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1,2,4-Triazole Fused Heterocycles; Part 3. Preparation of 1-(1-Phenylethenyl)-5-(*N*-substituted amino)-1,2,4-triazoles and 4*H*-1,2,4-Triazolo[1,5-*c*][1,3,5]oxadiazines

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Received June 12, 1995

The reaction of acetophenone 1-ureidoethylidenehydrazones **6** with a mixture of triphenylphosphine, carbon tetrachloride, and triethylamine in dichloromethane provides a general route to 1-(1-phenylethenyl)-5-(*N*-substituted amino)-1,2,4-triazoles **11** *via* the electrocyclization of the expected azino carbodiimide intermediates **9** to give the resonance stabilized azomethine imine **10a** followed by a proton abstraction from the methyl group by amide anion. However, the same reaction of benzaldehyde 1-ureidoethylidenehydrazones **5** was unsuccessful. Under the same conditions, the reactions of benzaldehyde 1-*N*-acylureidoethylidenehydrazones **7** or acetophenone 1-*N*-acylureidoethylidenehydrazones **8** afforded 4*H*-1,2,4-triazolo[1,5-*c*][1,3,5]oxadiazines **16** or **17** *via* the zwitterionic species **15**, or a [4+2] intramolecular cycloaddition from the carbodiimide intermediates **14**, respectively.

Introduction

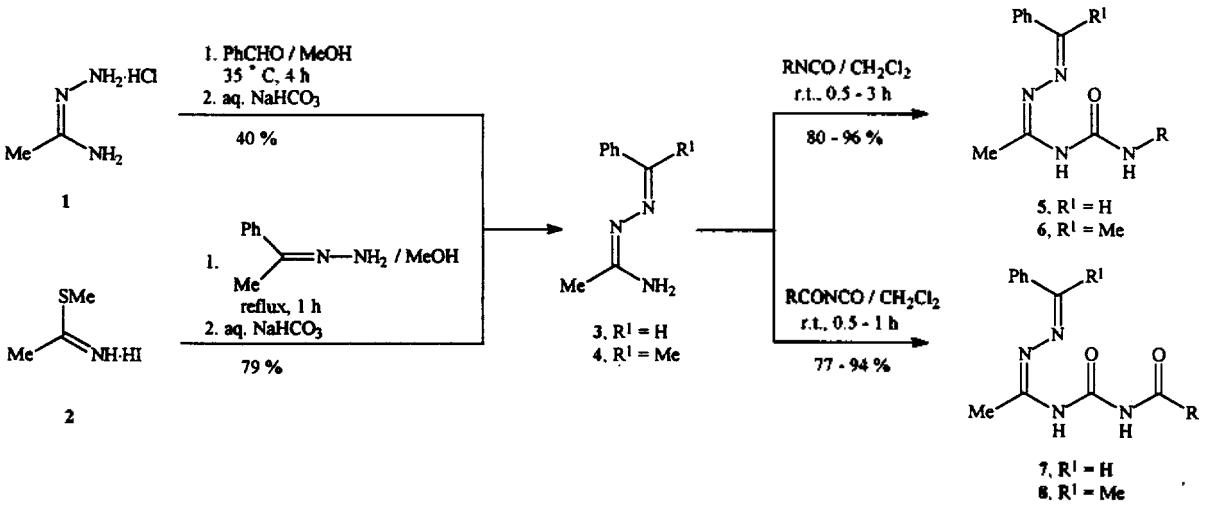
Recent interest in the electrocyclic reaction of conjugated heterocumulenes as a synthetic route to heterocycles,[1] prompted us to report on this subject. The previous papers in these series have shown that 1,2,4-triazole fused heterocyclic compounds with one of its nitrogen atom in a bridgehead position such as 5,10-dihydro-1,2,4-triazolo[5,1-*b*]quinazolines[2] and 4*H*-1,2,4-triazolo[1,5-*c*][1,3,5]oxadiazines[3] can readily be prepared from the reactions of benzophenone 1-ureidoethylidenehydrazones and benzophenone 1-*N*-acyl-ureidoethylidenehydrazones with a mixture of triphenylphosphine, carbon tetrachloride, and triethylamine in dichloromethane by dehydration[4] and subsequent electrocyclic ring closure of the azino carbodiimides. In the case of the reaction of benzophenone 1-ureidoethylidenehydrazones, either of two phenyl groups of benzophenone moiety was always participated in the ring closure process.[2]

