IMINOPHOSPHORANE-MEDIATED SYNTHESIS OF FUSED [1,3,4]THIADIAZOLES: PREPARATION OF IMIDAZO[2,1-b][1,3,4]THIADIAZOLES AND [1,3,4]THIADIAZOLO-[2,3-c][1,2,4]TRIAZINE DERIVATIVES

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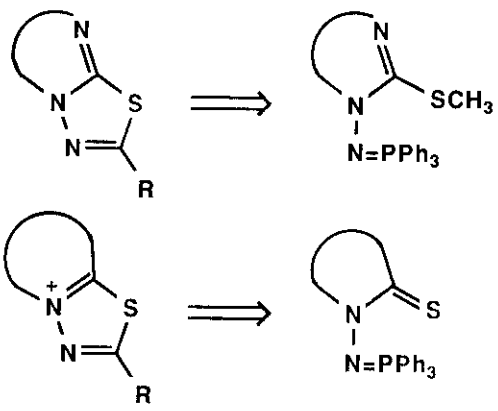
Abstract - A number of fused [1,3,4]thiadiazoles 4 and 7 have been prepared by treatment of iminophosphoranes 2 and 6 with acyl chlorides under neutral conditions.

As a part of an investigation on fused heterocycles we have reported the preparation of bridgehead nitrogen heterocycles which contain the [1,3,4]thiadiazole moiety e.g. [1,2,4]triazolo[3,4-b][1,3,4]thiadiazoles[1], [1,3,4]thiadiazolo[3,2-a]pyridines[2], [1,3,4]thiadiazolo[3,2-c]quinazolines[3], and [1,3,4]thiadiazolo[2,3-c][1,2,4]triazines[4].

We now describe a new general method for the preparation of fused [1,3,4]thiadiazoles such as imidazo[2,1-b][1,3,4]thiadiazoles and [1,3,4]thiadiazolo[2,3-c][1,2,4]triazines. On the other hand, it has become increasingly apparent that the aza-Wittig reaction of iminophosphoranes is a highly useful reaction in preparative heterocyclic chemistry. Consequently, improvements which increase the efficiency or enlarge its applicability are always desirable and the discovery of novel functionalized iminophosphoranes bearing a moiety able to react with the aza-Wittig product is important in this respect. In this context, our approach for the preparation of fused [1,3,4]thiadiazoles is based on the aza-Wittig reaction of iminophosphoranes derived from N-aminoheterocycles, which are conveniently functionalized in at least one of the adjacent positions to the endocyclic nitrogen atom by a thiocarbonyl or methylthio group, with acyl chlorides to give N-heteroaromatic imidoyl chlorides as highly reactive intermediates which undergo cyclization to give [1,3,4]thiadiazoles.

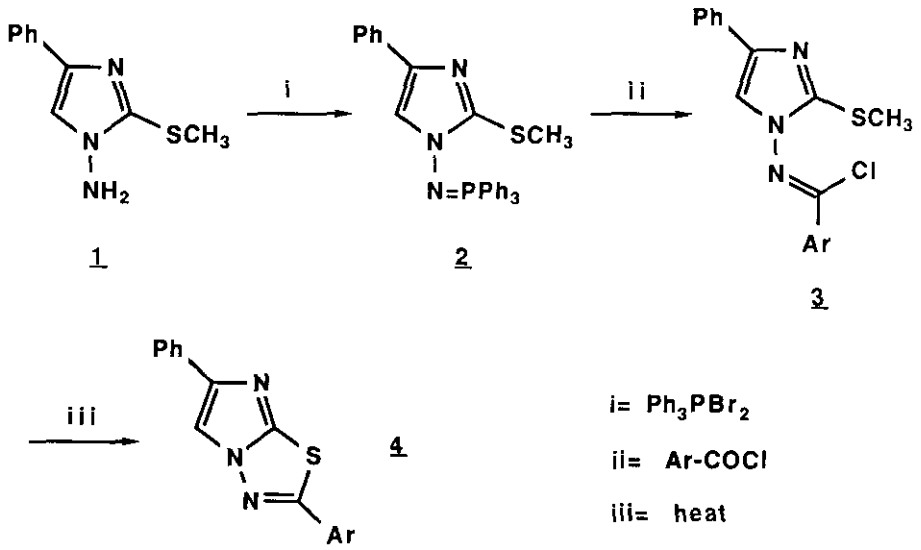
In the N-aminoazole series the presence of a thioiminoether group allows the preparation of neutral fused [1,3,4]thiadiazoles whereas the N-aminoazine bearing a thiocarbonyl group leads to fused [1,3,4]thiadiazoles which display cationic character.



