

**Iminophosphorane-mediated Syntheses of [1,2,4]Triazolo[5,1-*c*][1,2,4]triazines. The Unexpected Formation of *Z,Z*-1,3-Diazetidone-2,4-di-imines. X-Ray Molecular Structure of 7-(*p*-Chloroanilino)-8-(*p*-chlorophenyl)-3-methyl[1,2,4]triazolo[5,1-*c*][1,2,4]triazin-4(8*H*)-one and of 1,3-Bis-(*p*-chlorophenyl)-2,4-bis-(6-methyl-3-methylthio-5-oxo-4,5-dihydro-1,2,4-triazin-4-ylimino)-1,3-diazetidone**

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A number of [1,2,4]triazolo[5,1-*c*][1,2,4]triazine derivatives have been prepared. 6-Methyl-3-methylthio-4-triphenylphosphoranylideneamino-5-oxo-4,5-dihydro-1,2,4-triazine (**19**) reacts with aryl isocyanates to yield the corresponding 1,3-diaryl-2,4-bis-(6-methyl-3-methylthio-5-oxo-4,5-dihydro-1,2,4-triazin-4-ylimino)-1,3-diazetidines (**20**)—(**24**); these undergo ring cleavage on treatment with aqueous ethanol to give the 8-aryl-7-arylamino-3-methyl[1,2,4]triazolo[5,1-*c*][1,2,4]triazin-4(8*H*)-ones (**8**), (**12**), and (**16**)—(**18**). The reaction of the 3-arylmethylenehydrazino-6-methyl-5-oxo-4-triphenylphosphoranylideneamino-4,5-dihydro-1,2,4-triazines (**35**) and (**36**), available from the corresponding 4-amino-3-arylmethylenehydrazino-6-methyl-5-oxo-4,5-dihydro-1,2,4-triazine and triphenylphosphine dibromide, with alkyl or aryl isocyanates led directly to 7-arylamino-8-arylmethyleneamino-3-methyl[1,2,4]triazolo[5,1-*c*][1,2,4]triazin-4(8*H*)-ones (**37**)—(**46**). Also, iminophosphoranes (**5**)—(**7**), (**35**), and (**36**) react with acyl chlorides in the presence of triethylamine to give the triazolotriazinones (**25**)—(**31**) and (**50**)—(**55**) respectively. Structures of compounds (**20**)—(**24**) have been established by means of <sup>13</sup>C n.m.r. analysis and X-ray crystallography.

The [1,2,4]triazolo[5,1-*c*][1,2,4]triazine ring system has been prepared by different methods: (i) from hydrazino<sup>1-3</sup> or 3,4-diamino-1,2,4-triazines<sup>4</sup> and carbon-inserting reagents; (ii) from 3-hydrazino-1,2,4-triazoles and  $\alpha$ -dicarbonyl compounds,<sup>5-7</sup> and (iii) from 1,2,4-triazole-5-diazonium salts and active-methylene compounds.<sup>8-10</sup>

We now describe different synthetic procedures to obtain this heterocyclic system [(**8**)—(**18**), (**25**)—(**31**), (**47**)—(**49**), and (**50**)—(**58**)] from 4-amino-6-methyl-3-methylthio-5-oxo-4,5-dihydro-1,2,4-triazine (**1**). The first-row compounds of Scheme 1 [(**1**), (**2**)—(**4**), (**5**)—(**7**), and (**8**)—(**16**)] have already been described.<sup>11</sup>

## Results and Discussion

The iminophosphorane (**19**), readily available from amine (**1**) and triphenylphosphine dibromide, reacted with aryl isocyanates in dry benzene at room temperature to give the corresponding 1,3-diaryl-1,3-diazetidone-2,4-di-imines (**20**)—(**24**) as crystalline solids in good yield (55—76%) (Table 1).

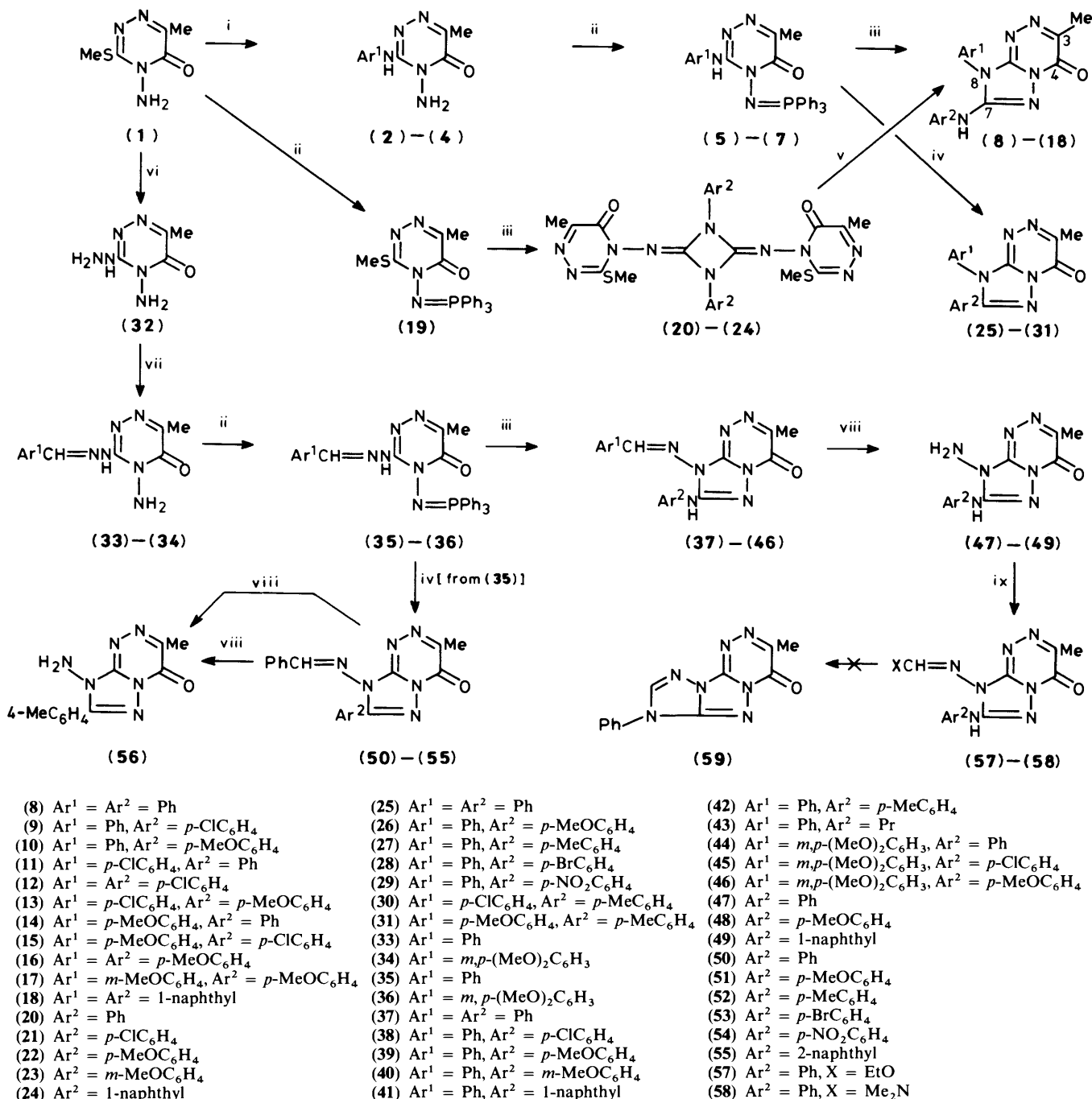
When compounds (**20**)—(**24**) were heated in aqueous ethanol for 14 h they underwent ring cleavage followed by cyclization to give the corresponding triazolotriazines (**8**), (**12**), and (**16**)—(**18**) as crystalline solids in good yield (51—77%) (Table 2).

This conversion is a useful alternative to the previously reported method<sup>11</sup> for the preparation of triazolotriazines from the iminophosphoranes (**5**)—(**7**) when Ar<sup>1</sup> = Ar<sup>2</sup>. On the other

hand, compound (**19**) reacted with *NN'*-diphenylthiourea in dry benzene at reflux to give a mixture of the triazolotriazine (**8**) and 7-anilino-3-methyl-4*H*-[1,3,4]thiadiazolo[2,3-*c*][1,2,4]triazin-4-one (**60**) as the major product.<sup>12</sup> We believe that this conversion (**19**)—(**8**) must follow the mechanism suggested<sup>13</sup> for the reaction of iminophosphoranes with *NN'*-disubstituted thioureas. This involves the formation of the guanidine derivative (**61**) which undergoes cyclization followed by elimination of methanethiol to give compound (**8**) (Scheme 2, pathway a). Presumably, the conversion (**19**)—(**60**) involves displacement of the methylthio group at position 3 by the sulphur atom of the thiourea to give the intermediate (**62**), which by [2 + 2]cycloaddition followed by elimination of aryliminophosphorane leads to product (**60**) (pathway b).

Compound (**1**) reacted with anhydrous hydrazine to give the hydrazino derivative (**32**) which, by action of aryl aldehydes in equimolecular amounts in ethanol solution, led to the hydrazones (**33**) and (**34**). Preparation of iminophosphoranes (**35**) and (**36**) was achieved by reaction of triphenylphosphine dibromide with hydrazones (**33**) and (**34**) in the presence of triethylamine. Compounds (**35**) and (**36**) in turn reacted with alkyl and aryl isocyanates in dry benzene at room temperature to give the corresponding triazolotriazines (**37**)—(**46**) in excellent yield (77—97%) (Table 3). Similar results were achieved by using isothiocyanates in place of isocyanates.

Iminophosphoranes (**5**)—(**7**) and (**35**), (**36**) react with acyl



**Scheme 1.** Reagents and conditions: i, Ar<sup>1</sup>NH<sub>2</sub>; heat; ii, Br<sub>2</sub>PPh<sub>3</sub>-Et<sub>3</sub>N; iii, Ar<sup>2</sup>NCO; iv, Ar<sup>2</sup>COCl-Et<sub>3</sub>N; v, aq. EtOH, heat (Ar<sup>1</sup> = Ar<sup>2</sup>); vi, NH<sub>2</sub>NH<sub>2</sub>; vii, Ar<sup>1</sup>CHO; viii, NH<sub>2</sub>NH<sub>2</sub>, heat; ix, HC(OEt)<sub>3</sub> or Me<sub>2</sub>NCH(OMe)<sub>2</sub>

**Table 1.** 1,3-Diaryl-1,3-diazetidines (20)—(24)

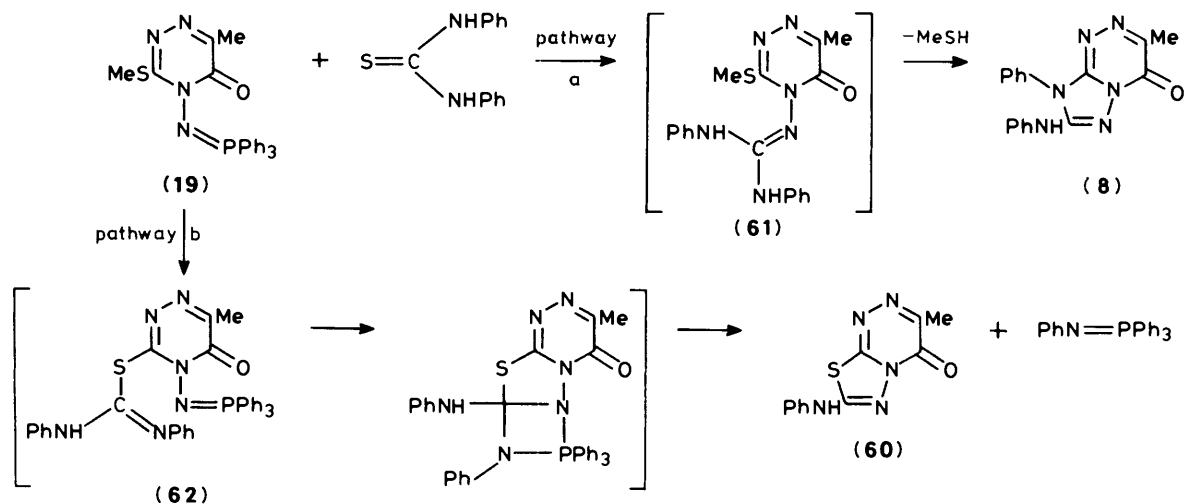
Compd.	Crystal form	Yield (%)	M.p. (°C)	Solvent	Found (%)			Formula	Required (%)		
					C	H	N		C	H	N
(20)	White plates	55	210—202	CH <sub>2</sub> Cl <sub>2</sub> -ether	52.7	4.0	25.5	C <sub>24</sub> H <sub>22</sub> N <sub>10</sub> O <sub>2</sub> S <sub>2</sub>	52.73	4.06	25.62
(21)	White prisms	75	202—205	CH <sub>2</sub> Cl <sub>2</sub> -ether	46.7	3.1	22.7	C <sub>24</sub> H <sub>20</sub> Cl <sub>2</sub> N <sub>10</sub> O <sub>2</sub> S <sub>2</sub>	46.83	3.27	22.76
(22)	White prisms	76	203—204	CH <sub>2</sub> Cl <sub>2</sub> -ether	51.4	4.3	22.9	C <sub>26</sub> H <sub>26</sub> N <sub>10</sub> O <sub>4</sub> S <sub>2</sub>	51.47	4.32	23.08
(23)	White prisms	58	100—102	CHCl <sub>3</sub> -ether	51.4	4.3	23.0	C <sub>26</sub> H <sub>26</sub> N <sub>10</sub> O <sub>4</sub> S <sub>2</sub>	51.47	4.32	23.08
(24)	White prisms	67	210—212	CHCl <sub>3</sub> -ether	59.4	4.0	21.6	C <sub>32</sub> H <sub>26</sub> N <sub>10</sub> O <sub>2</sub> S <sub>2</sub>	59.43	4.05	21.66

