Reaction of 2-Dimethylaminomethylene-1,3-diones with Dinucleophiles. VIII. Synthesis of Ethyl and Methyl 2,4-Disubstituted 5-Pyrimidinecarboxylates [1]

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Received May 5, 1989

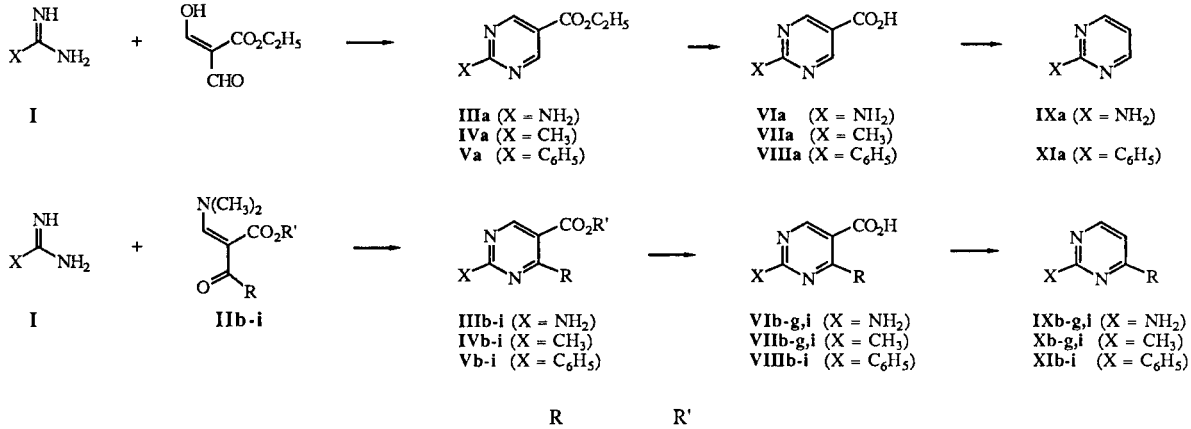
Reaction of ethyl or methyl 2-dimethylaminomethylene-3-oxoalkanoates with *N*-C-*N* dinucleophiles such as guanidine, acetamidine or benzamidine afforded in high yields the relative esters of 4-substituted 2-amino-, 2-methyl- or 2-phenyl-5-pyrimidinecarboxylic acids, respectively. These esters were hydrolyzed to the corresponding carboxylic acids, which were converted by heating to 4-substituted 2-pyrimidinamines, 2-methyl or 2-phenylpyrimidines, respectively, generally in excellent yields. The 4-unsubstituted ethyl 2-amino-, 2-methyl- and 2-phenyl-5-pyrimidinecarboxylates were obtained in moderate yields by reaction of the above dinucleophiles with ethyl 2,2-diformylacetate. These esters were hydrolyzed and the corresponding acids (with the exception of the 2-methyl derivative) were decarboxylated to give 2-pyrimidinamine and 2-phenylpyrimidine in satisfactory yields.

J. Heterocyclic Chem., **27**, 295 (1990).

In a previous paper of this series [2] some of us reported the efficient reaction of ethyl or methyl 2-dimethylaminomethylene-3-oxoalkanoates **IIb,d-i** with a *N-N* dinucleophile such as phenylhydrazine to give the corresponding esters of 5-substituted 1-phenyl-1*H*-pyrazole-4-carboxylic acids as sole products. Later, such a reaction of synthons **IIb,d-i** was extended to a *C*-C-*N* dinucleophile like cyanoacetamide to afford esters of 2-substituted 5-cyano-1,6-dihydro-6-oxo-3-pyridinecarboxylic acids with cardiotonic activity [3].

As a consequence of the neat reactivity of the above synthons and taking into account our former work on the reaction of open-chain *sym*-2-dimethylaminomethylene-1,3-diones with *N*-C-*N* dinucleophiles such as guanidine and amidines **I** to give efficiently a number of 2-substituted 5-acylpyrimidines [4], we have now employed the unsymmetrical synthons **IIb-i** in the reaction with guanidine, acetamidine and benzamidine for the synthesis of 2,4-disubstituted ethyl or methyl 5-pyrimidinecarboxylates **IIIb-i**, **IVb-i** and **Vb-i**.

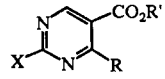
The reactions of **IIb-i** [2,5] with guanidine acetate, acetamidine and benzamidine hydrochloride were carried out in the presence of sodium ethoxide or methoxide in refluxing ethanol or methanol, respectively, to give, generally in 60-88% yields, 4-substituted ethyl or methyl 2-amino-5-pyrimidinecarboxylates **IIIb-i**, 2-methyl-5-pyrimidinecarboxylates **IVb-i** and 2-phenyl-5-pyrimidinecarboxylates **Vb-i** (Table I) as sole products. The low



	R	R'
a	H	C_2H_5
b	CH_3	C_2H_5
c	CH_2OCH_3	CH_3
d	C_2H_5	C_2H_5
e	$(CH_2)_2CH_3$	C_2H_5
f	$CH(CH_3)_2$	C_2H_5
g	$C(CH_3)_3$	C_2H_5
h	$CH_2C_6H_5$	CH_3
i	C_6H_5	C_2H_5

Table I

Esters of 2-Substituted and 2,4-Disubstituted 5-Pyrimidinecarboxylic Acids **IIIa-i, IVa-i, Va-i**



Formula Number	X	R	R'	Reflux Time (hours)	Yield %	Mp °C or bp/mm	Molecular Formula	Analyses % Calcd./Found C	H	N
IIIa	NH_2	H	C_2H_5	4	35	145-147 [a] [b]	$C_7H_9N_3O_2$	50.29 50.34	5.43 5.45	25.14 24.91
IIIb	NH_2	CH_3	C_2H_5	1	81	225-226 [a] [c]	$C_8H_{11}N_3O_2$	53.03 52.77	6.12 6.07	23.19 23.38
IIIc	NH_2	CH_2OCH_3	CH_3	1	66	144-145 [d]	$C_8H_{11}N_3O_3$	48.73 48.72	5.62 5.56	21.31 21.49
IIId	NH_2	C_2H_5	C_2H_5	1	74	164-165 [a]	$C_9H_{13}N_3O_2$	55.37 55.25	6.71 6.72	21.52 21.76
IIIe	NH_2	$(CH_2)_2CH_3$	C_2H_5	1	73	124-125 [a]	$C_{10}H_{15}N_3O_2$	57.40 57.14	7.22 7.23	20.08 20.23
IIIf	NH_2	$CH(CH_3)_2$	C_2H_5	1	70	74-75 [e]	$C_{10}H_{15}N_3O_2$	57.40 57.15	7.22 7.14	20.08 20.03
IIIg	NH_2	$C(CH_3)_3$	C_2H_5	2	81	86-87 [e]	$C_{11}H_{17}N_3O_2$	59.17 59.21	7.67 7.72	18.82 18.85
IIIh	NH_2	$CH_2C_6H_5$	CH_3	1	37	186-187 [a]	$C_{13}H_{13}N_3O_2$	64.19 64.43	5.39 5.29	17.27 17.42
IIIi	NH_2	C_6H_5	C_2H_5	1	80	155-156 [a] [f]	$C_{13}H_{13}N_3O_2$	64.19 64.35	5.39 5.34	17.27 17.20
IVa	CH_3	H	C_2H_5	4	22	110-115/20 [g]	$C_8H_{10}N_2O_2$	57.82 57.48	6.06 6.12	16.86 16.58
IVb	CH_3	CH_3	C_2H_5	24	65	80-81/0.6 [h]	$C_9H_{12}N_2O_2$	59.98 60.07	6.71 6.63	15.54 15.59
IVc	CH_3	CH_2OCH_3	CH_3	24	64	80-85/0.1	$C_9H_{12}N_2O_3$	55.09 54.75	6.16 6.19	14.28 14.58
IVd	CH_3	C_2H_5	C_2H_5	24	67	84-85/0.4	$C_{10}H_{14}N_2O_2$	61.84 62.00	7.26 7.33	14.42 14.32
IVe	CH_3	$(CH_2)_2CH_3$	C_2H_5	24	62	85-90/0.4	$C_{11}H_{16}N_2O_2$	63.44 63.40	7.74 7.49	13.45 13.08
IVf	CH_3	$CH(CH_3)_2$	C_2H_5	24	85	80-82/0.5	$C_{11}H_{16}N_2O_2$	63.44 63.40	7.74 7.60	13.45 13.55
IVg	CH_3	$C(CH_3)_3$	C_2H_5	48	88	85-90/0.7	$C_{12}H_{18}N_2O_2$	64.84 64.88	8.16 8.18	12.60 12.72
IVh	CH_3	$CH_2C_6H_5$	CH_3	24	13	125-130/0.5	$C_{14}H_{14}N_2O_2$	69.40 69.59	5.82 5.81	11.56 11.37
IVi	CH_3	C_6H_5	C_2H_5	24	68	124-126/0.5	$C_{14}H_{14}N_2O_2$	69.40 69.51	5.82 5.60	11.56 11.33
Va	C_6H_5	H	C_2H_5	1	38	85-87 [e]	$C_{13}H_{12}N_2O_2$	68.41 68.24	5.30 5.28	12.27 12.20
Vb	C_6H_5	CH_3	C_2H_5	1	68	95-96 [i] [l]	$C_{14}H_{14}N_2O_2$	69.40 69.36	5.82 5.70	11.56 11.67
Vc	C_6H_5	CH_2OCH_3	CH_3	1	67	97-98 [a]	$C_{14}H_{14}N_2O_3$	65.10 64.93	5.46 5.43	10.85 10.80

