Triazolo[4,5-*d*]pyrimidines. XII.[1] Reactions of 6-Benzoyl-6,7-dihydro-3-phenyl-3*H*-1,2,3-triazolo-[4,5-*d*]pyrimidines (Triazolopyrimidine Reissert Compounds) with Acid, Base, and Electrophile

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In the treatment of 6-benzoyl-6,7-dihydro-3-phenyl-3*H*-1,2,3-triazolo[4,5-*d*]pyrimidine-7-carbonitrile (1, triazolopyrimidine Reissert compound) and 6-benzoyl-6,7-dihydro-5-methyl-3-phenyl-3*H*-1,2,3-triazolo[4,5-*d*]pyrimidine-7-carbonitrile (2, 5-methyltriazolopyrimidine Reissert compound) with an acid, the ring fission of the pyrimidine ring proceeded to give the triazole derivatives (3—7). Alkaline hydrolysis of 2 and 1 gave 5-methyl-3-phenyl- (10) and 3-phenyl-3*H*-1,2,3-triazolo[4,5-*d*]pyrimidines (9), respectively. The anions, generated from 1 and 2 with sodium hydride (NaH), underwent aromatization to give the 3*H*-1,2,3-triazolo[4,5-*d*]pyrimidine-7-carbonitriles (12 and 14). Compounds 1 and 2 reacted with arylaldehydes in the presence of NaH to give corresponding 3*H*-1,2,3-triazolo[4,5-*d*]pyrimidin-7-ylmethyl benzoates (15 and 17).

Keywords 3*H*-1,2,3-triazolo[4,5-*d*]pyrimidine; Reissert compound; ring fission; aromatization; Reissert compound anion; 3*H*-1,2,3-triazolo[4,5-*d*]pyrimidin-7-ylmethyl benzoate

We have elucidated the reactivities of 3-benzoyl-3,4-dihydro-4-quinazolinecarbonitrile (quinazoline Reissert compound),[2a,b] 3-benzoyl-3,4-dihydro-2-methyl-4-quinazolinecarbonitrile (2-methylquinazoline Reissert compound),[3] 5-benzoyl-4,5-dihydro-1-phenyl-1*H*-pyrazolo-[3,4-*d*]pyrimidine-4-carbonitrile (pyrazolopyrimidine Reissert compound),[4] and 1-benzoyl-1,6-dihydro-9-phenyl-9*H*-purine-6-carbonitrile (purine Reissert compound)[5] with acid, alkali, sodium hydride, and electrophiles. As a continuation of these studies, the chemical reactivities of 6-benzoyl-6,7-dihydro-3-phenyl-3*H*-1,2,3-triazolo[4,5-*d*]-pyrimidine-7-carbonitrile (**1**, triazolopyrimidine Reissert compound) and 6-benzoyl-6,7-dihydro-5-methyl-3-phenyl-3*H*-1,2,3-triazolo[4,5-*d*]pyrimidine-7-carbonitrile (**2**, 5-methyltriazolopyrimidine Reissert compound) with acid, base, and electrophiles were investigated. In the present paper, we describe the results obtained in the above reactions, and compare the reactivities of **1** and **2** with those of quinazoline and 2-methylquinazoline Reissert compounds.

According to the procedure[6] reported previously, compounds **2** and **1** were prepared from 5-methyl- and 3-phenyl-3*H*-1,2,3-triazolo[4,5-*d*]pyrimidines in satisfactory yields.

Acid Hydrolysis It is known that the quinazoline Reissert compound[2a] is hydrolyzed in an acid medium to give the ring fission product, 2-(2-aminophenyl)-2-benzamidacetonitrile. The 2-methylquinazoline Reissert compound reacted with aqueous hydrochloric acid in a different way, yielding the oxazole derivative, 4-(2-acetamidophenyl)-5-amino-2-phenyloxazole.

