A New Route to 1,3-Diacyl-2,3-dihydro-1*H*-imidazoles

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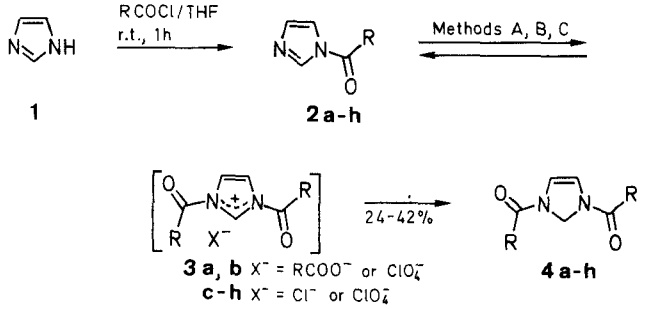
Preparative amounts of the title compounds can be prepared in high purity by hydrogenation of the corresponding 1,3-diacylimidazolium salts with sodium borohydride. Structures are confirmed by spectroscopic methods and in two cases by X-ray structure determination.

Little is known about 2,3-dihydro-1*H*-imidazoles **4**. Most syntheses yielding this heterocyclic ring[1] lead to *C*-substituted derivatives. Moreover, methods successfully used in the synthesis of the *O*-analogous 2,3-dihydrooxazoles,[2] and 1,3-dioxoles[3] are not applicable in this case.[4]

A convenient precursor for this synthesis is imidazole **1**. Since direct hydrogenation fails,[5] activation of the heteroaromatic compound by formation of imidazolium salts **3**[6] is necessary. Catalytic hydrogenation of **3** with platinum (IV) oxide[7] offers a route to **4**.

However, this method is limited to the preparation of the acetyl derivative **4a** since acetic anhydride is used as solvent. On the other hand, compounds **3** are able to undergo electrophilic reactions[8] with several arenes and heteroarenes resulting in C-2-substituted 2,3-dihydro-1*H*-imidazoles. Thus, it is conceivable that they may react with a hydride anion yielding compounds **4**.

Complex hydrides, e.g., sodium borohydride or lithium aluminum hydride are frequently used to hydrogenate 1,3-dialkylbenzimidazolium ions,[9] but result in ring-cleavage reactions[10] when applied to 1,3-dialkylimidazolium ions. In striking contrast, sodium borohydride is an excellent hydrogenation reagent for acyl-substituted imidazolium ions **3** when acetonitrile is the solvent (Scheme A).[11]



2–4	R	2–4	R
a	Me	**e**	n-$C_{11}H_{23}$
b	Et	**f**	Ph
c	i-Pr	**g**	4-$MeOC_6H_4$
d	t-Bu	**h**	4-(t-Bu)C_6H_4

Method A, for **4a, b**: 1. $(RCO)_2O$/MeCN, r.t.,
2. $NaBH_4$, r.t.; 2 h.
Method B, for **4c–h**: 1. RCOCl/MeCN, r.t., ½ h;
2. $NaBH_4$, −30 °C, 1 h then r.t., 2 h.
Method C: 1. $LiClO_4$/RCOCl/MeCN, r.t., 1 h;
2. $NaBH_4$, −30 °C, 1 h then r.t., 2 h.

Scheme A

Acylation of the easily available 1-acylimidazoles **2**[12] yields equilibrium mixtures of the salts **3** and starting material **2**. The equilibrium depends[13] on the substituent R and the counterion X^-. Since the sodium borohydride undergoes reaction not only with the imidazolium ions **3** but also with **2**, the desired products are obtained in varying and sometimes low yields (Table 1). Byproducts obtained in this reaction are esters, alcohols and aldehydes derived from the corresponding acyl compounds.

Higher yields are obtained by acylation of **2** with carboxylic anhydrides (Method A) instead of chlorides (Method B), but it seems that this variation of the rection is limited to the aliphatic derivatives **4a, b**, since with other substituents none of the target compounds **4** can be isolated.

Products of highest purity are obtained, when the reaction is carried out with acylium perchlorates (Method C), which are formed *in situ* via exchange of the chloride, employing lithium perchlorate in acetonitrile.[14] Lowering of the temperature to a certain limit raises the yield, but below −30 °C no reaction can be observed.

