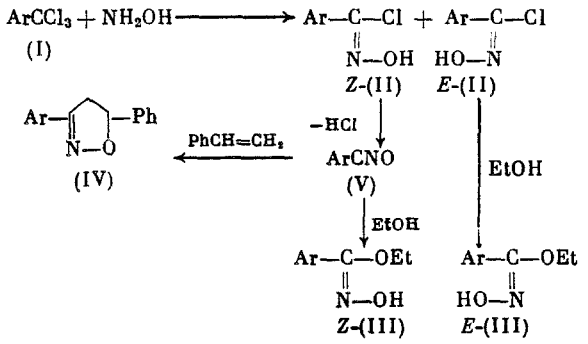
A NEW PATHWAY FOR THE FORMATION OF ARENECARBONITRILE OXIDES

D. B. Brokhovetskii, L. I. Belen'kii, and M. M. Krayushkin

UDC 542.953:547.539.232.3:547.238

The reaction of trichloromethylarenes (Ia)-(Ic) with hydroxylamine in pyridine involves reductive condensation. The primary products of this reaction are the oximes of the corresponding substituted benzaldehydes [1]. We have found that carrying out this reaction in ethanol using an eight-fold molar excess of hydroxylamine at ~20°C, instead of in pyridine, is not accompanied by reduction and leads to ~1:1 mixtures of the Z and E isomers of benzhydroximoyl chlorides (IIa)-(IIc). A mixture of the most sterically hindered Z- and E-2,4,6--trimethylbenzhydroximoyl chlorides (IIc) was separated in about 40% yield. The other hydroximoyl chlorides (IIa) and (IIb) could not be separated and mixtures of Z- and E-hydroximates (IIIa) and (IIIb) are the products (the yields were 60-65%). Upon carrying out the reaction of trichloromethylarenes (Ia)-(Ic) with NH_2OH in ethanol in the presence of styrene gives isoxazolines (IVa)-(IVc) in 10-20% yield, which are the products of 1,3-dipolar cycloaddition of the nitrile oxides (Va)-(Vc), formed as intermediates generated from the Z-chlorides [2], in addition to ~30% E-esters (IIIa) and (IIIb) and ~20% E-chloride (IIc). This opens a new pathway for the formation for the formation of arenecarbonitrile oxides in the single-step reaction of trichloromethylarenes with hydroxylamine.



Ar = 2,4-$Me_2C_6H_3$ (a); 2,4,5-$Me_3C_6H_2$ (b); 2,4,6-$Me_3C_6H_2$ (c).

The structures of (II)-(IV) established by IR and PMR spectroscopy and mass spectrometry were supported by elemental analysis and, in the case of (IIc) and (IVc), agreement of the physical indices and spectral data with those described by Grundmann [3] and Exner [4].

LITERATURE CITED

1. D. B. Brokhovetskii, L. I. Belen'kii, and M. M. Krayushkin, Izv. Akad. Nauk SSSR, Ser. Khim., No. 3, 748 (1989).
2. C. Grundmann and P. Grünanger, The Nitrile Oxides, Springer Verlag, Berlin (1971).
3. C. Grundmann and J. M. Dean, J. Org. Chem., 30, 2809 (1965).
4. O. Exner and G. Barbaro, J. Chem. Soc., Perkin Trans. 2, 1051 (1980).

N. D. Zelinskii Institute of Organic Chemistry, Academy of Sciences of the USSR, Moscow. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 7, pp. 1692-1693, July, 1990. Original article submitted March 5, 1990.

 0568-5230/90/3907-1538$12.50