The triazolopyrimidine Reissert compound **1** was hydrolyzed in the same medium to give the ring fission products, 5-amino-α-benzamido-1-phenyl-1*H*-1,2,3-triazole-4-acetonitrile (**3**) and 5-amino-α-benzamido-1-phenyl-1*H*-1,2,3-triazole-4-acetamide (**4**), in the same way as observed for the quinazoline Reissert compound. In the case of **2**, under the same conditions, two types of ring fission occurred, yielding 5-acetamido-α-benzamido-1-phenyl-1*H*-1,2,3-triazole-4-acetonitrile (**5**), 5-acetamido-α-benzamido-1-phenyl-1*H*-1,2,3-triazole-4-acetamide (**6**) and 5-acetamido-4-(5-amino-2-phenyl-4-oxazolyl)-1-phenyl-1*H*-1,2,3-triazole (**7**). The mechanism of the formation of the ring fission products might be similar to that already proposed by us[2a,3] for the reaction of the quinazoline and 2-methylquinazoline Reissert compounds with an acid.

Alkaline Hydrolysis It is known that the hydrolysis of quinazoline[2a] and 2-methylquinazoline[3] Reissert compounds in an alkaline medium gives quinazoline and 2-methylquinazoline,[3] respectively, *via* attack of the hydroxide ion at the carbonyl carbon, followed by loss of a cyanide ion.

A similar reaction between **2** and 2 N sodium hydroxide in methanol gave 5-methyl-3-phenyl-3*H*-1,2,3-triazolo-

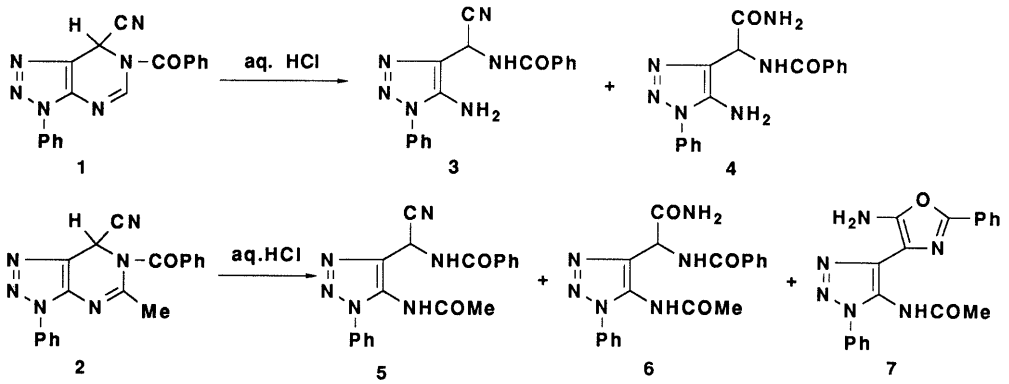

Chart 1

[4,5-*d*]pyrimidine (**10**), together with methyl benzoate (**11**). In contrast, compound **1** underwent ring fission under the same conditions and α-benzamido-5-(methoxymethyleneamino)-1-phenyl-1*H*-1,2,3-triazole-4-acetonitrile (**8**) was obtained, together with 3-phenyl-3*H*-1,2,3-triazolo[4,5-*d*]pyrimidine (**9**) and **11**.

The mechanism of formation of the ring fission product **8** is assumed to involve preferential addition of methoxide ion to the C^5,N^4-double bond, followed by cleavage of the C^5,N^6-single bond.

Reaction with Sodium Hydride It is known that the anions generated from 1-benzoyl-1,2-dihydro-2-quinolinecarbonitrile (quinoline Reissert compound)[7] and 2-benzoyl-1,2-dihydro-1-isoquinolinecarbonitrile (isoquinoline Reissert compound)[8] undergo rearrangement through aziridine intermediates in an intramolecular process, giving 2-benzoylquinoline and 1-benzoylisoquinoline, respectively. In contrast, that of the quinazoline Reissert compound[2a] undergoes aromatization to give 4-quinazolinecarbonitrile and that of the 2-methylquinazoline Reissert compound[3] undergoes both rearrangement and aromatization, giving 4-benzoyl-2-methylquinazoline and 2-methyl-4-quinazoline-carbonitrile.

