(t, 12H, $CH_3$).

**5,11,17,23-Tetrahydroxy-25,26,27,28-tetrakis(n-hexyloxy)calix[4]arene (7) and 5,11,17-Trihydroxy-25,26,27,28-tetrakis(n-hexyloxy)calix[4]arene (8).** General lithiation procedure was followed except that 1 g (0.93 mmol) of *p*-bromo compound 3, 100 mL of dry THF, and 16.0 mL (27.2 mmol) of 1.7 M *t*-BuLi-pentane solution were used. The lithiate was quenched with 4.2 mL of $B(OMe)_3$ (36.98 mmol). The mixture was then warmed to room temperature and stirred for 2 h. After the mixture was cooled again to −78 ℃, 10 mL of 1 : 1 3 N NaOH-28% $H_2O_2$ solution was added and slowly warmed to room temperature. The mixture was stirred for 2 h and then 8 g of $Na_2S_2O_3 \cdot 5H_2O$ was carefully added. After stirring for 1 h, the solvent was removed under reduced pressure and then the residue was partitioned between 1 N HCl and ether. The organic phase was washed with water, brine and then dried over anhydrous $MgSO_4$. The solvent was evaporated, and the crude mixture was chromatographed on a silica gel gravity column (2.5×26 cm, hexane : EtOAc=1 : 2). The best portions of each products were collected, concentrated and then recrystallized from a mixture of acetone and hexane to give 231 mg of the tetrol 7 (30%) and 124 mg of the triol 8 (16%): Tetrol 7: mp 267-268 ℃; $^1$H NMR (300 MHz, DMSO-$d_6$) δ 8.50 (s, 4H, O*H*), 6.15 (s, 8H, Ar*H*), 4.20 (d, *J*=12.6 Hz, 4H, *endo*-ArC*H*), 3.69 (t, *J*=7.5 Hz, 8H, $OCH_2$), 2.90 (d, *J*=12.6 Hz, 4H, *exo*-ArC*H*), 1.86 (br s, 8H, $OCH_2CH_2$), 1.33 (br s, 24H, $(CH_2)_3CH_3$), 0.90 (br s, 12H, $CH_3$); FAB$^+$ MS (thioglycerol), m/z 956 (M+Na$^+$+Matrix, 100%), 848 (M+Na$^+$, 40%), 825 (M$^+$, 76%); FT-IR (KBr), 3310 cm$^{-1}$ ($\nu_{O-H}$): Triol 8: mp. 180.8-182 ℃; $^1$H NMR (300 MHz, $CDCl_3$) δ 7.03 (d, *J*=6.7 Hz, 2H, H-Ar*H*), 6.85 (t, *J*=6.8 Hz, 1H, *H*-ArH), 6.53 (s, 2H, HO-Ar*H*), 6.24 (br s, 1H, O*H*), 6.07 (br s, 2H, O*H*), 5.83 (s, 2H, HO-Ar*H*), 5.68 (s, 2H, HO-Ar*H*), 4.41 (d, *J*=13.5 Hz, 2H, *endo*-ArC*H*), 4.36 (d, *J*=13.5 Hz, 2H, *endo*-ArC*H*), 4.00 (t, 2H, $OCH_2$), 3.92 (t, 2H, $OCH_2$), 3.68 (t, 4H, $OCH_2$), 3.08 (d, *J*=13.5 Hz, 2H, *exo*-ArC*H*), 2.99 (d, *J*=13.5 Hz, 2H, *exo*-ArC*H*), 1.90 (m, 8H, $OCH_2CH_2$), 1.55-1.30 (m, 24H, $(CH_2)_3CH_3$), 0.92 (m, 12H, $CH_3$); FAB$^+$ MS (thioglycerol), m/z 940 (M+Na$^+$+Matrix, 63%), 832 (M+Na$^+$, 56%), 809 (M$^+$, 100%); FT-IR (KBr) 3323 cm$^{-1}$ ($\nu_{O-H}$).

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# 1,2,4-Triazole Fused Heterocycles; Part 2. Preparation of 4*H*-1,2,4-Triazolo[1,5-c][1,3,5]oxadiazines

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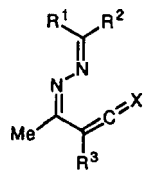
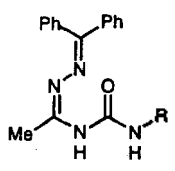
It has been shown[1,2] that cumulated azines 1 proved to be versatile synthons for a large variety of pyrazolo-fused heterocycles. Recently we reported[3] the synthesis of 5,10-dihydro-1,2,4-triazolo[5,1-*b*]quinazolines based on the dehydra-




