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CYCLOADDITION OF HETEROCUMULENES TO SOME 1,3-HETERODIENES INVOLVING UNUSUAL ASSISTANCE OF METHYL GROUP

JANUSZ MOSKAL

Department of Organic Chemistry, University School of Kielce*
25020 Kielce, Poland

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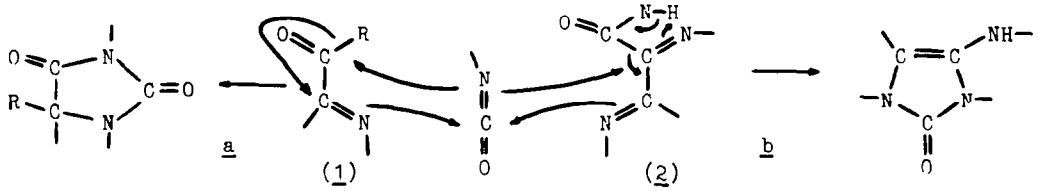
Abstract - Highly substituted 1,4-diazabutadienes react with aroyl isothiocyanates in a 1,3-dipolar cycloaddition node yielding five-membered thiohydantoin-type heterocycles. The cycloaddition is accompanied by 1,4 shift of hydrogen from a methyl group attached to C2 of the 1,4-diazabutadiene moiety. The mechanism of this reaction is discussed in comparison with similar cycloadditions with aryl isocyanates.

Sterically congested 1,3-heterodienes containing 1-oxa-4-azabutadiene and 1,4-diazabutadiene systems[2] have proved to be efficient "masked 1,3-dipoles" in a number of 1,3-dipolar cycloadditions with heterocumulenes. Thus, 1-oxa-4-azabutadienes (1) were prone to react with aryl isocyanates yielding five-membered heterocycles as a result of 1,3-dipolar cycloaddition combined with synchroneous 1,2 migration of a substituent attached to C2 of the 1-oxa-4-azabutadiene skeleton (path a)[3]. In these cycloadditions C2 and N4 were an electrophilic and a nucleophilic centrum, respectively. Also 1,4-diazabutadienes (2) reacted readily with aryl isocyanates in a 1,3-cycloaddition node, however, in a reverse manner, i.e., employing their N1 and C3 as a nucleophilic and an electrophilic centrum, respectively. These cycloadditions were accompanied by 1,4-sigmatropic shift of hydrogen from an arylamide substituent joined to C3 and a spontaneous elimination of this substituent as aryl isocyanate (path b)[4]:



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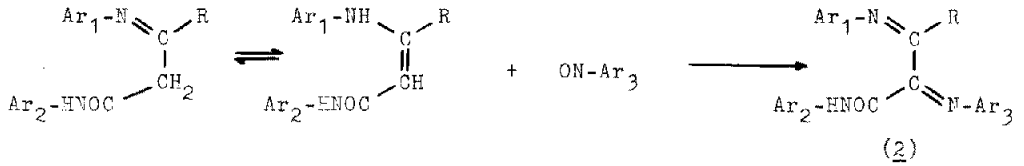
This particular reactivity of the sterically congested 1,3-heterodienes results from their specific "pseudo-gauche" conformation[5] in which conjugation between heteroene fragments is in fact supressed due to interaction of bulky substituents causing a twist around the C2,C3 bond and forcing their more or less perpendicular arrangement. In such conformation unshared electrons of azomethine nitrogens play an important rôle.

In present investigation attention has been directed towards reactions of the 1,4-diazabutadienes with organic isothiocyanates as a potential easy source of various 2-imidazolidinethiones which might be of interest because of their biological activity[6].

* Present address: Department of Organic Chemistry, Groningen University, 9747 AG Groningen, The Netherlands

RESULTS AND DISCUSSION

1,4-Diazabutadienes (2) chosen for cycloaddition with organic isothiocyanates were obtained according to the method described before, based on a base promoted condensation of β-anils of acet- and/or benzoyl-acetic acid anilides with nitrosoarenes[7] :



(2)

