1-Hydroxyimidazole Derivatives IV. Quaternary Salts Derived from 1-Hydroxy-1*H*-imidazoles

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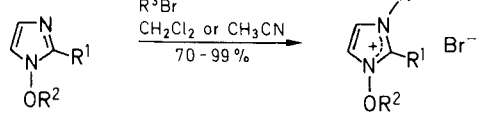
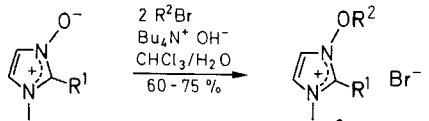
General procedures for the synthesis of 3-substituted 1-alkyloxy, 1-arylmethyloxy, and 1-phenyloxyimidazolium salts are described. 1,3-Bis(arylmethyloxy)imidazolium salts can be prepared using phase transfer conditions for the alkylation of 1-hydroxy-1*H*-imidazole 3-oxides. When the hydroxy group of 1-hydroxy-1*H*-imidazoles is protected during quaternization, 1-substituted imidazole 3-oxides are obtained.

An imidazole skeleton is commonly found in pharmaceutical drugs, fungicides, and herbicides. Therefore, new synthetic entries to this class of compounds may be desirable. The preparation of 1-hydroxy-1*H*-imidazoles **5a–c** from 1-hydroxy-1*H*-imidazole 3-oxides **3a–c**, and the transformation to 1-alkyloxy-, 1-arylmethyloxy-, and 1-phenyloxyimidazoles of type **1** have been reported only recently.[4–6] We now wish to present the synthesis of quaternary salts derived from these compounds.

Quaternization of compounds **1a–i** is straightforwardly performed by treating them with arylmethyl bromides in acetonitrile (Method A), or with aroylmethyl bromides in dichloromethane (Method B). The salts **2a–n** thus obtained are sensitive to heat, and especially **2a–i** (where R^1 = H) are decomposed rapidly by alkaline reagents. A convenient way to prepare 1,3-bis(arylmethyloxy)-imidazolium salts **4** is by the use of tetrabutylammonium hydroxide (TBAH) as a basic phase-transfer reagent for the alkylation of 1-hydroxy-1*H*-imidazole 3-oxides **3** in a two-phase system. However, only 2-substituted *N*-oxides like **3b,c** are suited for the reaction, and the method fails with the parent compound **3a**. When **3a** is treated with benzyl bromide under the above conditions, a strong odor of benzaldehyde develops, indicating cleavage of the N-O bond in the preformed product.

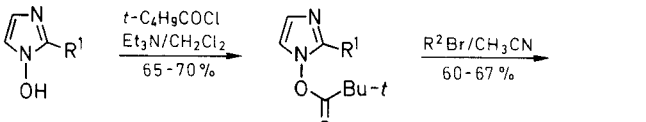


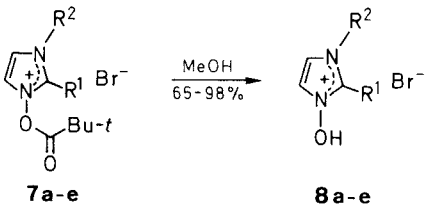


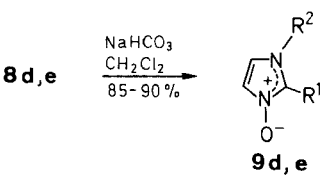
1	R^1	R^2	3	R^1
a	H	Me	a	H
b	H	Et	b	Me
c	H	CH_2=$CHCH_2$	c	Et
d	H	$PhCH_2CH_2$		
e	H	Ph		
f	Me	2,4-$Cl_2C_6H_3CH_2$		
g	Et	$PhCH_2$		
h	Et	2,4-$Cl_2C_6H_3CH_2$		
i	Et	Ph		

Again, this fact may be explained by the ready removal of the proton H-2 from the quaternary heterocycle in the presence of the basic TBAH, thus inducing the further decomposition. It is noteworthy, that we have not been able to prepare a monoalkylation product of **3b,c**, namely a 2-alkyl-1-arylmethyloxy-3-hydroxyimidazolium salt, by this method so far.

