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SYNTHESIS OF SUBSTITUTED 1*H*-4,5-DIHYDROIMIDAZOLIUM SALTS BY DEHYDROGENATION OF IMIDAZOLIDINES

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ABSTRACT: A study is presented on the scope of the method to obtain 1*H*-4,5-dihydroimidazolium salts **3** by dehydrogenation of 1,3-di and 1,2,3-trisubstituted imidazolidines **2**. Of the dehydrogenating agents used, N-bromoacetamide leads to the best results, providing a simple and general method to prepare salts **3**.

A search of the literature shows that N-alkyl substituted 1*H*-4,5-dihydroimidazolium salts **3** have been traditionally synthesized by direct alkylation of 1*H*-4,5-dihydroimidazoles due to the ease of quaternization of these compounds.[1] However, the method is limited by the availability of precursor dihydroimidazoles and the nature of the alkylating agent as conditioned by the mechanism of the reaction, typically SN_2. Alternatively, cyclocondensation of N,N'-dialkylethylenediamines with acids and derivatives has not been exhausted.[2,3]

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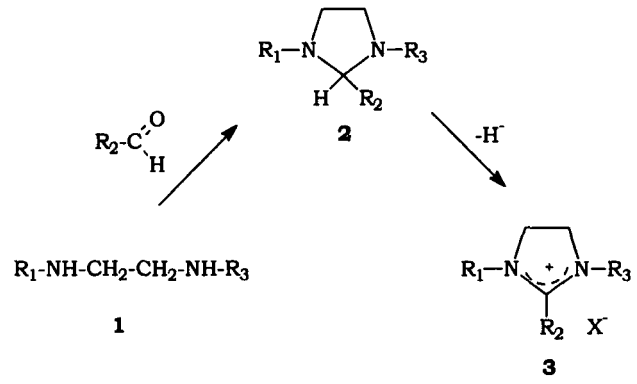
In turn, treatment of electron-rich alkenes (bisimidazolidinylidene derivatives) in acid medium[4] and cyclization of N-acyl derivatives of ethylenediamines[5,6] as a method to synthesize salts **3** has an even more restricted application and has been limited to the preparation of 1,3-diaryl-1*H*-4,5-dihydroimidazolium salts unsubstituted in C_2.

Although dehydrogenation of imidazolidines **2** may afford an attractive general method, it has only been used to obtain salts **3** with aryl groups on both nitrogen atoms.[5,7] The easy preparation of compounds **2** starting from suitably substituted ethylenediamines **1** and aldehydes[8] contributes an advantage for their use as synthetic precursors in this method. In turn, the development of new synthetic strategies to obtain selectively N,N'-disubstituted ethylenediamines allows the procedure to be enlarged.[9,8d]

In order to examine the capacity of imidazolidines **2** as precursors of 1*H*-4,5-dihydroimidazolium salts **3** and determine the scope of application for the method, we studied the reaction of compounds **2a-k** (Scheme) with the following available dehydrogenating agents: *N-bromosuccinimide* (NBS), *N-bromoacetamide* (NBA), *N-iodosuccinimide* (NIS), *2,3-dichloro-5,6-dicyano-1,4-benzoquinone* (DDQ), *tetrachloro-p-benzoquinone* (chloranil), *carbon tetrachloride*, *mercuric acetate/ ethylenediaminetetraacetic acid* (Hg(II)/EDTA) and *pyridinium chlorochromate* (PCC).

NBS, NBA, NIS and DDQ proved general dehydrogenating agents for imidazolidines with any substitution pattern, all leading to salts **3a-k**, although reaction times with the first three agents depended on the presence or absence of

Scheme



Compounds 1,2,3	R_1	R_2	R_3
a	C_6H_5	C_6H_5	CH_3
b	*p*-$CH_3C_6H_4$	C_6H_5	CH_3
c	*p*-$CH_3OC_6H_4$	C_6H_5	CH_3
d	*p*-ClC_6H_4	H	$CH_2C_6H_5$
e	*p*-ClC_6H_4	H	*p*-ClC_6H_4
f	*p*-$CH_3C_6H_4$	H	*p*-$CH_3C_6H_4$
g	*p*-$C_2H_5OC_6H_4$	H	*p*-$C_2H_5OC_6H_4$
h	C_6H_5	CH_3	C_6H_5
i	C_6H_5	C_6H_5	C_6H_5
j	CH_3	C_6H_5	CH_3
k	*p*-$CH_3OC_6H_4CH_2$	H	*p*-$CH_3OC_6H_4CH_2$

C_2 substituents. NBA afforded the best results, with higher yields and purer reaction products.

