294. Photochemische Reaktionen

91. Mitteilung [1]

Photochemistry of Imidazolides. I. The Photo-*Fries*-Type Rearrangement of N-Substituted Imidazoles

by **Shigeo Iwasaki**[1])

Organisch-chemisches Laboratorium der Eidg. Technischen Hochschule, CH-8092 Zürich

(6. X. 76)

Summary. A number of N-substituted imidazoles **1a–1i** have been found to photo-isomerize to give the corresponding 2-substituted- and 4(or 5)-substituted imidazoles (**2a–2i** and **3a–3i**). The role of a dissociative path in these reactions has been demonstrated.

The role of N-acyl imidazoles (imidazolides) in acyl transfer and in connection with the mode of action of hydrolytic enzymes, as well as their specific reactivity in nucleophilic reactions, have attracted much attention [2]. Formally they can be classed as amides; but the latter are relatively inert to hydrolysis or alcoholysis and in this respect and with other nucleophilic reactions there is little resemblance between the two types of compounds. There is, however, some analogy, in that the bathochromic shift in the UV. spectra of imidazolides (30–35 nm) relative to the maximum absorption of imidazole itself (207–208 nm) indicates interaction between the acyl carbonyl group with the π-electrons of the heterocyclic ring (in the particular case of N-alkoxycarbonyl of N-carbamoyl imidazoles this shift is less pronounced though there is some increase in relative intensity).

These facts led us to study the photochemical reactivity of imidazolides which has so far attracted little attention. *A priori* we expected to encounter the following types of reactions:

a) Migration of substituents from nitrogen to give C-acyl or C-alkyl isomers, as exemplified by anilides and enamides [3] and by the more closely related N-acetyl pyrrole [4a, b], N-acetyl-carbazole [4c] and by N-acyl indoles [5];

b) Photochemical transformations specifically involving the carbonyl group, either in the N-acyl imidazoles and/or their N → C migration products as produced under (a), such as of Type I (α-fission), Type II (γ-hydrogen abstraction), or photoreduction.

In the paper we describe the photo-*Fries*-type rearrangement of a number of N-acyl and other N-substituted imidazoles.

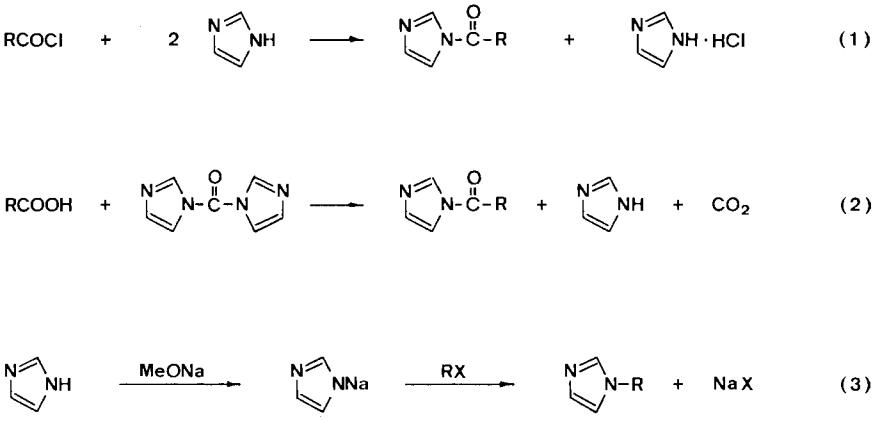
Results. – N-Acyl, N-methoxycarbonyl, and N-carbamoylimidazoles were prepared either by reaction of imidazole (two equivalents) with the corresponding acyl chloride in benzene (eq. *1*) [6] (*method a*), or by treatment of the corresponding

---

[1]) On leave from *Institute of Applied Microbiology*, University of Tokyo, Tokyo, Japan.

carboxylic acid with one equivalent or slight excess of N,N'-carbonyldiimidazole (eq. *2*) [7] (*method b*). Both methods gave the desired products in almost theoretical yield. Those prepared by *method b* were irradiated as formed *in situ* and thus in the presence of imidazole formed in the reaction.

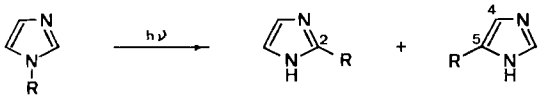
Scheme 1



N-Sulfonylimidazoles were prepared by treatment of imidazole (two equivalents) with the corresponding sulfonyl chloride. N-Benzyl-, N-crotyl-, and N-geranylimidazole were prepared according to *Godefroi* [8] by alkylation of the sodium salt of imidazole with the corresponding halide (eq. *3*).

Irradiation of N-acyl-, N-methoxycarbonyl-, N-carbamoyl-, and N-benzylimidazole (**1**) was found in each case to lead to rearrangement and the production of the corresponding 2-substituted and 4 (or 5)-substituted imidazole (**2** and **3**)[2]) in reasonable yield.

Scheme 2



The structural assignment of these products is described below. On a preparative scale either 0.02–0.04 M solutions of the pure imidazolides (obtained by *method a*), or 0.02–0.44 M solutions of the corresponding carboxylic acids to which 1.3 equivalents of N,N'-carbonyldiimidazole had been added (*method b*), were irradiated. Results obtained using the first procedure (yields were not optimised) are shown in Table 1; those obtained by the second procedure were found to be practically the same. They

[2]) Positions 4 and 5 are normally indistinguishable in N-unsubstituted imidazoles because of rapid proton interchange.

Table 1. *Yields of* **2** *and* **3** *by irradiation of* **1a–1i**

Compound **1**	R	Solvent	Yield of **2** (%)	Yield of **3** (%)
a	CH_3CO	THF[a]	26	30
b	n-$C_7H_{15}CO$	CH_3CN[a]	37	16
c	cyclo-$C_6H_{11}CO$	THF[a]	39	29
d	$(CH_3)_3CCO$	CH_3CN[a]	28	30
e	C_6H_5CO	THF[a]	13	23
f	$(CH_3)_2C{=}CHCO$	THF[a]	16	31
g	CH_3OCO	CH_3OH[b]	16 (25)[c]	10 (18)[c]
h	$(C_2H_5)_2NCO$	CH_3OH[b]	8 (17)[c]	10 (21)[c]
i	$C_6H_5CH_2$	THF[b]	45	35

[a] Irradiation with a low pressure lamp.
[b] Irradiation with a medium pressure lamp.
[c] Yields calculated from converted **1**.

show that this type of reaction constitutes a facile route to various 2-substituted or 4(or 5)-substituted imidazoles, compounds whose synthesis is difficult in that imidazole cannot easily be acylated or alkylated by *Friedel-Crafts* type reactions[3][4][5][6]. Alternative routes generally involve many tedious steps [14]. Use of a medium-pressure mercury lamp in the irradiation of compounds **1a–1f** did not improve the yield of N → C migration products; apparently this led to further transformation of these products[7]).

From both a synthetic and a mechanistic point of view the behaviour of N-aroylimidazoles was now of interest, and the irradiation of *p*-methoxybenzoyl- and of *p*-nitrobenzoylimidazole was studied. These appeared to react very rapidly, but no acyl migration products could be detected (by TLC).

Both N-methoxycarbonyl- and N-carbamoylimidazole (**1g** and **1h**) reacted more sluggishly than compounds **1a–1f** and a medium pressure lamp had to be employed in these cases. The N-benzyl compound **1i** was found to give the best yield of the rearranged products **2i** and **3i** among all the compounds studied; the N-crotyl and N-geranyl derivatives were found to be quite stable to irradiation and any product obtained (apart from unchanged material) was found to be a complex mixture. N-Sulfonylimidazoles were also found to be rather unreactive.

Discussion. – The reactions described above are mechanistically analogous to the photo-rearrangements of phenol esters (Photo-*Fries* rearrangement), and of enol esters, anilides and enamides [3]. Additional, more closely related reactions are the

[3] The 2-acetylation of imidazole, by treatment of its magnesium salt with acetyl chloride, has been reported in unstated yield, by *Oddo et al.* [8].

[4] Hydroxymethylations of substituted imidazoles have been reported by *Roel* [9], and by *Godefroi et al.* [10].

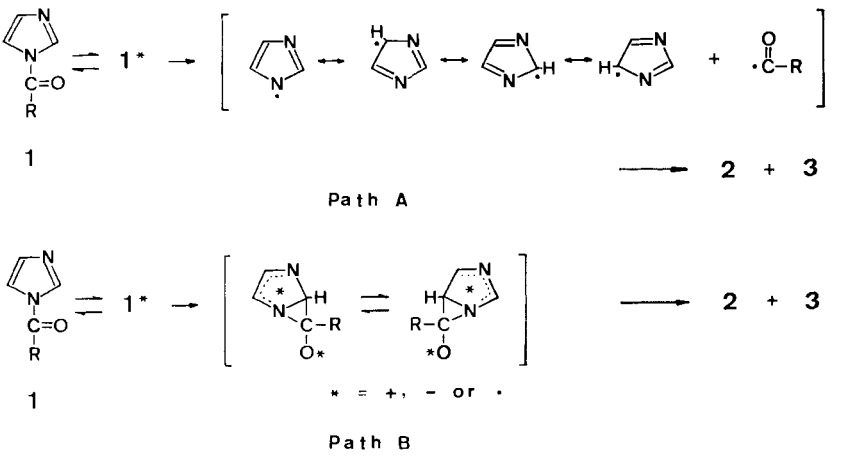
[5] *Matsuura et al.* have described the photochemical addition of ketones [11] and of acrylonitrile [12] to substituted imidazoles.