Another goal was the synthesis of 1-substituted imidazole 3-oxides. Since the direct alkylation of 1-hydroxy-1*H*-imidazoles **5a–c** yields only a mixture of *N*- and *O*-alkyl derivatives, protection of the hydroxy group during quaternization is necessary to effect selective *N*-alkylation. An acyl group would be a suitable protective group. Several attempts to obtain 1-acyloxy-1*H*-imidazoles (e.g. benzoyl, acetyl) have shown that these compounds are very unstable. However, the sterically hindered 1-(2,2-dimethylpropanoyloxy)-1*H*-imidazoles **6a–c** proved to be sufficiently stable, thus allowing the preparation of the protected quaternary salts **7a–e**, which are crystalline solids in the cases of **7a–c**, but less stable in the cases of **7d,e**. In all cases they are readily converted to 1-substituted 3-hydroxyimidazolium bromides **8a–e** by methanolysis of the acyl group. Neutralization of compounds **8d,e** gives 1-arylmethyl-imidazole 3-oxides **9d,e** but not so with the salts **8a–c**, due to enolization at the aroylmethyl moiety.







5, 6	R^1	7–9	R^1	R^2
a	H	a	H	4-$ClC_6H_4COCH_2$
b	Me	b	Me	4-$ClC_6H_4COCH_2$
c	Et	c	Et	4-$ClC_6H_4COCH_2$
		d	H	2,4-$Cl_2C_6H_3CH_2$
		e	H	3,4,5-$(MeO)_3C_6H_2CH_2$