2	R	Ar_1	Ar_2	Ar_3
a	phenyl	phenyl	phenyl	phenyl
b	phenyl	4-methoxyphenyl	phenyl	phenyl
c	methyl	4-methoxyphenyl	2,5-dichlorphenyl	phenyl
d	methyl	4-methylphenyl	2,5-dichlorphenyl	phenyl
e	methyl	4-ethoxyphenyl	phenyl	phenyl
f	methyl	4-dimethylaminophenyl	phenyl	phenyl
g	methyl	4-methoxyphenyl	phenyl	4-bromphenyl
h	methyl	4-diethylaminophenyl	phenyl	phenyl
i	methyl	4-methoxyphenyl	phenyl	phenyl

Despite the expectations 1,4-diazabutadienes (2) did not react with aryl isothiocyanates even when the strong electron-releasing substituents were placed in the aryl ring attached to N1 nitrogen in order to increase its nucleophility. However, replacement of an aryl by an aroyl group within the organic isothiocyanate molecule enhanced sufficiently electrophility of the isothiocyanate carbon and crystalline products (3) were obtained after short warming of a benzene solution containing both reagents, i.e., a 1,4-diazabutadiene (2) and an aroyl isothiocyanate. There was an additional requirement for the initial 1,4-diazabutadienes (2), namely, a methyl group at C2 carbon. The 1,4-diazabutadienes (2) containing a phenyl at C2 carbon did not react under analogous conditions.

Combustion analysis showed composition of the products (3) corresponding to the simple 1:1 adducts regarding both reactants. The ir spectra revealed strong absorptions in the region of stretching vibrations of the NH bond supporting the presence not only of the anilide NH group but an additional amino functionality as well. Sharp absorptions between 1650 and 1700 cm^{-1} evidenced both anilide and aroyl carbonyl groups indicating that the carbon, nitrogen double bond of aroyl isothiocyanates was involved in the cycloaddition. The ^1H nmr spectra showed anilide and amino protons as broad singulets sensitive to changes of the solvent polarity. The anilide NH signal was shifted from approx. 8.4 ppm to 10.1 ppm and the amino proton signal from 5.3 to 5.7 ppm when $CDCl_3$ was replaced by deuterated DMSO. Two one proton doublets were observed between 4.7 and 5.3 ppm but no signal corresponding to a methyl group. The doublets showed the small coupling constant 2.3Hz typical for geminal coupling[8]. This suggested participation of the methyl group at C2 in the cycloaddition.

The ^{13}C nmr spectrum of the representatively chosen and the best soluble compound (3d) proved finally the structure of the products (3) as 3-aroyl-1-aryl-4-arylamido-4-arylamino-5-methylidene imidazolidine-2-thiones. All the carbon signals were recognized and ascribed, partly on the basis of comparison with the spectra of similarly substituted 2-imidazolidinones, 2,4-imidazolidindiones, and 2-imidazolidinethiones[9,10,11]. The thione group carbon produced a signal at 175.3 ppm which was consistent with the carbon resonance ascribed to such carbon of a number of 2-imidazolidinethiones[11]. A singulet at 78.7 ppm evidenced the quaternary carbon of the imidazolidine ring. this was in good agreement with the resonance determined

for these carbons of 5,5-disubstituted 2,4-imidazolidindiones[10]. The carbonyl carbon singulets were typically positioned in the spectrum as reported for amides[8]. Also the carbon resonancies of all the three aryl rings corresponded well to those ascribed for analogously substituted rings joined to nitrogen in the imidazolidine derivatives. Coupling constants J_{CH} of aromatic carbons varied from 161 to 163 Hz. These of aliphatic carbons were about 135 Hz. The coupling constant of the methylidene carbon was 158.3 Hz.