1, X = $R^4R^5C$ or $R^4N$ or S

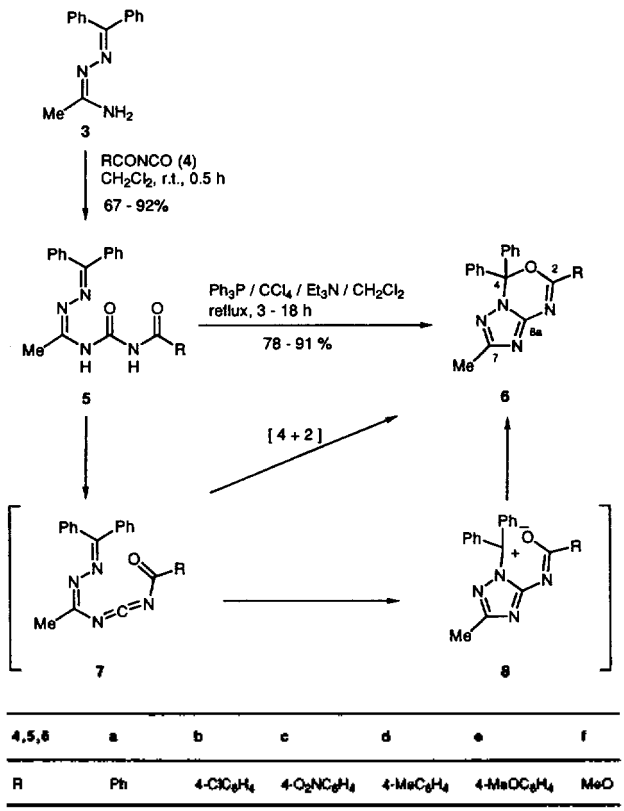



2, R = alkyl or aryl

**Table 1.** Benzophenone 1-*N*-acylureidoethylidenehydrazones **5**

| Product | Yield[a] (%) | Mp (°C) | Molecular Formula[b] | $^1$H NMR (DMSO-$d_6$/TMS), δ, *J*(Hz) | | | |
|---|---|---|---|---|---|---|---|
| | | | | $CH_3$[c] | Aromatic | two NH[c] | Others[c] |
| **5a** | 88 | 220-221 | $C_{23}H_{20}N_4O_2$ (384.4) | 2.35 | 7.24-7.26 (m, 2H), 7.46-7.69 (m, 9H), 7.81-7.83 (m, 2H), 8.02-8.04 (m, 2H) | 11.21, 12.43 | |
| **5b** | 92 | 201-202 | $C_{23}H_{19}ClN_4O_2$ (418.9) | 2.34 | 7.22-7.26 (m, 2H), 7.43-7.50 (m, 6H), 7.62 (d, *J*=8.6, 2H), 7.79-7.82 (m, 2H), 8.03 (d, *J*=8.6, 2H) | 11.25, 12.34 | |
| **5c** | 83 | 210-211 | $C_{23}H_{19}N_5O_4$ (429.4) | 2.35 | 7.24-7.27 (m, 2H), 7.44-7.51 (m, 6H), 7.79-7.83 (m, 2H), 8.22 and 8.37 (two d, *J*=9.0, each 2H) | 11.55, 12.28 | |
| **5d** | 81 | 209-210 | $C_{24}H_{22}N_4O_2$ (398.5) | 2.33 | 7.23-7.26 (m, 2H), 7.36 (d, *J*=8.3, 2H), 7.42-7.48 (m, 6H), 7.80-7.83 (m, 2H), 7.95 (d, *J*=8.3, 2H) | 11.08, 12.45 | 2.36 ($CH_3$) |
| **5e** | 74 | 195-196 | $C_{24}H_{22}N_4O_3$ (414.5) | 2.31 | 7.05 (d, *J*=8.9, 2H), 7.21-7.23 (m, 2H), 7.40-7.45 (m, 6H), 7.78-7.81 (m, 2H), 8.04 (d, *J*=8.9, 2H) | 10.96, 12.45 | 3.83 ($OCH_3$) |
| **5f** | 67 | 195 | $C_{18}H_{18}N_4O_3$ (338.4) | 2.28 | 7.21-7.24 (m, 2H), 7.39-7.48 (m, 6H), 7.71-7.75 (m, 2H) | 10.69, 11.63 | 3.75 ($OCH_3$) |

[a]Yield of pure isolated product. [b]Satisfactory microanalyses obtained: C± 0.25, H± 0.15, N± 0.24. [c]All singlets.