With our continued interest in the reactions of azine substituted heterocumulenes to prepare fused triazolo ring systems, we chose to examine the reactions of benzaldehyde 1-ureidoethylidenehydrazones **5** or acetophenone 1-ureidoethylidenehydrazones **6** with triphenylphosphine, carbon tetrachloride, and triethylamine to see whether different triazole products such as **12** or **13** can be formed, because of the possibility of the participation of phenyl group in benzaldehyde or acetophenone, *N*-substituted aromatic group, or methyl group in the ring forming step (Scheme 2).

Results and Discussion

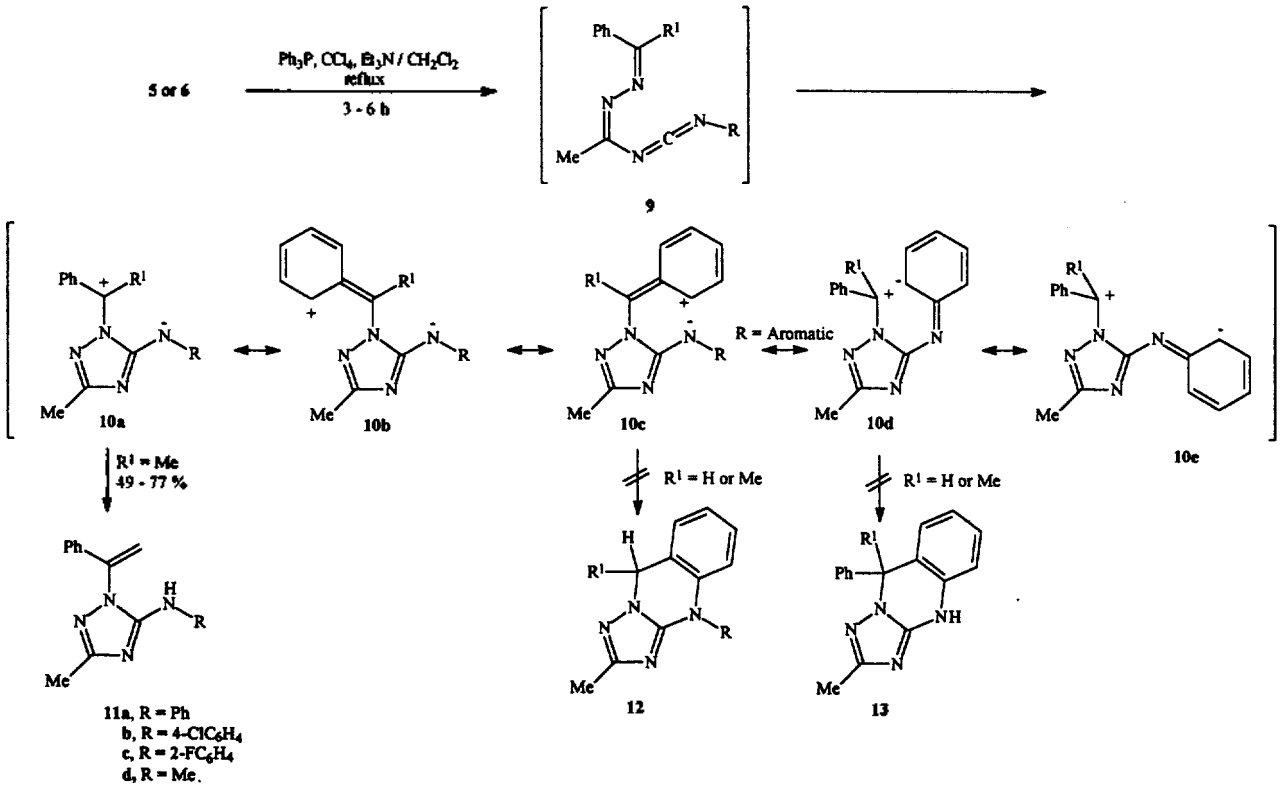
The starting compounds, benzaldehyde 1-aminoethylidenehydrazone (**3**) and acetophenone 1-aminoethylidenehydrazone (**4**), were obtained by the reaction of acetamidrazone hydrochloride (**1**) with benzaldehyde,[5] and by the reaction of acetophenone hydrazone with *S*-methylthioacetimidate hydroiodide (**2**), respectively. The ureas **5** and **6** were produced by the reactions of hydrazones **3** and **4** with isocyanates in dichloromethane at room temperature (Scheme 1). Thin layer chromatography showed one spot (silica gel, ethyl acetate-hexane, 1 : 1), however, ^{1}H NMR showed a mixture of two isomers, and the ratios found were 1.7-3.6/1 for the ureas **5** and 1.9-3.5/1 for the ureas **6** (Table 1). When the reaction of ureas **5** with triphenylphosphine, carbon tetrachloride, and triethylamine in dichloromethane was heated at reflux temperature for 4-5 h, the reaction mixture turned brown solution and thin layer chromatography showed the disappearance of **5** and the formation of a number of very small products along with triphenylphosphine oxide. All attempts to separate these complex mixture proved fruitless except triphenylphosphine oxide. We presume that although the azino carbodiimide intermediate **9** was formed, the electrocyclic reaction of **9** to give **12** or **13** did not occurr, but decomposed under the reaction conditions. These facts suggest that the steric interactions between phenyl and R groups push force the *N*-aromatic group into a transoid position relative to the triazole-*N*-substituents to give resonance form such as **10e**. Thus the resonance forms **10c** and **10d** are not favored to produce 1,2,4-triazoloquinazolines **12** or **13** (Scheme 2).