Table I (continued)

Formula Number	X	R	R'	Reflux Time (hours)	Yield %	Mp °C or bp/mm	Molecular Formula	Analyses % Calcd./Found C	H	N
Vd	C_6H_5	C_2H_5	C_2H_5	1	71	68-70 [m]	$C_{15}H_{15}N_2O_2$	70.29 70.57	6.29 6.42	10.93 11.10
Ve	C_6H_5	$(CH_2)_2CH_3$	C_2H_5	1	80	39-40 [e]	$C_{16}H_{18}N_2O_2$	71.09 71.21	6.71 6.60	10.36 10.48
Vf	C_6H_5	$CH(CH_3)_2$	C_2H_5	1	60	77-78 [m]	$C_{16}H_{18}N_2O_2$	71.09 71.19	6.71 6.76	10.36 10.52
Vg	C_6H_5	$C(CH_3)_3$	C_2H_5	18	75	160-164/0.5	$C_{17}H_{20}N_2O_2$	71.81 71.73	7.09 6.94	9.85 10.06
Vh	C_6H_5	$CH_2C_6H_5$	CH_3	1	22	60-62 [i]	$C_{19}H_{16}N_2O_2$	74.98 74.61	5.30 5.27	9.20 9.25
Vi	C_6H_5	C_6H_5	C_2H_5	1	72	59-61 [m][n]	$C_{19}H_{16}N_2O_2$	74.98 75.03	5.30 5.24	9.20 9.29

[a] From 95% ethanol. [b] Reference [12], mp 147-149°, reference [13], mp 140-141°. [c] Reference [6], mp 220-222°, 74% yield. [d] From ethyl acetate. [e] From petroleum ether, bp 40-70°. [f] Reference [7], mp 156°, 59% yield; reference [10], mp 153-154°, 84% yield. [g] Reference [14], bp 70-71°/0.45. [h] Reference [8], bp 113-115°/12, 73% yield. [i] From diethyl ether. [l] Reference [9], mp 99-100°. [m] From diethyl ether-petroleum ether 1:1. [n] Reference [10], mp 58-59°, 49% yeild.

Table II

UV, IR and ^{1}H NMR Spectral Data of Compounds **IIIa-i, IVa-i, Va-i**

Compound	UV, λ max nm (log ε)	IR, cm^{-1}	^{1}H NMR, δ
IIIa	260.5 (4.38)	3540, 3430, 1710,1608, 1554 [b]	1.30 (t, J = 6.6, 3H, CH_3), 4.28 (q, J = 6.6, 2H, CH_2), 7.55 (bs, 2H, NH_2; disappears with deuterium oxide), 8.75 (s, 2H, H-4 + H-6) [d]
IIIb	258.5 (4.38)	3290, 3130, 1712,1682, 1592, 1545 [a]	[c]
IIIc	260 (4.38)	3330, 3165, 1710,1655, 1585, 1527 [a]	3.50 (s, 3H, CH_3O), 3.86 (s, 3H, CH_3O), 4.87 (s, 2H, CH_2), 6.89 (bs, 2H, NH_2; disappears with deuterium oxide), 8.83 (s, 1H, H-6) [e]
IIId	258 (4.32)	3295, 3130, 1718,1670, 1587, 1535 [a]	1.16 (t , J = 7.2, 3H, 4-ethyl CH_3), 1.29 (t , J = 7.2, 3H, O-ethyl CH_3), 2.92 (q, J = 7.2, 2H, 4-ethyl CH_2), 4.24 (q, J = 7.2, 2H, O-ethyl CH_2), 7.35 (bs, 2H, NH_2; disappears with deuterium oxide), 8.28 (s, 1H, H-6) [d]
IIIe	257.5 (4.335)	3310, 3140, 1720,1665, 1585, 1535 [a]	0.94 (t , J = 7.2, 3H, propyl CH_3), 1.31 (t , J = 7.2, 3H, ethyl CH_3), 1.57 (mc, 2H, propyl CH_2), 2.90 (t, J = 7.2, 2H, propyl CH_2), 4.25 (q, J = 7.2, 2H, ethyl CH_2), 7.35 (bs, 2H, NH_2; disappears with deuterium oxide), 8.71 (s, 1H, H-6) [d]
IIIf	258.5 (4.33)	3395, 3315, 3190,1710, 1650, 1592,1535 [a]	1.16 [d, J = 5.4, 6H, $(CH_3)_2C$], 1.30 (t, J = 6.6, 3H, ethyl CH_3), 3.6-4.2 (m, 1H, $CHMe_2$), 4.25 (q, J = 6.6, 2H, CH_2), 7.30 (bs, 2H, NH_2; disappears with deuterium oxide), 8.68 (s, 1H, H-6) [d]
IIIg	253 (4.14) 288 sh (3.63)	3390, 3315, 3205,1720, 1665, 1585,1527 [a]	1.32 [mc, 12H, $(CH_3)_3C$ + ethyl CH_3], 4.25 (q, J = 7.2, 2H, CH_2), 7.05 (bs, 2H, NH_2; disappears with deuterium oxide), 8.38 (s, 1H, H-6) [d]
IIIh	259.5 (4.25) 290 sh (3.67)	3315, 3150, 1718, 1664, 1580, 1535 [a]	3.76 (s, 3H, CH_3O), 4.30 (s, 2H, CH_2), 7.26 (s, 5H, C_6H_5), 7.45 (bs, 2H, NH_2; disappears with deuterium oxide), 8.74 (s, 1H, H-6) [d]
IIIi	254 (4.35) 302 sh (3.66)	3405, 3320, 3185, 1690, 1642, 1583, 1570, 1528 [a]	1.02 (t, J = 7.2, 3H, CH_3), 4.06 (q, J = 7.2, 2H, CH_2), 7.46 (near s, 7H, C_6H_5 + NH_2; two protons disappear with deuterium oxide), 8.73 (s, 1H, H-6) [d]