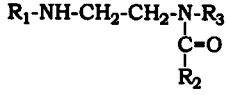
Chloranil and carbon tetrachloride[10] proved to be selective agents for the dehydrogenation of imidazolidines unsubstituted in C_2 **2d-g,k**.

Reaction yields with the quinones ranges from 60% to 80% and the method is certainly the fastest of all those employed. However, due to the presence of the highly unstable counterion (*p*-hydroxyphenoxide), an anion change (to perchlorate) was required, resulting in low yields (30%).

Although in theory the dehydrogenation process could be expected to culminate with the obtention of the corresponding aromatic imidazolium salts, with the dehydrogenating agents mentioned above there was no evidence in any case of the presence of such compounds nor of their hydrolysis products.

Structural assignments of compounds **3** were based on microanalyses (Table 1), and spectroscopic properties (Table 2).

Although treatment of imidazolidines **2** with the Hg(II)/EDTA complex and PCC leads in all cases to the corresponding salts, the use of such agents is not suitable. Reactions afford a quantity of side products (probably related to over-dehydrogenation processes), separation of the obtained products from the crude mixture is troublesome and acetates prepared with Hg(II)/EDTA are very unstable. In such cases, products were isolated as the corresponding hydrolysis products **4**[11] obtained by passage through an alumina column.



4

On the basis of the results achieved, it may be concluded that, for a given dehydrogenating agent, differences observed as regards selectivity and reaction times, among others, is mainly due to the presence of C_2 substituents in the imidazolidine, but practically unrelated to the nature of the substituents on the nitrogen atoms.

By resorting to N-haloamides or imides, the presented method affords the advantages of being both simple and general for the synthesis of 1*H*-4,5-dihydroimidazolium salts with diverse substitution patterns, with the additional benefit that raw materials are readily available, reaction techniques easy and yields particularly good with NBA.

Experimental

Melting points were determined with a Büchi capillary apparatus and are uncorrected. NMR spectra were recorded on a Bruker MSL 300 MHz spectrometer using deuteriochloroform as the solvent. Chemical shifts are reported in ppm (δ) relative to TMS as an internal standard. D_2O was employed to confirm exchangeable protons (ex). Splitting multiplicities are reported as singlet (s), broad signal (bs), doublet (d), triplet (t), quartet (q) and multiplet (m). Mass spectra (EI) were recorded with a GC-MS Shimadzu QP-1000 spectrometer operating at 20 eV. TLC analyses were carried out on aluminium sheets silica gel 60 F_{254} using chloroform-methanol (9:1) as the solvent.

N,N′-Disubstituted Ethylenediamines 1.

N-Aryl-N′-methylethylenediamines **1a**[12], **1b** and **1c**[12] were prepared from N-(2-bromoethyl)methylamine and the corresponding arylamine following literature

Table 1

Physical Data and Elemental Analyses of 1*H*-4,5-Dihydroimidazolium Salts 3.

