Quaternary Salts of 2*H*-Imidazoles

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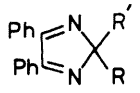
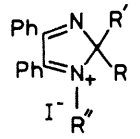
Treatment of the 4,5-diphenyl-2*H*-imidazoles (1a—e) with alkyl iodides gives novel 1*H*$^+$,2*H*-imidazolium salts (2) and (3). The metho-salt (2) *N*-methyl protons are readily exchanged for deuterium, and anions formed by the action of base give, with *m*-chlorobenzaldehyde, 2,3,5,7a-tetrahydroimidazo[5,1-*b*]-oxazoles (4), hydrolysable in acid to 2-(3-chlorophenyl)-2-hydroxyethylamine (6). Borohydride reduction of the metho-salt (2a) gave a dihydro-1*H*-imidazole (7) which with acid yielded 2-methylamino-1,2-diphenylethanone (8), and with methyl iodide a metho-salt (10). Direct (peracid) oxidation of 2*H*-imidazoles to *N,N'*-dioxides is reported for the first time.

2*H*-Imidazoles have been relatively infrequently mentioned in the literature.[1] Weiss [2] first synthesised 2,2,4,5-tetrasubstituted 2*H*-imidazoles from benzil, a ketone, and ammonium acetate and discovered their lability towards heat and acids. Further examples from benzil have been reported [3] and this synthesis has given 4,5-bis(ethoxycarbonyl) derivatives.[4] Other less convenient synthetic approaches have been also described.[5-7] 2*H*-Imidazole 1-oxides result from (*a*) reactions of α-dioximes with certain aldehydes or ketones and subsequent alkali [8,9] or acid [10] treatment, (*b*) photochemical dimerisation of a chloronitrosoalkane,[11] (*c*) acid-catalysed condensation of diphenylmethanimine with α-hydroxyimino ketones,[12] and (*d*) the action of bromine on 3-imidazoline † nitroxyl radicals.[13] Apparently only a single 2*H*-imidazole 1-oxide has been prepared by N-oxidation of the corresponding 2*H*-imidazole.[12] However, several 4*H*-imidazoles have been converted into *N,N'*-dioxides by lead dioxide.[14] Monoquaternisation of 4-amino-2*H*-imidazoles with methyl iodide at a ring nitrogen atom has been described.[15]

We now report the synthesis of a series of novel 2,2-disubstituted 4,5-diphenyl-2*H*-imidazoles, their quaternisation, and some additional reactions having potential synthetic applications.

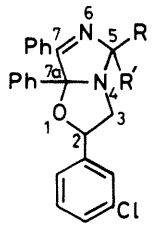


(1)

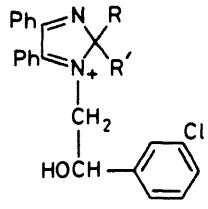


(2) R″ = Me
(3) R″ = Et

a; R = Me, R′ = Me
b; R = Me, R′ = Et
c; R = Me, R′ = $CH_2CH_2CO_2Et$
d; R = Me, R′ = Ph
e; R = Et, R′ = Et



(4)



(5)

a; R = Me, R′ = Me
b; R = Et, R′ = Et

Results and Discussion

Benzil, when treated with ketones and ammonium acetate afforded, by Weiss'[2] procedure, 2,2-disubstituted 4,5-diphenyl-2*H*-imidazoles (1a—e) (75—85%) (Table 1).

Quaternisations of the 2*H*-imidazoles with methyl iodide gave the corresponding 2,2-disubstituted 1-methyl-4,5-diphenyl-2*H*-imidazolium iodides (2a—e) (average 80%) (Table 2). However, quaternisation with ethyl iodide was more difficult and the corresponding 2,2-disubstituted 1-ethyl-4,5-diphenyl-2*H*-imidazolium iodides (3a and e) were obtained in only *ca.* 10% yield.

^{1}H N.m.r., i.r. (Table 3), and elemental analyses (Tables 1 and 2) were consistent with the proposed structures. Few reported n.m.r. spectra of these compounds are available.[1] We find absorptions at δ_H 1.7—1.9 (2-CH_3, Table 3) for the 2*H*-imidazoles (1a—e), at the same position as reported for (1a),[3] 2,2-dimethyl-4-phenyl-2*H*-imidazole,[16] 4-substituted 2,2-dimethyl-5-phenyl-2*H*-imidazoles,[17] and 4,5-diaryl-2,2-dimethyl-2*H*-imidazoles [18] (δ_H 1.6—1.9). Absorptions due to CH_2 attached to C-2 appear at δ_H 2.0—2.5 (Table 3), whilst that reported [3] for the corresponding CH_2 in (1e) is at δ_H 2.2.