Table 1. Compounds **2a–n** Prepared

Product	R^1	R^2	R^3	Method	Yield (%)	mp (°C)	Molecular Formula[a]	IR (KBr) ν(cm^{-1})	^{1}H-NMR (DMSO-d_6/TMS)[b] δ, J(Hz)
2a	H	Me	3,4,5-$(MeO)_3C_6H_4CH_2$	A	71	138	$C_{14}H_{19}BrN_2O_4$ (359.2)	1320, 1105	3.63 (s, 3H), 3.77 (s, 6H), 4.23 (s, 3H), 5.30 (s, 2H), 6.87 (s, 2H), 7.90 (t, 1H, J = 2), 8.20 (t, 1H, J = 2), 9.90 (t, 1H, J = 2)
2b	H	Et	4-$O_2NC_6H_4CH_2$	A	88	120	$C_{12}H_{14}BrN_3O_3$ (328.2)	1510, 1340, 1315, 1000	1.33 (t, 3H, J = 7), 4.50 (q, 2H, J = 7), 5.63 (s, 2H), 7.67–8.30 (AA'BB', 4H), 7.90 (t, 1H, J = 2), 8.13 (t, 1H, J = 2), 10.03 (t, 1H, J = 2)
2c	H	Et	2,4-$Cl_2C_6H_4CH_2$	A	99	134	$C_{12}H_{13}BrCl_2N_2O$ (352.1)	1470, 1010	1.30 (t, 3H, J = 7), 4.50 (q, 2H, J = 7), 5.55 (s, 2H), 7.50–7.73 (m, 3H), 7.83 (t, 1H, J = 2), 8.27 (t, 1H, J = 2), 9.90 (t, 1H, J = 2)
2d	H	CH_2=$CHCH_2$	3,4-(methylenedioxy)C_6H_3	A	85	137	$C_{14}H_{15}BrN_2O_3$ (339.2)	1490, 1290, 1245	4.93 (d, 2H, J = 6), 5.20–5.57 (m, 2H), 5.33 (s, 2H), 5.67–6.40 (m, 1H), 5.97 (s, 2H), 6.73–7.13 (m, 3H), 7.87 (t, 1H, J = 2), 8.17 (t, 1H, J = 2), 9.97 (t, 1H, J = 2)
2e	H	CH_2=$CHCH_2$	2,4-$Cl_2C_6H_3$	A	93	117	$C_{13}H_{13}BrCl_2N_2O$ (364.1)	1465, 1315	4.93 (d, 2H, J = 6), 5.17–6.30 (m, 3H), 5.50 (s, 2H), 7.47–7.67 (m, 3H), 7.77 (t, 1H, J = 2), 8.20 (t, 1H, J = 2), 9.83 (t, 1H, J = 2)
2f	H	$PhCH_2CH_2$	2,4-$Cl_2C_6H_3$	A	79	138	$C_{18}H_{17}BrCl_2N_2O$ (428.2)	1550, 945, 745	3.03 (t, 2H, J = 7), 4.67 (t, 2H, J = 7), 5.50 (s, 2H), 7.17 (s, 5H), 7.40–7.57 (m, 3H), 7.73 (t, 1H, J = 2), 8.17 (t, 1H, J = 2), 9.83 (t, 1H, J = 2)
2g	H	Me	4-$ClC_6H_4COCH_2$	B	84	156	$C_{12}H_{12}BrClN_2O_2$ (331.6)	1700, 1240, 1095	4.27 (s, 3H), 6.07 (s, 2H), 7.50–8.15 (AA'BB', 4H), 7.73 (t, 1H, J = 2), 8.30 (t, 1H, J = 2), 9.70 (t, 1H, J = 2)
2h	H	Et	4-$ClC_6H_4COCH_2$	B	98	130	$C_{13}H_{14}BrClN_2O_2$ (345.6)	1690, 1585	1.33 (t, 3H, J = 7), 4.50 (q, 2H, J = 7), 6.07 (s, 2H), 7.50–8.10 (AA'BB', 4H), 7.73 (t, 1H, J = 2), 8.23 (t, 1H, J = 2), 9.63 (t, 1H, J = 2)
2i	H	Ph	4-$Me_2NC_6H_4COCH_2$	B	70	141	$C_{19}H_{20}BrN_3O_2$ (402.3)	1660, 1590, 1260, 1190	3.06 (s, 6H), 5.98 (s, 2H), 6.81 (d, 2H, J = 9), 7.19–7.22 (m, 2H), 7.33–7.38 (m, 1H), 7.52–7.58 (m, 2H), 7.88 (d, 2H, J = 9), 7.95 (t, 1H, J = 2), 8.47 (t, 1H, J = 2), 10.04 (t, 1H, J = 2)
2j	Me	2,4-$Cl_2C_6H_4CH_2$	4-$ClC_6H_4COCH_2$	B	80	105	$C_{19}H_{16}BrCl_3N_2O_2$ (490.6)	1695, 1675, 1590	2.50 (s, 3H), 5.60 (s, 2H), 6.00 (s, 2H), 7.50–8.10 (m, 8H), 8.17 (d, 1H, J = 2)
2k	Et	$PhCH_2$	3,4,5-$(MeO)_3C_6H_2CH_2$	A	75	159	$C_{22}H_{27}BrN_2O_4$ (463.4)	1335, 1210, 1125	1.03 (t, 3H, J = 7), 2.97 (q, 2H, J = 7), 3.63 (s, 3H), 3.73 (s, 6H), 5.30 (s, 2H), 5.47 (s, 2H), 6.70 (s, 2H), 7.37 (s, 5H), 7.83 (d, 1H, J = 2), 8.27 (d, 1H, J = 2)
2l	Et	$PhCH_2$	2,4-$Cl_2C_6H_3CH_2$	A	78	144	$C_{19}H_{19}BrCl_2N_2O$ (442.2)	1460, 1320	0.97 (t, 3H, J = 7), 2.87 (q, 2H, J = 7), 5.46 (s, 2H), 5.50 (s, 2H), 7.40–7.55 (m, 8H), 7.63 (d, 1H, J = 2), 8.37 (d, 1H, J = 2)
2m	Et	2,4-$Cl_2C_6H_3CH_2$	4-$NO_2C_6H_4CH_2$	A	74	130	$C_{19}H_{18}BrCl_2N_3O_3$ (476.1)	1520, 1350, 870	1.01 (t, 3H, J = 7), 2.96 (q, 2H, J = 7), 5.63 (s, 2H), 5.67 (s, 2H), 7.53–7.80 (m, 3H), 7.57–8.30 (AA'BB', 4H), 7.90 (d, 1H, J = 2), 8.35 (d, 1H, J = 2)
2n	Et	Ph	4-$ClC_6H_4COCH_2$	B	82	171	$C_{19}H_{18}BrClN_2O_2$ (421.7)	1700, 1585, 1225	1.07 (t, 3H, J = 7), 3.04 (q, 2H, J = 7), 6.22 (s, 2H), 7.14–7.17 (m, 2H), 7.32–7.37 (m, 1H), 7.53–7.58 (m, 2H), 7.73, 8.11 (AA'BB', 4H), 7.90 (d, 1H, J = 2), 8.43 (d, 1H, J = 2)