Comp.	$X^- = Cl^-$		$X^- = Br^-$		$X^- = ClO_4^-$		$X^- = I^-$	
	MP (°C) Recryst. solvent	Formula Analyses Calc./Found %C %H %N	MP (°C) Recryst. solvent	Formula Analyses Calc./Found %C %H %N	MP (°C) Recryst. solvent	Formula Analyses Calc./Found %C %H %N	MP (°C) Recryst. solvent	Formula Analyses Calc./Found %C %H %N
3a	-	-	250 anh. methanol	$C_{16}H_{17}N_2Br$ 60.58 5.40 8.83 60.47 5.30 8.94	250 anh. ethanol	$C_{16}H_{17}N_2ClO_4$ 57.06 5.09 8.32 57.18 5.20 8.20	208[a] anh. ethanol	-
3b	-	-	238 anh. methanol	$C_{17}H_{19}N_2Br$ 61.64 5.78 8.46 61.72 5.68 8.27	240 anh. ethanol	$C_{17}H_{19}N_2ClO_4$ 58.21 5.46 7.99 58.01 5.58 7.76	148[b] 2-propanol	-
3c	-	-	248 anh. methanol	$C_{17}H_{19}N_2BrO$ 58.80 5.51 8.07 58.69 5.60 8.17	232 anh. ethanol	$C_{17}H_{19}N_2O_5Cl$ 55.67 5.22 7.64 55.51 5.30 7.55	187[c] 2-propanol	-
3d	198 anh. ethanol	$C_{16}H_{16}N_2Cl_2$ 62.55 5.25 9.12 62.40 5.34 9.16	210 anh. ethanol	$C_{16}H_{16}N_2BrCl$ 54.65 4.59 7.97 54.75 4.50 7.68	-	-	167 anh. methanol	$C_{16}H_{16}N_2ClI$ 48.20 4.05 7.03 48.35 4.13 6.95

3e	262 water	$C_{15}H_{13}N_2Cl_3$ 54.99 4.00 8.55 54.75 4.11 8.78	255 anh. methanol	$C_{15}H_{13}N_2Cl_2Br$ 48.42 3.52 7.53 48.60 3.49 7.41	268 anh. ethanol	$C_{15}H_{13}N_2Cl_3O_4$ 46.00 3.35 7.15 46.15 3.42 7.02	215 anh. methanol	$C_{15}H_{13}N_2Cl_2I$ 42.99 3.13 6.68 42.72 3.05 6.55
3f	275 water	$C_{17}H_{19}N_2Cl$ 71.19 6.68 9.77 71.25 6.63 9.68	265 anh. methanol	$C_{17}H_{19}N_2Br$ 61.64 5.78 8.46 61.51 5.82 8.29	271 anh. ethanol	$C_{17}H_{19}N_2ClO_4$ 58.21 5.46 7.99 58.12 5.52 7.82	198 anh. methanol	$C_{17}H_{19}N_2I$ 53.98 5.06 7.41 53.75 5.12 7.29
3g	290 water	$C_{19}H_{23}N_2ClO_2$ 65.79 6.68 8.08 65.89 6.59 8.15	280 anh. methanol	$C_{19}H_{23}N_2BrO_2$ 58.32 5.92 7.16 58.41 5.82 8.25	285 anh. ethanol	$C_{19}H_{23}N_2ClO_6$ 53.54 5.64 6.82 53.38 5.70 6.73	204 anh. methanol	$C_{19}H_{23}N_2IO_2$ 52.07 5.29 6.39 52.20 5.38 6.42
3h	-	-	222 anh. methanol	$C_{16}H_{17}N_2Br$ 60.58 5.40 8.83 60.41 5.45 8.75	233[d] anh. ethanol	-	220 anh. methanol	$C_{16}H_{17}N_2I$ 52.76 4.70 7.69 52.61 4.78 7.78
3i	-	-	228 anh. methanol	$C_{21}H_{19}N_2Br$ 66.50 5.05 7.39 66.29 5.11 7.28	243[e] anh. ethanol	-	197 anh. methanol	$C_{21}H_{19}N_2I$ 59.17 4.49 6.57 59.28 4.41 6.68
3j	-	-	-	-	-	-	190[f] anh. methanol	-
3k	oil	$C_{19}H_{23}N_2ClO_2$ 65.79 6.68 8.08 65.66 6.53 8.17	-	-	-	-	-	-

a- Lit. mp 208 °C (ref. 20). b- Lit. mp 148 °C (ref. 16). c- Lit. mp 187 °C (ref. 1a). f- Lit. mp 190°C (ref. 21). d- Lit. mp 233 °C (ref. 7a). e- Lit. mp 243 °C (ref. 7a)