Imidazo[2,1-b][1,3,4]thiadiazoles

All the methods described so far for the preparation of imidazo[2,1-b][1,3,4] thiadiazoles are based on the reaction of 5-amino[1,3,4]thiadiazole derivatives with α-halo carbonyl compounds[5].

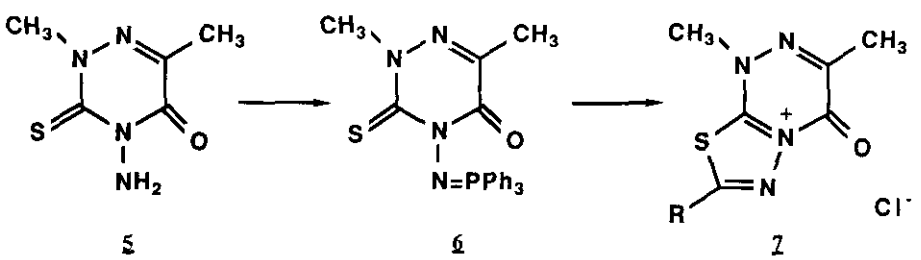
We report here an apparently widely applicable synthesis of 2-aryl-6-phenylimidazo[2,1-b][1,3,4]thiadiazoles 4 in synthetically useful yields based on the annelation of the 1,3,4 thiadiazole ring into a preexisting imidazole one. The aminoheterocycle 1-amino-2-methylthio-4-phenylimidazole 1, readily available by condensation of isothiosemicarbazone derived from benzaldehyde with phenacyl bromide and subsequent hydrazinolysis[6], reacts with triphenylphosphine dibromide in dry benzene to give 2-methylthio-4-phenyl-1-triphenylphosphoranylidenaminoimidazole 2 as crystalline solid in 95% yield. Compound 2 reacts with aroyl chlorides in dry toluene at reflux temperature to give the corresponding 2-aryl-6-phenylimidazo[2,1-b][1,3,4]thiadiazoles 4 in moderate to good yields (55-77%) (Table 1). The conversion 2-- 4 involves initial aza-Wittig reaction between iminophosphorane 2 and the acyl chloride to give the N-heteroaromatic imidoyl chloride 3 as intermediate[7] which undergoes cyclization and elimination of methyl chloride to give 4. This assumption is supported by the isolation, in all cases, of imidoyl chlorides 3 in moderate yields (47-60%) (Table 1) and the demostration that they are converted by heating into the corresponding fused [1,3,4]thiadiazoles 4 in moderate yields (30-57%). The ir spectra of compounds 3 show bands in the region 1628-1636 cm^{-1} due to the C=N bond and the ^{1}H-nmr spectra show among others a signal as a singlet at δ 2.65-2.75 ppm due to the S-methyl group. Mass spectra of 3 show the expected molecular ion peaks in high intensity, significative peaks are also found at m/z [M^+-CH_3Cl], [Ar-CN], 103 and 189. Similarly, mass spectra of compounds 4 show the expected molecular ion peaks in high intensity and fragments at m/z [M^+-Ar-CN], [Ar-CN], 147, 116 and 103.



1 2 3 4

[1,3,4]Thiadiazolo[2,3-c][1,2,4]triazines

Methods for the synthesis of [1,3,4]thiadiazolo[2,3-c][1,2,4]triazines may be conveniently classified into two main groups: construction of the [1,2,4]triazine portion of the fused ring system onto a preformed [1,3,4]thiadiazole ring[8], and ring closure of an appropriate 4-amino-[1,2,4]-triazine with a carbon-inserting reagent which supplies the carbon of the [1,3,4]thiadiazole moiety[9]. In this context, we report now that iminophosphorane 6, readily available from 4-amino-2,6-dimethyl-5-oxo-3-thioxo-2,3,4,5-tetrahydro[1,2,4]triazine 5 and triphenylphosphine dibromide, reacts with acyl chlorides in dry benzene at room temperature to give the corresponding [1,3,4]thiadiazolo[2,3-c][1,2,4]triazinium chlorides 7 in moderate to good yields (Table 2). Structural elucidation of 7 is accomplished on the basis of the spectral and microanalytical data. The ir spectra of all cationic derivatives 7 show a strong absorption band in the region 1748-1738 cm^{-1} attributable to the carbonyl group. In the ^{1}H-nmr spectra of 7 the chemical shifts of N-CH_3 and C_6-CH_3 groups are characteristic at δ 4.36-4.25 and δ 2.68-2.56 ppm, respectively, while in the ^{1}H-nmr spectrum of compound 6 these groups appear at δ 3.93 and δ 2.11 ppm, respectively. The EI-mass spectra show peaks at masses corresponding to the fragments [M^+-Cl], significative peaks are also found at m/z [M^+-Cl-CO], [R-CN], and [R-CS].