The only 1,3-diacyl-2,3-dihydro-1*H*-imidazole described so far is the diacetyl derivative **4a**.[5] A critical reinvestigation of another paper,[15] reporting the preparation of 1,3-dibenzoyl-2,3-dihydro-1*H*-imidazole **4f** via reduction of **3f** with zinc, indicates that most likely **4f** was not isolated. The reported melting point[15] is much higher (300–301 °C) than that of **4f** (156–158°) and the mass spectrum exhibits a strong signal at $m/z = 277$ instead of $m/z = 278$ (M^+) in the spectrum of **4f** obtained according to our method. Applying the method described[15] on **3d** we find $m/z = 237$ instead of $m/z = 238$ (M^+) in the mass spectrum of **4d**.

The 1,3-diacyl-2,3-dihydro-1*H*-imidazoles **4** are poorly soluble even in polar solvents, but may be recrystallized from water or alcohols. They form bright crystals and are stable towards air and moisture.

The ^{1}H-NMR spectra exhibit signals of different conformers coalescenting at elevated temperatures. Most likely indicating a hindered rotation around the N–CO bond,[16] the signals are assigned to the possible conformers by means of their chemical shifts, taking into account the deshielding effect of the carbonyl group (Scheme **B**, Figure 1). In case of derivatives **4a–c** in dimethyl sulfoxide the *endo,endo*-conformers (Table 2) are preferred, shifting the signals of their olefinic protons downfield and of the CH_2-bridge upfield. In the case of the *exo,exo*-conformers the shifts are reverse. The *endo,exo*-conformers, which because of their lower dipole moments

Table 1. 1,3-Diacyl-2,3-dihydro-1*H*-imidazoles **4a–h** Prepared

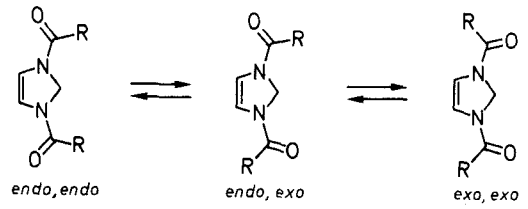
Compound	Yield (%)	Method	mp (°C)[a]	Molecular Formula[b] or Lit. mp (°C)	IR (KBr)[c] ν (cm^{-1}) C=O; C=CH$_{cis}$	UV (MeCN)[d] λ_{max} (nm) (log ε)	MS (70 eV)[e] *m/z* (%)
4a	31	A	249–251	238–240[7]	1645; 875, 749	276 (4.27)	154 (M^+, 14), 69 (100)
4b	42	A	208–210	$C_9H_{14}N_2O_2$ (182.2)	1635; 875, 748	278 (4.27)	182 (M^+, 21), 69 (100)
4c	28	C	148–149	$C_{11}H_{18}N_2O_2$ (210.3)	1645; 860, 752	278 (4.40)	210 (M^+, 20), 43 (100)
4d	31	C	216	$C_{13}H_{22}N_2O_2$ (238.3)	1630; 870, 762	279 (4.21)	238 (M^+, 10), 57 (100)
4e	24	B	147	$C_{27}H_{50}N_2O_2$ (434.7)	1640; 885, 747	278 (4.15)	434 (M^+, 1), 135 (100)
4f	42	B	156–158	$C_{17}H_{14}N_2O_2$ (278.3)	1640; 865, 715	296 (4.09)	278 (M^+, 19), 105 (100)
4g	38	C	194	$C_{19}H_{18}N_2O_4$ (338.4)	1615; 845, 740	298 (4.12)	338 (M^+, 4), 135 (77)
4h	34	B	185–187	$C_{25}H_{30}N_2O_2$ (390.5)	1630; 850, 730	295 (4.16)	390 (M^+, 4), 161 (46)

[a] Uncorrected, measured with a Büchi apparatus (type of Dr. Tottoli).
[b] Satisfactory microanalyses obtained on a Hereaus CHN Rapid apparatus: C ±0.35 (exc. **4e** −1.51), H ±0.23, N ±0.12.
[c] Recorded on a Perkin-Elmer 377 infrared spectrophotometer.
[d] Measured using a Perkin-Elmer 320 spectrometer.
[e] Measured using a Varian MAT 212 spectrometer, E.I. 70 eV, 1 mA.