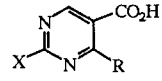
Table II (continued)

Compound	UV, λ max nm (log ε)	IR, cm^{-1}	^1H NMR, δ
IVa	221 (4.07) 250 sh (3.18) 257 sh (2.99) 287 (2.585)	1723, 1593, 1558 [b]	1.44 (t, J = 7.2, 3H, ethyl CH_3), 2.83 (s, 3H, CH_3-2), 4.47 (q, J = 7.2, 2H, CH_2), 9.22 (near s, 2H, H-4 + H-6) [e]
IVb	221.5 (4.06) 248 sh (3.51) 278 sh (3.07)	1722, 1582, 1545 [b]	1.42 (t, J = 7.2, 3H, ethyl CH_3), 2.74 (s, 3H, CH_3-2), 2.78 (s, 3H, CH_3-4), 4.42 (q, J = 7.2, 2H, CH_2), 9.03 (s, 1H, H-6) [e]
IVc	217 (3.985) 248 sh (3.54)	1723, 1577, 1545 [b]	2.72 (s, 3H, CH_3-2), 3.40 (s, 3H, CH_3O), 3.91 (s, 3H, CH_3O), 4.77 (s, 2H, CH_2), 8.98 (s, 1H, H-6) [e]
IVd	222 (3.99) 250 sh (3.47)	1722, 1578, 1545 [b]	1.29 (t, J = 7.2, 3H, 4-ethyl CH_3), 1.41 (t, J = 7.2, 3H, O-ethyl CH_3), 2.75 (s, 3H, CH_3-2), 3.14 (q, J = 7.2, 2H, 4-ethyl CH_2), 4.41 (q, J = 7.2, 2H, O-ethyl CH_2), 9.02 (s, 1H, H-6) [e]
IVe	222.5 (3.99) 250 sh (3.49) 280 (3.00)	1722, 1577, 1543 [b]	1.02 (t, J = 7.2, 3H, propyl CH_3), 1.41 (t, J = 7.2, 3H, ethyl CH_3), 1.68 (mc, 2H, propyl CH_2), 2.75 (s, 3 H, CH_3-2),3.11 (mc, 2H, propyl, CH_2), 4.41 (q, J = 7.2, 2H, ethyl CH_2), 9.02 (s, 1H, H-6) [e]
IVf	221.5 (3.99) 250 sh (3.51) 278 (3.15)	1720, 1578, 1535 [b]	1.27 [d, J = 7.2, 6H, $(CH_3)_2C$], 1.39 (t, J = 7.2, 3H, ethyl CH_3), 2.73 (s, 3H, CH_3-2), 3.88 (mc, 1H, $CHMe_2$), 4.40 (q, J = 7.2, 2H, ethyl CH_2), 8.95 (s, 1H, H-6) [e]
IVg	214 (3.71) 251 (3.45)	1725, 1574, 1525 [b]	1.39 [mc, 12H, $(CH_3)_3C$ + ethyl CH_3], 2.70 (s, 3H, CH_3-2), 4.41 (q, J = 7.2 2H, CH_2), 8.60 (s, 1H, H-6) [e]
IVh	256 (3.67) 281 (3.83) 315 sh (3.65)	1723, 1573, 1540 [b]	2.75 (s, 3H, CH_3-2), 3.86 (s, 3H, CH_3O), 4.51 (s, 2H, CH_2), 7.26 (s, 5H, C_6H_5), 9.05 (s, 1H, H-6) [e]
IVi	214 sh (4.12) 268 (4.00)	1722, 1566, 1534 [b]	1.11 (t, J = 7.2, 3H, ethyl CH_3), 2.83 (s, 3H, CH_3-2), 4.20 (q, J = 7.2, 2H, CH_2), 7.51 (mc, 5H, C_6H_5), 9.01 (s, 1H, H-6) [e]
Va	281 (4.22)	1722, 1588, 1545 [b]	1.40 (t, J = 7.2, 3H, CH_3), 4.44 (q, J = 7.2, 2H, CH_2), 7.54 (mc, 3H, 2H ar *m* + 1H ar *p*), 8.54 (mc, 2H, 2H ar *o*), 9.32 (s, 2H, H-4 + H-6) [e]
Vb	279 (4.43)	1718, 1570, 1534 [b]	1.38 (t, J = 7.2, 3H, ethyl CH_3), 2.86 (s, 3H, CH_3-4), 4.39 (q, J = 7.2, 2H, CH_2), 7.50 (mc, 3H, 2H ar *m* + 1H ar *p*), 8.52 (mc, 2H, 2H ar *o*), 9.18 (s, 1H, H-6) [e]
Vc	280 (4.40)	1720, 1567, 1533 [b]	3.55 (s, 3H, CH_3O), 3.94 (s, 3H, CH_3O), 4.97 (s, 2H, CH_2), 7.52 (mc, 3H, 2H ar *m* + 1H ar *p*), 8.57 (mc, 2H, 2H ar *o*), 9.20 (s, 1H, H-6) [e]
Vd	278 (4.39)	1717, 1565, 1530 [b]	1.38 (t, J = 7.2, 6H, $2CH_3$), 3.23 (q, J = 7.2, 2H, 4-ethyl CH_2), 4.39 (q, J = 7.2, 2H, O-ethyl CH_2), 7.50 (mc, 3H, 2H ar *m* + 1H ar *p*), 8.56 (mc, 2H, 2H ar *o*), 9.17 (s, 1H, H-6) [e]
Ve	279 (4.39)	1718, 1566, 1530 [b]	1.05 (t, J = 6.6, 3H, propyl CH_3), 1.37 (t, J = 7.2, 3H, ethyl CH_3), 1.85 (mc, 2H, propyl CH_2), 3.19 (t, J = 6.6, 2H, propyl CH_2), 4.38 (q, J = 7.2, 2H, ethyl CH_2), 7.49 (mc, 3H, 2H ar *m* + 1H ar *p*), 8.54 (mc, 2H, 2H ar *o*), 9.16 (s, 1H, H-6) [e]
Vf	278.5 (4.39)	1715, 1566, 1528 [b]	1.42 [mc, 9H, $(CH_3)_2C$ + ethyl CH_3], 4.00 (mc, 1H, $CHMe_2$), 4.42 (q, J = 7.2, 2H, CH_2), 7.51 (mc, 3H, 2H ar *m* + 1H ar *p*),8.58 (mc, 2H, 2H ar *o*), 9.15 (s, 1H, H-6) [e]
Vg	269 (4.35)	1720, 1562, 1512 [b]	1.37 (t, J = 7.2, 3H, ethyl CH_3), 1.50 [s, 9H, $(CH_3)_3C$], 4.41 (q, J = 7.2, 2H, CH_2), 7.51 (mc, 3H, 2H ar *m* + 1H ar *p*), 8.52 (mc, 2H, 2H ar *o*), 8.78 (s, 1H, H-6) [e]
Vh	281 (4.40)	1723, 1566, 1530 [b]	3.89 (s, 3H, CH_3O), 4.60 (s, 2H, CH_2), 7.1-7.7 (m, 8H, 2H ar *m* + 1H ar *p* + C_6H_5), 8.54 (mc, 2H, 2H ar *o*), 9.20 (s, 1H, H-6) [e]
Vi	269 (4.495)	1712, 1560, 1527 [b]	1.12 (t, J = 7.2, 3H, CH_3) 4.23 (q, J = 7.2 , 2H, CH_2), 7.53 (mc, 8H, 2H ar *m* + 1H ar *p* + C_6H_5-4), 8.57 (mc, 2H, 2H ar *o*), 9.16 (s, 1H, H-6) [e]

[a] In potassium bromide. [b] In chloroform. [c] The product was insufficiently soluble in the common solvents for nmr measurement. [d] In DMSO-d_6. [e] In deuteriochloroform.

