# Extensive degradation of the heterocyclic system in the reaction of 1,2,4-triazolo[5,1-*c*]triazin-7(4*H*)-ones with resorcinol and its derivatives

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**2-R$^1$-1,2,4-triazolo[5,1-*c*]triazin-7(4*H*)-ones react with resorcinols in trifluoroacetic acid yielding 5-R$^2$-6-hydroxy-3-(5′-R$^2$-2′,4′-dihydroxyphenyl)benzo[*b*]furan-2(3*H*)-one. The reaction with resorcinol ether gave 2,2-bis(2′,4′-dimethoxyphenyl)acetic acid.**

It has been established that reactions of 6-nitrotriazolo-[5,1-*c*]triazin-7(4*H*)-ones with N-, S- and O-nucleophiles or hydrogen halides usually lead to substitution of the nitro group with retention of the bicyclic system.[1] However, some O-nucleophiles, such as water and the hydroxyl ion, cause opening of the 1,2,4-triazine ring accompanied by elimination of the C(7)-atom. In particular, the hydrolysis of 6-nitroazolotriazines was found to give triazolylhydrazones of nitroformaldehyde.[2] Also, elimination of the N(5)–C(6)–C(7) fragment and the formation of 5-*N*-alkylaminoazoles have been observed in the reaction of 4-alkyl-6-nitroazolo[5,1-*c*]triazinones with hydrazine.[1]

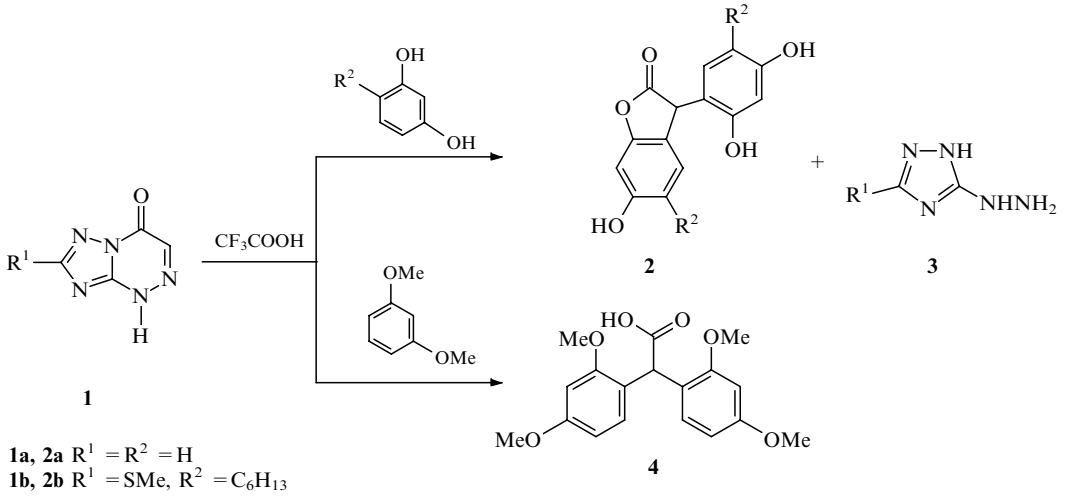
We have studied the reaction of 2-R-1,2,4-triazolo[5,1-*c*]triazin-7(4*H*)-ones **1** with polyphenols and have found that an unexpected ring-opening of the 1,2,4-triazine system occurred. In the course of the reaction of **1** with resorcinol or its derivatives in trifluoroacetic acid the heterocyclic system loses two atoms, yielding the 5-R$^2$-6-hydroxy-3-(5′-R$^2$-2′,4′-dihydroxyphenyl)benzo[*b*]furan-2(3*H*)-ones **2**. The second product of this reaction is 5-R$^1$-3-hydrazinotriazole **3**.

In contrast to the adduct formation in the reaction of 3-aryl-1,2,4-triazin-5(2*H*)-ones with phenols,[3] the mono-addition of resorcinol to 1,2,4-triazolo[5,1-*c*]triazin-7(4*H*)-ones **1** has not been observed.

4-*n*-Hexylresorcinol was found to react in a similar manner to resorcinol, thus indicating that the presence of a long alkyl group does not result in steric hindrance in this reaction.

Interaction of the triazinones **1** with 1,3-dimethoxybenzene under the same conditions gave 2,2-bis(2′,4′-dimethoxyphenyl)acetic acid **4**. $^1$H NMR spectral data† for the compounds **2** and **4** confirm their structures, also the lactone **2a** was found to be identical to one obtained by straightforward synthesis from resorcinol and glyoxylic acid.[4]

These results allow one to suggest the following reaction mechanism (Schemes 1 and 2). The triazolotriazinone **1** is protonated in trifluoroacetic acid at the N(5)-position, yielding cation **5**. In this form triazolotriazine becomes very susceptible to nucleophilic attack. At the same time, the adduct **6** formed can also be protonated. The aliphatic atom N(5) in the intermediate **6** is more basic than it is in **5**. Therefore, the formation of the addition product **8** proceeds faster than the formation of the adduct **6**. This can explain the absence of 6-(resorcyl-6′)-5,6-dihydro-1,2,4-triazolo[5,1-*c*]triazin-7(4*H*)-one **6** in the reaction mixture.




