# Reactions of 1,2,4-Triazin-5(2*H*)-ones with Phenols and Aromatic Amines



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1,2,4-Triazin-5(2*H*)-ones **1** react as well with phenols, resorinol and its dimethyl ethers, as with dimethyland diethylaniline, yielding 6-aryl-1,6-didydro-1,2,4-triazin-5(2*H*)-ones **2**, **4-8**, **12-15**. Oxidation of the 1,6-dihydroadducts **2a,b** gives the corresponding 3-aryl-6-hydroxyphenyl-1,2,4-triazin-5(2*H*)-ones **3a,b**. Rection of 1,2,4-triazinones **1** with 2-naphthylamine leads to destruction of the 1,2,4-triazine ring yielding benzo[*e*]indole-2,3-dione **19**.

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Recently we have shown that reaction of 1,2,4-triazin-5(2*H*)-ones **1** with electron-rich heterocycles, such as indoles, *N*-methylpyrrole, and aminothiazole in acetic anhydride gives in good yields the $C_6$-adducts, accompanied by acylation of the 1,2,4-triazine ring [1]. It has also been established that nonacylated adducts are formed in the reaction of 1,2,4-triazinones with indole in a mixture of trifluoroacetic acid and chloroform or in pure acetic acid.

In order to explore the scope of this reaction and it's selectivity we have studied the reaction of 3-aryl-1,2,4-triazine-5(2*H*)-ones with aromatic *C*-nucleophiles, such as phenols, their ethers and aromatic amines. One can expect interesting biological activities of the compounds produced.

Reactions with Phenols.

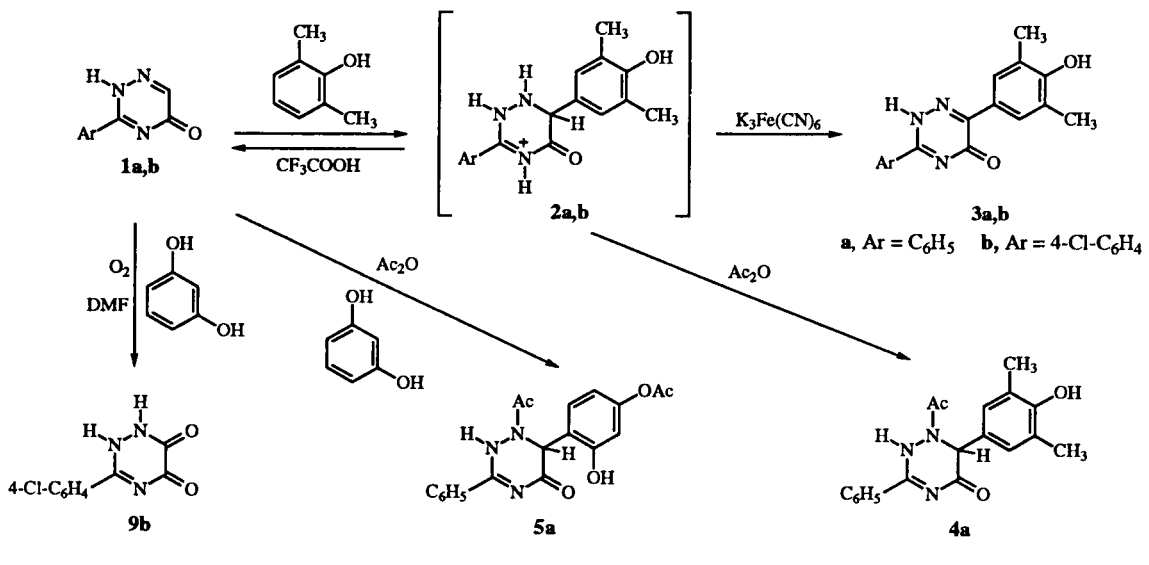
When studying the reactivity of 3-aryl-1,2,4-triazin-5(2*H*)-ones **1a-c** towards phenols we found that in spite of the electron-deficient character of 1,2,4-triazines they react with phenols only after activation of the 1,2,4-triazine ring by protonation.

Dissolving 3-aryl-1,2,4-triazin-5(2*H*)-ones **1a,b** in trifluoroacetic acid gives the $N^1$-protonation products. Reaction of the latter with 2,6-dimethylphenol leads to the adducts **2a,b** (Scheme 1). These adducts are stable only under strong acidic conditions and can be characterized by $^1$H-nmr spectroscopy. Attempts to isolate these compounds failed, due to their easy decomposition into the starting materials.

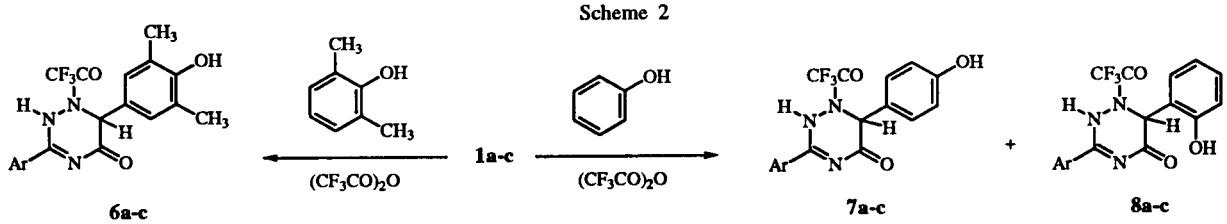
However, introduction of phenolic residues into the 1,2,4-triazines **1** is possible, when the adducts **2a,b** are oxidized in the reaction solution by potassium ferricyanide. The isolated 3-aryl-6-hydroxyphenyl-1,2,4-triazines **3a,b** are the products of nucleophilic aromatic substitution of hydrogen in **1**.