Table 2. NMR-Data of Compounds **4a–h**[a]

Compound	^{1}H-NMR[b] (DMSO-d_6/TMS) δ, J(Hz)				^{13}C-NMR[d] (DMSO-d_6/TMS)
	Ratio of Conformers[e]	H-2 (s, 2H)	H-4,5	R	δ
4a	58 *endo,endo* 38 *exo,endo* 4 *exo,exo*	5.16 5.40	6.73 (s, 2H) {6.74 (d, 1H, J = 3.0) 6.63 (d, 1H, J = 3.0)} 6.65 (s, 2H)	2.00 (s, 6H, *endo*-CH_3), 2.07 (s, 6H, *exo*-CH_3)	20.6 (*exo*-CH_3), 21.9 (*endo*-CH_3), 62.4 (*endo,endo*-C-2), 62.7 (*endo,exo*-C-2), 63.0 (*exo,exo*-C-2), 113.6 (*exo,exo* + *endo,exo*-C-4,5), 114.7 (*endo,endo*-C-4,5), 115.2 (*endo,exo*-C-4,5), 164.0 (CO)
4b	57 *endo,endo* 40 *exo,endo* 3 *exo,exo*	5.18 5.39 5.58	6.75 (s, 2H) {6.77 (d, 1H, J = 3.0) 6.65 (d, 1H, J = 3.0)} 6.66 (s, 2H)	1.00 (t, 6H, *endo*-CH_3, J = 7.5), 1.02 (t, 6H, *exo*-CH_3, J = 7.3), 2.27 (q, 4H, *endo*-CH_2, J = 7.5), 2.39 (q, 4H, *exo*-CH_2, J = 7.3)	8.0 (*endo*-CH_3), 8.5 (*exo*-CH_3), 25.5 (*exo*-CH_2), 26.7 (*endo*-CH_2), 61.8 (*exo,exo*-C-2), 62.3 (*exo,endo*-C-2), 62.6 (*endo,endo*-C-2), 113.7 (*exo,exo*-C-4,5), 113.6, 114.3 (*exo,endo*-C-4,5), 114.1 (*endo,endo*-C-4,5), 166.9 (*exo,exo*-CO), 166.6, 167.2 (*exo,endo*-CO), 167.3 (*endo,endo*-CO)
4c	71 *endo,endo* 26 *exo,endo* 3 *exo,exo*	5.16 5.48 5.76	6.89 (s, 2H) {6.91 (d, 1H, J = 3.4) 6.67 (d, 1H, J = 3.4)} 6.68 (s, 2H)	1.04 (d, 12H, *exo*-CH_3, J = 7.0), 1.08 (d, 12H, *endo*-CH_3, J = 7.0), 2.42 (sept, 2H, *endo*-CH, J = 7.0), 2.89 (sept, 2H, *exo*-CH, J = 7.0)	18.4 (*endo*-CH_3), 18.6 (*exo*-CH_3), 30.3 (*exo*-CH), 31.8 (*endo*-CH), 62.5 (*exo,exo*, *endo,exo*-C-2), 62.8 (*endo,endo*-C-2), 114.1 (*exo,exo* + *exo,endo*-C-4,5), 114.5 (*endo,endo* + *endo,exo*-C-4,5), 170.0 (*exo*-CO), 170.4 (*endo*-CO)
4d		5.21 (br)	6.90 (s, 2H)	1.21 (18H, CH_3)	26.7 (CH_3), 38.1 ($\underline{C}(CH_3)_3$), 65.9 (C-2), 114.3 (C-4,5), 171.0 (CO)
4f[c]	66 *exo,exo* 34 *exo,endo*	5.82 5.65	6.30 (s, 2H) {6.46 (br, 1H) 6.87 (br, 1H)}	7.43–7.62 (m, 10H$_{arom}$)	64.6 (*exo,exo*-C-2), 65.5 (*exo,endo*-C-2), 115.5 (*exo,exo* + *endo,exo*-C-4,5), 115.4 (*exo,endo*-C-4,5), 127.8, 128.7, 131.2 (CH$_{arom}$), 133.8 (C$_{arom}$), 164.0 (*endo*-CO), 164.7 (*exo*-CO)
4g[c]	62 *exo,exo* 38 *exo,endo*	5.75 (br) 5.75 (br)	6.37 (br, 2H) {6.43 (br, 1H) 6.95 (br, 1H)}	6.95 (d, 4H$_{arom}$, J = 8.8), 7.58 (d, 4H$_{arom}$, J = 8.8), 3.85 (s, 6H, OCH_3)	64.9 (C-2), 55.4 (OCH_3), 115.6 (C-4,5), 114.0 (CH$_{arom}$), 126.0 (C$_{arom}$), 129.8 (CH$_{arom}$), 161.9 (C$_{arom}$), 164.4 (CO)
4h[c]	66 *endo,endo* 34 *exo,endo*	5.80 (br) 5.67 (br)	6.36 (s, 2H) {6.49 (br, 1H) 6.85 (br, 1H)}	7.47 (d, 4H$_{arom}$, J = 8.0), 7.54 (d, 4H$_{arom}$, J = 8.0), 2.02 (s, 18H, CH_3)	31.1 (CH_3), 34.9 ($\underline{C}(CH_3)_3$), 64.6 (*exo,exo*-C-2), 65.3 (*exo,endo*-C-2), 115.5 (*exo,exo*-C-4,5), 115.9, 116.2 (*endo,exo*-C-4,5), 125.6, 127.7 (CH$_{arom}$), 130.8, 154.6 (C$_{arom}$), 164.6 (CO)

