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99. Mitteilung[1])

Photochemistry of *N*-Acylimidazoles. IV. Structural Factors Leading to *Norrish* Type II Elimination and to Cyclobutanol Formation in the Photolysis of Acylimidazoles

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Summary

Conformational factors leading to Type II elimination and to cyclobutanol formation were studied in the irradiation of *N*-acylimidazoles with simple acyl groups as well as of their photochemical acyl migration products.

Results and Discussion. Several *N*-acylimidazoles possessing hydrogen atoms at C(4') (γ to the carbonyl group) were found to undergo efficient cleavage of acyl chain between C(2') and C(3') *via* a *Norrish* Type II process [2], and pathways leading to this cleavage were discussed in the preceding paper [1].

The best conformation leading to efficient Type II cleavage was suggested to be one in which the *p*-orbitals at C(1') and C(4') of the intermediate biradical generated by the photochemical hydrogen abstraction by the carbonyl group are both parallel to the C(2')–C(3') bond [3]. A biradical intermediate in an unfavorable conformation for cleavage can instead undergo bond formation between C(1') and C(4') yielding a cyclobutanol derivative which is also of synthetic importance.

In view of the potential practical importance of the photoreactions of *N*-acylimidazoles as a mean of degradation and modification of naturally occurring carboxylic acids and related compounds, it was decided to study the influence of steric factors on these reactions, using *N*-acylimidazoles formed from carboxylic acids attached to ring systems and thus introducing conformational factors.

The *N*-acylimidazoles of such carboxylic acids were prepared *in situ* using *N*,*N*'-carbonyl-diimidazole (NCD) as coupling reagent and were irradiated in tetrahydrofuran (THF) using a low pressure mercury lamp (lamp A) with a quartz immersion well (254 nm light) (cf. [2]). The resulting primary photo-rearrangement products (*e.g.* **1** and **3**) were irradiated further in methanol using a medium pressure mercury lamp (lamp B) with a pyrex immersion well (> 280 nm light). The

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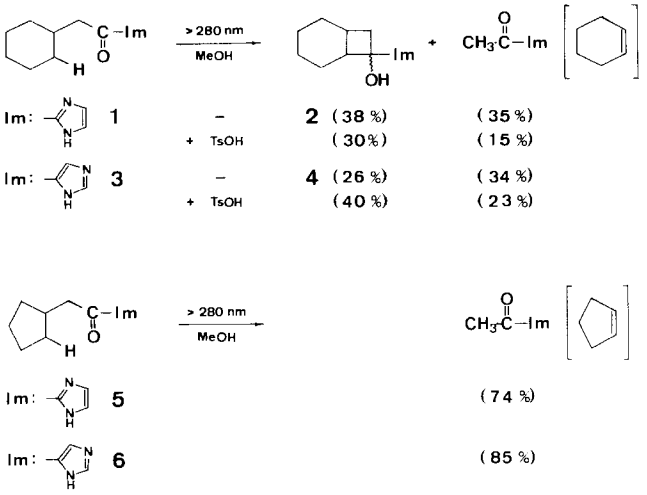
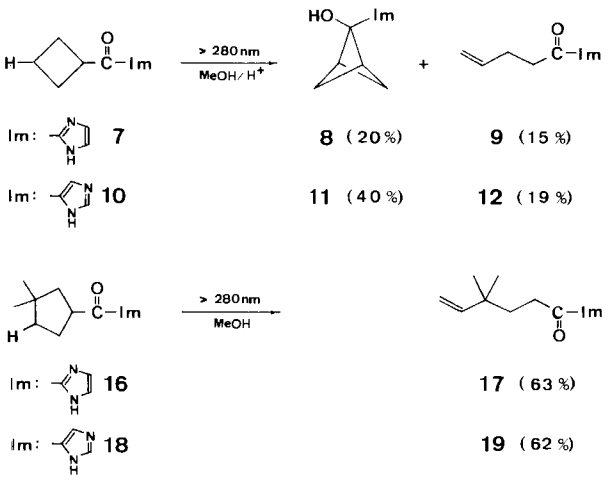
Scheme 1



ratio of cyclobutanol formation *versus* C(2′)–C(3′) cleavage for some acylimidazoles is shown in *Schemes 1* and *2*.

2- (**1**) and 4(5)-(cyclohexylacetyl)imidazole (**3**) are expected to assume preferably a conformation with an equatorial side chain on the cyclohexane ring, and this conformation is presumably unfavorable for elimination. In fact **1** and **3**, on irradiation in neutral medium, afforded the cyclobutanols **2** and **4**, respectively, and the fragmentation products in comparable yields; the yields of the former in comparison to the ones of the latter were increased when the irradiation was carried out in the presence of *p*-toluenesulfonic acid. This effect on product distribution might be caused by protonation of the imidazole ring which increases the relative bulk of the side chain groups.

Scheme 2



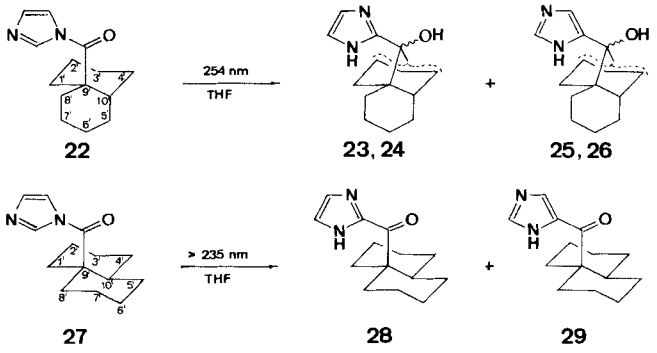
On the other hand irradiation of 2- (**5**) and 4 (5)-(cyclopentylacetyl)imidazole (**6**) gave only elimination products, and these in good yields. This result is understandable from the generally accepted conformation of the cyclopentane ring which should provide satisfactory overlapping of the *p*-orbitals of the generated radicals with the bond to be cleaved.

The relatively efficient formation of the highly strained 2-phenylbicyclo-[1.1.1]-pentan-2-ol (38% yield) by irradiation of cyclobutyl phenyl ketone has been reported [4]; and this fact was cited as the best evidence for the dominant effect of intermediate conformation over product stability in reaction path control [3]. In our hands irradiation of 2- (**7**) and 4(5)-(cyclobutylcarbonyl)imidazole (**10**) in the presence of acid gave the cyclobutanols **8** and **11** in higher yields than the corresponding elimination products **9** and **12**, respectively. Without acid the reaction proceeded very slowly, no product could be isolated even after prolonged irradiation.

Irradiation of 2- (**16**) and 4(5)-(3′,3′-dimethylcyclopentyl-carbonyl)imidazole (**18**)[3]) led to unexpected results, namely to the preferential formation of the ring opened products **17** and **19**. This is contrary to our premise concerning the intermediate conformation required for the Type II elimination, because according to the model the bonds cleaved seem to be almost perpendicular to the radical orbital at the ring carbon atom. A similar result has been reported in the photolysis of cyclopentyl phenyl ketone which gave none of the bridged cyclobutanol [5].

In view of the importance of the six-membered ring among alicyclic compounds, the photoreactivity of *N*-acylimidazoles of carboxylic acids attached directly to a cyclohexane ring was studied. Since simple (cyclohexylcarbonyl)imidazoles were found to give no Type II reaction products – perhaps because the side chain assumes an equatorial conformation – *cis*- (**20**) and *trans*-decalin-9-carboxylic acid (**21**) were prepared (see exper. part). In **20** and **21** the carboxyl group is axial in relation to one and both cyclohexane rings, respectively.