Aromatization proceeded in the reaction of **1** with sodium hydride (NaH), yielding 3-phenyl-3*H*-1,2,3-triazolo[4,5-*d*]pyrimidine-7-carbonitrile (**12**), together with **9**. In the case of **2**, only aromatization took place in the different way from that of the 2-methylquinazoline Reissert compound, resulting in the formation of 5-methyl-3-phenyl-3*H*-1,2,3-triazolo[4,5-*d*]pyrimidine-7-carbonitrile (**14**), **10**, α,3-diphenyl-5-methyl-3*H*-1,2,3-triazolo[4,5-*d*]pyrimidin-7-ylmethyl benzoate (**15**), and 7,7′-bis[5-methyl-3-phenyl-3*H*-1,2,3-triazolo[4,5-*d*]pyrimidine] (**16**). The mechanism of aromatization may be similar to that for the reaction of the quinazoline[2a] and pyrazolopyrimidine[4] Reissert com-

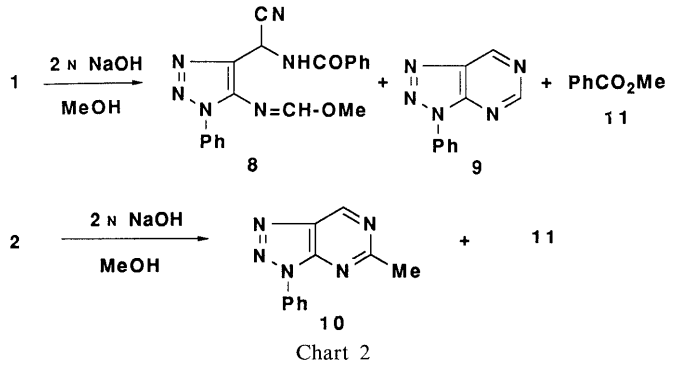

Chart 2

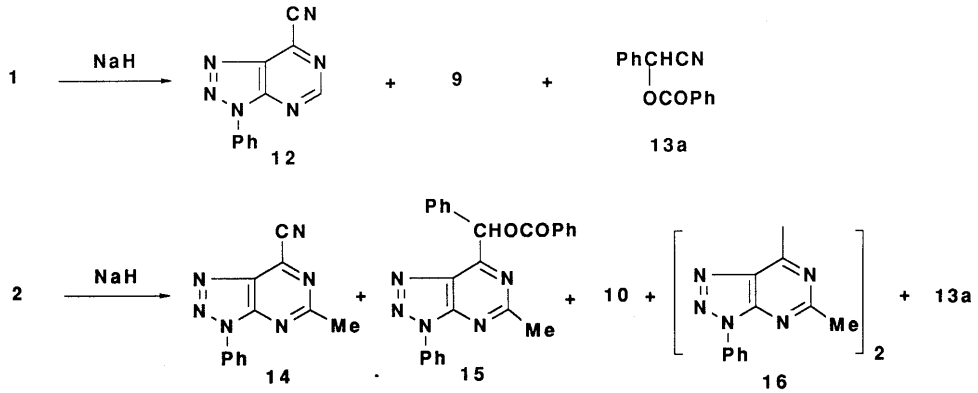

Chart 3

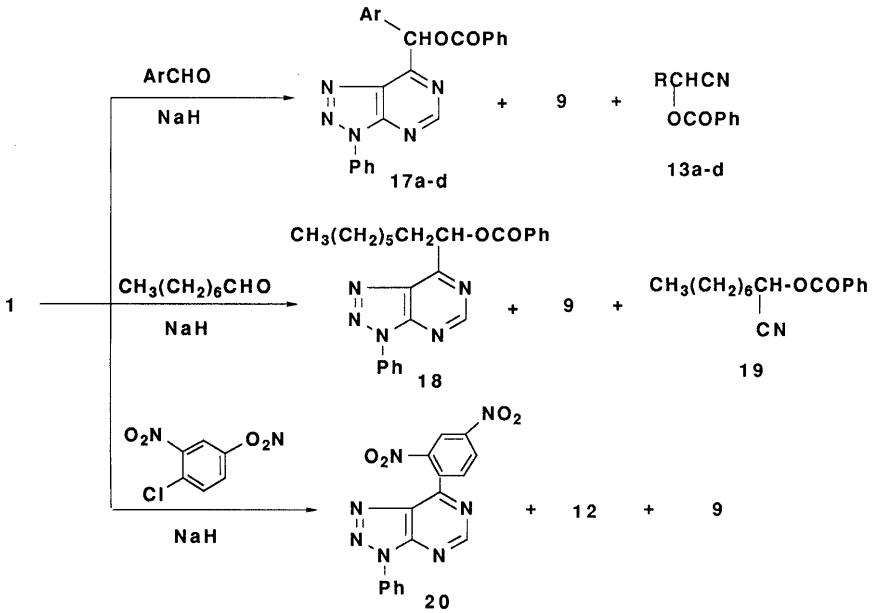

Chart 4

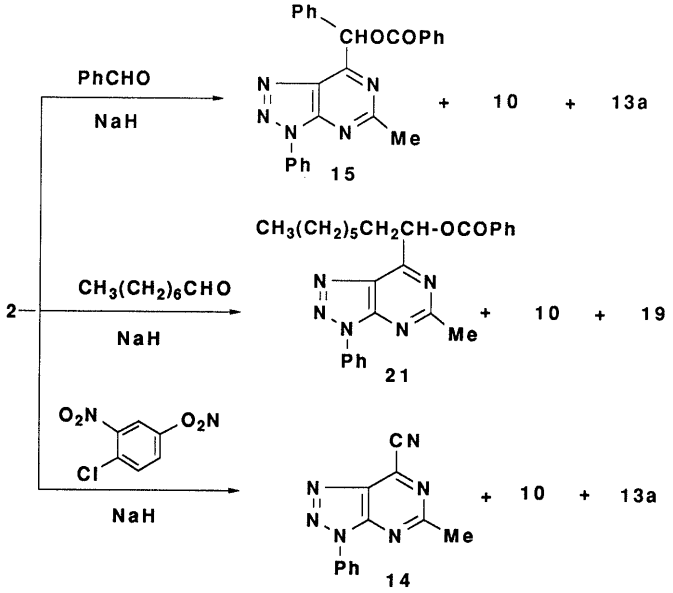

Chart 5

pounds with sodium hydride, already reported.

Reaction with Electrophiles The introduction of carbon chains into the 4-position on the quinazoline ring was achieved by reactions of quinazoline[2b] and 2-methylquinazoline[3] Reissert compound anions with aldehydes and aryl (alkyl) halides.

In connection with reactions involving the formation of Reissert compound anions, the reactions of **1** and **2** with aldehydes in the presence of NaH were investigated. The anions of **1** and **2** reacted with arylaldehydes and octanal, affording the corresponding benzoates (**17a—d**, **18**, **15**, and **21**) and by-products (**9**, **13**, **19**, and **10**) which were formed by aromatization.

In the treatment of **1** with 2,4-dinitrochlorobenzene in the presence of NaH, arylation occurred to give 4-(2,4-dinitrophenyl)-3-phenyl-3*H*-1,2,3-triazolo[4,5-*d*]-pyrimidine (**20**), together with **12** and **9**. In the case of **2**, only aromatization proceeded under the same conditions, yielding **10**, **13a**, and **14**.