5 6 7

TABLE 1. Preparation of N-Heteroaromatic Imidoyl Chlorides 3 and Imidazo[2,1-b][1,3,4]thiadiazoles 4.

Entry	Ar	Mp(°C)	Yield (%)	Found C	Found H	Found N	Molecular Formula	Required C	Required H	Required N
3a	C_6H_5	108	60	62.29	4.28	13.05	$C_{17}H_{14}ClN_3S$	62.28	4.30	12.82
3b	$4\text{-}H_3C\text{-}C_6H_4$	116-117	60	63.35	4.66	12.38	$C_{18}H_{16}ClN_3S$	63.24	4.72	12.29
3c	$4\text{-}Cl\text{-}C_6H_4$	126-127	47	56.03	4.38	11.66	$C_{17}H_{13}Cl_2N_3S$	55.90	4.41	11.50
3d	$4\text{-}H_3CO\text{-}C_6H_4$	118	40	60.35	4.58	11.60	$C_{18}H_{16}ClN_3OS$	60.41	4.51	11.74
3e	$C_6H_5\text{-}CH{=}CH$	127-128	52	64.60	4.53	11.99	$C_{19}H_{16}ClN_3S$	64.49	4.56	11.87
3f	$2\text{-}C_{10}H_7$	142-143	50	65.73	5.41	10.85	$C_{21}H_{21}ClN_3S$	65.87	5.53	10.97
4a	C_6H_5	206	57	69.17	4.03	15.03	$C_{16}H_{11}N_3S$	69.29	4.00	15.15
4b	$4\text{-}H_3C\text{-}C_6H_4$	218	65	69.95	4.46	14.55	$C_{17}H_{13}N_3S$	70.08	4.50	14.42
4c	$4\text{-}Cl\text{-}C_6H_4$	263	60	61.69	3.29	13.46	$C_{16}H_{10}ClN_3S$	61.64	3.23	13.48
4d	$4\text{-}H_3CO\text{-}C_6H_4$	227	55	66.58	4.36	13.77	$C_{17}H_{13}N_3OS$	66.43	4.26	13.67
4e	$C_6H_5\text{-}CH{=}CH$	230	67	71.42	4.21	13.96	$C_{18}H_{13}N_3S$	71.26	4.32	13.85
4f	$2\text{-}C_{10}H_7$	244	77	73.46	3.98	12.99	$C_{20}H_{13}N_3S$	73.37	4.00	12.83

TABLE 2. Preparation of [2,3-c][1,2,4]triazinium Salts 7.

Entry	Ar	Mp(°C)	Yield (%)	Found C	Found H	Found N	Molecular Formula	Required C	Required H	Required N
7a[a]	CH_3	219-220	65	29.43	3.16	19.85	$C_7H_9BF_4N_4OS$	29.60	3.19	19.72
7b	C_6H_5	198-200	75	49.03	3.61	18.92	$C_{12}H_{11}ClN_4OS$	48.89	3.76	19.01
7c	$4\text{-}H_3C\text{-}C_6H_4$	195-197	72	50.42	4.36	18.21	$C_{13}H_{13}ClN_4OS$	50.56	4.24	18.14
7d	$4\text{-}H_3CO\text{-}C_6H_4$	150-152	55	47.93	4.15	17.34	$C_{13}H_{13}ClN_4O_2S$	48.07	4.03	17.25
7e	$4\text{-}Cl\text{-}C_6H_4$	163-165	60	43.91	2.97	17.18	$C_{12}H_{10}Cl_2N_4OS$	43.78	3.06	17.01
7f	$4\text{-}Br\text{-}C_6H_4$	160-162	55	38.35	2.75	15.16	$C_{12}H_{10}BrClN_4OS$	38.57	2.69	14.99
7g	$2\text{-}C_{10}H_7$	225-227	55	55.63	3.84	16.19	$C_{16}H_{13}ClN_4OS$	55.73	3.79	16.24

[a] Isolated as tetrafluoroborate.