Scheme 3



22 **23, 24** **25, 26**

27 **28** **29**

[3]) **16** and **18** were prepared from 3,3-dimethylcyclopentyl-carboxylic acid (**15**) *via* the *N*-acylimidazole, and **15** was obtained from 2-chloro-4,4-dimethylcyclohexanone (**13**) by rearrangement to methyl 3,3-dimethylcyclopentyl-carboxylate (**14**) and subsequent hydrolysis. Acid **15** in which one of the carbon atoms in γ-position to the carbonyl group is fully substituted was prepared in order to avoid secondary reactions involving hydrogen atoms at this position (s. exper. part).

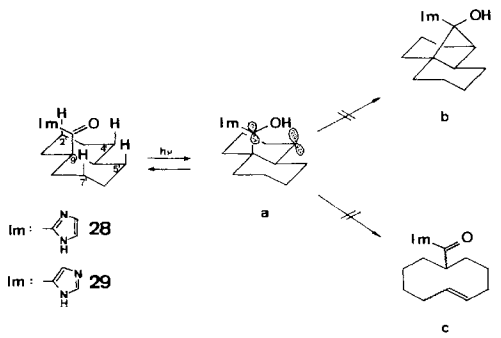
Irradiation of the *N*-acylimidazole **22** derived from the *cis*-acid **20** with 254-nm-light in THF gave the cyclobutanol derivatives **23** (5%) and **24** (17%) which could each be isolated as the pure compound, and a mixture of **25** and **26** (30%) *(Scheme 3)*; neither intermediate acyl migration product nor Type II cleavage products were isolated. These results indicate that hydrogen abstraction in the acyl migration products proceeded faster than the initial migration step. This might be due to the 1,3-diaxial interaction between the carbonyl substituent and the axial hydrogen atoms at the 2′ and/or 4′ position of the decalin ring favoring the probability of hydrogen abstraction.

On the other hand, the *N*-acylimidazole **27** derived from the *trans*-acid **21** was found to be much more stable on irradiation than **22**. Using >235-nm-light **27** led to the formation of the acyl migration products **28** and **29** in 13 and 25% yield, respectively (calculated from 78% conversion of **21**). **28** and **29** were in turn irradiated in methanol with >280-nm-light but were found to be stable, and no product could be isolated even by irradiation after addition of hydrochloric acid.

There is no clear explanation for the stability to irradiation of **27**. Perhaps there is some connection with the fact that *N*-acylimidazoles with hindered *N*-acyl groups are always formed much more slowly from the corresponding acids and *N,N′*-carbonyldiimidazole and that these *N*-acylimidazoles are photolised more sluggishly and eventually give complex product mixtures.

A perhaps more convincing argument for the stability of **28** and **29**, in spite of the *a priori* facile abstraction of axial hydrogen atoms at the 4′ and 5′ position of the decalin ring, is the following: Hydrogen abstraction by the carbonyl group from the 2′-(or 7′)-position is unfavorable because of steric interaction between the imidazole ring and the axial hydrogen atom at the 7′-(or 2′)-position in the transition state, so that the axial hydrogen atom at the 4′-(or 5′)-position would be expected to be abstracted to give the biradical intermediate **a** *(Scheme 4)*. But a hydroxy-imidazolyl-methano bridge between C(4′) and C(9′) (**b**) might be expected to give rise to considerable steric interference between the imidazole ring and axial *β*-hydrogen atoms, so that **b** isn't formed. On the other hand, Type II elimination to form a much less strained 10-membered ring **c** cannot proceed because of the fixed conformation of the biradical intermediates in which the radical orbitals at both the carbonyl carbon atom and at C(4′) of the decalin ring could hardly overlap with the C(9′)–C(10′) bond. As the result a reverse 1,5-hydrogen transfer would take place giving back the starting compounds.

Scheme 4



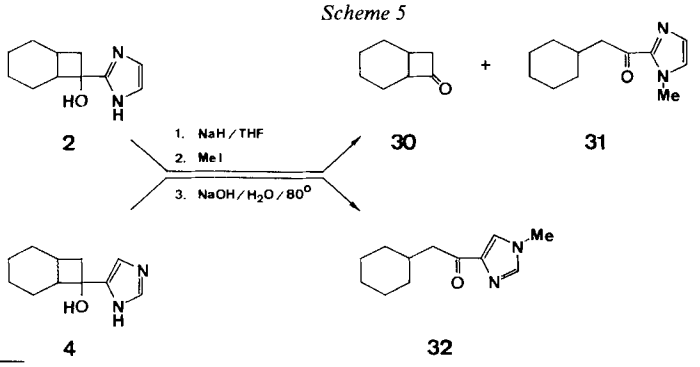
Structures of products. The structures of all the photoproducts are based essentially on their spectral and analytical data (s. exper. part). The substitution patterns on the imidazole ring of the acylimidazole derivatives were assigned

according to previous work [6]. In addition strong IR. bands appearing at *ca.* 1400 cm^{-1} and bands appearing at *ca.* 1550 cm^{-1} with weak to medium intensities are considered to be specific of 2-acyl- and 4(5)-acylimidazoles, respectively. These bands appear much sharper in the case of *N*(1)-methylated compounds such as **31** and **32** (s. below), and they are probably due to C(2)=N(3) and C(4)=C(5) bonds conjugated with acyl carbonyl groups.

Mass spectra and elemental analyses of **2** and **4** showed that they were isomers of **1** and **3**[4]). Their IR. spectra showed no carbonyl band. In the ^{1}H-NMR. spectra **2** exhibited a multiplet at 7.00–6.86 ppm due to the hydrogen atoms at C(4) and C(5) of the imidazole moiety and **4** showed two singlets at 7.68 and 6.93 ppm arising from H–C(2) and H–C(4 or 5) of the imidazole ring. In their ^{13}C-NMR. spectrum both compounds showed a singlet at 78.3 ppm due to the carbon atom substituted by the hydroxy and imidazolyl group. The signals of C(2), C(4) and C(5) of the imidazole ring appeared at 153.6 (1*s*) and 122.1 ppm (2*d*) for **2**, and at 135.8 (1*d*), 143.9 (1*s*) and 116.5 ppm (1*d*) for **4**. The NMR. data of **2** and **4** clearly indicate the substitution pattern on the imidazole ring and the presence of a fully substituted carbon atom bearing a hydroxy and an imidazolyl group. Similar conclusions can be drawn from data of other compounds possessing similar cyclobutanol moieties such as **8**, **11** and **23–26**, which are described in the exper. part.

Treatment of the sodio-derivative of **2** (from **2** and sodium hydride) with an excess of methyl iodide gave a quaternary salt (possibly a mixture), whose treatment with aqueous alkali at 80° led to fragmentation giving products **30** and **31** (2:1 mixture). The former was shown by its IR. spectrum (carbonyl band at 1780 cm^{-1}) to be a cyclobutanone[5]). Compound **31** apparently was formed by base-catalyzed ring opening of the cyclobutanol ring followed by *N*-demethylation. This assumption is based on the fact that the *N*(1)-methyl derivative of **2** was stable to alkali treatment. **31** was also synthetized by methylation of compound **1**.

