

LETTERS TO THE EDITOR

THE INFLUENCE OF THE NATURE OF THE SUBSTITUENTS ON THE FORMATION OF THE SYDNONE IMINE RING

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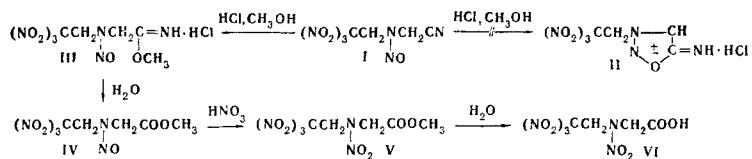
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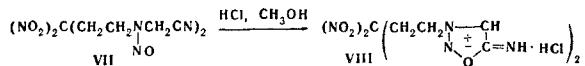
We have studied the influence of gem-trinitroethyl and gem-dinitropropyl substituents on the reactivity of N-nitroso derivatives of  $\alpha$ -aminoacetonitriles under the conditions of the formation of sydnone imines [1-6].

On reaction with hydrogen chloride in methanol ( $0^\circ\text{ C}$ ; 2.5 hr), (cyanomethyl)(2,2,2-trinitroethyl)nitrosoamine (I) (*mp* 59–60° C. Found, %: C 19.24; H 1.52; N 29.38. Calculated for  $\text{C}_4\text{H}_4\text{N}_6\text{O}_7$ , %: C 19.35; H 1.61; N 29.57) forms, in place of the expected sydnone imine (II) the imidic ester III [*mp* 88–90° C (decomp.). Found, %: C 19.49; H 2.62; N 26.37. Calculated for  $\text{C}_5\text{H}_9\text{N}_6\text{O}_8\text{Cl}$ , %: C 19.57; H 2.62; N 26.58].

The structure of III was shown by its hydrolysis to the ester IV (*mp* 41–42° C. Found, %: C 21.24; H 2.41; N 24.76. Calculated for  $\text{C}_5\text{H}_7\text{N}_5\text{O}_3$ , %: C 21.35; H 2.49; N 24.91). The nitric acid nitration of the ester IV converted it into the N-nitro analog V, which was saponified to give nitroamino(2,2,2-trinitroethyl)acetic acid (VI) [7].



In contrast to I, the N,N'-dinitroso derivative of 3,3-dinitropentane-1,5-diamine-N,N'-diacetonitrile (VII) (undistillable yellow oil) gives the bis(sydnone imine) VIII [*mp* 217–218° C (decomp.). Found, %: C 26.89; H 3.46; N 27.76. Calculated for  $\text{C}_9\text{H}_{14}\text{N}_8\text{O}_6\text{Cl}_2$ , %: C 27.00; H 3.50; N 28.00].



The results presented illustrate the previously unknown influence of the position of the electron-accepting nitro group on the formation of the sydnone imines.

REFERENCES

1. V. G. Yashunskii and L. E. Kholodov, *ZhOKh*, **32**, 3661, 1962.
2. V. G. Yashunskii and L. E. Kholodov, *ZhOKh*, **32**, 865, 1962.
3. V. G. Yashunskii, V. F. Vasil'eva, L. E. Kholodov, and M. N. Shechukina, *ZhOKh*, **32**, 162, 1962.
4. F. Stewart, *Chem. Rev.*, **64**, 129, 1964.
5. W. Baker and W. Ollis, *Quart. Rev.*, **11**, 15, 1957.
6. V. G. Yashunskii and Yu. N. Sheinker, *ZhOKh*, **32**, 1681, 1962.
7. H. Feuer, G. Bachmann, C. Coller, and W. Swarts, *Tetrah.*, **19**, 165, 1963.

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