Table 2

Comp.	X^-	^{1}H-NMR δ (ppm)
3a	Br^-	3.10 (s, 3H), 4.25 (t, 2H), 4.40 (t, 2H), 7.15-7.60 (m, 10H).
	ClO_4^-, I^-	3.01 (s, 3H), 4.43 (m, 2H), 4.50 (m, 2H), 7.10-7.20 (m, 3H), 7.20-7.40 (m, 4H), 7.50 (t, 1H), 7.65 (d, 2H).
3b	Br^-	2.20 (s, 3H), 3.10 (s, 3H), 4.25 (t, 2H), 4.45 (t, 2H), 7.00 (d, 2H), 7.15 (d, 2H), 7.50-7.70 (m, 5H).
	ClO_4^-, I^-	2.20 (s, 3H), 3.15 (s, 3H), 4.47 (m, 2H), 4.60 (m, 2H), 6.90 (d, 2H), 7.35 (d, 2H), 7.37-7.42 (m, 2H), 7.45 (t, H), 7.65 (d, 2H).
3c	Br^-	3.00 (s, 3H), 3.65 (s, 3H), 4.25 (t, 2H), 4.45 (t, 2H), 6.70 (d, 2H), 7.15 (d, 2H), 730-7.60 (m, 5H).
	ClO_4^-, I^-	3.00 (s, 3H), 3.50 (s, 3H), 4.40 (m, 2H), 4.50 (m, 2H), 6.80 (d, 2H), 7.90 (d, 2H), 7.24-7.35 (m, 2H), 7.45 (t, 1H), 7.60 (d, 2H).
3d	Br^-,Cl^-, ClO_4^-, I^-	4.10 (bs, 2H), 4.40 (bs, 2H), 5.10 (s, 2H), 7.20-7.60 (m, 9H), 11.40 (s, 1H).
3e	Br^-,Cl^-, ClO_4^-, I^-	4.51 (s, 4H), 7.20 (d, 4H), 7.40 (d, 4H), 9.90 (s, 1H).
3f	Br^-,Cl^-, ClO_4^-, I^-	2.20 (s, 6H), 4.45 (s, 4H), 7.30 (d, 4H), 7.60 (d, 4H), 10.10 (s, 1H).
3g	Br^-,Cl^-, ClO_4^-, I^-	1.25 (t, 6H), 4.00 (c, 4H), 4.45 (s, 4H), 6.90 (d, 4H), 7.40 (d, 4H), 9.85 (s, 1H).
3h	Br^-,Cl^-, ClO_4^-, I^-	2.30 (s, 3H), 4.50 (s, 4H), 7.50-7.70 (m, 10H).
3i	Br^-,Cl^-, ClO_4^-, I^-	4.55 (s, 4H), 7.30-7.70 (m, 15H).
3j	I^-	3.00 (s, 6H), 4.20 (s, 4H), 7.20-7.4 (m, 5H).
3k	Cl^-,Br^-	3.65 (s, 4H), 3.80 (s, 6H), 4.74 (s, 4H), 6.80 (d, 4H), 7.30 (d, 4H), 10.2 (s, 1H).

procedure[13]. The physical data and elemental analyses of the new compound are as follows:

N-Methyl-N'-(p-methylphenyl)ethylenediamine (**1b**).

The product was isolate as an oil, bp 132-135° (5 mm).

MS: m/z 164 (M^+).

^{1}H-NMR: δ 7.10 (d, 2H, *p*-$CH_3C_6H_4$, 2 *meta* H), 6.60 (d, 2H, *p*-$CH_3C_6H_4$, 2 *ortho* H), 3.50 (t, 2H, CH_2NHAr), 3.30 (s, ex, 1H, *H*NAr), 2.75 (t, 2H, CH_2NHCH_3), 2.45 (s, ex, 1H, *H*NCH_3), 2.35 (s, 3H, NCH_3) and 2.15 (s, 3H, $CH_3C_6H_4$).