**Table 2.** 8-Aryl-7-arylamino-3-methyl[1,2,4]triazolo[5,1-c][1,2,4]triazin-4(8*H*)-ones

Compd.	Crystal form	Yield (%)	M.p. (°C)	Lit. <sup>a</sup> m.p. (°C)	Found (%)			Formula	Required (%)		
					C	H	N		C	H	N
(8)	Prisms	77	336—338	335—337							
(12)	White prisms	51	181—183	183—185							
(16)	White needles	65	283—284	282—284							
(17)	Prisms	71	221—223		60.2	4.8	22.2	C <sub>19</sub> H <sub>18</sub> N <sub>6</sub> O <sub>3</sub>	60.31	4.79	22.21
(18)	Plates	74	278—280		71.7	4.4	19.9	C <sub>25</sub> H <sub>18</sub> N <sub>6</sub> O	71.76	4.33	20.08

<sup>a</sup> Ref. 11.**Table 3.** 7-Arylamino-8-arylmethyleneamino-3-methyl[1,2,4]triazolo[5,1-c][1,2,4]triazin-4(8*H*)-ones (37)—(46)

Compd.	Crystal form	Yield (%)	M.p. (°C)	Solvent	Found (%)			Formula	Required (%)		
					C	H	N		C	H	N
(37)	White plates	80	265—266	EtOH	62.5	4.4	28.4	C <sub>18</sub> H <sub>15</sub> N <sub>7</sub> O	62.60	4.38	28.39
(38)	White needles	93	262—263	EtOH	56.95	3.6	25.7	C <sub>18</sub> H <sub>14</sub> ClN <sub>7</sub> O	56.92	3.71	25.81
(39)	White needles	84	260—262	EtOH	60.7	4.5	26.1	C <sub>19</sub> H <sub>17</sub> N <sub>7</sub> O <sub>2</sub>	60.79	4.56	26.12
(40)	White needles	77	232—234	EtOH	60.8	4.5	26.05	C <sub>19</sub> H <sub>17</sub> N <sub>7</sub> O <sub>2</sub>	60.79	4.56	26.12
(41)	White prisms	86	288—289	EtOH	66.7	4.35	24.8	C <sub>22</sub> H <sub>17</sub> N <sub>7</sub> O	66.82	4.33	24.79
(42)	White needles	95	242—244	EtOH	63.4	4.7	27.2	C <sub>19</sub> H <sub>17</sub> N <sub>7</sub> O	63.50	4.77	27.28
(43) <sup>a</sup>	White needles	69	204—206	EtOH	57.8	5.4	31.4	C <sub>18</sub> H <sub>17</sub> N <sub>7</sub> O	57.87	5.50	31.49
(44)	White needles	92	214—216	EtOH	59.3	4.6	24.1	C <sub>20</sub> H <sub>19</sub> N <sub>7</sub> O <sub>3</sub>	59.25	4.72	24.18
(45)	White needles	97	210—212	EtOH	54.5	4.1	22.3	C <sub>20</sub> H <sub>18</sub> ClN <sub>7</sub> O <sub>3</sub>	54.61	4.12	22.29
(46)	White needles	95	222—224	EtOH	57.8	4.7	22.4	C <sub>21</sub> H <sub>21</sub> N <sub>7</sub> O <sub>4</sub>	57.92	4.86	22.52

<sup>a</sup> This compound is the 7-propylamino derivative.

Scheme 2.

chlorides in dry benzene at reflux temperature in the presence of triethylamine to give the triazolotriazines (25)—(31) and (50)—(55) respectively (Table 4).

Hydrazinolysis of compounds (37)—(46) and (50)—(55) gave the corresponding 8-aminotriazolotriazines (47)—(49) and (56) in good yield (59—73%) (Table 5).

Compound (47) reacted with triethyl orthoformate, and compound (48) with *NN*-dimethylformamide dimethyl acetal, to afford respectively compounds (57) (*X* = OEt, Ar<sup>2</sup> = Ph) and (58) (*X* = NMe<sub>2</sub>, Ar<sup>2</sup> = *p*-MeOC<sub>6</sub>H<sub>4</sub>). Attempted cyclization of compounds (57) and (58) to the tricyclic derivative (59) by heating failed.

*Synthesis, Structure, and Reactivity of the 1,3-Diazetidino-2,4-di-imines (20)—(24).*—The first indication of a diazetidine

structure was obtained from electron-impact mass spectrometry: all the compounds showed an intense peak at *M*<sup>+</sup>/2. Since another intense peak corresponded to a [Ar<sup>2</sup>N=C=NAr<sup>2</sup>]<sup>+</sup> mass, it was concluded that the compounds probably had a 'dissymmetrical' structure as shown in Figure 1.

Chemical-ionization mass spectra showed that the molecular-ion peak had very low intensity; peaks are also found at *M*<sup>+</sup> - 56.

<sup>1</sup>H and <sup>13</sup>C n.m.r. spectra clearly showed that there was only one group of signals for the Ar<sup>2</sup> residue. In order to determine the molecular structure, a sample of compound (21) (Ar<sup>2</sup> = *p*-ClC<sub>6</sub>H<sub>4</sub>) was dissolved in aqueous ethanol at room temperature, and by slow evaporation white crystals were obtained which were suitable for an X-ray study. The structure was solved and surprisingly enough it was that of compound

**Table 4.** 7-Aryl-8-aryl(arylmethyleneamino)-3-methyl[1,2,4]triazolo[5,1-c][1,2,4]triazin-4(8*H*)-ones. (25)—(31) and (50)—(55)

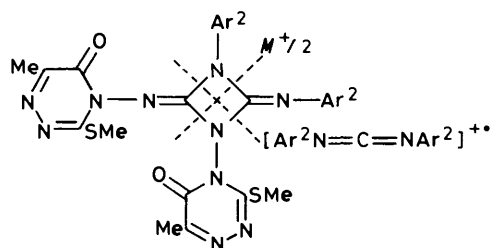
Compd.	Crystal form	Yield (%)	M.p. (°C)	Solvent	Found (%)			Formula	Required (%)		
					C	H	N		C	H	N
(25)	White needles	72	263—265	CHCl <sub>3</sub>	67.4	4.3	23.0	C <sub>17</sub> H <sub>13</sub> N <sub>5</sub> O	67.32	4.32	23.09
(26)	White needles	70	238—240	EtOH	64.8	4.5	20.9	C <sub>18</sub> H <sub>15</sub> N <sub>5</sub> O <sub>2</sub>	64.86	4.54	21.01
(27)	Yellow plates	57	274—276	EtOH	68.1	4.6	22.0	C <sub>18</sub> H <sub>15</sub> N <sub>5</sub> O	68.13	4.76	22.07
(28)	White prisms	81	252—254	EtOH	53.4	3.0	18.3	C <sub>17</sub> H <sub>12</sub> BrN <sub>5</sub> O	53.42	3.16	18.32
(29)	Yellow prisms	77	123—125	EtOH	58.6	3.3	24.0	C <sub>17</sub> H <sub>12</sub> N <sub>6</sub> O <sub>3</sub>	58.62	3.47	24.13
(30)	Yellow prisms	65	221—223	CHCl <sub>3</sub>	61.4	3.9	19.8	C <sub>18</sub> H <sub>14</sub> ClN <sub>5</sub> O	61.46	4.01	19.91
(31)	White prisms	76	283—285	CHCl <sub>3</sub>	65.6	4.9	20.1	C <sub>19</sub> H <sub>17</sub> N <sub>5</sub> O <sub>2</sub>	65.69	4.93	20.16
(50)	White needles	72	205—206	EtOH	65.4	4.2	25.3	C <sub>18</sub> H <sub>14</sub> N <sub>6</sub> O	65.45	4.27	25.44
(51)	White plates	73	240—241	EtOH	63.2	4.4	23.3	C <sub>19</sub> H <sub>16</sub> N <sub>6</sub> O <sub>2</sub>	63.33	4.48	23.32
(52)	White needles	80	242—243	Benzene	66.3	4.6	24.3	C <sub>19</sub> H <sub>16</sub> N <sub>6</sub> O	66.27	4.68	24.40
(53)	White needles	83	249—250	Benzene	52.8	3.2	20.5	C <sub>18</sub> H <sub>13</sub> BrN <sub>6</sub> O	52.83	3.20	20.53
(54)	White needles	71	262—263	Benzene	57.6	3.5	26.1	C <sub>18</sub> H <sub>13</sub> N <sub>7</sub> O <sub>3</sub>	57.56	3.42	26.17
(55)	White needles	68	234—236	Benzene	69.4	4.2	22.0	C <sub>22</sub> H <sub>16</sub> N <sub>6</sub> O	69.46	4.24	22.09

**Table 5.** 8-Amino-7-aryl(arylamino)-3-methyl[1,2,4]triazolo[5,1-c][1,2,4]triazin-4(8*H*)-ones. (47)—(49) and (56)

Compd.	Crystal form	Yield (%)	M.p. (°C)	Solvent	Found (%)			Formula	Required (%)		
					C	H	N		C	H	N
(47)	White needles	68	312—313	EtOH	51.2	4.3	38.0	C <sub>11</sub> H <sub>11</sub> N <sub>7</sub> O	51.36	4.31	38.11
(48)	White prisms	70	322—324	EtOH	50.2	4.6	34.0	C <sub>12</sub> H <sub>13</sub> N <sub>7</sub> O <sub>2</sub>	50.17	4.56	34.13
(49)	White needles	73	312—314	EtOH	58.6	4.2	31.8	C <sub>15</sub> H <sub>13</sub> N <sub>7</sub> O	58.63	4.26	31.90
(56)	White plates	59	270—272	EtOH	56.3	4.7	32.7	C <sub>12</sub> H <sub>12</sub> N <sub>6</sub> O	56.24	4.72	32.79

**Table 6.** Geometry of the hydrogen interactions (see Figure 2 for symmetry codes)

X—H...Y	Symmetry	X—H (Å)	X...Y (Å)	H...Y (Å)	X—H...Y (°)
O(W1)—H(1A)—O(24)	ii	0.91(18)	> 3.5	2.73(18)	162(13)
O(W1)—H(1B)—N(2)	iv	1.03(10)	2.703(8)	1.81(11)	144(8)
N(10)—H(10)—O(W1)	i	0.86(5)	2.796(8)	1.95(5)	166(5)
O(W2)—H(2A)—N(2')	iv	0.99(10)	2.831(6)	1.94(10)	149(8)
O(W2)—H(2B)—O(24)	ii	1.19(18)	2.988(6)	1.96(17)	142(12)
N(10')—H(10')—O(W2)	iii	0.95(4)	2.791(5)	1.90(4)	157(4)

**Figure 1.**

(12) ( $\text{Ar}^1 = \text{Ar}^2 = p\text{-ClC}_6\text{H}_4$ ). Thus the isomerization we carried out by heating for 14 h in aqueous ethanol took place by simple dissolution at room temperature.

