Synthesis, NMR Characterization and *ab initio* 6-31G* Study of 1-Aryl-2,3-dialkyl-1,4,5,6-tetrahydropyrimidinium Salts

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We describe the synthesis of a series of 1-aryl-2,3-dialkyl-1,4,5,6-tetrahydropyrimidinium salts **1**, by alkylation of the corresponding 1,4,5,6-tetrahydropyrimidines **2**. We analyze the changes in the ^{1}H and ^{13}C NMR spectra of compounds **2** induced by protonation and quaternization. The results of an *ab initio* theoretical study on amidine **2a**, and the cations resulting from its protonation (**2aH**$^{+}$) and quaternization (**1a**$^{+}$) are presented. A qualitative correlation was found between ^{13}C NMR and theoretical data in the case of protonation. The influence of the substitution patterns in the ^{1}H and ^{13}C NMR spectra of compounds **1** is also discussed.

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Introduction.

Cyclic amidinium salts have been studied as models of the natural cofactor N^{5},N^{10}-methenyltetrahydrofolic acid, involved in biochemical transfer of one carbon units at the oxidation level of formic acid [1]. Such reaction takes place *via* N^{10}-formyltetrahydrofolic acid, which plays a key role in the synthesis of purine nucleotides [2]. In an attempt to mimic the biological processes, transference of C2 unit to several nucleophiles was investigated in cyclic amidinium salts in which C2 is linked to two nitrogen atoms of different basicities, as occurs in the natural cofactor [3,4]. Such compounds were also employed as synthetic intermediates for the preparation of selectively substituted alkylenediamine derivatives [3,5-7]. The major part of the research in this area is devoted to 1*H*-4,5-dihydroimidazolium salts [3,5], while six membered homologues have been less studied [6,7]. Both acyclic and six-membered cyclic amidines and also their quaternary salts have found application as suitable probes to evaluate the importance of stereoelectronic effects in the hydrolysis of tetrahedral intermediates [8]. 1,3-Dimethyl-5-phenyl-1,4,5,6-tetrahydropyrimidinium ion was studied in order to assess the operativity of stereoelectronic control in the formation of tetrahedral intermediates derived from additions of carbon nucleophiles to nitrogen heterocycles [9].

In previous work we reported the alkaline hydrolysis of 1-aryl-3-alkyl-2-unsubstituted-1,4,5,6-tetrahydropyrimidinium salts [10]. The regioselective opening of the heterocyclic ring was analyzed in the light of the stereoelectronic control theory, with the aid of theoretical calculations. In connection to our investigation about nucleophilic additions and related stereoelectronic effects in amidinium systems, we recently needed to prepare some 2-alkyltetrahydropyrimidines and their quaternary salts. Due to our previous work on the spectral and stereochemical features of six-membered 1,3-diazaheterocycles [11], we were also interested in evaluating the perturbations derived from protonation and alkylation of the parent amidines. The effects of protonation and quaternization on the spectral features of nitrogen containing heterocyclic compounds have been studied in detail, employing theoretical calculations in some cases. The reported data are devoted to aromatic heterocycles such as pyridine and diazines [12], and also to saturated azaheterocyles like piperidine and its derivatives and pyrrolidine [13]. To our knowledge, however, partially saturated heterocycles like cyclic amidines have not been investigated yet. A clear understanding of steric and electronic features operating in such systems, and the perturbations induced by protonation and quaternization of the amidine functionality seemed therefore interesting. In this sense, NMR spectroscopy represents a valuable probe for the study of conformational and electronic features of organic compounds. Theoretical studies are also a helpful tool to investigate such characteristics.

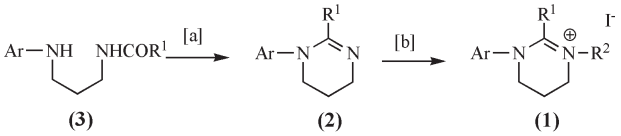
Here we present the synthesis of a series of 1-aryl-2,3-dialkyl-1,4,5,6-tetrahydropyrimidinium salts **1a-i** and their NMR spectroscopic characterization. We analyze the effects of protonation and quaternization of the heterocyclic nucleus in the light of theoretical calculations performed with an *ab initio* method. We also discuss the influence of the substitution patterns in the ^{1}H and ^{13}C NMR spectra of compounds **1**.

Results and Discussion.

