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 procedure⁶⁾ 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-benz-

amidacetonitrile. 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-methylquinazoline³⁾ 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 C⁵,N⁴-double bond, followed by cleavage of the C⁵,N⁶-single bond.

Reaction with Sodium Hydride It is known that the

Chart 2

anions generated from 1-benzoyl-1,2-dihydro-2-quinoline-carbonitrile (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 compound³⁾ 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 pyrazolopyrimidine⁴⁾ Reissert com-

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-methylquinazoline³) 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-3H-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 (¹H-NMR) spectra were taken at 60 MHz and 23 °C with a Hitachi R-24B ¹H-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 CHCl₃. The crude product was purified by SiO₂ column chromatography. The fraction elut-

ed with CHCl₃ gave 5-amino- α -benzamido-1-phenyl-1H-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 CHCl₃-MeOH (100:1) gave 5-amino- α -benzamido-1-phenyl-1H-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 SiO₂ column chromatography with CHCl₃ as an eluent gave 5-acetamido-4-(5-amino-2-phenyl-4-oxazolyl)-1-phenyl-1H-1,2,3-triazole (**7**) as colorless needles from CHCl₃-MeOH, mp 199–202 °C. Yield 32 mg (9%). The first fraction eluted with CHCl₃-MeOH (100:1) gave 5-acetamido- α -benzamido-1-phenyl-1H-1,2,3-triazole-4-acetonitrile (**5**) as colorless crystals from CHCl₃-MeOH, mp 97–99 °C. Yield 212 mg (59%). The second fraction eluted with CHCl₃-MeOH (100:1) gave 5-acetamido- α -benzamido-1-phenyl-1H-1,2,3-triazole-4-acetamide (**6**) as colorless prisms from CHCl₃-MeOH, mp 232–236 °C. Yield 64 mg (17%).

Alkaline Hydrolysis of 1 A mixture of **1** (0.33 g, 1 mmol), 2N 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 CHCl₃. The crude product was purified by SiO₂ 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-1H-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-CHCl₃ (1:1) gave 3-phenyl-3H-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 2N NaOH in the same manner as described for alkaline hydrolysis of **1**, the first fraction obtained from SiO₂ column chromatography with benzene as an eluent gave **11** (84 mg, 62%). The second fraction eluted with benzene gave 5-methyl-3-phenyl-3H-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 CHCl₃. The crude product was purified by SiO₂ 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-3H-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-CHCl₃ (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 SiO₂ column chromatography with petroleum benzin-benzene (1:1) gave **13a**. Yield 48 mg (41%). The fraction eluted with benzene gave 5-methyl-3-phenyl-3H-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-CHCl₃ (1:1) gave α ,3-diphenyl-5-methyl-3H-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-CHCl₃ (1:1) gave **10**. Yield 59 mg (28%). The third fraction eluted with benzene-CHCl₃ (1:1) gave 7,7'-bis-[5-methyl-3-phenyl-3H-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 CHCl₃. The crude product was purified by SiO₂ column chromatography. The fraction eluted with petroleum benzin gave **13a**. The fraction eluted with benzene gave the corresponding α -aryl-3-phenyl-5-methyl-3H-1,2,3-triazolo[4,5-d]pyrimidin-7-ylmethyl benzoate (**17a—d**). The fraction eluted with benzene-CHCl₃ (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 SiO₂ 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 (%)			MS Calcd (Observed)
			Calcd (Found)			
			C	H	N	
3	178–180	C ₁₇ H ₁₄ N ₆ O	64.14 (64.00)	4.43 (4.42)	26.40 (26.06)	
4	Oil	C ₁₇ H ₁₆ N ₆ O ₂				336.1335 (336.1319)
5	97–99	C ₁₉ H ₁₆ N ₆ O ₂				360.1335 (360.1346)
6	232–236	C ₁₉ H ₁₈ N ₆ O ₃	60.31 (60.36)	4.80 (4.80)	22.21 (22.32)	
7	199–202	C ₁₉ H ₁₆ N ₆ O ₂				360.1335 (360.1341)
8	130–131	C ₁₉ H ₁₆ N ₆ O ₂	63.32 (62.79)	4.48 (4.47)	23.32 (23.00)	
14	149–151	C ₁₂ H ₈ N ₆	61.01 (61.09)	3.41 (3.39)	35.58 (35.61)	
15	104–105	C ₂₅ H ₁₉ N ₅ O 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 (%)			MS Calcd (Observed)
			Calcd (Found)			
			C	H	N	
17a	148–150	C ₂₄ H ₁₇ N ₅ O ₂	70.75 (70.66)	4.20 (4.22)	17.19 (16.93)	
17b	130–131	C ₂₄ H ₁₆ ClN ₅ O ₂	65.23 (65.03)	3.65 (3.63)	15.85 (15.77)	
17c	125–126	C ₂₅ H ₁₉ N ₅ O ₂	71.25 (71.08)	4.54 (4.53)	16.62 (16.61)	
17d	127–130	C ₂₅ H ₁₉ N ₅ O ₃	68.64 (68.17)	4.38 (4.42)	16.01 (15.52)	
18	Oil	C ₂₅ H ₂₄ N ₅ O ₂	69.91 (69.82)	6.34 (6.47)	16.30 (15.84)	
20	158–159	C ₁₆ H ₁₉ N ₇ O ₄	52.90 (53.11)	2.50 (2.49)	26.99 (26.70)	
21	Oil	C ₂₆ H ₂₉ N ₅ O ₂				443.2336 (443.2328)