Table III

2-Substituted and 2,4-Disubstituted 5-Pyrimidinecarboxylic Acids **VIa-g, i, VIIa-g,i, VIIIa-i**



Formula Number	X	R	Yield %	Mp °C	Molecular Formula	Analyses % Calcd./Found C	H	N
VIa	NH_2	H	60	>300 [a]	$C_5H_5N_3O_2$	43.17 43.02	3.62 3.64	30.21 29.98
VIb	NH_2	CH_3	93	>300 [b]	$C_6H_7N_3O_2$	47.06 46.95	4.61 4.58	27.44 27.49
VIc	NH_2	CH_2OCH_3	74	267 dec [c]	$C_7H_9N_3O_3$	45.90 46.06	4.95 4.96	22.94 23.07
VId	NH_2	C_2H_5	99	>300 [c]	$C_7H_9N_3O_2$	50.29 50.33	5.43 5.53	25.14 25.09
VIe	NH_2	$(CH_2)_2CH_3$	99	279-280 [c]	$C_8H_{11}N_3O_2$	53.03 53.07	6.12 6.20	23.19 23.24
VIf	NH_2	$CH(CH_3)_2$	92	285-287 [c]	$C_8H_{11}N_3O_2$	53.03 53.23	6.12 6.20	23.19 23.14
VIg	NH_2	$C(CH_3)_3$	67	238-240 [d]	$C_9H_{13}N_3O_2$	55.37 55.43	6.71 6.78	21.52 21.72
VIi	NH_2	C_6H_5	94	275-276 [c] [e]	$C_{11}H_9N_3O_2$	61.39 61.29	4.21 4.23	19.52 19.57
VIIa	CH_3	H	88	195-196 [f] [g] [h]	$C_6H_6N_2O_2$	52.17 52.31	4.38 4.45	20.28 20.06
VIIb	CH_3	CH_3	72	154-155 [f] [g]	$C_7H_8N_2O_2$	55.25 55.34	5.30 5.34	18.41 18.30
VIIc	CH_3	CH_2OCH_3	60	149-150 [f] [g]	$C_8H_{10}N_2O_3$	52.74 52.71	5.53 5.65	15.38 15.28
VIId	CH_3	C_2H_5	86	163-164 [f]	$C_8H_{10}N_2O_2$	57.82 58.05	6.06 6.13	16.86 16.79
VIIe	CH_3	$(CH_2)_2CH_3$	77	100-101 [i]	$C_9H_{12}N_2O_2$	59.98 59.87	6.71 6.88	15.54 15.28
VIIf	CH_3	$CH(CH_3)_2$	99	170-171 [d]	$C_9H_{12}N_2O_2$	59.98 60.17	6.71 6.80	15.54 15.30
VIIg	CH_3	$C(CH_3)_3$	77	158-159 [c]	$C_{10}H_{14}N_2O_2$	61.84 62.12	7.26 7.42	14.42 14.36
VIIi	CH_3	C_6H_5	85	216-217 [c]	$C_{12}H_{10}N_2O_2$	67.28 67.21	4.70 4.70	13.08 13.10
VIIIa	C_6H_5	H	88	283-285 [c]	$C_{11}H_8N_2O_2$	65.99 65.82	4.03 3.98	13.99 13.92
VIIIb	C_6H_5	CH_3	90	247-248 [c] [l]	$C_{12}H_{10}N_2O_2$	67.28 67.06	4.70 4.64	13.08 13.00
VIIIc	C_6H_5	CH_2OCH_3	96	192-193 [c]	$C_{13}H_{12}N_2O_3$	63.93 64.04	4.95 4.95	11.47 11.50
VIIId	C_6H_5	C_2H_5	94	222-224 [c]	$C_{13}H_{12}N_2O_2$	68.41 68.11	5.30 5.21	12.27 12.21

Table III (continued)

Formula Number	X	R	Yield %	Mp °C	Molecular Formula	Analyses % Calcd./Found C	H	N
VIIIe	C_6H_5	$(CH_2)_2CH_3$	99	186-187 [c]	$C_{14}H_{14}N_2O_2$	69.40 69.13	5.82 5.80	11.56 11.74
VIIIf	C_6H_5	$CH(CH_3)_2$	99	216-217 [c]	$C_{14}H_{14}N_2O_2$	69.40 69.56	5.82 5.79	11.56 11.72
VIIIg	C_6H_5	$C(CH_3)_3$	99	180-181 [c]	$C_{15}H_{16}N_2O_2$	70.29 70.01	6.29 6.34	10.93 10.75
VIIIh	C_6H_5	$CH_2C_6H_5$	61	239-240 [c]	$C_{18}H_{14}N_2O_2$	74.47 74.22	4.86 4.78	9.65 9.55
VIIIi	C_6H_5	C_6H_5	99	186-187 [c]	$C_{17}H_{12}N_2O_2$	73.90 73.94	4.38 4.36	10.14 10.20

[a] From water; reference [12], mp >300°; reference [13], mp >290°. [b] From water - DMSO 1:1; reference [6], mp 313-316° dec. [c] From 95% ethanol. [d] From diethyl ether. [e] Reference [7], mp 271-274° dec; 75% yield. [f] From ethyl acetate. [g] This acid was obtained by hydrolysis of the corresponding ester with 2*N* sodium hydroxide at room temperature (see Experimental). [h] Reference [14], mp 196°. [i] From diethyl ether-petroleum ether 1:1. [l] Reference [8], mp 243° dec.

yields obtained with synthon **IIh** in the above reaction could be ascribed to its difficult purification; consequently, **IIh** was used crude and this led probably to poor yields.

The structure of esters **IIIb,i**, **IVb** and **Vb** was proved by comparison with the products obtained from esters of 2-ethoxymethylene-3-oxoalkanoic acids which were formerly used in few instances in the reaction with guanidine [6,7], acetamidine [8] and benzamidine [9]. Moreover, for these and the remaining compounds **III**, **IV** and **V**, other evidence was provided by their conversion to 4-substituted 2-pyrimidinamines **IXb-g,i** 2-methylpyrimidines **Xb-g,i** and 2-phenylpyrimidines **XIb-i**, respectively (see later). Finally, the ir and ^1H nmr spectral data of esters **IIIb-i**, **IVb-i** and **Vb-i** (Table II) were in agreement with the proposed structures.

Esters **IIIi** and **Vi** were the sole products described in the literature which were prepared by our procedure, starting from synthon **IIi** [10].

The 4-unsubstituted ethyl 2-amino-, 2-methyl- and 2-phenyl-5-pyrimidinecarboxylates **IIIa**, **IVa** and **Va** were prepared in moderate yields by reaction of ethyl 2,2-diformylacetate [11] with guanidine, acetamidine and benzamidine, respectively. Esters **IIIa** and **IVa** were already known [12-14], therefore their structure was proved by comparison with the products obtained by other routes.