No n.m.r. data on the quaternised 2*H*-imidazolium salts (2a—e), (3a), and (3e) were previously available. Signals for methyl groups attached to the positively charged nitrogen appear at δ_H 4.0—4.2, whilst those for CH_2 at the same position are in the range δ_H 4.5—4.6. Substituents attached to C-2 are shifted 0.5 p.p.m. downfield from their position in the corresponding 2*H*-imidazoles (1).

I.r. data of several aryl-2*H*-imidazoles have been reported; [16-19] a band near 1 610 cm^{-1} [(1a—e), Table 3] was assigned to the carbon–nitrogen double bonds. A band between 1 490—1 500 cm^{-1}, characteristic of these compounds,[19] was also found in the spectra of compounds (1a—e).

No literature i.r. data are available for the 2*H*-imidazolium salts (2a—e), (3a), and (3e) (Table 3). A characteristic band between 1 600 and 1 620 cm^{-1} corresponds to $\nu_{C=N}$ found for the parent 2*H*-imidazoles.

† 2,5-Dihydro-1*H*-imidazole.

Table 1. Preparation of 2,2-disubstituted 4,5-diphenyl-2*H*-imidazoles (1)

Compound	Crystal form [a]	M.p. (°C)	Yield (%)	Analysis (%) Found (Required) C	H	N	Formula
(1a)	Needles	78—80 [b]	75				
(1b)	Prisms	sublimes 92	85	82.5 (82.4	6.9 6.9	10.6 10.7)	$C_{18}H_{18}N_2$
(1c)	—	Oil	75	75.2 (75.5	6.6 6.6	8.2 8.4)	$C_{21}H_{22}N_2$
(1d)	Plates	80—82	80	85.0 (85.2	5.9 5.8	8.9 9.0)	$C_{23}H_{18}N_2$
(1e)	Needles	104—106 [c]	85				

[a] Crystallisation solvent was light petroleum (b.p. 37—52 °C). [b] Lit.,[1] 79—80 °C. [c] Lit.,[2] 105—106 °C.

Table 2. Preparation of 2,2-disubstituted 1-alkyl-4,5-diphenyl-2*H*-imidazolium iodides (2) and (3)

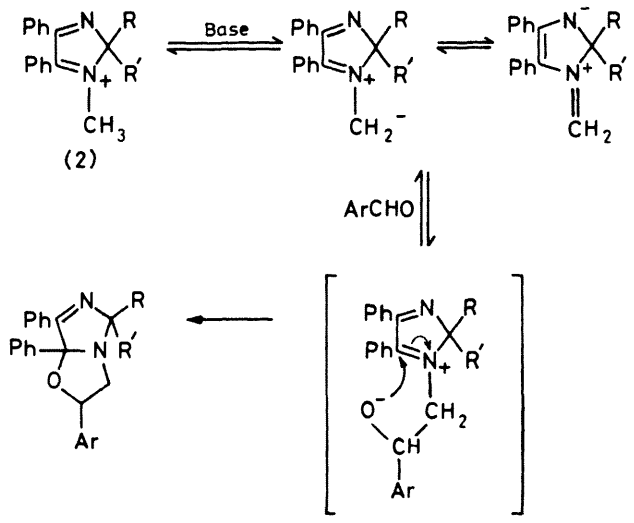
Compound	Crystal form [a]	M.p. (°C)	Yield (%)	Analysis (%) Found (Required) C	H	N	Formula
(2a)	Needles	191—192	65	55.1 (55.4	4.9 4.9	7.4 7.1)	$C_{18}H_{19}IN_2$
(2b)	Needles	169—171	70	56.4 (56.7	5.3 5.4	6.9 6.9)	$C_{19}H_{21}IN_2$
(2c)	Prisms	136—138	90	55.4 (55.5	5.3 5.2	5.9 5.8)	$C_{22}H_{25}IN_2O_2$
(2d)	Prisms	173—175	55	61.1 (61.1	4.7 4.6	6.1 6.2)	$C_{18}H_{19}IN_2$
(2e)	Plates	173—175	95	57.4 (57.4	5.5 5.5	6.6 6.7)	$C_{20}H_{23}IN_2$
(3a)	Prisms	180—181	10	56.5 (56.7	5.3 5.4	6.9 6.9)	$C_{19}H_{21}IN_2$
(3e)	Needles	188—190	10	58.3 (58.4	5.8 5.7	6.4 6.5)	$C_{21}H_{25}IN_2$

[a] Crystallisation solvent was absolute EtOH.