1-Aryl-2,3-dialkyltetrahydropyrimidinium salts **1** were synthesized by alkylation of the corresponding tetrahydropyrimidines **2**, themselves obtained by cyclization of aminoamides **3** (Scheme I). Physical constants and MS data of salts **1a-i** are given in the experimental section. ^{1}H and ^{13}C spectra will be discussed separately.

We examined first the changes induced by protonation and quaternization on the ^{1}H and ^{13}C NMR spectra of tetrahydropyrimidine **2a**, taken as model compound. For this purpose, resonances of compounds **2a** and **1a** were unequivocally assigned by means of the corresponding HMQC and HMBC spectra, with the exception of 2'- and 4'- signals of the phenyl ring in **1a**, which appear as a broad singlet in the proton spectrum. Those resonances

Scheme 1



(3) **(2)** **(1)**

Compound **1,2**	Ar	R^1	R^2
a	C_6H_5	*tert*-C_4H_9	CH_3
b	4-$CH_3OC_6H_4$	*tert*-C_4H_9	CH_3
c	4-$NO_2C_6H_4$	*tert*-C_4H_9	CH_3
d	4-ClC_6H_4	*tert*-C_4H_9	CH_3
e	4-ClC_6H_4	*iso*-C_3H_7	CH_3
f	4-ClC_6H_4	C_2H_5	CH_3
g	4-ClC_6H_4	CH_3	CH_3
h	4-ClC_6H_4	C_2H_5	C_2H_5
i	4-ClC_6H_4	C_2H_5	*iso*-C_3H_7

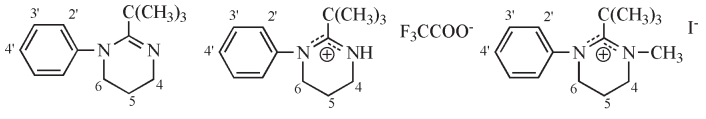
[a] PPSE/Cl_2CH_2, reflux, 6 hs; [b] R^2I/Cl_2CH_2, Reflux, 1-6 hs.

were assigned by comparison with the aromatic signals of compounds **1b,c,d** (see below). ^{1}H NMR spectra of tetrahydropyrimidine **2a**, its trifluoroacetate **2aH** and quaternary salt **1a** are listed in Table I.

For a better understanding of the spectral features of amidine **2a** and amidinium cations **2aH$^+$** and **1a$^+$**, the electron delocalization in such systems must be considered. In the tetrahydropyrimidine, the presence of a phenyl substituent on N1 results in a cross-conjugated system where competitive amidine and arylamine-type electron delocalization are possible (Scheme II, structures **I** and **II**, respectively). A comparison between the aromatic chemical shifts of compound **2a** and *N*-phenyltrimethylenediamine (H2: 6.44, H3,5: 7.17, H4: 6.69 ppm) [14] shows that shielding of the *ortho* and *para* hydrogen atoms is less significative in the amidine. This would be the consequence of competitive amidine-like resonance, enhanced by steric hindrance of the vicinal 2-*tert*-butyl group, which forces the phenyl group out of the plane of the amidine system. To further study resonance and steric effects in this heterocycle, we performed the complete optimization of compound **2a** using the HF 6-31G* method [15], and examined some relevant geometric parameters. The calculated N1-C2 bond length in **2a** (1.416 Å) is longer than the one measured by X-ray diffraction for the C-NH_2 bond of acetamidine (1.344 Å) [16], while C2-N3 distance (1.256 Å) is shorter than the corresponding

Table I

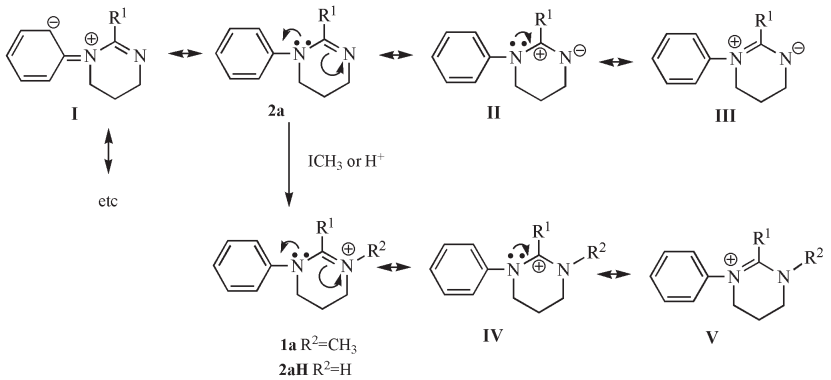
^{1}H NMR Spectra of compounds **2a**, **2aH**, **1a**