Esters **IIIa-g,i**, **IVd-g,i** and **Va-i** were converted in 61-99% yields to the corresponding 4-substituted 2-aminopyrimidine-5-carboxylic acids **VIa-g,i**, 2-methylpyrimidine-5-carboxylic acids **VIIa,d-g,i** and 2-phenylpyrimidine-5-carboxylic acids **VIIIa-i** (Tables III and IV), by saponification with potassium hydroxide in boiling ethanol followed by acidification. Hydrolysis of esters **IVa-c** with the above procedure gave no appreciable results; therefore these compounds were saponified in 60-88% yields following the method already described for **IVa** [14], namely treatment with 2*N* sodium hydroxide at room temperature. Esters **IIIh** and **IVh** were not saponified owing to the small quantity of compounds to our disposal. Finally, decarboxylation of the above 5-pyrimidinecarboxylic acids by simply heating at temperatures above their melting points led to 2-pyrimidinamines **IXa-g,i**, 2-methylpyrimidines **Xb-g,i** and 2-phenylpyrimidines **XIa-i** (Table V) in 55-99% yields. The sole exception was acid **VIIa**, whose attempted decarboxylation gave no appreciable results.

Several of these pyrimidines, prepared by other routes, are already known; therefore, the identity of their physical constants and spectral data with those of our compounds (Table VI) unequivocally established the structures of pyrimidines **IX**, **X**, **XI** and consequently also those of starting esters **III**, **IV**, **V**.

In conclusion, the reaction of esters of 2-dimethylaminomethylene-3-oxoalkanoic acids with guanidine and amidines seems to offer another useful synthetic pathway to functionalized pyrimidines, whose interest as naturally occurring and biologically active substances is well known (*cf* [4]). Work is in progress to extend the above reaction to other synthons like **IIb**-i and other *N*-C-*N* dinucleophiles.

Table IV

UV, IR and ^{1}H NMR Spectral Data of Compounds **VIa-g,i, VIIa-g,i, VIIIa-i**

Compound	UV, λ max nm (log ε)	IR, cm^{-1} (potassium bromide)	^{1}H NMR, δ (DMSO-d_6)
VIa	253.5 (4.13)	3440, 3325, 3210, 3000-2300, 1675,1632, 1598	[a]
VIb	253.5 (3.95)	3270, 3120, 2900-2500, 1665, 1583, 1535	2.55 (s, 3H, CH_3), 7.27 (s, 2H, NH_2; disappears with deuterium oxide), 8.70 (s, 1H, H-6)
VIc	256 (4.26)	3405, 3310, 3205, 2700-2400, 1687, 1653, 1597, 1530	3.35 (s, 3H, CH_3), 4.68 (s, 2H, CH_2), 7.42 (s, 2H, NH_2; disappears with deuterium oxide), 8.70 (s, 1H, H-6)
VId	255 (3.93)	3295, 3125, 3000-2500, 1664, 1585, 1533	1.16 (t, J = 7.2, 3H, CH_3), 2.96 (q, J = 7.2, 2H, CH_2), 7.27 (s, 2H, NH_2; disappears with deuterium oxide), 8.69 (s, 1H, H-6)
VIe	254.5 (4.28)	3330, 3180, 2700-2400, 1665, 1580, 1530	0.93 (t, J = 7.2, 3H, CH_3), 1.58 (m, 2H, CH_2), 2.94 (t, J = 7.8, 2H, CH_2), 7.25 (s, 2H, NH_2; disappears with deuterium oxide), 8.70 (s, 1H, H-6). ~11.5 (bs, 1H, CO_2H; disappears with deuterium oxide)
VIf	254 (4.235)	3380, 3330, 3205, 2800-2500, 1698, 1656, 1585, 1527	1.17 (d, J = 6.5, 6H, $2CH_3$), 4.00 (h, J = 6.5, 1H, $CHMe_2$), 7.20 (bs, 3H, NH_2 + CO_2H; disappears with deuterium oxide), 8.70 (s, 1H, H-6)
VIg	249 (4.09) 287 sh (3.62)	3490, 3300, 2900-2400, 1728, 1657, 1620, 1594	1.39 [s, 9H, $(CH_3)_3C$], 8.64 (s, 1H, H-6), ~10.75 (bs, 3H, NH_2 + CO_2H; disappears with deuterium oxide)
VIi	252 (4.36) 307 (3.70)	3290, 3190, 3000-2400, 1680, 1628, 1586, 1527	7.37 (s, 3H, NH_2 + CO_2H; disappears with deuterium oxide), 7.47 (s, 5H, C_6H_5), 8.75 (s, 1H, H-6)
VIIa	217 (4.02) 251 (3.25)	3000-2300, 1715, 1600, 1575	2.72 (s, 3H, CH_3), 9.12 (s, 2H, H-4 + H-6)
VIIb	221 (3.94) 251 (3.36)	3100-2300, 1722, 1590, 1547	2.65 (s, 3H, CH_3-4), 2.71 (s, 3H, CH_3-2), 8.99 (s, 1H, H-6), ~12.2 (bs, 1H, CO_2H; disappears with deuterium oxide)
VIIc	214 (3.95) 252 (3.40)	2900-2200, 1712, 1587, 1540	2.72 (s, 3H, CH_3-2), 3.40 (s, 3H, CH_3O), 4.82 (s, 2H, CH_2), 9.03 (s, 1H, H-6), ~13.5 (bs, 1H, CO_2H; disappears with deuterium oxide)
VIId	218.5 (3.89) 250 (3.40)	2900-2400, 1708, 1583, 1535	1.24 (t, J = 7, 3H, CH_3), 2.68 (s, 3H, CH_3-2), 3.11 (q, J = 7, 2H, CH_2), 9.00 (s, 1H, H-6), ~12 (bs, 1H, CO_2H; disappears with deuterium oxide)
VIIe	220 (3.95) 251 (3.51)	2800-2400, 1712, 1584, 1546	0.94 (t, J = 7.2, 3H, CH_3), 1.64 (mc, 2H, CH_2), 2.65 (s, 3H, CH_3-2), 3.06 (t, J = 7.2, 2H, CH_2), 8.99 (s, 1H, H-6), ~12.95 (bs, 1H, CO_2H; disappears with deuterium oxide)
VIIf	221 (3.95) 251 (3.47)	2800-2400, 1707, 1576, 1542	1.22 [d, J = 6.5, 6H, $(CH_3)_2C$], 2.68 (s, 3H, CH_3-2), 3.97 (h, J = 6.5, 1H, $CHMe_2$), 8.98 (s, 1H, H-6), ~11.25 (bs, 1H, CO_2H; disappears with deuterium oxide)
VIIg	252.5 (3.53)	2800-2400, 1708, 1583, 1530	1.39 [s, 9H, $(CH_3)_3C$], 2.64 (s, 3H, CH_3-2), 8.70 (s, 1H, H-6), ~12 (bs, 1H, CO_2H; disappears with deuterium oxide)
VIIi	253 (4.08) 274.5 (4.31)	2800-2400, 1725, 1572, 1532	2.73 (s, 3H, CH_3-2), 7.57 (mc, 5H, C_6H_5), 9.02 (s, 1H, H-6)
VIIIa	277 (4.39)	3000-2400, 1678, 1583, 1542	7.65 (mc, 3H, 2H ar *m* + 1H ar *p*), 8.52 (mc, 2H, 2H ar *o*), 9.34 (s, 2H, H-4 + H-6)
VIIIb	276.5 (4.38)	3000-2500, 1694, 1567, 1530	2.83 (s, 3H, CH_3), 7.60 (mc, 3H, 2H ar *m* + 1H ar *p*), 8.48 (mc, 2H, 2H ar *o*), 9.18 (s, 1H, H-6)
VIIIc	277.5 (4.39)	3000-2400, 1705, 1572, 1530	3.49 (s, 3H, CH_3O), 4.92 (s, 2H, CH_2), 7.61 (mc, 3H, 2H ar *m* + 1H ar *p*), 8.50 (mc, 2H, 2H ar *o*), 9.21 (s, 1H, H-6)
VIIId	271.5 (4.33)	2800-2300, 1692, 1567, 1528	1.33 (t, J = 7.2, 3H, CH_3), 3.22 (q, 7.2, 2H, CH_2), 7.60 (mc, 3H, 2H ar *m* + 1H ar *p*), 8.51 (mc, 2H, 2H ar *o*), 9.20 (s, 1H, H-6)
VIIIe	271 (4.33)	2900-2500, 1683, 1558, 1522	1.01 (t, J = 7.2, 3H, CH_3), 1.82 (sext, J = 7.2, 2H ,CH_2), 3.20 (t, J = 7.2, 2H, CH_2), 7.60 (mc, 3H, 2H ar *m* + 1H ar *p*), 8.50 (mc, 2H, 2H ar *o*), 9.22 (s, 1H, H-6), ~11.5 (bs, 1H, CO_2H; disappears with deuterium oxide)