The crystal structure of compound (12) is shown in Figure 2. There is a molecule of water, per molecule of (12), involved in a network of hydrogen interactions (see Table 6) which pack the two independent molecules in such way that there is almost a translation between both, except for the relative position of one *p*-chlorophenyl ring which has a different torsion angle in the adjoining bond [see Figure 2: C(7)—N(8)—C(17)—C(22) 56.5(8) *vs.* C(7')—N(8')—C(17')—C(22') -66.1(7)°]. The other two torsion angles have similar values, C(11)—N(10)—C(7)—N(6) -2.0(8), C(7)—N(10)—C(11)—C(12) 6.5(8)° *vs.* -12.2(8) and 15.8(8)° for the corresponding ones in the primed molecule (Figure 2). Table 7 gives the main bond lengths and angles, the

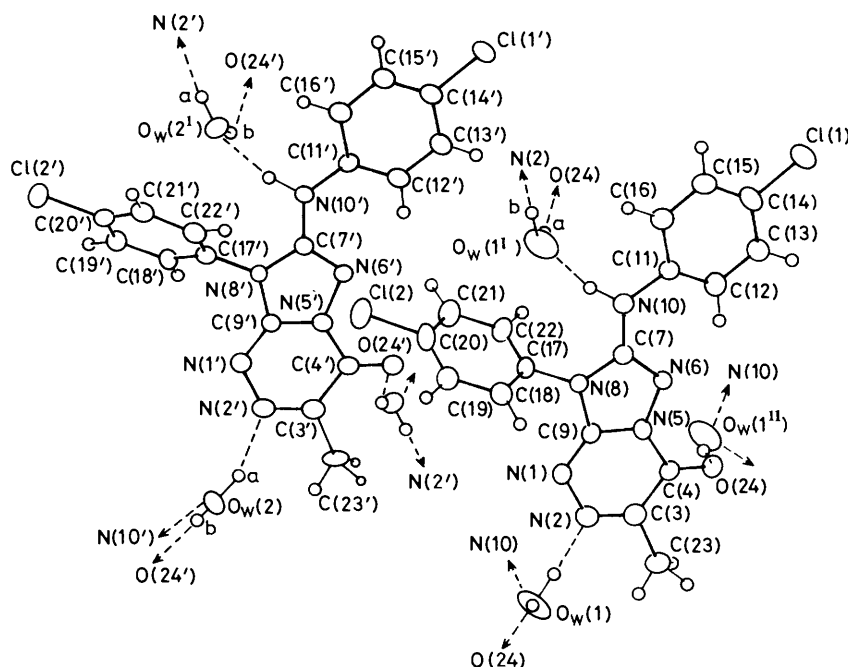
ranges of values for the phenyl rings being [1.358(9)—1.408(7) Å and 118.3(5)—122.2(6)°]. The bridging N atoms are planar, with angles of 125.8(4), 117(4), and 117(4)°, and 126.9(4), 114(3), and 119(3)° for N(10) and N(10') respectively. The reader should note the asymmetry in the angular values of the external junctions to the atoms C(11), C(7), N(8), and C(4) (and the corresponding primed ones), and the irregular distribution in the values of the intracyclic ring angles in the triazolotriazine system.

Using dichloromethane as solvent (see Table 1) we obtained, by slow evaporation at room temperature, true crystals of diazetidine (21). The structure is shown in Figure 3. Table 8 gives the main geometrical parameters of the molecule (21), the ranges in the aromatic rings being 1.359(12)—1.400(15) Å and 118.1(8)—122.6(9)°. It should be noted that the values of the internal bonds angles at N(1) and N(3) are lower than the corresponding ones at C(2) and C(4), carbon atoms that present more asymmetry in the values of the bond angles external to the ring. The relative twist of one *p*-chlorophenyl ring with respect to the other (see Figure 3) and torsion angles at N(1)—C(19) and at N(3)—C(25) are also noteworthy.

The crystal contains one molecule of dichloromethane in the unit cell. The structure shows two important facts: (i) the diazetidine is 'symmetrically' substituted (as represented in Scheme 1); (ii) both heterocyclic rings are turned towards one *p*-chlorophenyl substituent (*Z,Z*-configuration). These two properties can be described by the values of the torsion angles at

**Table 7.** Selected geometrical parameters for the two molecules (unprimed and primed respectively) in compound (12)

Bond lengths (Å)					
N(1)–N(2)	1.383(6)	1.385(6)	N(5)–N(6)	1.398(6)	1.409(5)
N(1)–C(9)	1.303(6)	1.298(6)	N(2)–C(3)	1.299(7)	1.301(7)
N(5)–C(9)	1.344(6)	1.353(6)	N(5)–C(4)	1.386(6)	1.385(6)
N(6)–C(7)	1.312(6)	1.305(6)	N(8)–C(9)	1.381(6)	1.374(6)
N(8)–C(7)	1.382(6)	1.383(6)	N(8)–C(17)	1.443(6)	1.437(6)
N(10)–C(7)	1.355(6)	1.351(6)	N(10)–C(11)	1.419(6)	1.415(6)
C(3)–C(4)	1.468(6)	1.466(7)	C(3)–C(23)	1.504(6)	1.494(8)
C(4)–O(24)	1.203(6)	1.214(6)	Cl(1)–C(14)	1.750(6)	1.751(5)
Cl(2)–C(20)	1.747(6)	1.735(5)			
Bond angles (°)					
C(9)–N(1)–N(2)	113.0(4)	113.8(4)	C(3)–N(2)–N(1)	122.9(4)	122.5(4)
N(2)–C(3)–C(4)	125.0(5)	124.8(5)	C(3)–C(4)–N(5)	108.6(5)	107.4(4)
C(4)–N(5)–C(9)	123.0(4)	122.5(4)	N(5)–C(9)–N(1)	127.4(5)	127.0(4)
C(3)–C(4)–O(24)	127.6(5)	127.0(5)	N(5)–C(4)–O(24)	123.7(5)	123.6(5)
C(4)–N(5)–N(6)	123.8(4)	125.4(4)	N(1)–C(9)–N(8)	127.8(5)	127.6(5)
C(9)–N(5)–N(6)	113.2(4)	112.1(4)	N(5)–N(6)–C(7)	102.5(4)	102.8(4)
N(6)–C(7)–N(8)	113.1(4)	113.4(4)	C(7)–N(8)–C(9)	106.3(4)	106.4(4)
N(8)–C(9)–N(5)	104.8(4)	105.4(4)	C(9)–N(8)–C(17)	123.6(4)	124.9(4)
C(7)–N(8)–C(17)	129.8(4)	128.6(4)	N(8)–C(7)–N(10)	121.3(5)	120.0(4)
N(6)–C(7)–N(10)	125.6(5)	126.6(4)	N(10)–C(11)–C(12)	124.1(5)	124.1(4)
N(10)–C(11)–C(16)	116.6(5)	116.3(4)	N(8)–C(17)–C(18)	119.1(5)	118.5(4)
N(8)–C(17)–C(22)	119.4(5)	120.1(5)			

**Figure 2.** A view of the two crystallographically independent molecules of compound (12), showing the hydrogen-bond network; the italic letters denote the symmetry operations involved:

$$i = 1 - x, -\frac{1}{2} + y, \frac{1}{2} - z; \text{ii} = x, \frac{3}{2} - y, \frac{1}{2} + z; \text{iii} = 2 - x, y - \frac{1}{2}, \frac{3}{2} - z; \text{iv} = x, y, z$$

C(2)–N(5) and C(7)–S(1), plus the corresponding ones on the other site (see Table 8). This explains the n.m.r. spectra. For instance, that of compound (21) recorded at 300 MHz in  $\text{CDCl}_3$  (Figure 4) shows two AA'BB' systems, which are tentatively assigned.

To assign the  $^{13}\text{C}$  n.m.r. spectra of compound (21) it is necessary to study those of compounds (1) and (19) (Table 9). Long-range coupling constants, in particular with  $^{31}\text{P}$  in the iminophosphorane, allow the assignment of all signals (Table 9).

It is now possible to discuss the spectra of compound (21) recorded at 75 MHz in  $\text{CDCl}_3$  (Figure 5). The most remarkable feature is the great difference in chemical shifts between carbons *ortho* to the diazetidene ring in *p*-chlorophenyl substituents (119.4 and 129.1 or 129.7 p.p.m.). Similar behaviour was observed in *N*-phenylpyrazoles (the effect of a *meta* chlorine is insignificant).<sup>14</sup>

The n.m.r. study confirms that the compound has the same structure in the solid state and in solution: a 1,3-diaryl-1,3-

**Table 8.** Selected geometrical parameters for compound (21)

Bond lengths (Å)			
N(1)–C(2)	1.408(12)	N(1)–C(4)	1.398(9)
N(3)–C(2)	1.387(9)	N(3)–C(4)	1.410(12)
N(6)–C(7)	1.352(12)	N(13)–C(14)	1.392(12)
N(6)–C(11)	1.395(11)	N(13)–C(18)	1.392(10)
N(1)–C(19)	1.400(10)	N(3)–C(25)	1.412(11)
C(2)–N(5)	1.266(11)	C(4)–N(12)	1.276(11)
C(7)–N(8)	1.303(12)	C(14)–N(15)	1.276(10)
C(10)–N(9)	1.264(15)	C(17)–N(16)	1.292(14)
N(5)–N(6)	1.440(11)	N(12)–N(13)	1.381(8)
N(8)–N(9)	1.403(11)	N(15)–N(16)	1.393(11)
C(7)–S(1)	1.734(8)	C(14)–S(2)	1.738(8)
C(33)–S(1)	1.802(20)	C(34)–S(2)	1.797(18)
C(10)–C(31)	1.501(25)	C(17)–C(32)	1.503(14)
C(10)–C(11)	1.482(16)	C(17)–C(18)	1.446(11)
C(11)–O(1)	1.199(14)	C(18)–O(2)	1.217(12)
C(22)–Cl(1)	1.727(10)	C(28)–Cl(2)	1.751(11)
C(40)–Cl(3)	1.768(11)	C(40)–Cl(4)	1.723(14)
Bond angles (°)			
C(2)–N(1)–C(4)	88.4(6)	C(2)–N(3)–C(4)	88.7(6)
C(2)–N(1)–C(19)	134.7(7)	C(2)–N(3)–C(25)	133.3(7)
C(4)–N(1)–C(19)	136.0(7)	C(4)–N(3)–C(25)	136.8(7)
N(1)–C(2)–N(3)	91.7(6)	N(1)–C(4)–N(3)	91.1(6)
N(1)–C(2)–N(5)	126.7(7)	N(1)–C(4)–N(12)	125.7(7)
N(3)–C(2)–N(5)	141.6(8)	N(3)–C(4)–N(12)	143.1(7)
N(5)–N(6)–C(7)	119.1(6)	N(12)–N(13)–C(14)	115.7(6)
N(5)–N(6)–C(11)	116.7(7)	N(12)–N(13)–C(18)	121.0(6)
C(7)–N(6)–C(11)	122.9(7)	C(14)–N(13)–C(18)	120.5(7)
C(7)–S(1)–C(33)	99.7(6)	C(14)–S(2)–C(34)	100.8(5)
Torsion angles (°)			
C(2)–N(1)–C(19)–C(20)	162.8(8)	C(2)–N(3)–C(25)–C(30)	–117.3(10)
C(4)–N(1)–C(19)–C(20)	–2.1(13)	C(4)–N(3)–C(25)–C(30)	46.3(13)
N(6)–N(5)–C(2)–N(1)	–173.1(7)	N(13)–N(12)–C(4)–N(1)	–177.2(7)
N(6)–N(5)–C(2)–N(3)	6.8(15)	N(13)–N(12)–C(4)–N(3)	6.7(16)
C(2)–N(5)–N(6)–C(7)	–126.0(8)	C(4)–N(12)–N(13)–C(14)	–144.0(7)
N(6)–C(7)–S(1)–C(33)	–177.8(8)	N(13)–C(14)–S(2)–C(34)	–171.3(7)

**Table 9.**  $^{13}\text{C}$  Chemical shifts (p.p.m. from  $\text{SiMe}_4$  and coupling constants (Hz) of compounds (1) and (19) in  $\text{CDCl}_3$ 

Compound	C-3	C-5	C-6	SMe	6-Me	X	
(1) X = $\text{H}_2$	160.4 $^3J$ 3.5(Me)	152.5 $^3J$ 2.8(Me)	153.6 $^2J$ 7.0(Me)	13.8 $^1J$ 142.0	17.0 $^1J$ 129.2		
(19) X = $\text{PPh}_3^a$	161.7 $^3J$ 3.8 (Me)	153.5 $^3J$ 3.0(Me)	151.4 $^2J$ 7.0(Me)	14.9 $^1J$ 141.7	17.5 $^1J$ 129.2	130.2( $\text{C}_i$ )	$^1J$ 100.7( $^{31}\text{P}$ )
	$^3J$ 11.4( $^{31}\text{P}$ )	$^3J$ 3.8( $^{31}\text{P}$ )				132.8( $\text{C}_o$ )	$^2J$ 9.7( $^{31}\text{P}$ )
						128.5( $\text{C}_m$ )	$^3J$ 12.4( $^{31}\text{P}$ )
						131.8( $\text{C}_p$ )	$^4J$ 2.8( $^{31}\text{P}$ )

<sup>a</sup> The assignment of phenyl chemical shifts and coupling constants ( $^{13}\text{C}$ – $^{31}\text{P}$ ) in the iminophosphorane are consistent with literature results (B. E. Mann and B. F. Taylor,  $^{13}\text{C}$  NMR Data for Organometallic Compounds, Academic Press, London, 1981, p. 127.

diazetidone-2,4-di-imine of *Z,Z*-configuration. To explain the formation of a fragment  $[\text{Ar}^2\text{N}=\text{C}=\text{NAr}^2]^{++}$  in the mass spectrum from a structure like (21) ( $m/z$  262 and 264) it is necessary to assume that the product is in equilibrium with the other, non-symmetric, structure (Figure 6).