The triazolopyrimidine and 5-methyltriazolopyrimidine Reissert compounds have almost the same reactivities as the quinazoline and 2-methylquinazoline Reissert compounds, respectively, with acid, alkali, and sodium hydride. The anions of **1** and **2** reacted with aldehydes to give the benzoates, and the formation of the benzoates indicates that **1** and **2** are potentially available as synthetic intermediates for introduction of a functionalized group at the 7-position by the use of electrophiles.

Experimental

All melting points are uncorrected. Infrared (IR) spectra were measured with a JASCO A-102 diffraction grating IR spectrophotometer. Proton nuclear magnetic resonance (^{1}H-NMR) spectra were taken at 60 MHz and 23 °C with a Hitachi R-24B ^{1}H-NMR spectrometer. Chemical shifts are expressed in parts per million (ppm) downfield from tetramethylsilane as an internal standard. The following abbreviations are used: s = singlet, d = doublet, t = triplet, m = multiplet, b = broad.

Acid Hydrolysis of the Triazolopyrimidine Reissert Compound (1) A solution of **1**[6] (0.33 g, 1 mmol) and 20% aqueous HCl (4 ml) in dimethyl sulfoxide (DMSO) (4 ml) was stirred at room temperature for 30 min. The mixture was poured onto ice-water and extracted with $CHCl_3$. The crude product was purified by SiO_2 column chromatography. The fraction eluted with $CHCl_3$ gave 5-amino-α-benzamido-1-phenyl-1*H*-1,2,3-triazole-4-acetonitrile (**3**) as colorless needles from benzene–MeOH, mp 178—180 °C. Yield 64 mg (20%). The fraction eluted with $CHCl_3$–MeOH (100 : 1) gave 5-amino-α-benzamido-1-phenyl-1*H*-1,2,3-triazole-4-acetamide (**4**) as a pale yellow oil. Yield 235 mg (70%).