[6] A homolytic alkylation of imidazole to give exclusive 2-alkylations was reported by *Bertini et al.* [13].

[7] Subsequent photo-reactions of 2-acyl and 4(or 5)-acylimidazoles are described in the following paper [15].

photo-rearrangements of N-acetyl pyrrole to give 2-acetyl pyrrole [4a, b], and of N-acyl indoles, which lead to the 3-, 4-, and 6-substituted isomers [5]. Mechanisms proposed for the photo-rearrangement of phenol esters and of N-acetyl pyrrole [4b] suggest that there might be several different directions in which N-acyl and other N-substituted imidazoles might rearrange on irradiation. On the basis of two such possibilities, a dissociative path **A** and a non-dissociative concerted one **B** are suggested in *Scheme 3*.

Scheme 3



In order to distinguish between an intramolecular and an intermolecular path we decided to prepare N-acetylimidazole-d_3 (**1j**) and N-acetyl-d_3-imidazole (**1k**). A 1:1

Scheme 4

1j **1k**

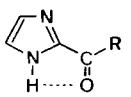
mixture of these deuteriated products was now irradiated in solution under two different conditions: (1) in 0.45 M concentration for 15 hours, (2) in 0.018 M concentration for 3 hours (in each case with a low pressure mercury lamp). In both cases the reaction products were isolated in pure form and their deuterium content was determined by mass spectrometry. The results are shown in Table 5. Under conditions (1) four or five deuterium atoms were incorporated in both the resulting 2-acetylimidazole and in the 4(or 5)-acetylimidazole: this cannot occur in a purely intramolecular process and hence indicates a significant contribution by the dissociative path **A**. A simple calculation, relating the observed values for d_4 and d_5 with the expected figures for the purely intramolecular and intermolecular processes, shows that the latter must be involved to the extent of *ca.* 30%. This figure, however, is a lower limit, since

deuterium exchange may occur within the mass spectrometer (and conceivably during the work-up process as well) and hence the actual yields of d_4 and d_5 may be even higher than observed. The result obtained under conditions (2) is more in line with that expected for the intramolecular process but does not necessarily contradict the conclusions derived from conditions (1), since obviously there is more chance for radical pairs from the same parent molecule to recombine at higher dilution.

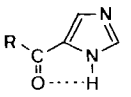
More evidence suggesting an intermolecular process contribution was obtained when a mixture of N-acetylimidazole-d_3 (**1j**) and N-cyclohexanecarbonylimidazole (**1c**) was irradiated in 0.36 M concentration, which resulted in the formation of the four expected C-acyl imidazoles. The deuterium incorporation in both 2-cyclohexanecarbonylimidazole (d_1 *ca.* 7%, d_2 *ca.* 17%) and in 4(or 5)-cyclohexanecarbonylimidazole (d_1 *ca.* 8%, d_2 *ca.* 15%) showed that cross recombination between acetyl- and cyclohexanecarbonylimidazole had occurred to the extent of about 25%.

Structures and spectra of products. – The mass spectra of products **2** and **3** (molecular ion and fragment peaks) suggest that these are positional isomers of the starting materials. The IR. spectra in solution of **2a**–**2h** and of **3a**–**3h** show bands at 3440–3430 cm^{-1} (sharp) and 3270–3240 cm^{-1} (broad) due to non-bonded and bonded –NH– respectively. In compounds **2a**–**2d**, **2f**, **3a**–**3d** and **3f** carbonyl bands appear at 1670–1660 cm^{-1} (broad) and in compounds **2e** and **3e** at 1635 cm^{-1}. The lower frequencies of all these as compared with acetophenone (1690 cm^{-1}) and benzophenone (1675 cm^{-1}) as well as their greater band width suggest intramolecular hydrogen bonding between –CO– and –NH–. The same tendency is observed on comparing the IR. spectra of the N-carbamoyl derivatives **2h** and **3h** with those of N-disubstituted benzamides. These data might suggest a significant contribution of tautomeric structures **2'** and **3'** in solution even though positions 1 and 3 in imidazoles are normally equivalent in view of rapid –NH– proton interchange.

Scheme 5



2'



3'

The IR. spectra of the methoxycarbonylimidazoles **2g** and **3g** were measured in KBr, and their carbonyl bands appear at 1720 and 1715 cm^{-1} respectively.

The positions of the substituents on the imidazole ring are clearly indicated by comparing the ^{1}H-NMR. spectra of the pairs of product **2** and **3**. Inspection of the data obtained for the imidazole ring protons (see Table 2) shows that in 2-acylimidazoles **2a**–**2h** these occur at δ 7.1–7.4 and hence are not assignable to a proton next to (and deshielded by) a neighbouring nitrogen proton H–C(2). On the other hand, those shown in 4 (or 5)-acylimidazoles **3a**–**3g** appear at lower field than δ 7.7 and those of **3h** appear at δ 7.42 and δ 7.64. Paramagnetic shifts shown by the H–C(4 or

Table 2. *^{1}H-NMR.-Spectra of acylimidazoles and related substituted imidazoles*[a])

Compound	R	1-R-Imidazole **1**	2-R-Imidazole **2**	4(or 5)-R-Imidazole **3**
	H	H—C(2) 7.66 (br. *s*) [b]) H—C(4) and H—C(5); 7.05 (*d*, 1.0) (CD_3OD)		
a	CH_3CO	H—C(2) 8.12 (br. *s*) [c]) H—C(4) 7.09 (*q*, 1.0) H—C(5) 7.46 (*q*, 1.0)	H—C(4) and H—C(5); 7.26 (br. *s*) (CD_3OD)	H—C(2) and H—C(4 or 5); 7.84, 7.81 (2*s*) (CD_3OD)
b	*n*-$C_7H_{15}CO$	H—C(2) 8.14 (br. *s*) H—C(4) 7.10 (*q*, 1.0) H—C(5) 7.41 (*q*, 1.0)	H—C(4) and H—C(5); 7.3–7.2 (*m*) +D_2O 7.25, 7.22 (2*s*)	H—C(2) 7.86 (*s*) H—C(4 or 5) 7.79 (*s*)
c	*cyclo*-$C_6H_{11}CO$	H—C(2) 8.15 (br. *s*) H—C(4) 7.10 (*q*, 1.0) H—C(5) 7.47 (*q*, 1.0)	H—C(4) and H—C(5); 7.3–7.2 (*m*) +D_2O 7.27, 7.23 (2*s*)	H—C(2) 7.86 (*s*) [d]) H—C(4 or 5) 7.79 (*s*)
d	$(CH_3)_3CCO$	H—C(2) 8.29 (br. *s*) H—C(4) 7.07 (*q*, 1.0) H—C(5) 7.55 (*q*, 1.0)	H—C(4) and H—C(5); 7.27, 7.15 (2*q*, 1.0)	H—C(2) and H—C(4 or 5); 7.79 (*s*)
e	C_6H_5CO	H—C(2) 8.07 (br. *s*) H—C(4) 7.16 (*q*, 1.0) H—C(5) 7.51 [e])	H—C(4) and H—C(5); 7.38, 7.24 (2*q*, 1.0) +D_2O 7.38, 7.24 (2*d*, 1.0)	H—C(2) 7.95 (*s*) [d]) H—C(4 or 5) 7.76 (*s*)
f	$(CH_3)_2C{=}CHCO$	H—C(2) 8.16 (br. *s*) H—C(4) 7.08 (*q*, 1.0) H—C(5) 7.50 (*q*, 1.0)	H—C(4) and H—C(5); 7.3–7.2 (*m*) +D_2O 7.26, 7.20 (2*s*)	H—C(2) 7.81 (*s*) H—C(4 or 5) 7.75 (*s*)
g	CH_3OCO	H—C(2) 8.11 (br. *s*) H—C(4) 7.07 (*q*, 1.0) H—C(5) 7.41 (*q*, 1.0)	H—C(4) and H—C(5); 7.22 (*s*) (CD_3OD)	H—C(2) 7.77 (*d*, 1.0) H—C(4 or 5) 7.73 (*d*, 1.0)
h	$(C_2H_5)_2NCO$	H—C(2) 7.89 (br. *s*) H—C(4) 7.10 (*q*, 1.0) H—C(5) 7.21 (*q*, 1.0)	H—C(4) and H—C(5); 7.18, 7.10 (2 br. *s*)	H—C(2) 7.64 (br. *s*) H—C(4 or 5) 7.42 (br. *s*)
i	$C_6H_5CH_2$	H—C(2) 7.53 (br. *s*) H—C(4) 7.09 (*q*, 1.0) H—C(5) 6.89 (*q*, 1.0)	H—C(4) and H—C(5); 6.90 (*s*)	H—C(2) 7.42 (br. *s*) H—C(4 or 5) 6.70 (br. *s*)
	CH_3	H—C(2) 7.47 [f]) H—C(4) 7.08 H—C(5) 6.88	H—C(4) and H—C(5); 6.96 [f])	H—C(2) 7.47 [f]) H—C(4 or 5) 6.81

[a]) Unless specified otherwise, $CDCl_3$ was used as the solvent. The data are recorded as in the experimental part.

[b]) The chemical shifts measured in $CDCl_3$ have been reported to be H—C(2) 7.86 and H—C(4 or 5) 7.25 [16].

