

SYNTHESIS OF S-TRIAZOLO[4,3-a]PYRIDINIUM SALTS BY ANODIC OXIDATION OF HYDRAZONES IN THE PRESENCE OF PYRIDINE<sup>1</sup>

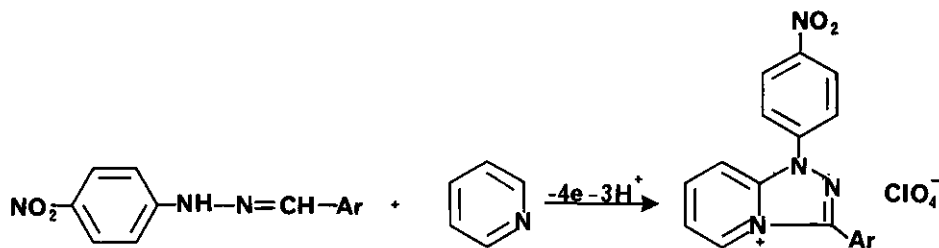
Ibro Tabaković and Senka Crljenak

Faculty of Technology, University "Djuro Pucar Stari", 78000 Banjaluka, Yugoslavia

**Abstract** — The anodic oxidation of some aldehyde hydrazones in the presence of pyridine was investigated. From the reaction mixture derivatives of s-triazolo[4,3-a]pyridinium salts were isolated in 45-80% yield and identified. The mechanism of these transformations is outlined and discussed.

Numerous and systematic studies have been reported on the anodic oxidation of the organic compounds containing nitrogen<sup>2</sup>, but relatively little attention has been paid to that of hydrazone derivatives<sup>3</sup>.

In our continuing on the anodic synthesis of heterocycles we have investigated the oxidation of the aldehyde hydrazones in the presence of pyridine to exploit a simple practical procedure for the preparation of s-triazolo[4,3-a]pyridinium salts according to the general scheme:



1a, Ar =  $p\text{-CH}_3\text{O-C}_6\text{H}_5\text{-}$

2a

1b, Ar =  $p\text{-(CH}_3)_2\text{N-C}_6\text{H}_5\text{-}$

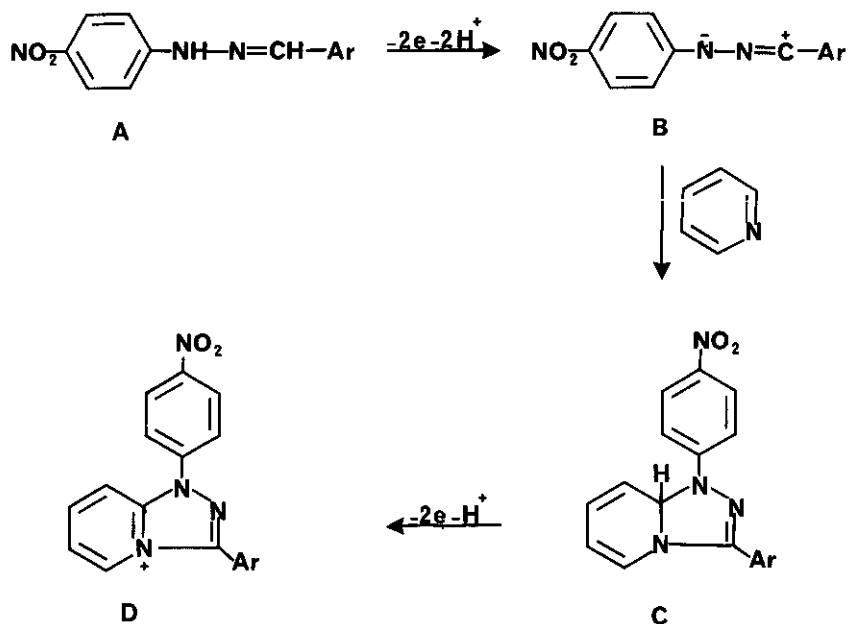
2b

1c, Ar =  $p\text{-CH}_3\text{-C}_6\text{H}_5\text{-}$

2c

All conversions were carried out in a divided electrolytic cell at Pt-gauze (3 x 5 cm) using controlled potential electrolysis as previously described<sup>4</sup>. The n-value determined by the coulometry at controlled potential<sup>5</sup> was in the range 3.0 - 3.6 F/mole.

The formation of the above mentioned s-triazolo[4,3-a]pyridinium salts can be explained in terms of the formation of the nitrilimine (B) as an intermediate by initial two electron oxidation of the starting hydrazone (A). We can envisage the intermolecular attack of pyridine followed by intramolecular cyclisation leading to the intermediate (C), which is further oxidised at the applied potential by loss of two electrons and one proton giving rise to s-triazolo[4,3-a]pyridinium salt (D).



It is necessary to point out that the electrochemical generation of nitrilimine, as a possible intermediate, provides entrance to the wide range of heterocyclic systems via anodic oxidation of aldehyde hydrazones through 1,3-dipolar cycloaddition reaction of the nitrilimine intermediates involved.

Anodic oxidation of 1a was carried out as follows: The hydrazone 1a (0.5 g) and 2 ml of pyridine were added to the anodic compartment of the cell filled with 0.1 molar solution of  $\text{Et}_4\text{NClO}_4$  in  $\text{CH}_3\text{CN}$  (100 ml). The potential is maintained at 1.05 V vs SCE by means of potentiostat, with initial current of about 200 mA.

