Azinoiminophosphorane Mediated 4*H*,8*H*-1,2,4-Triazolo[1,5-*c*]-[1,3]oxazepin-4-ones and 5,6-Dihydro-7*H*,12*H*-naphtho[2,1-*f*]-[1,2,4]triazolo[1,5-*c*][1,3]oxazepin-7-ones Synthesis

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The aza-Wittig reactions of benzaldehyde-, acetophenone- and benzophenone 1-[(triphenylphosphoranylidene)amino]ethylidenehydrazones (**1**) with 2,3-furandiones **6** provide a new route to 4*H*,8*H*-1,2,4-triazolo[1,5-*c*][1,3]oxazepin-4-ones **14** or 5,6-dihydro-7*H*,12*H*-naphtho[2,1-*f*][1,2,4]triazolo[1,5-*c*]-[1,3]oxazepin-7-ones **17** *via* the thermal reaction of the expected azinoimine vinylogous lactones.

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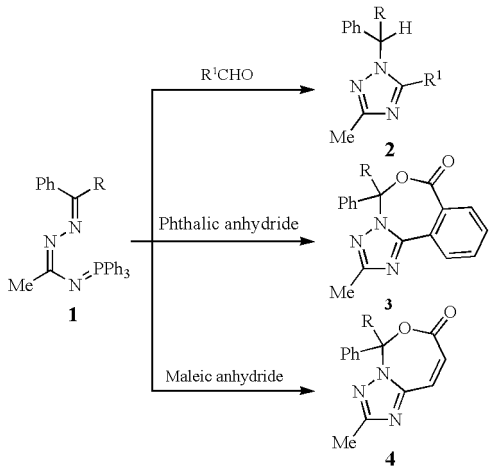
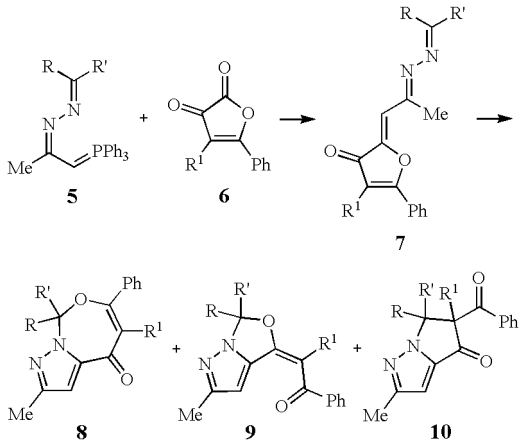
In recent years, there has been a significant interest in the chemistry of iminophosphoranes because of their utility in the synthesis of a wide variety of nitrogen heterocycles, and many interesting heterocyclization reactions involving functionalized iminophosphoranes have been reviewed [1]. Also, we reported that aza-Wittig reactions of azinoiminophosphoranes **1** with aromatic aldehydes [2],

Scheme I



phthalic anhydride and maleic anhydride [3] gave trisubstituted 1,2,4-triazoles **2**, 5*H*,7*H*-1,2,4-triazolo[1,5-*c*]-[1,3]benzoxazepin-7-ones **3** and 6*H*,8*H*-1,2,4-triazolo-[1,5-*a*][1,3]oxazepin-6-ones **4** by thermal rearrangement of intermediate azinoimines, respectively (Scheme I). In addition, Schweizer and co-workers described that the reactions of azine ylides **5** with 2,3-furandiones **6** would give the 4*H*,8*H*-pyrazolo[1,5-*c*][1,3]oxazepin-4-ones **8**, 4*H*,6*H*-pyrazolo[1,5-*c*]oxazol-4-ylidines **9** and/or 4*H*-pyrrolo[1,2-*b*]pyrazol-4-ones **10** depending upon R and R^1 substituents [4] (Scheme II). With their results in mind, we tried to apply this methodology to the synthesis of 4*H*,8*H*-1,2,4-triazolo[1,5-*c*][1,3]oxazepin-4-ones **14** and 5,6-dihydro-7*H*,12*H*-naphtho[2,1-*f*][1,2,4]triazolo[1,5-*c*]-[1,3]oxazepin-7-ones **17** by the reaction of known azinoiminophosphoranes **1a-c** with furandiones **6a-c** (Scheme III and IV).

