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OXIDATIVE CYCLIZATION OF ARYLSULFONYL HYDRAZIDES OF 2,4-DIOXOBUTANOIC ACID TO 3,4-DIHYDRO-3,4-PYRIDAZINEDIONE

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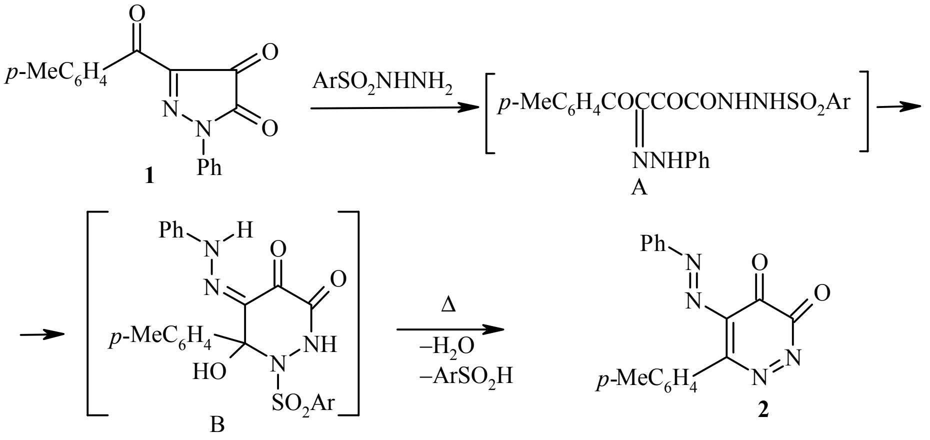
1-Phenyl-3-*p*-toluoyl-4,5-dihydro-4,5-pyrazoledione (**1**) reacts with tosyl hydrazide or *p*-chlorophenylsulfonyl hydrazide in dioxane at room temperature to form a mixture of arylsulfonyl hydrazides of 2,4-dioxo-3-phenyl-4-*p*-tolylhydrazonobutanoic acid (**A**) and their ring isomers (**B**), attempts to recrystallize which from ethanol result in their oxidation to 5-phenylazo-6-*p*-tolyl-3,4-dihydro-3,4-pyridazinedione (**2**).



Ar = p-MeC_6H_4, p-ClC_6H_4

Probably in the first step of the reaction, the arylsulfonyl hydrazides, like arylamines [1] and hydrazine [2], open the ring of the pyrazoledione **1** at the $N_{(1)}$–$C_{(5)}$ bond, and the arylsulfonyl hydrazides **A** formed, as in the case of unsubstituted hydrazides [2], convert to the corresponding ring forms **B**. The latter, even when heated only slightly, undergo thermolytic breaking of the N–S bond, accompanied by reduction of the SO_2 group, by cleavage of the arylsulfinic acids and oxidation of the hydrazino moiety of the heterocycle to an azo moiety. Such thermal oxidation–reduction cleavage has been previously observed for noncyclic arylsulfonyl

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hydrazides, and has been accompanied by liberation of a nitrogen molecule [3]. The existence of arylsulfonyl hydrazide **B** in the form of a six-membered ring makes elimination of nitrogen unfavorable, and the reaction ends in the step of formation of the N=N double bond in the heterocycle.

5-Phenylazo-6-*p*-tolyl-3,4-dihydro-3,4-pyridazinedione (2). Tosyl hydrazide (0.19 g, 1 mmol) was added to a solution of pyrazoledione **1** (0.29 g, 1 mmol) [4] in absolute dioxane and stirred at room temperature for 1 h. The solvent was evaporated and the residue was recrystallized from ethanol. Yield 0.16 g (53%), yellow crystals; mp 145-146°C. When *p*-chlorophenylsulfonyl hydrazide (0.21 g, 1 mmol) was used instead of tosyl hydrazide, the yield of compound **2** was 0.25 g (82%). IR spectrum (vaseline oil), ν, cm^{-1}: 1690, 1680 ($C_{(3)}$=O, $C_{(4)}$=O), 1632 w (C=C, N=N). ^1H NMR spectrum (300 MHz, DMSO-d_6, TMS, δ, ppm, *J*, Hz): 2.42 (3H, s, CH_3); 7.44 (5H, m, C_6H_5); 7.90 and 8.20 (4H, 2d, *J* = 10, C_6H_4). Mass spectrum (*m*/*z*, intensity, %): 304 (100, $M^{+\cdot}$); 278 (2, M-28); 105 (19, PhNN). Found, %: C 67.21; H 4.05; N 18.61. $C_{17}H_{12}N_4O_2$. Calculated, %: C 67.10; H 3.97; N 18.41.

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