EXPERIMENTAL

Melting points were obtained on a Kofler hot-stage apparatus and are uncorrected. Ir spectra were run using NaCl plates on a Nicolet FT-5DX spectrophotometer in Nujol emulsions. ^{1}H-Nmr spectra were obtained on a Varian FT-80 spectrometer at 80 MHz. The EI-mass spectra were obtained with a Hewlett-Packard 5993C spectrometer. Elemental analysis were performed with a Perkin Elmer 240C instrument.

2-Methylthio-4-phenyl-1-triphenylphosphoranylidenamino-1H-imidazole 2. Bromine (1.44 g, 9 mmol) in dry benzene (15 ml) was added dropwise to a stirred solution of triphenylphosphine (2.36 g, 9 mmol) in dry benzene (20 ml) at 0-5°C under nitrogen. The mixture was stirred for 1 h and then allowed to warm to room temperature. A solution of 1-amino-2-methylthio-4-phenyl-1H-imidazoles (1.85 g, 9 mmol) and triethylamine (1.82 g, 18 mmol) in dry benzene (20 ml) was added, after heating under reflux for 12 h, triethylammonium bromide was deposited. The salt was separated by filtration and the filtrate concentrated to dryness to afford a crude product which recrystallized from benzene/hexane (1:1, v/v), gave the iminophosphorane 2 (3.95 g, 95%) as colourless prisms, mp 194-195 °C; (Found: C, 72.15; H, 5.18; N, 8.98. $C_{28}H_{24}N_3PS$ requires C, 72.24; H, 5.20; N, 9.02); Ir ν_{max} (Nujol) 1602, 1546, 1314, 1189, 1115, 1070, 1030, 996, 982, 964, 941, 752, 737, 721, 694 cm^{-1}; ^{1}H-nmr δ ($CDCl_3$) 8.00-7.20(21H), 2.50(3H,s); m/z(%) 465(M^+,41), 450(5), 418(7), 348(16), 347(74), 263(14), 262(56), 184(20), 183(100), 160(53), 152(14), 133(14), 116(56), 108(72), 102(84), 77(14), 69(12), 57(15).

General Procedure for the Formation of Aryl-N-[2-methylthio-4-phenyl-imidazol-1-yl]imidoyl Chlorides 3. To a solution of 2-methylthio-4-phenyl-1-triphenylphosphoranylidenamino-1H-imidazole 2 (0.93g, 2mmol) in dry toluene (25 ml), the appropriate aroyl chloride (2 mmol) was added. The reaction mixture was stirred at reflux temperature for 15 h. After cooling, the solvent was removed off under reduced pressure and the residual material was slurried with ether (20 ml) and the separated solid was collected by filtration and recrystallized from ether/dichloromethane (1:1 , v/v) to give 3 as yellow prisms (see Table 1).

General Procedure for the Formation of 2-Aryl-6-phenylimidazo[2,1-b][1,3,4]thiadiazoles 4.

Method A. The appropriate aryl-N-[2-methylthio-4-phenyl-imidazol-1-yl]imidoyl chloride 3 (2 mmol) was heated at a temperature slightly its melting point (180-210°C) under reduced pressure. After cooling, the residual material was recrystallized from hexane/dichloromethane (2:1, v/v) to give 4 as colourless prisms.

Method B. To a solution of 2-methylthio-4-phenyl-1-triphenylphosphoranylidenamino-1H-imidazole 2 (0.93 g, 2 mmol) in dry toluene (25 ml), the appropriate aroyl chloride (2 mmol) was added. The reaction mixture was heated at reflux temperature for 60 h. After cooling, the solvent was removed off under reduced pressure

TABLE 3. Spectral Data of Compounds 3, 4, and 7.