On the other hand, treatment of ureas **6** with triphenylphosphine, carbon tetrachloride, and triethylamine in dichloromethane at reflux temperature smoothly afforded the 1-(1-phenylethenyl)-5-(*N*-substituted amino)-1,2,4-triazoles **11** pre-



5, 6	R	7, 8	R
a	Ph	a	Ph
b	4-ClC$_6$H$_4$	b	4-ClC$_6$H$_4$
c	2-FC$_6$H$_4$	c	4-O$_2$NC$_6$H$_4$
d	Me	d	4-MeC$_6$H$_4$
		e	4-MeOC$_6$H$_4$

Scheme 1.



Scheme 2.

Table 1. Benzaldehyde 1-Ureidoethylidenehydrazones **5** and Acetophenone 1-Ureidoethylidenehydrazones **6** Prepared

Compound[a]	Reaction Time (h)	Yield[b] (%)	mp (℃)	^{1}H NMR (DMSO-d_6/TMS) δ, J (Hz)				
				CH_3[c]	Aromatic[d]	Two NH[e]	Others	Ratio[f]
5a	0.5	96	177-178	2.33 (2.42)	7.03-7.97 (m, 10H)	9.68, 11.80 (9.44, 9.92)	8.61 (s, 1H, CH) (8.46)	1.7/1
5b	0.5	94	195-196	2.33 (2.41)	7.35-7.97 (m, 9H)	9.76, 11.88 (9.45, 9.99)	8.62 (s, 1H, CH) (8.47)	1.7/1
5c	0.5	95	202-203	2.34 (2.42)	7.10-8.27 (m, 9H)	9.86, 12.13 (9.68, 9.73)	8.42 (s, 1H, CH) (8.46)	3.6/1
5d	3[g]	80	165-166	2.23 (2.34)	7.43-7.93 (m, 5H)	9.06 (q, J=4.4, 1H), 9.26 (h), (9.13)	8.47 (s, 1H, CH), (8.39), 2.76 (d, J=4.6, 3H, NCH_3) (2.64, d, J=4.6)	2.7/1
6a	0.5	92	188-189	2.30 (2.41)	7.02-8.00 (m, 10H)	9.68, 11.69 (9.16, 9.80)	2.45 (s, 3H, CH_3)	2.0/1
6b	0.5	96	192-193	2.29 (2.41)	7.33-8.00 (m, 9H)	9.77, 11.77 (9.18, 9.95)	2.44 (s, 3H, CH_3)	1.9/1
6c	0.5	94	183-184	2.28 (2.44)	7.09-8.23 (m, 9H)	9.81, 11.60 (9.44, 9.68)	2.39 (s, 3H, CH_3)	3.5/1
6d	3[g]	86	172-173	2.19 (2.37)	7.34-7.86 (m, 5H)	9.09 (q, J=4.5, 1H), 9.31 (h), (8.89)	2.31 (s, 3H, CH_3), 2.79 (d, J=4.7, 3H, NCH_3) (2.62, d, J=4.5)	2.0/1

