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BRIEF COMMUNICATIONS

Anticorrosion Properties of Products of *N*-(2-Vinyloxyethyl)-1,2-ethylenediamine Condensation with Carbonyl Compounds

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Abstract—*N*-(2-Vinyloxyethyl)-*N*'-cyclohexylidene-1,2-ethylenediamine and *N*,*N*',*N*''-tris-[2-(2-vinyloxyethyl)-aminoethyl]hexahydro-1,3,5-triazine were synthesized by reactions of *N*-(2-vinyloxyethyl)-1,2-ethylenediamine with cyclohexanone and formaldehyde with yields of 91 and 90%, respectively. The IR and ^{1}H and ^{13}C NMR spectral data and the results of studying their anticorrosion properties are given.

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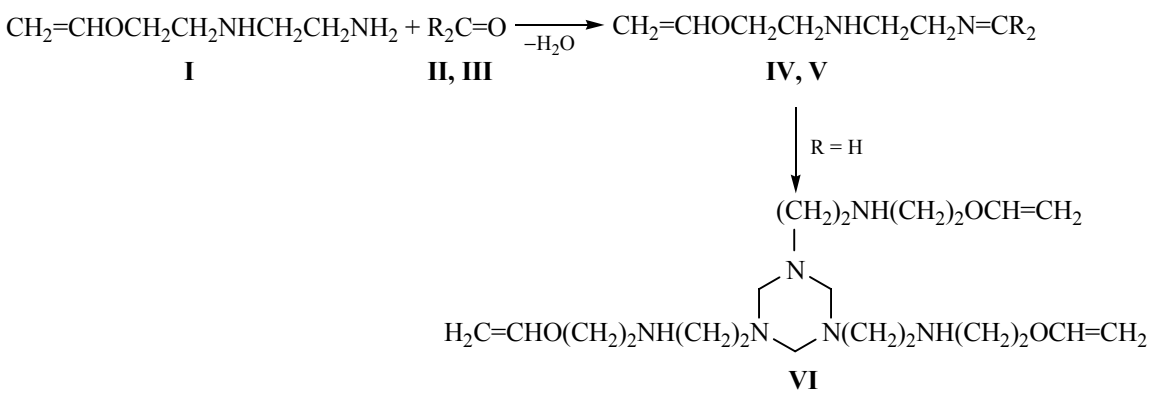
Nitrous bases [1, 2], in particular some vinyl ethers of amino alcohols and their derivatives [3, 4], are known to exhibit anticorrosion properties.

To detect anticorrosion properties of vinyl ether *N*-(2-amino-ethyl)-1,2-aminoethanol (**I**) and its derivatives, in the present work we have carried out the condensation of this ether with carbonyl compounds, which are accessible large-tonnage products: cyclohexanone and formaldehyde (in the form of paraformaldehyde).

The condensation was carried out at boiling of an equimolar mixture of reagents in toluene with azeotropic distilling off water. As a result imine (**IV**) was obtained from cyclohexanone (**II**) and amine (**I**) with a yield of 91%. As it is known for imines, which are derivatives of formaldehyde [5], imine (**V**) formed intermediately in the reaction of formaldehyde (**III**) with amine (**I**) is trimerized into triazine (**VI**). The yield of triazine (**VI**) was 90%:



$R_2 = (CH_2)_5$ (**II**), (**IV**); R = H (**III, V**).

The trimeric structure of product **VI** is confirmed by the absence of signals of protons and of the carbon atom of the $=CH_2$ group from the ^{1}H and ^{13}C NMR spectra, the presence of signals of protons and of the carbon atom of the NCH_2N group, and also by a high boiling point essentially exceeding the boiling point of imine **IV**.

To estimate inhibiting properties of initial vinyl ether of amino alcohol **I** and compounds **IV** and **VI** obtained from it, we have studied their effect on the corrosion of St.20 steel in 20% hydrochloric acid. The rate of metal dissolution was determined by a gravimetric method using 2×20×6 mm steel samples according to GOST 9.505-86 at 20°C and exposure time of 3 h. At the concentration of compounds **I** and **IV** 10^{-2} M and of compound **VI** 3.33×10^{-3} M the following protective effect Z (%) was obtained: 97.5 (**IV**), 94.4 (**VI**), and 34.9 (**I**). Thus, it has been shown that though *N*-(2-vinyloxyethyl)-1,2-ethylenediamine (**I**) itself does not inhibit the acid corrosion process, the products of its condensation with carbonyl compounds **IV** and **VI** possess a good protective effect. It shows searching for new corrosion inhibitors among such compounds is promising.

EXPERIMENTAL

Commercial paraformaldehyde (purity of 98.3%) and cyclohexanone purified by fractionation up to a base material content of no less than 99.8% were used for the synthesis. *N*-(2-Vinyloxyethyl)-1,2-ethylenediamine was obtained by a procedure described in [6].