Acid Hydrolysis of the 5-Methyltriazolopyrimidine Reissert Compound (2) When **2**[6] (0.34 g, 1 mmol) was treated with 20% aqueous HCl in the same manner as described for acid hydrolysis of **1**, the fraction obtained from SiO_2 column chromatography with $CHCl_3$ as an eluent gave 5-acetamido-4-(5-amino-2-phenyl-4-oxazolyl)-1-phenyl-1*H*-1,2,3-triazole (**7**) as colorless needles from $CHCl_3$–MeOH, mp 199—202 °C. Yield 32 mg (9%). The first fraction eluted with $CHCl_3$–MeOH (100 : 1) gave 5-acetamido-α-benzamido-1-phenyl-1*H*-1,2,3-triazole-4-acetonitrile (**5**) as colorless crystals from $CHCl_3$–MeOH, mp 97—99 °C. Yield 212 mg (59%). The second fraction eluted with $CHCl_3$–MeOH (100 : 1) gave 5-acetamido-α-benzamido-1-phenyl-1*H*-1,2,3-triazole-4-acetamide (**6**) as colorless prisms from $CHCl_3$–MeOH, mp 232—236 °C. Yield 64 mg (17%).

Alkaline Hydrolysis of 1 A mixture of **1** (0.33 g, 1 mmol), 2 N NaOH (0.5 ml), and MeOH (20 ml) was stirred at 0 °C for 5 min. The reaction mixture was poured onto ice-water, acidified with acetic acid, and extracted with $CHCl_3$. The crude product was purified by SiO_2 column chromatography. The first fraction eluted with benzene gave methyl benzoate (**11**) (38 mg, 28%). The second fraction eluted with benzene gave α-benzamido-5-methoxymethyleneamino-1-phenyl-1*H*-1,2,3-triazole-4-acetonitrile (**8**) as colorless needles from benzene, mp 130—131 °C. Yield 158 mg (44%). The fraction eluted with benzene–$CHCl_3$ (1 : 1) gave 3-phenyl-3*H*-1,2,3-triazolo[4,5-*d*]pyrimidine (**9**) as yellow needles, mp 113—115 °C (lit.[9] mp 114—115 °C). Yield 85 mg (43%).

Alkaline Hydrolysis of 2 When **2** (0.34 g, 1 mmol) was treated with 2 N NaOH in the same manner as described for alkaline hydrolysis of **1**, the first fraction obtained from SiO_2 column chromatography with benzene as an eluent gave **11** (84 mg, 62%). The second fraction eluted with benzene gave 5-methyl-3-phenyl-3*H*-1,2,3-triazolo[4,5-*d*]pyrimidine (**10**) as colorless needles, mp 156—157 °C (lit.[6] mp 158—159 °C). Yield 171 mg (81%).

Reaction of 1 with Sodium Hydride Sodium hydride (60% in oil; 50 mg, 1.25 mmol) was added to a solution of **1** (0.33 g, 1 mmol) in tetrahydrofuran (THF) (14 ml). The mixture was refluxed for 7 min. The reaction mixture was poured onto ice-water, neutralized with acetic acid, and extracted with $CHCl_3$. The crude product was purified by SiO_2 column chromatography. The first fraction eluted with petroleum benzin–benzene (1 : 1) gave *O*-benzoylmandelonitrile (**13a**). Yield 67 mg (32%). The second fraction gave 3-phenyl-3*H*-1,2,3-triazolo[4,5-*d*]pyrimidine-7-carbonitrile (**12**) as colorless scales from petroleum benzin–benzene, mp 166—167 °C (lit.[10] mp 166—167 °C). Yield 38 mg (30%). The fraction eluted with benzene–$CHCl_3$ (1 : 1) gave **9**. Yield 27 mg (20%).