Table IV (continued)

Compound	UV, λ max nm (log ε)	IR, cm^{-1} (potassium bromide)	^1H NMR, δ (DMSO-d_6)
VIIIf	270 (4.34)	2900-2500, 1682, 1556, 1522	1.35 (d, J = 6.5, 6H, $2CH_3$), 4.09 (h, J = 6.5, 1H, $2CHMe_2$), 7.62 (mc, 3H, 2H ar *m* + 1H ar *p*), 8.54 (mc, 2H, 2H ar *o*), 9.21 (s, 1H, H-6), ~13 (bs, 1H, CO_2H)
VIIIg	266 (4.305)	2800-2300, 1718, 1587, 1570, 1510	1.52 [s, 9H, $(CH_3)_3C$], 7.61 (mc, 3H, 2H ar *m* + 1H ar *p*), 8.49 (mc, 2H, 2H ar *o*), 8.95 (s, 1H, H-6)
VIIIh	270 (4.32)	2800-2500, 1688, 1566, 1528	4.62 (s, 2H, CH_2), 7.35 (s, 5H, C_6H_5), 7.4-7.8 (m, 3H, 2H ar *m* + 1H ar *p*), 8.48 (mc, 2H, 2H ar *o*), 9.27 (s, 1H, H-6), ~13.5 (bs, 1H, CO_2H; disappears with deuterium oxide)
VIIIi	259.5 (4.47)	2900-2300, 1725, 1660, 1587, 1560, 1528	7.64 (mc, 8H, 2H ar *m* + 1H ar *p* + C_6H_5), 8.53 (mc, 2H, 2H ar *o*), 9.24 (s 1H, H-6)

[a] The product was insufficiently soluble in the common solvents for nmr measurement.

EXPERIMENTAL

The uv spectra were measured in 95% ethanol with a Perkin-Elmer Model Lambda 3 spectrophotometer. The ir spectra were taken on a Perkin-Elmer Model 398 spectrophotometer and the ^1H nmr spectra were recorded on a Perkin-Elmer Model R-100 instrument (60 MHz, TMS as internal standard, J in Hz). Melting points were determined with a Fisher-Johns apparatus.

General Procedure for Esters of 2,4-Disubstituted 5-Pyrimidinecarboxylic Acids **IIIb-i, IVb-i, Vb-i.**

To a solution of sodium ethoxide or methoxide (in the case of **IIc,h**) in ethanol or methanol, prepared from sodium (0.23 g, 10 mmoles) and anhydrous ethanol or methanol, respectively (50 ml), guanidine acetate or acetamidine, benzamidine hydrochloride (10 mmoles) was added at room temperature, followed by a solution of **IIb-i** [2,5] (10 mmoles) in anhydrous ethanol or methanol (50 ml). The solution was refluxed for a certain time (see Table I), evaporated under reduced pressure and the residue was treated with water (150 ml). In the case of **IIIb-i** and **Vb-d,f,h,i**, a crystalline precipitate separated, which was filtered and recrystallized from a suitable solvent. In all the other cases, the resulting mixture was extracted thoroughly with diethyl ether. The extracts were dried (magnesium sulfate) and evaporated to give a residue which was recrystallized from a suitable solvent or purified by bulb-to-bulb distillation *in vacuo*.

General Procedure for 2-Substituted Ethyl 5-Pyrimidinecarboxylates **IIIa, IVa, Va.**

By proceeding as above, a solution of ethyl 2,2-diformylacetate [11] (1.44 g, 10 mmoles), sodium ethoxide (10 mmoles), guanidine acetate or acetamidine, benzamidine hydrochloride (10 mmoles) in anhydrous ethanol was refluxed for a certain time and worked up as described above. In the case of **IIIa** and **Va**, the compounds were purified by recrystallization, whereas **IVa** was obtained pure by distillation *in vacuo*.

Elemental analyses, reflux times, yields and mp or bp of these esters are reported in Table I; uv, ir and ^1H nmr spectral data in Table II.

General Procedure for 2,4-Disubstituted 5-Pyrimidinecarboxylic Acids **VIa-g,i, VIId-g,i, VIIIa-i.**

Potassium hydroxide (1.68 g, 30 mmoles) dissolved in methanol or 95% ethanol (10 ml) was added to a solution of the corresponding ester **III, IV** or **V** (10 mmoles) in the same solvent (10 ml). The resulting solution was refluxed with stirring for 5 hours, the solvent was evaporated under reduced pressure and the residue was dissolved with water (50 ml). The solution was acidified with 6*N* hydrochloric acid (*p*H ~ 1) and the white solid which separated was filtered, washed with water, dried in a vacuum oven at 100° and purified by recrystallization from a suitable solvent (Table III).

General Procedure for 2-Methyl-5-pyrimidinecarboxylic Acids **VIIa-c.**

Esters **IVa-c** (10 mmoles) were added to 2*N* sodium hydroxide (5 ml) and the mixture was stirred at room temperature for 1 hour. The final solution was acidified with concentrated hydrochloric acid (*p*H ~ 1), the white precipitate was filtered, dried in a vacuum oven at 100° and purified by recrystallization from ethyl acetate.

Elemental analyses, yields and mp of these acids are reported in Table III; uv, ir and ^1H nmr spectral data in Table IV.

General Procedure for 2-Substituted and 2,4-Disubstituted Pyrimidines **IXa-g,i, Xb-g,i, XIa-i.**

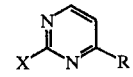
Acids **VI, VII** or **VIII** (about 10 mmoles) were decarboxylated by heating at temperatures above their melting points for a certain time (Table V) until the evolution of carbon dioxide subsided. The products were purified by distillation *in vacuo* or by recrystallization from a suitable solvent.

Acknowledgements.

The authors wish to thank Mr. A. Panaro for the microanalyses and Mr. F. Fasce and C. Rossi for the uv, ir and ^1H nmr spectra. Financial support from CNR, Rome, is gratefully acknowledged.