2a **2aH** **1a**

Compound	H4	H6	H5	Aromatics	$C(CH_3)_3$	N-CH_3
2a	3.56 (t)	3.38 (t)	1.73 (p)	2´:7.03 (dd) 3´:7.30 (dt) 4´:7.14 (dt)	1.03 (s)	-
2aH	3.65-3.68 (m)		2.14 (p)	7.25-7.51 (m)	1.15 (s)	-
1a	4.09 (t)	3.84 (t)	2.21 (p)	7.34-7.40 (m)	1.25 (s)	3.72 (s)

Scheme II



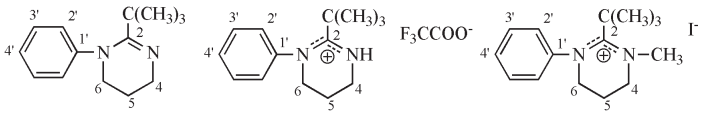
C=N bond in the acyclic amidine (1.298 Å). Besides, dihedral angle C2'-C1'-N1-C6 has a calculated value of –102.9° in **2a**. These results suggest that, due to the steric effect of the *tert*-butyl, aniline-type resonance is partially inhibited, but this does not result in an enhanced participation of the N1 lone pair in amidine-type resonance.

Data reported in Table I indicate that both protonation and quaternization induce a paramagnetic shift of all the ^{1}H resonances, the effect of *N*-alkylation being more pronounced. An analogous effect upon protonation was previously reported by Pugmire for pyridine and diazines [12] and by Morishima for piperidine and pyrrolidine [13]. The observed deshielding was attributed to a predominance of polarization effects due to the presence of a positively charged nitrogen atom in the cations [13]. In our case, however, changes in electron delocalization induced by *N*-substitution may additionally be involved in the observed shifts. In order to understand resonance effects in the amidinium salts, we performed a geometry optimization of cations **2aH$^+$** and **1a$^+$**, employing the same method as for the amidine. The resulting optimized structures showed very close values for N1-C2 and C2-N3 bond distances (**2aH$^+$**: 1.324 and 1.317 Å, **1a$^+$**: 1.337 and 1.326 Å, respectively). On the other hand, N1-C1' bond was comparatively longer in the cations than in the parent amidine (**2a**: 1.427 Å, **2aH$^+$**: 1.448 Å, **1a$^+$**: 1.447 Å, respectively). Both changes suggest that electron delocalization involving the amidinium system (Scheme II, structures **IV**, **V**) will predominate in the cations. In fact, the small shielding effect shown by the 2- and 4-phenyl hydrogen atoms in the amidine disappears upon *N*-substitution, indicating the loss of aniline-type resonance. The amidinium moiety becomes thus an electron withdrawing group acting on the phenyl ring mainly by inductive effect.

The ^{13}C spectra of compounds **2a**, **2aH** and **1a** are presented in Table II. At variance with ^{1}H resonances, which were all shifted to higher frequencies by N3 substitution, the effect on ^{13}C chemical shifts is different for protonation than for quaternization. Protonation of compound **2a** induced deshielding of C2, C4, C6 and shielding of the *tert*-butyl carbons, C5 and C1'. In saturated five and six-membered azaheterocycles [13] and also in acyclic aliphatic amines [17], protonation induces a diamagnetic shift of primary and secondary carbons α to the nitrogen atom, while tertiary and quaternary α carbons are deshielded. This was explained considering that *N*-protonation is accompanied by electronic redistribution with polarization of C-H bonds, producing C(δ-)-H(δ+) structures, and thus electron density on the hydrogen atoms is transmitted through the hydrocarbon chain towards the positively charged nitrogen atom. Therefore, electron density on the carbon atoms remains constant or may actually increase. Other interesting features described by Morishima were the alternation of shielding and deshielding effects along the hydrocarbon chain and the conformational dependence of the protonation induced ^{13}C shifts. Both effects were reproduced by the author by calculation of the electron densities on C and H atoms using the semiempirical method CNDO/2. At variance with the reported data, in our case protonation induces an unexpected deshielding of the α carbon atoms. In order to understand the effects of protonation and quaternization on the ^{13}C resonances of tetrahydropyrimidine **2a**, we calculated the atom charges of the neutral molecule and the corresponding cations derived from its protonation and quaternization (**2aH$^+$** and **1a$^+$**, respectively), using the HF 6-31G* method (Table III). An analysis of the results shows a correlation between changes in atomic charges and shielding/ deshielding effects on the ^{13}C resonances of **2a** and **2aH$^+$**. The correlation is only qualitative for protonation, and does not hold for quaternization. In the latter case, the effect of changes in the electron densities of the carbon atoms are probably overcome by standard β and γ-shifts to higher frequencies due to the presence of a methyl group on N3 [18].