[a]Satisfactory microanalyses were obtained: C± 0.26, H± 0.20, N± 0.28. [b]Yield of pure isolated product. [c]All singlets. [d]Values are both isomers. [e]All broad singlets, except for **5d** and **6d**. [f]Ratios based on 300 MHz ^{1}H NMR of methyl protons. Parentheses values are minor compounds. [g]Reflux temperature. [h]Unable to assign.

Table 2. Benzaldehyde 1-*N*-Acylureidoethylidenehydrazones **7** and Acetophenone 1-*N*-Acylureidoethylidenehydrazones **8** Prepared

Compound[a]	Yield[b] (%)	mp (℃)	^{1}H NMR (DMSO-d_6/TMS) δ			
			CH_3[c]	Aromatic	Two NH[c]	Others[c]
7a	79	220-221	2.48	7.47-8.05 (m, 10H)	11.16, 12.52	8.51 (1H, CH)
7b	94	203-204	2.50	7.49-8.06 (m, 9H)	11.25, 12.46	8.51 (1H, CH)
7c	79	223-224	2.48	7.49-8.38 (m, 9H)	11.53, 12.39	8.53 (1H, CH)
7d	77	202-203	2.47	7.34-8.04 (m, 9H)	11.06, 12.54	8.50 (1H, CH), 2.39 (3H, CH_3)
7e	90	194-196	2.49	7.07-8.08 (m, 9H)	11.01, 12.59	8.50 (1H, CH), 3.86 (3H, OCH_3)
8a	79	211-212	2.45	7.45-8.20 (m, 10H)	11.16, 12.33	2.51 (3H, CH_3)
8b	86	207-208	2.45	7.46-8.19 (m, 9H)	11.23, 12.27	2.50 (3H, CH_3)
8c	81	190-191	2.45	7.45-8.36 (m, 9H)	11.43, 12.16	2.51 (3H, CH_3)
8d	94	204-205	2.44	7.34-8.19 (m, 9H)	11.02, 12.33	2.50 (3H, CH_3), 2.39 (3H, CH_3)
8e	89	192-193	2.44	7.05-8.19 (m, 9H)	10.98, 12.41	2.50 (3H, CH_3), 3.34 (3H, OCH_3)

[a]Satisfactory microanalyses were obtained: C± 0.19, H± 0.13, N± 0.24. [b]Yield of pure isolated product. [c]All singlets.

sumably *via* a proton abstraction from the methyl group[6] by amide ion in the resonance structure **10a**, but no 1,2,4-triazoloquinazolines **12** or **13** were found to form (Table 3). A reasonable mechanistic pathway for these transformation was shown in Scheme 2.

In a similar manner, the reactions of **7** and **8**, which were readily obtainable by the reaction of the corresponding hydrazones **3** and **4** with acyl isocyanates (Scheme 1, Table 2),[7] with triphenylphosphine, carbon tetrachloride, and triethylamine in dichloromethane at reflux temperature gave the expected 4*H*-1,2,4-triazolo[1,5-*c*][1,3,5]oxadiazines[3] **16** or **17** in good yields *via* the zwitterionic species **15** or a [4+2] intramolecular cycloaddition from the carbodiimide intermediates **14** (Scheme 3, Table 4). In the case of the reaction of **8**, no triazole compound **18** involving a methyl proton abstraction was formed.