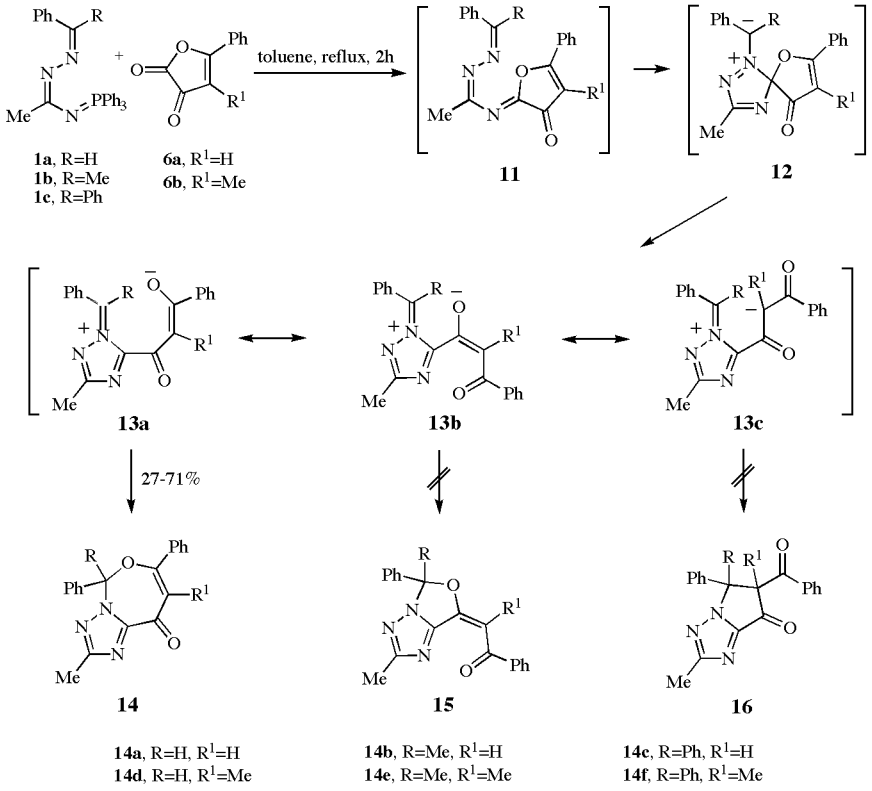
Scheme II



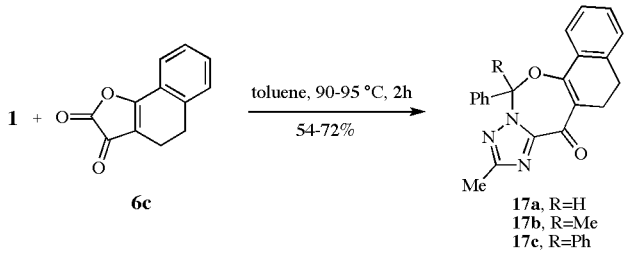
The aza-Wittig reactions of **1a-c** with furandiones **6a** and **6b** in toluene at reflux temperature led directly to 27-71 % yields of a single product, hitherto unknown 4*H*,8*H*-1,2,4-triazolo[1,5-*c*][1,3]oxazepin-4-ones **14a-f**. Both possible five-membered ring closure products **15** and **16** were not produced. When the reactions were carried out at room temperature and monitored by thin-layer chromatography, no reactions occurred. The reactions of iminophosphoranes **1a-c** with furandione **6c** were also investigated and reacted smoothly at 90-95 °C [5] to afford 54-72 % yields of 5,6-dihydro-7*H*,12*H*-naphtho[2,1-*f*][1,2,4]triazolo-[1,5-*c*][1,3]oxazepin-7-ones **17a-c** (Scheme IV).

