Oxamic Acid Derivatives in Heterocyclic Synthesis: Preparation of 1,4-Oxazine and 1,2,4-Triazino[5,6-*e*][1,3,4]oxadiazine Derivatives

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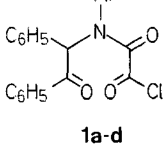
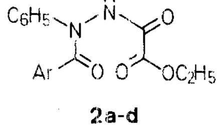
A number of derivatives of the 1,4-oxazine ring system have been prepared by reaction of *N*-aryl-*N*-(α-phenylphenacyl)oxamoyl chlorides **1** with amines. Reaction of *N*-aroyl-N'-ethoxyoxalyl-phenylhydrazines **2** with unsubstituted amidrazones leads to functionalized 1,2,4-triazines which undergo ring-closure to give 1,2,4-triazino[5,6-*e*][1,3,4]oxadiazine derivatives.

Synthetic applications of oxamic acid derivatives in heterocyclic chemistry remain almost unexplored. It has only been mentioned that oxalyl chloride reacts with aryl hydrazones in the presence of aluminium chloride to give isatin derivatives which rearrange on reaction with base giving 3-aryl-quinoline-4-carboxylic acids[1] (Stollé-Becker synthesis) and with 1,1,3-trisubstituted ureas,[2,3] carbodiimides[4] or aldehyde semicarbazones[5] to give parabanic acid derivatives. Recently, we have reported[6] that *N*-phenyl-*N*-(α-phenylphenacyl)oxamoyl chloride reacts with unsubstituted amidrazones to give imidazo[1,2-*d*][1,2,4]triazine derivatives. As a continuation of our interest in the preparation of fused heterocycles, we wish to report now the reaction of oxamic acid derivatives **1** and **2** with several nitrogen nucleophiles such as amines, hydrazines and unsubstituted amidrazones.



1a-d

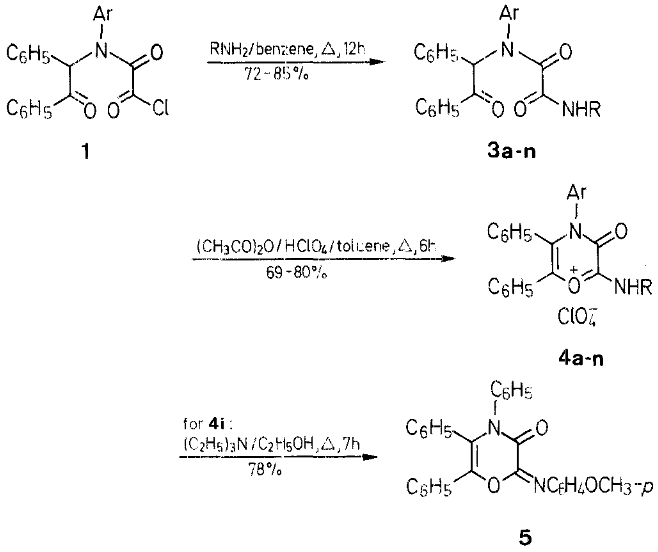


2a-d

1, 2	Ar
a	C_6H_5
b	4-$CH_3C_6H_4$
c	4-$CH_3OC_6H_4$
d	4-ClC_6H_4

N-Aryl-*N*-(α-phenylphenacyl)oxamoyl chlorides **1**, themselves readily available from benzoin by sequential treatment with aromatic amines and oxalyl chloride, react with amines, hydrazine and arylhydrazines in dry benzene at reflux temperature for 12 h to give the corresponding oxamide derivative **3** in good yield. Compounds **3** undergo cyclization by action of acetic anhydride/perchloric acid in dry toluene at reflux temperature for 6 h to give the corresponding 1,4-oxazinium perchlorates **4** as crystalline solids in excellent yields (Table 1). When ethanolic solution of **4i** is treated with triethylamine at room temperature, 1,4-oxazine derivative **5** is isolated. Treatment of **5** with perchloric acid leads to **4i** in near quantitative yields.

Support for the formulation **3** and **4** is clearly provided by their elemental analysis and spectral data. The IR spectra of **3** show the absorption bands due to the carbonyl groups around 1690, 1660 and 1630 cm^{-1} respectively. Mass spectra show the expected molecular ion peak; peaks are also found at $m/e = 105$ and for $[C_6H_5-CH=N-Ar]^+$. The IR spectra of **4** show absorptions due to the amino group at 3475 cm^{-1} and around 1680 cm^{-1} attributable to the carbonyl group. Mass spectra show the expected ion peak at $[M^+-ClO_4^-]$ and $[M^+-HClO_4]$ as the base peak.



3, 4	Ar	R
a	C_6H_5	p-$CH_3C_6H_4CH_2$
b	C_6H_5	p-$ClC_6H_4CH_2$
c	C_6H_5	$C_6H_5CH_2$
d	C_6H_5	C_2H_5
e	C_6H_5	p-$NO_2C_6H_4NH$
f	C_6H_5	NH_2
g	C_6H_5	C_6H_5NH
h	C_6H_5	C_6H_5
i	C_6H_5	p-$CH_3OC_6H_4$
j	C_6H_5	p-$CH_3C_6H_4$
k	p-$CH_3C_6H_4$	C_6H_5
l	p-$CH_3C_6H_4$	C_6H_5NH
m	p-$CH_3OC_6H_4$	$C_6H_5CH_2$
n	p-ClC_6H_4	p-$CH_3C_6H_5CH_2$

On the other hand, the unreported *N*-aroyl-*N'*-ethoxyoxalyl-phenylhydrazines **2**, available from phenylhydrazine by sequential treatment with diethyl oxalate and aroyl chlorides, react with unsubstituted amidrazones in dry toluene at reflux temperature to give the corresponding functionalized 1,2,4-triazin-6-ones **6** in excellent yields. Compounds **6** undergo ring-closure by action of thionyl chloride to give 1,2,4-triazino[5,6-*e*][1,3,4]oxadiazinium chlorides **7** as hydrochlorides in good yields (Table 2). Compounds **7** by treatment with bases, such as aqueous potassium carbonate or triethylamine, undergo ring-opening of the oxadiazine moiety to give **6**.