Scheme 5



[4]) **2** and **4** were always obtained as mixtures consisting of a major (80–90%) and a minor stereoisomer. The composition differed depending on irradiation conditions and on the purification procedures. The data given in the exper. part refer to a 9:1 mixture, the ^{13}C-NMR. data to the major component in each mixture.

[5]) This fragmentation to a cyclobutanone was found to be applicable to 1-(2-imidazolyl)cyclobutanols in general.

Similar treatment of the sodio-derivative of **4** afforded only **32** which was also the sole methylation product of **3**. The position of the *N*-methyl substitution in **32** was deduced from the ^{1}H-NMR. chemical shift of this methyl group (3.70 ppm) as compared to the corresponding *N*(1)-methyl signal of **31** (3.96 ppm) having the acyl substituent next to the CH_3N group.

The ^{1}H-NMR. spectra of **8** and **11** show close analogy to that of 2-phenylbicyclo-[1.1.1]pentan-2-ol [4] and the assignment of the proton signals of **8** and **11** is based on that of the latter compound (see exper. part, *Scheme 6*).

Compounds **9** and **12** were identical with products obtained from the parallel irradiation of *N*-(allylacetyl)imidazole, and the structures of **17** and **19** were unambiguously clear from their ^{1}H-NMR. spectra (see exper. part).

The ^{1}H-NMR. spectra of **23** and **24** demonstrated substitution at C(2) of the imidazole moiety (signals due to H–C(4) and H–C(5)). Moreover, quaternization of **23** followed by alkali-induced fragmentation as described above for compound **2** led to a product whose IR. spectrum once again appeared to be that of a cyclobutanone **33** (1775–1765 cm^{-1}, broad)[6]). Compound **24** treated in the same way as **23** gave also compound **33** identified by its IR. spectrum and GLC. retention time. This shows that **23** and **24** differ only in the configuration at the hydroxy-imidazolyl-methano carbon atom. However, the degradation does not determine the position of the photochemical hydrogen abstraction on the decalin ring.

25 and **26** were obtained as a mixture as indicated by the ^{13}C-NMR. spectrum. The spectroscopic properties of **25/26** showed close analogy with those of **23** and **24**, except for the NMR. signals of the imidazole group. In **25/26** one of the attachment of the hydroxy-imidazolyl-methano bridge as well as the configuration of the latter in each compound remain unknown.

The ^{13}C-NMR. of compound **28** exhibited 6 signals due to the decalin group indicating the presence of a symmetry plane along the C(9′)–C(10′) bond. The acyl substitution pattern of the imidazole ring is indicated by the UV., IR., and NMR. spectra. The ^{1}H-NMR. spectrum of **28** showed a two-proton multiplet at 3.18 ppm which might be assigned to the equatorial hydrogen atoms at C(1′) and C(8′) of the decalin ring, their shift being induced by the anisotropic effect of the imidazole ring.

The structure of **29** was similarly assigned. Its ^{1}H-NMR. spectrum likewise showed a two-proton multiplet shifted to 2.53 ppm and possibly assignable to the equatorial hydrogen atoms at C(1′) and C(8′).

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Experimental Part

General. See [1].

Preparation of acylimidazole 1, 3, 5–7, 10, 16 and 18. – These acylimidazoles were synthetized *in situ* by irradiation (lamp A) of the corresponding *N*-acylimidazoles prepared from the corresponding

[6]) The carbonyl band of bicyclo[3.1.1]heptan-6-one appears at 1775 cm^{-1} [7]. Based on the spectroscopic properties two structures are proposed for **33**: tricyclo[7.1.1.0^{4,9}]undecan-10-one and tricyclo[5.3.1.0^{7,2}]undecan-11-one.

acid and *N,N'*-carbonyl-diimidazole (NCD) in THF. The products were separated by column chromatography on silicagel, eluting with either chloroform/methanol 9:1 or ethyl acetate/methanol 9:1.

2-(Cyclohexylacetyl)imidazole (**1**), yield 19%, m.p. 146–147° (from benzene/heptane). – UV. (EtOH): 280 (12200). – IR. (CCl_4): 3450*m*, 3270*m*, 2920*s*, 2850*m*, 1665*s*, 1450*m*, 1430*s*, 1300*w*, 1110*w*, 1078*w*, 940*w*. – ^{1}H-NMR. ($CDCl_3$): 7.32–7.18 (*m*, H–C(4) and H–C(5)); 2.99 (*d*, J=7.0, CH_2CO); 2.3–0.8 (*m*, 11 H). – MS.: 192 (M^+, 26), 175 (3), 164 (4), 149 (4), 135 (6), 121 (2), 110 (*100*), 95 (13), 82 (36), 68 (25), 55 (10).

$C_{11}H_{16}N_2O$ (192.25) Calc. C 68.72 H 8.39 N 14.57% Found C 68.75 H 8.31 N 14.57%

4(5)-(Cyclohexylacetyl)imidazole (**3**), yield 24%, m.p. 169° (from acetone/hexane). – UV. (EtOH): 258 (13900). – IR. ($CHCl_3$): 3430*m*, 3150*m*, 2930*s*, 2855*m*, 1655*s*, 1550*m*, 1450*m*, 1370*m*, 1125*m*, 1090*m*, 975*w*, 840*w*. – ^{1}H-NMR. ($CDCl_3$): 7.82 (*s*, H–C(2)); 7.75 (*s*, H–C(4 or 5)); 2.73 (*d*, J=6.0, CH_2CO); 2.3–0.7 (*m*, 11 H). – MS.: 192(M^+, 4), 149 (7), 110 (*100*), 95 (26), 81 (5), 69 (6), 68 (6), 55 (8), 41 (9).

$C_{11}H_{16}N_2O$ (192.25) Calc. C 68.72 H 8.39 N 14.57% Found C 68.60 H 8.21 N 14.61%

2-(Cyclopentylacetyl)imidazole (**5**), yield 18%, m.p. 154–155° (from benzene/heptane). – UV. (EtOH): 280 (12800). – IR. (CCl_4): 3450*m*, 3280*s*, 2960*s*, 2875*m*, 1665*s*, 1415*s*, 1300*w*, 1160*m*, 1115*m*, 1080*m*, 1030*w*, 950*w*, 870*w*. – ^{1}H-NMR. ($CDCl_3$): 7.32–7.18 (*m*, H–C(4) and H–C(5)); 3.15 (*d*, J=7.0, CH_2CO); 2.46 (*m*, $CHCH_2CO$); 2.1–1.0 (*m*, 8 H). – MS.: 178 (M^+, 36), 161 (4), 149 (17), 135 (13), 122 (6), 121 (6), 110 (*100*), 95 (34), 85 (52), 68 (56), 55 (17), 41 (28).

$C_{10}H_{14}N_2O$ (178.23) Calc. C 67.38 H 7.92 N 15.72% Found C 67.28 H 7.93 N 15.52%

4(5)-(Cyclopentylacetyl)imidazole (**6**), yield 28%, m.p. 121–122° (from acetone/benzene). – UV. (EtOH): 257 (11100). – IR. ($CHCl_3$): 3440*m*, 3250*m*, 2960*s*, 2870*m*, 1660*s*, 1550*m*, 1410*m*, 1370*m*, 1320*w*, 1128*m*, 1095*m*, 965*w*, 920*w*, 845*w*. – ^{1}H-NMR. ($CDCl_3$): 7.84 (*s*, H–C(2)); 7.76 (*s*, H–C(4 or 5)); 2.89 (*d*, J=7.0, CH_2CO); 2.42 (*m*, $CHCH_2CO$); 2.1–1.0 (*m*, 8 H). – MS.: 178 (M^+, 5), 149 (4), 135 (3), 123 (3), 110 (*100*), 95 (44), 82 (3), 68 (9), 55 (4), 41 (10).

