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# CHARACTERISTIC FEATURES OF CONVERSIONS OF 3,6-SUBSTITUTED 1,2,4-TRIAZINE-4-OXIDES WITH 1,3-DIMETHYLBARBITURIC ACID

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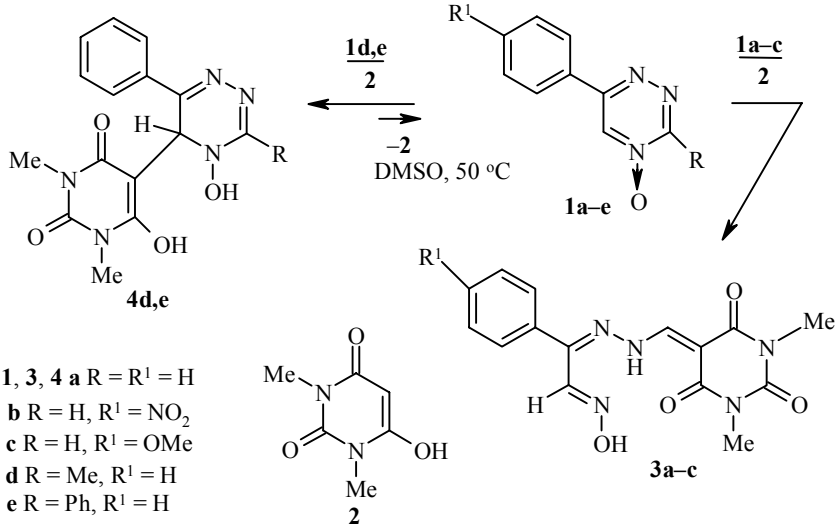
When 3,6-diphenyl-1,2,4-triazine-4-oxide was heated with indoles in butanol in the presence of trifluoroacetic acid, 5-indolyl-substituted 3,6-diphenyl-1,2,4-triazines were obtained [1]. 6-Phenyl-1,2,4-triazine-4-oxide reacts with CH acids in the presence of base with opening of the triazine ring at the C(3)–N(4) bond and formation of the corresponding enhydrazino derivatives [2].

In this work, we observed that when 6-phenyl-1,2,4-triazine-4-oxides **1a-c** are heated in butanol with 1,3-dimethylbarbituric acid **2** without addition of catalysts for 3 h, the enhydrazino derivatives **3a-c** are formed. The latter exist in dimethylsulfoxide in the form of acyclic enhydrazines, which obviously are stabilized by formation of pseudopolycyclic systems with participation of hydrogen bonds (in the $^1$H NMR spectra of solutions of compounds **3** in DMSO-$d_6$, we observe doublets from protons of adjacent methine CH and NH groups, typical for such enhydrazines [3, 4]).

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In contrast, when 3,6-disubstituted 1,2,4-triazine-4-oxides **1d,e** are heated even briefly (for 15-20 min) with 1,3-dimethylbarbituric acid **2** in butanol, from the hot solution of the reaction mass we isolate colorless high-melting crystalline compounds **4d,e**. It is interesting that with the help of $^1$H NMR spectroscopy, we can observe over time the complete conversion of a mixture of equimolar amounts of compounds **1d** (or **1e**) and **2**, at room temperature in dimethylsulfoxide, to adduct **4**. At the same time, at 50°C, along with signals from adduct **4d**, signals from the starting components **1** and **2** appear again in the spectrum.

Usually reactions of 1,2,4-triazine-4-oxides with C-nucleophiles occur smoothly with reagents that have been activated by acquiring a charge, while the conversions with 1,3-dimethylbarbituric acid that we observed occur on reaction of neutral reagents. The σ complexes obtained are of interest for further study as possible intermediates in a nucleophilic substitution reactions or other transformations in the 1,2,4-triazine series.