We observed that acylation of the adducts **2** increases their stability. When the adduct **2a** obtained from 1,2,4-

Scheme 1



Scheme 2



a, Ar = $C_6H_5$, b, Ar = 4-Cl-$C_6H_4$, c, Ar = 4-$CH_3$-$C_6H_4$

triazinone **1a** and 2,6-dimethylphenol in trifluoroacetic acid was treated with acetic anhydride the 1-acetyl-3-phenyl-6-(3,5-dimethyl-4-hydroxyphenyl)-1,2,4-triazin-5(2*H*)-one **4a** was isolated from the reaction mixture.

Acetic anhydride can be used not only as a stabilizing agent for the adducts, but also as activating agent and a solvent for these reactions. Thus, reaction of resorcinol with 3-phenyl-1,2,4-triazin-5(2*H*)-one **1a** in acetic anhydride results in the formation of **5a** in nearly quantitative yield.

Table 1

Yields and Ratio of *para*- and *ortho*-Isomers in the Addition of Phenol and Anisole to 3-Aryl-1,2,4-triazine-5(2*H*)-ones **1a-c**

| Compound | Yield, % | Ratio of isomers |
|---|---|---|
| **7a, 8a** | 98 | 19: 1 |
| **7b, 8b** | 99 | 14: 1 |
| **7c, 8c** | 97 | 15: 1 |
| **12a, 13a** | 99 | 2,5: 1 |
| **12b, 13b** | 99 | 3,0: 1 |
| **12c, 13c** | 98 | 3,4: 1 |

The less nucleophilic phenol and 2,6-dimethylphenol do not react with 1,2,4 triazinones **1** under the same reaction conditions. The addition products could not be detected by tlc or spectroscopic methods even after 2 weeks, and only acylated 1,2,4-triazinones were isolated from the reaction mixture. Use of trifluoroacetic anhydride gave better results; the products **6a-c**, **7a-c**, **8a-c** of nucleophilic addition of 2,6-dimethylphenol and phenol to the 1,2,4-triazinones **1a-c** were obtained in very high yields (Scheme 2). It should be noted that the reaction of phenol with 1,2,4-triazinones **1** gave a mixture of *ortho*- **8** end *para*-isomers **7** (Table 1).

Without acids or their anhydrides the reaction proceeds by a different way; refluxing of 3-(4-chlorphenyl)-1,2,4-triazin-5(2*H*)-one (**1b**) with resorcinol in DMF leads to the formation of 3-(4-chlorophenyl)-1,2,4-triazine-5,6(1*H*,2*H*)-dione **9b** in 81% yield (Scheme 1).

Reactions with Phenol Ethers.

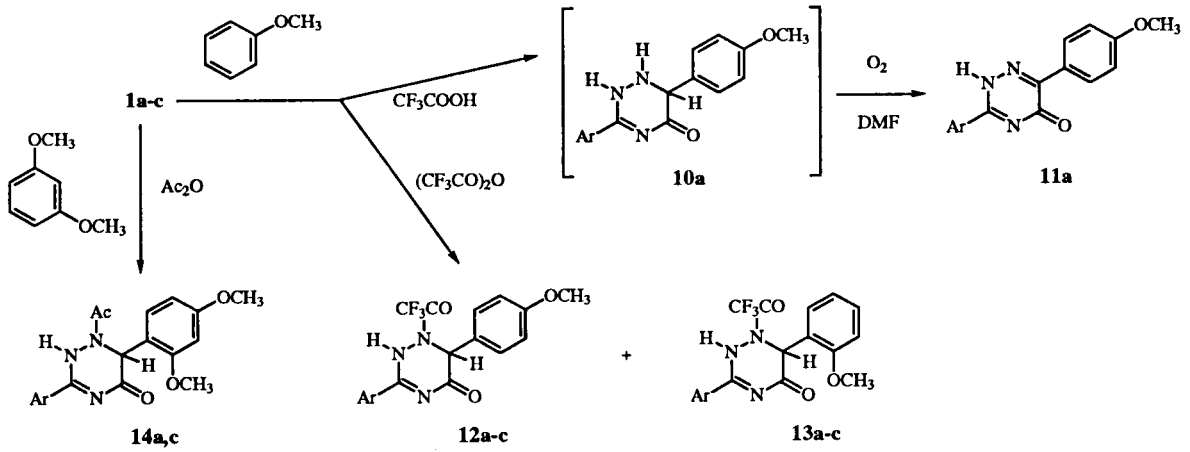
Phenol ethers react with 1,2,4-triazinones **1** in a similar way (Scheme 3). Refluxing 3-phenyl-1,2,4-triazin-5(2*H*)-one **1a** with anisol in trifluoroacetic acid for a long time gives the adduct **10a**, which is oxidized by air to 3-phenyl-6-(4-methoxyphenyl)-1,2,4-triazin-5(2*H*)-one **11a**.