A proposed mechanism for the formation of 1,2,4-triazoles **14** is shown in Scheme III based on literature [4]. The presumed intermediate azinoimine vinylogous lactones **11** were too unstable to isolate under the reaction condition, so nucleophilic attack by the imine nitrogen on the exocyclic imine bond in **11** would yield the azomethine imine intermediate **12** which could open to zwitterionic intermediates **13a-c**. Ring closure from **13a** would yield the seven-membered 1,2,4-triazole-fused vinylogous lactones **14**. Presumably the seven-membered ring closure is a 7-*Endo-Trig* process and is favored. Both five-membered ring closures to give **15** and **16** would be a 5-*Endo-Trig* process and would be disfavored by Baldwin's rule [6].

Scheme III



Scheme IV



Structural elucidation of **14** and **17** was accomplished on the basis of spectral data. The ^{13}C nmr spectra showed a characteristic peak at δ = 175.2-177.5 for the vinylogous lactone carbonyl carbon, and two triazole carbons resonated in δ = 152.8 to 153.5 region and δ = 158.0 to 161.6 region. Their infrared spectra showed absorption at 1619-1638 cm^{-1} for the carbonyl band. Their mass spectra showed molecular ion peaks in all cases.

In conclusion, it has been demonstrated that the aza-Wittig reactions between azinoiminophosphoranes and furandiones provides a new synthesis of 4*H*,8*H*-1,2,4-triazolo[1,5-*c*][1,3]oxazepin-4-ones **14** and 5,6-dihydro-7*H*,12*H*-naphtho[2,1-*f*][1,2,4]triazolo[1,5-*c*][1,3]-oxazepin-7-ones **17** *via* the azinoimine vinylogous lactones. This method is useful because we have found no previous reports of the preparation of this ring system.

EXPERIMENTAL

All reagents and solvents were reagent grade or were purified by standard methods before use and the reactions were routinely carried out under an inert atmosphere. Silica gel 60 (70-230 mesh ASTM) used for column chromatography was supplied by E. Merck. Analytical thin layer chromatography (tlc) was performed on silica gel with fluorescent indicator coated on aluminium sheets. Melting points were taken using an Electrothermal melting point apparatus and are uncorrected. Microanalyses were obtained using a Carlo Erba EA 1180 element analyzer. Mass spectra were obtained using a ThermoQuest Polaris Q mass spectrometer operating at 70 eV. Infrared spectra were recorded on a Nicolet Magna 550 FTIR spectrometer. The ^1H and ^{13}C nmr spectra were measured on a Gemini 300 spectrometer. All chemical shifts are reported in parts per million (δ) relative to tetramethylsilane in deuteriochloroform solvent.

The benzaldehyde-, acetophenone- and benzophenone 1-[(triphenylphosphoranylidene)amino]ethylidenehydrazones (**1a-c**) [2,7] and furandiones **6a-c** [8] were prepared following literature procedures.

4H,8H-1,2,4-Triazolo[1,5-*c*][1,3]oxazepin-4-ones **14a-f** and 5,6-Dihydro-*7H,12H*-naphtho[2,1-*f*][1,2,4]triazolo[1,5-*c*][1,3]-oxazepin-7-ones **17a-c**. General Procedure.

To a solution of iminophosphorane **1** (1.5 mmoles) in 15 ml of toluene was added furandione **6** (2.25 mmoles) and this solution was stirred at reflux temperature or at 90-95 °C [9] for 2 hours. After cooling to room temperature the solvent was removed on a rotary evaporator. The residue was chromatographed on silica

Table 1

4*H*,8*H*-1,2,4-Triazolo[1,5-*c*][1,3]oxazepin-4-ones **14a-f** and
5,6-Dihydro-7*H*,12*H*-naphtho[2,1-*f*][1,2,4]triazolo[1,5-*c*][1,3]oxazepin-7-ones **17a-c**