Compound No.	IR $\nu(cm^{-1})$	^{1}H-NMR δ(ppm)	MS m/z(%)
3a	1634,1603,1489,1292, 1229,1167,1092,1026, 939,918,787,773,760, 719.	8.35-7.26(11H,m); 2.75(3H,s).	329(M^++2,23),327(M^+,64), 277(11),190(14),189(100), 184(19),182(50),145(21), 121(10),118(16),116(24), 103(81),102(22),91(12), 89(57),77(45).
3b	1631,1602,1489,1285, 1234,1161,1087,1030, 1019,934,917,821, 798,770,768,691.	8.20-7.30(10H,m); 2.65(3H,s); 2.45(3H,s).	343(M^++2,15),341(M^+,43), 196(19),189(50),147(19), 145(18),130(11),121(16), 118(21),116(43),104(16), 103(100),102(87),91(31), 89(39),77(26).
3c	1636,1618,1605,1597, 1587,1516,1491,1323, 1227,1171,1160,1092, 1011,966,935,835, 760,706.	8.42-7.07(10H,m); 2.75(3H,s);	365(M^++4,14),363(M^++2,69) 361(M^+,100),311(23),218 (23),216(33),190(12),189 (88),147(21),137(13),123 (18),116(18),103(51),89 (13),76(18).
3d	1628,1605,1578,1559, 1506,1315,1260,1240, 1179,1165,1090,1028, 937,916,853,775,712.	8.23-6.87(10H,m); 3.87(3H,s); 2.77(3H,s).	359(M^++2,19),357(M^+,54), 307(15),310(8),189(100), 133(56),116(15),107(48), 103(79),102(37),89(13), 76(25).
3e	1628,1605,1572,1555, 1315,1294,1188,1167, 1146,1094,1026,953, 795,750,714.	8.31-7.06(13H,m); 2.77(3H,s).	355(M^++2,14)353(M^+,42), 278(34),277(82),208(35), 199(30),189(100),183(25) 157(21),152(20),147(21), 116(29),115(55),103(70), 102(44),89(25),77(65).
3f	1631,1602,1552,1506, 1314,1302,1194,1167, 1128,1094,1071,970, 922,899,851,827,773, 752,708.	8.65-7.07(13H,m); 2.73(3H,s).	379(M^++2,10),377(M^+,25), 327(21),232(34),189(100) 174(23),153(91),147(51), 139(44),130(10),127(36), 121(11),116(22),103(88),

TABLE 3 (Cont.)

			102(20),89(15),76(19).
4a	1603,1573,1520,1317, 1295,1260,1071,1025, 966,937,911,804,757, 715,692.		277(M^+,33),174(33),148 (10),147(70),146(14),116 (10),104(10),103(100), 102(3),77(10).
4b	1603,1535,1315,1293, 1256,1214,1071,1025, 964,935,013,846,815, 785,770,735.	8.02-7.20(10H,m); 2.40(3H,s).	291(M^+,53),174(26),148 (10),147(73),146(15),120 (10),117(19),116(27),104 (10),103(100),91(10),90 (15),76(15).
4c	1593,1572,1514,1318, 1295,1256,1016,965, 914,826,773,750,722, 694.		313(M^++2,23),311(M^+,68) 174(73),148(10),147(93), 146(19),139(7),137(22), 116(12),104(10),103(100), 102(18),76(20).
4d	1608,1577,1530,1498, 1312,1304,1250,1116, 1072,1032,969,913, 829,771,725,693.	8.10-7.00(10H,m); 3.90(3H,s).	307(M^+,68),174(43),148 (10),147(67),146(12),133 (18),116(10),104(10),103 (100),90(14),76(16).
4e	1631,1602,1578,1535, 1504,1493,1294,1258, 1238,1202,1109,1071, 1026,952,934,912, 818,770,748,717.		303(M^+,86),174(44),148 (10),147(81),146(14),129 (15),128(10),120(5),116 (10),103(100),102(14).
4f	1602,1540,1512,1281, 1260,1196,1132,1072, 1026,990,937,866, 831,754,744,692.		327(M^+,42),174(34),163 (10),152(12),146(18), 153(60),147(83),146(14), 126(21),116(10),103(100), 77(10).
7a	1740,1604,1543,1303, 1273,1217,1104,1060, 957,896,748,699,647, 610.	4.33(3H,s); 3.04(3H,s); 2.60(3H,s).	197(M^+-BF_4,5),169(5),157 (30),137(15),129(14),128 (7),117(7),99(8),97(18) 88(13),83(23),73(23),70 (14),69(22),59(35),57(28) 49(100),41(10).

TABLE 3 (Cont.)