**Scheme 1.**

tion[4] followed by an electrocylic ring closure of azino ureas **2** using a mixture of triphenylphosphine, carbon tetrachloride, and triethylamine in dichloromethane. Continuing our interest in the reactions of azine substituted heterocumulenes to prepare fused triazolo ring systems, we chose to explore the reaction of *N*-azinyl-*N'*-acylcarbodiimide species **7** that could be used to prepare 4*H*-1,2,4-triazolo[1,5-*c*][1,3,5]oxadiazines **6**. In this paper we wish to reveal an extension of the usefulness of azino ureas **5** as an excellent intermediate for the perparation of fused triazolo species **6**.

The starting compounds, benzophenone 1-*N*-acylureidoethylidenehydrazones (**5**), were obtained by the reaction of benzophenone 1-aminoethylidenehydrazone (**3**) with acyl isocyanates **4** in dichloromethane at room temperature (see Table 1). Treatment of *N*-aziny-*N'*-acylureas **5** with triphenylphosphine, carbon tetrachloride, and triethylamine in dichloromethane at reflux temperature smoothly afforded the desired 4*H*-1,2,4-triazolo[1,5-*c*][1,3,5]oxadiazines **6** in yields ranging from 78 to 91% (see Table 2). Although the isolation of *N*-azinyl-*N'*-acylcarbodiimides **7** was unsuccessful under the reaction conditions, the corresponding triazoloxadiazine **6** can be assumed to proceed by ring closure *via* the zwitterionic species **8**, or may have been formed directly *via* a [4+2] intramolecular cycloaddition from the carbodiimides **7**. A reasonable mechanistic pathway for the transformation of **5** into **6** is depicted in Scheme 1.[2]

All compounds were characterized by their $^1$H and $^{13}$C NMR spectra and microanalytical data (see Table 2 and Table 3). Thus, it has been shown that good to excellent yields of the hitherto unknown 4*H*-1,2,4-triazolo[1,5-*c*][1,3,5]oxadiazines **6** can be produced readily from *N*-azinyl-*N'*-acylureas **5**.

## Experimental

$CCl_4$ and $CH_2Cl_2$ were dried and distilled from $P_2O_5$. $Et_3N$ 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 analyzer. $^1$H and $^{13}$C NMR spectra were measured on

**Table 2.** 4,4-Diphenyl-7-methyl-4*H*-1,2,4-triazolo[1,5-*c*][1,3,5]oxadiazines **6**

| Product | Reaction Time (h) | Yield[a] (%) | Mp (℃) (EtOH) | Molecular Formula[b] | $^1$H NMR ($CDCl_3$/TMS) δ, *J* (Hz) | | |
|---|---|---|---|---|---|---|---|
| | | | | | C7-$CH_3$[c] | Aromatic | Others[c] |
| **6a** | 3 | 91 | 174-175 | $C_{23}H_{18}N_4O$ (366.4) | 2.44 | 7.27-7.50 (m, 13H), 8.23 (d, *J*=8.4, 2H) | |
| **6b** | 3 | 82 | 210-211 | $C_{23}H_{17}ClN_4O$ (400.9) | 2.43 | 7.31-7.45 (m, 12H), 8.16 (d, *J*=7.8, 2H) | |
| **6c** | 6 | 78 | 257-258[d] | $C_{23}H_{17}N_5O_3$ (411.4) | 2.44 | 7.31-7.46 (m, 10H), 8.31 and 8.39 (two d, *J*=8.9, each 2H) | |
| **6d** | 10 | 83 | 183-184 | $C_{24}H_{20}N_4O$ (380.4) | 2.42 | 7.27 (d, *J*=8.3, 2H), 7.35-7.41 (m, 10H), 8.12 (d, *J*=8.3, 2H) | 2.43 ($CH_3$) |
| **6e** | 18 | 80 | 154-155 | $C_{24}H_{20}N_4O_2$ (396.4) | 2.42 | 6.96 (d, *J*=8.9, 2H), 7.32-7.44 (m, 10H), 8.18 (d, *J*=8.9, 2H) | 3.87 ($OCH_3$) |
| **6f** | 8 | 79 | 156-157 | $C_{18}H_{16}N_4O_2$ (320.3) | 2.35 | 7.28-7.43 (m, 10H) | 3.98 ($OCH_3$) |

[a]Yield of pure isolated product. [b]Satisfactory microanalyses obtained: C± 0.20, H± 0.22, N± 0.21. [c]All singlets. [d]Recrystallized from MeOH/$CH_2Cl_2$.