[c]) Reported to be H—C(2) 8.15, H—C(4) 7.08 and H—C(5) 7.46 [17].

[d]) Signal assignment was made with the compound with an unequally deuterated imidazole (see footnote 8).

[e]) The signal overlap with those of the phenyl ring protons.

[f]) These values are taken from reference [14b].

Table 3. *^{13}C-NMR. of acylimidazoles and related substituted imidazoles*[a])

Compound	R	2-R-Imidazole **2**		4(or 5)-R-imidazole **3**	
a	CH_3CO	C(1')[b])	170.0 (*s*)	C(1')	192.9 (*s*)
		C(2)	146.2 (*s*)	C(2)	139.3 (*d*)
		C(4), C(5)	132–120 (br. *s*)	C(4), C(5)	128.7 (*d*) ? (*s*)[c])
b	*n*-$C_7H_{15}CO$	C(1')	192.8 (*s*)	C(1')	193 (br. *s*)
		C(2)	145.3 (*s*)	C(2)	138.5 (*d*)
		C(4), C(5)	131.1 (*d*) 120.5 (*d*)	C(4), C(5)	131.0 (*d*) ? (*s*)[c])
c	*cyclo*-$C_6H_{11}CO$	C(1')	195.7 (*s*)	C(1')	197 (br. *s*)
		C(2)	144.7 (*s*)	C(2)	138.7 (*d*)
		C(4), C(5)	131.1 (*d*) 120.5 (*d*)	C(4), C(5)	131.0 (*d*) ? (*s*)[c])
e	C_6H_5CO	C(1')	182.2 (*s*)	C(1')	186.5 (*s*)
		C(2)	145.2 (*s*)	C(2)	138.9 (*d*)
		C(4), C(5)	131.7 (*d*) 120.4 (*d*)	C(4), C(5)	132.1 (*d*) 138.0 (*s*)
g	CH_3OCO	C(1')	160.4 (br. *s*)	C(1')	164.2 (*s*)
		C(2)	139.2 (br. *s*)	C(2)	138.5 (*d*)
		C(4), C(5)	126.8 (2*d*)	C(4), C(5)	126.7 (br. *d*) 131.2 (br. *s*)
i	$C_6H_5CH_2$	C(1')[d])	34.6 (*t*)	C(1')	33.3 (*t*)
		C(2)	147.0 (*s*)	C(2)	134.8 (*d*)
		C(4), C(5)	121.4 (2*d*)	C(4), C(5)	117.6 (*d*) 136.3 (*s*)

a) For **2a**, **3a**, **2g** and **3g** CD_3OD, and for the other compounds $CDCl_3$ were used as the solvents. The data are recorded as in the experimental part.

b) Numbering 1', 2, 4 and 5 are given for the carbonyl carbon atom, and 2, 4 and 5 positions of imidazole ring, respectively.

c) The signal of C(4 or 5) bearing the substituent was not assignable in the spectrum because of the signal broadening.

d) Numbering 1' is given for benzyl carbon atom.

Table 4. *UV.-Spectra of acylimidazoles*

Compound	R	1-R-Imidazole **1** nm (ε)	2-R-Imidazole **2** nm (ε)	4(or 5)-R-Imidazole **3** nm (ε)
a	CH_3CO	244 (4180)[a])	277 (12700)	255 (13100)
b	*n*-$C_7H_{15}CO$	244 (4500)[a])	277 (13100)	257 (12200)
c	*cyclo*-$C_6H_{11}CO$	244 (5500)[a])	279 (12900)	257 (12300)
d	$(CH_3)_3CCO$	245 (5500)[a])	278 (13100)	257 (12300)
e	C_6H_5CO	240 (11200)	260 (8800)	257sh (11000)
		272sh (2900)[a])	297 (14800)	276 (13400)
f	$(CH_3)_2C{=}CHCO$	245 (13900)[a])	297 (17500)	279 (16900)
g	CH_3OCO	209 (12000)	258 (12900)	236 (11200)
h	$(C_2H_5)_2NCO$	209 (11000)	258 (9800)	237 (7500)
i	$C_6H_5CH_2$	209 (14200)	212 (11100)	212 (11500)

a) THF was used as solvent. Otherwise ethanol was used as solvent. sh = shoulder.

5) are probably due to the anisotropic effect of the acyl carbonyl group. Assignments for H–C(2) and H–C(4 or 5) in compounds **3b–3h** were made on the basis of those established from the spectra of 4-(or 5)-cyclohexanecarbonyl- and 4-(or 5)-benzoylimidazole-d_2 (D–C(2), 85%; D–C(4 or 5), 92.5%)[8]).

In compounds **2** spin-spin coupling between protons on the imidazole ring carbon atoms and those on nitrogen were observed (broad multiplets or two quartets for H–C(4) and N–C(5) which were simplified after adding D_2O to exchange protons on nitrogen). The observed relatively slow exchange of –NH– and its appearance at low field (below δ 10.5) support the contribution of the tautomeric form **2'**, at any rate in $CDCl_3$ solution. This proton appears at similarly low field in compounds **3a–3h** and thus supports a similar contribution of structure **3'**.

Assignments for protons in the benzyl derivatives **1i**, **2i** and **3i** are based on data for 1-, 2-, and 4(or 5)-methyl-imidazoles (see Table 2).

In spite of solubility problems the ^{13}C-NMR. spectra of some of the acyl- and benzylimidazoles could be determined.

An additional problem encountered here was due to possible hydrogen migration from nitrogen to nitrogen and resulting magnetic site exchange, leading to signal line broadening and thus to difficulty in assignment for some carbon atoms.

The data listed in Table 3 show that in the 2-substituted imidazoles the C(2)signal appears downfield by *ca.* 10 ppm. relative to imidazole [18]; this also applies to one of the two signals for C(4) and C(5) but not the other – this again demonstrates non-identity for C(4) and C(5) in 2-acylimidazoles.

Further evidence on substitution pattern can be deduced from UV. spectra. On comparing imidazoles substituted by acyl, methoxycarbonyl and carbamoyl groups at C(2) on the one hand and at C(4 or 5) on the other (see Table 4), a bathochromic shift (*ca.* 20 nm) can be discerned for the former relative to the latter[9]). However, in both 2-benzyl- and in 4(or 5)-benzylimidazole the absorption maximum occurs at *ca.* 212 nm; and hence in these cases UV. spectra are of no value in structure determination.

All these data are admittedly for a limited number of examples but nevertheless they appear to constitute useful information (so far lacking in the literature) on the substitution pattern of imidazoles.

Financial support by *Schweiz. Nationalfonds zur Förderung der wissenschaftlichen Forschung*, and by *Ciba-Geigy AG*, Basel, are gratefully acknowledged. The author wishes to thank Prof. *H. J. Eli Loewenthal* of *Israel Institute of Technology*, Haifa, Israel, for his helpful advice in the preparation of the manuscript.

Experimental Part

General. – *Melting points* (m.p.) were taken using an oil apparatus (*Büchi*, type Dr. *Tottoli*) and are not corrected. – *Ultraviolet spectra* were measured on a *Perkin-Elmer* apparatus (model 402) and are recorded as follows: UV. (solvent), maxima and inflections in nm (extinction ε). –

---

[8]) Deuteriated imidazole (as prepared for the synthesis of N-acetylimidazole-d_3 (**1j**)) was acylated and then irradiated in order to prepare these compounds.

[9]) The following data have been reported; 2-formylimidazole, λ_{max}^{EtOH} 285 nm (ε 12500) [19]; 4(or 5)-formylimidazole, λ_{max}^{EtOH} 257 nm (ε 11900) [20].

Infrared spectra were measured on a *Perkin-Elmer*-spectrophotometer (model 257) and are recorded as follows: IR. (support), frequency in cm^{-1}, intensity as *w* = weak, *m* = medium, *s* = strong. – *Mass spectra* were measured on a *Hitachi-Perkin-Elmer* RMU-6M instrument and are recorded as follows: MS. *m/e* (relative intensity). – *Proton magnetic resonance* spectra were measured on a *Varian* H-100 or XL-100 instrument (100 MHz) and are recorded as follows: ^{1}H-NMR. (solvent), chemical shift (in δ) with TMS ($\delta = 0$) as internal standard (assignment, multiplicity: *s* = singlet, *d* = doublet, *t* = triplet, *q* = quartet, *m* = multiplet, br. = broad, coupling constant *J* in Hz, $\omega_{1/2}$ = half width in Hz). – *^{13}C-nuclear magnetic resonance* spectra were measured on a *Varian* XL-100 instrument (25 MHz) and are recorded as follows: ^{13}C-NMR. (solvent), chemical shift (in δ) with TMS ($\delta = 0$) as internal standard (assignment, multiplicity as above).

Thin layer chromatography was carried out on *Merck* DC.-Fertigplatten Kieselgel 60 F-254, developed with chloroform/methanol 5:1 or ethyl acetate/methanol 5:1. – *Column chromatography* was carried out on silicagel *Merck* (0.063–0.200 mm) and, unless specified otherwise, chloroform/methanol 9:1 was used for elution. – *Abreviations*: *i.V.* = *in vacuo*, i.HV. = in high vacuum; RT. = room temperature.