7b	1740,1661,1525,1307, 1261,1084,899,793, 739,706.	8.10-7.65(5H,m); 4.25(3H,s); 2.56(3H,s).	259(M^+-Cl,6),232(16),231 (100),191(12),141(11), 128(20),121(77),104(12), 103(81),88(13),77(49), 76(37),75(10),74(8),70 (15),51(22).
7c	1748,1601,1524,1500, 1321,1307,1290,1194, 1062,1035,897,824, 704.	7.95(2H,d,J=7Hz); 7.48(2H,d,J=7Hz); 4.27(3H,s); 2.58(3H,s); 2.50(3H,s).	273(M^+-Cl,5)246(15),245 (100),135(33),134(10), 128(20),91(13),69(5).
7d	1742,1599,1578,1528, 1315,1267,1186,1121, 1020,895,849,704.	8.10(2H,d,J=9Hz); 7.20(2H,d,J=9Hz); 4.26(3H,s); 3.95(3H,s); 2.60(3H,s).	289(M^+-Cl,4),261(24),246 (5),157(8),153(7),151 (100),136(16),134(12), 133(65),128(12),108(20), 90(38),76(16),69(15).
7e	1740,1599,1526,1314, 1292,1265,1090,1070, 1050,1010,988,899, 849,835,740,723,706.	8.10(2H,d,J=9Hz); 7.70(2H,d,J=9Hz); 4.30(3H,s); 2.62(3H,s).	295(M^++2-Cl,1),293 (M^+-Cl,3),267(38),265 (100),157(31),155(91), 139(9),137(18),128(26), 113(8),111(22),75(24), 69(23).
7f	1738,1603,1587,1523, 1263,1068,1006,898, 831,740,706.	7.95(4H,s); 4.34(3H,s); 2.65(3H,s).	339(M^++2-Cl,1),337 (M^+-Cl, 3),311(99),309 (100),201(47),199(47), 183(8),181(8),128(30), 121(7),119(7),102(14), 94(8),69(16).
7g	1742,1597,1553,1520, 1317,1269,1061,1026, 995,899,876,835,771, 734,702.	8.50-7.70(7H,m); 4.36(3H,s); 2.68(3H,s).	309(M^+-Cl,3),281(63),172 (13),171(100),153(22),128 (30),127(52),126(22),85 (37),69(20).

[a] Obtained as solutions in $CDCl_3$ + CF_3COOH, except for compounds 3 which were recorded in $CDCl_3$.

and the residual material was slurried with ethanol (35 ml), the separated solid was collected by filtration dried and recrystallized from hexane/dichloromethane (2:1, v/v) to give 4 (see Table 1).

2,6-Dimethyl-4-triphenylphosphoranylidenamino-5-oxo-3-thioxo-2,3,4,5-tetrahydro[1,2,4]triazine 6. Bromine (7.29 g, 45.65 mmol) in dry benzene (45 ml) was added dropwise to a stirred solution of triphenylphosphine (11.87 g, 45.65 mmol) in dry benzene (50 ml) at 0-5°C under nitrogen. The mixture was stirred for 1 h and then allowed to warm to room temperature. A solution of 4-amino-2,6-dimethyl-5-oxo-3-thioxo-2,3,4,5-tetrahydro 1,2,4 triazine 5 (6.54 g, 38 mmol) and triethylamine (9.24 g, 91.30 mmol) in dry benzene (40 ml) was added, after heating under reflux for 24 h, triethylammonium bromide was deposited. The salt was separated by filtration and the filtrate concentrated to dryness to afford a crude product which was slurried with hexane and the formed solid was recrystallized from dichloromethane to give the iminophosphorane 6 (13.13 g, 80%) as pale yellow prisms, mp 223°C (Found: C, 63.66; H, 5.08; N, 12.84. $C_{23}H_{21}N_4OPS$ requires C, 63.87; H, 4.92; N, 12.95); Ir ν_{max} (Nujol) 1670, 1319, 1268, 1178, 1110, 1030, 1020, 986, 894, 844, 747, 725, 661 cm^{-1}; ^{1}H-nmr δ ($CDCl_3$) 7.96-7.89(6H,m), 7.54-7.40(9H,m), 3.93(3H,s), 2.11(3H,s); m/z (%) 432(M^+,21), 308(22), 277(13), 276(56), 263(11), 262(58), 261(11), 185(13), 184(21), 183(100), 152(12), 108(61), 107(18), 77(12), 73(24).

General Procedure for the Formation of 1,3-Dimethyl-7-substituted-4-oxo-4H-[1,3,4]thiadiazolo[2,3-c][1,2,4]triazinium Chlorides 7.
To a solution of 2,6-dimethyl-4-triphenylphosphoranylidenamino-5-oxo-3-thioxo-2,3,4,5-tetrahydro[1,2,4]triazine 6 (0.43 g, 1 mmol) in dry benzene (15 ml), the appropriate acyl chloride (1 mmol) was added. The reaction mixture was stirred at room temperature for 24 h. Whereupon the precipitated solid was collected by filtration, washed with ether (10 ml), dried and recrystallized from ethanol/ether (1:1, v/v) to give 7 (see Table 2).

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