Coming back to the chemistry, there are two points to discuss: the mechanism of formation of compound (21) and the mechanism of the transformation (21)  $\rightarrow$  (12), choosing as examples the molecules whose structures have been established by X-ray crystallography.

The formation of the diazetidone presumably involves an initial aza-Wittig reaction between the phosphorane (19) and *p*-chlorophenyl isocyanate to give a carbodi-imide which, under reaction conditions, undergoes a  $[\pi_2^s + \pi_2^s]$  cycloaddition to give the diazetidone (21). This assumption is supported by the fact that attempts to prepare compounds (20)–(24) from compound (19) and 1,3-diaryl-1,3-diazetidone-2,4-diones, available from aryl isocyanates and tributylphosphine,<sup>15</sup> were unsuccessful.

Although the *N*-aminoheterocycles 1-amino-4,6-diphenyl-2-

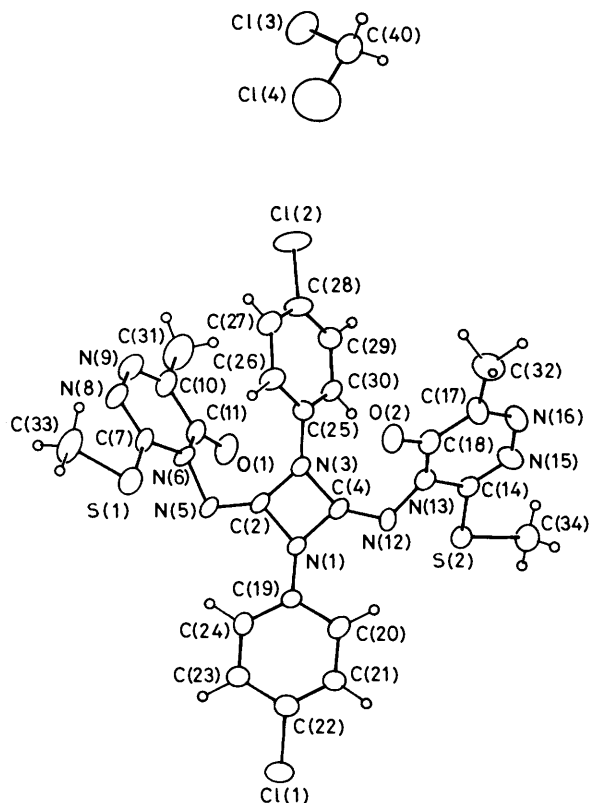


Figure 3. A view of the structure of compound (21), as seen projected onto the best plane through the diazetidene ring

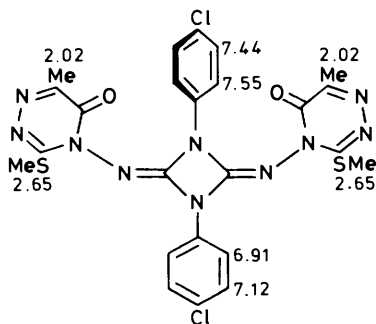


Figure 4.

pyridone and (1) show structural similarity, their iminophosphoranes (63) and (19) exhibit striking differences in their reactions toward aryl isocyanates. The former leads to mesoionic derivatives of the 1,3,4-oxadiazolo[3,2-*a*]pyridine ring system (64)<sup>16</sup> whereas the latter leads to 1,3-diaryl-1,3-diazetidene-2,4-di-imines (20)–(24).

The formation of 1,3-diazetidene-2,4-di-imines by dimerization of carbodi-imides is a case of pericyclic reaction of cumulenes.<sup>17</sup> It has been known for a long time (for instance, the dimerization of diphenylcarbodi-imide)<sup>18</sup> but all examples thus far concern symmetrical compounds (Figure 6, A = B). Thus, there is no problem of regioselectivity. Moreover, no *X*-ray structure of a 1,3-diazetidene-2,4-di-imine having been determined, the configuration of the imino groups was unknown (there are reports on the molecular structure of 1,3-diazetidene-2,4-diones, dimers of isocyanates).<sup>19</sup> In the case of endocyclic

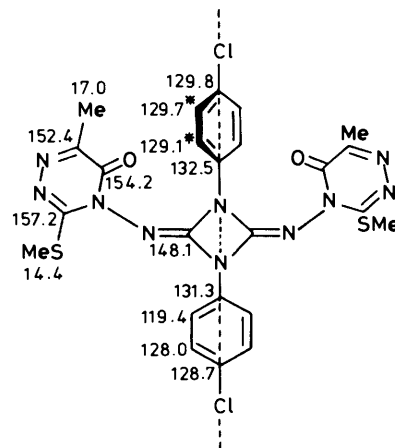


Figure 5.

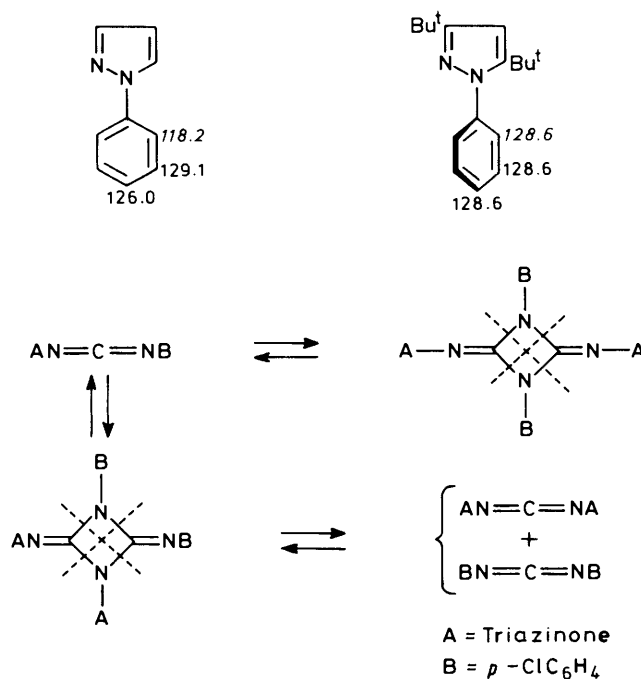
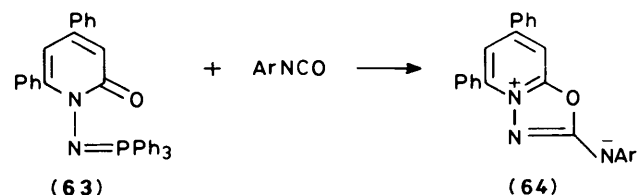


Figure 6.



carbodi-imides, the bond between the substituents imposes a *E,E*-configuration for the di-imine.<sup>20,21</sup>

Since the *Z,Z*-configuration of compound (21) is more crowded than the *E,E*-configuration, the kinetic product here described for the first time would be useful to test whether or not the allowed [ $\pi_s^2 + \pi_a^2$ ] mechanism was concerted.

The last point concerns the transformation (21)  $\rightarrow$  (12) and, in general, of 1,3-diazetidene-2,4-di-imines (20)–(24) into triazolotriazines (8)–(18). We have established that the re-





**Table 11.** Final atomic co-ordinates for compound (12), with e.s.d.s in parentheses

Atom	x	y	z
Cl(1)	0.286 43(13)	0.185 09(9)	-0.168 20(17)
Cl(2)	0.714 59(11)	0.496 87(10)	0.617 04(12)
N(1)	0.469 57(29)	0.673 47(22)	0.173 08(36)
N(2)	0.435 78(30)	0.728 68(23)	0.102 04(39)
C(3)	0.388 75(37)	0.718 78(29)	0.001 31(48)
C(4)	0.364 22(37)	0.649 27(27)	-0.050 36(47)
N(5)	0.401 19(27)	0.596 94(21)	0.025 15(33)
N(6)	0.390 69(27)	0.524 32(20)	0.003 26(35)
C(7)	0.434 69(32)	0.495 90(26)	0.097 02(42)
N(8)	0.473 95(28)	0.545 69(21)	0.175 40(34)
C(9)	0.449 88(32)	0.611 28(26)	0.128 08(40)
N(10)	0.442 73(29)	0.425 52(22)	0.119 19(36)
C(11)	0.402 91(33)	0.370 31(26)	0.046 19(45)
C(12)	0.357 02(36)	0.380 77(29)	-0.062 05(43)
C(13)	0.321 30(40)	0.324 10(31)	-0.129 09(50)
C(14)	0.332 14(39)	0.257 03(31)	-0.084 61(52)
C(15)	0.377 16(45)	0.245 03(30)	0.022 87(56)
C(16)	0.412 91(40)	0.302 01(31)	0.088 57(50)
C(17)	0.534 49(34)	0.536 03(26)	0.282 71(42)
C(18)	0.513 61(36)	0.564 01(29)	0.374 69(45)
C(19)	0.571 34(43)	0.553 73(32)	0.478 34(47)
C(20)	0.646 48(40)	0.515 07(31)	0.485 74(47)
C(21)	0.669 41(39)	0.489 78(36)	0.394 20(52)
C(22)	0.611 86(36)	0.500 44(33)	0.290 48(44)
C(23)	0.355 46(47)	0.782 49(32)	-0.069 53(54)
O(24)	0.320 72(29)	0.637 25(21)	-0.142 77(32)
Cl(1')	0.764 89(10)	0.138 94(7)	0.339 28(14)
Cl(2')	1.196 81(12)	0.435 29(9)	1.122 21(12)
N(1')	0.964 70(30)	0.623 81(20)	0.687 85(36)
N(2')	0.931 99(30)	0.682 22(21)	0.623 02(38)
C(3')	0.888 05(34)	0.676 60(26)	0.519 84(45)
C(4')	0.867 01(36)	0.609 47(26)	0.459 75(43)
N(5')	0.901 46(26)	0.553 72(19)	0.529 67(34)
N(6')	0.893 76(27)	0.481 33(19)	0.500 80(33)
C(7')	0.934 04(32)	0.450 00(23)	0.593 00(40)
N(8')	0.968 65(27)	0.496 87(20)	0.678 25(32)
C(9')	0.946 48(32)	0.563 67(25)	0.636 46(41)
N(10')	0.943 28(27)	0.379 37(20)	0.610 52(34)
C(11')	0.898 55(31)	0.324 82(24)	0.540 53(40)
C(12')	0.853 56(35)	0.334 70(26)	0.431 27(45)
C(13')	0.811 48(38)	0.277 60(28)	0.368 10(48)
C(14')	0.817 39(34)	0.210 72(26)	0.418 14(45)
C(15')	0.862 15(39)	0.200 22(28)	0.525 37(52)
C(16')	0.903 11(38)	0.256 57(27)	0.587 48(50)
C(17')	1.023 27(32)	0.481 89(23)	0.787 03(39)
C(18')	1.109 49(35)	0.506 25(28)	0.814 37(45)
C(19')	1.162 21(38)	0.492 04(30)	0.918 25(47)
C(20')	1.129 29(37)	0.452 74(25)	0.991 57(41)
C(21')	1.043 58(40)	0.428 07(28)	0.964 58(46)
C(22')	0.989 98(38)	0.443 59(27)	0.860 97(43)
C(23')	0.855 62(53)	0.742 97(32)	0.457 26(62)
O(24')	0.827 39(26)	0.601 79(19)	0.363 41(30)
O(W1)	0.470 64(85)	0.862 09(32)	0.180 10(56)
O(W2)	0.923 61(28)	0.814 36(22)	0.727 71(35)