Reaction of 2 with Sodium Hydride When **2** (0.34 g, 1 mmol) was treated with sodium hydride in the same manner as described for reaction of **1** with sodium hydride, the fraction obtained from SiO_2 column chromatography with petroleum benzin–benzene (1 : 1) gave **13a**. Yield 48 mg (41%). The fraction eluted with benzene gave 5-methyl-3-phenyl-3*H*-1,2,3-triazolo[4,5-*d*]pyrimidine-7-carbonitrile (**14**) as colorless needles from petroleum benzin–benzene, mp 149—151 °C. Yield 111 mg (47%). The first fraction eluted with benzene–$CHCl_3$ (1 : 1) gave α,3-diphenyl-5-methyl-3*H*-1,2,3-triazolo[4,5-*d*]pyrimidin-7-ylmethyl benzoate (**15**) as colorless needles from petroleum benzin–benzene, mp 104—106 °C. Yield 34 mg (8%). The second fraction eluted with benzene–$CHCl_3$ (1 : 1) gave **10**. Yield 59 mg (28%). The third fraction eluted with benzene–$CHCl_3$ (1 : 1) gave 7,7′-bis-[5-methyl-3-phenyl-3*H*-1,2,3-triazolo[4,5-*d*]pyrimidine] (**16**) as red scales from ethyl acetate, mp 274—276 °C. Yield 17 mg (8%).

General Procedure for the Reaction of 1 with Arylaldehydes in the Presence of Sodium Hydride Sodium hydride (60% in oil; 50 mg, 1.25 mmol) was added to a solution of **1** (0.33 g, 1 mmol) and an arylaldehyde (1 mmol) in THF (14 ml). The mixture was refluxed for 7 min. The reaction mixture was poured onto ice-water, neutralized with acetic acid, and extracted with $CHCl_3$. The crude product was purified by SiO_2 column chromatography. The fraction eluted with petroleum benzin gave **13a**. The fraction eluted with benzene gave the corresponding α-aryl-3-phenyl-5-methyl-3*H*-1,2,3-triazolo[4,5-*d*]pyrimidin-7-ylmethyl benzoate (**17a—d**). The fraction eluted with benzene–$CHCl_3$ (1 : 1) gave **9**.

Reaction of 1 with Octanal in the Presence of Sodium Hydride When **1** (0.33 g, 1 mmol) was treated with octanal in the same manner as described for reaction of **1** with arylaldehydes, the fraction obtained from SiO_2 column chromatography with benzene as an eluent gave 1-cyanoctyl

TABLE I. Melting Points, Elemental Analytical, and Mass Spectral Data for **3**—**8** and **14**—**16**

Compd.	mp (°C)	Formula	Analysis (%) Calcd (Found) C	H	N	MS Calcd (Observed)
3	178—180	$C_{17}H_{14}N_6O$	64.14 (64.00)	4.43 (4.42)	26.40 (26.06)	
4	Oil	$C_{17}H_{16}N_6O_2$				336.1335 (336.1319)
5	97—99	$C_{19}H_{16}N_6O_2$				360.1335 (360.1346)
6	232—236	$C_{19}H_{18}N_6O_3$	60.31 (60.36)	4.80 (4.80)	22.21 (22.32)	
7	199—202	$C_{19}H_{16}N_6O_2$				360.1335 (360.1341)
8	130—131	$C_{19}H_{16}N_6O_2$	63.32 (62.79)	4.48 (4.47)	23.32 (23.00)	
14	149—151	$C_{12}H_8N_6$	61.01 (61.09)	3.41 (3.39)	35.58 (35.61)	
15	104—105	$C_{25}H_{19}N_5O_2$	71.24 (70.75)	4.54 (4.61)	16.62 (16.31)	
16	274—276	$C_{22}H_{16}N_{10}$				420.1558 (420.1552)

TABLE II. Melting Points, Elemental Analytical, and Mass Spectral Data for **17a**—**d**, **18**, **20**, and **21**

Compd.	mp (°C)	Formula	Analysis (%) Calcd (Found) C	H	N	MS Calcd (Observed)
17a	148—150	$C_{24}H_{17}N_5O_2$	70.75 (70.66)	4.20 (4.22)	17.19 (16.93)	
17b	130—131	$C_{24}H_{16}ClN_5O_2$	65.23 (65.03)	3.65 (3.63)	15.85 (15.77)	
17c	125—126	$C_{25}H_{19}N_5O_2$	71.25 (71.08)	4.54 (4.53)	16.62 (16.61)	
17d	127—130	$C_{25}H_{19}N_5O_3$	68.64 (68.17)	4.38 (4.42)	16.01 (15.52)	
18	Oil	$C_{25}H_{24}N_5O_2$	69.91 (69.82)	6.34 (6.47)	16.30 (15.84)	
20	158—159	$C_{16}H_{19}N_7O_4$	52.90 (53.11)	2.50 (2.49)	26.99 (26.70)	
21	Oil	$C_{26}H_{29}N_5O_2$				443.2336 (443.2328)