Using acetic anhydride in the reaction of **1a,c** with resocinol dimethyl ether leads to the isolation of the *N*-acyl adducts **14a,c.** Reaction of **1a-c** with anisol in trifluoroacetic anhydride afforded a mixture of *ortho*- **13a-c** and*para*-isomers **12a-c.** The ratio of the *para*-isomers 1-trifluoroacetyl-3-aryl-6-(4-methoxyphenyl)-1,2,4-triazin-5(2*H*)-ones **12a-c** to the *ortho*-isomers **13a-c** is 10:4 to 17:5 (see Table 1), while the *para*-isomer **7** in the adduct with phenol is dominant (95%).

Reactions with Aromatic Amines.

Dimethylaniline, unlike phenols, does not react with 1,2,4-triazinones **1a,c** in trifluoroacetic acid. Use of the weaker acetic acid leads to the formation of 3-aryl-6-(4-

Scheme 3



a, Ar = $C_6H_5$, b, Ar = 4-Cl-$C_6H_4$, c, Ar = 4-$CH_3$-$C_6H_4$

dimethylaminophenyl)-1,6-dihydro-1,2,4-triazin-5(2*H*)-ones **15a-c** (Scheme 4). Compounds **15a-c** can be considered as intermediates in the nucleophilic substitution of hydrogen in 1,2,4-triazin-5(2*H*)-ones. Indeed, aromatization of the adduct **15a**, occuring either spontaneously or by bubbling air through its solution in DMF, affords 3-phenyl-6-(4-dimethylaminophenyl)-1,2,4-triazin-5(2*H*)-one **16a**.

Reaction of 1,2,4-triazinones **1a-c** with *N,N*-dialkylanilines in acetic anhydride proceeds similar to the reaction of **1** with resorcinol, yielding the stable 1-acetyl-1,6-dihydro-compounds **17a-c, 18b**.

Aniline and *N*-methylaniline do not react with compounds **1** under the conditions mentioned above. Reaction of 1,2,4-triazinones **1a,b** with 2-naphthylamine in acetic acid leads to the destruction of the 1,2,4-triazine ring: reaction of equimolar amounts of **1a,b** and 2-naphthylamine led to the isolation of benzo[*e*]indole-2,3-dione **19**, while **1a** and two moles of 2-naphthylamine gave 3-(2-naphthylamino)-benzo[*e*]indol-2-one **20** (Scheme 5).

Table 2

Yields, Melting Points and Analytical Data of 3-Ar-6-Ar'-1,2,4-triazin-5(2*H*)-ones **3, 11, 16** and 3-Ar-6-Ar'-1,6-dihydro-1,2,4-triazin-5(2*H*)-ones **4-8, 12-15. 17, 18**