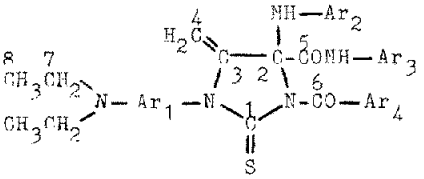
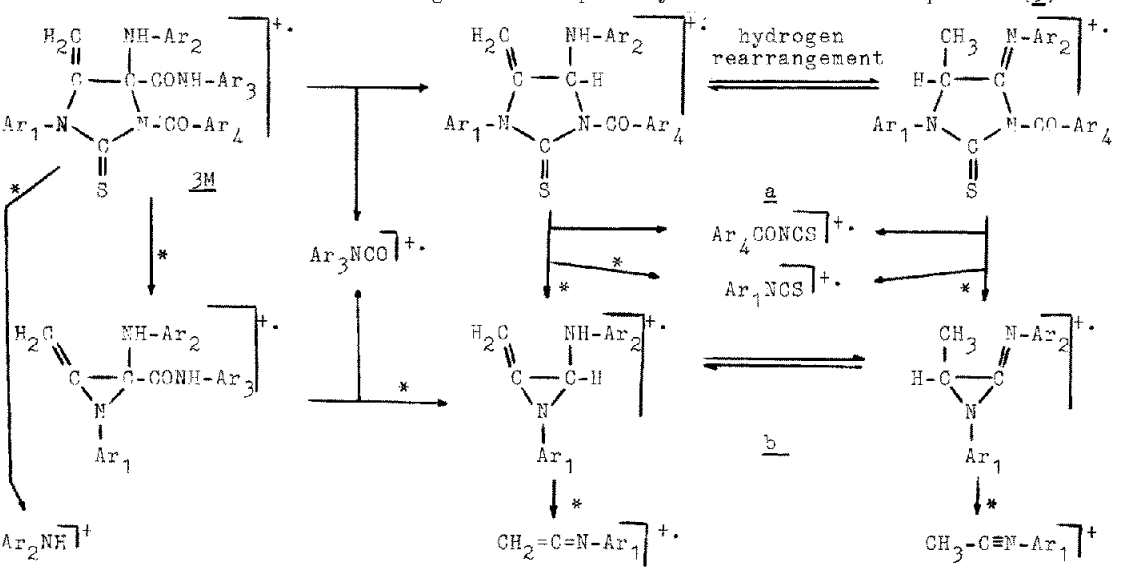


Table 1. Carbon resonancies (ppm) found for (3δ)

Carbon	δ ppm	Carbon	δ ppm
C1	175.3	Ar_2 : C1	147.5
C2	78.7	C2,6	111.7
C3	144.4	C3,5	129.0
C4	95.1	C4	115.6
C5	166.6	Ar_3 : C1	138.3
C6	169.6	C2,6	121.2
C7	43.8	C3,5	128.8
C8	12.4	C4	124.4
Ar_1 : C1	119.5	Ar_4 : C1	135.8
C2,6	111.5	C2,6	128.6
C3,5	128.0	C3,5	128.3
C4	148.3	C4	132.4

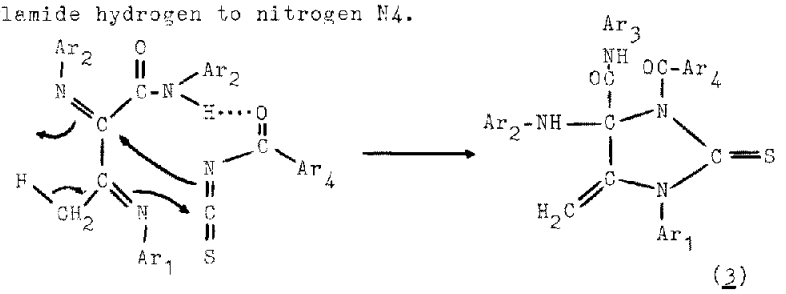
Electron impact induced fragmentation of the compounds (3) showed great resemblance to that determined for 2-imidazolidinones and 2,4-imidazolidindiones[12]. The molecular ions (3M) lost first the aryl isocyanate molecule producing stable 4-arylimino-5-methylidene imidazolidine-2-thione radical ions (a) responsible for the prominent peaks in the spectra. The radical ions (a) detached the aroyl isothiocyanate molecule forming aziridine-type ions (b) characteristic for electron impact fragmentation of imidazolidine derivatives.

Scheme 1. The main fragmentation pathways found for the compounds (3)



Formation of these rather uncommon derivatives of 2-imidazolidinethione could be explained by the 1,3-dipolar cycloaddition employing N1 and C3 of the 1,4-diazabutadienes (2) and the C=N double bond of aroyl isothiocyanates, and combined with or followed by 1,4 shift of hydrogen from a methyl group joined to C2 of the 1,4-diazabutadiene skeleton. However, a question arouse why in this case hydrogen migrated from not very favourable position compared with that of the arylamide group. According to the model reaction of α,β-diimine of α,β-diketobutyric acid amide with isocyanic acid two center contact between nitrogen N4 (chiefly its p_x and p_y orbitals) and amide hydrogen was entirely acceptable. Analogously, migration of this hydrogen would give 4-arylimino-imidazolidine-2-thiones[13].

