Reaction of 2-{^{15}N}-1a with HCl. A 3 *M* ether solution of HCl (0.8 mL, 2.4 mmol HCl) was added to a solution of 2-{^{15}N}-**1a** (220 mg, 1.1 mmol) in abs. ether (2 mL) at 0 °C. The precipitate that formed was filtered off. The yield of phenyldiazonium chloride 2-{^{15}N}-**2a** was 147 mg (95%). The product was dissolved in 30% aqueous HBF_4 (2 mL), and ether (5 mL) was added. The residue was filtered off, washed with ether, and dried *in vacuo*. The yield of labeled phenyldiazonium tetrafluoroborate was 0.1 g (50%). ^{15}N NMR (DMSO-d_6), δ: −67.96 (see Ref. 10: $Ph-\overset{\oplus}{N}\overset{1}{\equiv}\overset{2}{N}\ \overset{\ominus}{BF_4}$ (complex with 18-crown-6 in $CHCl_3$): −150.2 (N-1) and −57.2 (N-2).

Reaction of 2-{^{15}N}-1a with dimethylamine. A solution of BDO 2-{^{15}N}-**1a** (280 mg, 1.39 mmol) in CD_2Cl_2 (0.3 mL) was added to a solution of Me_2NH (184 mg, 4.1 mmol) in CD_2Cl_2 (0.7 mL) with stirring and cooling to −30 °C. The mixture was stored for 5 min at −20 °C and analyzed by ^{1}H NMR using internal standard. The yield of 3,3-dimethyl-1-phenyltriazene 2-{^{15}N}-**3a** was 80%. ^{15}N NMR (CD_2Cl_2), δ: 65.48 (see Ref. 11: $Ph-\overset{1}{N}=\overset{2}{N}-\overset{3}{NMe_2}$ in $CDCl_3$: −19.8 (N-1), 72.2 (N-2), −224.6 (N-3).

Reaction of BDO 1a with morpholine. Morpholine (254 mg, 2.9 mmol) was added to a solution of BDO **1a** (201 mg, 1 mmol) in CCl_4 (2 mL) and stored for 2 h at 20 °C. The reaction mixture was analyzed by ^{1}H NMR using internal standard. The yields of 1-phenylazomorpholine and *N*-bromomorpholine were 95 and 90%, respectively (the products were identified by comparison with the authentic samples). The solvent was evaporated *in vacuo*, and the product was purified by column chromatography (silica gel, $CHCl_3$ as eluent). The yield of triazene **3b** was 172 mg (90%, identical to the authentic sample in its IR spectrum).

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Unexpected transformations of *O*-vinylacetophenone oxime in the system Bu^{t}OK—THF

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Transformation of *O*-vinylacetophenone oxime in the system Bu^{t}OK—THF was studied. The reaction at 60—65 °C was shown to afford not the anticipated 2-phenylpyrrole, but, instead, 2,4-diphenylpyrrole (21% yield) and oligomer products (40% yield). The latter have the same elemental composition as the starting *O*-vinyl oxime but do not contain vinyloxy groups or pyrrole fragments.

Key words: *O*-vinyl oximes, *O*-vinylacetophenone oxime, 2-phenylpyrrole, 2,4-diphenylpyrrole.

O-Vinyl oximes are precursors of the pyrroles that are formed from ketoximes and acetylene in the system KOH—DMSO[1—4]. In light of said data, we obtained an unexpected result when heating acetophenone *O*-vinyloxime (**1**) with Bu^{t}OK in THF at 60—65 °C: instead of 2-phenylpyrrole[4], we isolated 2,4-diphenylpyrrole (**2**) in

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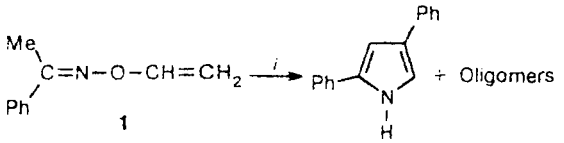
21% yield and intense colored oligomers (in 40% yield), which have the identical elemental composition with the starting oxime **1** but double (or more) molecular weight. Moreover, acetophenone (3%) and traces only of 2-phenylpyrrole were detected among the reaction products.



i: Bu^{t}OK/THF, 60—65 °C, 1 h.

Pyrrole **2** results apparently from autocondensation (analogous to aldol condensation) of *O*-vinyl oxime **1** with the formation of dimer **3**, which later, similarly to the crotonization process, is transformed to azadiene **4**. The latter isomerizes under the action of a strong base into butadiene **5**, which undergoes cyclization into dihydropyrrole **6**. Elimination of vinyl alcohol from the latter compound and isomerization of 3*H*-pyrrole **7** terminate the conversion sequence.

The oligomeric products we obtained are insoluble in hexane, scarcely soluble in ether, and readily soluble in acetone, chloroform, and CCl_4 (with film formation upon the evaporation of solvent); they are much better retained on Al_2O_3 than the starting oxime **1** and 2,4-diphenylpyrrole and are eluted with difficulty with the ether:hexane (1:1) system, but better with pure ether; the latter fact indicates the presence of polar groups, such as C=O, N—H, O—H, in their structure.