Preparations of 1-acylimidazoles (*1a–f*), 1-carbomethoxyimidazole (*1g*) and 1-carbamoylimidazole (*1h*). – *1-Acetylimidazole* (**1a**). a) To 13.6 g (0.3 mol) of imidazole suspended in 200 ml dry benzene was added 7.8 g (0.15 mol) of acetyl chloride dissolved in 250 ml of dry benzene. The mixture was stirred for 24 h at RT. After filtration of imidazole hydrochloride the filtrate was evaporated *i.V.* to give crude crystals of **1a** (*ca.* 12 g) which were recrystallized from dry benzene giving 9.3 g of **1a**, m.p. 102–104° (lit. 104° [2a]). – UV. (THF): 244 (4180). – IR. ($CHCl_3$): 3160*w*, 3130*w*, 2980*m*, 1740*s*, 1485*m*, 1383*s*, 1360*w*, 1285*s*, 1095*m*, 1060*m*, 1050*m*, 958*m*, 950*w*. – MS.: 110 (23, M^+), 82 (25), 68 (*100*), 54 (2), 52 (2), 43 (72). – ^{1}H-NMR. ($CDCl_3$): 8.12 (br. *s*, H–C(2)); 7.46 (*q*, *J* = 1.0, H–C(5)); 7.09 (*q*, *J* = 1.0, H–C(4)); 2.64 (*s*, H_3CCO–N(1)).

$C_5H_6N_2O$ (110.11) Calc. C 54.54 H 5.49 N 25.44% Found C 53.62 H 5.47 N 25.03%

b) To a solution of 1.2 g (0.02 mol) of acetic acid in 30 ml dry THF was added 4.8 g (0.03 mol) of N,N'-carbonyldiimadazole. CO_2 was evolved immediately. The solution was kept for 20–30 min at RT. and was then used for the irradiation directly without separation of imidazole generated in the reaction.

All of the other 1-acyl-, 1-methoxycarbonyl- and 1-carbamoylimidazoles (**1b–f**, **1g** and **1h**) were prepared in the same way as for **1a**.

1-Capryloylimidazole (**1b**). Needles from heptane, m.p. 46.5–47° (lit. 47° [2a]). – UV. (THF): 244 (4500). – IR. ($CHCl_3$): 3160*w*, 3130*w*, 2960*s*, 2920*s*, 2855*m*, 1740*s*, 1470*s*, 1380*s*, 1300*m*, 1270*s*, 1105*m*, 1095*m*, 1075*m*, 900*m*. – MS.: 194 (7, M^+), 166 (2), 127 (38), 110 (4), 109 (5), 98 (4), 95 (4), 84 (3), 83 (3), 82 (3), 69 (70), 57 (*100*), 43 (37), 41 (34). – ^{1}H-NMR. ($CDCl_3$): 8.14 (br. *s*, H–C(2)); 7.41 (*q*, *J* = 1.0, H–C(5)); 7.10 (*q*, *J* = 1.0, H–C(4)); 2.88 (*t*, *J* = 7.0, H_2CCO–N(1)); 1.83 (*m*, H_2CCH_2CO–N(1)); 1.6–1.15 (*m*, 8H); 0.91 (*t*, *J* = 7.0, terminal H_3C).

$C_{11}H_{18}N_2O$ (194.27) Calc. C 68.00 H 9.34 N 14.42% Found C 67.90 H 9.32 N 14.45%

1-Cyclohexanecarbonylimidazole (**1c**). Needles, m.p. 86–87° (from benzene/heptane). – UV. (THF): 244 (5500). – IR. (CCl_4): 3160*w*, 3130*w*, 2940*s*, 2860*m*, 1735*s*, 1470*s*, 1455*m*, 1395*s*, 1420*m*, 1267*s*, 1220*s*, 1205*s*, 1210*m*, 1200*m*, 1180*m*, 1140*m*, 960*s*, 898*m*. – MS.: 178 (5, M^+), 150 (1), 128 (1), 111 (37), 83 (*100*), 69 (23), 68 (23), 55 (41), 41 (20). – ^{1}H-NMR. ($CDCl_3$): 8.15 (br. *s*, H–C(2)); 7.47 (*q*, *J* = 1.0, H–C(5)); 7.10 (*q*, *J* = 1.0, H–C(4)); 2.92 (*m*, HCO–N(1)); 2.15–1.10 (*m*, 10H).

$C_{10}H_{14}N_2O$ (178.23) Calc. C 67.38 H 7.92 N 15.72% Found C 67.23 H 7.91 N 15.66%

1-Pivaloylimidazole (**1d**). Needles from benzene/heptane, m.p. 56° (lit. 56° [2a]). – UV. (THF): 245 (5500). – IR. (CCl_4): 3160*w*, 3140*w*, 2900*m*, 1730*s*, 1475*m*, 1465*m*, 1410*m*, 1365*m*, 1285*s*, 1205*s*, 1107*m*, 1090*m*, 1080*m*, 1057*m*, 947*s*, 900*w*, 850*w*. – MS.: 152 (7, M^+), 109 (1), 85 (25), 68 (46), 57 (*100*), 41 (43). – ^{1}H-NMR. ($CDCl_3$): 8.29 (br. *s*, H–C(2)); 7.55 (*q*, *J* = 1.0, H–C(5)); 7.07 (*q*, *J* = 1,0, H–C(4)); 1.05 (*s*, $3H_3CCO$–N(1)).

$C_8H_{12}N_2O$ (152.19) Calc. C 63.13 H 7.95 N 18.41% Found C 62.98 H 7.90 N 18.23%

1-Benzoylimidazole (**1e**). Solid at low temperature. – UV. (EtOH): 240 (11200), 272 shoulder (2900). – IR. (CCl_4): 3160*w*, 3140*w*, 3090*w*, 3070*w*, 3040*w*, 1715*s*, 1603*m*, 1465*m*, 1453*m*, 1370*s*, 1300*s*, 1243*m*, 1190*m*, 1100*m*, 1065*m*, 1033*m*, 1020*m*, 900*s*, 720*m*, 700*m*, 680*m*. – MS.: 172 (8, M^+), 122 (5), 105 (100), 82 (2), 77 (52), 68 (3), 51 (18), 40 (4). – ^{1}H-NMR. ($CDCl_3$): 8.07 (br. *s*, H–C(2)); 7.86–7.72 (*m*, 2H on phenyl); 7.72–7.44 (*m*, 3H on phenyl); 7.55 (H–C(5), overlap with phenyl protons; assignment is based on comparison with the derivatives deuteriated on imidazole ring); 7.16 (*q*, J = 1.0, H–C(4)).

1-(3-Methyl-2-butenoyl)imidazole (**1f**). M.p. 63–64° (from benzene/heptane). – UV. (THF): 245 (13900). – IR. (CCl_4): 3160*w*, 3120*w*, 3110*w*, 2990*w*, 2970*w*, 2957*w*, 1710*s*, 1635*s*, 1470*s*, 1450*m*, 1395*m*, 1380*m*, 1370*m*, 1295*m*, 1270*s*, 1235*s*, 1190*m*, 1125*m*, 1095*s*, 1060*m*, 985*m*. – MS.: 150 (9, M^+), 100 (2), 83 (*100*), 68 (8), 55 (48), 39 (15). – ^{1}H-NMR. ($CDCl_3$): 8.16 (br. *s*, H–C(2)); 7.50 (*q*, J = 1.0, H–C(5)); 7.08 (*q*, J = 1.0, H–C(4)); 6.31 (*m*, HCCO–N(1)); 2.13 (*d*, J = 1.0, H_3C-*cis*); 2.11 (*d*, J = 1.0, H_3C-*trans*).

$C_8H_{10}N_2O$ (150.18) Calc. C 63.98 H 6.71 N 18.65% Found C 63.73 H 6.68 N 18.86%

1-Methoxycarbonylimidazole (**1g**). M.p. 35–39° (from benzene/heptane). – UV. (EtOH): 209 (12000). – IR. ($CHCl_3$): 3160*w*, 3130*w*, 2900*m*, 2800*m*, 1765*s*, 1470*m*, 1445*s*, 1385*s*, 1315*m*, 1295*s*, 1285*s*, 1165*m*, 1095*m*, 1060*m*, 1010*s*, 900*m*, 830*w*. – MS.: 126 (*100*, M^+), 95 (11), 82 (35), 81 (31), 68 (22), 59 (47), 55 (27), 54 (32), 40 (78). – ^{1}H-NMR. ($CDCl_3$): 8.11 (br. *s*, H–C(2)); 7.41 (*q*, J = 1.0, H–C(5)); 7.07 (*q*, J = 1.0, H–C(4)); 4.06 (*s*, H_3CO).

$C_5H_6N_2O_2$ (126.11) Calc. C 47.62 H 4.80 N 22.22% Found C 47.50 H 4.88 N 22.13%

1-(N,N-Diethylcarbamoyl)imidazole (**1h**). M.p. 41.5–43° (after distillation; lit. 48–49.5° [2a]). – UV. (EtOH): 209 (11000). – IR. ($CHCl_3$): 3160*w*, 3120*w*, 2990*m*, 2940*m*, 2900*m*, 2880*w*, 1695*s*, 1475*m*, 1423*s*, 1387*m*, 1357*m*, 1300*m*, 1280*s*, 1240*m*, 1217*m*, 1130*w*, 1100*m*, 1065*m*, 1025*m*, 900*m*, 860*m*. – MS.: 167 (11, M^+), 100 (96), 95 (2), 81 (2), 72 (*100*), 68 (9), 58 (5), 56 (9), 44 (43), 40 (18). – ^{1}H-NMR. ($CDCl_3$): 7.89 (br. *s*, H–C(2)); 7.21 (*q*, J = 1.0, H–C(5)); 7.10 (*q*, J = 1.0, H–C(4)); 3.47 (*q*, J = 7.0, $2H_2C$–N); 1.29 (*t*, J = 7.0, $2H_3C$).