Table II

^{13}C NMR Spectra of Compounds **2a**, **2aH**, **1a**

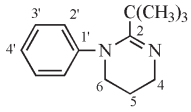


2a **2aH** **1a**

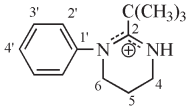
Compd.	C4	C6	C5	C2	$C(CH_3)_3$	$C(CH_3)_3$	N-CH_3	Aromatics 1'	2'	3'	4'
2a	46.3	53.3	21. 9	167.9	40.4	31.2	-	149.8	127.0	129.4	125.4
2aH	55.1	55.1	19.2	170.3	39.8	29.3	-	142.5	127.9 and 130.1		
1a	54.5	55.1	21.0	175.7	41.4	30.7	45.9	145.2	127.61	130.4	129.1

Table III

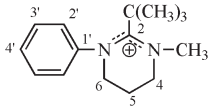
Selected HF 6-31G* Calculated Atom Charges for Compound **2a** and Cations **2aH**$^+$, **1a**$^+$



2a



2aH$^+$



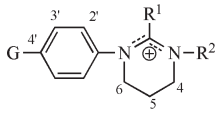
1a$^+$

Compd.	C4	C6	C5	C2	*C*$(CH_3)_3$	C(*C*$H_3)_3$[a]	Aromatics 1'	2'[a]	3'[a]	4'
2a	-0.122	-0.137	-0.360	0.554	-0.057	-0.470	0.250	-0.220	-0.196	-0.208
2aH$^+$	-0.114	-0.118	-0.383	0.839	-0.137	-0.510	0.202	-0.201	-0.200	-0.186
1a$^+$	-0.130	-0.113	-0.386	0.822	-0.139	-0.492	0.202	-0.198	-0.200	-0.189

[a]: averaged.

Table IV

^{1}H NMR Spectra of 1-Aryl-2,3-Dialkyl-1,4,5,6-tetrahydropyrimidinium Iodides **1b-k**



Compd.	G	R^1	R^2	H4	H6	H5	Ar	R^1	R^2
1b	CH_3O	$C(CH_3)_3$	CH_3	3.99 (t)	3.81 (t)	2.21 (p)	2': 7.36 (dd) 3': 6.89 (dd) CH_3O: 3.78 (s) [a]	1.27 (s)	3.70 (s) [a]
1c	NO_2	$C(CH_3)_3$	CH_3	4.12 (t)	3.94 (t)	2.28 (p)	2': 7.92 (dd) 3': 8.29 (dd)	1.35 (s)	3.80 (s)
1d	Cl	$C(CH_3)_3$	CH_3	4.05 (t)	3.86 (t)	2.25 (p)	2': 7.51 (dd) 3': 7.42 (dd)	1.33 (s)	3.74 (s)
1e	Cl	$CH(CH_3)_2$ (c) (d)	CH_3	3.97 (t)	3.93 (t)	2.33 (p)	2': 7.61 (dd) 3': 7.46 (dd)	c: 3.00 (m) d: 1.38 (d)	3.42 (s)
1f	Cl	CH_2CH_3 (c) (d)	CH_3	3.90 (t)	3.85 (t)	2.40 (p)	2': 7.69 (dd) 3': 7.46 (dd)	c: 2.55 (q) d: 1.17 (t)	3.41 (s)
1g	Cl	CH_3	CH_3	3.83 (t)	3.78 (t)	2.40 (p)	2': 7.62 (dd) 3': 7.40 (dd)	2.21 (s)	3.34 (s)
1h	Cl	CH_2CH_3 (c) (d)	CH_2CH_3 (e) (f)	3.90 (t)	3.86 (t)	2.37 (p)	2': 7.69 (dd) 3': 7.44 (dd)	c: 2.48 (q) d: 1.17 (t)	e: 3.65 (q) f: 1.45 (t)
1i	Cl	CH_2CH_3 (c) (d)	$CH(CH_3)_2$ (e) (f)	3.78 (t)	3.81 (t)	2.34 (p)	2': 7.78 (dd) 3': 7.44 (dd)	c: 2.51 (q) d: 1.18 (t)	e: 4.29 (m) f: 1.46 (d)
1j	Cl	H	CH_3	3.94 (t) [a]	3.58 (t) [a]	2.36 (p)	2': 7.57 (dd) 3': 7.38 (dd)	8.80 (s)	3.47 (s)
1k	Cl	C_6H_5	CH_3	4.06 (t)	4.19 (t)	2.57 (p)	2': 7.39 (dd) 3': 7.12 (dd)	2": 7.69-7.72 (m) 3",4": 7.30-7.32 (m)	3.08 (s)