Then it seemed reasonable that a transition state showing two center contacts $^{N1}(2) \longrightarrow C_{NCS}$ and $N_{NCS} \longrightarrow {}^{C3}(2)$ responsible for the virtual cycloaddition, was also conducive to an additional two center contact between the aroyl oxygen and the arylamide hydrogen $O_{ArCO} \longrightarrow H_{CONH}$. This prevented the probable migration of the arylamide hydrogen to nitrogen N4.



(3)

3	Ar_1	Ar_2	Ar_3	Ar_4
a	p-methoxyphenyl	phenyl	2,5-dichlorphenyl	phenyl
b	p-methylphenyl	phenyl	2,5-dichlorphenyl	phenyl
c	p-ethoxyphenyl	phenyl	phenyl	phenyl
d	p-diethylaminophenyl	phenyl	phenyl	phenyl
e	p-methoxyphenyl	p-bromphenyl	phenyl	phenyl
f	p-dimethylaminophenyl	phenyl	phenyl	phenyl
g	p-methoxyphenyl	phenyl	phenyl	p-chlorphenyl
h	p-diethylaminophenyl	phenyl	phenyl	p-chlorphenyl

The intramolecular hydrogen bond between the arylamide NH and aroyl CO groups was observed in the ir spectra of the products (3). The migration of hydrogen from the methyl group seemed to be forced by an increase of electron density on N4 (chiefly p_x and p_y orbitals) and rehybridization on C3 ($sp^2 \longrightarrow sp^3$) decreasing distance between N4 and hydrogen of the methyl group. The cycloaddition was hardly affected by solvent polarity (benzene and acetonitrile) that suggested rather synchroneous shift of hydrogen along with the virtual cycloaddition. This also eliminated the possible intramolecular processes of hydrogen transfer.

In conclusion, reactions of sterically congested 1,4-diazabutadienes (2) with aroyl isothiocyanates can be useful for synthesis of some 2-imidazolidinethiones. The 1,3-dipolar cycloaddition required uncommon assistance of a methyl group attached to C2 of the 1,4-diazabutadiene system that led in consequence to 5-methylidene imidazolidine-2-thione derivatives.

EXPERIMENTAL

1,4-Diazabutadienes (2), i.e., α,β-dianils of α,β-diketobutyric acid anilides (2c - 2i) and α,β-dianils of β-phenyl-α,β-diketopropionic acid anilides (2a,2b) were obtained by condensation of the appropriate β-anils of aceto- and aroylacetic acid anilides with nitrosobenzenes in the presence catalytic amounts of a base, as reported previously[4,13]. The chemical and spectral properties of these 1,4-diazabutadienes (2) were reported earlier[4,5] except of 2e and 2g .

β-p-Ethoxyanilo-α-anil of α,β-diketobutyric acid anilide (2e), : m.p.140-143°C; yellow prisms from t-butanol; yield 72%; for $C_{24}H_{23}N_3$, m.w.,385,2 , calc. %C 75.8 H 6.0 N 10.9, found %C 75.7 H 6.0 N 11.0.

Ir (KBr, cm^{-1}) : 3290-3185,w,broad, NH; 2845,m,OEt; 1670,s,CO_{an}; 1642,s,broad,C=N.

^1H nmr ($CDCl_3$,TMS) : 1.25-1.42,m,3H,$OCH_2\underline{CH_3}$; 1.80-2.45,seven singulets,3H,CH_3; 3.7-3.9,m,2H,$O\underline{CH_2}CH_3$; 6.3-8.2,m,14H_{ar}; 9.3-10.1,three singulets,1H,NH_{an}.

β-p-Methoxyanilo-α-p-bromanil of α,β-diketobutyric acid anilide (2g), : m.p., 154-156°C; pale yellow prisms from t-butanol; yield 78%; for $C_{23}H_{20}BrN_3O_2$, m.w., 450.1, calc. %C 61.3 H 4.5 N 9.3 Br 17.8, found %C 61.3 H 4.5 N 9.4 Br 17.7.

