ($CHCl_3$): 3440*m*, 3230*m*, 2960*s*, 2930*s*, 2870*m*, 1660*s*, 1550*s*, 1375*s*, 1130*s*, 1090*m*, 920*w*, 843*w*. – ^{1}H-NMR. ($CDCl_3$): 7.85 (*s*, H–C(2)); 7.78 (*s*, H–C(4 or 5)); 2.89 (*t*, *J* = 7.0, CH_2–COC(4 or 5)); 1.90–1.24 (*m*, 4 H); 0.95 (*t*, *J* = 7.0, terminal CH_3). – MS.: 152 (M^+, 11), 123 (8), 110 (*100*), 95 (93), 82 (3), 81 (2), 68 (11), 67 (6), 55 (1), 40 (14).

$C_8H_{12}N_2O$ (152.18) Calc. C 63.13 H 7.95 N 18.41% Found C 63.05 H 7.97 N 18.43%

Quantitative study of the photo-reactivities of acylimidazoles. – In all cases irradiations were carried out using lamp A or B through a quartz immersion well. Each compound to be irradiated was prepared as a $5 \cdot 10^{-2}$M solution from which 0.7 ml were taken in a standardized quartz or pyrex tube (3 mm inner diameter) placed at the same position. The reactions were followed repeatedly by GLC. and quantitatively by calibration with solutions of known concentration.

Rates of consumption of valerylimidazoles **1–3.** THF solutions of **1**, **2**, **3** and of *valerophenone* (**4**) were each irradiated under four different conditions; A) lamp A with quartz tubes (254 nm), B) lamp B with quartz tubes (> 235 nm), C) lamp B with pyrex tubes (> 280 nm), and D) 254 nm light (condition A) with the addition of 1.5 equiv. of HCl. The rates of decrease of **1**, **2** and **3** relative to that of **4** were determined by GLC. using QF-1 and *Apiezon* L column and were calculated from the early stages of their conversion. The result is shown in *Table 1*.

Yields of photo-rearrangement (**2** *and* **3**) *and photo-fragmentation products* (**5** *and* **6**) *on the irradiation of* **1**. The THF solution of **1** was irradiated using lamp A with quartz tubes, and the formation of **2**, **3**, 2-acetylimidazole (**5**) and 4(5)-acetylimidazole (**6**) was followed by GLC. using a QF-1 and an *Apiezon* L column. Yields at various stages of conversion of **1** were calculated from the plotted lines and are shown in *Table 2.*

Yields of **2** and **5** by irradiation of **1** using lamp B with quartz tubes were determined similarly[4]). The result is shown in *Table 4.*

Yields of 1-hexadecene (**10**) *on irradiation of the stearoylimidazoles* **7–9**. **7–9** were irradiated under four different conditions; A) lamp A with quartz tubes, in THF (254 nm), B) lamp B with quartz tubes, in THF (>235 nm), C) >235 nm light, in ethanol (**8** and **9** only) and D) >235 nm light in ethanol with the addition of 1.5 equiv. of HCl (**8** and **9** only). In each irradiation the maximum yield of **10** was determined by GLC. using a QF-1 column. The result is shown in *Table 3.*

Photolysis of stearoylimidazoles. – *Photolysis of 2-stearoylimidazole* (**8**). 2.20 g of **8** in 300 ml of THF were irradiated for 100 min using lamp B with a quartz immersion well. The irradiation mixture was passed through a column of 100 g of silicagel. Elution with hexane/benzene 1:1 gave 760 ml of crude**10**, further elution with chloroform/methanol 1:1 *ca.* 1.5 g of a mixture. Repeated chromatographic separation of the latter afforded 140 mg **11**, 181 mg **12**, 136 mg **13a** and 177 mg **13b**. *2-(1'-Hydroxy-octadenyl)-imidazole* (**11**), m.p. 101–102° (from acetone). – UV. (THF): 231 (1260). – IR. (KBr): 3700–2500*m* br., 2920*s*, 2850*s*, 1550*w*, 1470*m*, 1375*w*, 1110*w*, 1090*w*, 1050*w*, 780*w*, 765*w*, 735*w*, 720*w*. – ^{1}H-NMR. (CF_3COOD): 7.52 (br. *s*, H–C(4) and H–C(5)); 6.34 (*t*, J=7.0, H–C(1')); 2.26 (br. *m*, $w_{1/2}$=18, 2 H–C(2')); 1.32 (*s*, 30 H); 0.90 (*t*, J=7.0, terminal CH_3). – MS.: 336 (M^+, 25), 318 (29), 303 (4), 291 (21), 277 (10), 275 (9), 261 (8), 247 (8), 233 (8), 219 (10), 205 (11), 191 (12), 177 (12), 167 (12), 163 (13), 153 (40), 149 (17), 135 (18), 121 (85), 111 (38), 107 (31), 98 (*100*), 95 (40), 82 (43), 69 (25), 57 (25), 55 (21).