$C_8H_{13}N_3O$ (167.21) Calc. C 57.46 H 7.84 N 25.13% Found C 57.40 H 7.91 N 25.06%

Preparation of 1-benzylimidazole (**1i**) [7]. Needles from benzene/hexane, m.p. 71–72° (lit. 70–71° [7]. – UV. (EtOH): 209 (14200). – IR. ($CHCl_3$): 3140–3040*m*, 2925*m*, 1500*s*, 1455*m*, 1440*m*, 1390*w*, 1355*w*, 1280*m*, 1230*m*, 1110*m*, 1070*s*, 1030*m*, 900*m*, 700*s*. – MS.: 158 (29, M^+), 91 (*100*), 77 (2), 65 (17), 51 (7), 39 (10). – ^{1}H-NMR. ($CDCl_3$): 7.53 (br. *s*, H–C(2)); 7.09 (*q*, J = 1.0, H–C(4)); 6.89 (*q*, J = 1.0, H–C(5)); 7.4–7.1 (*m*, phenyl protons); 5.12 (*s*, benzyl protons).

$C_{10}H_{10}N_2$ (158.20) Calc. C 75.92 H 6.37 N 17.17% Found C 75.92 H 6.42 N 17.67%

Photolysis of 1-substituted imidazoles (**1a–i**). – *General procedure.* a) A 500 ml solution containing 2–4 g of a 1-substituted imidazole was irradiated either with a low pressure mercury lamp (TNM 15132, *Quarzlampen GmbH*, Hanau; lamp A) or a 125 watt medium pressure mercury lamp (QM 125, *Meda*-Licht AG, Basel; lamp B). A quartz immersion well with water cooling was centered in a pyrex vessel filled with the solution to be irradiated. After irradiation the solvent was removed *i.V.* and the residue was passed through a column of 30 times its weight of basic alumina (*Woelm*, activity I) and eluted with $CHCl_3/CH_3OH$ 9:1 to remove the recovered acid. The reaction products were separated by chromatography using 50 times their weight of silicagel, and eluted with $CHCl_3$/MeOH 9:1, unless specified otherwise.

b) An acylimidazole solution prepared from the corresponding carboxylic acid and N,N'-carbonyldiimidazole was diluted to a solution of 500 ml THF; this solution was irradiated and then worked up as in a).

In both methods a) and b), the reaction and the separation were followed by TLC. and the products were detected by UV.-light (254 nm). It was noted that the 2-substituted derivatives so far obtained (**2a–i**) show the higher Rf values than the 4(or 5)-substituted isomers (**3a–i**) on TLC. plates developed either with $CHCl_3/CH_3OH$ 5:1 or with AcOEt/CH_3OH 5:1 and are, accordingly, eluted in fore-runs by chromatography on silicagel.

Photolysis of 1-acetylimidazole (**1a**). 2.2 g of **1a** was irradiated in THF for 16 h (lamp A). Chromatography afforded 530 mg of **2a** and 650 mg of **3a**.

2-Acetylimidazole (**2a**). M.p. 137–137.5° (from MeOH/benzene); lit. 135–137.5° [8]. – UV. (EtOH): 277 (12700). – IR. (KBr): 3350–2200*s*, 1680*s*, 1667*s*, 1410*s*, 1390*s*, 1455*m*, 1315*m*, 1155*m*, 1125*m*, 1100*m*, 1025*m*, 950*s*, 785*m*, 775*m*, 720*w*, 635*m*, 545*w*. – MS.: 110 (100, M^+), 95 (61), 82 (44), 68 (61), 54 (5), 43 (99). – ^{1}H-NMR. (CD_3OD): 7.26 (*s*, H—C(4) and H—C(5)); 2.58 (*s*, H_3CCO). – ^{13}C-NMR. (CD_3OD): 190.0 (*s*, CO); 146.2 (*s*, C(2)); 132–120 (br., C(4) and C(5)); 25.8 (*q*, H_3CCO).

$C_5H_6N_2O$ (110.11) Calc. C 54.54 H 5.49 N 25.46% Found C 54.45 H 5.49 N 25.46%

4(or 5)-Acetylimidazole (**3a**). M.p. 172° (from $CHCl_3$/acetone). – UV. (EtOH): 255 (13100). – IR. (KBr): 3350–2200*s*, 1660*s*, 1540*m*, 1510*m*, 1440*m*, 1370*m*, 1340*m*, 1230*m*, 1135*m*, 1090*m*, 960*m*, 860*m*, 820*m*, 630*s*. – MS.: 110 (49, M^+), 95 (*100*), 82 (2), 68 (13), 67 (17), 54 (2), 52 (2), 43 (16). – ^{1}H-NMR. (CD_3OD): 7.84 and 7.81 (2*s*, 2H on imidazole ring); 2.51 (*s*, H_3CCO). – ^{13}C-NMR. (CD_3OD): 192.9 (*s*, CO); 139.3 (*d*, C(2)); 128.7 (*d*, C(4)); 26.6 (*q*, H_3CCO).

$C_5H_6N_2O$ (110.11) Calc. C 54.54 H 5.49 N 25.44% Found C 54.48 H 5.48 N 25.49%

Photolysis of 1-capryloylimidazole (**1b**). 1.9 g of **1b** was irradiated in acetonitrile for 20 h (lamp A). Chromatography afforded 700 mg of **2b** and 300 mg of **3b**.

2-Capryloylimidazole (**2b**). Leaflets from acetone/hexane, m.p. 93.5–94.5°. – UV. (EtOH): 277 (13100). – IR. ($CHCl_3$): 3430*m*, 3270*m*, 2960*s*, 2925*s*, 2860*m*, 1670*s*, 1415*s*, 1390*m*, 1085*m*. – MS.: 194 (18, M^+), 179 (2), 177 (2), 166 (3), 165 (3), 151 (4), 137 (17), 123 (28), 110 (*100*), 95 (47), 82 (4), 68 (54), 57 (7), 55 (8), 41 (16). – ^{1}H-NMR. ($CDCl_3$): 7.3–7.2 (*m*, H—C(4) and H—C(5)) (on addition of D_2O: 7.25, *s* and 7.22, *s*); 3.14 (*t*, J = 8.0, H_2CCO); 1.76 (*m*, H_2CCH_2CO); 1.55–1.10 (*m*, 8H); 0.89 (*t*, J = 7.0, terminal H_3C). – ^{13}C-NMR. ($CDCl_3$): 192.8 (*s*, CO); 145.3 (*s*, C(2)); 131.1 and 120.5 (*d*, C(4), C(5)); 37.9 (*t*, H_2CCH_2CO); 31.7 (*t*); 29.3 (*t*); 29.0 (*t*); 24.3 (*t*); 22.6 (*t*); 14.0 (*q*, terminal H_3C).

$C_{11}H_{18}N_2O$ (194.27) Calc. C 68.00 H 9.34 N 14.42% Found C 68.03 H 9.31 N 14.46%

4(or 5)-Capryloylimidazole (**3b**). M.p. 129–130° (from MeOH/benzene). – UV. (EtOH): 257 (12200). – IR. ($CHCl_3$): 3430*m*, 3240*m*, 2960*s*, 2925*s*, 2850*m*, 1660*s*, 1550*m*, 1410*w*, 1360–1330*m*, 1140*m*, 1095*m*, 850*w*. – ^{1}H-NMR. ($CDCl_3$): 7.86 (*s*, H—C(2)); 7.79 (*s*, H—C(4 or 5)); 2.89 (*t*, J = 8.0, H_2CCO); 1.76 (*m*, H_2CCH_2CO); 1.55–1.10 (*m*, 8H); 0.89 (*t*, J = 7.0, terminal H_3C). – ^{13}C-NMR. ($CDCl_3$): 193 (*s*, CO); 138.5 (*d*, C(2)); 131 (*d*, C(4)); 39.1 (*t*, H_2CCH_2CO); 31.7 (*t*); 29.3 (*t*); 29.1 (*t*); 24.8 (*t*); 22.6 (*t*); 14.0 (*q*, terminal H_3C).

$C_{11}H_{18}N_2O$ (194.27) Calc. C 68.00 H 9.34 N 14.42% Found C 68.10 H 9.30 N 14.47%

Photolysis of 1-cyclohexanecarbonylimidazole (**1c**). 3.6 g of **1c** was irradiated in THF for 18 h (lamp A). Chromatography gave 1.4 g of **2c** and 1.0 g of **3c**.