benzoate (**19**). Yield 83 mg (32%). The first fraction eluted with benzene–CHCl₃ (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–CHCl₃ (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 aryl-aldehydes, the fraction obtained from SiO₂ column chromatography with benzene as an eluent gave **12**. Yield 9 mg (4%). The fraction eluted with benzene–CHCl₃ (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 CHCl₃ 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 CHCl₃. The crude product was purified by SiO₂ 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

TABLE III. IR and ¹H-NMR Spectral Data for **3–10**, **12**, **14**, and **15**

Compd.	IR $\nu_{\text{max}}^{\text{KBr}}$ (cm ⁻¹)	¹ H-NMR (CDCl ₃) (ppm)
3	3300 (NH) 3400 (NH)	5.90 (2H, s, NH ₂), 6.40 (1H, d, <i>J</i> = 6.0 Hz, CHCN), 7.30–8.20 (10H, m, aromatic H), 9.65 (1H, d, <i>J</i> = 6.0 Hz, NH)
4	1630 (C=O) 3300 (NH)	4.75–5.25 (2H, b, NH ₂), 5.75 (1H, d, <i>J</i> = 6.0 Hz, CHCN), 6.63–7.03 (2H, b, CONH ₂), 7.03–7.95 (10H, m, aromatic H), 8.10 (1H, d, <i>J</i> = 6.0 Hz, NH)
5	1645 (C=O)	2.15 (3H, s, CH ₃), 6.26 (1H, d, <i>J</i> = 8.0 Hz, CHCN), 7.20–7.95 (10H, m, aromatic H), 8.33 (1H, d, <i>J</i> = 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, <i>J</i> = 9.0 Hz, CHNH), 7.01–8.30 (12H, m, aromatic H and CONH ₂), 8.67 (1H, d, <i>J</i> = 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, <i>J</i> = 8.0 Hz, CHCN), 7.00–7.97 (10H, m, aromatic H), 8.05 (1H, s, N=CH), 8.47 (1H, d, <i>J</i> = 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) ¹H-NMR in DMSO-*d*₆.

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

Compd.	IR $\nu_{\text{max}}^{\text{KBr}}$ (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, <i>J</i> = 4.0 Hz, CH ₃ (CH ₂) ₅ CH ₂ CH), 1.10–2.00 (10H, m, CH ₃ (CH ₂) ₅ CH ₂ CH), 2.00–2.80 (2H, m, CH ₃ (CH ₂) ₅ CH ₂ CH), 6.50 (1H, t, <i>J</i> = 6.0 Hz, CH ₂ CH–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, <i>J</i> = 4.0 Hz, CH ₃ (CH ₂) ₅ CH ₂ CH–O), 1.08–2.02 (10H, m, CH ₃ (CH ₂) ₅ CH ₂ CH–O), 2.02–2.60 (2H, m, CH ₃ (CH ₂) ₅ CH ₂ CH–O), 2.85 (3H, s, C ⁵ -CH ₃), 5.53 (1H, t, <i>J</i> = 6.0 Hz, CH ₃ (CH ₂) ₅ CH ₂ CH–O), 7.10–7.70 (6H, m, aromatic H), 7.90–8.40 (4H, m, aromatic H)

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 SiO₂ column chromatography with benzene–CHCl₃ (1 : 1) as an eluent gave **19**. Yield 85 mg (33%). The second fraction eluted with benzene–CHCl₃ (1 : 1) gave α -heptyl-5-methyl-3-phenyl-3*H*-1,2,3-triazolo[4,5-*d*]pyrimidin-7-yl-methyl benzoate (**21**) as a colorless oil. Yield 208 mg (47%). The fraction

eluted with benzene-CHCl₃ (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 SiO₂ column chromatography with benzene as an eluent gave **13a**. Yield 43 mg (18%). The fraction eluted with benzene-CHCl₃ (1 : 1) gave **14**. Yield 64 mg (27%). The fraction eluted with CHCl₃ gave **10**. Yield 99 mg (47%).

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