(aldehyde proton). Signals of vinyloxy group protons (7.02, 4.14-4.67 ppm) and of a pyrrole ring (6.3-6.8 ppm) are practically absent; signals at 4.28-4.8 ppm (15), may be attributed apparently to O-CH(Me)-O and O-CH(Me)-N, and multiplets at 1.1-1.7 ppm may be proton signals of CH₃-CH; the signals at 3.2-3.9 ppm (9), 2.0-2.6 ppm (16), may be possibly the signals of protons of OH, C-CH(Me)-C, CH₂ and CH₃-C(Ph)= groups. The NMR ¹H spectrum of *O*-vinyl oxime (1) (δ , ppm): 7.31 (m, Ph), 7.02 (q, H_a), 4.67, 4.14 (dd, H_b-trans), 2.25 (s, Me).

MS of dimer $[m/z (I_{rel} (\%)]$: 44 (15.0), 51 (27.7), 56 (40.2), 77 (75.2), Ph; 83 (35.7), 84 (54.8), 91 (18.1), 102 (26.4), 104 (26.9), 105 (100), PhCO; 106 (11.0), 115 (20.8), 116 (12.0), 119 (18.3), 143 (44.9), 144 (17.6), 146 (31.7), 158 (15.6), 160 (11.0), 161 (27.7), 162 (75.0), M⁺⁺⁺ of monomer + 1 H; 187 (18.9), 208 (13.2), 215 (11.7), 232 (15.4), 320 (9.6), 321 (2.5), 322 (4.6), M⁺⁺⁺ of dimer.

Acctophenone and 2-phenylpyrrole were identified using GC/MS and IR spectroscopy.

2.4-Diphenylpyrrole (2). M.p. 182 °C (176-177 °C)⁷. Found (%): C, 87.69; H, 5.87; N, 6.27. $C_{16}H_{13}N$. Calculated (%): C, 87.67; H, 5.94; N, 6.39. 1R (CCl₄): 3470 cm⁻¹ (N-H). MS: M⁺⁺ 219. NMR ¹H (8, ppm); 8.44 (broad s, NH), 7.56, 7.52, 7.37, 7.22 (all m, 2 Ph), 7.14 (q, 3-H of pyrrole ring), 6.82 (q, 5-H of pyrrole ring). This work was financially supported by the Russian Foundation for Basic Research (Project No.95-03-09303a).

References

- B.A.Trofimov, A.I.Mikhaleva, N-Vinylpyrroles, Nauka, Novosibirsk, 1984, 262 p.
- B. A. Trotimov, Preparation of Pyrroles from Ketoximes and Acetylenes, Advances in Heterocyclic Chemistry, 1990, 51, 177.
- 3. B. A. Trofimov and A. I. Mikhaleva, *Heterocycles*, 1994, 37, 1193.
- O. A. Tarasova, S. E. Korostova, A. I. Mikhaleva, L. N. Sobenina, R.N. Nesterenko, S. G. Shevchenko, B. A. Trofimov, *Zhurn. Organ. Khim.*, 1994, 30, 810 [Rus. J. Org. Chem., 1994, 30, 810 (Engl. Transl.)].
- L. Bellami, Infrakrasnye spektry slozhnykh molekul, [zd. Inostr. Lit., Moscow, 1963, 590 p. [The Infrared Spectra of Complex Molecules, J. Wiley, New York, 1961].
- B. A. Trofimov, O. A. Tarasova, M. V. Sigalov, and A. I. Mikhaleva, *Tetrahedron Lett.*, 1995, 36, 9181.
- M. A. Yurovskaya, A. Z. Afanasyev, Yu. G. Bundel, *Khim. Geterotsikl. Soedin.*, 1984, 1077 [*Chem. Heterocycl. Compd.*, 1984 (Engl. Transl.)].

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Formation of nitrone in the reaction of *para*-nitroso-*N*, *N*-dimethylaniline with tetracyanoethylene

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*para-N*itroso-*N*,*N*-dimethylaniline reacts with tetracyanoethylene to give [4-(dimethylamino)phenylimino]malononitrile *N*-oxide 1 (65%) in addition to [4-(dimethylamino)phenylimino]malononitrile 2 (17%). The structures of the products are confirmed by spectral data and chemical transformations.

Key words: aromatic nitroso compounds, tetracyanoethylene, nitrones, cycloaddition reactions.

Reactions of aromatic nitroso compounds with nucleophilic olefins have been studied comprehensively,^{1,2} whereas only one electrophilic alkene, diethyl methylenemalonate, was involved in this reaction.³

In this work we studied the reaction of 4-nitroso-

N, N-dimethylaniline (NDMA) with a highly electrophilic alkene, tetracyanoethylene (TCE). We found that this reaction proceeds at room temperature in aprotic dipolar solvents (DMF and DMSO) to give products 1 and 2.