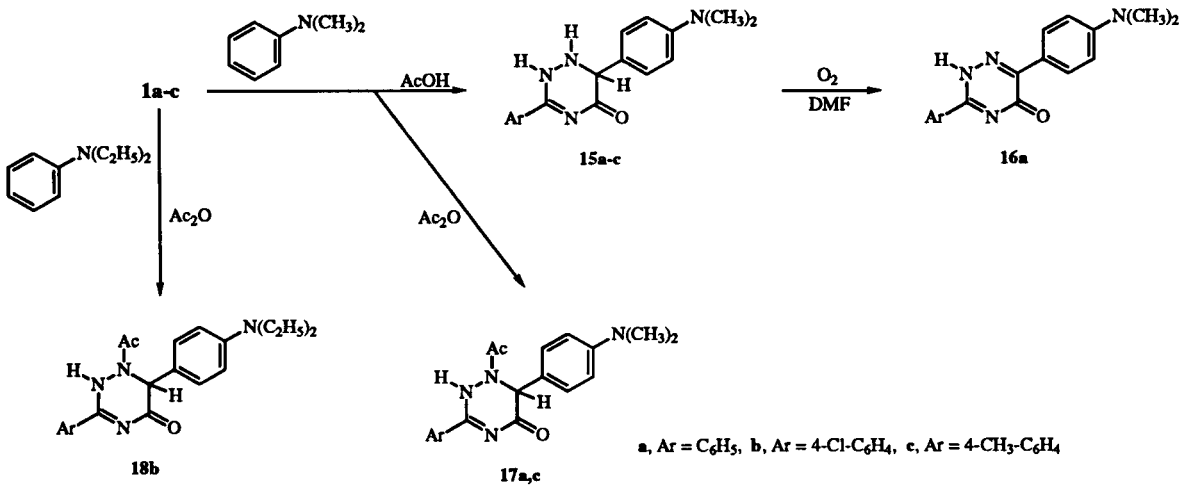
| Compound | Yield, % | mp, °C | Formula (Mol. mass) | Analysis Calcd. Found | C | H | N |
|---|---|---|---|---|---|---|---|
| 1 | 2 | 3 | 4 | 5 | 6 | | 7 |
| **3a** | 61 | 252-253 | $C_{17}H_{15}N_3O_2$ | Calcd. | 69.61 | 5.15 | 14.33 |
| | | | (293.3) | Found | 69.90 | 5.27 | 14.60 |
| **3b** | 84 | 302-304 | $C_{17}H_{14}N_3O_2Cl$ | Calcd. | 62.29 | 4.31 | 12.82 |
| | | | (327.7) | Found | 62.23 | 4.10 | 12.82 |
| **4a** | 45 | 260-263 | $C_{19}H_{19}N_3O_3$ | Calcd. | 67.64 | 5.67 | 12.45 |
| | | | (335.3) | Found | 67.78 | 5.40 | 12.50 |
| **5a** | 81 | 215-217 | $C_{19}H_{17}N_3O_5$ | Calcd. | 62.12 | 4.67 | 11.44 |
| | | | (367.3) | Found | 62.12 | 4.64 | 11.47 |
| **6a** | 98 | 258-259 | $C_{19}H_{16}N_3O_3F_3$ | Calcd. | 58.31 | 4.12 | 10.74 |
| | | | (367.3) | Found | 58.55 | 4.02 | 10.68 |
| **6b** | 99 | 251-253 | $C_{19}H_{15}N_3O_3ClF_3$ | Calcd. | 53.60 | 3.55 | 9.87 |
| | | | (425.8) | Found | 53.65 | 3.44 | 9.59 |
| **6c** | 97 | 253-254 | $C_{20}H_{18}N_3O_3F_3$ | Calcd. | 59.26 | 4.47 | 10.37 |
| | | | (405.4) | Found | 59.34 | 4.11 | 10.39 |
| **7a, 8a** | 98 | | $C_{17}H_{12}N_3O_3F_3$ | Calcd. | 56.20 | 3.33 | 11.57 |
| | | | (365.3) | Found | 56.18 | 3.26 | 11.53 |
| **7b, 8b** | 99 | | $C_{17}H_{11}N_3O_3F_3Cl$ | Calcd. | 51.33 | 2.78 | 10.56 |
| | | | (397.7) | Found | 51.66 | 2.95 | 10.39 |
| **7c, 8c** | 97 | | $C_{18}H_{14}N_3O_3F_3$ | Calcd. | 57.30 | 3.74 | 11.14 |
| | | | (377.3) | Found | 57.60 | 3.52 | 10.97 |
| **11a** | 86 | > 320 | $C_{16}H_{13}N_3O_2$ | Calcd. | 68.81 | 4.69 | 15.05 |
| | | | (279.2) | Found | 68.73 | 4.80 | 14.93 |
| **12a, 13a** | 99 | | $C_{18}H_{14}N_3O_3F_3$ | Calcd. | 57.30 | 3.74 | 11.14 |
| | | | (377.3) | Found | 57.48 | 3.91 | 10.84 |
| **12b, 13b** | 99 | | $C_{18}H_{13}N_3O_3ClF_3$ | Calcd. | 52.51 | 3.18 | 10.21 |
| | | | (411.7) | Found | 52.62 | 3.16 | 10.01 |
| **12c, 13c** | 98 | | $C_{19}H_{16}N_3O_3F_3$ | Calcd. | 58.31 | 4.12 | 10.74 |
| | | | (391.3) | Found | 58.35 | 4.37 | 10.53 |
| **14a** | 62 | 156-158 | $C_{19}H_{19}N_3O_4$ | Calcd. | 64.58 | 5.41 | 11.89 |
| | | | (353.4) | Found | 64.43 | 5.44 | 11.61 |
| **14c** | 50 | 168-170 | $C_{20}H_{21}N_3O_4$ | Calcd. | 65.38 | 5.76 | 11.44 |
| | | | (367.4) | Found | 65.36 | 5.88 | 11.10 |
| **15a** | 52 | 209-210 | $C_{17}H_{18}N_4O$ | Calcd. | 69.37 | 6.16 | 19.04 |
| | | | (294.3) | Found | 69.30 | 6.21 | 19.29 |
| **15b** | 40 | 274-276 | $C_{17}H_{17}N_4OCl$ | Calcd. | 62.10 | 5.21 | 17.04 |
| | | | (328.8) | Found | 62.03 | 4.95 | 17.33 |
| **15c** | 53 | 262-263 | $C_{18}H_{20}N_4O$ | Calcd. | 70.11 | 6.53 | 18.17 |
| | | | (308.4) | Found | 70.08 | 6.67 | 18.05 |
| **16a** | 52 | 315-317 | $C_{17}H_{16}N_4O$ | Calcd. | 69.84 | 5.51 | 19.17 |
| | | | (292.3) | Found | 69.88 | 5.52 | 19.16 |
| **17a** | 88 | 203 -205 | $C_{19}H_{20}N_4O_2$ | Calcd. | 67.84 | 5.99 | 16.66 |
| | | | (336.4) | Found | 67.95 | 6.03 | 16.44 |
| **17c** | 90 | 224-225 | $C_{20}H_{22}N_4O_2$ | Calcd. | 68.55 | 6.32 | 15.99 |
| | | | (350 4) | Found | 68.69 | 6.29 | 16.00 |
| **18b** | 89 | 245-247 | $C_{21}H_{23}N_4O_2Cl$ | Calcd. | 63.23 | 5.81 | 14.05 |
| | | | (398 9) | Found | 63.12 | 5.81 | 13.96 |