	Reaction Time (h)	Yield (%)	MP (°C)	Molecular Formula	Analysis (%) Calcd../Found C	H	N	Mass Spectra m/z (%)
14a	2	27	178-180	$C_{19}H_{15}N_3O_2$ (317.34)	71.91 71.75	4.76 4.61	13.24 13.02	317 (M^+, 7), 213 (15), 212 (100), 173 (20), 105 (53), 77 (36)
14b	2	47	185-187	$C_{20}H_{17}N_3O_2$ (331.37)	72.49 72.13	5.17 5.03	12.68 12.45	331 (M^+, 18), 227 (16), 226 (100), 221 (30), 105 (38), 77 (21)
14c	2	52	211-213	$C_{25}H_{19}N_3O_2$ (393.44)	76.32 76.08	4.87 4.59	10.68 10.40	393 (M^+, 100), 392 (37), 365 (27), 364 (28), 336 (57), 294 (47), 288 (57), 105 (27), 77 (28)
14d	2	68	207-209	$C_{20}H_{17}N_3O_2$ (331.37)	72.49 72.20	5.17 4.96	12.68 12.41	331 (M^+, 25), 226 (40), 105 (100), 77 (37)
14e	2	71	173-175	$C_{21}H_{19}N_3O_2$ (345.39)	73.03 69.74	5.54 5.32	12.17 11.82	345 (M^+, 14), 330 (12), 240 (100), 105 (84), 77 (36)
14f	2	56	174-176	$C_{26}H_{21}N_3O_2$ (407.46)	76.64 76.39	5.19 5.03	10.31 10.58	407 (M^+, 12), 365 (34), 330 (100), 314 (57), 302 (62), 297 (53), 285 (28), 207 (42), 105 (69), 77 (45)
17a	2	70	190-192	$C_{21}H_{17}N_3O_2$ (343.38)	73.45 72.23	4.99 4.70	12.24 12.02	343 (M^+, 41), 326 (42), 314 (20), 266 (69), 233 (100), 171 (21)
17b	2	54	198-200	$C_{22}H_{19}N_3O_2$ (357.41)	73.93 73.70	5.36 5.03	11.76 11.48	357 (M^+, 16), 324 (100), 247 (62), 253 (44), 198 (36)
17c	2	72	209-211 (419.47)	$C_{27}H_{21}N_3O_2$	77.31 77.10	5.05 4.87	10.02 9.76	419 (M^+, 19), 342 (71), 326 (100), 309 (66), 207 (60)