Ir (KBr, cm^{-1}) : 3290-3185,m,broad, NH; 2842,w, OMe; 1658,s,CO_{an}; 1635,s,broad C=N.
^1H nmr ($CDCl_3$, TMS) : 1.9-2.5,seven singulets,3H, CH_3; 3.7-3.8,three singulets,3H, OCH_3; 6.4-8.6,m,13H_{ar};9.3-10.1,three singulets,1H,NH.

Aroylisothiocyanates, i.e., benzoylisothiocyanate and p-chlorbenzoylisothiocyanate, were prepared according to the procedure reported before[14], based on reaction of the corresponding aroyl chlorides with lead isothiocyanate.

3-Aroyl-1-aryl-4-arylamido-4-arylamino-5-methylidene imidazolidine-2-thiones (3); Typical procedure :
2 mmols of an appropriate α,β-dianil of α,β-diketobutyric acid anilide (2) in 25 ml of dry benzene were mixed with a solution of 2.1 mmols of an aroyl isothiocyanate in 10 ml of dry benzene. The mixture was shortly refluxed (2 to 5 min) and put to stand for 12 h at room temperature. The crystalline product (yields from 35 to 60%) was filtered off, washed with petroleum ether and crystallized from CH_2Cl_2 or ethanol.
4-Anilino-3-benzoyl-4-2′,5′-dichloranilido-1-4′-methoxyphenyl-5-methylidene imidazolidine-2-thione (3a), : m.p., 210-211°C; white needls from ethanol; yield 39% for $C_{31}H_{24}Cl_2N_4O_3S$, m.w., 603.2, calc. %C 61.7 H 4.0 N 9.3 S 5.3 Cl 11.8, found %C 61.5 H 4.0 N 9.3 S 5.6 Cl 12.2.
Ir (Nujol, cm^{-1}) : 3340-3320,m,broad,NH; 1695,s,CO; 1628,s,CO_{an};550,m,C=S.
^1H nmr ($CDCl_3$, TMS, ppm) : 3.8,s,3H,OMe; 4.4,d,1H;4.8,d,1H, J_{HH}=2.3 Hz; 6.8-7.6,m, 15H_{ar}; 7.8,d,2H_{ar},J_{HH}=8 Hz; 8.4,s,1H,NH_{an}; 5.3,s,1H,NH.
Ms (m/z, rel.abundance) : M^+,602, 2.0; M +1,603, 1.5; M +2,604, 1.4; M-Ar_3NCO,415, 46.2; M-Ar_3NHCO,414, 26.8; M-Ar_4CONCS,439, 0.9; M-Ar_2NH,510, 0.9; $Ar_1N{=}C{=}CH_2^+$,147, 12.2; $Ar_1N{\equiv}C{-}CH_3^+$,148, 34.1; $Ar_3NCO^{+\cdot}$,187, 6.7; 189, 6.0; $Ar_4CONCS^{+\cdot}$,163, 3.5; $Ar_2NH_2^{+\cdot}$,93, 7.5; $PhCO^+$,105, 100; $Ar_1NCS^{+\cdot}$,165, 1.1.

4-Anilino-3-benzoyl-4-2′,5′-dichloranilido-1-4′-methylphenyl-5-methylidene imidazolidine-2-thione (3b), : m.p., 225-226°C; white needls from ethanol;yield 33%; for $C_{31}H_{24}Cl_2N_4O_2S$, m.w., 587.2, calc. %C 63.4 H 4.1 N 9.5 S 5.5 Cl 12.1, found %C 63.4 H 4.1 N 9.9 S 6.0 Cl 12.4.
Ir (Nujol/HCB, cm^{-1}) : 3330-3315,m,broad,NH; 1695,s,CO;1630,s,CO_{an}; 570,m,C=S.
^1H nmr ($CDCl_3$,TMS,ppm): 2.5,s,3H,Me; 4.5,d,1H; 4.9,d,1H, J_{HH}=2.3Hz; 5.3,s,1H,NH; 6.7-7.6,m,15H_{ar}; 7.8,d,2H_{ar},J_{HH}=8Hz; 8.4,s,1H,NH_{an}.
Ms (m/z, rel. abundances) : M^+,586, 2.9;M +1,587, 1.5;M +2,588, 2.3; M-Ar_3NCO,399, 33.1; M-Ar_3NHCO,398, 56.2; M-Ar_4CONCS,423, 1.1; M-Ar_2NH,494, 0.8; $Ar_1N{=}C{=}CH_2^{+\cdot}$,131, 2.8; $Ar_1N{\equiv}C{-}CH_3^+$,132, 15.0; $Ar_3NCO^{+\cdot}$,187, 9.1; 189, 6.8; $Ar_4CONCS^{+\cdot}$,163, 2.6; Ar_2NH_2 93, 100; $PhCO^+$,105, 100; $Ar_1NCS^{+\cdot}$,149, 1.8.

