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SYNTHESIS OF 3-ARYL(HETARYL)-4-(2-CYANOPHENYL)-Δ^2-1,2,4-TRIAZOLIN-5-ONES

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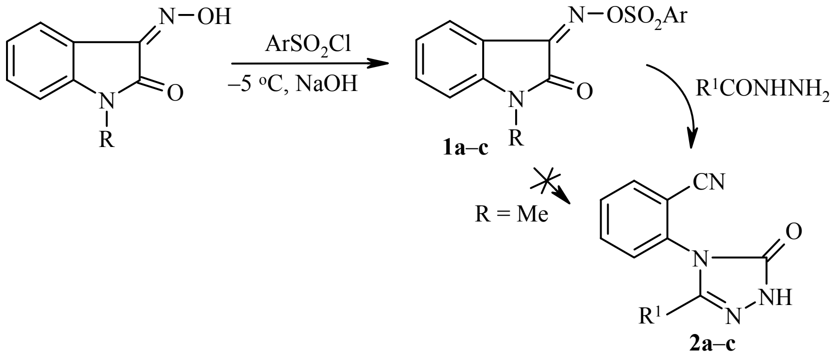
1-Unsubstituted O-arylsulfonyl derivatives of isatin 3-oximes in the presence of aliphatic and aromatic amines readily rearrange with breaking of the intercarbonyl bond to form N-(2-cyanoaryl)-N'-R-carbamides [1]. Hypothesizing that the corresponding semicarbazides will be formed upon reaction with substituted hydrazines, we studied the reaction of arylsulfonates **1a-c** with carboxylic acid hydrazides. In this case, we have established that even under relatively mild conditions (brief heating of the components in dioxane in the presence of triethylamine), compounds with molecular masses 18 units less than expected for the corresponding semicarbazides were formed in rather good yields. This indicated that under the reaction conditions, cyclodehydration of compounds **1a-c** occurred to form 3-aryl(hetaryl)-5-oxo(4H-4-(2-cyanophenyl)-1,2,4-triazolines **2a-c**.



1 a, **b** R = H, **c** R = Me, **a** Ar = Ph, **b, c** Ar = *p*-MeC$_6$H$_4$;
2 a R^1 = *p*-MeOC$_6$H$_4$, **b** R^1 = 4-Py, **c** R^1 = Ph

In fact, the molecular ion peaks had the maximum intensity in their mass spectra, indicating a cyclic structure for the compounds, while the fragmentation processes were mainly connected with elimination of predominantly CO molecules, 2-NCC$_6$H$_4$NCO, and also R'CN (*m/z* 159), which would not be possible in the case of a linear structure. We should note that N-substituted tosylate **1c** did not react with the hydrazides used, which allows us to hypothesize formation of highly reactive intermediate 2-cyanophenyl isocyanates under the reaction conditions. Investigations are continuing.

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4-(2-Cyanophenyl)-3-(4-methoxyphenyl)-Δ^2-1,2,4-triazolin-5-one (2a). Mixture of O-benzenesulfonate **1a** (3.02 g, 10 mmol) [1], *p*-methoxybenzoic acid hydrazide (3.32 g, 20 mmol), triethylamine (1 ml) in dioxane (10 ml) was heated for 45 min. After cooling down to room temperature, the mixture was diluted with water (20 ml), the substance was filtered off, washed with water, and recrystallized from acetic acid with activated carbon. Obtained 1.2 g (41%) of triazolinone **2a**; mp 302-303°C. Mass spectrum, *m*/*z* (*I*, %): 292 $[M]^+$ (100), 277 $[M–CH_3]^+$ (7), 264 $[M–CO]^+$ (6), 148 [M-144] (11), 144 $[2\text{-}NCC_6H_4NCO]^+$ (7), 133 $[R^1CN]^+$ (16), 119 (5), 105 (4), 103 (4), 90 (4), 76 (5).

4-(2-Cyanophenyl)-3-(4-pyridyl)-Δ^2-1,2,4-triazolin-5-one (2b) was obtained similarly from benzenesulfonate **1a** (3.02 g, 10 mmol), isonicotinic acid hydrazide (1.5 g, 11 mmol) and triethylamine (2 ml) in dioxane (10 ml). The mixture was boiled for 10 min and 1.1 g (42%) of compound **2a** were obtained; mp >300°C (acetic acid). Mass spectrum, *m*/*z* (*I*, %): 263 $[M]^+$ (100), 159 $[M–R^1CN]^+$ (4), 144 $[2\text{-}NCC_6H_4NCO]^+$ (8), 131 $[M–R^1CN–CO]^+$ (17), 119 $[M\text{-}144]^+$ (70), 104 $[R^1CN]^+$ (7), 103 (10), 92 (10), 91 (9), 78 (24), 76 (11), 50 (17).

4-(2-Cyanophenyl)-3-phenyl-Δ^2-1,2,4-triazolin-5-one (2c) was obtained similarly by boiling a mixture of tosylate **1b** (3.16 g, 10 mmol) [1], benzoic acid hydrazide (1.5 g, 11 mmol) and triethylamine (2 ml) in dioxane (10 ml) for 45 min. Yield 1.2 g (46%); mp >300°C (dioxane). Mass spectrum, *m*/*z* (*I*, %): 262 $[M]^+$ (100), 234 $[M–CO]^+$ (6), 159 $[M–R^1CN]^+$ (3), 144 $[2\text{-}NCC_6H_4NCO]^+$ (3), 131 $[M–R^1CN–CO]^+$ (6), 118 $[M–144]^+$ (70), 103 $[R^1CN]^+$ (15), 91 (14), 89 (10), 77 (11), 76 (10).

REFERENCES

1. A. P. Stankevicius, P. B. Terentiev, L. N. Janushene, and P. V. Vainauskas, *Khim. Geterotsikl. Soedin.*, 1868 (2003).