**1a, 2a** R$^1$ = R$^2$ = H
**1b, 2b** R$^1$ = SMe, R$^2$ = $C_6H_{13}$

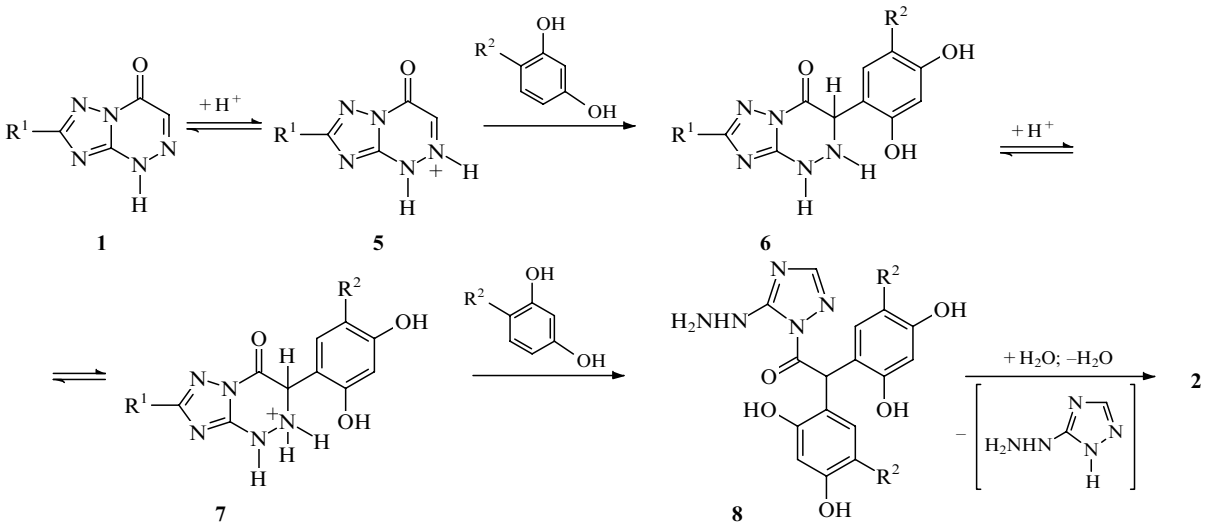
**Scheme 1**

† *General experimental procedure*. 5 mmol of 2-R-1,2,4-triazolo[5,1-*c*]triazin-7(4*H*)-ones and 10 mmol of polyphenol or its ether were dissolved in 5 ml of trifluoroacetic acid and the reaction mixture was kept overnight at room temperature. The solvent was then evaporated *in vacuo* and the residue was recrystallized from ethanol.
The 5-R$^1$-hydrazino-1,2,4-triazole **3** was identified as the hydrazine of *ortho*-nitrobenzaldehyde by TLS.
All new compounds **2a–c** and **4** gave satisfactory analytical and spectral data.

*Compound* **2a**: mp 280 °C; $^1$H NMR (300 MHz, [$^2H_6$]DMSO) $\delta$ 4.9 [s, 1H,H(3)], 6.2–7.0 (m, 6H, aromatic protons), 9.3 (s, 1H, OH), 9.5 (s, 1H, OH), 9.7 (s, 1H, OH); *m*/*z* (%) 258 (100) [M$^+$].

**2b**: mp 121–122 °C; $^1$H NMR (80 MHz, [$^2H_6$]DMSO) $\delta$ 1.10–1.70 (m, 26H, 2$C_6H_{13}$), 2.55 (s, 3H, $SCH_3$), 4.95 [s, 1H, H(3)], 6.00–7.00 (m, 4H, aromatic protons), 9.30 (s, 1H, OH), 9.45 (s, 1H, OH), 9.70 (s, 1H, OH).

**4**: mp 147 °C; $^1$H NMR (300 MHz, [$^2H_6$]DMSO) $\delta$ 3.79 (s, 12H, 4 $OCH_3$), 4.85 (s, 1H, OH), 5.46 [s, 1H, H(2)], 6.42 [dd, 2H, $^3J$ = 8.4 Hz, $^4J$ = 2.4 Hz, H(5′)], 6.48 [d, 2H, $^4J$ = 2.4 Hz, H(4′)], 6.97 [d, 2H, $^3J$ = 8.4 Hz, 2 H(6′)].



**Scheme 2**

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