Table 3

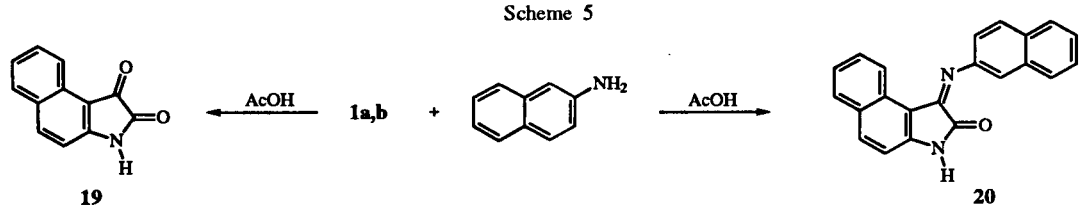
300 MHz (*100 MHz)- $^1$H-NMR Data of 3-Ar-6-Ar$^1$-1,2,4-triazin-5(2*H*)-ones **3**, **11**, **16** and 3-Ar-6Ar$^1$-1,6-Dihydro-1,2,4-triazin-5(2*H*)-ones **4-8**, **12-15**, **17**, **18**

| Compound 1 | Ar 2 | Ar$^1$ 3 | 6-H 4 | N$^1$H(Ac) 5 | N$^2$H 6 |
|---|---|---|---|---|---|
| **3a*** | 7.59-7.69 (m, 3H), 8.08-8.13 (m, 2H) | 2.23 (s, 6H), 7.68(s, 2H), 8.80 (s, 1H) | | | 14.17 (b s, 1H) |
| **3b*** | 7.68 (d, J = 8.5 Hz, 2H), 8.68 (d, J = 8.5 Hz, 2H) | 2.23 (s, 6H), 7.68 (s, 2H), 8.78 (s, 1H) | | | 14.10 (b s, 1H) |
| **11a** | 7.59-7.68 (m, 3H), 8.09-8.12 (m, 2H) | 3.00 (m, 3H), 6.77 (d, J = 9.1 Hz, 2H), 8.21 (d, J = 9.1 Hz, 2H) | | | 14.10 (b s, 1H) |
| **16a** | 7.59-7.68 (m, 3H), 8.10-8.13 (m, 2H) | 3.83 (m, 6H), 7.06 (d, J = 9.0 Hz, 2H), 8.23 (d, J = 9.0 Hz, 2H) | | | 14.10 (b s, 1H) |
| **4a** | 7.44-7.48 (m, 3H), 7.84-7.94 (m, 2H) | 2.23 (s, 6H), 6.86 (s, 2H), 8.38 (b s, 1H) | 5.90 (s, 1H) | 2.36 (s, 3H) | 11.50 (b s, 1H) |
| **5a** | 7.48-7.55 (m, 3H), 7.88-7.97 (m, 2H) | 2.28 (s, 3H), 6.94-7.04 (m, 3H), 9.89 (b s, 1H) | 6.06 (s, 1H) | 2.17 (s, 3H) | 11.55 (b s, 1H) |
| **6a** | 7.51-7.59 (m, 3H), 7.84-7.94 (m, 2H) | 2.11 (s, 6H), 6.83 (s, 2H), 8.80 (b s, 1H) | 5.78 (s, 1H) | — | 11.83 (b s, 1H) |
| **6b** | 7.61 (d, J = 8.7 Hz, 2H), 7.97 (d, J = 8.7 Hz, 2H) | 2.11 (s, 6H), 6.82 (s, 2H), 8.80 (b s, 1H) | 5.77 (s, 1H) | — | 11.88 (b s, 1H) |
| **6c** | 2.36 (s, 3H), 7.29-7.94 (m, 4H) | 2.12 (s, 6H), 6.82 (s, 2H), 8.80 (b s, 1H) | 5.77 (s, 1H) | — | 11.88 (b s, 1H) |
| **7a, 8a** | 7.49-7.60 (m, 3H), 7.81-7.95 (m, 2H) | 6.72-7.28 (m, 4H), 9.89 (b s, 1H) | 5.85 (s, 0.95H), 5.95 (s, 0.05H) | —<br>— | 11.50 (b s, 1H) |
| **7b, 8b** | 7.63 (d, J = 8.7 Hz, 2H), 7.91 (d, J = 8.7 Hz, 2H) | 6.44-6.55 (m, 2H), 6.69-7.04 (m, 2H), 9.96 (b s, 1H) | 5.84 (s, 0.93H), 5.93 (s, 0.07H) | —<br>— | 11.72 (b s, 1H) |
| **7c, 8c** | 2.35 (s, 3H), 7.34 (d, J = 8.0 Hz, 2H), 7.81 (d, J = 8.0 Hz, 2H) | 6.73-7.22 (m, 4H), 9.92 (b s, 1H) | 5.84 (s, 0.80H), 5.95 (s, 0.20H) | —<br>— | 11.85 (b s, 1H) |
| **12a, 13a** | 7.48-7.55 (m, 3H), 7.88-7.97 (m, 2H) | 3.66 (s, 2H), 3.72 (s, 1H), 6.88-7.57 (m, 4H) | 5.95 (s, 0.65H), 5.98 (s, 0.35H) | | 11.80 (b s, 1H) |
| **12b, 13b** | 7.64 (d, J = 8.7 Hz, 2H), 7.91 (d, J = 8.7 Hz, 2H) | 3.68 (s, 2.25H), 3.75 (s, 0.75H), 6.86-7.46 (m, 4H) | 5.92 (s, 0.75H), 5.99 (s, 0.25H) | | 11.80 (b s, 1H) |