$C_{10}H_{14}N_2O$ (178.23) Calc. C 67.38 H 7.92 N 15.72% Found C 67.20 H 8.01 N 15.58%

2-(Cyclobutylcarbonyl)imidazole (**7**), yield 33%, m.p. 143–144° (from benzene/heptane). – UV. (EtOH): 280 (14600). – IR. (CCl_4): 3450*m*, 3280*s*, 2990*m*, 2950*m*, 2870*w*, 1660*s*, 1415*s*, 1290*w*, 1272*w*, 1160*w*, 1123*m*, 1078*m*, 948*w*. – ^{1}H-NMR. ($CDCl_3$): 7.24 (br. *s*, H–C(4) and H–C(5)); 4.33 (*m*, CHCO); 2.6–1.6 (*m*, 6 H). – MS.: 150 (M^+, 19), 135 (40), 122 (90), 107 (10), 95 (62), 82 (52), 68 (*100*), 55 (45), 40 (24).

$C_8H_{10}N_2O$ (150.18) Calc. C 63.98 H 6.71 N 18.65% Found C 63.79 H 6.69 N 18.73%

4(5)-(Cyclobutylcarbonyl)imidazole (**10**), yield 41%, m.p. 174–175° (from acetone/benzene). – UV. (EtOH): 259 (11000). – IR. ($CHCl_3$): 3440*m*, 3240*m*, 2980*m*, 2950*m*, 2860*w*, 1655*s*, 1550*m*, 1375*m*, 1310*m*, 1130*m*, 1003*w*, 955*w*, 845*w*. – ^{1}H-NMR. ($CDCl_3$): 7.82 (*s*, H–C(2)); 7.67 (*s*, H–C(4 or 5)); 3.86 (*m*, CHCO); 2.6–1.8 (*m*, 6 H). – MS.: 150 (M^+, 16), 135 (9), 122 (7), 95 (*100*), 68 (8), 67 (8), 55 (13), 40 (10).

$C_8H_{10}N_2O$ (150.18) Calc. C 63.98 H 6.71 N 18.65% Found C 63.86 H 6.68 N 18.76%

2-(3',3'-Dimethylcyclopentyl-carbonyl)imidazole (**16**), yield 18%, m.p. 146–147° (from benzene/heptane). – UV. (EtOH): 277 (13200). – IR. ($CHCl_3$): 3440*m*, 3280*m*, 2960*s*, 2870*m*, 1670*s*, 1415*s*, 1125*m*, 1085*m*, 870*w*. – ^{1}H-NMR. ($CDCl_3$): 7.30–7.16 (*m*, H–C(4) and H–C(5)); 4.17 (*qi*, J=8, H–C(1')); 2.24–1.42 (*m*, 6 H); 1.06 and 1.04 (2*s*, 2 H_3C–C(3')). – MS.: 192 (M^+, 56), 177 (74), 164 (57), 159 (29), 149 (59), 135 (47), 123 (56), 108 (*100*), 96 (44), 81 (26), 68 (100), 55 (47).

$C_{11}H_{16}N_2O$ (192.25) Calc. C 68.72 H 8.39 N 14.57% Found C 68.55 H 8.39 N 14.64%

4(5)-(3',3'-Dimethylcyclopentyl-carbonyl)imidazole (**18**), yield 35%, m.p. 123–124° (from acetone/benzene). – UV. (EtOH): 255 (13200). – IR. ($CHCl_3$): 3440*m*, 3250*m*, 2960*s*, 2870*m*, 1660*s*, 1550*m*, 1382*m*, 1330*m*, 1130*m*, 1110*m*, 850*w*. – ^{1}H-NMR. ($CDCl_3$): 7.83 (*s*, H–C(2)); 3.68 (*qi*, J=9.0, H–C(1')); 2.20–1.40 (*m*, 6 H); 1.06 and 1.04 (2*s*, 2 H_3C–C(3')). – MS.: 192 (M^+, 22), 177 (8), 164 (6), 149 (5), 136 (9), 123 (46), 110 (6), 95 (46), 68 (*100*), 52 (22), 39 (15).

$C_{11}H_{16}N_2O$ (192.25) Calc. C 68.72 H 8.39 N 14.57% Found C 68.65 H 8.35 N 14.26%

Preparation of 3,3-dimethylcyclopentyl-carboxylic acid (**15**). – *2-Chloro-4,4-dimethylcyclohexanone* (**13**). 43.5 g of 4,4-dimethylcyclohexanone were chlorinated as described for cyclohexanone [8]. Distillation of the crude product gave 39 g of **13** (b.p. 110–120°/15 Torr) which decomposed slowly on standing at room temp. – IR. (CCl_4): 2960*s*, 2930*s*, 2450*m*, 1730*s*, 1460*m*, 1445*m*, 1425*m*, 1390*m*, 1370*m*, 1320*m*, 1310*m*, 1215*w*, 1150*m*, 1120*m*, 1090*m*, 1025*m*, 1005*m*, 870*w*. – ^{1}H-NMR. ($CDCl_3$): 4.64 ($d\times d$, J_1=13, J_2=6.0, H–C(2)); 2.7–1.6 (*m*, 6 H); 1.24 and 1.07 (2*s*, 2 H_3C–C(4)).

Methyl-3,3-dimethylcyclopentyl-carboxylate (**14**). 40 g of **13** were rearranged with sodium methoxide as described for 2-chlorocyclohexanon (giving methyl cyclopentyl-carboxylate) [9]. Distillation of the crude product yielded 23 g of **14** (b.p. 65–70°/15 Torr) which was purified by GLC. (5% SE-30 on *Chromosorb* W) for spectroscopic and elemental analysis. – IR. (CCl_4): 2960*s*, 2870*m*, 1735*s*, 1460*m*, 1435*m*, 1370*m*, 1320*m*, 1195*s*, 1165*s*, 1050*w*, 1025*w*. – ^{1}H-NMR. ($CDCl_3$): 3.66 (*s*, CH_3O); 2.91 (*qi*, J=8.0, H–C(1)); 2.12–1.20 (*m*, 6 H); 1.05 and 0.97 (2*s*, 2 H_3C–C(3)). – MS.: 156 (M^+, 11), 141 (20), 128 (*100*), 125 (22), 109 (35), 101 (30), 100 (30), 87 (73), 81 (95), 69 (39), 55 (82), 41 (59).

$C_9H_{16}O_2$ (156.22) Calc. C 69.19 H 10.32% Found C 68.92 H 10.39%

3,3-Dimethylcyclopentyl-carboxylic acid (**15**). 21.5 g of **14** were hydrolyzed with 5% ethanolic sodium hydroxide. The mixture was extracted with methylene chloride. Removal of the solvent gave 20.5 g of oil which was distilled affording 19 g of **15** (b.p. 63–65°/0.1 Torr). It was purified by GLC. (SE-30 on *Chromosorb* W) for spectra and elemental analysis. – IR. (CCl_4): 3500–2400 br., 2960*s*, 2870*m*, 1705*s*, 1460*m*, 1420*m*, 1370*m*, 1237*m*, 940*w*. – ^{1}H-NMR. ($CDCl_3$): 2.92 (*qi*, J=8.0, H–C(1)); 2.15–1.30 (*m*, 6 H); 1.04 and 0.97 (2*s*, 2 H_3C–C(3)). – MS.: 142 (M^+, 6), 127 (19), 114 (*100*), 109 (33), 97 (21), 87 (20), 81 (76), 69 (84), 55 (48), 41 (48).