[a] No data of **4e** available because of its low solubility.
[b] Recorded on a Varian VRX 300 (300 MHz).
[c] Measured in $CDCl_3$, because in DMSO poor soluble.
[d] Recorded on a Varian VRX 300 (74 MHz).
[e] Concerning CO-groups.



Scheme **B**

are the major conformers in $CDCl_3$, show signals due to two inequivalent coupling olefinic protons.

In the case of the benzoyl derivatives **4f–h** assignment of the observed shifts to different conformers is more difficult, because the phenyl substituents deshield themselves. Only signals due to a symmetric, probably the *exo,exo*-, and of the asymmetric *endo,exo*-conformer are

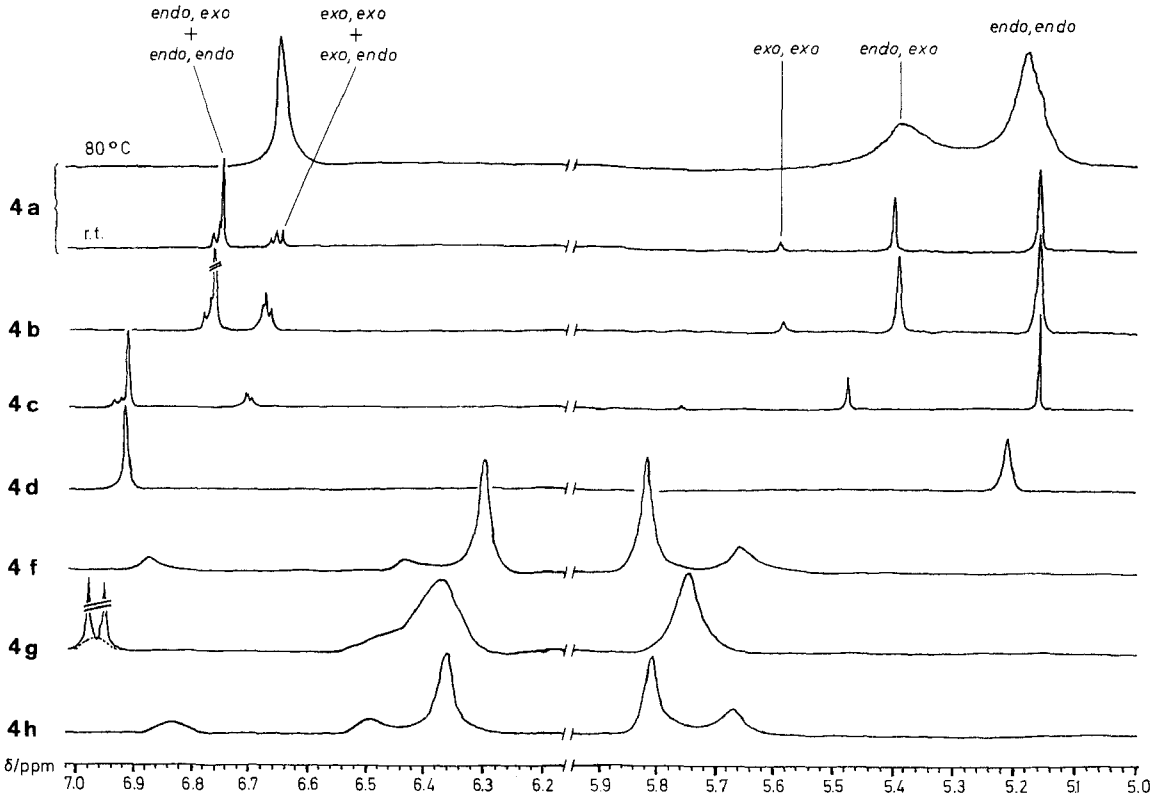


Figure 1. ^{1}H-NMR Signals of the Conformers of 1,3-Diacyl-2,3-dihydro-1*H*-imidazoles **4** (H-4,5 and H-2 showed)

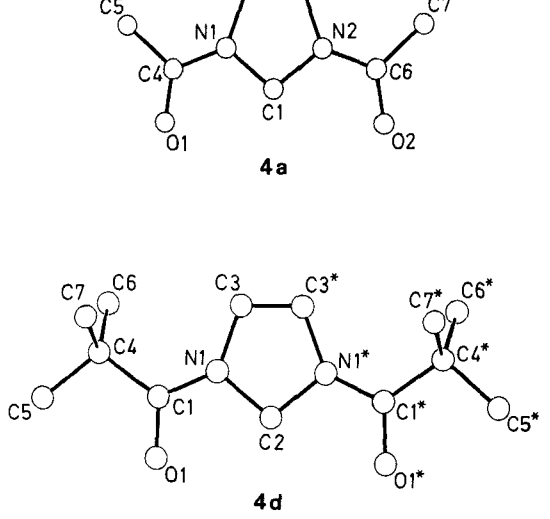


Figure 2. X-Ray Structures of the 1,3-Diacyl-2,3-dihydro-1*H*-imidazoles **4a** and **4d**

discernible. Corresponding observations were not mentioned in earlier reports[5] describing this class of compounds, while a similar study has been carried out in the case of 1,3-diacyl-2,3-dihydrobenzimidazoles.[17]

Well-seperated signals for the conformers occur only in the case of compounds **4a–c** containing small substituents. The pivaloyl derivative **4d** causes only one signal for each type of proton. This might be the result of a displacement of the pivaloyl group out of the plane of the heterocyclic ring, as reported for 1-pivaloylimidazole **3d**.[18]