| **12c, 13c** | 2.38 (s, 3H), 7.40 (d, J = 8.0 Hz, 2H), 7.81 (d, J = 8.0 Hz, 2H) | 3.68 (s, 2.25H), 3.75 (s, 0.75H), 6.86-7.46 (m, 4H) | 5.88 (s, 0.23H), 5.99 (s, 0.77H) | | 11.70 (b s,1H) |
| **14a** | 7.47-7.54 (m, 3H), 7.87-7.98 (m, 2H) | 3.65 (s, 3H), 3.73 (s, 3H), 6.42-6.51 (m, 2H), 6.99 (m, 1H) | 6.01 (s, 1H) | 2.34 (s, 3H) | 11.32 (b s, 1H) |
| **14c** | 2.24 (s, 3H), 3.64 (s, 3H), 7.76-7.87 (s, 2H) | 3.72 (s, 3H), 6.41-6.51(m, 2H), 7.08-7.35 (m, 3H) | 6.00 (s, 1H) | 2.36 (s, 3H) | 11.26 (b s, 1H) |
| **15a** | 7.38-7.41 (m, 3H), 7.72-7.76 (m, 2H) | 2.87 (s, 6H), 6.69 (d, J = (8.7 Hz, 2H), 7.13 (d, J = (8.7 Hz, 2H) | 4.52 (d, J = 1.2 Hz, 1H) | 7.59 (b s, 1H) | 10.86 (b s, 1H) |
| **15b** | 7.46 (d, J = 8.7 Hz, 2H), 7.74 (d, J = 8.7 Hz, 2H) | 2.86 (s, 6H), 6.68 (d, J = (8.7 Hz, 2H), 7.13 (d, J = (8.7 Hz, 2H) | 4.52 (b s, 1H) | 7.68 (b s, 1H) | 11.50 (b s, 1H) |
| **15c** | 2.32 (s, 3H), 7.21 (d, J = 8.1 Hz, 2H), 7.63 (d, J = 8.1 Hz; 2H) | 2.87 (s, 6H), 6.69 (d, J = (8.7 Hz, 2H), 7.15 (d, J = (8.7 Hz, 2H) | 4.50 (b s, 1H) | 7.50 (b s, 1H) | 11.50 (b s, 1H) |
| **17a** | 7.50-7.53 (m, 3H), 7.84-7.96 (m, 2H) 7.04 (d, J = (8.9 Hz, 2H) | 2.83 (s, 6H), 6.64 (d, J = (8.9 Hz, 2H), | 5.95 (s, 1H) | 2.35 (s, 3H) | 11.57 (b s, 1H) |
| **17c** | 2.35 (s, 3H), 7.27(d, J = 8.0 Hz, 2H), 7.79 (d, J = 8.0 Hz, 2H) | 2.83 (s, 6H), 6.64 (d, J = (8.9 Hz, 2H), 7.03 (d, J = (8.9 Hz, 2H) | 5.90 (s, 1H) | 2.34 (s, 3H) | 11.50 (b s, 1H) |
| **18b** | 7.54 (d, J = 8.7 Hz, 2H), 7.79 (d, J = 8.7 Hz, 2H) | 0.93-1.11 (m, 6H), 3.13-3.97 (m, 4H), 6.56 (d, J = (8.9 Hz, 2H), 6.99 (d, J = (8.9 Hz, 2H) | 5.91(s, 1H) | 2.34 (s, 3H) | 11.57 (b s, 1H) |

Scheme 4




Scheme 5




The spectral data of the products obtained (Table 3) are in agreement with the proposed structures. The following data confirm that the acyl-group in **4a**, **5a**, **6a-c**, **7a-c**, **8a-c**, **12a-c**, **13a-c**, **14a,c**, **17a,c**, **18b** is bound to $N^1$ of the triazine ring: i) In the $^1$H-nmr spectra of the nonacetylated compounds **15a-c** the signal for $H^6$ is observed as broadened singlet or doublet around 4.8 ppm, due to spin-spin coupling with the proton at $N^1$, which gives a signal around 7 ppm; the spin-spin coupling was confirmed by double resonance experiments. ii) In the $^1$H-nmr spectra of the acylated products the signal for $H^6$ is observed as a singlet, and signals in the area of 7-8 ppm could not be detected.