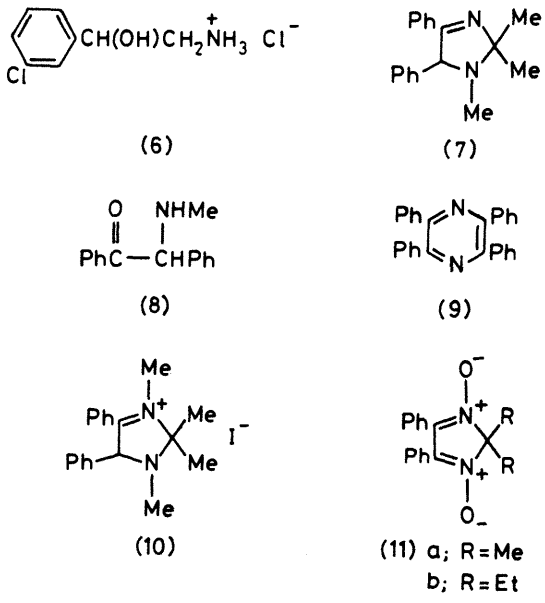
Table 3. Spectroscopic data for 2,2-disubstituted 4,5-diphenyl-2*H*-imidazoles (1) and 2,2-disubstituted 1-alkyl-4,5-diphenyl-2*H*-imidazolium iodides (2) and (3)

Compound	Chemical shift (δ_H) [a] Aromatic	R''	R	R'	$\nu_{max.}$ [b] (cm^{-1})
(1a)	7.2—8.1 [c]	—	1.7	1.7	1 600m, 1 550s, 1 490s, 1 440s, 1 355w, and 1 260s
(1b)	7.2—8.1 [c]	—	1.68	0.8,[d] 2.2 [e]	1 600m, 1 550s, 1 490s, 1 440s, 1 355w, and 1 260s
(1c)	7.2—8.1 [c]	—	1.7	1.2,[d] 2.0—2.7,[f] 4.1 [e]	1 740s, 1 600s, 1 550m, 1 490m, 1 450s, and 1 350s
(1d)	7.4—7.9 [g]	—	1.90	*h*	3 060m, 1 600s, 1 550s, 1 490s, and 1 250s
(1e)	7.3—8.2 [c]	—	0.75,[d] 2.25 [e]	0.75,[d] 2.25 [e]	1 600s, 1 550m, and 1 480m
(2a)	7.3—8.2 [c]	4.0	2.0	2.0	1 600s, 1 560s, 1 450s, and 1 390s
(2b)	7.3—8.2 [c]	4.1	2.2	0.8,[d] 2.5 [e]	2 820s, 1 620s, 1 600s, 1 490s, and 1 400s
(2c)	7.3—8.2 [c]	4.0	2.3	1.2,[d] 2.3—3.0,[f] 4.1 [e]	2 920s, 1 600m, 1 500m, and 1 290s
(2d)	7.2—8.1 [g]	4.0	1.9	*h*	2 920s, 1 600s, 1 300s, and 1 050w
(2e)	7.3—8.2 [c]	4.2	0.85,[d] 2.7 [e]	0.85,[d] 2.7 [e]	2 910s, 1 600m, 1 550s, and 1 440s
(3a)	7.3—8.0 [c]	1.3,[d] 4.55 [e]	2.2	2.2	2 920s, 1 600s, 1 550m, and 1 450m
(3e)	7.3—7.8 [c]	1.45,[d] 4.65 [e]	1.0,[d] 2.8 [e]	1.0,[d] 2.8 [e]	2 920s, 1 600m, 1 450m, and 1 290m

[a] 60 MHz; $CDCl_3$ as solvent; $SiMe_4$ as internal reference; singlets unless otherwise indicated. [b] Mull in $CHBr_3$. [c] 10 H, multiplet. [d] 3 H, triplet. [e] 2 H, quartet. [f] 4 H, multiplet. [g] 15 H, multiplet. [h] Included in aromatic region.