Electrolysis is discontinued when the current drops to 20 mA. The n-value determined was 3.4. After electrolysis acetonitrile is evaporated to a volume of  $\sim 5$  ml and 100 ml of benzene was added. The precipitate was filtered and dissolved in  $\sim 5$  ml of  $\text{CH}_3\text{CN}$ . Into this solution 100 ml of water, containing few drops of  $\text{HClO}_4$  was added. The precipitated 1-p-nitrophenyl-3-anisyl-s-triazolo[4,3-a]pyridinium perchlorate, 2a, was isolated by filtration (0.454 g; 55%). The product was recrystallized from the mixture acetonitrile/benzene (2 : 3) and showed m.p. 279 - 281 $^\circ$ . IR(KBr): 3120, 1645, 1610, 1520, 1350, 1260, 1100, 760  $\text{cm}^{-1}$ . NMR ( $\text{DMSO}-d_6$ ):  $\delta = 3.95$  (s, 3H,  $\text{CH}_3\text{O}$ ); 7.3 - 9.2 ppm (m, 12H, arom.); M. S.: m/e (rel. abundance): 396 (4), 378 (14), 369 (4), 364 (8), 363 (14), 362 (62), 334 (14), 333 (28), 297 (20), 296 (100), 225 (18), 221 (10), 173 (24), 135 (69), 134 (34), 133 (98), 121 (46), 92 (38), 91 (18), 90 (92). Analysis, calculated for  $\text{C}_{19}\text{H}_{15}\text{ClN}_4\text{O}_7$ : C, 51.06; H, 3.36; N, 12.54. Found: C, 50.78; H, 3.37; N, 12.71.

Anodic oxidation of 1b (0.5 g) ( $E_{\text{appl.}} = 0.7$  V vs SCE;  $n = 3.6$ ) and isolation of product 1-p-nitrophenyl-3-(N,N-dimethylaminophenyl)-s-triazolo[4,3-a]pyridinium perchlorate, 2b, were performed on the same way as described above for the conversion 1a  $\longrightarrow$  2a. The product obtained (0.65 g; 80%) was recrystallized from mixture acetonitrile/benzene (1 : 3) and showed m.p. 280 - 282 $^\circ$ . IR(KBr): 3100, 1640, 1610, 1520, 1350, 1100, 760  $\text{cm}^{-1}$ . NMR ( $\text{DMSO}-d_6$ ):  $\delta = 3.1$  (s, 6H,  $(\text{CH}_3)_2\text{N}$ ); 6.9 - 9.2 ppm (m, 12H, arom.). Analysis, calculated for  $\text{C}_{20}\text{H}_{18}\text{ClN}_5\text{O}_6$ : C, 52.24; H, 3.94; N, 15.23. Found: C, 52.37; H, 4.20; N, 15.42.

Anodic oxidation of 1c (0.5 g) ( $E_{\text{appl.}} = 1.25$  V vs SCE;  $n = 3.0$ ) and isolation of product 1-p-nitrophenyl-3-tolyl-s-triazolo[4,3-a]pyridinium perchlorate, 2c, were performed on the same way as described for the conversion 1a  $\longrightarrow$  2a. The product obtained (0.38 g, 45 %) was recrystallized from mixture acetonitrile/benzene (3 : 2) and showed m.p. 286 - 288 $^\circ$ . IR(KBr): 3100, 1640, 1520, 1360, 1100, 760  $\text{cm}^{-1}$ . NMR ( $\text{DMSO}-d_6$ ):  $\delta = 2.5$  (s, 3H,  $\text{CH}_3$ ); 7.4 - 9.2 ppm (m, 12H, arom.). Analysis,

calculated for  $C_{19}H_{15}ClN_4O_6$ : C, 52.97; H, 3.51, N, 13.00. Found: C, 53.09; H, 3.81; N, 12.71.

This work was supported in part by grant from the Republic's Association for Scientific Work of Bosnia and Hercegovina.

#### REFERENCES

1. Paper IX in the series "Electrochemical Synthesis of Heterocyclic Compounds", For paper VIII see. Ž. Čeković and I. Tabaković, Bull. Soc. Chim. (Beograd), 1979, 44, 409.
2. N. L. Weinberg, "Technique of Electroorganic Synthesis", ed. N. L. Weinberg, John Wiley and Sons, New York (1974).
3. (a) G. Barbey, J. Juguet, and C. Caullet, Compt. rend., 1972, 275 C, 435; (b) G. Barbey, M. Genies, M. Libert, and C. Caullet, Bull. Soc. Chim. France, 1973, 1942; (c) G. Barbey and C. Caullet, Tetrahedron Lett., 1974, 1717; (d) M. Lačan, K. Jakopčič, V. Rogić, Sh. Damoni, O. Rogić, and I. Tabaković, Synth. Commun., 1974, 4, 219; (e) I. Tabaković, M. Lačan, and Sh. Damoni, Electrochim. Acta, 1976, 21, 621; (f) I. Tabaković, M. Trkovnić, and D. Galijaš, J. Electroanal. Chem., 1978, 86, 241.
4. M. Lačan, I. Tabaković, and Ž. Čeković, Tetrahedron, 1974, 30, 2911.
5. During controlled potential electrolysis an electronic integrator was used to record the quantity of electricity passed.

Received, 18th September, 1980