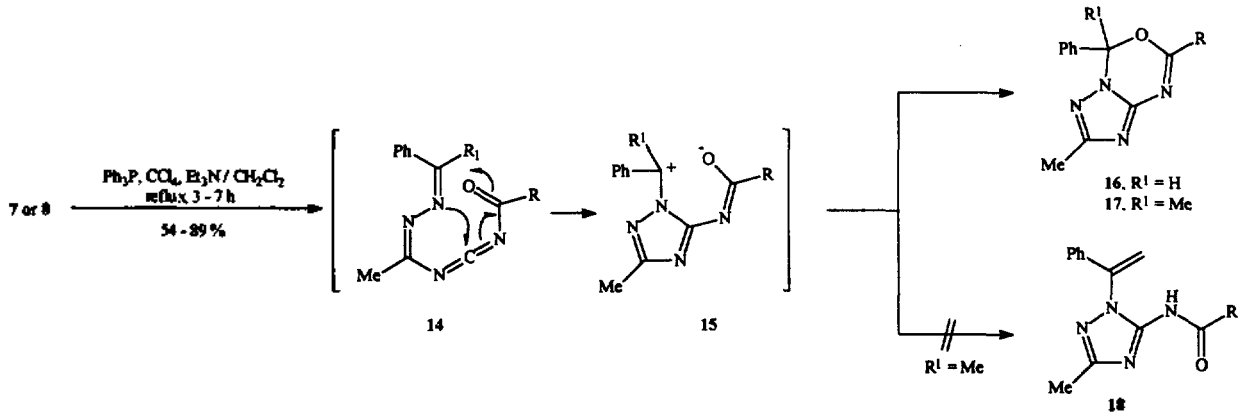
Experimental

Carbon tetrachloride and dichloromethane were dried and distilled from phosphorus pentoxide. Triethylamine was dried and distilled from sodium metal. Silica gel EM 7747 for column chromatography was used throughout for product separation. Melting points were taken using an Electrothermal melting point apparatus and are uncorrected. Microanalyses were obtained using a Perkin-Elmer 240 DS element

Table 3. 3-Methyl-1-(1-phenylethenyl)-5-(*N*-substituted amino)-1,2,4-triazoles **11** Prepared

Compound[a]	Reaction Time (h)	Yield[b] (%)	mp (℃)	^{1}H NMR ($CDCl_3$/TMS) δ					Selected ^{13}C NMR ($CDCl_3$) δ					
				CH_3[c]	$=CH_2$[c]	NH[c]	Aromatic	Others	C3	C5	C3-CH3	N1-C	$=CH_2$	Others
11a	3	73	119-120	2.40	5.58, 5.73	6.04	6.97-6.99 (m, 1H), 7.01-7.44 (m, 9H)		159.5	152.0	15.0	134.9	112.1	
11b	3	77	111-112	2.38	5.56, 5.73	6.07	7.18-7.44 (m, 9H)		159.4	151.6	15.0	134.7	112.2	
11c	3	75	94-95	2.40	5.58, 5.72	6.38	6.88-7.43 (m, 8H), 8.33-8.40 (m, 1H)		159.5	151.3	15.0	134.7	112.0	
11d	6	49	86-87	2.29	5.40, 5.56	3.97	7.31-7.50 (m, 5H)	2.93 (s, 3H, NCH_3)	159.1	156.9	14.8	135.0	110.9	31.0 (NCH_3)

[a]Satisfactory microanalyses were obtained: C± 0.25, H± 0.18, N± 0.23. [b]Yield of pure isolated product. [c]All singlets.



16, 17	a	b	c	d	e
R	Ph	4-ClC_6H_4	4-$O_2NC_6H_4$	4-MeC_6H_4	4-$MeOC_6H_4$

Scheme 3.