Scheme.



The 1-methyl protons in the quaternised salts (2) are active: they were exchanged almost completely for deuterium at 25 °C after 48 h in deuterium oxide and [$^2H_6$]acetone (concentration *ca.* 0.2M) in the presence of triethylamine or pyridine. These protons have an activity similar to that of the α-protons in pyridinium cations (50% exchange in 21 h at 20 °C; concentration 0.3M; piperidine as base),[20,21] whilst they exchange faster than the corresponding *N*-methyl protons in 1-methylpyridiniums (complete exchange in 8 d at room temperature; concentration 0.3M; piperidine as base).[20,21] 1,3-Dimethylimidazolium iodides exchange only at the ring positions.[22]

The salts (2) are acidic enough to undergo aldol reactions with aldehydes using triethylamine as a catalyst. Thus, 1,2,2-trimethyl-4,5-diphenyl-2*H*-imidazolium (2a) and 2,2-diethyl-1-methyl-4,5-diphenyl-2*H*-imidazolium (2e) iodide reacted with *m*-chlorobenzaldehyde to give the bicyclic compounds (4a) (70%) and (4b) (70%), respectively. We consider the irreversible final cyclization to be responsible for the success of this reaction (Scheme). The bicyclic compounds (4a) and (4b) were identified by their spectroscopic properties and elemental analysis. ^1H N.m.r. spectra showed in both cases a characteristic ABX system for the 2-H (δ 4.45) and 3-H_2 (δ 3.65 and 2.95) protons.

The ^{13}C n.m.r. spectrum of compound (4b) confirmed the proposed structure, the characteristic absorptions being δ_C 110.4 (C-7a), 95.3 (C-5), 79.8 (C-2), and 54.6 p.p.m. (C-3). The imino carbon signal appeared at δ_C 165.6 p.p.m. The signals were assigned by chemical shift considerations and off-resonance decoupled spectra.

Treatment of compound (4a) with perchloric or fluoroboric acid did not cause ring-opening to the monocyclic structure (5a). However, hydrolysis with hydrochloric acid afforded the hydroxy amine hydrochloride (6) (20%). The ^1H n.m.r. spectrum of this compound showed a characteristic AA'X system (for protons at C-1 and C-2), and it was fully characterized by ^{13}C n.m.r. and elemental analysis (see Experimental section).

This reaction between an aromatic aldehyde and 1,3,3-trimethyl-4,5-diphenyl-2*H*-imidazolium iodide (2a) with subsequent hydrolysis of the bicyclic product (4a) offers an alternative method to the reaction with nitromethane, followed by reduction, for the preparation of compounds of type (6) in cases where a reduction step is undesirable.

Treatment of 1,2,2-trimethyl-4,5-diphenyl-2*H*-imidazolium iodide (2a) with sodium borohydride afforded 1,2,2-trimethyl-4,5-diphenyl-2,5-dihydro-1*H*-imidazole (7). No further reduction occurred even with excess of borohydride. Some similar cases are found in the literature for related 4*H*-imidazoles,[23] and for 2*H*-imidazole 1,3-dioxides.[10] With lithium aluminium hydride, 2*H*-imidazole 1-oxides form 1,2-dihydro compounds only at low temperature.[12]

Hydrolysis (heat; 2M-HCl; 1 h) of the 2,5-dihydro-1*H*-imidazole (7) afforded the α-amino ketone (8). Thus, successive formation of the 2*H*-imidazole, quaternisation, reduction, and finally hydrolysis is a potentially useful way to convert α-diketones into α-(*N*-alkylamino) ketones. Asinger [6] described a similar hydrolysis for the corresponding 5-methyl-4-ethyl compound. Hydrolyses of 2,5-dihydro-1*H*-imidazoles unsubstituted on nitrogen have been reported for the 5-ethyl-4-methyl [6] and 4,5-diphenyl [24] compounds.