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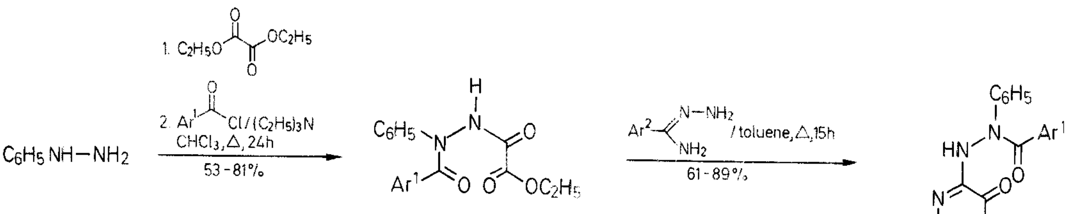
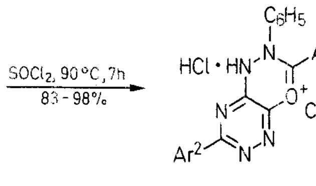


2a-d

6a-i

6, 7	Ar^1	Ar^2
a	C_6H_5	C_6H_5
b	C_6H_5	p-$CH_3C_6H_4$
c	C_6H_5	p-$CH_3OC_6H_4$
d	p-CH_3–C_6H_4	C_6H_5
e	p-$CH_3C_6H_4$	p-$CH_3C_6H_4$
f	p-$CH_3C_6H_4$	p-$CH_3OC_6H_4$
g	p-$CH_3OC_6H_4$	p-$CH_3C_6H_4$
h	p-$CH_3OC_6H_4$	p-$CH_3OC_6H_4$
i	p-BrC_6H_4	p-$CH_3OC_6H_4$



7a-i

Compounds **6** and **7** are characterized on the basis of their elemental analysis and spectral data. The IR spectra of **6** show absorption bands around 3200 cm^{-1} due to the amino group, and two bands around 1680 and 1660 cm^{-1} attributable to the two carbonyl groups. Mass spectra show the expected molecular ion peak; peaks are also found at $[Ar^2-CN]^+$ and $[Ar^1-CO]^+$ as the base peak. The IR spectra of **7** show absorption bands at around 2700, 1640 and 1600 cm^{-1}; mass spectra show the ion peak at $[M^+-HCl-Cl^-]$ and $[Ar-CO]^+$ as the base peak.

Table 1. Compounds **3** and **4** Prepared

Product	Yield[a] (%)	m.p.[b] (°C) (Solvent)	Molecular Formula[c]	IR (Nujol)[d] ν (cm^{-1})	^{1}H-NMR[e] δ (ppm)	MS[f] m/e (%)
3a	85	178–179 ($CHCl_3$)	$C_{30}H_{26}N_2O_3$ (462.6)	3386, 1680, 1651, 1596, 1539, 1493, 1452, 1398, 1226, 1022, 981, 814, 751, 738, 704, 690, 650	2.3 (s, 3H); 4.3 (d, 2H, J = 6 Hz); 6.25 (s, 1H); 7.0–7.9 (m, 19H)	462 (M^+, 2), 357 (27), 315 (1), 314 (6), 195 (2), 183 (14), 182 (100), 181 (9), 180 (33), 147 (1), 120 (2), 119 (2), 105 (59), 91 (4), 77 (67)
3b	78	152–154 ($CHCl_3$)	$C_{29}H_{23}ClN_2O_3$ (483.0)	3392, 1681, 1653, 1596, 1528, 1494, 1460, 1381, 1223, 1092, 1019, 979, 826, 701, 690	4.3 (d, 2H, J = 6 Hz); 6.25 (s, 1H); 6.8–7.8 (m, 19H)	484 (M^+ + 2, 2), 482 (M^+, 5), 379 (29), 377 (77), 315 (2), 314 (7), 195 (2), 183 (14), 182 (100), 181 (9), 180 (15), 168 (1), 167 (6), 140 (2), 139 (1), 127 (17), 125 (48), 119 (1), 111 (1), 105 (14), 77 (18)
3c	72	188–190 ($CHCl_3$)	$C_{29}H_{23}N_2O_3$ (447.5)	3386, 1681, 1653, 1596, 1640, 1493, 1458, 1394, 1224, 1115, 1058, 979, 883, 747, 730, 696, 650	4.3 (d, 2H, J = 6 Hz); 6.25 (s, 1H); 6.9–7.9 (m, 20H)	448 (M^+, 10), 343 (98), 315 (2), 314 (6), 195 (1), 183 (4), 182 (100), 181 (3), 180 (5), 106 (1), 105 (13), 91 (12), 77 (12)
3d	75	182–184 ($CHCl_3$)	$C_{24}H_{22}N_2O_3$ (386.5)	3330, 1693, 1670, 1640, 1596, 1540, 1494, 1455, 1398, 1381, 1245, 1223, 1177, 1149, 979, 854, 769, 730, 696, 650	1.0 (t, 3H, J = 6.5 Hz); 3.20 (m, 2H); 6.25 (s, 1H), 7.0–7.8 (m, 15H)	386 (M^+, 3), 314 (4), 313 (2), 281 (47), 195 (1), 183 (16), 182 (100), 181 (9), 180 (15), 119 (2), 105 (19), 77 (6), 72 (10), 71 (1), 44 (20), 43 (2), 29 (31), 15 (1)
3e	80	220–222 ($CHCl_3$)	$C_{28}H_{22}N_4O_5$ (494.5)	3269, 1715, 1689, 1629, 1589, 1496, 1469, 1377, 1310, 1224, 1177, 1111, 978, 846, 764, 756, 709, 696	6.25 (s, 1H); 6.8–7.9, (m, 19H)	494 (M^+, 7), 389 (9), 314 (20), 313 (52), 195 (16), 194 (2), 183 (10), 182 (100), 181 (23), 180 (89), 152 (11), 138 (8), 122 (2), 119 (3), 105 (32), 77 (99)
3f	82	185–187 ($CHCl_3$)	$C_{27}H_{19}N_3O_3$ (373.4)	3330, 3290, 3262, 1698, 1664, 1596, 1494, 1455, 1432, 1376, 1313, 1206, 1132, 1075, 1007, 973, 928, 820, 752, 713, 696	6.25 (s, 1H); 7.0–8.0 (m, 15H)	373 (M^+, 1), 314 (2), 268 (48), 195 (3), 194 (1), 183 (15), 182 (100), 181 (7), 180 (15), 179 (1), 178 (1), 119 (2), 105 (17), 77 (39), 59 (3)
3g	85	213–215 ($CHCl_3$)	$C_{28}H_{23}N_3O_3$ (449.5)	3313, 3211, 1699, 1676, 1659, 1597, 1495, 1455, 1376, 1308, 1246, 1223, 1076, 979, 889, 860, 781, 758, 730, 696	6.25 (s, 1H); 6.9–8.1 (m, 20H)	449 (M^+, 6), 344 (6), 314 (10), 255 (1), 254 (1), 195 (10), 194 (1), 183 (15), 182 (100), 181 (15), 180 (25), 135 (2), 119 (2), 107 (16), 105 (31), 93 (11), 91 (6), 77 (68)
3h	80	157–159 (Toluene)	$C_{28}H_{22}N_2O_3$ (434.5)	3296, 1681, 1649, 1641, 1603, 1595, 1535, 1494, 1449, 1404, 1313, 1245, 1223, 1189, 1177, 1075, 979, 860, 758, 701, 684	6.25 (s, 1H); 7.0–8.1 (m, 20H); 9.3 (s, 1H)	434 (M^+, 4), 329 (46), 314 (4), 315 (1), 195 (2), 183 (15), 182 (100), 181 (7), 180 (13), 120 (3), 119 (8), 105 (14), 92 (12), 77 (68)