Anal. calcd. for $C_{10}H_{16}N_2$: C 73.13, H 9.82, N 17.06; found: C 73.25, H 9.72, N 17.19.

N-Benzyl-N'-(*p*-chlorophenyl)ethylenediamine[9a] (**1d**), N,N'-diphenylethylenediamine[5] (**1h**), N,N'-di(*p*-chlorophenyl)ethylenediamine[14] (**1e**), N,N'-di(*p*-methylphenyl)ethylenediamine[5] (**1f**), N,N'-di(*p*-ethoxyphenyl)-ethylenediamine[5] (**1g**) and N,N'-di(*p*-methoxybenzyl)ethylenediamine[15] (**1k**) were prepared following literature procedures.

Imidazolidines 2.

Compounds **2** were obtained by reaction of the corresponding N,N'-disubstituted ethylenediamines **1** and aldehydes in ethanol.[8d] Yields: **2a**[16] (87%), **2b**[16] (88%), **2c**[16] (91%), **2e**[14] (89%), **2f**[5] (85%), **2g**[5] (88%), **2h**[17] (89%), **2i**[18] (86%), **2j**[19] (89%), **2k** [15] (80%).

1-Benzyl-3-(p-chlorophenyl)imidazolidine (**2d**) (91%); mp 87°C.

MS: m/z 272 ($M^{+\cdot}$).

^{1}H-RMN: δ 7.50-7.20 (m, 5H, C_6H_5), 7.15 (d, 2H, *p*-ClC_6H_4, 2H *meta*), 6.45 (d, 2H, *p*-ClC_6H_4, 2H *ortho*), 4.00 (s, 2H, NCH_2N), 3.70 (s, 2H, $CH_2C_6H_5$), 3.40 (t, 2H, CH_2-NAr) and 3.00 (t, 2H, CH_2-$NCH_2C_6H_5$).

Anal. calcd. for $C_{16}H_{17}N_2Cl$: C 70.45, H 6.28, N 10.27; found: C 70.53 , H 6.16, N 10.35.

Synthesis of 1*H*-4,5-Dihydroimidazolium Salts.

Melting points and elemental analyses are given in Table 1. The ^{1}H-RMN data are given in Table 2.

Reaction of Imidazolidines 2 with Carbon Tetrachloride. General Procedure.

A solution of imidazolidine (0.5 mmole) in carbon tetrachloride (100 ml) was refluxed for 4 hours. The resulting solids were filtered and recrystallized from methanol-water. Yields (X^-=Cl^-): **3d** (64%), **3e** (58%), **3f** (61%), **3g** (67%), **3k** (68%).

Reaction of Imidazolidines 2 with 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) and Chloranil. General Procedure.

To a stirred solution of imidazolidines **2** (1 mmole) in benzene (75 ml), DDQ or chloranil (1 mmole) was added in two portions at 10 minutes intervals. Stirring was continued at room temperature for 30 minutes. The products were removed by filtration and washed with benzene and chloroform.

Yields employing DDQ (X^-=$HOC_6Cl_2(CN)_2O^-$): **3a** (69%), **3b** (73%), **3c** (75%), **3d** (75%), **3e** (74%), **3f** (73%), **3g** (66%), **3h** (77%), **3i** (68%).

Yields employing chloranil (X= $HOC_6Cl_4O^-$): **3d** (70%), **3e** (75%), **3f** (70%), **3g** (69%).

Perchlorates were prepared from these salts and perchloric acid in methanol and recrystallized from water.

Yields (X^-=ClO_4^-): 22-31%.

Reaction of Imidazolidines 2 with N-Bromosuccinimide, N-Bromoacetamide and N-Iodosuccinimide. General Procedure.

To a stirred solution of compounds **2** (10 mmole) in 1,2-dimethoxyethane (30 ml), the corresponding dehydrogenating agent (10 mmole) was added in two portions at 10 minutes intervals. Stirring was continued at room temperature for 30 minutes. Salts precipitate in variable times (30 minutes-12 hours). The products

were collected, washed with 1,2-dimethoxyethane and recrystallized from anhydrous methanol.