**1-(α)-Hydroximinobenzhydrazonylmethylene)-3,5-dimethylhexahydropyrimidine-2,4,6-trione (3a).** Yield 35-40%; mp 239-240°C. $^1$H NMR spectrum (DMSO-$d_6$), δ, ppm: 3.20 (6H, s, 2×$NCH_3$); 7.30-7.50 (3H, m, CH arom.); 7.70-7.90, 2H, m, CH arom.); 8.40 (1H, s, CH); 8.49 (1H, d, CH); 12.77 (1H, br. s, OH), 14.20 (1H, d, NH). Found, %: C 54.3; H 4.8; N 21.0. $C_{15}H_{15}N_5O_4$. Calculated, %: C 54.7; H 4.6; N 21.3.

**1-(α-Hydroximino-*p*-nitrobenzhydrazonylmethylene)-3,5-dimethylhexahydropyrimidine-2,4,6-trione (3b).** Yield 20-25%; mp 249-250°C. $^1$H NMR spectrum (DMSO-$d_6$), δ, ppm: 3.22 (3H, s, $NCH_3$); 3.25 (3H, s, $NCH_3$); 8.10 (2H, d, CH arom.); 8.25 (2H, d, CH arom.); 8.47 (1H, s, CH); 8.55 (1H, d, CH); 12.81 (1H, s, NOH); 14.25 (1H, d, NH). Found, %: C 48.0, H 4.0, N 22.2. $C_{15}H_{14}N_6O_6$. Calculated, %: C 48.1; H 3.8; N 22.4.

**1-( α-Hydroximino-*p*-methoxybenzhydrazonylmethylene)-1,3-dimethylhexahydropyrimidine-2,4,6-trione (3c).** Yield 65-70%; mp 231-232°C. $^1$H NMR spectrum (DMSO-$d_6$), δ, ppm: 3.10 (3H, s, $NCH_3$); 3.12 (3H, s, $NCH_3$); 3.82 (3H, s, $OCH_3$); 6.98 (2H, d, CH arom.); 7.75 (2H, d, CH arom.); 8.36 (1H, s, CH); 8.49 (1H, d, CH); 12.65 (1H, s, NOH); 14.00 (1H, d, NH). Found, %: C 53.2; H 5.0; N 19.3. $C_{16}H_{17}N_5O_5$. Calculated, %: C 53.5; H 4.8; N 19.5.

**4-Hydroxy-5-(6-hydroxy-1,3-dimethyl-2,4-dioxohexahydropyrimidin-5-yl)-3-methyl-6-phenyl-4,5-dihydro-1,2,4-triazine (4d).** Yield 90-95%; mp > 250°C. $^1$H NMR spectrum (DMSO-$d_6$), δ, ppm: (at 20°) 2.25 (3H, s, $CCH_3$); 3.05 (6H, s, 2×$NCH_3$); 6.19 (1H, s, 5-H); 7.35-7.50 (3H, m, CH arom.); 7.87 (2H, m, CH arom.); 11.57 (1H, s, OH); 12.41 (1H, s, OH); (at 50°); 2.27 (3H, s, $CCH_3$); 2.54* (signals from compound **2**) (3H, s, $NCH_3$); 2.68* (3H, s, $NCH_3$); 3.00*[2] (signals from compound **1a**) (3H, s, $CH_3$); 3.04 (6H, s, 2×$NCH_3$); 3.70* (2H, br. s, $CH_2$); 6.20 (1H, s, CH); 7.35-7.48 (3H, m, CH arom.); 7.55-7.65*[2] (3H, m, CH arom.); 7.85-7.95 (2H, m, CH arom.); 8.15-8.25*[2] (2H, m, CH arom.); 9.23*[2] (1H, s, CH); 11.50 (1H, br. s, OH); 12.35 (1H, s, OH). Found, %: C 54.2; H 5.2; N 21.0. $C_{16}H_{17}N_5O_4$. Calculated, %: C 54.4; H 5.2; N 21.1.

**4-Hydroxy-5-(6-hydroxy-1,3-dimethyl-2,4-dioxohexahydropyrimidin-5-yl)-3,6-diphenyl-4,5-dihydro-1,2,4-triazine (4e).** Yield 45-50%; mp 215-216°C. Found, %: C 61.9; H 4.8; N 17.0. $C_{21}H_{19}N_5O_4$. Calculated, %: C 62.2; H 4.7; N 17.3.

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