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Table 1: (Continued)

Product	Yield[a] (%)	m.p.[b] (°C) (Solvent)	Molecular Formula[c]	IR (Nujol)[d] ν (cm^{-1})	^{1}H-NMR[e] δ (ppm)	MS[f] m/e (%)
3i	73	185–187 (Toluene)	$C_{29}H_{24}N_2O_4$ (464.5)	3294, 1698, 1664, 1653, 1593, 1514, 1493, 1456, 1379, 1271, 1250, 1224, 1174, 1024, 977, 835, 777, 761, 746, 698, 611	3.75 (s, 3H); 6.25 (S, 1H), 6.8–8.1 (m, 19H); 9.3 (lc, 1H)	464 (M$^+$, 4), 359 (22), 315 (1), 314 (4), 195 (2), 183 (15), 182 (100), 181 (6), 180 (2), 150 (2), 149 (3), 122 (16), 107 (1), 105 (13), 77 (22)
3j	75	173–175 (Toluene)	$C_{29}H_{24}N_2O_3$ (448.5)	3307, 1695, 1678, 1643, 1595, 1512, 1494, 1456, 1394, 1311, 1240, 1226, 1194, 1076, 977, 866, 817, 763, 736, 698, 609	2.3 (s, 3H); 6.25 (s, 1H); 7.0–8.1 (m, 19H); 9.3 (s, 1H)	448 (M$^+$, 4), 343 (49), 315 (2), 314 (5), 195 (1), 183 (15), 182 (100), 181 (8), 180 (15), 134 (4), 133 (9), 106 (9), 105 (14), 91 (7), 77 (26)
3k	75	168–169 (Toluene)	$C_{29}H_{24}N_2O_3$ (448.5)	3311, 1700, 1664, 1649, 1603, 1550, 1540, 1494, 1448, 1394, 1315, 1253, 1224, 1194, 981, 866, 798, 761, 750, 727, 700, 677	2.2 (s, 3H); 6.25 (s, 1H); 7.9–8.2 (m, 19H); 9.3 (s, 1H)	448 (M$^+$, 4), 343 (47), 329 (2), 328 (5), 197 (16), 196 (100), 195 (9), 194 (13), 120 (5), 119 (11), 105 (12), 92 (8), 77 (24)
3l	82	199–201 ($CHCl_3$)	$C_{29}H_{25}N_3O_3$ (463.5)	3314, 3211, 1678, 1663, 1605, 1595, 1499, 1460, 1448, 1377, 1313, 1244, 1228, 979, 891, 860, 789, 767, 754, 727, 698	2.2 (s, 3H); 6.25 (s, 1H); 6.9–8.0 (m, 19H)	463 (M$^+$, 15), 358 (8), 328 (12), 268 (2), 267 (3), 197 (17), 196 (100), 195 (16), 194 (22), 135 (1), 133 (2), 107 (11), 105 (19), 92 (20), 77 (22)
3m	72	190–192 ($CHCl_3$)	$C_{30}H_{26}N_2O_4$ (478.6)	3386, 1681, 1653, 1596, 1511, 1494, 1460, 1376, 1245, 1223, 1030, 979, 832, 735, 696	3.75 (s, 3H); 4.3 (d, 2H, J = 6 Hz); 6.25 (s, 1H); 6.9–7.9 (m, 19H)	478 (M$^+$, 5), 373 (45), 344 (10), 343 (3), 213 (16), 212 (100), 211 (12), 210 (8), 195 (3), 149 (3), 134 (8), 133 (1), 107 (2), 106 (5), 105 (21), 91 (68), 77 (26)
3n	72	162–164 ($CHCl_3$)	$C_{30}H_{25}ClN_2O_3$ (497.0)	3386, 1681, 1653, 1596, 1534, 1381, 1223, 1092, 1019, 979, 809, 775, 758, 701, 690	2.3 (s, 3H); 4.3 (d, 2H, J = 6 Hz); 6.25 (s, 1H); 6.8–7.9 (m, 19H)	498 (M$^+$ + 2, 1), 496 (M$^+$, 1), 393 (2), 391 (7), 350 (1), 349 (2), 348 (2), 347 (4), 219 (5), 218 (30), 217 (18), 216 (100), 215 (20), 214 (22), 195 (1), 153 (2), 147 (2), 120 (7), 119 (2), 111 (4)
4a	70	197–199 (C_2H_5OH)	$C_{30}H_{25}ClN_2O_6$ (545.0)	3488, 1672, 1630, 1589, 1489, 1463, 1377, 1310, 1104, 759, 699, 626	2.1 (s, 3H); 5.1 (s, 2H); 6.9–7.7 (m, 19H)	445 (M$^+$ − ClO_4^-, 8), 444 (M$^+$ − $HClO_4$, 100), 417 (3), 416 (8), 340 (97), 180 (36), 178 (2), 120 (18), 119 (2), 105 (21), 91 (2), 77 (31), 28 (3)
4b	70	208–210 (C_2H_5OH)	$C_{29}H_{22}Cl_2N_2O_6$ (565.4)	3501, 1675, 1630, 1589, 1496, 1463, 1377, 1310, 1098, 865, 839, 792, 759, 719, 699, 626	5.1 (s, 2H); 6.7–7.9 (m, 19H)	467 (M$^+$ + 2-ClO_4, 11), 466 (M$^+$ + 2-$HClO_4$, 38), 465 (M$^+$ − ClO_4, 43), 464 (M$^+$ − $HClO_4$, 100), 438 (2), 436 (4), 180 (6), 178 (2), 142 (3), 140 (11), 127 (6), 125 (17), 119 (1), 113 (1), 111 (2), 105 (3), 77 (25), 28 (8)
4c	72	130–132 (C_2H_5OH)	$C_{29}H_{23}ClN_2O_6$ (531.0)	3451, 1675, 1630, 1589, 1489, 1456, 1377, 1310, 1104, 759, 702, 699, 622	5.1 (s, 2H); 6.9–7.5 (m, 20H)	431 (M$^+$ − ClO_4^-, 30), 430 (M$^+$ − $HClO_4$, 100), 403 (1), 402 (3), 312 (5), 311 (31), 326 (1), 180 (5), 178 (1), 119 (2), 106 (8), 105 (2), 91 (7), 77 (6), 28 (15)
4d	75	210–212 (C_2H_5OH)	$C_{24}H_{21}ClN_2O_6$ (468.9)	3475, 1662, 1625, 1590, 1496, 1463, 1377, 1317, 1104, 759, 706, 626	1.3 (t, 3H, J = 6.5 Hz); 4.10 (m, 2H); 6.9–7.7 (m, 15H)	369 (M$^+$ − ClO_4^-, 27), 368 (M$^+$ − $HClO_4$, 100), 341 (12), 340 (45), 180 (36), 178 (5), 119 (2), 105 (12), 77 (96), 44 (3), 29 (4), 28 (5)
4e	74	233–235 (C_2H_5OH)	$C_{28}H_{21}ClN_4O_8$ (577.0)	3335, 1669, 1630, 1596, 1489, 1463, 1377, 1337, 1250, 1111, 845, 759, 712	6.9–7.9 (m, 19H)	477 (M$^+$ − ClO_4^-, 1), 476 (M$^+$ − $HClO_4$, 1), 341 (27), 340 (100), 339 (3), 312 (32), 311 (19), 180 (20), 178 (2), 152 (2), 138 (4), 122 (5), 119 (2), 105 (29), 77 (17), 28 (7)
4f	69	210–212 (C_2H_5OH)	$C_{22}H_{18}ClN_3O_6$ (455.9)	3335, 1702, 1630, 1590, 1489, 1463, 1377, 1310, 1098, 759, 719, 699, 626	7.0–8.1 (m, 15H)	356 (M$^+$ − ClO_4^-, 13), 355 (M$^+$ − $HClO_4$, 48), 341 (25), 340 (100), 312 (57), 311 (55), 180 (35), 178 (5), 119 (6), 77 (32), 31 (2), 28 (3), 17 (2)
4g	70	220–222 (C_2H_5OH)	$C_{28}H_{22}ClN_3O_6$ (532.0)	3290, 1672, 1640, 1589, 1491, 1464, 1446, 1379, 1097, 787, 760, 698, 624	6.8–7.9 (m, 20H)	432 (M$^+$ − ClO_4^-, 2), 431 (M$^+$ − $HClO_4$, 7), 341 (24), 340 (100), 312 (26), 311 (12), 180 (33), 178 (2), 119 (3), 107 (4), 105 (68), 93 (47), 92 (6), 77 (47), 28 (2)