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## EXPERIMENTAL

Melting points are uncorrected: Kofler plate; $^1$H-nmr Tesla BS-597A (100 MHz) or Bruker WM 300 (300 MHz); in DMSO-$d_6$ with TMS as internal standard; ms: Varian MAT-311A; ir (potassium bromide pellets): Perkin-Elmer-IR-spectrometer Model 297.

General Procedure for the Preparation of 3-Aryl-6-(3,5-dimethyl-4-hydroxyphenyl)-1,2,4-triazin-5(2*H*)-ones **3a,b** (Tables 2,3).

To 3-aryl-1,2,4-triazin-5(2*H*) one **1a,b** (0.3 mmole) in trifluoroacetic acid (2 ml) 2,6-dimethylphenol (36.6 mg, 0.3 mmole) was added. After 15 hours stirring at room temperature, potassium ferricyanide (197.5 mg, 0.6 mmole) and water (0.1 ml) were added. The reaction mixture was stirred for 1 hour and the residue was filtered. Addition of water to the filtrate gave an additional amount of product. The product was recrystallized from acetonitrile.

1-Acetyl-3-phenyl-6-(3,5-dimethyl-4-hydroxyphenyl)-1,6-hydro-1,2,4-triazin-5(2*H*)-one (**4a**) (Tables 2,3).

2,6-Dimethylphenol (35 mg, 0.29 mmole) was added to a solution of 3-phenyl-1,2,4-triazin-5(2*H*)-one (**1a**, 50.2 mg, 0.29 mmole) in trifluoroacetic acid (2 ml) and the mixture stirred for 15 hours at room temperature. Acetic anhydride (90 mg, 0.87 mmole) was added, the mixture stirred overnight at room temperature and then evaporated to dryness. The residue was recrystallized from ethanol.

1-Acetyl-3-phenyl-6-(2,4-dihydroxy-phenyl)-1,6-dihydro-1,2,4-triazin-5(2*H*)-one (**5a**) (Tables 2,3).

Resorcinol (49.5 mg, 0.45 mmole) and 3-phenyl-1,2,4-triazin-5(2*H*)-one **1a** (51.9 mg, 0.3 mmole) were dissolved in acetic anhydride (2 ml) by heating. The mixture was stirred for 36 hours at room temperature. The white precipitate was filtered and recrystallized from methanol.

General Procedure for the Preparation of 1-Triflouroacetyl-3-aryl-6-(hydroxyphenyl)-1,6-dihydro-1,2,4-triazin-5(2*H*)-ones, **6a-c**, **7a-c**, **8a-c** (Tables 1,2,3).

The corresponding phenol (0.45 mmole) was added to a solution of 3-aryl-1,2,4-triazin-5(2*H*)-one **1a-c** (0.3 mmole) in trifluoroacetic anhydride (2 ml) and the mixture stirred for 0.5 hours at room temperature. The residue was filtered, the filtrate was evaporated to dryness and the residue washed with ether. The product is recrystallized from methanol. The ratio of *ortho* -**8** end *para*-isorners **7** is shown in Table 1.

3-(4-Chlorophenyl)-1,2,4-triazin-5,6(1*H*, 2*H*)-dione (**9b**).

3-(4-Chlorophenyl)-1,2,4-triazin-5(2*H*)-one **1b** (430 mg, 2.5 mmoles) and resorcinol (330 mg, 3 mmoles) were refluxed in DMF (20 ml) for 8 hours. After cooling the residue was filtered and recrystallized from DMF, yield 450 mg (81%), mp 305-307°; 300 MHz $^1$H-nmr (DMSO-$d_6$): δ = 7.65 (d, J = 8.7 Hz, 2H), 7.84 (d, J = 8.7 Hz, 2H); ms: (70 eV), m/z (%) 223 (76) [M$^+$], 195 (40), [M$^+$-CO], 152 (100) [M$^+$-CO-CONH], 138 (53), 137 (34), 125 (33), 75 (50); ir (potassium bromide): ν = 1720 cm$^{-1}$ (CO).

*Anal.* Calcd. for $C_9H_6N_3O_2Cl$ (223.6): C, 48.34; H, 2.70; N, 18.79. Found: C, 48.21; H, 2.84; N, 18.53.

6-(4-Dimethylaminophenyl)-3-phenyl-1,2,4-triazin-5(2*H*)-one (**11a**) (Tables 2, 3).

3-Phenyl-1,2,4-triazin-5(2*H*)one (**1a**) (173 mg, 1 mmole) and anisol (108 mg, 1 mmole) in trifluoroacetic acid (6 ml) were refluxed for 72 hours. The solvents was evaporated, the residue dissolved in DMF (10 ml) and the solution refluxed for 10 hours with bubbling air through the solution. The solvent was evaporated, the residue stirred with water, filtered and recrystallized from methanol.

General Procedure for the Preparation of 1-Triflouroacetyl-3-aryl-6-(methoxy-phenyl)-1,6-dihydro-1,2,4-triazin-5(2*H*)-ones **12a-c, 13a-c** (Tables 1, 2, 3).