$C_8H_{14}O_2$ (142.19) Calc. C 67.57 H 9.93% Found C 67.30 H 9.84%

Photolysis of acylimidazoles 1, 3, 5–7, 10, 16 and 18. – *Photolysis of* **1**. 1) 250 mg of **1** in 40 ml of methanol were irradiated (lamp B; >280 nm) for 1.5 h. Column chromatography on silicagel afforded 87 mg of **2** and 46 mg of *2-acetylimidazole* [7] besides 20 mg of **1**. 2) 250 mg of **1** and 1 g of *p*-toluenesulfonic acid in 40 ml of methanol were irradiated (lamp B, >280 nm) for 1 h. Column chromatography on silicagel afforded 75 mg of **2** and 21 mg of *2-acetylimidazole*. *2-(7'-Hydroxybicyclo[4.2.0]oct-7'-yl)imidazole* (**2**)[3]), m.p. 197–198° (from chloroform). – IR. (KBr): 3700–2200 br., 2930*s*, 2855*s*, 1550*w*, 1440*m*, 1288*m*, 1233*m*, 1170*m*, 1110*m*, 1100*m*, 1070*w*, 988*w*, 735*s*. – ^{1}H-NMR. (CD_3OD): 7.00–6.86 (*m*, H–C(4) and H–C(5)); 2.30–1.10 (*m*, 12 H). – ^{13}C-NMR. (CD_3OD): 153.6 (*s*, C(2)); 122.1 (2*d*, C(4) and C(5)); 78.3 (*s*, C(7')); 54.5 (*d*, C(6')); 43.3 (*t*, C(8')); 39.0 (*d*, C(1')); 32.4 (*t*); 27.6 (*t*); 27.0 (*t*); 26.7 (*t*). – MS.: 192 (M^+, 20), 175 (6), 164 (4), 149 (11), 145 (4), 137 (11), 135 (11), 123 (33), 110 (*100*), 95 (22), 82 (83), 69 (39), 55 (9).

$C_{11}H_{16}N_2O$ (192.25) Calc. C 68.72 H 8.39 N 14.57% Found C 68.30 H 8.31 N 14.64%

Treatment of **2** with 1 mol-equiv. of sodium hydride in THF followed by methylation with an excess of methyl iodide afforded a quaternary salt (or salts) which was heated to 80° in 10% aqueous sodium hydroxide to give an oily mixture. This was extracted with ether and worked-up. The crude product consisted of two compounds **30** and **31** in the ratio 2:1 (IR. determination), which were separated by GLC. *Bicyclo[4.2.0]octan-7-one* (**30**), liquid. – IR. (CCl_4): 2930*s*, 2855*m*, 1780*s*, 1450*w*, 1035*w*. – MS.: 124 (M^+, 13), 95 (2), 82 (67), 68 (*100*), 54 (41), 41 (18).

1-Methyl-2-(cyclohexylacetyl)imidazole (**31**), liquid. – UV. (EtOH): 281 (11900). – IR. (CCl_4): 2920*s*, 2860*m*, 1673*s*, 1448*m*, 1410*s*, 1280*m*, 1155*w*, 1077*w*, 1020*w*, 1000*w*, 955*w*, 913*m*. – ^{1}H-NMR.

($CDCl_3$): 7.10 and 6.99 (2*s*, H–C(4) and H–C(5)); 3.96 (*s*, CH_3N); 2.97 (*d*, *J* = 7, CH_2CO); 2.40–1.70 (*m*, 10 H). – MS.: 206 (M^+, 22), 189 (2), 178 (2), 163 (2), 149 (5), 138 (5), 124 (*100*), 109 (51), 96 (34), 82 (48), 55 (34), 43 (52).

Photolysis of **3**. 1) Irradiation (5 h) and work-up as for **1** (s. 1)) afforded 60 mg of **4** and 43 mg of *4(5)-acetylimidazole* [7] besides 30 mg of **3**. 2) Irradiation in the presence of *p*-toluenesulfonic acid and work-up as for **1** (s. 2)) afforded 90 mg of **4** and 30 mg of *4(5)-acetylimidazole* besides 23 mg of **3**. *4(5)-(7′-Hydroxybicyclo[4.2.0]oct-7′-yl)imidazole* (**4**)[3], m.p. 161–163° (from chloroform). – IR. (KBr): 3600–2200 br., 2920*s*, 2835*s*, 1500*w*, 1470*m*, 1440*m*, 1400*w*, 1300*w*, 1215*w*, 1205*w*, 1180*w*, 1153*m*, 1143*m*, 1130*m*, 1113*m*, 1100*m*, 975*m*, 825*m*, 620*m*. – ^{1}H-NMR. (CD_3OD): 7.68 (br. *s*, H–C(2)); 6.93 (br. *s*, H–C(4 or 5)); 2.40–1.00 (*m*, 12 H). – ^{13}C-NMR. (CD_3OD): 143.9 (*s*, C(4)); 135.8 (*d*, C(2)); 116.5 (*d*, C(4 or 5)); 78.3 (*s*, C(7′)); 54.8 (*d*, C(6′)); 43.4 (*t*, C(8′)); 39.1 (*d*, C(1′)); 32.5 (*t*); 27.7 (*t*); 27.1 (*t*); 26.8 (*t*). – MS.: 192 (M^+, 7), 174 (23), 159 (7), 146 (11), 145 (11), 123 (34), 110 (*100*), 95 (41), 82 (25), 68 (18), 55 (7), 41 (11).

$C_{11}H_{16}N_2O$ (192.25) Calc. C 68.72 H 8.39 N 14.57% Found C 68.66 H 8.18 N 14.20%

Methylation of **4** followed by alkali treatment of the obtained quaternary salt (or salts) as in the case of **2** yielded only the liquid *1-methyl-4-(cyclohexylacetyl)imidazole* (**32**) which was prepared also by methylation of **3**. – UV. (EtOH): 257 (12100). – IR. (CCl_4): 3140*w*, 2925*s*, 2855*s*, 1673*s*, 1530*s*, 1445*s*, 1420*s*, 1350*m*, 1303*w*, 1275*w*, 1222*s*, 1215*m*, 1175*s*, 1163*m*, 1123*w*, 1045*m*, 950*m*, 925*s*, 830*w*. – ^{1}H-NMR. ($CDCl_3$): 7.54 (*d*, *J* = 1.0, H–C(2)); 7.42 (*d*, *J* = 1.0, H–C(5)); 3.70 (*s*, CH_3N); 2.80 (*d*, *J* = 7.0, CH_2CO); 2.20–0.70 (*m*, 11 H). – MS.: 206 (M^+, 5), 149 (6), 138 (25), 124 (*100*), 109 (59), 96 (13), 82 (26), 69 (2), 55 (6), 42 (9).