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Table 1: (Continued)

Prod-uct	Yield[a] (%)	m.p.[b] (°C) (Solvent)	Molecular Formula[c]	IR (Nujol)[d] ν (cm⁻¹)	¹H-NMR[e] δ (ppm)	MS[f] m/e (%)
4h	80	190–191 (C_2H_5OH)	$C_{28}H_{21}ClN_2O_6$ (516.9)	3482, 1681, 1630, 1590, 1494, 1455, 1376, 1313, 1098, 928, 832, 752, 718, 696, 622	6.7–7.6 (m, 20H)	417 ($M^+ - ClO_4^-$, 22), 416 ($M^+ - HClO_4$, 100), 389 (12), 388 (38), 180 (6), 178 (3), 120 (3), 119 (2), 105 (6), 93 (48), 92 (4), 91 (4), 77 (96), 28 (3)
4i	72	240–243 (C_2H_5OH)	$C_{29}H_{23}ClN_2O_7$ (547.0)	3482, 1669, 1625, 1590, 1509, 1489, 1463, 1377, 1303, 1257, 1118, 812, 752, 726, 699, 626	3.8 (s, 3H); 6.8–7.9 (m, 19H)	447 ($M^+ - ClO_4^-$, 33), 446 ($M^+ - HClO_4$, 100), 419 (16), 418 (50), 180 (7), 178 (5), 122 (1), 121 (3), 120 (1), 119 (2), 107 (4), 105 (5), 77 (8), 28 (3)
4j	70	210–212 (C_2H_5OH)	$C_{29}H_{23}ClN_2O_6$ (531.0)	3471, 1664, 1625, 1585, 1511, 1494, 1466, 1375, 1325, 1109, 803, 752, 724, 701, 622	2.1 (s, 3H); 6.6–7.6 (m, 19H)	431 ($M^+ - ClO_4^-$, 33), 430 ($M^+ - HClO_4$, 100), 403 (14), 402 (46), 180 (6), 178 (5), 120 (1), 119 (3), 106 (1), 105 (3), 91 (3), 77 (4), 28 (3)
4k	75	271–272 (Toluene)	$C_{29}H_{23}ClN_2O_6$ (531.0)	3482, 1669, 1629, 1582, 1489, 1456, 1377, 1323, 1098, 805, 752, 726, 699, 626	2.2 (s, 3H); 6.7–7.9 (m, 19H)	431 ($M^+ - ClO_4^-$, 33), 430 ($M^+ - HClO_4$, 100), 403 (12), 402 (40), 194 (7), 178 (3), 134 (1), 133 (2), 105 (3), 93 (36), 92 (3), 91 (3), 77 (40), 28 (3)
4l	71	229–232 (C_2H_5OH)	$C_{29}H_{24}ClN_3O_6$ (546.0)	3290, 1670, 1628, 1596, 1511, 1494, 1460, 1376, 1087, 803, 758, 724, 701, 622	2.1 (s, 3H); 6.8–7.9 (m, 19H)	446 ($M^+ - ClO_4^-$, 1), 445 ($M^+ - HClO_4$, 3), 355 (25), 354 (100), 326 (10), 325 (7), 194 (30), 192 (2), 133 (3), 107 (4), 105 (49), 93 (47), 91 (37), 77 (58), 28 (3)
4m	73	136–138 (C_2H_5OH)	$C_{30}H_{25}ClN_2O_7$ (561.0)	3450, 1670, 1630, 1596, 1511, 1489, 1460, 1376, 1302, 1251, 1104, 832, 764, 730, 707, 622	3.25 (s, 3H); 5.1 (s, 2H); 6.8–7.8 (m, 19H)	461 ($M^+ - ClO_4^-$, 9), 460 ($M^+ - HClO_4$, 100), 433 (7), 432 (28), 342 (52), 341 (28), 210 (97), 178 (2), 107 (10), 106 (3), 105 (5), 91 (14), 77 (18), 28 (4)
4n	75	204–206 (C_2H_5OH)	$C_{30}H_{24}Cl_2N_2O_6$ (579.4)	3396, 1675, 1630, 1600, 1489, 1460, 1376, 1308, 1098, 764, 724, 701, 628	2.1 (s, 3H); 5.1 (s, 2H); 6.8–7.9 (m, 19H)	481 ($M^+ + 2-ClO_4^-$, 2), 480 ($M^+ + 2-HClO_4$, 16), 479 ($M^+ - ClO_4^-$, 7), 478 ($M^+ - HClO_4$, 100), 376 (30), 374 (96), 216 (5), 214 (14), 178 (2), 155 (2), 153 (3), 120 (2), 113 (2), 111 (5), 105 (6), 91 (2), 28 (8)