2-Cyclohexanecarbonylimidazole (**2c**). Needles from benzene, m.p. 158–160°. – UV. (EtOH): 279 nm (12900). – IR. (CCl_4): 3440*s*, 3270*s*, 2940*s*, 2860*m*, 1665*s*, 1455*m*, 1415*s*, 1160*w*, 1145*w*, 1115*m*, 1080*m*, 1060*w*, 1030*w*, 1000*m*, 950*m*. – MS.: 178 (46, M^+), 150 (33), 135 (32), 123 (14), 121 (14), 108 (4), 96 (41), 95 (34), 82 (25), 68 (*100*), 55 (27), 41 (29). – ^{1}H-NMR. ($CDCl_3$): 7.3–7.2 (*m*, H—C(4) and H—C(5)) (on addition of D_2O: 7.27, *s* and 7.23, *s*); 3.62 (*m*, HCCO); 2.2–1.1 (*m*, 10H). – ^{13}C-NMR. ($CDCl_3$): 195.7 (*s*, CO); 144.7 (*s*, C(2)); 131.1 and 120.5 (2*d*, C(4), C(5)); 45.2 (*d*, HCCO); 29.0 (2*t*); 25.9 (*t*); 25.6 (2*t*).

$C_{10}H_{14}N_2O$ (178.23) Calc. C 67.38 H 7.91 N 15.72% Found C 67.43 H 7.91 N 15.80%

4(or 5)-Cyclohexanecarbonylimidazole (**3c**). Needles from acetone/benzene, m.p. 170–172°. – UV. (EtOH): 257 (12300). – IR. ($CHCl_3$): 3430*s*, 3250*s*, 2940*s*, 2860*m*, 1660*s*, 1550*m*, 1450–1410*m*, 1365*s*, 1145*m*, 1130*m*, 1100*m*, 925*m*, 850*w*. – MS.: 178 (27, M^+), 163 (2), 161 (2), 150 (3), 149 (4), 137 (8), 135 (6), 123 (49), 110 (58), 95 (*100*), 82 (17), 68 (30), 55 (32), 41 (20). – ^{1}H-NMR. ($CDCl_3$): 7.86 (*s*, H—C(2)); 7.79 (*s*, H—C(4 or 5)); 3.10 (*m*, HCCO); 2.1–1.1 (*m*, 10H). – ^{13}C-NMR. ($CDCl_3$): 197 (br. *s*, CO); 138.7 (*d*, C(2)); 131 (br. *d*, C(4)); 41.7 (*d*, HCCO); 29.5 (2*t*); 25.7 (3*t*).

$C_{10}H_{14}N_2O$ (178.23) Calc. C 67.38 H 7.92 N 15.72% Found C 67.33 H 7.87 N 15.67%

Photolysis of 1-pivaloylimidazole (**1d**). 2 g of **1d** was irradiated in acetonitrile for 20 h (lamp A). Chromatography afforded 550 mg of **2d** and 590 mg of **3d**.

2-Pivaloylimidazole (**2d**). Needles from benzene, m.p. 140–141°. – UV. (EtOH): 278 (13100). – IR. (CCl_4): 3445*s*, 3300*s*, 2970*m*, 2960*m*, 2935*m*, 2875*w*, 1668*s*, 1652*s*, 1485*m*, 1410*s*, 1400*s*, 1390*m*, 1367*m*, 1305*w*, 1295*w*, 1120*m*, 1083*s*, 1050*w*, 1000*s*, 945*s*, 940*s*, 920*s*, 915*s*, 870*w*. – MS.: 152 (17, M^+), 137 (7), 124 (18), 123 (8), 109 (7), 96 (41), 81 (2), 68 (*100*), 57 (18), 50 (20), 41 (14). – ^{1}H-NMR. ($CDCl_3$): 7.20 and 7.15 (2*q*, J = 1.0, H–C(4), H–C(5)); 1.51 (*s*, $3H_3C$).

$C_8H_{12}N_2O$ (152.19) Calc. C 63.13 H 7.95 N 18.41% Found C 63.04 H 7.90 N 18.46%

4(or 5)-Pivaloylimidazole (**3d**). M.p. 105–107° (from benzene/heptane). – UV. (EtOH): 257 (12300). – IR. (CCl_4): 3430*m*, 3280*m*, 2990*m*, 2930*m*, 2910*w*, 1650*s*, 1535*w*, 1480*m*, 1340*s*, 1240*s*, 1093*m*, 950*m*, 915*m*, 850*w*. – MS.: 152 (46, M^+), 137 (5), 124 (5), 109 (8), 95 (*100*), 68 (85), 57 (79), 41 (44). – ^{1}H-NMR. ($CDCl_3$): 7.79 (*s*, H–C(2) and H–C(4 or 5)); 1.42 (*s*, $3H_3C$).

$C_8H_{12}N_2O$ (152.19) Calc. C 63.13 H 7.95 N 18.41% Found C 63.22 H 7.88 N 18.42%

Photolysis of 1-benzoylimidazole (**1e**). 2 g of **1e** was irradiated in THF for 16 h (lamp A). Chromatography afforded 250 mg of **2e** and 450 mg of **3e**.

2-Benzoylimidazole (**2e**). Needles from benzene, m.p. 159–159.5° (lit. 161–162° [21]). – UV. (EtOH): 260 (8800), 297 (14800). – IR. ($CHCl_3$): 3430*s*, 3250*s*, 2950*m*, 1640*s*, 1600*m*, 1575*m*, 1450*m*, 1410*s*, 1390*s*, 1300*m*, 1085*m*, 900*s*. – MS.: 172 (44, M^+), 144 (*100*), 117 (27), 105 (72), 95 (9), 90 (6), 86 (3), 77 (92), 68 (3), 63 (3), 51 (29), 40 (10). – ^{1}H-NMR. ($CDCl_3$)[10]: 8.55 (*octet*, J_1 = 8.0, J_2 = 2.0, J_3 ≈ 1.0, H–C(2') and H–C(6')); 7.64–7.44 (*m*, H–C(3'), H–C(4'), H–C(5')); 7.38 and 7.24 (2*q*, J = 1.0, H–C(4) and H–C(5)) (on addition of D_2O: 7.38, *s* and 7.24, *s*). – ^{13}C-NMR. ($CDCl_3$)[10]: 182.2 (*s*, CO); 145.2 (*s*, C(2)); 135.6 (*s*, C(1')); 133.2 (*d*, C(4')); 131.7–120.4 (2*d*, C(4) and C(5)); 130.9 (2*d*, C(2') and C(6')); 128.2 (2*d*, C(3') and C(5')).

$C_{10}H_8N_2O$ (172.18) Calc. C 69.75 H 4.68 N 16.27% Found C 69.80 H 4.76 N 16.21%

4(or 5)-Benzoylimidazole (**3e**). Needles from acetone/hexane, m.p. 142°. – UV. (EtOH): 257 shoulder (11000), 276 (13400). – IR. ($CHCl_3$): 3430*m*, 3250*m*, 2900*m*, 1635*s*, 1600*w*, 1575*w*, 1540*m*, 1445*w*, 1410*w*, 1360*s*, 1095*m*, 895*m*. – MS.: 172 (60, M^+), 145 (26), 117 (4), 105 (42), 95 (54), 89 (4), 78 (*100*), 77 (50), 67 (10), 63 (5), 51 (27), 40 (12). – ^{1}H-NMR. ($CDCl_3$)[10]: 7.96 (*q*, J_1 = 8.0, J_2 = 2.0, H–C(2') and H–C(6')); 7.95 (*s*, H–C(2)); 7.76 (*s*, H–C(4 or 5)); 7.64–7.40 (*m*, H–C(3'), H–C(4') and H–C(5')). – ^{13}C-NMR. ($CDCl_3$)[10]: 186.5 (*s*, CO); 138.9 (*d*, C(2)); 138.0 (*s*, C(5)); 134.8 (*s*, C(1')); 132.5 (*d*, C(4')); 132.1 (*d*, C(4)); 129.0 and 128.7 (2*d* and 2*d*, C(2'), C(3'), C(5'), C(6')).

Photolysis of 1-(3-methyl-2-butenoyl)imidazole (**1f**). 2 g of **1f** was irradiated in THF for 25 h (lamp A). Chromatography on silicagel and elution with $CHCl_3$/MeOH 9:1 gave 310 mg of **2f** and crude **3f** which was rechromatographed and eluted with ethyl acetate/MeOH 9:1 to give 610 mg of pure **3f**.

2-(3-Methyl-2-butenoyl)imidazole (**2f**). M.p. 143–144° (from benzene). – UV. (EtOH): 297 (17500). – IR. (CCl_4): 3430*m*, 3250*m*, 1660*s*, 1655*s*, 1445*s*, 1415*s*, 1395*m*, 1375*m*, 1297*m*, 1280*m*, 1123*m*, 1080*m*, 1030*m*, 960*m*, 860*m*, 850*m*. – MS.: 150 (73, M^+), 149 (*100*), 135 (15), 122 (24), 121 (22), 107 (25), 95 (28), 82 (78), 69 (29), 68 (17), 55 (32), 42 (14), 39 (30). – ^{1}H-NMR. ($CDCl_3$): 7.28 (*m*, HCCO); 7.32–7.18 (*m*, H–C(4) and H–C(5)) (on addition of D_2O: 7.26, *d* and 7.20, *d*); 2.36 (*d*, J = 1.0, H_3C-*cis*); 2.09 (*d*, J = 1.0, H_3C-*trans*).