[a] Microanalyses obtained: C, H, N ±0.50.

[b] Compounds **2i**, **m**, **n** were measured at 300 MHz, rest at 60 MHz.

Table 2. Compounds **4** Prepared

Product	R^1	R^2	Yield (%)	mp (°C) (dec)	Molecular Formula[a]	IR (KBr) ν(cm^{-1})	^{1}H-NMR (DMSO-d_6/TMS) δ, J(Hz)
4a	Me	4-$BrC_6H_4CH_2$	60	174	$C_{18}H_{17}Br_3N_2O_2$ (533.0)	3050, 1490, 850	2.47 (s, 3H), 5.46 (s, 4H), 7.50, 7.67 (AA'BB', 8H), 8.20 (s, 2H)
4b	Me	2,4-$Cl_2C_6H_3CH_2$	75	190	$C_{18}H_{15}BrCl_4N_2O_2$ (513.0)	1590, 1480, 1105, 865	2.47 (s, 3H), 5.53 (s, 4H), 7.56 (dd, 2H, J = 2, 8), 7.67 (d, 2H, J = 8), 7.79 (d, 2H, J = 2), 8.16 (s, 2H)
4c	Me	4-$O_2NC_6H_4CH_2$	60	168	$C_{18}H_{17}BrN_4O_6$ (465.2)	1525, 1350, 1110, 855	2.60 (s, 3H), 5.66 (s, 4H), 7.86 (d, 4H, J = 9), 8.25 (s, 2H), 8.30 (d, 4H, J = 9)
4d	Et	4-$BrC_6H_4CH_2$	60	170	$C_{19}H_{19}Br_3N_2O_2$ (547.1)	3040, 1490, 850	1.05 (t, 3H, J = 7), 2.86 (q, 2H, J = 7), 5.48 (s, 4H), 7.49, 7.67 (AA'BB', 8H), 8.30 (s, 2H)
4e	Et	2,4-$Cl_2C_6H_3CH_2$	65	176	$C_{19}H_{17}BrCl_4N_2O_2$ (527.1)	3040, 1580, 1470	1.11 (t, 3H, J = 7), 2.91 (q, 2H, J = 7), 5.58 (s, 4H), 7.57 (dd, 2H, J = 2, 8), 7.70 (d, 2H, J = 8), 7.79 (d, 2H, J = 2), 8.28 (s, 2H)
4f	Et	2,6-$Cl_2C_6H_3CH_2$	60	156	$C_{19}H_{17}BrCl_4N_2O_2$ (527.1)	1580, 1440, 940	1.05 (t, 3H, J = 7), 2.82 (q, 2H, J = 7), 5.73 (s, 4H), 7.54–7.64 (m, 6H), 8.44 (s, 2H)
4g	Et	4-$NO_2C_6H_4CH_2$	75	169	$C_{19}H_{19}BrN_4O_6$ (479.3)	1515, 1350, 850	1.15 (t, 3H, J = 7), 3.00 (q, 2H, J = 7), 5.66 (s, 4H), 7.85 (d, 4H, J = 9), 8.30 (d, 4H, J = 9), 8.31 (s, 2H)

[a] Microanalyses obtained: C, H, N ±0.50.