$C_{21}H_{40}N_2O$ (336.55) Calc. C 74.94 H 11.98 N 8,32% Found C 74.39 H 12.03 N 8.22%

To 35 mg of **11** in 1 ml of glacial acetic acid were added 30 mg of CrO_3. The mixture was stirred for 1 h at room temp., water was added to the solution and the separated solid extracted with $CHCl_3$ and worked-up. Removal of solvent and recrystallization from carbon tetrachloride gave a product found to be identical with *2-stearoylimidazole* (**8**).

2-(1'-Hydroxy-2'-tetradecylcyclobutyl)imidazole (**12**), m.p. 115–116° (from acetone). – UV. (THF): 231 (2100). – IR. ($CHCl_3$): 3600–3000*m* br., 2925*s*, 2845*s*, 1540*w*, 1460*m*, 1370*w*, 1070*m*. – ^{1}H-NMR. ($CDCl_3$): 6.95 (*s*, H–C(4) and H–C(5)); 3.0–2.4 (*m*, 2 H); 2.3–1.4 (*m*, 7 H); 1.0–1.4 (br. *s*, 22 H); 0.88 (*t*, J=7.0, terminal CH_3). – MS.: 334 (M^+, 32), 316 (3), 306 (5), 301 (1), 287 (1), 278 (6), 273 (0.5), 263 (1), 259 (1), 249 (1), 245 (0.5), 235 (2), 231 (0.5), 221 (1), 217 (0.5), 207 (2), 203 (1), 193 (3), 189 (1), 179 (3), 175 (1), 165 (3), 161 (3), 151 (5), 147 (6), 137 (8), 133 (5), 123 (8), 110 (*100*), 95 (9), 82 (29), 69 (17), 55 (9).

$C_{21}H_{38}N_2O$ (334.53) Calc. C 75.39 H 11.45 N 8.37% Found C 75.30 H 11.39 N 8.25%

To 70 mg of **12** in 1 ml of dry THF were added at 0° 10 mg of sodium hydride dispersion (50–60% in oil) and the suspension was stirred for 1 h. To the solution were added 100 mg of methyl iodide and the mixture was stirred for 2 h at room temp. After evaporation of the solvent the residue was dissolved in 10% sodium hydroxide and heated in a closed flask to 80° for 1 h. After cooling the separated solid was extracted with hexane and the extract was washed with diluted hydrochloric acid and water. Solvent removal gave a solid which was purified by GLC. (QF-1 colmn) to give *2-(tetradecyl)-1-cyclobutanone* (**17**). – IR. ($CHCl_3$): 2925*s*, 2855*s*, 1780*s*, 1460*m*, 1390*w*, 1375*w*, 1090*w*. – ^{1}H-NMR. ($CDCl_3$): 3.24 (*m*, 1 H); 3.1–2.86 (*m*, 2 H); 2.18 (*m*, 1 H); 1.86–1.40 (*m*, 5 H); 1.26 (br. *s*, 22 H); 0.88 (*t*, J=6.0, terminal CH_3). – MS.: 266 (M^+, 4), 248 (3), 238 (5), 222 (3), 194 (2), 180 (1), 166 (1), 152 (1), 138 (1), 124 (5), 112 (36), 98 (*100*), 84 (30), 69 (20), 55 (35).

$C_{18}H_{34}O$ (266.47) Calc. C 81.13 H 12.86% Found C 80.97 H 13.43%

2-[1'-Hydroxy-1'-(2''-tetrahydrofuryl)octadecyl]imidazole. Isomer (**13a**), m.p. 90° (from acetone). – UV. (THF): 228 (1130). – IR. ($CHCl_3$): 3600–3000*m* br., 2925*s*, 2855*s*, 1460*m*, 1380*w*, 1150*w*, 1065*m*. – ^{1}H-NMR. ($CDCl_3$): 6.98 (br. *s*, H–C(4) and H–C(5)); 4.18 (*t*, J=7.0, H–C(2'')); 3.80 (br. *t*, J=6.0, 2 H–C(5'')); 2.1–1.6 (*m*, 6 H); 1.4–1.1 (*m*, 30 H); 0.85 (*t*, J=7.0, terminal CH_3). – MS.: 406 (M^+, 7), 388

(24), 336 (90), 335 (*100*), 317 (4), 277 (3), 261 (3), 247 (3), 233 (3), 219 (4), 205 (4), 191 (14), 177 (9), 164 (18), 163 (19), 149 (7), 135 (6), 123 (6), 111 (40), 95 (11), 82 (7), 71 (24), 69 (36), 57 (9), 55 (8).