[a] Yield of isolated pure product.
[b] Uncorrected.
[c] The microanalyses were in good agreement with the calculated values: C ±0.26, H ±0.28, N ±0.25.
[d] Recorded on a Nicolet FT 5DX spectrometer.
[e] Recorded at 60 MHz on a Varian EM-360A spectrometer with TMS as internal standard. For compounds **3** $CDCl_3$ was used as solvent except for **3c**, **3e**, **3f** and **3l** where $CDCl_3$/TFA was used. For compounds **4** $CDCl_3$/TFA was used as solvent.
[f] Recorded at 70 eV on a Hewlett-Packard 5993 C instrument.

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N-Aryl-N-(α-phenylphenacyl)oxamoyl Chlorides 1; General Procedure: Compounds **1b–d** are prepared according to the method previously described[6] for **1a**.

N-p-Tolyl-N-(α-phenylphenacyl)oxamoyl Chloride (**1b**); yield: 82%; colourless crystals; m.p. 165–166 °C (chloroform).

$C_{23}H_{18}ClNO_3$	calc.	C 70.49	H 4.62	N 3.57
(391.9)	found	70.37	4.71	3.48

IR (Nujol): ν = 1783, 1704, 1660 cm⁻¹.

¹H-NMR ($CDCl_3$/TMS): δ = 2.3 (s, 3H); 5.45 (s, 1H); 6.7–7.6 ppm (m, 14H).

MS (70 eV): m/e (%) = 393 (M^+ + 2, 7); 391 (M^+, 21); 195 (100).

N-(p-Methoxyphenyl)-N-(α-phenylphenacyl)oxamoyl Chloride (**1c**); yield: 79%; colourless crystals; m.p. 153–155 °C (chloroform).

$C_{23}H_{18}ClNO_4$	calc.	C 67.73	H 4.44	N 3.43
(407.9)	found	67.61	4.35	3.58

IR (Nujol): ν = 1784, 1699, 1667 cm⁻¹.

¹H-NMR ($CDCl_3$/TMS): δ = 3.8 (s, 3H); 5.45 (s, 1H); 6.8–7.6 ppm (m, 14H).

MS (70 eV): m/e (%) = 409 (M^+ + 2, 8); 407 (M^+, 23); 211 (100).

N-(p-Chlorophenyl)-N-(α-phenylphenacyl)oxamoyl Chloride (**1d**); yield: 77%; colourless crystals; m.p. 147–148 °C (chloroform).

$C_{22}H_{15}Cl_2NO_3$	calc.	C 64.09	H 3.66	N 3.39
(412.3)	found	63.91	3.58	3.47

IR (Nujol): ν = 1779, 1708, 1655 cm⁻¹.

¹H-NMR ($CDCl_3$/TMS): δ = 5.45 (s, 1H); 6.8–7.7 ppm (m, 14H).

MS (70 eV): m/e (%) = 415 (M^+ + 4, 2); 413 (M^+ + 2, 15); 411 (M^+, 24); 215 (100).

N-Aroyl-N′-ethoxyoxalyl Phenylhydrazines 2; General Procedure: To a solution of ethoxyoxalyl phenylhydrazine (2 g, 10 mmol) in chloroform (50 ml), the appropriate aroyl chloride (10 mmol) and triethylamine (1.01 g, 10 mmol) are added. The mixture is refluxed for 24 h. After cooling, the solution is washed with water (2 × 100 ml) and the organic layer is dried with sodium sulfate and the solvent removed under reduced pressure. The resulting oil is triturated with ether (30 ml) and the precipitated solid is collected by filtration and recrystallized from ethanol/ether (1 : 2) to give **2**.