Aromatic substituents in conjugation with the carbonyl group diminish the cross-conjugation with the nitrogen of the ring,[19] lowering the rotational barrier and thus broadening the signals.

In the case of **4a** and **4d** single crystals of a quality sufficient for X-ray structure determination were obtained (Figure 2). Geometric parameters are given in Tables 3 and 4.

The five-membered rings of both molecules are essentially planar. The carbonyl groups are fixed in the *exo,exo*-positions. With 1.316(4) Å in **4a** and 1.302(4) Å in **4d** the interatomic distances between the termini of the C=C double bonds are close to the lower limit for olefinic double bonds. Both, the C=O and N-(CO) bond lengths lie in the upper range usually specified for acylated tertiary amides.[20] In the crystal lattice the molecules of **4d** slightly deviate from planarity in that one pivaloyl group lies somewhat above and the other marginally below the plane defined by the atoms of the five-membered ring. Given by space group symmetry, **4d** is characterized by a twofold axis passing through carbon atom C2 and the centre of the C=C bond. In contrast, **4a** is essentially of C_s symmetry in the solid state, with its approximate mirror plane being perpendicular to the plane of the ring and passing through C1 and the centre of the C=C bond. Interatomic distances and bond angles are quite similar in both molecules, the higher steric demands of the *tert*-butyl groups compared with the methyl groups being reflected by a somewhat wider C–C–N angle of the NCOR-segment in the case of **4d**.