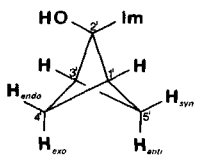
Photolysis of **5**. Irradiation (4 h) and work-up as for **1** (s. 1)) afforded 115 mg of *2-acetylimidazole* and *ca.* 10 mg of a mixture of alcohols which was not purified further.

Photolysis of **6**. Irradiation (10 h) and work-up as for **1** (s. 1)) gave 118 mg of *4(5)-acetylimidazole* and 5 mg of a mixture of alcohols besides 30 mg of **6**.

Photolysis of **7**. 300 mg of **7** in 50 ml of methanol and 0.3 ml of conc. hydrochloric acid were irradiated (lamp B, > 280 nm) for 5 h. Silicagel chromatography of the mixture afforded 60 mg of **8** and 46 mg of **9**. *2-(2′-Hydroxybicyclo[1.1.1]pent-2′-yl)imidazole* (**8**), m.p. 218–219° (chloroform). – IR. (KBr): 3650–2000 br., 3160*s*, 3090*s*, 3000*s*, 2970*s*, 2930*s*, 1560*w*, 1440*m*, 1290*m*, 1230*m*, 1207*m*, 1198*m*, 1170*m*, 1140*m*, 1130*s*, 1105*m*, 1087*m*, 1073*m*, 1013*m*, 980*m*, 920*m*, 727*s*. – ^{1}H-NMR. (MeOH): 6.94 (*s*, H–C(4) and H–C(5)); 2.96 (*s*, H–C(1′) and H–C(3′)); 2.84 (*d* × *d*, $J_{5'syn,4'endo}$ = 10.0, $J_{4'endo,4'exo}$ = 2.0, H*endo*-C(4′)); 1.78 (*d*, $J_{4'endo,4'exo}$ = 2.0, H*exo*-C(4′)); 1.61 (*d*, $J_{5'syn,5'anti}$ = 3.0, H*anti*-C(5′)); 1.39 (*qa*, $J_{5'syn,4'endo}$ = 10.0, $J_{5'syn,5'anti}$ = 3.0, H*syn*-C(5′)). ^{1}H-NMR. (CF_3COOD): 7.55 (*s*, H–C(4) and H–C(5)); 3.59 (*s*, H–C(1′) and H–C(3′)); 2.78 (*qa*, $J_{5'syn,4'endo}$ = 11.0, $J_{4'endo,4'exo}$ = 4.0, H*endo*-C(4′)); 2.25 (*d*, $J_{4'endo,4'exo}$ = 4.0, H*exo*-C(4′)); 2.24 (*d*, $J_{5'syn,5'anti}$ = 5.5, H*anti*-C(5′)); 1.56 (*d* × *d*, $J_{5'syn,4'endo}$ = 11.0, $J_{5'syn,5'anti}$ = 5.5, H*syn*-C(5′)). – ^{13}C-NMR. (MeOH): 150.0 (*s*); 122.1 (2*d*); 86.9 (*s*); 44.2 (*d*); 43.3 (2*d*); 41.1 (*d*). – MS.: 150 (M^+, 13), 149 (13), 135 (40), 122 (41), 107 (19), 95 (43), 82 (15), 68 (*100*), 55 (16), 42 (17).

$C_8H_{10}N_2O$ (150.18) Calc. C 63.98 H 6.71 N 18.65% Found C 63.83 H 6.72 N 18.47%

Scheme 6



2-(4′-Pentenoyl)imidazole (**9**), m.p. 103–104° (from acetone/hexane). – UV. (EtOH): 279 (12200). – IR. (CCl_4): 3450*m*, 3380*s*, 3080*w*, 2980*w*, 2920*w*, 1665*s*, 1415*s*, 1290*w*, 1160*m*, 1115*m*, 1080*m*, 990*w*, 945*m*, 915*m*, 865*w*. – ^{1}H-NMR. ($CDCl_3$): 7.29 (br. *s*, H–C(4) and H–C(5)); 6.15–5.68 (*m*, H–C(4′)); 5.22–4.90 (*m*, 2 H–C(5′)); 3.26 (*t*, *J* = 7.0, 2 H–C(2′)); 2.70–2.38 (*m*, 2 H–C(3′)). – ^{13}C-NMR. (CD_3OD):

150.0 (*s*); 122.1 (2*d*); 86.9 (*s*); 44.2 (*t*); 43.3 (2*d*); 41.1 (*t*). – MS.: 150 (M^+, 24), 135 (34), 122 (66), 107 (28), 95 (59), 82 (14), 68 (*100*), 55 (21), 40 (28).

$C_8H_{10}N_2O$ (150.18) Calc. C 63.98 H 6.71 N 18.65% Found C 63.89 H 6.81 N 18.56%

Photolysis of **10**. Irradiation (9 h) and work-up as for **7** afforded 120 mg of **11** and 42 mg of **12**. *4(5)-(2'-Hydroxybicyclo[1.1.1]pent-2'-yl)imidazole* (**11**), m.p. 162–163° (from chloroform/methanol). – IR. (KBr): 3700–2000 br., 3080*m*, 2950*s*, 1480*m*, 1470*m*, 1450*m*, 1435*m*, 1340*w*, 1375*w*, 1342*w*, 1322*m*, 1309*m*, 1298*m*, 1113*m*, 1088*m*, 1013*m*, 985*w*, 950*m*, 900*m*, 810*m*, 650*m*. – ^{1}H-NMR. (CD_3OD): 7.58 (*d*, J = 1.0, H–C(2)); 6.91 (*d*, J = 1.0, H–C(4 or 5)); 2.87 (*s*, H–C(1') and H–C(3')); 2.85 (*d*×*d*, $J_{5'syn,4'endo}$ = 11.0, $J_{4'endo,4'exo}$ = 2.0, H*endo*-C(4')); 1.76 (*d*, $J_{4'endo,4'exo}$ = 2.0, H*exo*-C(4')); 1.58 (*d*, $J_{5'syn,5'anti}$ = 3.0, H*anti*-C(5')); 1.52 (*d*×*d*, $J_{5'syn,4'endo}$ = 11.0, $J_{5'syn,5'anti}$ = 3.0, H*syn*-C(5')). – ^{13}C-NMR. (CD_3OD): 138.3 (*s*); 135.5 (*d*); 119.3 (*d*); 86.3 (*s*); 143.1 (*d*); 44.6 (*t*); 41.7 (*t*). – MS.: 150 (M^+, 5), 149 (5), 135 (25), 123 (12), 108 (6), 107 (5), 106 (5), 105 (4), 104 (4), 97 (25), 95 (*100*), 81 (6), 78 (5), 68 (42), 55 (9), 53 (7), 41 (16).

$C_8H_{10}N_2O$ (150.18) Calc. C 63.98 H 6.71 N 18.65% Found C 63.89 H 6.79 N 18.50%

4(5)-(4'-Pentenoyl)imidazole (**12**), m.p. 124–126° (from acetone/hexane). – UV. (EtOH): 257 (13900). – IR. ($CHCl_3$): 3440*m*, 3250*m*, 3080*w*, 2980*m*, 2850*w*, 1665*s*, 1550*m*, 1412*m*, 1370*m*, 1320*w*, 1130*m*, 1095*m*, 920*m*, 850*w*. – ^{1}H-NMR. ($CDCl_3$): 7.85 (*s*, H–C(2)); 7.79 (*s*, H–C(4 or 5)); 6.12–5.68 (*m*, H–C(4')); 5.22–4.92 (*m*, 2 H–C(5')); 3.00 (*t*, J = 7.0, 2 H–C(2')); 2.66–2.38 (*m*, 2 H–C(3')). – MS.: 150 (M^+, 14), 135 (5), 122 (7), 108 (7), 95 (*100*), 81 (5), 68 (12), 55 (6), 40 (13).