***N*-(2-Vinyloxyethyl)-*N*'-cyclohexylidene-1,2-ethylenediamine (IV).** A mixture of 26 g (0.2 mol) of *N*-(2-vinyloxyethyl)-1,2-ethylenediamine (**I**), 19.6 g (0.2 mol) of cyclohexanone, and 100 ml of toluene were boiled with a Dyne–Stark trap up to the termination of water separation. The reaction mixture was cooled and distilled. Yield of compound **IV** 38.2 g (91%), bp 119–121°C (3 mm Hg), n_D^{20} 1.500. IR spectrum, ν, cm^{-1}: 1605, 1615, 1660, 3040, 3065, 3100, 3285. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 6.44 d.d (OCH=C, 1H, $^3J_{cis}$ 6.7, $^3J_{trans}$ 14.3), 4.13 d.d (*trans*-CH=C, 1H, $^2J_{hem}$ 1.8, $^3J_{trans}$ 14.3), 3.95 d.d (*cis*-CH=C, 1H, $^2J_{hem}$ 1.8, $^3J_{cis}$ 6.7), 3.73 t (OCH_2, 2H, ^3J 6.1), 3.25 br.s (NH, 1H), 3.01 t (=NCH_2, 2H, ^3J 6.9), 2.86 t (=NCH_2CH_2, 2H, 3*J* 6.9), 2.75 t (OCH_2CH_2N, 2H, ^3J 6.1), 1.30–1.80 m (C_5H_{10}, 10H). ^{13}C NMR spectrum, δ, ppm: 172.92 (N=C), 153.13 (OCH=), 87.80 (=CH_2), 69.01 (OCH_2), 52.69 (CH_2N=), 49.88 ($NHCH_2$·CH_2N=), 49.39 (OCH_2CH_2NH), 32.81 (CH_2CH_2·$CH_2CH_2CH_2$), 28.35 (*sin*-CN=CCH_2CH_2), 27.45 (*anti*-CN=CCH_2CH_2), 25.11 ($CH_2CH_2CH_2CH_2CH_2$). Found, %: C 68.64, H 10.62, N 13.17. $C_{12}H_{22}N_2O$. Calculated, %: C 68.53, H 10.54, N 13.32.

***N*,*N*',*N*''-Tris-[2-(2-vinyloxyethyl)aminoethyl]-hexahydro-1,3,5-triazine (VI)**. Similarly to the previous synthesis from 25.6 g (90%) of compound **VI**, bp 175–178°C (3 mm Hg), d_4^{20} 1.0218, n_D^{20} 4960, was obtained from 26 g (0.2 mol) of *N*-(2-vinyloxyethyl)-1,2-ethylenediaminea (**I**) and 6 g (0.2 mol) of paraformaldehyde (**III**). IR spectrum, ν, cm^{-1}: 1605, 1625, 3025, 3075, 3110, 3280. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 6.43 d.d (OCH=C, 1H, $^3J_{cis}$ 6.9, $^3J_{trans}$ 14.3), 4.10 d.d (*trans*-CH=C, 1H, $^2J_{hem}$ 1.8, $^3J_{trans}$ 14.3), 3.93 d.d (*cis*-CH=C, 1H, $^2J_{hem}$ 1.8, $^3J_{cis}$ 6.9), 3.44 s(NCH_2N, 2H), 3.73 t (OCH_2, 2H, 3J 5.6), 3.01 t ($NHCH_2CH_2N$, 2H, ^3J 7.1), 2.73 t ($NHCH_2CH_2O$, 2H, ^3J 5.6), 2.62 t ($NHCH_2CH_2N$, 2H, ^3J 7.1), 1.83 br.s (NH, 1H). ^{13}C NMR spectrum, δ, ppm: 151.60 (OCH=), 86.34 (=CH_2), 75.32 (NCH_2N), 66.66 (OCH_2), 53.54 (NCH_2CH_2NH), 52.69 (NCH_2CH_2NH), 50.39 ($NHCH_2CH_2O$). Found, %: C 59.33, H 10.03, N 19.51. $C_{21}H_{42}N_6O_3$. Calculated, %: C 59.12, H 9.92, N 19.70.

CONCLUSIONS

(1) It has been shown that products of *N*-(2-vinyloxyethyl)-1,2-ethylenediamine condensation with cyclohexanone and formaldehyde have the imine and symmetrical triazine structures, respectively.

(2) In the case of steel acid corrosion the protective effect *N*-(2-vinyloxyethyl)-*N*'-cyclohexylidene-1,2-ethylenediamine and *N,N*',*N*''-tris-[2-(2-vinyloxyethyl)aminoethyl]hexahydro-1,3,5-triazine is 94.4–97.5%.

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