$C_8H_{10}N_2O$ (150.18) Calc. C 63.98 H 6.71 N 18.65% Found C 64.15 H 6.76 N 18.80%

4(or 5)-(3-Methyl-2-butenoyl)imidazole (**3f**). M.p. 129–130° (from benzene). – UV. (EtOH): 279 (13400). – IR. ($CHCl_3$): 3440*s*, 3230*s*, 2900*s*, 1655*s*, 1615*s*, 1605*s*, 1545*s*, 1455*m*, 1390*m*, 1365*m*, 1330*m*, 1130*s*, 1105*m*, 1080*w*, 1033*w*, 980*m*, 840*s*. – MS.: 150 (30, M^+), 149 (22), 135 (7), 133 (7), 122 (37), 107 (8), 95 (*100*), 82 (27), 78 (38), 68 (18), 67 (23), 55 (28), 40 (37), 39 (37). – ^{1}H-NMR. ($CDCl_3$): 7.81 (*s*, H–C(2)); 7.75 (*s*, H–C(4 or 5)); 6.68 (*m*, HCCO), 2.33 (*d*, J = 1.0, H_3C-*cis*); 2.05 (*d*, J = 1.0, H_3C-*trans*).

$C_8H_{10}N_2O$ (150.18) Calc. C 63.98 H 6.71 N 18.65% Found C 63.78 H 6.69 N 18.75%

---

[10] Numbering of the ring atoms of imidazole and phenyl groups are given as 1 to 5 and 1' to 6', respectively.

Photolysis of 1-methoxycarbonylimidazole (**1g**). 2.4 g of **1g** was irradiated in MeOH for 24 h (lamp B). Chromatography afforded 400 mg of **2g** and 250 mg of **3g** with the recovery of 1.3 g of **1g**.

2-Methoxycarbonylimidazole (**2g**). M.p. 194–195° (dec., from MeOH/benzene). – UV. (EtOH): 258 (12900). – IR. (KBr): 3300–2100*s*, 1730*s*, 1727*s*, 1540*s*, 1455*s*, 1437*w*, 1430*s*, 1380*s*, 1320*m*, 1220*s*, 1150*s*, 1127*s*, 1105*m*, 990*m*, 790*m*. – MS.: 126 (28, M^+), 109 (3), 95 (38), 82 (9), 68 (*100*), 59 (10), 54 (7), 44 (20), 40 (25). – ^{1}H-NMR. (CD_3OD): 7.22 (*s*, H–C(4) and H–C(5)); 3.91 (*s*, H_3CO). – ^{13}C-NMR. (CD_3OD): 160.4 (*s*, CO); 139.2 (*s*, C(2)); 126.8 (2*d*, C(4) and C(5)); 51.8 (*q*, H_3CO).

$C_5H_6N_2O_2$ (126.11) Calc. C 47.62 H 4.80 N 22.20% Found C 47.52 H 4.81 N 22.30%

4(or 5)-Methoxycarbonylimidazole (**3g**). M.p. 154–154.5° (from MeOH/benzene). – UV. (EtOH): 236 (11300). – IR. (KBr): 3300–2200*s*, 1715*s*, 1515*m*, 1445*s*, 1350*s*, 1325*m*, 1290*m*, 1197*s*, 1170*s*, 1090*s*, 1000*s*, 934*w*, 900*w*, 845*s*. – MS.: 126 (60, M^+), 109 (3), 95 (*100*), 82 (2), 68 (13), 67 (21), 59 (1), 53 (1), 40 (21). – ^{1}H-NMR. (CD_3OD): 7.77 (*d*, J = 1.0, H–C(2)); 7.73 (*d*, J = 1.0, H–C(4 or 5)); 3.84 (*s*, H_3CO). – ^{13}C-NMR. (CD_3OD): 164.2 (*s*, CO); 138.5 (*d*, C(2)); 131.2 (*s*, C(5)); 126.7 (*d*, C(4)); 51.8 (*q*, H_3CO).

$C_5H_6N_2O_2$ (126.11) Calc. C 47.62 H 4.80 N 22.22% Found C 47.63 H 4.86 N 22.30%

Photolysis of 1-(N,N-diethylcarbamoyl)imidazole (**1h**). 2.6 g of **1h** was irradiated in MeOH for 9 h (lamp B). The separation of the products was carried out by successive chromatography on two columns, eluting from the first with $CHCl_3$/MeOH 9:1 and from the second using ethyl acetate/MeOH 9:1, to give 200 mg of **2h** which was solidified after standing and 250 mg of **3h** as liquid with the recovery of 1.4 g of **1h**.

2-(N,N-Diethylcarbamoyl)imidazole (**2h**). – UV. (EtOH): 258 (9800). – IR. (CCl_4): 3440*s*, 3200*s*, 2980*m*, 2940*m*, 2880*w*, 1605*s*, 1485*s*, 1463*m*, 1450*m*, 1440*m*, 1415*w*, 1380*m*, 1365*m*, 1305*m*, 1143*m*, 1120*w*, 1100*m*, 1075*w*, 862*m*. – MS.: 167 (1, M^+), 152 (1), 138 (1), 124 (1), 110 (1), 100 (3), 96 (28), 72 (*100*), 68 (24), 58 (37), 44 (7), 42 (12), 40 (11). – ^{1}H-NMR. ($CDCl_3$): 7.18 and 7.09 (2 br. *s*, H–C(4), H–C(5)); 4.28 and 3.58 (2*q*, J = 6.0, $2H_2CN$); 1.34 and 1.27 (2*t*, J = 6.0, $2H_3CCH_2N$).

4(or 5)-(N,N-Diethylcarbamoyl)imidazole (**3h**). – UV. (EtOH): 237 (7500). – IR. (CCl_4): 3150*m*, 2980*m*, 2940*m*, 2900*w*, 2840*w*, 1590*s*, 1500*w*, 1465*w*, 1430*w*, 1385*w*, 1330*m*, 1300*w*, 1215*m*, 1140*m*. – MS.: 167 (18, M^+), 152 (7), 138 (4), 124 (1), 95 (82), 72 (46), 68 (15), 58 (*100*), 44 (30), 40 (18). – ^{1}H-NMR. ($CDCl_3$): 7.64 (br. *s*, H–C(2)); 7.42 (br. *s*, H–C(4)); 3.67 (*m*, $\omega_{1/2}$ = 22, $2H_2CN$); 1.50 (*t*, J = 6.0, $2H_3CCH_2N$).

Photolysis of 1-benzylimidazole (**1i**). 2 g of **1i** was irradiated in THF for 15 h (lamp B). Repeated chromatography afforded 900 mg of **2i** and 700 mg of **3i**.

2-Benzylimidazole (**2i**). Needles from benzene, m.p. 121–122.5° (lit. 125–126° [21]). – UV. (EtOH): 212 (11100). – IR. ($CHCl_3$): 3300–2300*s*, 1613*m*, 1602*w*, 1495*m*, 1380*m*, 920*m*. – MS.: 158 (81, M^+), 157 (*100*), 130 (12), 116 (5), 103 (12), 91 (21), 81 (8), 78 (10), 77 (12), 65 (12), 54 (2), 51 (10), 39 (6). – ^{1}H-NMR. ($CDCl_3$): 7.4–7.1 (*m*, 5H on phenyl); 6.90 (*s*, H–C(4) and H–C(5)); 4.04 (*s*, H_2C). – ^{13}C-NMR. ($CDCl_3$)[10]: 147.0 (*s*, C(2)); 137.8 (*s*, C(1')); 128.4 (4*d*, C(2'), C(3'), C(5'), C(6')); 126.4 (*d*, C(4')); 121.4 (2*d*, C(4) and C(5)); 34.6 (*t*, H_2C).

$C_{10}H_{10}N_2$ (158.20) Calc. C 75.92 H 6.37 N 17.71% Found C 75.86 H 6.38 N 17.74%

4(or 5)-Benzylimidazole (**3i**). M.p. 77–80° (after distillation; lit. 84–85° [22]). – UV. (EtOH): 212 (11500). – IR. (CCl_4): 3400–2300*s*, 1610*w*, 1497*s*, 1475*m*, 1457*m*, 1108*m*, 1090*m*, 1030*m*, 990*m*, 945*m*, 715*s*, 705*s*, 700*s*. – MS.: 158 (*100*, M^+), 130 (53), 103 (18), 91 (9), 81 (36), 77 (24), 71 (10), 65 (11), 63 (8), 51 (20), 39 (13). – ^{1}H-NMR. ($CDCl_3$): 7.42 (br. *s*, H–C(2)); 7.22 (*m*, 5H on phenyl); 6.70 (br. *s*, H–C(4 or 5)); 3.95 (*s*, H_2C). – ^{13}C-NMR. ($CDCl_3$)[10]: 139.7 (*s*, C(1')); 136.3 (*s*, C(4 or 5)); 134.8 (*d*, C(2)); 128.7 and 128.3 (4*d*, C(2'), C(3'), C(5') and C(6')); 126.1 (*d*, C(4')); 117.5 (*d*, C(4)); 33.3 (*t*, H_2C).

$C_{10}H_{10}N_2$ (158.20) Calc. C 75.92 H 6.37 N 17.71% Found C 75.61 H 6.01 N 17.58%

Preparation and photolysis of deuterated compounds. – *Deuteriation of Imidazole.* Two glass cylinders, each of which contained 2.5 g of imidazole dissolved in 25 ml D_2O (d_2 = 99.5%), were sealed and heated to 230–235° for 6 h. On cooling, D_2O was removed by distillation to give crude crystals of the deuteriated imidazole which was recrystallized from benzene (plates, m.p. 85–87°). Their deuterium content was found (mass spectrum) as follows: d_0 = 4%, d_1 = 3%, d_2 = 16%, d_3 = 59%, d_4 = 18% (total 71%).