Table 3. Bond Lengths (Å), Bond Angles (deg), and Dihedral Angles (deg) for **4a**

Atoms		Atoms	
O1–C4	1.226(5)	C6–N2–C3	128.9(3)
O2–C6	1.235(5)	N1–C1–N2	102.7(3)
N1–C4	1.357(4)	O1–C4–N1	119.1(3)
N1–C2	1.424(5)	N2–C3–C2	109.6(3)
N2–C6	1.352(4)	O1–C4–C5	122.7(3)
N2–C3	1.423(5)	N1–C4–C5	118.2(3)
C1–N1	1.452(4)	O2–C6–N2	118.4(3)
C1–N2	1.450(4)	O2–C6–C7	123.0(3)
C3–C2	1.316(4)	N2–C6–C7	118.7(3)
C4–C5	1.497(5)	N1–C2–C3	109.4(3)
C6–C7	1.493(5)		
C1–N1–C4	121.3(3)	C1–N1–C4–O1	1.9(6)
C1–N1–C2	109.1(2)	C2–N1–C4–O1	177.3(4)
C4–N1–C2	129.5(3)	N1–C2–C3–N2	0.2(5)
C1–N2–C6	121.8(3)	C1–N2–C6–O2	−1.1(6)
C1–N2–C3	109.1(2)	C3–N2–C6–O2	−177.3(4)

Table 4. Bond Lengths (Å), Bond Angles (deg), and Dihedral Angles (deg) for **4d**

Atoms		Atoms	
N1–C1	1.356(3)	N1*–C2–N1	103.3(2)
N1–C2	1.460(3)	C3*–C3–N1	110.3(3)
N1–C3	1.425(3)	C1–C4–C5	107.2(3)
O1–C1	1.240(4)	C1–C4–C6	109.9(2)
C1–C4	1.525(4)	C1–C4–C7	110.5(2)
C3–C3*	1.302(4)	C5–C4–C6	108.5(2)
C4–C5	1.532(5)	C5–C4–C7	108.8(3)
C4–C6	1.526(5)	C6–C4–C7	111.8(3)
C4–C7	1.528(5)	C2–N1–C1–O1	1.3(3)
C1–N1–C3	133.8(2)	C2–N1–C1–C4	180.0(2)
C1–N1–C2	118.0(2)	C3–N1–C1–O1	176.9(2)
C3–N1–C2	108.9(2)	C3–N1–C1–C4	−4.3(4)
O1–C1–N1	116.3(2)	O1–C1–C4–C5	0.2(3)
O1–C1–C4	121.8(2)	O1–C1–C4–C6	−117.5(3)
N1–C1–C4	121.8(2)	O1–C1–C4–C7	118.7(3)

The simple preparative methods described above provide access to an interesting class of compounds. Thus, due to the electron-rich double bond of the 1,3-diacyl-2,3-dihydro-1*H*-imidazoles **4** which is part of a endiamine structure, their reactivity should be comparable to that of 2,3-dihydrooxazoles[21] and 1,3-dioxoles.[22] Explorative experiments confirm the expected reactivity, and a full account of this work will be published soon.

All solvents are dried and stored under N_2, $NaBH_4$ and the salts are dried *in vacuo* or used as commercially available anhydrous products. All other reagents are used as commercially available without further purification. The reactions are carried out under moisture free conditions.

1-Acylimidazoles 2; General Procedure:
The imidazole (**1**; 136 g, 2.0 mol) is dissolved in THF (400 mL). A solution of the acyl chloride (1.0 mol) in THF (100 mL) is added at a moderate rate and the mixture is stirred for 1 h. The precepitated imidazole hydrochloride is removed by filtration and the solvent of the filtrate is evaporated yielding the moisture sensitive 1-acylimidazoles **2**, which are used without purification.

1,3-Diacyl-2,3-dihydro-1*H*-imidzaoles 4; General Procedures:
Method A (for **4a,b**): To a stirred solution of 1-acylimidazole **2** (1.0 mol) in MeCN (200 mL) a solution of the carboxylic anhydride (2.0 mol) in acetonitrile (100 mL) is added slowly, followed by $NaBH_4$ (38 g, 1 mol) in small portions. After 2 h of stirring (may be continued overnight) the MeCN is evaporated, the residue poured into H_2O (500 mL), and extracted with CH_2Cl_2 (4 × 200 mL). After evaporation of the solvent, the crude product **4** is recrystallized (MeOH), filtered and dried *in vacuo*.