Table 4. 4*H*-1,2,4-Triazolo[1,5-*c*][1,3,5]oxadiazines **16** and **17** Prepared

Compound[a]	Reaction Time (h)	Yield[b] (%)	mp (℃)	^{1}H NMR ($CDCl_3$/TMS) δ		
				CH_3[c]	Aromatic	Others[c]
16a	4	84	144-145	2.40	7.37-7.60 (m, 8H), 8.14-8.17 (m, 2H)	7.24 (1H, CH)
16b	5	67	164-165	2.40	7.41-7.50 (m, 7H), 8.06-8.09 (m, 2H)	7.23 (1H, CH)
16c	6	54	200-201	2.43	7.40-7.53 (m, 5H), 8.28-8.35 (m, 4H)	7.27 (1H, CH)
16d	5	70	138-139	2.40	7.24-7.47 (m, 7H), 8.03-8.06 (m, 2H)	7.21 (1H, CH), 2.41 (3H, CH_3)
16e	5	72	183-184	2.40	6.92-6.95 (m, 2H), 7.40-7.48 (m, 5H) 8.08-8.12 (m, 2H)	7.19 (1H, CH), 3.87 (3H, OCH_3)
17a	3	89	137-138	2.38	7.27-7.50 (m, 8H), 8.19-8.22 (m, 2H)	2.48 (3H, C4-CH_3)
17b	3	78	158-159	2.36	7.23-7.43 (m, 7H), 8.10-8.13 (m, 2H)	2.46 (3H, C4-CH_3)
17c	4	60	165-166	2.42	7.21-7.36 (m, 5H), 8.29-8.38 (m, 4H)	2.49 (3H, C4-CH_3)
17d	3	69	169-171	2.36	7.26-7.30 (m, 7H), 8.08-8.11 (m, 2H)	2.47 (3H, C4-CH_3), 2.42 (3H, CH_3)
17e	3	76	173-174	2.32	6.89-7.26 (m, 7H), 8.11-8.14 (m, 2H)	2.44 (3H, C4-CH_3), 3.79 (3H, OCH_3)

[a]Satisfactory microanalyses were obtained: C± 0.23, H± 0.15, N± 0.26. [b]Yield of pure isolated product. [c]All singlets.

analyzer. ^{1}H and ^{13}C NMR spectra were measured on a Varian Gemini 300 spectrometer.

The acetamidrazone hydrochloride (**1**),[8] *S*-methylthioacetimidate hydroiodide (**2**),[9] acetophenone hydrazone,[10] and acyl isocyanates[11] were prepared following the literature procedures.

Benzaldehyde 1-Aminoethylidenehydrazone (3). To a solution of acetamidrazone hydrochloride (**1**) (4.38 g, 40 mmol) in methanol (30 mL) was added benzaldehyde (4.24 g, 40 mmol) and this solution was stirred at 35 ℃ for 4 h. The solution was concentrated to dryness, and the residual material was dissolved in dichloromethane (100 mL) and washed with 10% sodium hydrogen carbonate solution (30 mL). The organic layer was separated, dried with magnesium sulfate, concentrated under reduced pressure. The residual material was chromatographed (silica gel; ethyl acetate-hexane, 2 : 1) to give **3** as a white solid after crystallization from petroleum ether; yield 2.58 g (40%); mp 86-88 ℃.

^{1}H NMR ($CDCl_3$/TMS) : δ=2.07 (s, 3H, CH_3), 5.45 (br s, 2H, NH_2), 7.27-7.40 (m, 3 H_{arom}), 7.71-7.75 (m, 2 H_{arom}), 8.37 (s, 1H, CH).

Anal. Calcd. for $C_9H_{11}N_3$: C, 67.06; H, 6.86; N, 26.07. Found: C, 66.82; H, 6.79; N, 25.78.

Acetophenone 1-Aminoethylidenehydrazone (4). To a solution of *S*-methylthioacetimidate hydroiodide (**2**) (9.55 g, 44 mmol) in methanol (150 mL) was added acetophenone hydrazone (5.53 g, 40 mmol) and this solution was stirred at reflux temperature for 1 h. After cooling, the solution was concentrated to dryness, and the residual material was dissolved in dichloromethane (300 mL) and washed with 10% sodium hydrogen carbonate solution (200 mL). The organic layer was separated, dried with magnesium sulfate, concentrated to dryness, and crystallized from petroleum ether to give the product **4**; yield 5.57 g (79%); mp 76-77 ℃.

^{1}H NMR ($CDCl_3$/TMS): δ=2.10 (s, 3H, CH_3), 2.40 (s, 3H, CH_3), 5.29 (br s, 2H, NH_2), 7.27-7.46 (m, 3 H_{arom}), 7.80-7.87 (m, 2 H_{arom}).