4-Anilido-4-anilino-3-benzoyl-1-4′-ethoxyphenyl-5-methylidene imidazolidine-2-thione (3c),: m.p., 230-231°C; white prisms from dichloromethane; yield 44%;for $C_{32}H_{28}N_4O_3S$ m.w., 548.3, calc., %C 70.0 H 5.2 N 10.2 S 5.9, found %C 70.2 H 5.4 N 9.9 S 5.4.
Ir (Nujol/HCB, cm^{-1}) : 3375,m,NH; 3330-3325,m,broad,NH_{an};1685,s,CO; 1660,s,CO_{an};550, m,C=S.
^1H nmr ($CDCl_3$, TMS, ppm) : 1.5,t,3H,J_{HH}=7.2Hz; 4.1 ,q,2H,J_{HH}=7.2Hz; 4.3,d,1H,J_{HH}=2.3 Hz; 4.8,d,1H,J_{HH}=2.3Hz; 5.3,s,1H,NH; 6.6-7.5,m,17H_{ar}; 7.9,d,2H_{ar},J_{HH}=8.0Hz; 8.3,s, 1H,NH_{an}.
Ms (m/z, rel. abundance) : M^+,548, 6.6; M +1,549, 3.0; M-Ar_3NCO,429, 23.6; M-Ar_3NHCO 428, 73.4; M-Ar_4CONCS,385, 7.9; M-Ar_2NH,456, 5.4; $Ar_1N{=}C{=}CH_2$+.,161, 1.1; $Ar_1N{\equiv}C{-}CH_3^+$ 162, 11.8; $Ar_3NCO^{+\cdot}$,119, 16.9; $Ar_4CONCS^{+\cdot}$,163, 6.6; $Ar_1NCS^{+\cdot}$,179, 5.8; $Ar_2NH_2^{+\cdot}$,93, 39.0; $PhCO^+$,105, 100.

4-Anilido-4-anilino-3-benzoyl-1-4′-diethylaminophenyl-5-methylidene imidazolidine-2-thione (3d), : m.p., 219-220°C; white prisms from dichlormethane; yield 58%; for $C_{34}H_{33}N_5O_2S$, m.w., 575.3, calc., %C 70.9 H 5.8 N 12.2 S 5.6, found %C 70.8 H 5.8 N 12.2 S 5.6.

Ir (Nujol/HCB, cm^{-1}) : 3340,m,NH; 3320-3300,w,broad,NH_{an}; 1690,s,CO; 1640,s,CO_{an}; 560,m, C=S.
^1H nmr ($CDCl_3$, TMS, ppm) : 1.2,t,6H,J_{HH}=7.1Hz; 3.4,q,4H,J_{HH}=7.1Hz; 4.6,d,1H,J_{HH}=2.3 Hz; 4.8,d,1H,J_{HH}=2.3Hz; 5.3,s,1H,NH; 6.7-7.5,m,17H_{ar}; 7.9,d,2H_{ar},J_{HH}=8.1Hz; 8.3,s, 1H,NH_{an}.
Ms (m/z, rel.abundance) : M^+,575, 13.8; M +1,576, 6.9; M-Ar_3NCO,456, 27.6; M-Ar_3NHCO,455, 37.9; M-Ar_4CONCS,412, 6.9; M-Ar_2NH,483, 3.4; $Ar_1N{=}C{=}CH_2^{+\cdot}$,188, 8.3; $Ar_1N{\equiv}C{-}CH_3^+$ 189, 22.2; $Ar_3NCO^{+\cdot}$,119, 27.6; $Ar_4CONCS^{+\cdot}$ 163, 0.9; $Ar_1NCS^{+\cdot}$,206, 6.9; $Ar_2NH_2^{+\cdot}$,93, 50.9; $PhCO^+$,105, 100.