Table V

2-Substituted and 2,4-Disubstituted Pyrimidines **IXa-g,i, Xb-g,i, XIa-i**



Formula Number	X	R	Heating Time (hours)	Yield %	Mp °C [a] or bp/mm	Literature mp °C of bp/mm	Molecular Formula	Analyses % Calcd./Found C	H	N
IXa	NH_2	H	3	74	125-126	127-128 [15] 122-126 [16]	$C_4H_5N_3$			
IXb	NH_2	CH_3	2	83	155-157	159-160 [17] 158-159 [18]	$C_5H_7N_3$			
IXc	NH_2	CH_2OCH_3	2	55	120-121	123-124 [19]	$C_6H_9N_3O$			
IXd	NH_2	C_2H_5	1.5	66	135-136	139-141 [20] 136 [18]	$C_6H_9N_3$			
IXe	NH_2	$(CH_2)_2CH_3$	1.5	71	122-123	122-123 [18] [21]	$C_7H_{11}N_3$			
IXf	NH_2	$CH(CH_3)_2$	2	91	116-117	117-118 [22] 116.5-119 [23]	$C_7H_{11}N_3$			
IXg	NH_2	$C(CH_3)_3$	7	83	100-102 [b]	103-105.5 [24] 102.5-104 [25]	$C_8H_{13}N_3$			
IXi	NH_2	C_6H_5	2	50	162-163	166 [29] 165 [21] [31] 160-161 [18]	$C_{10}H_9N_3$			
Xb	CH_3	CH_3	6	85	50-55/18	146/760 [30]	$C_6H_8N_2$			
Xc	CH_3	CH_2OCH_3	6	74	75-80/18	82-83/15 [34]	$C_7H_{10}N_2O$			
Xd	CH_3	C_2H_5	20	80	60-65/18	57-58/16 [26]	$C_7H_{10}N_2$			
Xe	CH_3	$(CH_2)_2CH_3$	36	68	75-80/16	98/50 [27]	$C_8H_{12}N_2$	70.55 70.30	8.88 8.87	20.57 20.78
Xf	CH_3	$CH(CH_3)_2$	22	78	60-65/16		$C_8H_{12}N_2$	70.55 70.65	8.88 9.00	20.57 20.71
Xg	CH_3	$C(CH_3)_3$	36	80	75-80/16	[28]	$C_9H_{14}N_2$	71.96 71.70	9.39 9.36	18.65 18.80
Xi	CH_3	C_6H_5	4	99	50-51	54 [29]	$C_{11}H_{10}N_2$			
XIa	C_6H_5	H	2	92	37 [b]	37-38 [33]	$C_{10}H_8N_2$			
XIb	C_6H_5	CH_3	5	96	110-115/0.8	279/762; 22.5 [30] 275-279/760; 25 [18]	$C_{11}H_{10}N_2$			
XIc	C_6H_5	CH_2OCH_3	5	67	110-120/0.3		$C_{12}H_{12}N_2O$	71.98 72.00	6.04 6.02	13.99 13.94
XId	C_6H_5	C_2H_5	5	90	108-110/0.5	135-140/5 [18] 113-115/12 [27]	$C_{12}H_{12}N_2$			
XIe	C_6H_5	$(CH_2)_2CH_3$	16	86	105-110/0.3	153-155/10 [18] 130/2 [27]	$C_{13}H_{14}N_2$			
XIf	C_6H_5	$CH(CH_3)_2$	5	90	114-116/0.6		$C_{13}H_{14}N_2$	78.75 78.70	7.12 7.07	14.13 14.20
XIg	C_6H_5	$C(CH_3)_3$	8	94	95-100/0.05		$C_{14}H_{16}N_2$	79.21 79.31	7.60 7.75	13.20 13.26
XIh	C_6H_5	$CH_2C_6H_5$	5	95	82-84		$C_{17}H_{14}N_2$	82.90 82.64	5.73 5.70	11.37 11.31
XIi	C_6H_5	C_6H_5	5	96	69-70	71-72 [18] 71 [31]	$C_{16}H_{12}N_2$			

[a] From diethyl ether. [b] From petroleum ether.

Table VI

UV, IR and ^{1}H NMR Spectral Data of Compounds **IXa-g,i, Xa-g,i, XIa-i**

Compound	UV, λ max nm (log ε)	IR, -cm^{-1}	^{1}H NMR, δ
IXa	226 (4.16) 297 (3.50)	3535, 3430, 1607, 1566, 1465, 1448 [a]	5.81 (bs, 2H, NH_2; disappears with deuterium oxide), 6.58 (t, J = 5, 1H, H-5), 8.30 (d, J = 5, 2H, H-4 + H-6) [e]
IXb	226 (4.16) 292 (3.63)	3535, 3422, 1604, 1582, 1565, 1458 [a]	2.24 (s, 3H, CH_3), 6.45 (d, J = 5, 1H, H-5), ~6.5 (bs, 2H, NH_2; disappears with deuterium oxide), 8.10 (d, J = 5, 1H, H-6) [c]
IXc	226.5 (4.17) 295 (3.61)	3330, 3170, 1657, 1570, 1480 [b]	3.37 (s, 3H, CH_3), 4.28 (s, 2H, CH_2), 6.62 (d, J = 5, 3H, H-5 and NH_2; two protons disappear with deuterium oxide), 8.27 (d, J = 5, 1H, H-6) [c]
IXd	226 (4.17) 292 (3.64)	3330, 3160, 1655, 1570, 1560, 1467 [b]	1.15 (t, J = 7.2, 3H, CH_3), 2.50 (q, J = 7.2, 2H, CH_2), 6.46 (d, J = 5, 1H, H-5), 6.50 (s, 2H, NH_2; disappears with deuterium oxide), 8.14 (d, J = 5, 1H, H-6) [c]
IXe	226.5 (4.14) 293 (3.63)	3335, 3170, 1657, 1583, 1562, 1473 [b]	0.90 (t, J = 7.2, 3H, CH_3), 1.58 (sex, J = 7.2, 2H, CH_2), 2.47 (t, J = 7.2, 2H, CH_2), 6.45 (d, J = 5, 2H, H-5), 6.50 (s, 2H, NH_2; disappears with deuterium oxide), 8.14 (d, J = 5, 1H, H-6) [c]
IXf	225.5 (4.13) 291.5 (3.62)	3330, 3165, 1657, 1570, 1462 [b]	1.15 (d, J = 6, 6H, $2CH_3$), 2.73 (mc, 1H, $CHMe_2$), 6.46 (d, J = 5, 1H, H-5), 6.50 (s, 2H, NH_2; disappears with deuterium oxide), 8.15 (d, J = 5, 1H, H-6) [c]
IXg	225 (4.09) 290 (3.59)	3405, 3315, 3185, 1635, 1577, 1552, 1465 [b]	1.19 [s, 9H, $(CH_3)_3C$], 6.40 (s, 2H, NH_2 ; disappears with deuterium oxide), 6.56 (d, J = 5, 1H, H-5), 8.16 (d, J = 5, 1H, H-6) [c]
IXi	240 (4.15) 314 (3.74)	3320, 3170, 1643, 1552, 1467 [b]	6.73 (s, 2H, NH_2 ; disappears with deuterium oxide), 7.14(d, J = 5, 1H, H-5), 7.54 (mc, 3H, 2H ar *m* + 1H ar *p*), 8.10 (mc, 2H, 2H ar *o*), 8.38 (d, J = 5, 1H, H-6) [c] [d]
Xb	239.5 (3.54) 275 sh (2.61)	1585, 1563, 1442 [a]	2.50 (s, 3H, CH_3-4), 2.70 (s, 3H, CH_3-2), 7.01 (d, J = 5, 1H, H-5), 8.51 (d, J = 5, 1H, H-6) [e]
Xc	249.5 (3.63) 277 (2.72)	1585, 1563, 1440, 1410 [a]	2.72 (s, 3H, CH_3-2), 3.50 (s, 3H, CH_3O),4.53 (s, 2H, CH_2), 7.31 (d, J = 5, 1H, H-5), 8.67 (d, J = 5, 1H, H-6) [e] [f]
Xd	248 (3.57) 275 (2.53)	1582, 1554, 1430, 1400 [a]	1.29 (t, J = 7.2, 3H, ethyl CH_3), 2.70 (s, 3H, CH_3-2), 2.76 (q, J = 7.2, 2H, CH_2), 7.00 (d, J = 5, 1H, H-5), 8.52 (d, J = 5, 1H, H-6) [e] [g]
Xe	249 (3.62) 276 (2.65)	1582, 1553, 1440, 1402 [a]	0.98 (t, J = 7, 3H, propyl CH_3), 1.5-2.0 (m, 2H, CH_2), 2.71 (s, 3H, CH_3-2), 2.71 (t, J = 7, 2H, CH_2), 6.98 (d, J = 5.5, 1H, H-5), 8.51 (d, J = 5.5, 1H, H-6) [e] [h]
Xf	248 (3.75) 275 (2.82)	1579, 1552, 1440, 1400 [a]	1.28 (d, J = 7.2, 6H, $2CH_3$), 2.70 (s, 3H, CH_3-2), 2.8-3.4 (m, 1H, $CHMe_2$), 7.00 (d, J = 5, 1H, H-5), 8.53 (d, J = 5, 1H, H-6) [e]
Xg	248 (3.60) 279 (2.61)	1578, 1547, 1437, 1393 [a]	1.33 [s, 9H, $(CH_3)_3C$], 2.69 (s, 3H, CH_3-2), 7.12 (d, J = 5.5, 1H, H-5), 8.54 (d, J = 5.5, 1H, H-6) [e]
Xi	250 sh (3.98) 254 (3.99) 276 (4.22)	1573, 1548, 1432, 1393 [a]	2.79 (s, 3H, CH_3-2), 7.44 (d, J = 5.5, 1H, H-5), 7.49 (mc, 3H, 2H ar *m* + 1H ar *p*), 8.07 (mc, 2H, 2H ar *o*), 8.63 (d, J = 5.5, 1H, H-6) [e] [i]
XIa	255 (4.29)	1570, 1557, 1418 [a]	7.07 (t, J = 5, 1H, H-5), 7.50 (mc, 3H, 2H ar *m* + 1H ar *p*), 8.53 (mc, 2H, 2H ar *o*), 8.76 (d, J = 5, 2H, H-4 + H-6) [e]
XIb	254 (4.24)	1587, 1570, 1553, 1422, 1384 [a]	3.52 (s, 3H, CH_3), 6.96 (d, J = 5, 1H, H-5), 7.46 (mc, 3H, 2H ar *m* + 1H ar *p*), 8.3-8.6 (mc, 2H, 2H ar *o*), 8.60 (d, J = 5, 1H, H-6) [e] [l]
XIc	254 (4.30)	1587, 1560, 1430, 1392 [a]	3.45 (s, 3H, CH_3), 4.55 (s, 2H, CH_2), 7.28 (d, J = 5, 1H, H-5), 7.45 (mc, 3H, 2H ar *m* + 1H ar *p*), 8.48 (mc, 2H, 2H ar *o*), 8.73 (d, J = 5, 1H, H-6) [e]
XId	254.5 (4.30)	1587, 1570, 1550, 1426, 1386 [a]	1.30 (t, J = 7.2, 3H, CH_3), 2.78 (q, J = 7.2, 2H, CH_2), 6.94 (d, J = 5, 1H, H-5), 7.45 (mc, 3H, 2H ar *m* + 1H ar *p*), 8.48 (mc, 2H, 2H ar *o*), 8.62 (d, J = 5, 1H, H-6) [e] [m]
XIe	255.5 (4.29)	1587, 1570, 1550, 1426, 1384 [a]	0.97 (t, J = 7.2, 3H, CH_3), 1.78 (sext, J = 7.2, 2H, CH_2), 2.74 (t, J = 7.2, 2H, CH_2), 6.93 (d, J = 5, 1H, H-5), 7.46 (mc, 3H, 2H ar *m* + 1H ar *p*), 8.46 (mc, 2H, 2H ar *o*), 8.61(d, J = 5, 1H, H-6) [e] [n]