Experimental

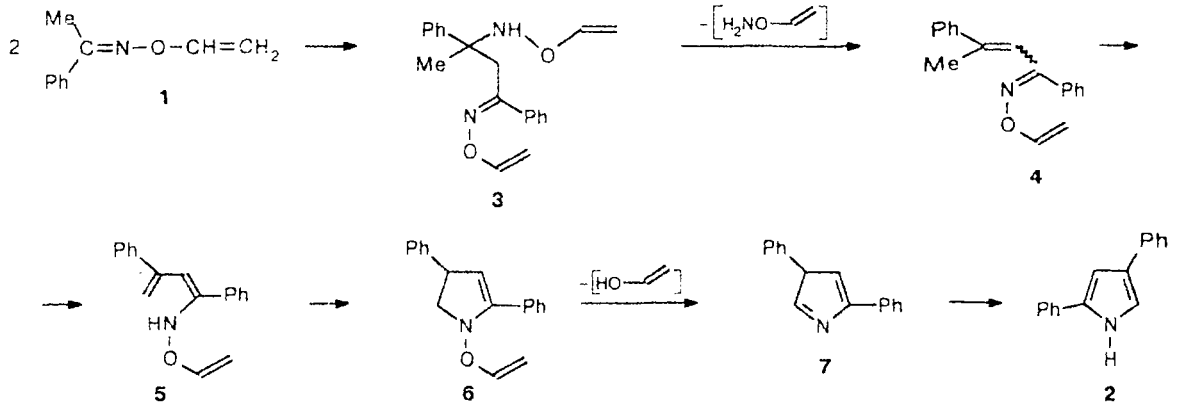
IR-spectra of the compounds were obtained on a Specord-75 IR instrument (liquids as microlayers, oligomers as films). NMR ^{1}H spectra were recorded on a Varian VXR-500S spectrometer (500 MHz) in $CDCl_3$, TMC being the internal standard. Mass spectra were obtained on an LKB-2091/152 spectrometer.

Starting *O*-vinyl oxime **1** was prepared according to[4].

Action of Bu^{t}OK in THF on acetophenone *O*-vinyloxime (1). A mixture of 3.36 g (30 mmol) of Bu^{t}OK and 4.03 (25 mmol) of oxime **1** in 25 ml of THF was heated at 60—65 °C and stirred for 1 h, THF was removed *in vacuo*, the residue was treated with ether. The fraction that is practically insoluble in ether (0.62 g) is a dark-colored polymer. Found (%): C, 75.44; H, 6.95; N, 8.68. $(C_{10}H_{11}NO)_n$. Calculated (%): C, 74.53; H, 6.83; N, 8.70. The ethereal extract was washed with water, dried with Na_2SO_4. After removal of ether and Bu^{t}OH *in vacuo* (5 Torr, 40—50 °C, 30 min), 3.14 g of dark viscous mass was obtained, 2.42 g from which were deposited on Al_2O_3 column in the ether—hexane (1:3) system. Successive eluting with ether—hexane system (firstly 1:3, then 1:1) and with pure ether afforded 0.8 g of starting oxime **1** (80% conversion), 0.45 g of 2,4-diphenylpyrrole **2** (yield 21%), 0.07 g (3%) of acetophenone, 0.36 g of brown oligomer and 0.3 g of reddish oligomer. MS, *m/z*: 322 (corresponds to a dimer of oxime **1**, however, according to NMR ^{1}H spectrum this is a mixture of oligomers). Found (%): C, 75.36; H, 7.02; N, 8.64. $(C_{10}H_{11}NO)_n$. Calculated (%): C, 74.53; H, 6.83; N 8.70. Total yield of oligomers and of polymer is 1.28 g (40%). The yields are calculated to the unreacted *O*-vinyl oxime **1**.

The IR-spectra of all the isolated oligomers include the same set of bands (ν/cm^{-1}): 685 s, 750 s, 850 w, 1020 w, 1065 w, 1150 w, 1220 w, 1280 w, 1370 w, 1445 m, 1485 w, 1520 w, 1570 w, 1590 m, 1620 w, 1670 s, 2860 m, 2920 m, 2970 m, 3050 m, 3300 (broad band). The bands differ somewhat in intensity depending on the oligomer molecular weight. The intense absorption at 685 and 750 cm^{-1}, which is present as well at IR-spectra of acetophenone and *O*-vinyl oxime (**1**), is related to deformational oscillations of the benzene ring[5]. The intense absorption at 1670 cm^{-1} may be attributed either to valent oscillations of the C=O group conjugated with the benzene ring, or to oscillations of C=C and C=N bonds in the pyridine ring[5]; the band at 3300 cm^{-1} relates to the valent oscillations of NH- or OH-groups. The vinyloxy group demonstrates strong absorption in the starting oxime (**1**) at 1610 and 1635 cm^{-1} (νC=C); in acetophenone, 1680 cm^{-1} ν(C=O); in acetophenone oxime, 1625 cm^{-1} (medium) ν(C=N); and in CH_2=C(C_6H_5)—NHCOCH=CH_2, 1650 cm^{-1} (s) ν(C=O).[6]

The NMR ^{1}H spectrum of the fraction of oligomers containing a dimer (mass spectrum data) contains signals of phenyl groups at 7.1—7.6 ppm (total integral intensity 98), and signals at 7.76—8.1 ppm (19), which may be attributed to pyridine protons or to an HC=N—; singlet at 9.2 ppm (2)



(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 CH_3—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, CH_2 and CH_3—C(Ph)= groups. The NMR ^{1}H 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), $M^{+\cdot}$ 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), $M^{+\cdot}$ of dimer.

Acetophenone 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. IR (CCl_4): 3470 cm^{-1} (N—H). MS: $M^{+\cdot}$ 219. NMR ^{1}H (δ, 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).

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

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para-Nitroso-*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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