4-Anilido-3-benzoyl-4-4′-bromanilino-1-4′-methoxyphenyl-5-methylidene imidazolidine 2-thione (3e), : m.p., 200-201°C; white needls from ethanol; yield 36%;
for $C_{31}H_{25}BrN_4O_3S$, m.w., 613.2, calc., %C 60.7 H 4.1 N 9.1 S 5.2 Br 13.0, found %C 60.4 H 4.1 N 9.0 S 5.2 Br 12.9.
Ir (Nujol/HCB, cm^{-1}) : 3335-3320,m, broad NH; 1690,s,CO; 1635,s,CO_{an}; 542,m,C=S.
^1H nmr ($CDCl_3$, TMS, ppm) : 3.9,s,3H,OMe; 4.5,d,1H,J_{HH}=2.3Hz; 4.9,d,1H,J_{HH}=2.3Hz; 5.3,s,1H,NH; 6.8-7.6,m,16H_{ar}; 7.9,d,2H_{ar},J_{HH}=8.3Hz; 8.4,s,1H,NH_{an}.
Ms (m/z, rel.abundance) : M^+,612, 1.2; M +1,613, 0.7; M +2,614, 1.1; M-Ar_3NCO,493, 6.6; 495, 7.2; M-Ar_3NHCO,492, 6.4; 494, 7.2; M-Ar_4CONCS,449, 1.2; 451, 1.2;M-Ar_2NH, 440, 0.9; $Ar_1N{=}C{=}CH_2^{+\cdot}$,147, 1.1; $Ar_1N{\equiv}C{-}CH_3^+$,148, 8.3; $Ar_3NCO^{+\cdot}$,119, 8.3; Ar_4CONCS, 163, 0.9; $Ar_1NCS^{+\cdot}$,165, 1.9; $Ar_2NH_2^{+\cdot}$,93, 100.

4-Anilido-4-anilino-3-benzoyl-1-4′-dimethyaminophenyl-5-methylidene imidazolidine-2-thione (3f), : m.p., 237-238°C; grey prisms from ethanol; yield 60%;
for $C_{32}H_{29}N_5O_2S$, m.w., 547.3, calc., %C 70.2 H 5.3 N 12.8 S 5.9, found %C 70.1 H 5.4 N 12.7 S 5.7.
Ir (Nujol/HCB, cm^{-1}) : 3400,m,NH; 3335-3325,m,broad NH_{an}; 1695,s,CO; 1640,s,CO_{an}; 540,m,C=S.
^1H nmr ($CDCl_3$, TMS, ppm) : 3.0,s,3H,N-Me; 4.5,d,1H,J_{HH}=2.4 Hz;4.9,d,1H,J_{HH}=2.4Hz; 5.3,s,1H,NH; 6.7-7.6,m,17H_{ar}; 7.9,d,2H_{ar},J_{HH}=8.0Hz; 8.4,s,1H,NH_{an}.
Ms (m/z, rel.abundance) : M^+,547, 13.9; M +1, 548, 5.3; M-Ar_3NCO,428, 7.9;M-Ar_3NHCO 427, 9.9; M-Ar_4CONCS,384, 3.1; M-Ar_2NH,455,1.3; $Ar_1N{=}C{=}CH_2^{+\cdot}$,160, 2.7; $Ar_1N{\equiv}C{-}CH_3^+$, 161, 14.3; $Ar_3NCO^{+\cdot}$,119, 21.3; $Ar_4CONCS^{+\cdot}$,163, 2.2; $Ar_1NCS^{+\cdot}$,178, 3.8; $Ar_2NH_2^{+\cdot}$,93, 36.4; $PhCO^+$,105, 100.