benzoate (**19**). Yield 83 mg (32%). The first fraction eluted with benzene–$CHCl_3$ (1 : 1) gave α-heptyl-3-phenyl-3*H*-1,2,3-triazolo[4,5-*d*]pyrimidin-7-ylmethyl benzoate (**18**) as a pale yellow oil. Yield 52 mg (12%). The second fraction eluted with benzene–$CHCl_3$ (1 : 1) gave **9**. Yield 40 mg (19%).

Reaction of 1 with 2,4-Dinitrochlorobenzene in the Presence of Sodium Hydride When **1** (0.33 g, 1 mmol) was treated with 2,4-dinitrochlorobenzene in the same manner as described for reaction of **1** with arylaldehydes, the fraction obtained from SiO_2 column chromatography with benzene as an eluent gave **12**. Yield 9 mg (4%). The fraction eluted with benzene–$CHCl_3$ (1 : 1) gave 7-(2,4-dinitrophenyl)-3-phenyl-3*H*-1,2,3-triazolo[4,5-*d*]pyrimidine (**20**) as yellow prisms from petroleum benzin–benzene, mp 158—159 °C. Yield 26 mg (7%). The fraction eluted with $CHCl_3$ gave **9**. Yield 16 mg (8%).

Reaction of 2 with Benzaldehyde in the Presence of Sodium Hydride Sodium hydride (60% in oil; 50 mg, 1.25 mmol) was added to a solution of **2** (0.34 g, 1 mmol) and benzaldehyde (116 mg, 1 mmol) in THF (14 ml). The mixture was refluxed for 30 min. The reaction mixture was poured onto ice-water, neutralized with acetic acid, and extracted with $CHCl_3$. The crude product was purified by SiO_2 column chromatography. The fraction eluted with petroleum benzin gave **13a**. Yield 119 mg (50%). The first fraction eluted with benzene gave **15**. Yield 215 mg (51%). The second fraction eluted with benzene gave **10**. Yield 63 mg (30%).

Reaction of 2 with Octanal in the Presence of Sodium Hydride When **2** (0.34 g, 1 mmol) was treated with octanal in the same manner as described for reaction of **2** with benzaldehyde, the first fraction obtained from SiO_2 column chromatography with benzene–$CHCl_3$ (1 : 1) as an eluent gave **19**. Yield 85 mg (33%). The second fraction eluted with benzene–$CHCl_3$ (1 : 1) gave α-heptyl-5-methyl-3-phenyl-3*H*-1,2,3-triazolo[4,5-*d*]pyrimidin-7-ylmethyl benzoate (**21**) as a colorless oil. Yield 208 mg (47%). The fraction

TABLE III. IR and ^{1}H-NMR Spectral Data for **3**—**10**, **12**, **14**, and **15**

Compd.	IR ν_{max}^{KBr} (cm^{-1})	^{1}H-NMR ($CDCl_3$) (ppm)
3	3300 (NH) 3400 (NH)	5.90 (2H, s, NH_2), 6.40 (1H, d, J=6.0 Hz, CHCN), 7.30—8.20 (10H, m, aromatic H), 9,65 (1H, d, J=6.0 Hz, NH)
4	1630 (C=O) 3300 (NH)	4.75—5.25 (2H, b, NH_2), 5.75 (1H, d, J=6.0 Hz, CHCN), 6.63—7.03 (2H, b, $CONH_2$), 7.03—7.95 (10H, m, aromatic H), 8.10 (1H, d, J=6.0 Hz, NH)
5	1645 (C=O)	2.15 (3H, s, CH_3), 6.26 (1H, d, J=8.0 Hz, CHCN), 7.20—7.95 (10H, m, aromatic H), 8.33 (1H, d, J=8.0 Hz, NH), 9.11 (1H, s, NHAc)
6[a]	1640 (C=O) 1680 (C=O)	2.02 (3H, s, $COCH_3$), 5.82 (1H, d, J=9.0 Hz, CHNH), 7.01—8.30 (12H, m, aromatic H and $CONH_2$), 8.67 (1H, d, J=9.0 Hz, CHNH), 10.25 (1H, s, NHAc)
7	1680 (C=O)	2.12 (3H, s, CH_3), 6.02 (2H, b, NH_2), 7.16—8.80 (10H, m, aromatic H), 10.34 (1H, s, NH)
8	1650 (C=O)	3.80 (3H, s, OCH_3), 6.37 (1H, d, J=8.0 Hz, CHCN), 7.00—7.97 (10H, m, aromatic H), 8.05 (1H, s, N=CH), 8.47 (1H, d, J=8.0 Hz, NHCH)
9		7.40—8.50 (5H, m, N^3-Ph), 9.31 (1H, s, C^5-H), 9.68 (1H, s, C^7-H)
10		2.93 (3H, s, CH_3), 7.40—8.50 (5H, m, N^3-Ph), 9.50 (1H, s, C^7-H)
12[a]		7.50—8.50 (5H, m, N^3-Ph), 9.58 (1H, s, C^5-H)
14		2.98 (3H, s, CH_3), 7.30—7.85 (3H, m, N^3-Ph), 7.90—8.40 (2H, m, N^3-Ph)
15	1720 (C=O)	2.82 (3H, s, CH_3), 7.00—8.40 (16H, m, CH–O– and aromatic H)