Hydrolysis under milder conditions (25 °C) but for a longer time (one week) gave a product of high melting point (248—250 °C), with no aliphatic protons in the ^1H n.m.r. spectrum, and which was characterized by elemental analysis and its mass spectrum as 2,3,5,6-tetraphenylpyrazine (9) (lit.,[25] m.p. 249—250 °C).

Following our study of the chemical properties of the imidazoline (7), it was quaternised with methyl iodide giving compound (10) in 60% yield.

Only one oxidation of a 2*H*-imidazole to its *N*-oxide has been reported.[12] We find that oxidation of compounds (1a) and (1e) with hydrogen peroxide in acetic acid gives the corresponding *N*,*N*'-dioxides (11a) and (11b). Elemental analysis, i.r., n.m.r., and mass spectra were consistent with the assigned structures. The mass spectra did not show the molecular ion, but the $(M - 1)^+$ peak was present. No intense $(M - 16)^+$ or $(M - 17)^+$ peaks, frequently observed with heterocyclic *N*-oxides,[26-28] were apparent, in accord with the findings in the 3,4-dihydro-2*H*-pyrrole [29] and 2,2-diphenyl-2*H*-imidazole [12] *N*-monoxides series; the latter compounds were, however, all reported to show a molecular ion.

Experimental

M.p.s were obtained in a Bristolscope hot-stage apparatus and are uncorrected. I.r. spectra were run as $CHBr_3$ mulls on a Perkin-Elmer 283B spectrophotometer, using NaCl plates. ^1H N.m.r. spectra were recorded on Varian A-60A and Varian EM 360L (60 MHz) instruments, and ^{13}C n.m.r.

spectra on a JEOL FX 100 instrument; $SiMe_4$ was used as internal reference.

2,2-*Disubstituted* 4,5-*Diphenyl*-2H-*imidazoles* (1).—*General procedure* (*Tables* 1 *and* 3). Benzil (10.5 g, 0.05 mol), ammonium acetate (40 g), and the appropriate ketone (0.05 mol) in glacial AcOH (100 ml) were boiled under reflux for 2 h. The solution was cooled, poured into ice–water (150 ml), and extracted with diethyl ether (3 × 50 ml). The combined extracts were washed with water until the washings were neutral, and were then dried ($MgSO_4$) and evaporated (30 °C; 30 mmHg). The product was recrystallised from light petroleum (b.p. 37—52 °C).

2,2-*Disubstituted* 1-*Methyl- and* 1-*Ethyl*-4,5-*diphenyl*-2H-*imidazolium Iodides* (2) and (3).—*General procedure* (*Tables* 2 *and* 3). Methyl (or ethyl) iodide (0.0080 mol) was added to the 2,2-disubstituted 4,5-diphenyl-2*H*-imidazole (0.0080 mol) in $MeNO_2$ (15 ml) and the solution was stirred under reflux until t.l.c. (silica gel; EtOAc) showed no starting material (5—6 h). The solution was cooled, the iodide salts were precipitated with diethyl ether (50 ml), dried under reduced pressure 40 °C; 0.5 (mmHg; 6 h) and recrystallised (absolute EtOH).

Deuterium–Proton Exchange of the N-*Methyl Protons of Compound* (2a).—A solution of the salt (2a) (0.150 g) in [$^2H_6$]acetone (2 ml) was stirred with a 10% solution of either Et_3N or pyridine (as base) in D_2O (0.1 ml). After 48 h exchange was shown to be complete by the disappearance of the N^+–Me protons (δ 4.0) in the ^1H n.m.r. spectrum.