Table 2. Compounds **6** and **7** Prepared

Product	Yield[a] (%)	m.p.[b] (°C) (Solvent)	Molecular Formula[c]	IR (Nujol)[d] ν (cm^{-1})	^{1}H-NMR[e] δ (ppm)	MS[f] m/e (%)
6a	76	213–214 (C_2H_5OH)	$C_{22}H_{17}N_5O_2$ (383.4)	3284, 1698, 1659, 1613, 1493, 1462, 1359, 1308, 1221, 1137, 1016, 986, 942, 923, 896, 883, 784, 758, 732, 704, 691, 622, 607	6.86–7.85 (m, 15H)	383 (M$^+$, 10), 279 (1), 278 (1), 212 (1), 197 (1), 172 (1), 144 (1), 106 (9), 105 (100), 104 (1), 103 (2), 77 (30)
6b	78	213–216 (C_2H_5OH)	$C_{23}H_{19}N_5O_2$ (397.4)	3216, 1698, 1663, 1613, 1506, 1491, 1458, 1365, 1215, 1170, 1151, 1076, 1024, 987, 895, 854, 825, 768, 761, 738, 698	2.40 (s, 3H); 7.18–8.30 (m, 14H)	397 (M$^+$, 10), 293 (1), 292 (2), 212 (1), 197 (2), 186 (3), 158 (1), 118 (3), 117 (7), 106 (9), 105 (100), 91 (3), 77 (31)
6c	89	228–229 (C_2H_5OH)	$C_{23}H_{19}N_5O_3$ (413.4)	3216, 1698, 1653, 1613, 1506, 1455, 1365, 1255, 1178, 1030, 985, 896, 839, 794, 764, 742, 698	3.9 (s, 3H); 8.30–7.10 (m, 14H)	413 (M$^+$, 7), 309 (4), 308 (1), 212 (1), 202 (3), 197 (1), 174 (1), 134 (5), 133 (9), 107 (3), 106 (8), 105 (100), 77 (32)
6d	62	220–224 (C_2H_5OH)	$C_{23}H_{19}N_5O_2$ (397.4)	3188, 1687, 1664, 1613, 1494, 1466, 1404, 1353, 1285, 1183, 1155, 1115, 1030, 985, 884, 854, 832, 748, 730, 696	2.28 (s, 3H); 7.15–8.10 (m, 14H)	397 (M$^+$, 97), 279 (8), 278 (2), 226 (1), 211 (2), 172 (3), 144 (1), 120 (9), 119 (100), 104 (3), 103 (4), 91 (15), 77 (4)
6e	77	204–207 (C_2H_5OH)	$C_{24}H_{21}N_5O_2$ (411.5)	3211, 1688, 1667, 1622, 1557, 1523, 1506, 1491, 1456, 1365, 1215, 1170, 985, 895, 857, 825, 775, 769, 740, 698	2.24 (s, 3H); 2.33 (s, 3H); 7.07–7.97 (m, 13H)	411 (M$^+$, 30), 293 (2), 292 (1), 226 (1), 211 (1), 186 (3), 158 (1), 120 (9), 119 (100), 118 (4), 117 (5), 91 (21), 77 (8)
6f	87	184–187 (C_2H_5OH)	$C_{24}H_{21}N_5O_3$ (427.5)	3220, 1684, 1666, 1615, 1523, 1504, 1491, 1462, 1442, 1355, 1312, 1254, 1184, 1153, 1030, 981, 897, 856, 840, 838, 799, 783, 747, 733, 700, 645, 620	2.36 (s, 3H); 3.91 (s, 3H); 6.80–8.36 (m, 13H)	427 (M$^+$, 10), 309 (2), 308 (1), 226 (1), 202 (2), 174 (1), 134 (3), 133 (7), 120 (9), 119 (100), 107 (1), 91 (19), 77 (6)
6g	67	196–199 (C_2H_5OH)	$C_{24}H_{21}N_5O_3$ (427.5)	3167, 1686, 1661, 1609, 1563, 1512, 1505, 1495, 1456, 1353, 1307, 1268, 1175, 1152, 1030, 984, 897, 857, 832, 759, 737, 732, 695, 653, 601	2.35 (s, 3H); 3.85 (s, 3H); 6.95–8.00 (m, 13H)	427 (M$^+$, 32), 293 (3), 292 (1), 242 (1), 227 (1), 186 (1), 158 (1), 136 (8), 135 (100), 118 (4), 117 (5), 107 (4), 91 (2), 77 (2)
6h	63	198–202 (C_2H_5OH)	$C_{24}H_{21}N_5O_4$ (443.5)	3189, 1684, 1663, 1615, 1561, 1505, 1464, 1402, 1354, 1310, 1267, 1256, 1177, 1152, 1119, 1030, 982, 897, 858, 839, 759, 746, 732, 651, 620, 602	3.72 (s, 3H); 3.80 (s, 3H); 6.81–7.90 (m, 13H)	443 (M$^+$, 30), 309 (24), 308 (1), 242 (2), 227 (5), 202 (2), 174 (1), 136 (9), 135 (100), 134 (4), 133 (3), 107 (4), 77 (5)
6i	61	236–239 (C_2H_5OH)	$C_{23}H_{18}BrN_5O_3$ (492.3)	3258, 1701, 1665, 1614, 1564, 1505, 1462, 1404, 1312, 1276, 1256, 1179, 1169, 1138, 1113, 1030, 990, 898, 858, 837, 799, 751, 733, 692	3.83 (s, 3H); 6.86–8.03 (m, 13H)	493 (M$^+$ + 2,2), 491 (M$^+$, 2), 309 (3), 308 (1), 292 (1), 290 (1), 277 (2), 275 (2), 202 (2), 186 (6), 185 (97), 184 (6), 183 (100), 174 (1), 157 (2), 155 (2), 134 (4), 133 (6), 107 (2), 77 (1)
7a	89	183–185 (CH_3CN)	$C_{22}H_{17}Cl_2N_5O$ (438.3)	2720, 1636, 1602, 1561, 1498, 1416, 1352, 1305, 1291, 1246, 1230, 1186, 1169, 1145, 1116, 1057, 1029, 1002, 982, 884, 848, 789, 770, 715, 675	6.75–7.98 (m, 15H); 11.67 (s, 1H)	366 (M$^+$ – HCl–Cl$^-$, 3), 365 (M$^+$ – 2HCl, 10), 261 (4), 197 (14), 186 (1), 180 (4), 171 (2), 170 (15), 145 (33), 106 (7), 105 (100), 104 (5), 103 (15), 77 (70)
7b	87	173–176 (CH_3CN)	$C_{23}H_{19}Cl_2N_5O$ (452.3)	2616, 1655, 1613, 1591, 1555, 1499, 1456, 1341, 1317, 1306, 1288, 1229, 1184, 1175, 1150, 1024, 1007, 982, 957, 932, 826, 778, 733, 720, 681, 669	2.34 (s, 3H); 6.74–7.99 (m, 14H); 11.71 (s, 1H)	380 (M$^+$ – HCl–Cl$^-$, 7), 379 (M$^+$ – 2HCl, 22), 275 (4), 200 (5), 197 (15), 185 (6), 184 (20), 180 (5), 159 (38), 118 (12), 117 (21), 106 (9), 105 (100), 91 (20), 77 (32)
7c	97	112–115 (dec.) (CH_3CN)	$C_{23}H_{19}Cl_2N_5O_2$ (468.3)	2684, 1640, 1611, 1557, 1497, 1414, 1348, 1302, 1289, 1277, 1229, 1181, 1121, 1065, 1023, 1007, 983, 899, 880, 843, 795, 770, 737, 710, 679, 664, 625	3.80 (s, 3H); 7.02–8.05 (m, 14H); 11.70 (s, 1H)	396 (M$^+$ – HCl–Cl$^-$, 2), 395 (M$^+$ – 2HCl, 6), 291 (7), 216 (2), 201 (8), 200 (4), 197 (7), 180 (3), 175 (8), 134 (4), 133 (10), 107 (3), 106 (8), 105 (100), 77 (16)
7d	88	163–165 (CH_3CN)	$C_{23}H_{19}Cl_2N_5O$ (452.3)	2666, 1641, 1611, 1597, 1576, 1565, 1512, 1500, 1487, 1301, 1250, 1195, 1143, 1046, 1031, 1012, 982, 973, 960, 891, 835, 823, 777, 763, 718, 680	2.25 (s, 3H); 7.08–8.13 (m, 14H); 11.75 (s, 1H)	380 (M$^+$ – HCl–Cl$^-$, 2), 379 (M$^+$ – 2HCl, 8), 261 (2), 211 (5), 194 (3), 186 (1), 171 (2), 170 (4), 145 (41), 120 (6), 119 (100), 104 (6), 103 (13), 91 (19), 77 (22)
7e	83	218–222 (CH_3CN)	$C_{24}H_{21}Cl_2N_5O$ (466.4)	2672, 1640, 1611, 1593, 1576, 1564, 1508, 1487, 1300, 1248, 1233, 1192, 1142, 1048, 1022, 982, 974, 959, 893, 828, 762, 734, 718, 681	2.25 (s, 3H); 2.34 (s, 3H); 7.08–7.91 (m, 13H); 11.67 (s, 1H)	394 (M$^+$ – HCl–Cl$^-$, 2), 393 (M$^+$ – 2HCl, 9), 275 (2), 211 (27), 200 (5), 194 (6), 185 (6), 184 (34), 159 (25), 120 (9), 119 (100), 118 (11), 117 (11), 91 (49), 77 (6)