(2.16 g, 0.0135 mol) in dry benzene (15 ml) was added dropwise to a stirred solution of triphenylphosphine (3.53 g, 0.0135 mol) in dry benzene (60 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-6-methyl-3-methylthio-5-oxo-4,5-dihydro-1,2,4-triazine (1) (2.32 g, 0.0135 mol) and triethylamine (2.73 g, 0.037 mol) in dry benzene (25 ml) was added; after the mixture had been heated for 4 h under reflux, triethylammonium bromide was deposited. The salt was separated by filtration and the filtrate was concentrated to dryness to afford a crude product, which was crystallized from ethanol to give the *title phosphorane* (19) (3.56 g, 61%) as yellow

**Table 12.** Final atomic co-ordinates for compound (21), with e.s.d.s in parentheses

Atom	x	y	z
S(1)	0.674 5(2)	0.022 9(1)	0.265 7(3)
Cl(1)	0.948 9(3)	-0.155 7(1)	-0.430 0(4)
S(2)	1.001 3(2)	0.312 4(1)	-0.309 9(2)
Cl(2)	0.575 6(3)	0.481 2(2)	0.252 3(3)
N(1)	0.858 8(6)	0.121 6(4)	-0.063 7(8)
C(2)	0.764 7(7)	0.135 2(5)	-0.002 9(8)
N(3)	0.811 7(6)	0.217 9(4)	0.039 3(7)
C(4)	0.901 3(7)	0.205 5(5)	-0.029 0(8)
N(5)	0.677 8(6)	0.082 3(4)	0.000 1(8)
N(6)	0.586 8(6)	0.117 5(4)	0.053 4(7)
C(7)	0.569 9(7)	0.090 9(4)	0.174 1(8)
N(8)	0.482 5(7)	0.114 9(4)	0.222 3(8)
N(9)	0.399 9(7)	0.168 8(5)	0.140 0(10)
C(10)	0.407 6(8)	0.191 8(6)	0.021 5(11)
C(11)	0.501 2(8)	0.165 0(5)	-0.043 2(11)
O(1)	0.506 4(6)	0.181 8(4)	-0.160 1(7)
N(12)	0.987 5(6)	0.242 6(4)	-0.064 4(7)
C(14)	1.051 5(8)	0.367 2(5)	-0.023 5(9)
N(13)	1.025 9(5)	0.325 5(4)	-0.018 0(7)
N(15)	1.109 7(8)	0.440 5(4)	-0.085 5(8)
N(16)	1.154 2(8)	0.480 9(4)	0.067 3(10)
C(17)	1.138 6(8)	0.443 5(5)	0.171 5(10)
C(18)	1.074 5(7)	0.360 4(5)	0.138 7(10)
O(2)	1.063 6(6)	0.321 7(4)	0.234 9(7)
C(19)	0.880 8(7)	0.054 7(4)	-0.148 4(8)
C(20)	0.961 2(8)	0.067 9(5)	-0.226 6(10)
C(21)	0.981 9(9)	0.002 4(5)	-0.309 2(11)
C(22)	0.925 2(8)	-0.074 5(5)	-0.319 0(10)
C(23)	0.846 7(8)	-0.088 0(5)	-0.238 4(10)
C(24)	0.824 8(7)	-0.022 6(5)	-0.155 8(9)
C(25)	0.765 8(7)	0.285 0(5)	0.096 3(9)
C(26)	0.755 4(8)	0.285 8(5)	0.236 3(9)
C(27)	0.695 1(8)	0.346 7(5)	0.284 9(11)
C(28)	0.654 6(8)	0.406 2(5)	0.194 5(10)
C(29)	0.671 9(8)	0.408 3(5)	0.060 3(10)
C(30)	0.727 9(8)	0.346 0(5)	0.010 4(11)
C(31)	0.318 4(16)	0.250 8(15)	-0.060 1(33)
C(32)	1.193 8(18)	0.487 8(9)	0.336 8(13)
C(33)	0.611 9(16)	0.002 8(10)	0.407 3(17)
C(34)	1.075 3(17)	0.381 1(8)	-0.393 9(16)
Cl(3)	0.339 7(3)	0.763 4(2)	0.401 8(3)
Cl(4)	0.545 3(6)	0.663 6(3)	0.474 9(9)
C(40)	0.513 5(10)	0.762 6(7)	0.465 5(14)

prisms, m.p. 220–221 °C (Found: C, 63.9; H, 4.8; N, 12.9.  $C_{23}H_{21}N_4OPS$  requires C, 63.87; H, 4.89; N, 12.95%);  $\nu_{max}$  (Nujol) 3 090, 1 640, 1 490, 1 470, 1 438, 1 382, 1 350, 1 270, 1 120, 1 080, 1 040, 1 030, 885, 760, 730, 720, 710, and 695  $cm^{-1}$ ;  $\delta_H$ ( $CDCl_3$ ) 8.3–7.5 (15 H, m), 2.60 (3 H, s), and 2.30 (3 H, s);  $m/z$  (%) 432 ( $M^+$ , 10), 276 (12), 263 (13), 262 (70), 261 (10), 185 (13), 183 (5), 152 (16), 131 (16), 122 (9), 108 (100), 107 (27), 77 (15), and 73 (30).

*General Procedure for the Preparation of 1,3-Diaryl-2,4-bis-(6-methyl-3-methylthio-5-oxo-4,5-dihydro-1,2,4-triazin-4-ylimino)-1,3-diazetidines (20)–(24).*—To a solution of 6-methyl-3-methylthio-5-oxo-4-triphenylphosphoranylideneamino-4,5-dihydro-1,2,4-triazine (19) (1 g, 0.0023 mol) in dry benzene (15 ml) was added the appropriate aryl isocyanate (0.0023 mol). The colourless solution quickly turned deep red. The reaction mixture was stirred for 18 h at room temperature; the white solid which separated from the pale-yellow solution was collected by filtration, dried, and crystallized from dichloromethane–ether (1:1 v/v) to give the corresponding 1,3-diazetidine-2,4-di-imine (20)–(24) as a crystalline solid. If no precipitation occurred during the reaction, the final solution

was concentrated to dryness and the residue was scratched with cold ethanol (5 ml) to give a precipitate of crude diazetidine.

The following compounds were obtained (yields, m.p.s, and analyses are given in Table 1): 1,3-diphenyl (**20**),  $\nu_{\max}$  (Nujol) 1 765, 1 695, 1 625, 1 500, 1 470, 1 385, 1 315, 1 230, 1 070, 755, 750, 720, 695, and 690  $\text{cm}^{-1}$ ;  $\delta_{\text{H}}$  ( $\text{CDCl}_3$ ) 8.0—7.2 (5 H, m), 2.70 (3 H, s), and 2.00 (3 H, s);  $m/z$  (%) 273 (53), 258 (5), 197 (17), 194 (97), 187 (10), 165 (11), 161 (16), 156 (11), 129 (12), 120 (16), 119 (100), 118 (24), 115 (37), 103 (31), 91 (77), and 77 (65). 1,3-Bis-(4-chlorophenyl) (**21**),  $\nu_{\max}$  (Nujol) 1 765, 1 700, 1 630, 1 515, 1 495, 1 470, 1 310, 1 085, 1 015, 825, and 750  $\text{cm}^{-1}$ ;  $\delta_{\text{H}}$  ( $\text{CDCl}_3$ ) 8.6—6.9 (4 H, m), 2.70 (3 H, s), and 2.00 (3 H, s);  $m/z$  (%) 309 (13), 307 (37), 264 (10), 262 (17), 165 (7), 153 (16), 152 (11), 151 (27), 137 (24), 125 (10), 115 (100), 102 (15), 101 (13), 99 (39), 83 (19), and 75 (21). 1,3-Bis-(4-methoxyphenyl) (**22**),  $\nu_{\max}$  (Nujol) 1 765, 1 685, 1 625, 1 505, 1 470, 1 300, 1 250, 1 165, 1 035, 830, 750, and 715  $\text{cm}^{-1}$ ;  $\delta_{\text{H}}$  ( $\text{CDCl}_3$ ) 8.1—6.5 (8 H, m), 3.90 (3 H, s), 3.80 (3 H, s), 2.65 (6 H, s), and 2.05 (6 H, s);  $m/z$  (%) 303 (47), 255 (6), 254 (32), 240 (6), 239 (37), 205 (5), 157 (17), 149 (15), 148 (47), 147 (100), 134 (15), 133 (57), 116 (15), 105 (16), 86 (17), 84 (25), and 77 (12). 1,3-Bis-(3-methoxyphenyl) (**23**),  $\nu_{\max}$  (Nujol) 1 766, 1 698, 1 630, 1 601, 1 470, 1 377, 1 313, 1 246, 1 070, 843, 786, 765, 747, 718, and 690  $\text{cm}^{-1}$ ;  $\delta_{\text{H}}$  ( $\text{CDCl}_3$ ) 7.9—6.6 (8 H, m), 4.00 (3 H, s), 3.80 (3 H, s), 2.65 (6 H, s), and 2.00 (6 H, s);  $m/z$  (%) 303 (38), 277 (7), 255 (6), 254 (33), 161 (10), 149 (55), 148 (20), 147 (17), 133 (15), 119 (25), 115 (100), 106 (18), 103 (16), 95 (48), 92 (22), 91 (23), 83 (35), 77 (34), and 69 (48). 1,3-Bis-(1-naphthyl) (**24**),  $\nu_{\max}$  (Nujol) 1 695, 1 630, 1 537, 1 470, 1 376, 1 306, 1 066, 1 014, 964, 804, 777, 754, 721, and 653  $\text{cm}^{-1}$ ;  $\delta_{\text{H}}$  ( $\text{CDCl}_3$ ) 9.0—7.4 (7 H, m), 2.60 (3 H, s), and 1.85 (3 H, s);  $m/z$  (%) 323 (5), 295 (5), 294 (6), 169 (100), 141 (57), 140 (57), 114 (42), 113 (22), 85 (67), 83 (95), 74 (19), and 63 (20).

**General Procedure for the Preparation of 8-Aryl-7-arylamino-3-methyl[1,2,4]triazolo[5,1-c][1,2,4]triazin-4(8H)-ones (8)–(18).**—A solution of the appropriate 1,3-diaryl-1,3-diazetidene-2,4-di-imine (**20**)—(0.0033 mol) in aqueous ethanol (85%; 20 ml) was heated at reflux temperature for 14 h; evolution of methanethiol was clearly detected (by its odour). After the mixture had cooled, the precipitated crude product was filtered off, dried, and recrystallized from ethanol to give the corresponding triazolo [5,1-c][1,2,4]triazin-4-one as a crystalline solid. The following compounds were obtained (yields, m.p.s, and analyses are given in Table 2); (**8**), (**12**), and (**16**), which have already been described,<sup>12</sup> and two new compounds: 8-(3-methoxyphenyl)-7-(*m*-anisidino) (**17**),  $\nu_{\max}$  (Nujol) 3 352, 1 670, 1 619, 1 574, 1 495, 1 438, 1 329, 1 273, 1 230, 1 203, 1 183, 1 169, 1 088, 1 049, 1 034, 899, 850, 773, 766, 750, 731, and 686  $\text{cm}^{-1}$ ;  $\delta_{\text{H}}$  [ $(\text{CD}_3)_2\text{SO}$ ] 9.5 (1 H, s), 8.0—6.8 (8 H, m), 3.90 (3 H, s), 3.80 (3 H, s), and 2.40 (3 H, s);  $m/z$  (%) 378 ( $M^+$ , 40), 350 (10), 280 (10), 240 (8), 203 (10), 159 (25), 148 (100), 134 (54), 119 (22), 118 (20), 107 (32), 95 (29), 92 (45), and 77 (59). 8-(1-Naphthyl)-7-(1-naphthylamino) (**18**),  $\nu_{\max}$  1 687, 1 597, 1 574, 1 506, 1 466, 1 330, 1 257, 1 092, 1 030, 985, 951, 806, 794, 780, 752, and 715  $\text{cm}^{-1}$ ;  $\delta_{\text{H}}$  [ $(\text{CD}_3)_2\text{SO}$ ] 9.70 (1 H, s), 8.6—7.4 (14 H, m), and 2.40 (3 H, s);  $m/z$  (%) 418 ( $M^+$ , 24), 390 (5), 223 (14), 182 (14), 179 (41), 168 (34), 154 (100), 143 (22), 140 (38), 127 (89), 115 (78), 101 (10), and 77 (18).