Anal. Calcd. for $C_{10}H_{12}N_3$: C, 82.25; H, 7.48; N, 23.98. Found: C, 82.11; H, 7.42; N, 23.83.

Benzaldehyde 1-Ureidoethylidenehydrazones 5 and Acetophenone 1-Ureidoethylidenehydrazones 6; General Procedure. To a stirred solution of benzaldehyde 1-aminoethylidenehydrazone (**3**) (1.61 g, 10 mmol) or acetophenone 1-aminoethylidenehydrazone (**4**) (1.75 g, 10 mmol) in dichloromethane (30 mL) was added isocyanate (11 mmol) at room temperature. After stirring for the time indicated in Table 1 at ambient temperature, the reaction mixture was concentrated and the resulting solid was triturated with ether, separated by filtration, and dried *in vacuo* to give **5** or **6** as white solid, respectively (Table 1).

Benzaldehyde 1-*N*-acylureidoethylidenehydrazones 7 and Acetophenone 1-*N*-acylureidoethylidenehydrazones 8; General procedure. To a stirred solution of benzaldehyde 1-aminoethylidenehydrazone (**3**) (0.80 g, 5 mmol) or acetophenone 1-aminoethylidenehydrazone (**4**) (0.87 g, 5 mmol) in dichloromethane (15 mL) was added acyl isocyanate (6 mmol) at room temperature. The pale yellow solid was precipitated as soon as addition was completed. After stirring for 0.5 h at room temperature, the precipitated solid was separated by filtration, washed with ether and dried *in vacuo* to give **7** or **8** (Table 2).

Table 5. Microanalytical Data[a]

Compounds	Molecular Formula	Analyses (%) C	Calcd./(Found) H	N
5a	$C_{16}H_{16}N_4O$	68.54	5.75	19.98
	(280.33)	(68.34)	(5.71)	(19.87)
5b	$C_{16}H_{15}ClN_4O$	61.05	4.80	17.80
	(314.77)	(60.88)	(4.75)	(17.58)
5c	$C_{16}H_{15}FN_4O$	64.42	5.09	18.78
	(298.32)	(64.27)	(4.89)	(18.70)
5d	$C_{11}H_{14}N_4O$	60.53	6.47	25.67
	(218.26)	(60.41)	(6.32)	(25.39)
6a	$C_{17}H_{16}N_4O$	69.37	6.16	19.03
	(294.36)	(69.18)	(6.02)	(18.77)
6b	$C_{17}H_{17}ClN_4O$	62.10	5.21	17.04
	(328.80)	(61.85)	(5.19)	(16.81)
6c	$C_{17}H_{17}FN_4O$	65.37	5.49	17.94
	(312.35)	(65.18)	(5.37)	(17.81)
6d	$C_{12}H_{18}N_4O$	62.08	6.95	24.13
	(234.30)	(61.82)	(6.84)	(23.87)
7a	$C_{17}H_{16}N_4O_2$	66.22	5.23	18.17
	(308.34)	(66.09)	(5.18)	(18.02)
7b	$C_{17}H_{15}ClN_4O_2$	59.57	4.41	16.34
	(342.78)	(59.73)	(4.53)	(16.50)
7c	$C_{17}H_{15}N_5O_4$	57.79	4.23	19.82
	(353.34)	(57.65)	(4.11)	(19.58)
7d	$C_{18}H_{18}N_4O_2$	67.07	5.63	17.38
	(322.37)	(66.88)	(5.60)	(17.22)
7e	$C_{18}H_{18}N_4O_3$	63.89	5.36	16.56
	(338.37)	(63.78)	(5.28)	(16.41)
8a	$C_{18}H_{17}N_4O_2$	67.07	5.63	17.38
	(321.36)	(66.95)	(5.57)	(17.25)
8b	$C_{18}H_{17}ClN_4O_2$	60.59	4.80	15.70
	(356.81)	(60.47)	(4.69)	(15.48)
8c	$C_{18}H_{17}N_5O_4$	58.85	4.66	19.06
	(367.36)	(58.75)	(4.55)	(18.88)
8d	$C_{19}H_{20}N_4O_2$	70.35	6.21	17.27
	(336.39)	(70.19)	(6.18)	(17.15)
8e	$C_{19}H_{20}N_4O_3$	67.05	5.92	16.46
	(352.39)	(66.87)	(5.79)	(16.28)
11a	$C_{17}H_{16}N_4$	73.89	5.84	20.07
	(276.34)	(73.81)	(5.80)	(19.84)
11b	$C_{17}H_{15}ClN_4$	65.70	4.86	18.03
	(310.79)	(65.49)	(4.68)	(17.83)
11c	$C_{17}H_{15}FN_4$	69.37	5.14	19.04
	(294.33)	(69.21)	(5.08)	(18.82)
11d	$C_{12}H_{14}N_4$	62.27	6.59	26.15
	(214.27)	(62.02)	(6.48)	(25.92)
16a	$C_{17}H_{14}N_4O$	70.33	4.86	19.30
	(290.32)	(70.15)	(4.80)	(19.15)
16b	$C_{17}H_{13}ClN_4O$	62.87	4.03	17.25
	(324.77)	(62.79)	(3.88)	(17.10)
16c	$C_{18}H_{16}N_5O_3$	60.89	3.91	20.89
	(335.32)	(60.79)	(3.90)	(20.68)
16d	$C_{18}H_{16}N_4O$	71.04	5.30	18.41
	(304.35)	(70.85)	(5.21)	(18.30)