Table 2

IR and NMR Data of Compounds **14** and **17**

	IR ν (cm^{-1}) (KBr)	^{1}H NMR δ (ppm) (Deuteriochloroform)	^{13}C NMR δ (ppm) (Deuteriochloroform)
14a	1638, 1596, 1568, 1487, 1429, 1335, 1269, 1219, 1114, 1048, 978, 838	2.46 (s, 3H), 6.51 (s, 1H), 7.38 (s, 1H), 7.34-7.58 (m, 8H), 7.77-7.79 (m, 2H)	13.9, 89.4 (d), 108.5, 126.7, 127.4, 128.0, 128.7, 129.3, 130.5, 132.0, 132.9, 152.8, 161.6, 165.0, 175.2
14b	1627, 1600, 1572, 1483, 1448, 1413, 1347, 1258, 1215, 1091, 765	2.51 (s, 3H), 2.57 (s, 3H), 6.33 (s, 1H) 6.77-6.79 (m, 2H), 7.21-7.30 (m, 3H), 7.49-7.58 (m, 3H), 7.86-7.89 (m, 2H)	13.9 (d), 30.5 (d), 96.3, 108.4 (d), 124.4, 127.2, 129.0, 129.1, 129.7, 132.2, 133.5, 139.0, 153.0, 160.7, 162.2, 175.3
14c	1631, 1603, 1572, 1475, 1444, 1339, 1258, 1122, 1048, 970, 897, 757	2.41 (s, 3H), 6.44 (s, 1H), 7.08-7.11 (m, 4H) 7.34-7.57 (m, 9H), 7.81-7.84 (m, 2H)	14.0, 99.1, 108.6 (d), 127.1, 127.5, 127.8, 128.5, 129.5, 130.2, 133.4, 138.1, 153.5, 160.4, 162.0, 175.3
14d	1627, 1600, 1475, 1429, 1332, 1300, 1223, 1153, 1044, 776	2.07 (s, 3H), 2.41 (s, 1H), 7.13 (s, 1H) 7.39-7.53 (m, 10H)	13.9, 16.9 (d), 89.1 (d), 117.6, 127.8, 128.4, 128.7, 129.9, 130.1, 131.2, 131.6, 134.5, 152.9, 161.4, 166.0, 176.9
14e	1634, 1588, 1565, 1491, 1444, 1332, 1312, 1277, 1227, 1145, 1095, 1021	1.76 (s, 3H), 2.39 (s, 3H), 2.56 (s, 3H) 6.89-6.92 (m, 2H), 7.28-7.33 (m, 3H), 7.46-7.55 (m, 5H)	14.0 (d), 16.3 (d), 30.0, 95.2, 118.1, 125.1, 128.4, 128.9, 129.4, 129.5, 130.6, 135.6, 138.6, 153.1, 160.7, 161.8, 177.1
14f	1619, 1586, 1561, 1479, 1452, 1421, 1328, 1258, 1149, 1044, 768	1.83 (s, 3H), 2.40 (s, 3H), 7.11-7.14 (m, 4H), 7.30-7.48 (m, 11H)	14.1, 16.0 (d), 98.1, 119.6, 127.8, 128.2, 128.5, 129.2, 129.7, 130.0, 135.6, 138.1, 153.3, 160.6, 161.1, 177.5
17a	1623, 1603, 1549, 1487, 1436, 1370, 1300, 1246, 1192, 1157, 1102, 733	2.46 (s, 3H), 2.71-2.87 (m, 4H), 7.21-7.46 (m, 8H), 7.81-7.83 (m, 1H)	13.9 (d), 22.2, 27.3, 89.0 (d), 118.1, 125.3, 125.4, 126.9, 127.7, 128.9, 130.1, 130.3, 131.8, 132.5, 140.4, 153.0, 160.3, 161.5, 175.3
17b	1627, 1600, 1561, 1479, 1421, 1363, 1312, 1161, 1102, 932, 854, 765	2.47 (s, 3H), 2.57 (s, 3H), 2.43-2.54 (m, 2H), 2.63-2.77 (m, 2H), 6.73-6.75 (m, 2H), 7.15-7.29 (m, 4H), 7.38-7.45 (m, 2H), 8.01-8.03 (m, 1H)	13.9 (d), 21.9, 27.2, 30.3 (d), 95.7, 118.0, 124.6, 125.0, 127.1, 127.6, 128.8, 129.5, 130.7, 131.5, 139.1, 140.5, 153.1, 158.0, 160.6, 175.4
17c	1627, 1600, 1557, 1479, 1448, 1417, 1355, 1308, 1153, 1095, 998, 765	2.41 (s, 3H), 2.62(s, 4H), 7.07-7.19 (m, 4H), 7.21-7.25 (m, 1H), 7.26-7.44 (m, 8H), 7.87-7.90 (m, 1H)	14.1 (d), 21.9, 27.2, 98.6, 118.7, 125.3, 125.4, 127.1, 127.7, 128.3, 129.8, 130.9, 131.5, 138.4, 140.4, 153.5, 158.0, 160.4, 175.5

gel column eluting with hexane-ethyl acetate 3:1 to give the product **14** or **17**. Purification was achieved by crystallization from ethyl ether.

The physical and spectral data of compounds **14** and **17** prepared by this general method are listed in Table 1 and Table 2.

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* Author to whom correspondence should be addressed.

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