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Scheme 1



Table 1. IR and mass spectra of compounds 1-3

Com- pound		IR spectrum, v/nm ⁻¹	Mass spectrum, $m/z (I_{rel})$	
	C≡N	C=N	=N-H	
1	2200, 2220	1595	_	214(100)[M ⁺], 198(28)[M ⁺ -O]. 197(36), 184(40), 150(15), 136(38), 133(22), 119(26)
2	2210, 2220	1600		198(100), 183(60), 168(50), 154(70)
3	2230	1615 (N(O)=C) 1630 (C=N-H)	3280	246(100)[M ⁺], 230(47)[M ⁺ -O], 215(27), 201(24), 185(10), 172(18), 162(27), 145(11)

The structure of nitrone 1 was confirmed by spectroscopic methods. Its mass spectrum contains a peak of the molecular ion of maximum intensity, and fragmentation with elimination of the oxygen atom is observed, which is typical of nitrones⁴ (Table 1). In the ¹⁴N NMR spectrum of compound 1 there is a comparatively narrow signal at δ -44, which is typical of *N*-oxide oxygen atoms. The theoretical chemical shift values (which

Table 2. ¹H and ¹³C NMR spectra of compounds 1-3

were calculated using ACD/CNMR 1.0 program and taking into account the chemical shifts of compound 2) are in a satisfactory agreement with the experimental values (Table 2). For comparison the spectral data for azomethine 2 are presented in Table 2.



At present, the mechanism for formation of nitrone 1 is not quite clear; however we may assume that zwitterion intermediate A is formed at the first step of the reaction. This intermediate probably reacts with the second molecule of NDMA, and the resulting adduct decomposes to give two molecules of nitrone 1.

The assumption about formation of the ionic intermediate is supported by the fact that nitrobenzene does not

react with TCE under similar conditions, because distribution of positive charge in the intermediate of this reaction is not so favorable. The ionic character of the reaction is also confirmed by the fact that it does not occur in slightly polar solvents (CHCl₃, C_6H_6).

Formally, the reaction of NDMA with TCE is similar to the reaction of nitrosobenzene with styrene, where the cleavage of the olefin C=C bond also occurs to form benzylidene-N-nitrone,⁵ however, mechanisms of these reactions must be different, because styrene is a nucleophilic olefin, and TCE is electrophilic. We also note the absence of cleavage of the olefin C=C bond in the reaction of nitrosobenzene with electrophilic diethyl methylenemalonate.³

The structure of the second reaction product (Scheme 1), azomethine 2, is confirmed by comparison with an authentic sample synthesized by the reaction of NDMA with malononitrile according to a well known procedure.⁶ Azomethine is apparently formed as a result of decomposition of oxazetidine, which is obtained by cyclization of zwitterion intermediate A.

Compound 1 is the first representative of nitrones containing two electronegative functional groups at the

Com-	Solvent	¹ Η NMR (δ, <i>J</i> /Hz)			¹³ C (δ)						
pound		H-2	H-3	Other signals	C-1	C-2	C-3	C-4	Me	-CN	C=N
14,5	CDCl ₃	7.74 d (J = 7.1)	6.65 d (J = 7.1)	3.15 s (Me ₂ N)	134.3 [138]	125.7 [118]	110.7 [114]	154.4 [149]	40.4	110.9, 111.4	93.2
2ª	Acetone-D ₆	7.79 d (J = 9.6)	6.92 d (J = 9.6)	3.25 s (Me ₂ N)	134.5 [140]	129.2 [122]	112.3 [112]	154.6 [148]	40.0	113.0, 115.6	93.4
3	CDCl ₃	7.59 d (J = 9.3)	6.65 d (J = 9.3)	3.1 s (Me ₂ N), 3.91 s (MeO), 10.36 s (NH)	136.1	125.2	110.6	153.0	40.2 (Me ₂ N 53.3 (MeO)	110.6 i)	125.6 (N(O)=C) 157.0 (H-N=C)

Note The calculated chemical shifts are given in brackets. All the signals were unambiguously assigned using the following procedures: a selective polarization transfer (SPT); b NOESY.

carbon. Like dicyanoazomethine 2,⁶ compound 1 adds MeOH to the triple bond $C \equiv N$ in the presence of Na_2CO_3 to give compound 3, whose structure is confirmed by the spectral data (Tables 1 and 2). This reaction is reversible: when compound 3 is stored in a solution, it eliminates MeOH to form nitrone 1. A similar transformation occurs in the course of melting compound 3: at 134–136 °C it melts: as the temperature increases it solidifies, and it melts again at 141–143 °C (this temperature corresponds to m.p. of nitrone 1).