Table 3. Compounds **6–9** Prepared

Product	Yield (%)	mp (°C)	Molecular Formula[a]	IR (neat or KBr) ν(cm^{-1})	^{1}H-NMR (DMSO-d_6/TMS)[b] δ, J(Hz)
6a	70	oil	$C_7H_{12}N_2O_2$ (156.2)	1800	1.33 (s, 9H), 6.90 (t, 1H, J = 1.2), 7.35 (t, 1H, J = 1.2), 7.78 (t, 1H, J = 1.2)
6b	65	oil	$C_8H_{14}N_2O_2$ (170.2)	1785	1.33 (s, 9H), 2.10 (s, 3H), 6.78 (d, 1H, J = 1.4), 7.30 (d, 1H, J = 1.4)
6c	65	oil	$C_9H_{16}N_2O_2$ (184.2)	1785	1.13 (t, 3H, J = 7), 1.33 (s, 9H), 2.44 (q, 2H, J = 7), 6.72 (d, 1H, J = 1.4), 7.20 (d, 1H, J = 1.4)
7a	67	166	$C_{16}H_{18}BrClN_2O_3$ (401.7)	1800, 1700	1.07 (s, 9H), 6.00 (s, 2H), 7.62 (t, 1H, J = 2), 7.71, 8.06 (AA'BB', 4H), 7.90 (t, 1H, J = 2), 9.33 (t, 1H, J = 2)
7b	63	140	$C_{17}H_{20}BrClN_2O_3$ (415.7)	1810, 1690	1.10 (s, 9H), 2.50 (s, 3H), 6.05 (s, 2H), 7.59 (d, 1H, J = 2), 7.71, 8.06 (AA'BB', 4H), 7.93 (d, 1H, J = 2)
7c	60	184	$C_{18}H_{22}BrClN_2O_3$ (429.8)	1815, 1690	1.10 (s, 9H), 1.14 (t, 3H, J = 7), 2.95 (q, 2H, J = 7), 6.09 (s, 2H), 7.61 (d, 1H, J = 2), 7.71, 8.07 (AA'BB', 4H), 7.95 (d, 1H, J = 2)
8a	90	202	$C_{11}H_{10}BrClN_2O_2$ (317.6)	2600, 1700	6.09 (s, 2H), 7.69, 8.06 (AA'BB', 4H), 7.74 (t, 1H, J = 2), 7.99 (t, 1H, J = 2), 9.45 (t, 1H, J = 2)
8b	98	200	$C_{12}H_{12}BrClN_2O_2$ (331.6)	2570, 1685	2.52 (s, 3H), 6.08 (s, 2H), 7.62 (d, 1H, J = 2), 7.72, 8.07 (AA'BB', 4H), 7.93 (d, 1H, J = 2)
8c	96	199	$C_{13}H_{14}BrClN_2O_2$ (345.6)	2550, 1680	1.16 (t, 3H, J = 7), 2.97 (q, 2H, J = 7), 6.12 (s, 2H), 7.63 (d, 1H, J = 2), 7.72, 8.08 (AA'BB', 4H), 7.96 (d, 1H, J = 2)
8d	80	115	$C_{10}H_9BrCl_2N_2O$ (324.0)	2550	5.47 (s, 2H), 7.30–7.70 (m, 4H), 7.83 (t, 1H, J = 2), 9.40 (t, 1H, J = 2)
8e	65	190	$C_{13}H_{17}BrN_2O_4$ (345.2)	2600, 1125	3.64 (s, 3H), 3.78 (s, 6H), 5.27 (s, 2H), 6.87 (s, 2H), 7.84 (t, 1H, J = 2), 7.91 (t, 1H, J = 2), 9.64 (t, 1H, J = 2)
9d	90	156	$C_{10}H_5Cl_2N_2O$ (243.1)	1320	5.25 (s, 2H), 7.20–7.90 (m, 5H), 8.43 (t, 1H, J = 2)
9e	85	80	$C_{13}H_{16}N_2O_4$ (264.3)	1310, 1130	3.65 (s, 3H), 3.77 (s, 6H), 4.97 (s, 2H), 6.70 (s, 2H), 7.03 (t, 1H, J = 2), 7.20 (t, 1H, J = 2), 8.35 (t, 1H, J = 2)

[a] Satisfactory microanalyses obtained: C ±0.35, H ±0.40, N ±0.30.
[b] The resonance signal of OH is too broad to be detected.