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Table 2: (Continued)

Product	Yield[a] (%)	m.p.[b] (°C) (Solvent)	Molecular Formula[c]	IR (Nujol)[d] ν (cm^{-1})	^{1}H-NMR[e] δ (ppm)	MS[f] m/e (%)
7f	95	142–147 (CH_3CN)	$C_{24}H_{21}Cl_2N_5O_2$ (482.4)	2682, 1641, 1613, 1576, 1565, 1506, 1292, 1256, 1186, 1142, 1028, 982, 974, 961, 885, 837, 762, 739, 718, 704, 690, 680	2.25 (s, 3H); 3.81 (s, 3H); 6.68–8.01 (m, 13H); 11.68 (s, 1H)	410 (M^+ − HCl−Cl^-, 6), 409 (M^+ − 2HCl, 20), 291 (5), 216 (2), 211 (30), 201 (9), 200 (52), 194 (13), 175 (89), 134 (24), 133 (30), 120 (11), 119 (100), 107 (4), 91 (46), 77 (10)
7g	98	142–145 (CH_3CN)	$C_{24}H_{21}Cl_2N_5O_2$ (482.4)	2690, 1645, 1603, 1587, 1508, 1487, 1445, 1395, 1323, 1190, 1148, 1015, 982, 974, 961, 876, 843, 774, 754, 735, 698, 677, 648, 604	2.35 (s, 3H); 3.72 (s, 3H); 6.72–8.00 (m, 13H); 11.68 (s, 1H)	410 (M^+ − HCl−Cl^-, 1), 409 (M^+ − 2HCl, 2), 275 (2), 227 (6), 210 (2), 200 (3), 185 (2), 184 (4), 159 (7), 136 (9), 135 (100), 118 (5), 117 (5), 107 (5), 91 (4), 77 (8)
7h	98	144–146 (CH_3CN)	$C_{24}H_{21}Cl_2N_5O_3$ (498.4)	2700, 1641, 1606, 1555, 1510, 1487, 1445, 1397, 1323, 1283, 1264, 1188, 1146, 1065, 1022, 976, 961, 880, 844, 801, 776, 756, 738, 704, 677, 605	3.73 (s, 3H); 3.81 (s, 3H); 6.53–8.07 (m, 13H); 11.68 (s, 1H)	426 (M^+ − HCl−Cl^-, 6), 425 (M^+ − 2HCl, 25), 291 (5), 227 (27), 216 (5), 210 (6), 201 (6), 200 (38), 175 (12), 136 (9), 135 (100), 134 (3), 133 (14), 107 (4), 77 (4)
7i	94	181–183 (CH_3CN)	$C_{23}H_{18}BrCl_2N_5O_2$ (547.2)	2720, 1613, 1582, 1559, 1541, 1506, 1499, 1294, 1252, 1184, 1171, 1150, 1125, 1024, 984, 897, 839, 762, 743, 720, 696	3.82 (s, 3H); 7.08–8.05 (m, 13H); 11.67 (s, 1H)	476 (M^+ + 2-HCl−Cl^-, 8), 475 (M^+ + 2-2HCl, 4), 474 (M^+ − HCl−Cl^-, 8), 473 (M^+ − 2HCl, 5), 291 (2), 277 (2), 275 (2), 260 (1), 258 (1), 216 (3), 201 (4), 200 (10), 186 (2), 185 (96), 184 (1), 183 (100), 175 (88), 157 (2), 155 (2), 134 (17), 133 (24), 107 (1), 77 (3)

[a] Yield of isolated pure product.
[b] Uncorrected.
[c] The microanalyses were in good agreement with the calculated values: C ±0.22, H ±0.24, N ±0.24.
[d] Recorded on a Nicolet FT 5DX spectrometer.
[e] Recorded at 60 MHz on a Varian EM-360A spectrometer.
[f] Recorded at 70 eV on a Hewlett-Packard 5993 C instrument.