16e	$C_{19}H_{16}N_4O_2$	67.49	5.03	17.49
	(320.35)	(67.33)	(5.12)	(17.25)
17a	$C_{18}H_{16}N_4O$	71.04	5.30	18.41
	(304.35)	(70.81)	(5.25)	(18.30)
17b	$C_{18}H_{15}ClN_4O$	63.81	4.46	16.54
	(338.80)	(63.70)	(4.44)	(16.31)
17c	$C_{18}H_{15}N_5O_3$	61.89	4.33	20.25
	(349.35)	(61.78)	(4.28)	(20.13)
17d	$C_{19}H_{18}N_4O$	71.68	5.70	17.60
	(318.38)	(71.71)	(5.65)	(17.41)
17e	$C_{19}H_{18}N_4O_2$	68.25	5.43	17.76
	(334.38)	(68.22)	(5.33)	(17.50)

[a]Obtained using a Perkin-Elmer 240 DS element analyzer.

3-Methyl-1-(1-phenylethenyl)-5-(*N*-substituted amino)-1,2,4-triazoles 11; General Procedure. To a stirred suspension of the urea **6** (3.0 mmol) in dichloromethane (30 mL) was added triphenylphosphine (1.18 g, 4.5 mmol), carbon tetrachloride (1.16 mL, 12 mmol), triethylamine (0.63 mL, 4.5 mmol) at room temperature. The mixture was heated at reflux temperature for 3-6 h, and the resulting solution was concentrated to dryness. The residual material was chromatographed (silica gel; ethyl acetate-hexane, 1 : 3) to give **11** as a white solid after crystallization from petroleum ether (Table 3).

7-Methyl-4*H*-1,2,4-triazlo[1,5-**c**][1,3,5]oxadiazines **16** and **17**; General Procedure. To a stirred suspension of the urea **7** or **8** (3 mmol) in dichloromethane (30 mL) was added triphenylphosphine (1.18 g, 4.5 mmol), carbon tetrachloride (1.16 mL, 12 mmol), triethylamine (0.63 mL, 4.5 mmol) at room temperature. The mixture was heated at reflux temperature for the time indicated in Table 4, and the resulting reddish solution was concentrated under reduced pressure. The residual material was chromatographed (silica gel; ethyl acetate-hexane, 1 : 3) to give **16** or **17** as a white solid after crystallization from ether (Table 4).

Acknowledgment. The authors wish to thank the Korea Science and Engineering Foundation (Grant No. 941-0300-008-2) for financial support. Special thanks go to Dr. K. H. Lee of JINRO Company for obtaining the NMR spectra reported in this work.

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