A number of examples are listed in Tables 1–3. The IR spectra of compounds **6–9** reveal some remarkable features: (a) high values for the wave number of the C=O vibration of the acylated *N*-oxides **6, 7** ($\nu = \sim 1800\ cm^{-1}$);[7,8] (b) a broad band at $\nu = \sim 2600\ cm^{-1}$ in the spectra of the protonated *N*-oxides **8**;[9] and (c) in the mesoionic *N*-oxides **9d,e** a characteristic band at $\nu = \sim 1300\ cm^{-1}$.[9] In the ^{1}H-NMR spectra of all quaternary salts, when R^1 = H, the protons H-2 are exchangeable with deuterium oxide or methanol-d_4, thus confirming their acidic character.[10,11] As expected, the heteroaromatic protons appear as doublets when R^1 = alkyl, or as triplets when R^1 = H, respectively, due to the similar values of ^3J and ^4J (ca. 1.5 Hz).

In summary, new quaternary heterocyclic compounds are available by convenient procedures.

IR spectra were recorded on a Beckman Acculab 4 spectrophotometer. ^{1}H-NMR were obtained using either a Jeol JNM-PMX 60 spectrometer or a Bruker AM 300 instrument.

The requisite benzyl bromides, unless commercially available, were obtained from alcohols, prepared by $LiAlH_4$ reduction of the appropriate acid, ester or aldehyde. The benzyl alcohols were converted in the usual way to the bromides by the action of PBr_3. Bromination of acetophenones yielded the corresponding aroylmethyl bromides. 1-Methoxy-1*H*-imidazole **(1a)** was obtained from 1-hydroxy-1*H*-imidazole **(5a)** and diazomethane, as described below. Compounds **1b–i** were prepared by the procedure previously published.[6]

1-Methoxy-1*H*-imidazole (1a):
To a stirred suspension of 1-hydroxy-1*H*-imidazole (**5a**; 2.0 g, 23.8 mmol) in anhydrous Et_2O (10 mL) is added a solution of CH_2N_2 in Et_2O until the yellow color of the mixture persists. After 1 h at r.t. the mixture is filtered through diatomaceous earth, and the solvent is evaporated. Vacuum distillation of the remaining liquid affords pure 1-methoxy-1*H*-imidazole **(1a)**; yield: 1.05 g (45%); bp 50 °C/0.1 mbar; $n_D^{20} = 1.4788$.

$C_4H_6N_2O$	calc.	C 48.98	H 6.17	N 28.56
(98.1)	found	49.10	6.25	28.43

IR (neat): ν = 3120, 2940, 1355, 1115, 1030, 980 cm^{-1}.

^{1}H-NMR (CCl_4): δ = 4.00 (s, 3 H), 6.73 (t, 1 H, $J < 1$ Hz), 6.95 (t, 1 H, $J < 1$ Hz), 7.40 (t, 1 H, $J < 1$ Hz).

3-Substituted 1-Alkyloxy-, or 1-Aryloxyimidazolium Bromides 2a–n; General Procedure:

Method A: A solution of the appropriate 1-alkyloxyimidazole **1** (10 mmol) and arylmethyl bromide (12 mmol) in CH_3CN (35 mL) is stirred at r.t. for 24 h. The solvent is evaporated *in vacuo*, and the oily residue is treated repeatedly with Et_2O until it solidifies. After filtration the product is redissolved in CH_2Cl_2, precipitated with Et_2O and dried.

Method B: A solution of the appropriate 1-alkyloxy-, or 1-aryloxyimidazole **1** (10 mmol) and aroylmethyl bromide (10.5 mmol) in CH_2Cl_2 (50 mL) is stirred at r.t. for 12 h. The precipitation is completed by the addition of Et_2O (50 mL), and the product is purified as described above.