Cyclization of the 2,2-*Dialkyl*-1-*methyl*-4,5-*diphenyl*-2H-*imidazolium Iodides* (2a and e) *with* m-*Chlorobenzaldehyde*.—*With* (2e). Triethylamine (2.3 g, 0.0227 mol) and *m*-chlorobenzaldehyde (1.60 g, 0.0128 mol) were added to a solution of the salt (2e) (3.00 g, 0.0072 mol) in CH_2Cl_2 (30 ml) and the reaction mixture was heated under reflux for 9 h, after which no starting material was detected (silica gel; EtOAc). The deposited triethylammonium iodide was separated, the remaining liquid was washed with water (3 × 20 ml), and the organic layer was dried ($MgSO_4$) and evaporated (40 °C; 30 mmHg) to give 2-(3-*chlorophenyl*)-5,5-*diethyl*-7,7a-*diphenyl*-2,3,5,7a-*tetrahydroimidazo*[5,1-b]*oxazole* (4b) (70%) as prisms from acetone, m.p. 124—126 °C (Found: C, 75.0; H, 6.3; N, 6.5. $C_{27}H_{27}ClN_2O$ requires C, 75.25; H, 6.3; N, 6.5%); δ_H (CCl_4) 0.9 (3 H, t), 1.3 (3 H, t), 2.0 (4 H, m), 2.9 (1 H, dd), 3.7 (1 H, dd), 4.6 (1 H, dd), and 7.0—7.9 (14 H); δ_C ($CDCl_3$) 8.6 (CH_3), 9.9 (CH_3), 27.1 (CH_2), 32.1 (CH_2), 54.6 (C-3), 79.8 (C-2), 95.3 (C-5), 110.4 (C-7a), 123.0—142.5 (aromatic), and 165.6 p.p.m. (C-7); $\nu_{max.}$ 2 975m, 2 960m, 2 930m, 1 615m, 1 600m, 1 570m, 1 490m, and 1 355m cm^{-1}.

With (2a). Following the procedure for (2e), the salt (2a) (2.0 g, 0.0051 mol) was treated with *m*-chlorobenzaldehyde (0.79 g, 0.0063 mol) and triethylamine (2.3 g, 0.0227 mol) to give 2-(3-*chlorophenyl*)-5,5-*dimethyl*-7,7a-*diphenyl*-2,3,5,7a-*tetrahydroimidazo*[5,1-b]*oxazole* (4a) (70%) as prisms from acetone, m.p. 146—148 °C (Found: C, 74.4; H, 5.8; N, 6.9. $C_{25}H_{23}ClN_2O$ requires C, 74.5; H, 5.8; N, 7.0%); δ_H (CCl_4) 1.6 (3 H, s), 1.7 (3 H, s), 2.9 (1 H, dd), 3.6 (1 H, dd), 4.7 (1 H, dd), and 7.2—8.0 (14 H, m); $\nu_{max.}$ 2 975m, 2 960m, 2 930m, 1 615m, 1 600m, 1 570m, 1 490m, and 1 355m cm^{-1}.

Acid Hydrolysis of 2-(3-*Chlorophenyl*)-5,5-*dimethyl*-7,7a-*diphenyl*-2,3,5,7a-*tetrahydroimidazo*[5,1-b]*oxazole* (4a).—To a solution of compound (4a) (1 g, 0.0025 mol) in CH_2Cl_2 (10 ml) was added concentrated HCl (4 ml) and the mixture was kept for 24 h. The precipitated solid was filtered off and characterized as the *hydroxy amine hydrochloride* (6) (20%), which was crystallized as prisms from chloroform, m.p. 141 °C (analysed as the dihydrate: Found: C, 39.2; H, 5.7; N, 5.3. $C_8H_{11}Cl_2NO{\cdot}1H_2O$ requires C, 39.4; H, 6.1; N, 5.7%); δ_H (D_2O) 3.1 (2 H, m), 4.9 (1 H, dd), and 7.3 (4 H, m); δ_C (dioxane) 46.05 (CH), 69.78 (CH_2), and 125.20, 126.76, 129.44, and 131.34 p.p.m. (aromatic); $\nu_{max.}$ 3 400—2 500br and 1 160—1 010br cm^{-1}.

Reduction of 1,2,2-*Trimethyl*-4,5-*diphenyl*-2H-*imidazolium Iodide* (2a).—$NaBH_4$ (0.37 g, 0.010 mol) was added (0.5 h) to a solution of the imidazolium iodide (2a) (2.0 g, 0.0051 mol) in methanol (10 ml). After 2 h the solvent was evaporated off (40 °C; 30 mmHg), the residue was washed with water (2 × 20 ml), filtered off, dried *in vacuo* (25 °C; 0.5 mmHg; 4 h), and characterized as 1,2,2-*trimethyl*-4,5-*diphenyl*-2,5-*dihydro*-1H-*imidazole* (7) (85%) as prisms from acetonitrile, m.p. 85—87 °C (Found: C, 81.5; H, 7.6; N, 10.5. $C_{18}H_{20}N_2$ requires C, 81.8; H, 7.6, N, 10.6%); δ_H ($CDCl_3$) 1.6 (3 H, s), 1.8 (3 H, s), 2.6 (3 H, s), 4.9 (1 H, s), and 7.2—7.5 (10 H, m); $\nu_{max.}$ 3 030s, 2 980s, 2 240m, 1 620s, 1 500s, 1 450s, and 1 250s cm^{-1}.