4-Anilido-4-anilino-3-4′-chlorbenzoyl-1-4′-methoxyphenyl-5-methylidene imidazolidine-2-thione (3g), : m.p.,205-207°C; white prisms from dichlormethane; yield 42%;
for $C_{31}H_{25}ClN_4O_3S$, m.w., 568.8, calc., %C 65.4 H 4.4 N 9.9 S 5.6 Cl 6.2, found %C 65.5 H 4.5 N 9.8 S 5.5 Cl 6.0.
Ir (KBr, cm^{-1}) : 3365,m,NH; 3335-3320,m,broad,NH_{an};1692,s,CO; 1644,s,CO_{an}; 1175,s, C_{ar}-Cl; 542,m,C=S.
^1H nmr (DMSO-d6, TMS, ppm) : 3.6,s,3H,OMe; 4.6,d,1H,J_{HH}=2.2Hz; 5.2,d,1H,J_{HH}=2.2Hz; 5.6,s,1H,NH; 6.6-8.1,m,18H_{ar}; 10.1,s,1H,NH_{an}.
Ms (m/z, rel.abundance) : M^+,568, 0.9; M +2,570, 0.4; M-Ar_3NCO,449, 2.4;M-Ar_3NHCO, 448, 2.4; 450, 1.6; M-Ar_4CONCS,371, 2.9; M-Ar_2NH,477, 0.9; $Ar_1N{=}C{=}CH_2^{+\cdot}$,147, 13.9; $Ar_1N{\equiv}C{-}CH_3^+$,148, 18.3; $Ar_3NCO^{+\cdot}$,119, 45.3; $Ar_4CONCS^{+\cdot}$,197, 1.7; 199, 0.5; $Ar_1NCS^{+\cdot}$, 165, 2.0; $Ar_2NH_2^{+\cdot}$,93,100.

4-Anilido-4-anilino-3-4′-chlorbenzoyl-1-4′-diethylaminophenyl-5-methylidene imidazolidine-2-thione (3h), : m.p., 212-213°C; grey prisms from ethanol;yield 48%;
for $C_{34}H_{32}ClN_5O_2S$, m.w., 609.8, calc., %C 66.9 H 5.3 N 11.5 S 5.3 Cl 5.8, found %C 66.9 H 5.3 N 11.3 S 5.3 Cl 5.9 .
Ir (KBr, cm^{-1}) : 3360,m,NH; 3330-3310,m,broad,NH_{an};1680,s,CO; 1635,s,CO_{an}; 1170,s, C_{ar}-Cl; 560,m,C=S.
^1H nmr (DMSO-d6, TMS, ppm) : 1.2,t,6H,J_{HH}=7.3Hz; 3.4,q,4H,J_{HH}=7.3Hz; 4.5,d,1H,J_{HH}= 2.3Hz; 5.2,d,1H,J_{HH}=2.3Hz; 5.7,s,1H,NH; 6.7-8.0,m,18H_{ar}; 10.1,s,1H,NH_{an}.

Ms (m/z, rel.abundance) : $M^{+\cdot}$,609, 3.4; M +1,610, 1.3; M +2,611, 2.2; M-Ar_3NCO,490, 86.8; 492, 32.9; M-Ar_3NHCO,489, 26.8; 491, 34.1; M-Ar_4CONCS,412, 11.6; M-Ar_2NH,517, 0.6; $Ar_1N{=}C{=}CH_2^{+\cdot}$,188, 6.2; $Ar_1N{=}C{-}CH_3^{+}$,189, 54.9; $Ar_3NCO^{+\cdot}$,119, 11.4; $Ar_4CONCS^{+\cdot}$, 197, 1.8; 199, 0.9; $Ar_1NCS^{+\cdot}$, 206, 2.7; $Ar_2NH_2^{+\cdot}$,93, 9.7; 326, 100.

The ir spectra were recorded on an UR-10 Zeiss, IR-75 Zeiss, and a Perkin-Elmer 257 spectrophotometers using Nujol and hexachlorbutadiene (HCB) mulls or KBr pills. The symbols m,s,w, ar, an designated moderate, sharp, weak, aryl, anilide, respectively.

The ^1H nmr spectra were determined on aJeol-100, Tesla 80, and a Hitachi-Perkin-Elmer 60 spectrometers. The symbols s,d,t,q,m,ar,an designated singulet, doublet, triplet, quartet, multiplet, aryl, anilide, respectively. The ^{13}C nmr spectrum was recorded on a Varian XL-100 spectrometer, in $CDCl_3$ (standard TMS).

The mass spectra were determined on an LKB-9000S and a Micromass 3D8 spectrometers under standard conditions, i.e., electron voltage 70 eV, acc.voltage 3.5 kV, D.I. temp.,60-120°C, I.S.temp.,150-250°C.

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