2-Alkyl-1,3-bis(arylmethyloxy)imidazolium Bromides 4a–g; General Procedure:
2-Alkyl-1-hydroxyimidazole 3-oxide **3b** or **3c** is dissolved at 0 °C in aq 40% TBAH (4 g) and a solution of the appropriate arylmethyl bromide (10 mmol) in $CHCl_3$ (10 mL) is added. The mixture is stirred vigorously at r.t. for 3 h, diluted with H_2O (20 mL) and shaken. The aqueous layer is discarded, and the mixture again extracted with H_2O (20 mL). To the organic layer Et_2O is added to precipitate the product. Alternatively, the organic layer is evaporated prior to the addition of MeOH (4–5 mL) and Et_2O (10–20 mL). The product is filtered by suction, washed with H_2O and Et_2O and dried over P_2O_5.

1-(2,2-Dimethylpropanoyloxy)-1*H*-imidazoles 6a–c; General Procedure:
The appropriate 1-hydroxy-1*H*-imidazole **5a–c** (30 mmol) and Et_3N (3.03 g, 30 mmol) are stirred in dry CH_2Cl_2 (50 mL) for 10 min. The mixture is cooled to 0 °C and a solution of 2,2-dimethylpropanoyl chloride (3.62 g, 30 mmol) in CH_2Cl_2 (20 mL) is added dropwise. Stirring is continued for 2 h at r.t. After removal of the solvent, the residue is partitioned between Et_2O (20 mL) and H_2O (20 mL), the organic layer separated and extracted twice with H_2O (20 mL), sat. aq $NaHCO_3$ (20 mL) and at last twice with H_2O (10 mL), and dried ($MgSO_4$). All extractions should be carried out quickly. The solvent is evaporated to give the crude product as an oil, which should be used immediately or stored in a dry atmosphere for a maximum of 10 h.

1-(4-Chlorobenzoylmethyl)-3-(2,2-dimethylpropanoyloxy)imidazolium Bromides 7a–c; General Procedure:
To a solution of the freshly prepared appropriate 1-(2,2-dimethylpropanoyloxy)imidazole **6a–c** (3 mmol) in dry CH_3CN (10 mL) 4-chlorobenzoylmethyl bromide (0.7 g, 3 mmol) is added. The mixture is stirred at r.t. for 3 h. Then, Et_2O (10 mL) is added, and the product is filtered, washed with dry CH_3CN (10 mL) and dried.

1-Arylmethyl-3-(2,2-dimethylpropanoyloxy)imidazolium Bromides 7d,e; General Procedure:
To a solution of freshly prepared 1-(2,2-dimethylpropanoyloxy)-1*H*-imidazole (**6a**; 0.5 g, 3 mmol) in dry CH_3CN (10 mL) is added the appropriate arylmethyl bromide (3 mmol), and the mixture is stirred at r.t. for 12 h. Then, the solvent is removed, and the remaining oil is crystallized by repeated treatment with warm Et_2O. The product is very hygroscopic and should be used immediately for the next step.

1-Substituted 3-Hydroxyimidazolium Bromides 8a–e; General Procedure:
The appropriate 1-substituted 3-(2,2-dimethylpropanoyloxy)imidazolium bromide **7a–e** (1 mmol) is dissolved in MeOH (10 mL), and the solution is refluxed for 3 h. The solvent is evaporated, and the residue treated with Et_2O to give the crystalline product which further can be purified by recrystallization from boiling CH_3CN, cooling to r.t. and addition of Et_2O.

1-Arylmethylimidazole 3-oxides 9d,e; General Procedure:
The hydrobromide **8d** or **8e** (1 mmol) is dissolved in H_2O (10 mL), $KHCO_3$ (100 mg, 1 mmol) is added, and the solution is extracted with CH_2Cl_2 (5 × 20 mL). The combined organic layers are dried ($MgSO_4$) and evaporated. The residue is redissolved in CH_3CN (2 mL), Et_2O (8 mL) is added, and the mixture cooled to 0 °C. The product is filtered and dried.

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