a) ^{1}H-NMR in DMSO-d_6.

TABLE IV. IR and ^{1}H-NMR Spectral Data for **17a**—**d**, **18**, **20**, and **21**

Compd.	IR ν_{max}^{KBr} (cm^{-1})	^{1}H-NMR ($CDCl_3$) (ppm)
17a	1720 (C=O)	7.10—7.70 (6H, m, aromatic H), 7.70—8.40 (10H, m, aromatic H), 9.05 (1H, s, C^5-H)
17b	1720 (C=O)	7.10—7.90 (11H, m, aromatic H), 7.95—8.40 (4H, m, aromatic H), 9.03 (1H, s, C^5-H)
17c	1720 (C=O)	2.30 (3H, s, CH_3), 7.11—7.90 (11H, m, aromatic H), 8.00—8.45 (4H, m, aromatic H), 9.15 (1H, s, C^5-H)
17d	1720 (C=O)	3.78 (3H, s, OCH_3), 6.80—8.50 (15H, m, aromatic H), 9.10 (1H, s, C^5-H)
18	1720 (C=O)	0.83 (3H, t, J=4.0 Hz, $CH_3(CH_2)_5CH_2CH$), 1.10—2.00 (10H, m, $CH_3(CH_2)_5CH_2CH$), 2.00—2.80 (2H, m, $CH_3(CH_2)_5CH_2CH$), 6.50 (1H, t, J=6.0 Hz, CH_2CH–O), 7.30—7.90 (6H, m, aromatic H), 7.90—8.40 (4H, m, aromatic H), 9.10 (1H, s, C^5-H)
20	1350 (NO_2) 1550 (NO_2)	7.40—8.40 (5H, m, aromatic H), 8.40—9.00 (3H, m, aromatic H), 9.30 (1H, s, C^5-H)
21	1720 (C=O)	0.90 (3H, t, J=4.0 Hz, $CH_3(CH_2)_5CH_2CH$–O), 1.08—2.02 (10H, m, $CH_3(CH_2)_5CH_2CH$–O), 2.02—2.60 (2H, m, $CH_3(CH_2)_5CH_2CH$–O), 2.85 (3H, s, C^5–CH_3), 5.53 (1H, t, J=6.0 Hz, $CH_3(CH_2)_5CH_2CH$–O), 7.10—7.70 (6H, m, aromatic H), 7.90—8.40 (4H, m, aromatic H)

eluted with benzene–$CHCl_3$ (1 : 1) gave **10**. Yield 106 mg (50%).

Reaction of 2 with 2,4-Dinitrochlorobenzene in the Presence of Sodium Hydride When **2** (0.34 g, 1 mmol) was treated with 2,4-dinitrochlorobenzene in the same manner as described for reaction of **2** with benzaldehyde, the fraction obtained from SiO_2 column chromatography with benzene as an eluent gave **13a**. Yield 43 mg (18%). The fraction eluted with benzene–$CHCl_3$ (1 : 1) gave **14**. Yield 64 mg (27%). The fraction eluted with $CHCl_3$ gave **10**. Yield 99 mg (47%).

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