**General Procedure for the Preparation of 7,8-Diaryl-3-methyl[1,2,4]triazolo[5,1-c][1,2,4]triazin-4(8H)-ones (25)–(31).**—To a solution of an iminophosphorane (**5**), (**6**), or (**7**) (0.001 mol) in dry benzene (20 ml) were added the appropriate aryl chloride (0.0015 mol) and triethylamine (0.001 mol). After the mixture had been stirred and heated for 2 h under reflux, triethylammonium chloride was deposited. The salt was separated by filtration and the filtrate was concentrated to dryness to afford a crude product, which was crystallized from

the appropriate solvent to give the corresponding triazolo [5,1-c][1,2,4]triazin-4-one (**25**)—(**31**) as a crystalline solid. The following compounds were obtained (yields, m.p.s, and analyses are given in Table 3): 7,8-diphenyl (**25**),  $\nu_{\max}$  (Nujol) 3 040, 1 700, 1 568, 1 529, 1 500, 1 448, 1 383, 1 325, 1 295, 1 234, 1 166, 1 075, 1 036, 1 007, 854, 781, 754, 740, 694, and 636  $\text{cm}^{-1}$ ;  $\delta_{\text{H}}$  ( $\text{CDCl}_3$ ) 7.7—7.0 (10 H, m) and 2.65 (3 H, s);  $m/z$  (%) 304 (19), 303 ( $M^+$ , 100), 302 (61), 275 (14), 274 (18), 205 (10), 180 (15), 165 (11), 129 (5), 103 (11), and 77 (13). 7-(4-Methoxyphenyl)-8-phenyl (**26**),  $\nu_{\max}$  (Nujol) 3 040, 1 695, 1 608, 1 568, 1 540, 1 506, 1 495, 1 308, 1 262, 1 177, 1 080, 1 024, 843, 800, 752, 735, 721, and 696  $\text{cm}^{-1}$ ;  $\delta_{\text{H}}$  ( $\text{CDCl}_3$ ) 7.8—6.7 (9 H, m), 3.85 (3 H, s), and 2.55 (3 H, s);  $m/z$  (%) 334 (21), 333 ( $M^+$ , 100), 332 (40), 305 (20), 304 (9), 236 (6), 235 (18), 210 (30), 195 (13), 103 (66), and 77 (6). 8-Phenyl-7-(*p*-tolyl) (**27**),  $\nu_{\max}$  (Nujol) 3 040, 1 693, 1 593, 1 568, 1 506, 1 495, 1 456, 1 435, 1 331, 1 317, 1 234, 1 198, 1 093, 1 072, 827, 817, 758, 736, 692, and 664  $\text{cm}^{-1}$ ;  $\delta_{\text{H}}$  ( $\text{CDCl}_3$ ) 8.0—7.2 (9 H, m), 2.70 (3 H, s), and 2.45 (3 H, s);  $m/z$  (%) 318 (21), 317 ( $M^+$ , 100), 316 (58), 205 (27), 195 (9), 194 (53), 193 (12), 179 (32), 143 (18), 117 (30), 116 (21), 103 (43), 91 (28), 90 (17), 89 (18), and 77 (88). 7-(4-Bromophenyl)-8-phenyl (**28**),  $\nu_{\max}$  (Nujol) 3 040, 1 693, 1 591, 1 568, 1 532, 1 495, 1 426, 1 240, 1 121, 1 081, 1 007, 854, 820, 756, 748, 727, 696, and 644  $\text{cm}^{-1}$ ;  $\delta_{\text{H}}$  ( $\text{CDCl}_3$ ) 8.1—7.0 (9 H, m) and 2.25 (3 H, s);  $m/z$  (%) 384 (19), 383 (96), 382 (83), 381 ( $M^+$ , 100), 380 (66), 355 (30), 354 (24), 353 (28), 285 (15), 283 (13), 260 (33), 258 (35), 245 (13), 243 (13), 209 (12), 205 (50), 183 (27), 103 (24), 102 (14), and 77 (25). 7-(4-Nitrophenyl)-8-phenyl (**29**),  $\nu_{\max}$  (Nujol) 3 040, 1 700, 1 602, 1 568, 1 523, 1 495, 1 438, 1 347, 1 115, 1 081, 1 013, 960, 752, 724, and 696  $\text{cm}^{-1}$ ;  $\delta_{\text{H}}$  ( $\text{CDCl}_3$ ) 8.5—7.2 (9 H, m) and 2.55 (3 H, s);  $m/z$  (%) 349 (20), 348 ( $M^+$ , 100), 347 (61), 320 (28), 319 (22), 278 (39), 277 (78), 250 (5), 225 (9), 205 (8), 204 (10), 179 (8), 167 (7), 150 (9), and 77 (5). 8-(4-Chlorophenyl)-7-(*p*-tolyl) (**30**),  $\nu_{\max}$  (Nujol) 3 040, 1 695, 1 613, 1 590, 1 566, 1 508, 1 495, 1 458, 1 435, 1 377, 1 329, 1 232, 1 092, 1 085, 1 021, 829, 821, 756, 729, and 646  $\text{cm}^{-1}$ ;  $\delta_{\text{H}}$  ( $\text{CDCl}_3$ ) 8.0—7.1 (8 H, m), 2.65 (3 H, s), and 2.45 (3 H, s);  $m/z$  (%) 353 (35), 352 (36), 351 ( $M^+$ , 100), 350 (48), 325 (11), 324 (11), 323 (32), 322 (19), 239 (20), 228 (43), 219 (47), 213 (20), 143 (17), 139 (16), 137 (43), 117 (31), 116 (22), 113 (13), 111 (36), 102 (12), and 91 (30). 8-(4-Methoxyphenyl)-7-(*p*-tolyl) (**31**),  $\nu_{\max}$  (Nujol) 3 040, 1 687, 1 608, 1 568, 1 540, 1 512, 1 466, 1 373, 1 330, 1 302, 1 251, 1 172, 1 086, 1 022, 833, 823, 758, 733, and 652  $\text{cm}^{-1}$ ;  $\delta_{\text{H}}$  ( $\text{CDCl}_3$ ) 8.0—7.2 (8 H, m), 4.10 (3 H, s), 2.75 (3 H, s), and 2.45 (3 H, s);  $m/z$  (%) 348 (20), 347 (97), 346 ( $M^+$ , 100), 319 (13), 318 (30), 235 (10), 224 (10), 209 (11), 133 (15), 92 (7), 90 (7), and 77 (7).

**General Procedure for the Preparation of 4-Amino-3-[2-(arylmethylene)hydrazino]-6-methyl-5-oxo-4,5-dihydro-1,2,4-triazines (33) and (34).**—To a solution of 4-amino-3-hydrazino-6-methyl-5-oxo-4,5-dihydro-1,2,4-triazine (**32**) (2 g, 0.0128 mol) in ethanol (30 ml) were added the appropriate aryl aldehyde (0.0128 mol) and conc. hydrochloric acid (1 drop). The reaction mixture was heated at reflux temperature for 10 min while being stirred. After the mixture had cooled, the precipitated solid was collected by filtration, dried, and crystallized from ethanol to give the corresponding hydrazone as a crystalline solid. The following compounds were obtained: 3-benzylidenehydrazino (**33**) (2.9 g, 93%) as yellow plates, m.p. 249—251 °C (Found: C, 54.0; H, 4.9; N, 34.3.  $\text{C}_{11}\text{H}_{12}\text{N}_6\text{O}$  requires C, 54.09; H, 4.95; N, 34.41%);  $\nu_{\max}$  (Nujol) 3 352, 3 313, 3 165, 1 625, 1 603, 1 580, 1 555, 1 493, 1 296, 1 189, 1 030, 973, 911, 764, 730, 701, and 662  $\text{cm}^{-1}$ ;  $\delta_{\text{H}}$  [ $(\text{CD}_3)_2\text{SO}$ ] 12.4 (1 H, s), 8.50 (1 H, s), 8.2—7.4 (5 H, m), 5.90 (2 H, s), and 2.20 (3 H, s);  $m/z$  (%) 245 (16), 244 ( $M^+$ , 100), 243 (15), 167 (16), 141 (5), 90 (5), 89 (5), and 42 (5). 3-[3,4-Dimethoxybenzylidene]hydrazino (**34**) (3.5 g, 90%) as yellow needles, m.p. 227—228 °C (Found: C, 51.3; H, 5.2; N, 27.5.  $\text{C}_{13}\text{H}_{16}\text{N}_6\text{O}_3$  requires C, 51.3; H, 5.3; N, 27.6%);  $\nu_{\max}$  (Nujol) 3 340, 3 256, 1 619, 1 591, 1 568, 1 512, 1 440, 1 263, 1 236, 1 142,

1 070, 981, 929, 831, 819, 769, 681, and 661  $\text{cm}^{-1}$ ;  $\delta_{\text{H}}$  [(CD<sub>3</sub>)<sub>2</sub>SO] 12.4 (1 H, s), 8.40 (1 H, s), 7.90 (1 H, s) 7.50—6.90 (2 H, m) 5.90 (2 H, s) 3.90 (3 H, s), 3.80 (3 H, s), and 2.20 (3 H, s);  $m/z$  (%) 305 (16), 304 ( $M^+$ , 100), 303 (9), 165 (6), 164 (11), 163 (17), 150 (17), 141 (9), 135 (8), and 107 (5).

**General Procedure for the Preparation of 3-[(2-Arylmethyl-ene)hydrazino]-6-methyl-5-oxo-4-triphenylphosphoranylidene-amino-4,5-dihydro-1,2,4-triazines (35) and (36).**—A solution of bromine (1.18 g, 0.0074 mol) in dry benzene (10 ml) was added dropwise to a stirred solution of triphenylphosphine (1.93 g, 0.0074 mol) in dry benzene (40 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 the appropriate *N*-amino-heterocycle (33) or (34) (0.0074 mol) and triethylamine (1.48 g, 0.0148 mol) in dry benzene (20 ml) was added; after being heated for 4 h under reflux the mixture deposited triethylammonium bromide, which was separated by filtration; the filtrate was concentrated to dryness to afford a crude product, which was crystallized from benzene to give the corresponding iminophosphorane (35) or (36) as a crystalline solid. 3-Benzylidenehydrazino (35) (2.23 g, 60%) as yellow needles, m.p. 117—119 °C (Found: C, 69.2; H, 5.0; N, 16.5. C<sub>29</sub>H<sub>25</sub>N<sub>6</sub>OP requires C, 69.04; H, 4.99; N, 16.66%);  $\nu_{\text{max}}$  (Nujol) 3 228, 1 647, 1 608, 1 580, 1 545, 1 438, 1 325, 1 285, 1 110, 1 064, 1 007, 980, 894, 871, 758, 718, 696, and 684  $\text{cm}^{-1}$ ;  $\delta_{\text{H}}$  (CDCl<sub>3</sub>) 8.20 (1 H, s), 8.1—7.3 (21 H, m), and 2.10 (3 H, s);  $m/z$  (%) 505 (29), 504 ( $M^+$ , 84), 503 (10), 502 (16), 400 (8), 367 (28), 366 (100), 304 (5), 277 (17), 276 (50), 262 (23), 261 (10), and 183 (13). 3-[(3,4-Dimethoxybenzylidene)hydrazino] (36) (2.67 g, 64%) as yellow needles, m.p. 203—205 °C (Found: C, 65.8; H, 5.1; N, 14.8. C<sub>31</sub>H<sub>29</sub>N<sub>6</sub>O<sub>3</sub>P requires C, 65.95; H, 5.18; N, 14.89%);  $\nu_{\text{max}}$  (Nujol) 3 205, 1 648, 1 680, 1 545, 1 506, 1 466, 1 438, 1 330, 1 262, 1 183, 1 110, 1 024, 1 002, 877, 747, 718, 696, and 673  $\text{cm}^{-1}$ ;  $\delta_{\text{H}}$  [(CD<sub>3</sub>)<sub>2</sub>SO] 8.4—7.0 (20 H, m), 3.90 (3 H, s), 3.85 (3 H, s), and 2.00 (3 H, s);  $m/z$  (%) 565 (40), 564 ( $M^+$ , 100), 562 (16), 427 (19), 426 (57), 401 (14), 400 (25), 304 (8), 301 (10), 278 (7), 277 (23), 276 (64), 262 (20), 183 (11), and 77 (5).