N-Benzoyl-N'-ethoxyoxalyl Phenylhydrazine (**2a**); yield: 81%; white crystals; m.p. 141–142°C.

$C_{17}H_{16}N_2O_4$	calc.	C 65.38	H 5.16	N 8.97
(312.3)	found	65.56	5.05	8.70

IR (Nujol): ν = 3284, 1742, 1715, 1678 cm^{-1}.

^{1}H-NMR ($CDCl_3$/TMS): δ = 1.35 (t, 3H, J = 7.1 Hz); 4.42 (q, 2H, J = 7.1 Hz); 7.23–7.8 (m, 10H); 9.5 ppm (s, 1H).

MS (70 eV): m/e (%) = 312 (M^+, 26); 105 (100).

N-(p-Toluoyl)-N'-ethoxyoxalyl Phenylhydrazine (**2b**); yield: 73%; white crystals; m.p. 116–118°C.

$C_{18}H_{18}N_2O_4$	calc.	C 66.25	H 5.56	N 6.58
(326.3)	found	66.10	5.60	6.30

IR (Nujol): ν = 3262, 1740, 1702, 1685 cm^{-1}.

^{1}H-NMR ($CDCl_3$/TMS): δ = 1.34 (t, 3H, J = 7.1 Hz); 2.34 (s, 3H); 4.40 (q, 2H, J = 7.1 Hz); 7.1–7.7 (m, 9H); 9.43 ppm (s, 1H).

MS (70 eV): m/e (%) = 326 (M^+, 15); 119 (100).

N-(p-Methoxybenzoyl)-N'-ethoxyoxalyl Phenylhydrazine (**2c**); yield: 56%; white crystals; m.p. 136–138°C.

$C_{18}H_{18}N_2O_5$	calc.	C 63.15	H 5.30	N 8.18
(342.3)	found	63.40	5.15	8.20

IR (Nujol): ν = 3245, 1742, 1703, 1682 cm^{-1}.

^{1}H-NMR ($CDCl_3$/TMS): δ = 1.3 (t, 3H, J = 7.1 Hz); 3.72 (s, 3H); 4.29 (q, 2H, J = 7.1 Hz); 6.61 (d, 2H, J = 8.9 Hz); 7.19 (s, 5H); 7.4 (d, 2H, J = 8.9 Hz); 9.65 ppm (s, 1H).

MS (70 eV): m/e (%) = 342 (M^+, 10); 135 (100).

N-(p-Bromobenzoyl)-N'-ethoxyoxalyl Phenylhydrazine (**2d**); yield: 53%; white prisms; m.p. 113–115°C.

$C_{17}H_{15}BrN_2O_4$	calc.	C 52.19	H 3.86	N 7.16
(391.2)	found	51.90	3.70	7.06

IR (Nujol): ν = 3290, 1738, 1707, 1656 cm^{-1}.

^{1}H-NMR ($CDCl_3$/TMS): δ = 1.37 (t, 3H, J = 7.1 Hz); 4.3 (q, 2H, J = 7.1 Hz); 6.80–7.54 (m, 9H); 9.28 ppm (s, 1H).

MS (70 eV): m/e (%) = 392 (M^+ + 2, 13); 390 (M^+, 13); 185 (97); 183 (100).

Oxamide Derivatives 3; General Procedure:

To a solution of the appropriate *N*-aryl-*N*-(α-phenylphenacyl)oxamoyl chloride **1**, (2 mmol) in dry benzene, the corresponding amino compound (2 mmol) is added and the mixture is stirred under reflux for 12 h. After cooling the precipitated solid is separated by filtration and recrystallized from the appropriate solvent to give **3** (Table 1).

1,4-Oxazinium Perchlorates 4; General Procedure:

To a solution of the appropriate oxamide derivative **3**, (2 mmol) in dry toluene (20 ml), 70% perchloric acid (1.67 g, 2 mmol) and acetic anhydride (1 ml) are added. The resulting solution is stirred under reflux for 6 h. After cooling, cold ether (10 ml) is added and the precipitated solid is filtered off and recrystallized from ethanol to give **4** (Table 1).

Treatment of 4 with Triethylamine; Typical Procedure:

To a solution of **4i** (1.09 g, 2 mmol) in toluene (30 ml) triethylamine (0.202 g, 2 mmol) is added. The solution is refluxed for 7 h and on cooling the resulting solid is separated by filtration and recrystallized from ethanol to give **5**; yield; 0.69 g (78%); m.p. 172–173°C.

$C_{29}H_{22}N_2O_3$	calc.	C 78.00	H 4.96	N 6.27
(446.5)	found	78.13	4.77	6.10

IR (Nujol): ν = 1709, 1635 cm^{-1}.

^{1}H-NMR ($CDCl_3$/TMS): δ = 3.75 (s, 3H); 6.8–8.1 ppm (m, 19H).

MS (70 eV): m/e(%) = 446 (M^+, 100); 417 (18); 180 (8); 107 (6); 105 (5); 77 (14).

1,2,4-Triazin-6-ones 6; General Procedure:

To a solution of the appropriate *N*-aroyl-*N'*-ethoxyoxalyl phenylhydrazine **2**, (10 mmol) in dry toluene (30 ml), the corresponding unsubstituted amidrazones (10 mmol) is added and the reaction mixture is

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stirred under reflux for 15 h. After cooling, the solvent is removed under reduced pressure. The remaining solid is washed with ether (2 × 10 ml) and recrystallized from ethanol to give **6** (Table 2).

1,2,4-Triazino[5,6-*e*]-1,3,4-oxadiazinium Chlorides 7; General Procedure:

A mixture of the appropriate 1,2,4-triazin-6-one **6**, (3 mmol) and thionyl chloride (10 ml) is heated at 90 °C for 7 h. On cooling, the excess of thionyl chloride is removed under reduced pressure and the resulting solid is triturated with *n*-hexane. Recrystallization from dry acetonitrile gives **7** as their hydrochlorides (Table 2).

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