Table VI(continued)

Compound	UV, λ max nm (log ε)	IR, -cm^{-1}	^{1}H NMR, δ
XIf	255 (4.28)	1588, 1567, 1550, 1426, 1388 [a]	1.31 (d, J = 7.2, 6H, $2CH_3$), 3.03 (mc, 1H, $CHMe_2$), 6.97 (d, J = 5.5, 1H, H-5), 7.48 (mc, 3H, 2H ar *m* + 1H ar *p*), 8.62 (mc, 2H, 2H ar *o*), 8.65 (d, J = 5.5, 1H, H-6) [e]
XIg	255 (4.31)	1586, 1565, 1544, 1425, 1380 [a]	1.49 [s, 9H, $(CH_3)_3C$], 7.13 (d, J = 5, 1H, H-5), 7.48 (mc, 3H, 2H ar *m* + 1H ar *p*), 8.4-8.8 (m, 2H, 2H ar *o*), 8.68 (d, J = 5, 1H, H-6) [e]
XIh	257 (4.34)	1587, 1565, 1552, 1426, 1385 [a]	4.11 (bs, 2H, CH_2), 6.87 (d, J = 5, 1H, H-5), 7.29 (mc, 8H, C_6H_5 + 2H ar *m* + 1H ar *p*), 8.55 (mc, 2H, 2H ar *o*), 8.59 (d, J = 5, 1H, H-6) [e]
XIi	257 (4.55)	1585, 1563, 1544, 1422, 1382 [a]	7.48 (d, J = 5, 1H, H-5), 7.52 (bs, 6H, C_6H_5 + 1H ar *p*), 8.67 (mc, 2H, 2H ar *m*), 8.70 (mc, 2H ar *o*), 8.74 (d, J = 5, 1H, H-6) [e] [o]

[a] In chloroform. [b] In potassium bromide. [c] In DMSO-d_6. [d] Reference [31] (DMSO-d_6): δ 6.8 (s, 2H), 7.1 (d, J = 5, 1H), 7.4-7.65 (m. 3H), 8-8.2 (m, 2H), 8.4 (d, J = 5, 1H). [e] In deuteriochloroform. [f] Reference [35] (deuteriochloroform): δ 2.60 (s, 3H), 3.43 (s, 3H), 4.40 (s, 2H), 7.15 (d, J = 5, 1H), 8.50 (d, J = 5, 1H). [g] Reference [26] (deuteriochloroform): δ 1.26 (t, J = 7, ethyl CH_3), 2.67 (q, J = 7, CH_2). [h] Reference [27] (tetrachloromethane): δ 0.95 (t, J = 7, 3H), 1.4-2.1 (m, 2H), 2.60 (m, 3H), 2.65 (t, J = 7, 2H), 6.85 (d, J = 5, 1H), 8.40 (d, J = 5, 1H). [i] Reference [32] (deuteriochloroform): δ 2.80 (s, 3H, CH_3), ~7.50 (d, J = 5, 1H, CH-5), 7.50 (m, 3H, 2H ar *m* + 1H ar *p*), 8.10 (m, 2H, 2H ar *o*), 8.67 (d, J = 5, 1H, CH-6). [l] Reference [31] (deuteriochloroform): δ 2.6 (s, 3H),6.8 (d, J = 5, 1H), 7.3-7.55 (m, 5H), 8.55 (d, J = 5, 1H). [m] Reference [27] (tetrachloromethane): δ 1.22 (t, J = 7, 3H), 2.67 (q, J = 7, 2H), 6.75(d, J = 5, 1H), 7.3-7.6 (m, 3H), 8.4-8.6 (m, 3H). [n] Reference [27] (tetrachloromethane): δ 0.95 (t, J = 7, 3H), 1.5-2.1 (m, 2H), 2.70 (t, J = 7, 2H), 6.80 (d, J = 5, 1H), 7.3-7.6 (m, 3H), 8.4-8.7 (m, 3H). [o] Reference [31] (deuteriochloroform): δ 7.45-7.65 (m, 7H), 8.5-8.7 (m, 2H), 8.8 (d, J = 5, 1H).

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