**General Procedure for the Preparation of 7-Arylamino-8-arylmethyleneamino-3-methyl[1,2,4]triazolo[5,1-c][1,2,4]triazin-4(8H)-ones (37)–(46).**—To a solution of an iminophosphorane (35) or (36) (0.001 mol) in dry benzene (15 ml) was added the appropriate aryl isocyanate (0.001 mol). The resulting mixture was stirred for 2 h at room temperature and the precipitate was collected by filtration, dried, and crystallized from ethanol to give the corresponding triazolo [5,1-c][1,2,4]triazin-4(8H)-one (37)–(46) as a crystalline solid. The following compounds were obtained (yields, m.p.s, and analyses are given in Table 4). 7-Anilino-8-benzylideneamino (37),  $\nu_{\text{max}}$  (Nujol) 3 380, 1 693, 1 642, 1 602, 1 580, 1 551, 1 495, 1 410, 1 302, 1 209, 1 072, 1 040, 1 000, 972, 839, 769, 758, 748, 694, and 635  $\text{cm}^{-1}$ ;  $\delta_{\text{H}}$  [(CD<sub>3</sub>)<sub>2</sub>SO] 10.3 (1 H, s), 9.95 (1 H, s), 8.2—7.3 (10 H, m), and 2.50 (3 H, s);  $m/z$  (%) 346 (10), 345 ( $M^+$ , 41), 276 (5), 243 (14), 242 (100), 214 (9), 144 (27), 119 (7), 118 (35), 117 (5), 104 (22), 103 (13), 92 (6), 91 (7), 89 (7), and 77 (79). 8-Benzylideneamino-7-(4-chloroanilino) (38),  $\nu_{\text{max}}$  (Nujol) 3 381, 1 693, 1 636, 1 602, 1 574, 1 545, 1 494, 1 405, 1 330, 1 302, 1 075, 1 036, 973, 832, 817, 769, 778, 696, and 682  $\text{cm}^{-1}$ ;  $\delta_{\text{H}}$  [(CD<sub>3</sub>)<sub>2</sub>SO] 10.0 (1 H, s), 9.80 (1 H, s), 8.3—7.2 (9 H, m), and 2.35 (3 H, s);  $m/z$  (%) 382 (5), 381 (22), 380 (14), 379 ( $M^+$ , 61), 279 (5), 278 (33), 277 (16), 276 (100), 248 (7), 180 (6), 178 (18), 154 (8), 152 (26), 111 (19), 104 (10), 103 (12), 98 (8), and 77 (20). 8-Benzylideneamino-*p*-anisidino (39),  $\nu_{\text{max}}$  (Nujol) 3 400, 1 693, 1 647, 1 580, 1 545, 1 512, 1 432, 1 410, 1 302, 1 251, 1 177, 1 075, 1 036, 973, 826, 760, 748, 731, 698, 690, and 607  $\text{cm}^{-1}$ ;  $\delta_{\text{H}}$  [(CD<sub>3</sub>)<sub>2</sub>SO] 10.3 (1 H, s), 9.75 (1 H, s), 8.5—7.0 (9 H, m), 3.80 (3 H, s), and 2.40 (3 H, s);  $m/z$  (%) 376 (24), 375 ( $M^+$ , 100), 273 (12),

272 (75), 271 (8), 257 (44), 229 (6), 174 (24), 159 (6), 158 (6), 148 (9), 147 (14), 133 (16), 122 (24), 103 (9), and 77 (24). 8-Benzylideneamino-7-(*m*-anisidino) (40),  $\nu_{\text{max}}$  (Nujol) 3 307, 1 677, 1 625, 1 589, 1 575, 1 554, 1 496, 1 412, 1 338, 1 252, 1 201, 1 165, 1 093, 1 037, 979, 833, 761, 750, 702, and 684  $\text{cm}^{-1}$ ;  $\delta_{\text{H}}$  [(CD<sub>3</sub>)<sub>2</sub>SO] 10.2 (1 H, s), 9.75 (1 H, s), 8.5—6.6 (9 H, m), 3.85 (3 H, s), and 2.40 (3 H, s);  $m/z$  (%) 376 (14), 375 ( $M^+$ , 61), 273 (16), 270 (100), 174 (14), 148 (18), 134 (5), 107 (11), 105 (5), 104 (9), 103 (20), 92 (10), 90 (5), and 77 (28). 8-Benzylideneamino-7-(1-naphthylamino) (41),  $\nu_{\text{max}}$  (Nujol) 3 377, 1 700, 1 636, 1 619, 1 568, 1 540, 1 500, 1 415, 1 381, 1 072, 1 059, 966, 792, 775, 747, 698, and 684  $\text{cm}^{-1}$ ;  $\delta_{\text{H}}$  [(CD<sub>3</sub>)<sub>2</sub>SO] 10.3 (1 H, s), 10.15 (1 H, s), 8.5—7.5 (12 H, m), and 2.70 (3 H, s);  $m/z$  (%) 396 (19), 395 ( $M^+$ , 70), 293 (17), 292 (100), 194 (18), 168 (14), 154 (10), 140 (9), 127 (16), 115 (12), 103 (11), and 77 (12). 8-Benzylideneamino-7-(*p*-toluidino) (42),  $\nu_{\text{max}}$  (Nujol) 3 364, 1 693, 1 636, 1 574, 1 551, 1 500, 1 426, 1 410, 1 382, 1 336, 1 228, 1 081, 1 076, 968, 849, 820, 764, 747, 730, 696, and 605  $\text{cm}^{-1}$ ;  $\delta_{\text{H}}$  [(CD<sub>3</sub>)<sub>2</sub>SO] 10.5 (1 H, s), 9.95 (1 H, s), 8.1—7.3 (9 H, m), 2.40 (3 H, s), and 2.30 (3 H, s);  $m/z$  (%) 360 (15), 359 ( $M^+$ , 63), 257 (16), 256 (100), 228 (6), 158 (27), 132 (21), 131 (13), 118 (9), 106 (7), 104 (12), 91 (36), 89 (8), and 77 (27). 8-Benzylideneamino-7-propylamino (43),  $\nu_{\text{max}}$  (Nujol) 3 305, 1 676, 1 636, 1 580, 1 529, 1 416, 1 347, 1 240, 1 149, 1 093, 974, 849, 753, 709, and 696  $\text{cm}^{-1}$ ;  $\delta_{\text{H}}$  [(CD<sub>3</sub>)<sub>2</sub>SO] 10.0 (1 H, s), 8.4—7.4 (6 H, m), 3.40 (2 H, m), 2.40 (3 H, s), 1.70 (2 H, m), and 1.00 (3 H, t);  $m/z$  (%) 312 (9), 311 ( $M^+$ , 39), 208 (7), 193 (5), 180 (14), 179 (100), 166 (53), 151 (20), 138 (6), 110 (9), 104 (18), 103 (6), 90 (9), 89 (9), and 77 (29). 7-Anilino-8-(3,4-dimethoxybenzylideneamino) (44),  $\nu_{\text{max}}$  (Nujol) 3 386, 1 693, 1 664, 1 636, 1 591, 1 568, 1 545, 1 511, 1 421, 1 262, 1 160, 1 143, 1 085, 1 019, 979, 820, 758, and 691  $\text{cm}^{-1}$ ;  $\delta_{\text{H}}$  [(CD<sub>3</sub>)<sub>2</sub>SO] 10.3 (1 H, s), 10.00 (1 H, s), 8.4—7.3 (8 H, m), 4.10 (3 H, s), 4.05 (3 H, s), and 2.50 (3 H, s);  $m/z$  (%) 406 (12), 405 ( $M^+$ , 47), 328 (6), 305 (5), 304 (30), 302 (13), 289 (24), 288 (7), 287 (16), 257 (6), 243 (13), 242 (100), 163 (20), 118 (8), and 77 (5). 7-(4-Chloroanilino)-8-(3,4-dimethoxybenzylideneamino) (45),  $\nu_{\text{max}}$  (Nujol) 3 381, 1 676, 1 642, 1 602, 1 568, 1 511, 1 494, 1 432, 1 404, 1 268, 1 166, 1 138, 1 081, 1 013, 837, 762, 752, 722, and 697  $\text{cm}^{-1}$ ;  $\delta_{\text{H}}$  [(CD<sub>3</sub>)<sub>2</sub>SO] 10.0 (1 H, s), 9.80 (1 H, s), 8.1—7.0 (7 H, m), 4.00 (3 H, s), 3.95 (3 H, s), and 2.40 (3 H, s);  $m/z$  (%) 441 (9), 440 (10), 439 ( $M^+$ , 30), 330 (22), 329 (23), 328 (100), 327 (32), 313 (10), 305 (13), 304 (87), 303 (14), 302 (27), 290 (9), 289 (34), 287 (16), 278 (23), 276 (56), 248 (10), 164 (10), 163 (28), 148 (10), and 75 (25). 7-(*p*-Anisidino)-8-(3,4-dimethoxybenzylideneamino) (46),  $\nu_{\text{max}}$  (Nujol) 3 475, 1 670, 1 642, 1 596, 1 569, 1 516, 1 436, 1 410, 1 264, 1 164, 1 137, 1 051, 1 025, 965, 832, 812, 760, 752, and 698  $\text{cm}^{-1}$ ;  $\delta_{\text{H}}$  [(CD<sub>3</sub>)<sub>2</sub>SO] 10.1 (1 H, s), 9.70 (1 H, s), 8.1—6.9 (7 H, m), 4.00 (3 H, s), 3.95 (3 H, s), 3.80 (3 H, s), and 2.40 (3 H, s);  $m/z$  (%) 435 ( $M^+$ , 12), 273 (15), 272 (100), 257 (39), 229 (7), 163 (40), 148 (18), 133 (9), 120 (9), 105 (5), and 92 (5).