[a]: exchangeable assignment.

^{1}H NMR spectra of tetrahydropyrimidinium salts **1b-i** are presented in Table IV, together with compounds **1j** [19] and **1k** [6] included for comparison. Signals corresponding to the aromatic substituent and to the heterocyclic ring were attributed by analogy with the unequivocal assignment of compound **1a** (Table I). Some resonances, however, were assigned only tentatively, due to their very close values. Analysis of data reported in Table IV indicates that the more significant effects both on the trimethylene portion, the *N*–alkyl substituent and the aromatic moiety are associated to the substituent in position 2 (R^1).

A comparison between 2-alkyl derivatives **1d-g** and 2-phenyl derivative **1k** shows that the presence of a 2-aryl group shifts the signals of the trimethylene portion to

higher frequencies, while a shielding effect on *N*-methyl and 1-aryl resonances is observed. This may be explained by considering that the steric tension due to the presence of vicinal aryl substituents leads to twisting of such groups with respect to the ring, causing the 1-aryl and the *N*-methyl hydrogen atoms to be within the shielding region of the 2-phenyl group.

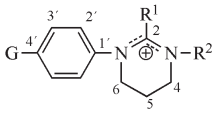
Comparing 2-*tert*-butyl derivatives with different *para* substituents **1a-d**, a progressive deshielding of the signals is observed on going from an electron donor such as CH_3O to a strong electron withdrawing substituent.

^{13}C NMR spectra of tetrahydropyrimidinium salts **1b-i** are presented in Table V together with compounds **1j,k,** included for comparison. Resonances corresponding to C2, C4, C5 and C6 were assigned by analogy with compound **1a**. For all the compounds, resonances corresponding to C4 and C6 show very close values and the proposed assignment is therefore tentative. For salts **1a-d**, signals corresponding to the 1-aryl carbons were attributed taking into account standard chemical shift contributions of the *para* substituents in benzene rings [20]. A comparison between salts **1g,j** shows that replacement of the 2-hydrogen atom by a methyl group induces a deshielding of *ca.* 10 ppm in C2 as a consequence of the α–effect. C4 and C6 signals are also shifted *ca.* 5 ppm to higher frequencies, while the *N*-methyl resonance is shielded. This can be explained taking into account the dihedral angle dependence of the γ–effect, which derives in a shielding effect when the mentioned angle between the methyl group and the considered carbon atom is 0º, and in the opposite effect when the angle is near 180º. Replacement of 2-methyl by a phenyl group (compounds **1g,k**) shifts C2 resonance to higher frequencies, due to delocalization of the positive charge density on C2 by the 2-aryl substituent.

For compounds **1d-g**, the increasing branching of R^1 induces the expected deshielding of C2 (β–effect). C4 and C6 are also shifted to higher frequencies, while the effect on the *N*-methyl is variable. For compounds **1h-i** increasing substitution on the N3-methyl induces a diamagnetic shift in C2 signal (γ–effect). The nature of the *para* substituent in the 1-aryl modifies the position of C2 signal, which is shielded in the case of the methoxy derivative **1b** and deshielded for $G=NO_2$. This effect can be related to an increase in the positive charge density of

Table V

^{13}C NMR Spectra of 1-Aryl-2,3-Dialkyl-1,4,5,6-tetrahydropyrimidinium iodides **1a-h**