Method B (for **4c–h**): To a stirred solution of acyl chloride (1.0 mol) in MeCN (200 mL) a solution of 1-acylimidazole **2** (1.0 mol) in MeCN (100 mL) is added. After stirring for 30 min the mixture is cooled to −30 °C (not below) and $NaBH_4$ (38 g, 1.0 mol) is added in small portions, while the temperature may rise to −25 °C. Subsequently the mixture is stirred at this temperature 1 h and then warmed to r.t. After stirring for 2 h (or overnight) the solvent is evaporated, the residue poured into H_2O (500 mL), and extracted with (4 × 200 mL). Evaporation of the solvent yields the crude product **4**, which is recrystallized (MeOH), filtered and dried *in vacuo*.

Method C: To a stirred suspension of $LiClO_4$ (106 g, 1.0 mol) in MeCN (200 mL) acyl chloride (1.0 mol) is added at a moderate rate, followed by the solution of 1-acylimidazole **2** (1.0 mol) in MeCN (100 mL). The mixture is stirred for 1 h while the LiCl precepitates. Subsequently the mixture is cooled to a temperature not below −30 °C (In case of **4f** to +10 °C because otherwise the mixture cannot be stirred) and $NaBH_4$ (38 g, 1 mol) is added in small portions, while the temperature may rise to −25 °C. After stirring for 1 h at this temperature, the mixture is warmed to r.t. and stirred for 2 h (or overnight). Then the solvent is evaporated, the residue poured into H_2O (500 mL), extracted with CH_2Cl_2 (4 × 200 mL), and the solvent evaporated again. The crude product **4** is then recrystallized (MeOH), filtered and dried *in vacuo*.

X-ray Structure Determination of 1,3-Diacetyl-2,3-dihydro-1*H*-imidazole (4a):[23] Crystals are monoclinic, spacegroup C2/c (No. 15) with cell constants a = 15.697(2) Å, b = 5.716(1) Å, c = 17.779(3) Å, and β = 110.70(1)°, corresponding to a cell volume of V = 1492.2 Å^3. With eight molecules in the unit cell the total number of electrons amounts to F (000) = 656 and the absorption coefficient is μ = 8.12 cm^{-1}.

3371 Reflections have been recorded on an ENRAF-NONIUS CAD4 diffractometer at r.t. (293 K) with Cu K_α radiation (λ =

1.54179 Å) in the range $1° < \theta < 75°$ ($\pm h + k + 1$) (1480 independent and 1163 observed reflections ($I > 2\,\sigma(I)$); internal consistency $R_{av} = 0.01$; $\sin\Theta/\lambda_{max} = 0.63$).

The structure has been solved employing the SIMPEL method[24] as implemented in the XTAL 2.6 program package.[25] A total number of 101 parameters has been refined (full matrix least squares) to a final R value of 0.070 ($R_w = 0.074$) and a residual electron density of $\varrho = 0.5\,e\,Å^{-3}$. The positions of all hydrogens could be located in the final difference Fourier maps, however, have been held fixed in the refinement process.

X-Ray Structure Determination of 1,3-Dipivaloyl-2,3-dihydro-1*H*-imidazole (4d):[23]

The compound crystallizes in orthorhombic space group Fdd2 (No. 43) with cell dimensions a = 19.370(3) Å, b = 24.675(3) Å, c = 5.908(1) Å, and V = 2823.8 Å.^{3} With eight molecules in the unit cell the total number of electrons is F(000) = 1040 and the absorption coefficient $\mu = 0.71\,cm^{-1}$ for Mo K_α radiation (λ = 0.71069 Å, graphite monochromator). 3222 reflections have been recorded on a ENRAF-NONIUS CAD 4 diffractometer at r.t. (293 K) in the range $1° < \theta < 27.44°$ ($\pm h \pm k + 1$) (885 independent and 780 observed reflections; ($I > 2\sigma$ (I)); internal consistency $R_{av} = 0.019$; $\sin\Theta/\lambda_{max} = 0.648$).

The structure has been solved using the GENTAN[26] routine as part of the XTAL 2.4 program package.[27] Employing a full matrix least squares procedure a total number of 121 parameters has been refined to a R index of 0.043 ($R_w = 0.040$) and a residual electron density of $\varrho = 0.5\,e\,Å^{-3}$. The positions of all hydrogens could be located and were included in the refinement process.

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