$C_{25}H_{46}N_2O_2$ (406.63) Calc. C 73.84 H 11.40 N 6.89% Found C 73.85 H 11.38 N 6.90%

Isomer (**13b**), m.p. 76–77° (from acetone). – UV. (THF): 230 (990). – IR. ($CHCl_3$): 3600–3000*m* br., 2920*s*, 2855*s*, 1465*m*, 1380*w*, 1060*m*. – ^{1}H-NMR. ($CDCl_3$): 6.98 (*s*, H–C(4) and H–C(5)); 4.23 (*t*, J = 6.0, H–C(2″)); 3.82 (*t*, J = 6.0, 2 H–C(5″)); 2.2–1.4 (*m*, 6 H); 1.4–1.1 (*m*, 30 H); 0.88 (*t*, J = 7.0, terminal CH_3). – MS.: 406 (M^+, 8), 388 (10), 336 (89), 335 (*100*), 317 (2), 277 (3), 261 (1), 247 (1), 233 (1), 191 (5), 177 (3), 164 (11), 163 (12), 149 (7), 137 (3), 135 (3), 123 (5), 111 (26), 95 (7), 85 (3), 82 (4), 71 (14), 69 (21), 57 (10), 55 (7).

$C_{25}H_{46}N_2O_2$ (406.63) Cal. C 73.84 H 11.40 N 6.89% Found C 73.68 H 11.48 N 6.93%

To 40 mg of **13a** in 1 ml of acetonitrile were added 60 mg of lead tetraacetate. The mixture was stirred for 2 h at room temp., and excess of lead tetraacetate was destroyed with sodium hydrogensulfite. After addition of a small amount of water the mixture was extracted with ether and the extract washed with water. Evaporation of the solvent gave crude **8** which was purified by silicagel chromatography.

13b was treated in the same way, and **8** obtained from both **13a** and **13b** was identified with an authentic sample.

Photolysis of 4(5)-stearoylimidazole (**9**). 2.20 g of **9** in 300 ml of THF were irradiated for 2.5 h using lamp B with a quartz immersion well. The irradiation mixture was passed through a column of 100 g of silicagel. Elution with hexane/benzene 2:1 gave 730 mg of crude **10**. Further elution with chloroform/methanol 1:1 gave a mixture. Repeated silicagel chromatography of this afforded 110 mg **14** and 130 mg **15**. The rest of the products could not be obtained in pure form. *4(5)-(1′-Hydroxy-octadecyl)imidazole* (**14**), m.p. 91–93° (from acetone). – UV. (THF): 232 (1060). – IR. (KBr): 3600–3000*m* br., 2920*s*, 2845*s*, 1465*m*, 1070*m*, 780*w*, 720*w*, 625*m*. – ^{1}H-NMR. (CF_3COOD): 8.83 (*d*, J = 1.0, H–C(2)); 7.63 (*d*, J = 1.0, H–C(4 or 5)); 6.14 (*t*, J = 7.0, H–C(1′)); 2.23 (*m*, 2 H–C(2′)); 1.32 (br. *s*, 30 H); 0.90 (*t*, J = 7.0, terminal CH_3). – MS.: 336 (M^+, 4), 318 (28), 303 (3), 289 (5), 275 (6), 261 (5), 247 (7), 233 (5), 221 (3), 219 (5), 205 (6), 191 (7), 177 (9), 163 (10), 149 (14), 135 (12), 121 (37), 107 (37), 97 (*100*), 82 (27), 69 (12), 55 (13).

$C_{21}H_{40}N_2O$ (336.55) Calc. C 74.94 H 11.98 N 8.32% Found C 74.55 H 11.76 N 8.22%

4(5)-(1′-Hydroxy-2′-tetradecylcyclobutyl)imidazole (**15**), m.p. 91° (from acetone). – UV. (THF): 231 (2114). – IR. ($CHCl_3$): 3600–3000*m* br., 2920*s*, 2850*s*, 1460*m*, 1370*w*, 1305*w*, 1110*m*, 1090*m*, 880*w*, 820*m*. – ^{1}H-NMR. ($CDCl_3$): 7.45 (br. *s*, H–C(2)); 6.88 (br. *s*, H–C(4 or 5)); 2.7–1.4 (*m*, 9 H); 1.23 (br. *s*, 22 H); 0.88 (*t*, J = 6.0, terminal CH_3). – MS.: 334 (M^+, 4), 316 (24), 306 (4), 301 (6), 291 (0.5), 287 (4), 278 (4), 273 (4), 263 (1), 259 (3), 249 (1), 245 (3), 235 (1), 231 (4), 221 (1), 217 (4), 207 (2), 203 (6), 193 (1), 189 (7), 179 (2), 175 (7), 165 (2), 161 (15), 151 (2), 147 (35), 133 (69), 123 (16), 110 (*100*), 95 (23), 81 (12), 69 (9), 55 (12).

$C_{21}H_{38}N_2O$ (334.53) Calc. C 75.39 H 11.45 N 8.37% Found C 75.21 H 11.66 N 8.48%

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