Compd.	G	R^1	R^2	C2	C4	C6	C5	Ar 1'	Ar 2'	Ar 3'	Ar 4'	R^1	R^2
1b	CH_3O	$C(CH_3)_3$ (d)(e)	CH_3	174.8	53.8 [a]	54.7 [a]	19.4		CH_3O: 55.5 [a]			d: 40.8 e: 31.5	45.3
								137.3	128.3	115.0	159.5		
1c	NO_2	$C(CH_3)_3$ (d)(e)	CH_3	176.3	54.4 [a]	54.5 [a]	20.3	150.1 [a]	128.5	125.4	146.9 [a]	d: 41.4 e: 31.5	45.7
1d	Cl	$C(CH_3)_3$ (d)(e)	CH_3	175.3	54.1 [a]	54.7 [a]	20.5	143.1	128.7	130.3	134.8	d:41.1 e:31.5	45.6
1e	Cl	$CH(CH_3)_2$ (d) (e)	CH_3	167.8	50.7 [a]	51.3 [a]	19.8	140.9	128.4	130.8	135.7	d:31.9 e:19.00	41.8
1f	Cl	CH_2CH_3 (d) (e)	CH_3	165.9	49.3 [a]	50.7 [a]	19.7	140.2	128.6	130.4	135.5	d:24.5 e:10.5	41.4
1g	Cl	CH_3	CH_3	162.5	49.5 [a]	50.6 [a]	19.6 [a]	140.6	128.6	130.4	135.4	19.7 [a]	42.2
1h	Cl	CH_2CH_3 (d) (e)	CH_2CH_3 (f) (g)	165.2	48.7 [a]	51.3 [a]	19.6	140.2	128.8	130.7	135.9	d: 24.0 e: 11.6	f: 45.9 g:13.2
1i	Cl	CH_2CH_3 (d) (e)	$CH(CH_3)_2$ (f) (g)	164.2	51.5 [a]	52.7 [a]	19.7	140.4	128.9	130.5	135.6	d: 24.1 e: 11.5	f: 39.5 g:19.7
1j	Cl	H	CH_3	152.5	45.9 [a]	45.7 [a]	18.8	139.7	124.0	130.0	134.0	-	43.3
1k	Cl	C_6H_5	CH_3	161.9	48.0	49.8	19.0	140.2			133.3	1": 127.3 4": 130.4	42.2
										128.6, 128.4, 128.1			

[a]: exchangeable assignment.

C2 due to the progressively higher inductive electron withdrawing effect of the 1-aryl substituent. This influence is stronger for quaternary carbons, where no compensatory release of electron density by attached hydrogen atoms can operate [13].

EXPERIMENTAL

Melting points were taken on a Büchi capillary apparatus and are uncorrected. ^{1}H and ^{13}C nmr spectra were recorded on a Bruker MSL 300 MHz spectrometer. Deuteriochloroform was used as the solvent, and the standard concentration of the samples was 10 mg/ml. HMQC and HMBC spectra were recorded in an AVANCE DRX300 spectrometer. Spectral data for compound **2aH** were obtained by addition of a twofold molar excess of trifluoroactic acid to a sample of compound **2a**. Chemical shifts are reported in ppm (δ) relative to TMS as an internal standard. Splitting multiplicities are reported as singlet (s), broad signal (bs), doublet (d), double doublet (dd), triplet (t), double triplet (dt), quartet (q), pentet (p) and multiplet (m). Electron impact mass spectra were recorded with a GC-MS Shimadzu QP-1000 spectrometer operating at 20 eV. Tlc analyses were carried out on aluminium sheets Alumina 60 F_{254} using chloroform as the solvent. Reagents, solvents and starting materials were purchased from standard sources and purified according to literature procedures. 1-Aryl-2-alkyl-1,4,5,6-tetrahydropyrimidines **2a-i** were described in the literature [21].

1-Aryl-2,3-dialkyl-1,4,5,6-tetrahydropyrimidinium Iodides **1**.

General Procedure.

A mixture of 1,4,5,6-tetrahydropyrimidine (**2**) (5 mmol) and alkyl iodide (6 mmol) in anhydrous methylene chloride (50 ml) was refluxed protected from moisture. The reaction was monitored by TLC (chloroform:methanol 9:1) until disappearance of the starting material. The solution was evaporated *in vacuo* and the residue purified by recrystalization or by flash column chromatography (silica gel, chloroform:methanol 9:1) to yield compounds (**1a-i**). ^{1}H nmr data of compounds **1a,b-k** are given in Tables I and IV, respectively. ^{13}C nmr data of compounds **1a,b-k** are given in Tables II and V, respectively. Yields, physical data and elemental analyses are as follows:

1-Phenyl-2-*tert*-butyl-3-methyl-1,4,5,6-tetrahydropyrimidinium Iodide (**1a**).