$C_8H_{10}N_2O$ (150.18) Calc. C 63.98 H 6.71 N 18.65% Found C 63.78 H 6.77 N 18.68%

Photolysis of **16**. Irradiation (345 mg of **16**, 50 ml of methanol, 0.3 ml of conc. hydrochloric acid, 3 h) and work-up as for **7** afforded 216 mg of *2-(4',4'-dimethyl-5'-hexenoyl)imidazole* (**17**), m.p. 135° (from acetone/hexane). – UV. (EtOH): 277 (13100). – IR. (CCl_4): 3450*m*, 3280*s*, 2965*m*, 2930*m*, 2875*w*, 1665*s*, 1415*s*, 1310*w*, 1160*w*, 1120*m*, 1080*m*, 1000*w*, 950*m*, 920*s*, 870*w*. – ^{1}H-NMR. ($CDCl_3$): 7.30–7.15 (*m*, H–C(4) and H–C(5)); 5.75 (*d*×*d*, J_1 = 18, J_2 = 11, H–C(5')); 4.91 (2 *d*×*d*, J_1 = 18, J_2 = 1.0, and J_1 = 11.0, J_2 = 1.0, 2 H–C(6')); 3.10–2.90 (*m*, 2 H–C(2')); 1.84–1.60 (*m*, 2 H–C(3')); 1.03 (*s*, 2 H_3C–C(4')). – MS.: 192 (M^+, 8), 177 (22), 164 (25), 149 (51), 136 (24), 135 (25), 123 (71), 110 (35), 95 (56), 82 (40), 69 (78), 55 (24), 41 (*100*).

$C_{11}H_{16}N_2O$ (192.25) Calc. C 68.72 H 8.39 N 14.57% Found C 68.40 H 8.30 N 14.47%

Photolysis of **18**. Irradiation (235 mg of **18**, 50 ml of methanol, 0.3 ml of conc. hydrochlorid acid, 3 h) and work-up as for **7** afforded 206 mg of *4(5)-(4',4'-dimethyl-5'-hexenoyl)imidazole* (**19**), m.p. 145° (from acetone/hexane). – UV. (EtOH): 257 (11300). – IR. (CCl_4): 3440*m*, 3240*m*, 2960*s*, 2870*w*, 1660*s*, 1550*m*, 1420*m*, 1365*s*, 1340*m*, 1130*m*, 1100*m*, 1000*w*, 960*w*, 920*m*, 850*m*, 650*m*. – ^{1}H-NMR. ($CDCl_3$): 7.80 (*s*, H–C(2)); 7.62 (*s*, H–C(4 or 5)); 5.75 (*d*×*d*, J_1 = 17, J_2 = 11.0, H–C(5')); 4.95 (*d*×*d*, J_1 = 17.0, J_2 = 1.0) and 4.82 (*d*×*d*, J_1 = 11.0, J_2 = 1.0, 2 H–C(6')); 2.85–2.65 (*m*, 2 H–C(2')); 1.83–1.62 (*m*, 2 H–C(3')); 1.03 (*s*, 2 H_3C–C(4')). – MS.: 192 (M^+, 27), 177 (13), 163 (14), 149 (11), 136 (27), 123 (36), 110 (64), 95 (*100*), 81 (15), 69 (47), 55 (11), 41 (32).

$C_{11}H_{16}N_2O$ (192.25) Calc. C 68.72 H 8.39 N 14.57% Found C 68.40 H 8.30 N 14.47%

Preparation of *cis*- and *-trans*-decalin-9-carboxylic acid (20 and 21) and photolysis of their *N*-acylimidazoles 22 and 27. A 1:9 mixture of **20/21** (ratio determined by GLC. with their ethyl esters) prepared according to the procedure of *Hussey et al.* [10][7]) was separated by silicagel chromatography. **20**, m.p. 122–124° (from acetone). – IR. (CCl_4): 3400–2300 br., 2930*s*, 2863*s*, 1693*s*, 1450*m*, 1400*w*, 1310*w*, 1300*m*, 1250*m*, 1157*m*, 1107*w*, 950*w*. – ^{1}H-NMR. ($CDCl_3$): 2.2 (*m*, 1 H); 1.80–1.10 (*m*, 16 H). –

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[7]) *Hussey et al.* isolated only the main acid and assigned to it the *cis*-configuration but later the assignment was corrected to *trans* [11].

^{13}C-NMR. ($CDCl_3$)[8]): 185.0 (*s*); 47.5 (*s*); 36.0 (*d*); 31.7 (2*t*); 28.3 (2*t*); 23.3 (2*t*); 22.9 (2*t*). – MS.: 182 (M^+, 47), 164 (15), 149 (9), 137 (*100*), 127 (38), 95 (79), 81 (87), 67 (34), 55 (21), 41 (32).

$C_{11}H_{18}O_2$ (182.25) Calc. C 72.49 H 9.96% Found C 72.43 H 10.03%

21, m.p. 133–134° (from ethanol). – IR. (CCl_4): 3400–2300 br., 2930*s*, 2860*s*, 1690*s*, 1450*m*, 1400*w*, 1320*w*, 1225*m*, 1153*w*, 1110*w*, 1087*w*, 973*w*. – ^{1}H-NMR. ($CDCl_3$): 2.3–0.9 (*m*, 17 H). – ^{13}C-NMR. ($CDCl_3$): 183.3 (*s*); 48.8 (*s*); 45.7 (*d*); 38.8 (2*t*); 29.4 (2*t*); 26.8 (2*t*); 23.6 (2*t*). – MS.: 182 (M^+, 45), 164 (15), 149 (3), 137 (*100*), 127 (38), 95 (71), 81 (94), 67 (31), 55 (22), 41 (26).

$C_{11}H_{18}O_2$ (182.25) Calc. C 72.49 H 9.96% Found C 72.55 H 9.97%

*Photolysis of 1-(*cis*-decal-9′-yl-carbonyl)imidazol* (**22**). **22**, prepared from 1.13 g of **20**, and a slight excess of NCD was irradiated *in situ* (lamp A) in THF for 16 h. The mixture was chromatographed on silicagel repeatedly affording 135 mg of a mixture of alcohols, 70 mg of **23**, 240 mg of **24** and 435 mg of a mixture of **25** and **26**. *2-[(*cis*-Decal-9′,2′-diyl)-hydroxy-methyl]imidazol* **23**, m.p. 138–140° (from acetone). – IR. ($CHCl_3$): 3580*m*, 3470*s*, 3300*m*, 2930*s*, 2860*s*, 1445*m*, 1370*w*, 1083*m*, 1030*w*, 973*m*, 930*w*. – ^{1}H-NMR. ($CDCl_3$): 6.94 (*s*, H–C(4) and H–C(5)); 2.50 (*m*, 1H); 2.25–1.00 (*m*, 15 H). – MS.: 232 (M^+, 54), 214 (18), 204 (23), 186 (9), 175 (9), 161 (27), 149 (27), 137 (18), 124 (*100*), 98 (95), 82 (60), 69 (81), 55 (14), 43 (31).