Scheme 2



Experimental

IR spectra were recorded on a UR-20 spectrometer. Mass spectra were obtained using a Varian CH-6 instrument. UV spectra were recorded on a Specord instrument. ¹H, ¹³C, and ¹⁴N (300.13, 75.5, and 21.5 MHz, respectively) were recorded on a Bruker AM-300 spectrometer. Chemical shifts (δ) in the ¹⁴N NMR spectra were measured with respect to MeNO₂ as the external standard. The course of the reactions was monitored by TLC (Silufol UV-54). Silica gel was used for column chromatography.

Reaction of 4-nitroso-N, N-dimethylaniline (NDMA) with tetracyanoethylene (TCE). A solution of TCE (180 mg, 1.4 mmol) in DMF (2 mL) was added to a solution of NDMA (100 mg, 0.7 mmol) in DMF (3 mL) at 20 °C with stirring. Thirty minutes later the mixture was poured into water (50 mL) and extracted with ether (3 \times 100 mL) (3 \times 100 mL). The extract was evaporated *in vacuo*, the residue was dissolved in benzene and chromatographed on a column filled with silica Lipilin et al.

gel (benzene as the eluent) to yield product 1 (95 mg, 65%) and product 2 (24 mg, 17%).

[4-(Dimethylamino)phenylimino]malononitrile N-oxide (1). Dark violet crystals, m.p. 141–143 °C. Found (%): C, 61.68; H, 4.67; N, 25.79. C₁₁H₁₀N₄O. Calculated (%): C, 61.67; H, 4.71; N, 26.16. ¹⁴N NMR (acetone-d₆), δ : -44 (N=N(O), $\Delta v_{1/2} = 50$ Hz), -100 (CN, $\Delta v_{1/2} = 600$ Hz), -320 (Me₂N, $\Delta v_{1/2} = 500$ Hz). UV (hexane), λ_{max} /nm: 465 (lge 3.5). UV (MeCN), λ_{nax} /nm 495.

[4-(Dimethylamino)phenylimino]malononitrile (2). Red crystals, m.p. 169–171 °C (Ref. 6: m.p. 168–169 °C, lit.⁶). ¹⁴N NMR (acetone-d₆), δ : -110 (CN, $\Delta v_{1/2}$ = 700 Hz), -310 (Me₂N, $\Delta v_{1/2}$ = 600 Hz).

Methyl [(4-dimethylamino)phenylimino]cyanoimidoacetate N-oxide (3). Anhydrous Na₂CO₃ (110 mg) was added to a solution of nitrone 1 (45 mg, 0.21 mmol) in MeOH (5 mL) at 20 °C with stirring; the reaction mixture was stirred for 4 h (Na₂CO₃ was dissolved almost completely). The resulting mixture was cooled, and the crystalline solid that precipitated was filtered off and washed with hexane on a filter. The mother liquor was concentrated to reduce the volume by 50%, and after cooling an additional portion of compound 3 was isolated by filtration. Both portions of orange-yellow crystals were combined and dried *in vacuo* to give the target product 3 (40 mg, 80%), m.p. 134-136 °C (decomp.). Found (%):C, 58.29; H, 6.11; N, 22.66. C₁₂H₁₄N₄O₂. Calculated (%): C, 58.53; H, 5.73; N, 22.75.

Decomposition of aitrone 3. A solution of nitrone 3 (30 mg, 0.12 mmol) in chloroform (2 mL) was kept for 7 days at 20 °C, and the starting nitrone 3 was quantitatively converted to nitrone 1 (23 mg). The product 1 was identical to the authentic sample.

References

- R. J. Kumbs in Comprehensive Organic Chemistry, Eds. D. Barton and E. D. Ollis, Pergamon Press, Oxford-New York, 1979.
- 2. G. T. Knight and B. Pepper, Tetrahedron, 1971, 27, 6201.
- 3. N. F. Hepfinger and C. E. Griffin, Tetrahedron Lett., 1963, 1365.
- R. G. Kostyanovskii, A. P. Pleshkova, V. N. Voznesenskii, A. I. Mishchenko, A. V. Prosyanik, and V. I. Markov, *Izv.* Akad. Nauk SSSR, Ser. Khim., 1980, 322. [Bull. Acad. Sci. USSR, Div. Chem. Sci., 1980, 29, 322 (Engl. Transl.)].
- 5. N. F. Hepfinger and C. E. Griffin, Tetrahedron Lett., 1963, 1361.
- 6. F. Sachs, Ber., 1900, 33, 963.

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