Anisole (62.6 mg, 0.58 mmole) was added to a solution of 3-aryl-1,2,4-triazin-5(2*H*)-one **1a-c** (0.3 mmole) in trifluoroacetic anhydride (2 ml) and the mixture stirred for 0.5 hours at room temperature. The solvent was evaporated, the residue dissolved in dry benzene and the solution was evaporated again. The residue was washed with ether and recrystallized from methanol. The yield of the two isomers **12** and **13** is quantitative.

General Procedure for the Preparation of 1-Acetyl-3-aryl-6-(2,4-dimethoxyphenyl)-1,6-dihydro- 1,2,4-triazin-5(2*H*)-ones **14a,c** (Tables 2,3).

To a solution of 3-aryl-1,2,4-triazin-5(2*H*)-one **1a,c** (0.50 mmole) in trifluoroacetic anhydride (2 ml) resorcinol dimethyl ether (80 mg, 0.58 mmole) was added and the mixture was stirred for 0.5 hours at room temperature. The solvent was evaporated, the residue dissolved in dry benzene and the solution was evaporated again. The residue was washed with ether and recrystallized from methanol.

General Procedure for the Preparation of 3-Aryl-6-(2,4-dimethylaminophenyl)-1,6-dihydro-1,2,4-triazin-5(2*H*)-ones **15a,c** (Tables 2,3).

3-Aryl-1,2,4-triazin-5(2*H*)-one **1a,c** (5 mmoles) and dimethylaniline (1.21 g, 10 mmoles) were refluxed in acetic acid (6 ml) for 2 hours. The solvent was evaporated, the residue washed with ether and recrystallized from methanol.

3-Phenyl-(4-dimethylaminophenyl)-1,2,4-triazin-5(2*H*)-one (**16a**) (Tables 2,3).

3-Phenyl-6-(dimethylaminophenyl)-1,6-dihydro-12,4-triazin-5(2*H*)-one (**15a**, 300 mg, 1 mmole) was refluxed in DMF (5 ml) for 8 hours with bubbling air through the solution. The solvent was evaporated, the residue stirred with water, filtered and recrystallized from methanol.

General Procedure for the Preparation of 1-Acetyl-3-aryl-6-(4-dialkylaminophenyl)-1,6-dihydro-1,2,4-triazin-5(2*H*)-ones **17a,c, 18b** (Tables 2,3).

*N,N*-Diallcylaniline (0.30 mmole) and 3-aryl-1,2,4-triazin-5(2*H*)-one **1a-c** (0.3 mmole) were dissolved by heating in acetic anhydride (2 ml). The mixture was stirred for 4 hours at room temperature. The white precipitate was filtered off and recrystallized from acetonitrile.

Benz[*e*]indole-2,3-dione **19**.

3-Phenyl-1,2,4-triazin-5(2*H*)-one (**1a**, 432.5 mg, 2.5 mmoles) or 3-(4-chlorophenyl)-1,2,4-triazin-5(2*H*)one (**1b**, 543.8 mg, 2.5 mmoles) and 2-naphthylamine (715 mg, 2.5 mmoles) were refluxed in acetic acid (7 ml) for 2 hours. The residue was filtered and recrystallized from ethanol, yield 350 mg (71%) **19** (from **1a**) or 400 mg (81%) (from **1b**); mp 250-251°; 60 MHz $^1$H-nmr (DMSO-$d_6$): δ = 7.10-8.50 (m, 12H), 10.90 (b s, 1H); ms: (70 eV) m/z (%) = 197 (98) [M$^+$], 169 (100) [M$^+$-CO], 142 (21), 141 (45) [M$^+$-CO-CO], 140 (30), 114 (51), 112 (19), 71 (18); ir (potassium bromide): ν = 1760, 1710 cm$^{-1}$ (CO).

*Anal.* Calcd. for $C_{12}H_7NO_2$ (197.2): C, 73.09; H, 3.57; N, 7.10. Found: C, 72.92; H, 3.54; N, 7.33.

3-(2-Naphthylamino)-benzo[*e*]indol-2-one **20**.

3-Phenyl-1,2,4-triazin-5(2*H*)-one (**1a**, 865 mg, 5 mmoles) and 2-naphthylamine (1.43 g, 10 mmoles) were refluxed in acetic acid (7 ml) for 1 hour. The residue was filtered off and recrystallized from DMF, yield 800 mg (51%), mp 264-265°; 60-MHz-$^1$H-nmr (DMSO-$d_6$): δ = 7.00-8.50 (m, 12H); 10.80 (b s, 1H); ms: (70 eV) m/z (%) 322 (78) [M$^+$], 295 (95), 294 (100) [M$^+$-CO], 293 (43), 127 (37); ir (potassium bromide): $\nu_{CO}$ = 1720 cm$^{-1}$.

*Anal.* Calcd. for $C_{22}H_{14}N_2O$ (322.4): C, 81.97; H, 4.37; N, 8.69. Found: C, 81.73; H, 4.36; N, 8.78.

## REFERENCES AND NOTES

[1] V. L. Rusinov, G. V. Zyryanov, T. L. Pilicheva, O. N. Chupalchin, and H. Neunhoeffer, *J. Heterocyclic Chem.*, in press.