$C_{14}H_{20}N_2O$ (232.32) Calc. C 72.38 H 8.68 N 12.06% Found C 72.26 H 8.82 N 11.84%

2-[(cis-Decal-9′,2′-diyl)-hydroxy-methyl]imidazol **24**, m.p. 183–184° (from methanol/acetone). – IR. (KBr): 3650–2200br., 2940*s*, 2875*s*, 1560*w*, 1480*m*, 1433*m*, 1290*m*, 1030*m*, 955*w*, 740*s*. – ^{1}H-NMR. (CD_3OD): 6.94 (*s*, H–C(4) and H–C(5)); 2.75–1.10 (*m*, 16 H). – ^{13}C-NMR. (CD_3OD): 150.1 (*s*); 122.1 (2*d*); 79.9 (*s*); 48.9 (*d*); 48.4 (*s*); 42.3 (*d*); 30.8 (*t*); 27.0 (*t*); 25.9 (*t*); 23.0 (*t*); 22.4 (*t*); 21.9 (*t*); 14.9 (*t*). – MS.: 232 (M^+, 22), 214 (28), 204 (28), 189 (34), 175 (22), 161 (20), 137 (22), 124 (75), 95 (*100*), 82 (54), 69 (78), 55 (12), 41 (29).

$C_{14}H_{20}N_2O$ (232.32) Calc. C 72.38 H 8.68 N 12.06% Found C 72.37 H 8.82 N 11.72%

To 100 mg of **24** in 3 ml of dry THF were added 21 mg of sodium hydride (55% in oil). Having stirred at room temp. for 4 h. 200 mg of methyl iodide were added, and the mixture was stirred at room temp. overnight. After evaporation of THF 4 ml of 10% aqueous sodium hydroxide were added, the mixture was heated to *ca.* 80° for 1 h, and then extracted with methylene chloride. The crude oil was purified by GLC.: **33** (*tricyclo[7.1.1.0^{4,9}]undecan-10-one* or *tricyclo[5.3.1.0^{7,2}]undecan-11-one*). – IR. (CCl_4): 2940*s*, 2875*s*, 1775–1765*s*, br., 1450*m*, 1270*w*, 1180*w*, 1155*w*, 1105*w*, 1040*w*, 995*w*, 973*w*, 960*w*. – ^{1}H-NMR. ($CDCl_3$): 3.14–2.94 (*m*, 1 H); 2.80–2.34 (*m*, 1 H); 2.16–1.10 (*m*, 14 H). – MS.: 165 (M^+, 1), 149 (2), 136 (85), 121 (36), 107 (51), 95 (68), 93 (68), 79 (*100*), 67 (48), 55 (14), 41 (37).

*4(5)-[(*cis*-Decal-9′,2′-diyl)-hydroxy-methyl]imidazol* **25/26**[9]), m.p. 180–181° (from methanol/acetone). – IR. (KBr). 3650–2200br., 2930*s*, 2850*s*, 1465*m*, 1448*m*, 1435*m*, 1330*w*, 1240*w*, 1120*m*, 1030*m*, 930*w*, 908*w*, 818*m*, 655*m*. – ^{1}H-NMR. (CD_3OD): 7.59 (br. *s*, H–C(2)); 6.90 (br. *s*, H–C(4 or 5)); 2.8–1.0 (*m*, 16 H). – ^{13}C-NMR. (CD_3OD): 136.0 (*s*); 135.7 (*d*); 135.6 (*d*); 121.4 (*d*); 119.9 (*d*); 80.2 (*s*); 79.7 (*s*); 51.6 (*s*); 49.5 (*d*); 48.7 (*s*); 42.8 (*d*); 42.4 (*d*); 40.4 (*d*); 34.0 (*t*); 31.4 (*t*); 30.9 (*t*); 30.2 (*t*); 27.2 (*t*); 26.9 (2*t*); 26.7 (*t*); 24.4 (*t*); 23.8 (*t*); 23.5 (*t*); 23.2 (*t*); 22.2 (*t*); 14.9 (*t*). – MS.: 232 (M^+, 1), 214 (*100*), 199 (30), 186 (98), 171 (38), 158 (53), 145 (30), 131 (20), 117 (20), 105 (10), 91 (28), 81 (23), 77 (20), 65 (13), 51 (10), 41 (15).

$C_{14}H_{20}N_2O$ (232.32) Calc. C 72.38 H 8.68 N 12.06% Found C 72.50 H 8.75 N 12.01%

*Photolysis of 1-(*trans*-decal-9′-yl-carbonyl)imidazole* (**27**). **27**, prepared from 1.82 g of **21** and a slight excess of NCD, was irradiated *in situ* (lamp B, >235 nm light) in THF for 16 h. Column

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[8]) These values were obtained at *ca.* 60°. At room temp. line broadening at each resonance was observed.

[9]) All data are given for the mixture.

chromatography of the mixture afforded 185 mg of **28** and 350 mg of **29** besides 495 mg of **21**. *2-(*trans-*Decal-9'-yl-carbonyl)imidazole* (**28**), m.p. 188–189° (from acetone/hexane). – UV. (EtOH): 281 (11700). – IR. (CCl_4): 3450*m*, 3300*m*, 2920*s*, 2855*s*, 1660–1645*s* br., 1445*m*, 1385*s*, 1275*w*, 1105*w*, 1078*m*, 1015*m*, 927*s*, 870*s*. – ^{1}H-NMR. ($CDCl_3$): 7.22 and 7.10 (2 *qa*, H–C(4) and H–C(5)); 3.18 (*m*, 2 H); 2.26–0.70 (*m*, 15 H). – ^{13}C-NMR. (CF_3COOD): 190.3 (*s*); 139.8 (*s*); 122.9 (2*d*); 55.3 (*s*); 48.7 (*d*); 39.2 (2*t*); 29.9 (2*t*); 27.6 (2*t*); 24.7 (2*t*). – MS.: 232 (M^+, 71), 204 (50), 189 (16), 175 (9), 161 (9), 149 (11), 137 (12), 124 (9), 96 (88), 81 (32), 68 (*100*), 55 (14), 41 (29).

$C_{14}H_{20}N_2O$ (232.32) Calc. C 72.38 H 8.68 N 12.06% Found C 72.36 H 8.68 N 11.98%

*4(5)-(*trans-*Decal-9'-yl-carbonyl)imidazole* (**29**), m.p. 166° (from acetone/hexane). – UV. (EtOH): 264 (11700). – IR. ($CHCl_3$): 3440*m*, 3300*m*, 2925*s*, 2855*s*, 1640*s*, 1530*m*, 1450*m*, 1405*w*, 1365*w*, 1330*s*, 1133*s*, 1090*s*, 915*s*, 867*s*. – ^{1}H-NMR. ($CDCl_3$): 7.74 (*s*, H–C(2)); 7.70 (*s*, H–C(4 or 5)); 2,53 (*m*, 2 H); 2.30–0.70 (*m*, 15 H). – MS.: 232 (M^+, 88), 214 (36), 204 (7), 189 (5), 177 (4), 161 (3), 149 (71), 137 (64), 123 (7), 111 (11), 95 (*100*), 68 (70), 55 (18), 41 (29).

$C_{14}H_{20}N_2O$ (232.32) Calc. C 72.38 H 8.68 N 12.06% Found C 72.21 H 8.56 N 12.18%

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