**Table 3.** Selected $^{13}$C NMR Chemical Shifts of 4,4-Diphenyl-7-methyl-4*H*-1,2,4-triazolo[1,5*c*][1,3,5]oxadiazines **6**[a]

| Product | C2 | C4 | C7 | C8a | C7-$CH_3$ | Others |
|---|---|---|---|---|---|---|
| **6a** | 152.0 | 96.8 | 161.3 | 160.7 | 14.8 | |
| **6b** | 151.8 | 97.0 | 161.4 | 159.8 | 14.8 | |
| **6c** | 151.3 | 97.6 | 161.8 | 158.6 | 14.7 | |
| **6d** | 152.1 | 96.6 | 161.2 | 160.9 | 14.8 | 21.8 ($CH_3$) |
| **6e** | 152.3 | 96.4 | 161.1 | 160.6 | 14.8 | 55.6 ($OCH_3$) |
| **6f** | 153.3 | 97.4 | 161.0 | 159.3 | 14.7 | 57.4 ($OCH_3$) |

[a]$CDCl_3$ solution. Numbering of **6** shown in Scheme 1. Assignments based on ref 2, and C7 and C8a may be reversed.

a Varian Gemini 300 spectrometer.

The benzophenone 1-aminoethylidenehydrazone (**3**) was produced by known methods.[3] The acyl isocyanates **4** employed were prepared according to Speziale and Smith.[5,6]

**Benzophenone 1-*N*-acylureidoethylidenehydrazones 5a-f**

**General Procedure.** To a stirred solution of benzophenone 1-aminoethylidenehydrazone (**3**; 1.18 g, 5 mmol) in $CH_2Cl_2$ (10 mL) was added acyl isocyanate (**4**, 6 mmol) at room temperature. The pale yellow solid was precipitated as soon as addition was completed. After stirring for 0.5 hour at ambient temperature, the precipitated solid was separated by filtration, washed with ether and dried in vacuo to give **5a-f** (see Table 1).

**4,4-Diphenyl-7-methyl-4*H*-1,2,4-triazolo[1,5-c][1,3,5]oxadiazines 6a-f**

**General Procedure.** To a stirred suspension of the appropriate urea **5** (2 mmol) in $CH_2Cl_2$ (20 mL) was added triphenylphosphine (0.78 g, 3 mmol), carbon tetrachloride (0.58 mL, 6 mmol), and triethylamine (0.42 mL, 3 mmol) at room temperature. The mixture was heated at reflux temperature with stirring for the time indicated in Table 2, and the resulting reddish solution was concentrated under reduced pressure. The residual material was chromatographed on a short silica gel column ($CH_2Cl_2$) to give **6** as a yellowish-white solid after crystallization with ether. An analytical sample was prepared by recrystallization from ethanol (see Table 2).

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Microanalytical Data[a]

| Product | Molecular formula | Analyses (%) C | H | calcd./(Found) N |
|---|---|---|---|---|
| **5a** | $C_{23}H_{20}N_4O_2$ (384.44) | 71.86 (71.73) | 5.24 (5.09) | 14.57 (14.70) |
| **5b** | $C_{23}H_{19}ClN_4O_2$ (418.88) | 65.95 (65.78) | 4.57 (4.55) | 13.38 (13.19) |
| **5c** | $C_{23}H_{19}N_5O_4$ (429.43) | 64.33 (64.08) | 4.46 (4.31) | 16.31 (16.40) |
| **5d** | $C_{24}H_{22}N_4O_2$ (398.46) | 72.34 (72.41) | 5.56 (5.70) | 14.06 (13.85) |
| **5e** | $C_{24}H_{22}N_4O_3$ (414.46) | 69.55 (69.30) | 5.35 (5.34) | 13.52 (13.28) |
| **5f** | $C_{18}H_{18}N_4O_3$ (338.37) | 63.89 (63.73) | 5.36 (5.23) | 16.56 (16.39) |

| | | | | |
|---|---|---|---|---|
| **6a** | $C_{23}H_{18}N_4O$ | 75.39 | 4.95 | 15.29 |
| | (366.42) | (75.24) | (4.94) | (15.25) |
| **6b** | $C_{23}H_{17}ClN_4O$ | 68.91 | 4.27 | 13.98 |
| | (400.87) | (68.84) | (4.34) | (13.97) |
| **6c** | $C_{23}H_{17}N_5O_3$ | 67.15 | 4.17 | 17.02 |
| | (411.42) | (66.95) | (3.95) | (16.89) |
| **6d** | $C_{24}H_{20}N_4O$ | 75.77 | 5.30 | 14.73 |
| | (380.45) | (75.79) | (5.45) | (14.80) |
| **6e** | $C_{24}H_{20}N_4O_2$ | 72.71 | 5.09 | 14.13 |
| | (396.45) | (72.53) | (5.22) | (13.95) |
| **6f** | $C_{18}H_{16}N_4O_2$ | 67.49 | 5.03 | 17.49 |
| | (320.35) | (67.31) | (5.05) | (17.70) |

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