Yields employing NBS (X^-=Br^-): **3a** (69%), **3b** (74%), **3c** (73%), **3d** (69%), **3e** (75%), **3f** (68%), **3g** (75%), **3h** (69%), **3i** (75%).

Yields employing NBA (X^-=Br^-): **3a** (88%), **3b** (84%), **3c** (88%), **3d** (83%), **3e** (85%), **3f** (89%), **3g** (83%), **3h** (87%), **3i** (88%), **3k** (81%).

Yields employing NIS (X^-=I^-): **3a** (57%), **3b** (54%), **3c** (59%), **3d** (57%), **3e** (63%), **3f** (62%), **3g** (64%), **3h** (59%), **3i** (61%); **3j** (64%).

Reaction of Imidazolidines 2 with Mercuric Acetate/EDTA.

Reactions were performed following literature procedure.[7b] The reaction mixtures showed a complex mixture of compounds (TLC). The crude products were taken up in chloroform and passed through an alumina column eluting with chloroform. Appropriate fractions were pooled and evaporated to dryness affording acyl derivatives **4**.

Compound **4a** (mp 87°C),[1a] **4c** (mp 61°C),[1a] **4f** (mp 77-78°C),[5] **4g** (mp 89-90°C),[5] **4h** (mp 126-127°C)[7b] and **4i** (mp 125-126°C)[7b] were identified by comparison with authentic samples.

N-Benzoyl-N-methyl-N'-(p-methylphenyl)ethylenediamine (**4b**) (30%); mp: 83°C (cyclohexane).

MS: m/z 268 ($M^{+\cdot}$).

^{1}H-NMR: δ 7.60-7.40 (m, 5H, C_6H_5), 6.90 (d, 2H, *p*-$CH_3C_6H_4$, 2 *meta* H), 6.25 (d, 2H, *p*-$CH_3C_6H_4$, 2 *ortho* H), 4.20 (sa, ex, 1H, NH), 3.70-3.15 (m, 4H, CH_2CH_2), 3.10 (s, 3H, NCH_3) and 2.30 (s, 3H, CH_3Ar).

Anal. calcd. for $C_{17}H_{20}N_2O$: C 76.09, H 7.51, N, 10.44; found: C 76.20, H 7.42, N 10.56.

N,N'-Di(p-clorophenyl)-N-formylethylenediamine (**4e**) (18%), mp:120-122°C (ethanol).

MS: m/z 308 (M^+).

^{1}H-RMN: δ 8.33 (s, 1H, CHO), 7.40 (dd, 2H, *p*-ClC_6H_4NCHO, 2H *meta*), 7.21 (dd, 2H, *p*-ClC_6H_4NCHO, 2H *ortho*), 7.10 (dd, 2H, *p*-ClC_6H_4NH, 2H *meta*), 6.51 (dd, 2H, *p*-ClC_6H_4NH, 2H *ortho*), 3.80 (m, 3H, CH_2N= and NH) and 3.20 (t, 2H, CH_2NH).

Anal. cald. for $C_{15}H_{14}N_2Cl_2O$: C 58.27, H 4.56, N 9.06; found: C 58.34, H 4.48, N 9.10.

Reaction of Imidazolidines 2 with PCC.

The corresponding imidazolidine **2** (5 mmole) in dichloromethane (10 ml) was rapidly added at room temperature to a suspension of PCC (10 mmole) in dichloromethane (10 ml). The mixture was stirred for 2 hours and the progress of the reaction followed by TLC. The mixture was filtered and processed as was described for the previous experiment with similar results.

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6. Unpublished results from our work group indicate that, unlike what occurs with N-formyl-N,N'-diarylethylenediamines,[5] N-acetyl and N-benzoyl derivatives remain unaffected in acid medium. Besides, N′-aryl-N-benzoyl-N-methylethylenediamines in acid medium rearranged with intramolecular N⟶N′-aroyl transfer.[1a]

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