**General Procedure for the Preparation of 7-Aryl-8-benzylideneamino-3-methyl[1,2,4]triazolo[5,1-c][1,2,4]triazin-4(8H)-ones (50)–(55).**—To a solution of the iminophosphorane (35) (0.50 g, 0.001 mol) in dry benzene (20 ml) were added the appropriate aryl chloride (0.0015 mol) and triethylamine (0.001 mol). After the mixture had been stirred and heated for 2 h under reflux, triethylammonium chloride was deposited. The salt was separated by filtration and the filtrate was concentrated to dryness to afford a crude product, which was crystallized from the appropriate solvent to give the corresponding triazolo[5,1-c][1,2,4]triazin-4-one, (50)–(55), as a crystalline solid. The following compounds were obtained (yields, m.p.s, and analyses are given in Table 3): 7-phenyl (50),  $\nu_{\text{max}}$  (Nujol) 3 050, 1 693, 1 563, 1 498, 1 449, 1 421, 1 359, 1 314, 1 228, 1 078, 1 063, 976, 910, 839, 767, 752, and 694  $\text{cm}^{-1}$ ;  $\delta_{\text{H}}$  (CDCl<sub>3</sub>) 10.4 (1 H, s), 8.5—7.3 (10 H, m), and 2.60 (3 H, s);  $m/z$  (%) 330 ( $M^+$ , 9), 228 (15), 227 (100), 199 (15), 129 (34), 104 (49), 103 (85), 77 (88),

76 (23), and 51 (39). 7-(4-Methoxyphenyl) (**51**),  $\nu_{\max}$ . (Nujol) 3 050, 1 693, 1 614, 1 568, 1 500, 1 438, 1 410, 1 359, 1 308, 1 262, 1 234, 1 180, 1 169, 1 117, 1 084, 1 064, 1 020, 976, 910, 840, 769, 750, 733, 698, and 661  $\text{cm}^{-1}$ ;  $\delta_{\text{H}}$  [(CD<sub>3</sub>)<sub>2</sub>SO] 10.6 (1 H, s), 8.7—7.4 (9 H, m), 4.05 (3 H, s), and 2.50 (3 H, s);  $m/z$  (%) 360 ( $M^+$ , 10), 258 (16), 257 (100), 159 (38), 134 (39), 133 (75), 104 (16), 103 (68), 90 (27), 89 (10), and 77 (52). 7-(*p*-Tolyl) (**52**),  $\nu_{\max}$ . (Nujol) 3 050, 1 693, 1 614, 1 568, 1 500, 1 427, 1 353, 1 228, 1 192, 1 084, 974, 912, 841, 826, 752, 724, 702, 686, and 653  $\text{cm}^{-1}$ ;  $\delta_{\text{H}}$  (CDCl<sub>3</sub>) 10.7 (1 H, s), 8.6—7.5 (9 H, m), 2.70 (3 H, s), and 2.55 (3 H, s);  $m/z$  (%) 344 ( $M^+$ , 10), 242 (15), 241 (100), 213 (11), 143 (34), 118 (38), 117 (53), 116 (18), 103 (16), 91 (23), 90 (16), 89 (17), and 77 (27). 7-(4-Bromophenyl) (**53**),  $\nu_{\max}$ . (Nujol) 3 050, 1 700, 1 608, 1 574, 1 483, 1 432, 1 381, 1 359, 1 228, 1 177, 1 075, 1 013, 979, 911, 837, 820, 764, 756, 723, 696, and 650  $\text{cm}^{-1}$ ;  $\delta_{\text{H}}$  (CDCl<sub>3</sub>) 10.35 (1 H, s), 8.3—7.1 (9 H, m), and 2.55 (3 H, s);  $m/z$  (%) 410 (15), 408 ( $M^+$ , 15), 308 (14), 307 (97), 306 (17), 305 (100), 279 (8), 277 (8), 209 (11), 207 (10), 183 (10), 181 (9), and 77 (5). 7-(4-Nitrophenyl) (**54**),  $\nu_{\max}$ . (Nujol) 3 090, 1 704, 1 575, 1 540, 1 517, 1 490, 1 432, 1 353, 1 296, 1 230, 1 177, 1 075, 1 062, 970, 914, 864, 856, 839, 758, 750, 702, 686, and 651  $\text{cm}^{-1}$ ;  $\delta_{\text{H}}$  [(CD<sub>3</sub>)<sub>2</sub>SO] 10.5 (1 H, s), 8.8—7.6 (9 H, m), and 2.45 (3 H, s);  $m/z$  (%) 376 (6), 375 ( $M^+$ , 25), 273 (15), 272 (100), 244 (5), 242 (9), 214 (7), 174 (6), 149 (7), 129 (5), 128 (13), 103 (9), 102 (9), and 77 (12). 7-(2-Naphthyl) (**55**),  $\nu_{\max}$ . (Nujol) 3 040, 1 704, 1 568, 1 529, 1 506, 1 468, 1 458, 1 419, 1 230, 1 084, 977, 866, 820, 752, 707, 690, and 653  $\text{cm}^{-1}$ ;  $\delta_{\text{H}}$  [(CD<sub>3</sub>)<sub>2</sub>SO] 10.15 (1 H, s), 8.8—7.5 (12 H, m), and 2.45 (3 H, s);  $m/z$  (%) 381 (10), 380 ( $M^+$ , 34), 278 (19), 277 (100), 179 (6), 154 (6), 153 (14), and 103 (7).

*General Procedure for the Preparation of 8-Amino-7-arylamino-3-methyl[1,2,4]triazolo[5,1-*c*][1,2,4]triazin-4(8H)-ones [(47)—(49) and (56)].*—To a solution of the appropriate 8-benzylideneaminotriazolo[5,1-*c*][1,2,4]triazin-4-one (**37**), (**39**), (**41**), or (**52**) (0.002 mol) in 2-methoxyethanol (15 ml) was added hydrazine hydrate (98%; 0.006 mol). The mixture was stirred and heated under reflux for 30 min. After the mixture had cooled, the white precipitated solid was collected by filtration, dried, and crystallized from ethanol to give the corresponding 8-aminotriazolo[5,1-*c*][1,2,4]triazin-4-one (**47**)—(**49**) or (**56**) as a crystalline solid. The following compounds were obtained (yields, m.p.s, and analyses are given in Table 5): 7-anilino (**47**),  $\nu_{\max}$ . (Nujol) 3 347, 3 262, 3 171, 1 670, 1 651, 1 626, 1 583, 1 548, 1 502, 1 341, 1 262, 1 234, 1 092, 1 030, 985, 752, and 696  $\text{cm}^{-1}$ ;  $\delta_{\text{H}}$  [(CD<sub>3</sub>)<sub>2</sub>SO] 9.95 (1 H, s), 8.2—7.1 (5 H, m), 6.30 (2 H, s), and 2.45 (3 H, s);  $m/z$  (%) 257 ( $M^+$ , 39), 243 (14), 242 (100), 214 (6), 190 (33), 175 (24), 174 (13), 160 (8), 146 (6), 144 (30), 143 (10), 119 (21), 118 (39), 104 (20), 103 (12), and 77 (22). 7-(*p*-Anisidino) (**48**),  $\nu_{\max}$ . (Nujol) 3 347, 3 245, 3 177, 1 670, 1 647, 1 591, 1 551, 1 517, 1 308, 1 251, 1 189, 1 092, 1 041, 826, 775, 752, 730, and 684  $\text{cm}^{-1}$ ;  $\delta_{\text{H}}$  [(CD<sub>3</sub>)<sub>2</sub>SO] 10.15 (1 H, s), 8.5—7.2 (4 H, m), 6.50 (2 H, s), 3.95 (3 H, s), and 2.45 (3 H, s);  $m/z$  (%) 287 ( $M^+$ , 100), 272 (23), 257 (7), 173 (23), 158 (13), 148 (65), 147 (24), 133 (24), 122 (24), 105 (9), 92 (7), and 77 (9). 7-(1-Naphthylamino) (**49**),  $\nu_{\max}$ . (Nujol) 3 352, 3 290, 3 177, 1 681, 1 636, 1 619, 1 580, 1 562, 1 506, 1 279, 1 155, 1 092, 1 070, 1 047, 972, 770, 752, 701, and 679  $\text{cm}^{-1}$ ;  $\delta_{\text{H}}$  [(CD<sub>3</sub>)<sub>2</sub>SO] 9.65 (1 H, s), 8.3—7.2 (7 H, m), 6.10 (2 H, s), and 2.40 (3 H, s);  $m/z$  (%) 308 (20), 307 ( $M^+$ , 100), 292 (27), 194 (7), 193 (8), 168 (29), 167 (6), 154 (9), 140 (6), 127 (7), and 115 (5). 7-(*p*-Tolyl) (**56**),  $\nu_{\max}$ . (Nujol) 3 284, 3 194, 1 687, 1 642, 1 585, 1 545, 1 506, 1 342, 1 277, 1 240, 1 178, 1 097, 1 076, 1 024, 862, 821, 756, 725, 702, and 690  $\text{cm}^{-1}$ ;  $\delta_{\text{H}}$  [(CD<sub>3</sub>)<sub>2</sub>SO] 8.6—7.5 (4 H, m), 6.60 (2 H, s), and 2.50 (6 H, s);  $m/z$  (%) 256 ( $M^+$ , 100), 241 (53), 207 (8), 174 (17), 143 (28), 131 (8), 118 (25), 117 (28), 116 (16), 104 (5), 103 (10), 91 (12), and 77 (5).

*Reaction of 8-Amino-7-anilino-3-methyl[1,2,4]triazolo[5,1-*c*][1,2,4]triazin-4(8H)-one (47) with Triethyl Orthoformate.*—A

solution of compound (**47**) (0.26 g, 0.001 mol) in triethyl orthoformate (10 ml) was heated at reflux temperature for 4.5 h. After the mixture had cooled, the precipitated solid was collected by filtration, washed with ether (2 × 10 ml), dried, and crystallized from ethanol-ether to give the 8-ethoxymethyl-eneamino derivative (**57**) (0.15 g, 60%) as orange prisms, m.p. 191—193 °C (Found: C, 53.7; H, 4.7; N, 31.3. C<sub>14</sub>H<sub>15</sub>N<sub>7</sub>O<sub>2</sub> requires C, 53.67; H, 4.82; N, 31.29%);  $\nu_{\max}$ . (Nujol) 3 260, 3 075, 1 676, 1 636, 1 603, 1 587, 1 572, 1 545, 1 500, 1 421, 1 308, 1 268, 1 228, 1 087, 1 041, 1 007, 945, 900, 860, 837, 752, 744, and 690  $\text{cm}^{-1}$ ;  $\delta_{\text{H}}$  (CDCl<sub>3</sub>) 10.1 (1 H, s), 8.0—7.1 (6 H, m), 4.50 (2 H, q), 2.60 (3 H, s), and 1.50 (3 H, t);  $m/z$  (%) 314 (19), 313 ( $M^+$ , 100), 295 (6), 284 (7), 270 (8), 268 (10), 243 (12), 242 (79), 214 (7), 144 (12), 143 (11), 77 (5), and 29 (8).

*Reaction of 8-Amino-7-(*p*-anisidino)-3-methyl[1,2,4]triazolo[5,1-*c*][1,2,4]triazin-4(8H)-one (48) with NN-Dimethylformamide Dimethyl Acetal.*—To a solution of compound (**48**) (0.43 g, 0.0015 mol) in toluene (15 ml) was added NN-dimethylformamide dimethyl acetal (0.18 g, 0.0015 mol). The mixture was stirred and heated at reflux temperature for 4 h. The precipitated solid was collected by filtration and crystallized from ethanol to give the 8-[(NN-dimethylamino)methyleneamino] derivative (**58**), m.p. 223—225 °C (Found: C, 52.5; H, 5.3; N, 32.65. C<sub>15</sub>H<sub>18</sub>N<sub>8</sub>O<sub>2</sub> requires C, 52.62; H, 5.26; N, 32.73%);  $\nu_{\max}$ . (Nujol) 3 345, 1 687, 1 642, 1 619, 1 585, 1 570, 1 545, 1 508, 1 425, 1 336, 1 245, 1 183, 1 110, 1 092, 1 030, 837, 781, 752, 701, and 673  $\text{cm}^{-1}$ ;  $\delta_{\text{H}}$  [(CD<sub>3</sub>)<sub>2</sub>SO] 9.25 (1 H, s), 8.75 (1 H, s), 8.1—7.0 (4 H, m), 3.85 (3 H, s), 3.20 (6 H, s), and 2.40 (3 H, s);  $m/z$  (%) 343 (20), 342 ( $M^+$ , 100), 273 (13), 272 (80), 257 (47), 229 (7), 174 (9), 173 (6), 158 (8), 148 (10), 147 (14), 133 (14), 122 (8), 98 (8), and 42 (9).

*Reaction of Iminophosphorane (19) with NN'-diphenylthiourea.*—A solution of the iminophosphorane (**19**) (0.5 g, 0.0011 mol) and NN'-diphenylthiourea (0.26 g, 0.0011 mol) in dry benzene (20 ml) was heated at reflux temperature for 14 h; evolution of methanethiol was detected. After the mixture had cooled, the precipitate was filtered off and the products were separated by silica gel column chromatography with a mixture of ethanol-ethyl acetate as eluant. Evaporation of the main fraction and crystallization from ethanol-chloroform gave 7-anilino-3-methyl-4*H*-[1,3,4]thiadiazolo[2,3-*c*][1,2,4]triazin-4-one (**60**) (0.16 g, 56%) as white prisms, m.p. 290—292 °C (lit.,<sup>12</sup> 291—293 °C). The column was then washed thoroughly with ethyl acetate, the solvent was evaporated off, and the residue was crystallized from ethanol to give the triazolotriazine (**8**) (0.03 g, 8%) as prisms, m.p. 336—338 °C (lit.,<sup>11</sup> 335—338 °C).

## Acknowledgements

We thank Prof. S. Garcia Blanco for the facilities given during this work and to the Comisión Asesora de Investigación Científica y Técnica for financial support

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Received 15th July 1985; Paper 5/1198