Acid Hydrolysis of 1,2,2-*Trimethyl*-4,5-*diphenyl*-2,5-*dihydro*-1H-*imidazole* (7).—(*a*) A solution of compound (7) (1 g, 0.0038 mol) in 2M-HCl (10 ml) was heated (steam-bath) for 1 h. After the solution had been cooled, CH_2Cl_2 (20 ml) was added and the organic layer was separated, dried ($MgSO_4$), and filtered. The solvent was evaporated off (40 °C; 30 mmHg) and the solid residue, obtained as prisms, m.p. 226 °C (from absolute ethanol), was characterized as the hydrochloride of the α-amino ketone (8) (90%) (Found: C, 68.8; H, 6.1; N, 5.2. Calc. for $C_{15}H_{16}ClNO$: C, 68.8; H, 6.1; N, 5.2%); δ_H ($CDCl_3$) 2.4 (3 H, s), 5.3 (1 H, s), and 7.2—8.2 (10 H, m); $\nu_{max.}$ 1 670s, 1 600s, 1 540s, and 1 400br cm^{-1}.

(*b*) A solution of compound (7) (1 g, 0.0038 mol) in EtOH (10 ml), H_2O (1.5 ml), and concentrated HCl (2 ml) was kept at 25 °C for 8 d. A solid was formed which, after filtration and recrystallization from chloroform (prisms, m.p. 248—250 °C) (lit.,[25] 249—250 °C), was characterized as 2,3,5,6-tetraphenylpyrazine (9) (8%) (Found: C, 87.2; H, 5.6; N, 7.2. Calc. for $C_{28}H_{20}N_2$: C, 87.5; H, 5.2; N, 7.3%); δ_H ($CDCl_3$) aromatics only; $\nu_{max.}$ 3 200s, 1 700s, 1 400s, and 1 300s cm^{-1}.

Quaternisation of 1,2,2-*Trimethyl*-4,5-*diphenyl*-2,5-*dihydro*-1H-*imidazole* (7).—The dihydro-1*H*-imidazole (7) (1 g, 0.0038 mol) was stirred with MeI (10 ml). A precipitate was immediately formed. After the mixture has been stirred for 10 h no starting material was detected by t.l.c. (silica gel; EtOAc). Evaporation of the solvent (30 °C; 30 mmHg) and recrystallization of the residue (absolute EtOH) gave 1,2,2,3-*tetramethyl*-4,5-*diphenyl*-3,4-*dihydro*-2H-*imidazolium iodide* (10) (60%) as prisms, m.p. 188—190 °C (Found: C, 56.2; H, 5.7; N, 6.9. $C_{19}H_{23}IN_2$ requires C, 56.2; H, 5.7; N, 6.9%); δ_H ($CDCl_3$) 1.8 (3 H, s), 2.2 (3 H, s), 2.9 (3 H, s), 3.7 (3 H, s), and 7.1—7.9 (10 H, m); $\nu_{max.}$ 2 920s, 1 630s, 1 570m, 1 470s, 1 450s, 1 380m, and 1 140br cm^{-1}.

2,2-*Dimethyl*-4,5-*diphenyl*-2H-*imidazole* 1,3-*Dioxide* (11a).—A solution of the 2*H*-imidazole (1a) (2.0 g, 0.0081 mol) in AcOH–30% H_2O_2 (20 ml; 5 : 1) was stirred at 25 °C for 2 h; water (100 ml) was then added and the N,N′-*dioxide* (11a) separated out (88%) and was recrystallized as prisms from acetone, m.p. 74—74.5 °C (Found: C, 73.0; H, 5.8; N, 9.9. $C_{17}H_{16}N_2O_2$ requires C, 72.8; H, 5.8; N, 10.0%); δ_H ($CDCl_3$) 1.6 (6 H, s) and 7.3—7.7 (10 H, m); $\nu_{max.}$ 1 445s, 1 340s, 1 290s, 750s, and 655s cm^{-1}.

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