This compound was obtained with 77 % yield; mp 96-98 ºC (anhydrous isopropanol); MS: m/z 231 (M-127$^+$).

Anal. Calcd. for $C_{15}H_{23}N_2I$: C, 50.29; H, 6.47; N, 7.82. Found: C, 50.12; H, 6.45; N, 7.84.

1-(4-Methoxyphenyl)-2-*tert*-butyl-3-methyl-1,4,5,6-tetrahydropyrimidinium iodide (**1b**).

This compound was obtained as an oil (74%); MS: m/z 261 (M-127$^+$).

Anal. Calcd. for $C_{16}H_{25}N_2OI$: C, 49.49; H, 6.49; N, 7.21. Found: C, 49.56; H, 6.52; N, 7.20.

1-(4-Nitrophenyl)-2-*tert*-butyl-3-methyl-1,4,5,6-tetrahydropyrimidinium Iodide (**1c**).

This compound was obtained with 69 % yield; mp 213-215 ºC (anhydrous tetrahydrofurane); MS: m/z 276 (M-127$^+$).

Anal. Calcd. for $C_{15}H_{22}N_3O_2I$: C, 44.68; H, 5.50; N, 10.42. Found: C, 44.80; H, 5.48; N, 10.38.

1-(4-Chlorophenyl)-2-*tert*-butyl-3-methyl-1,4,5,6-tetrahydropyrimidinium Iodide (**1d**).

This compound was obtained with 79 % yield; mp 102-104ºC (anhydrous isopropanol); MS: m/z 265 (M-127$^+$).

Anal. Calcd. for $C_{15}H_{22}N_2ClI$: C, 45.88; H, 5.65; N, 7.13. Found: C, 45.82; H, 5.66; N, 7.11.

1-(4-Chlorophenyl)-2-*iso*-propyl-3-methyl-1,4,5,6-tetrahydropyrimidinium Iodide (**1e**).

This compound was obtained as an oil (73%); MS: m/z 251 (M-127$^+$).

Anal. Calcd. for $C_{14}H_{20}N_2ClI$: C, 44.40; H, 5.32; N, 7.40. Found: C, 44.29; H, 5.34; N, 7.39.

1-(4-Chlorophenyl)-2-ethyl-3-methyl-1,4,5,6-tetrahydropyrimidinium Iodide (**1f**).

This compound was obtained in 81 % yield; mp 187-188ºC (anhydrous isopropanol); MS: m/z 237 (M-127$^+$).

Anal. Calcd. for $C_{13}H_{18}N_2ClI$: C, 42.82; H, 4.98; N, 7.68. Found: C, 42.71; H, 5.00; N, 7.69.

1-(4-Chlorophenyl)-2,3-dimethyl-1,4,5,6-tetrahydropyrimidinium Iodide (**1g**).

This compound was obtained in 83 % yield; mp 258-260ºC (anhydrous isopropanol); MS: m/z 223 (M-127$^+$).

Anal. Calcd. for $C_{12}H_{16}N_2ClI$: C, 41.11; H, 4.60; N, 7.99. Found: C, 41.20; H, 4.59; N, 8.00.

1-(4-Chlorophenyl)-2,3-diethyl-1,4,5,6-tetrahydropyrimidinium Iodide (**1h**).

This compound was obtained in 82 % yield; mp 144-145ºC (anhydrous isopropanol); MS: m/z 251 (M-127$^+$).

Anal. Calcd. for $C_{14}H_{20}N_2ClI$: C, 44.40; H, 5.32; N, 7.40. Found: C, 44.45; H, 5.30; N, 7.42.

1-(4-Chlorophenyl)-2-ethyl-3-*iso*-propyl-1,4,5,6-tetrahydropyrimidinium Iodide (**1i**).

This compound was obtained in 54 % yield; mp 174-176ºC (anhydrous isopropanol); MS: m/z 265 (M-127$^+$).

Anal. Calcd. for $C_{15}H_{22}N_2ClI$: C, 45.88; H, 5.65; N, 7.13. Found: C, 45.75; H, 5.65; N, 7.15.

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