1-Acetyl-imidazol-d_3 (**1j**). 2.8 g of deuteriated imidazole (described above) and 1.6 g of freshly distilled acetyl chloride were stirred in 80 ml of dry benzene for 24 h. Filtration of the hydrochloride and evaporation of the solvent afforded 2.3 g of crude material which was recrystallized from dry benzene, m.p. 102–104°. – IR. ($CHCl_3$): 2990*m*, 1740*s*, 1415*m*, 1377*s*, 1340*s*, 1287*m*, 1114*w*, 1040*w*, 982*w*, 975*w*, 964*w*, 947*m*, 824*m*. – Their deuterium content was found (mass spectrum) as follows; d_0 = 1%, d_1 = 3%, d_2 = 25%, d_3 = 71% (total 89%). The combination of the result with the data obtained from its ^{1}H-NMR. spectrum indicated that the deuterium content at the 2-, 4- and 5-positions were 85%, 92.5% and 92.5%, respectively.

1-Acetyl-d_3-imidazole (**1k**). 2.8 g of imidazole and 1.6 g of freshly distilled acetyl-d_3 chloride (*Merck Sharp & Dohme Canada Ltd.*, Montreal, Canada) were stirred in 80 ml dry benzene for 24 h. Filtration of the hydrochloride and evaporation of solvent afforded crude **1k** which was recrystallized repeatedly from dry benzene to give 1.3 g of **1k**, m.p. 100–104°. – IR. ($CHCl_3$): 3160*w*, 3130*w*, 2990*m*, 1740*s*, 1475*s*, 1375*s*, 1310*m*, 1290*s*, 1275*m*, 1140*w*, 1100*m*, 1068*w*, 1040*m*, 953*s*, 900*m*.

The deuterium content was found (mass spectrum) as follows: d_0 = 0%, d_1 = 0%, d_2 = 5%, d_3 = 95% (total 98%).

Photolysis of 1:1 mixtures of **1j** *and* **1k**. 1) Two quartz tubes each of which contained 100 mg of **1j** and 100 mg of **1k** dissolved in 10 ml THF were irradiated externally for 15 h (lamp A). The solvent was removed *i.V.* and the residue was subjected to chromatography (30 g of silicagel), elution with $CHCl_3$/MeOH 9:1 giving 84 mg of crude *2-acetylimidazole* (m.p. 136–137° after recrystallization from MeOH/benzene) and 85 mg of crude *4(or 5)-acetylimidazole* (m.p. 172° after recrystallization from CHCl/acetone). – Their deuterium contents were determined by mass spectrometry and the results are shown in Table 5. 2) **1j** and **1k**, 200 mg each, were dissolved in 500 ml THF and irradiated for 3 h (lamp A). The solvent was removed *i.V.* to give a complex mixture. Repeated chromatography afforded a few mg of *2-* and *4(or 5)- acetylimidazole* each. Their deuterium contents were determined by mass spectrometry and the results are shown in Table 5.

Table 5. *Deuterium contents of photolysis products*

	2-Acetylimidazole				4(or 5)-Acetylimidazole			
	Observed (%)		Expected (%)		Observed (%)		Expected (%)	
	Run 1	Run 2	Intra-molecul.	Inter-molecul.	Run 1	Run 2	Intra-molecul.	Inter-molecul.
d_0	9 ± 1	1 ± 1	0 ± 1	25 ± 1	6 ± 1	1 ± 1	1 ± 1	25 ± 1
d_1	7 ± 1	10 ± 1	8 ± 1	2 ± 1	10 ± 1	12 ± 1	10 ± 1	2 ± 1
d_2	40 ± 1	53 ± 1	44 ± 1	13 ± 1	38 ± 1	46 ± 1	41 ± 1	12 ± 1
d_3	37 ± 1	33 ± 1	48 ± 1	36 ± 1	37 ± 1	40 ± 1	48 ± 1	36 ± 1
d_4	2 ± 1	2 ± 1	0	5 ± 1	3 ± 1	1 ± 1	0	5 ± 1
d_5	6 ± 1	1 ± 1	0	20 ± 1	5 ± 1	1 ± 1	0	20 ± 1

Photolysis of a mixture of 1-acetyl-imidazole-d_3 (**1j**) *and 1-cyclohexanecarbonylimidazole* (**1c**). **1j** and **1c**, 540 mg each, were mixed in 20 ml THF and irradiated for 14 h externally (lamp A). The solvent was removed and the residual oil was passed through a column of 30 g of basic alumina (*Woelm*, activity I) and eluted with $CHCl_3$/MeOH 9:1. The resulting mixture was chromatographed repeatedly on silicagel. All of the four expected acylimidazoles were isolated in pure form and their deuterium contents were determined by mass spectrometry: *2-acetylimidazole*,

$d_0 = 12\%$, $d_1 = 10\%$, $d_2 = 74\%$, $d_3 = 4\%$ (expected values for intramolecular acyl migration: $d_0 = 3\%$, $d_1 = 13\%$, $d_2 = 84\%$); *4(or 5)-acetylimidazole*, $d_0 = 12\%$, $d_1 = 25\%$, $d_2 = 60\%$, $d_3 = 3\%$ (expected values for intramolecular acyl migration: $d_0 = 3\%$, $d_1 = 20\%$, $d_2 = 77\%$); *2-cyclohexanecarbonylimidazole*, $d_0 = 76\%$, $d_1 = 7\%$, $d_2 = 17\%$, $d_3 = 0\%$; *4(or 5)-cyclohexanecarbonylimidazole*, $d_0 = 77\%$, $d_1 = 8\%$, $d_2 = 15\%$, $d_3 = 0\%$.

Elementary analyses were carried out in the microanalysis laboratory of ETH Zürich (directed by *W. Manser*). For the measurement of NMR.-spectra Miss *B. Brandenberg* and Mr. *K. Hiltbrunner* (directed for the NMR.-service by Prof. *J. F. M. Oth*) are gratefully acknowledged. The author is indebted to Dr. *K. Müllen* for the interpretation of ^{13}C-NMR. spectra. The author also wishes to thank Prof. *J. Seibl* for helpful discussions on mass spectra and Mrs. *L. Golgowsky* for their measurements.

REFERENCES

[1] 90. Mitt.: *H. Eichenberger, H. R. Wolf & O. Jeger*, Helv. *59*, 1253 (1976).
[2] For reviews see: a) *H. A. Staab*, Angew. Chem., Int. Ed. *1*, 351 (1962), (containing original literature references), b) *E. A. Bernard & W. D. Stein*, Adv. in Enzymology, *20*, 51 (1958), c) *T. C. Bruice & S. J. Bekovic*, Bioorganic Mechanisms, Vol. *1*, W. A. Benjamin 1966.
[3] For a review, see: *D. Belluš*, Adv. in Photochemistry *8*, Wiley, New York, London 1971, p. 109.
[4] a) *H. Shizuka, E. Okutsu, Y. Mori & I. Tanaka*, Mol. Photochemistry *1*, 135 (1969), b) *H. Shizuka, S. Ono, T. Morita & I. Tanaka*, Mol. Photochemistry *3*, 203 (1971), c) *H. Shizuka, M. Kato, T. Ochiai, K. Matsui & T. Morita*, Bull. chem. Soc. Japan *43*, 67 (1970).
[5] *M. Somei & M. Natsume*, Tetrahedron Letters *1973*, 2451.
[6] *H. A. Staab, M. Lüking & F. H. Dürr*, Chem. Ber. *95*, 1275 (1962).
[7] *E. F. Godefroi*, J. org. Chemistry *33*, 860 (1968).
[8] *B. Oddo & F. Ingraffia*, Gazz. chim. Ital. *61*, 466 (1931).
[9] *A. M. Rosl*, J. chem. Soc. *1963*, 2195.
[10] *E. F. Godefroi, H. J. J. Loozen & J. Th. J. Luderer-Platje*, Rec. trav. Chim. Pays Bas *91*, 1383 (1972).
[11] *T. Matsuura, A. Banba & K. Ogura*, Tetrahedron *27*, 1211 (1971).
[12] *Y. Ito & T. Matsuura*, Tetrahedron Letters *1974*, 513.
[13] *F. Bertini, R. Galli, F. Minisci & O. Porta*, Chim. Ind. (Milan) *54*, 233 (1972).
[14] For general reviews on imidazole chemistry, see: a) *K. Hofmann*, 'Imidazole and Its Derivatives', Intersciences Publ., Inc., New York, part *1*, b) *M. R. Grimett*, Adv. in Heterocycl. Chem. *12*, 103 (1970).
[15] *S. Iwasaki*, Helv. *59*, 2753 (1976).
[16] *G. B. Barlin & T. J. Batterham*, J. chem. Soc. *B* 516 (1967).
[17] *G. S. Reddy, L. Mandell & J. H. Goldstein*, J. chem. Soc. *1963*, 1414.
[18] a) *R. J. Pugmire & D. M. Grant*, J. Amer. chem. Soc. *90*, 4232 (1968), b) *F. J. Weigert & J. D. Roberts*, ibid. *90*, 3543 (1968).
[19] *H. Schubert & W. D. Rudolf*, Angew. Chem. Int. Ed. *5*, 674 (1966).
[20] *K. Brocklehurst & J. R. Griffiths*, Tetrahedron *24*, 2407 (1968).
[21] *A. Sonn & P. Greif*, Chem. Ber. *66*, 1900 (1933).
[22] *S. Akabori & S. Numano*, ibid. *66*, 159 (1933).