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Dedicated to Full Member of the Russian Academy of Sciences B.A. Trofimov on the 65th Anniversary of His Birth

Reactivity of Benzophenone *O*-Vinyloxime

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Abstract—Benzophenone *O*-vinyloxime readily takes up bromine and hydrogen chloride to give benzophenone *O*-(1,2-dibromoethyl)oxime and benzophenone *O*-(1-chloroethyl)oxime, respectively. Its reactions with methanol, trifluoroacetic acid, and acetic acid lead to formation of the corresponding *O*-(1-methoxyethyl), *O*-(1-trifluoroacetoxyethyl), and *O*-(1-acetoxyethyl) derivatives. Slow heating of the title compound induces its decomposition with formation of benzophenone as the major product; fast heating leads to a complex mixture of products containing benzophenone, benzophenone imine, and acetaldehyde.

The chemistry of vinyl ethers, whose groundwork was laid by A.E. Favorskii [1], extensively developed in the midtwentieth century, when most fundamental transformations of these compounds were discovered (see [2, 3] and references therein). Later on, the most important studies concerning quantitative estimation of the reactivity of vinyl ethers and effects of functional substituents were performed by B.A. Trofimov and co-workers [4, 5]. The results of these studies gave rise to extensive application of functionalized vinyl ethers in organic synthesis, specifically in the preparation of polymers possessing various useful properties [4, 6].

We recently reported on the synthesis from ketone oximes and acetylene of ketone *O*-vinyloximes [7] and amide *O*-vinyloximes [8, 9] which can formally be regarded as vinyl ethers. These derivatives contain a highly reactive vinyl group directly attached to an oxime fragment, which extends the range of possible chemical transformations as compared to conventional vinyl ethers. For example, *O*-vinyloximes were used in the synthesis of trifluoroacetyl derivatives [10, 11] and new unsaturated heterocyclic compounds of the pyrrole [12–14], hydroxydihydropyrrole [12, 14], 3*H*-pyrrole [14, 15], oxazole [10], and oxadiazole series [9]. However, chemical and thermal instability of *O*-vinyloximes derived from dialkyl and alkyl aryl ketones [7] remains a serious obstacle to their wide application in the synthetic practice. Diaryl ketone *O*-vinyloximes, which have recently become available [16], are stable to storage and heating. These properties, in addition to high yields of these compounds, make them promising monomers and intermediate products, as well as model structures for studying the reactivity of the *O*-vinyloxime fragment.

In the present work we examined chemical properties of the simplest representative of diaryl ketone *O*-vinyloximes, benzophenone *O*-vinyloxime (**I**) with the goal of elucidating whether reactions typical of conventional vinyl ethers could be used for chemical modification of diaryl ketone *O*-vinyloximes, as well as of obtaining on that basis new intermediate products for organic synthesis.

Oxime **I** readily reacted with bromine at room temperature (reaction time 5 min) to afford 78% of benzophenone *O*-(1,2-dibromoethyl)oxime (**II**):

$$Ph_2C{=}N{-}OCH{=}CH_2$$

I

$$\xrightarrow{Br_2,\ CH_2Cl_2} Ph_2C{=}N{-}OCHBrCH_2Br$$

II

An analogous reaction pattern is typical of such representative of dialkyl ketone *O*-vinyloximes as

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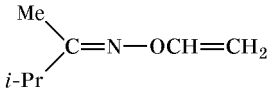
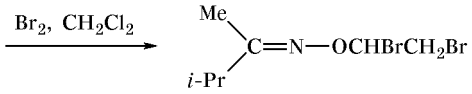
methyl isopropyl ketone *O*-vinyloxime (**III**). In this case, an appreciable amount of tars is formed, presumably as a result of bromine-initiated polymerization of initial *O*-vinyloxime **III**.



III

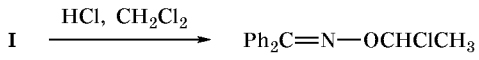


IV

Strong tarring was also observed in the bromination of conventional vinyl ethers. This process can be avoided by adding vinyl ether to bromine without a solvent, as was demonstrated for the first time by M.F. Shostakovskii [17]. The relatively ready and effective bromination of benzophenone *O*-vinyloxime may be explained by the presence in molecule **I** of bulky benzene rings which hinder polymerization due to their electronic effect and steric factor.

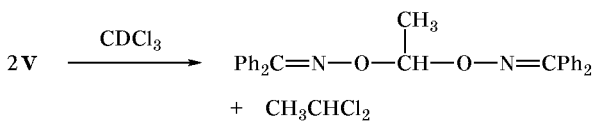
No addition at the double bond occurred in the reaction of oxime **I** with iodine. The process is likely to include a complex combination of various reactions whose products give rise to a complicated ^{1}H NMR spectral pattern. Likewise, polymerization processes predominated in similar reactions with vinyl ethers [17]. Probably, in the iodination of ketone *O*-vinyloximes, polymerization is accompanied by redox reactions involving iodine and oxime groups.

The reaction of benzophenone *O*-vinyloxime (**I**) with dry hydrogen chloride afforded exclusively the corresponding Markownikoff adduct, benzophenone *O*-(1-chloroethyl)oxime (**V**), in 87% yield.



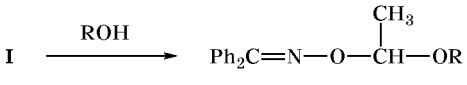
V

According to the ^{1}H NMR data, no further reaction of adduct **V** with hydrogen chloride was observed. The high selectivity was also noted for reactions of vinyl ethers with hydrogen chloride [17]. Adduct **V** (neat) is relatively stable at room temperature (over a week), while in $CDCl_3$ it undergoes appreciable disproportionation even in 12 h (^{1}H NMR data).



1-Haloethyl ethers derived from *O*-vinyl ethers are also known to be unstable [17]. The greater stability of benzophenone oxime *O*-(1-chloroethyl) ether to hydrolysis also follows from the fact that, unlike conventional α-chloro ethers [17], it does not fume on exposure to air.

Benzophenone *O*-vinyloxime (**I**) also exhibits a lower reactivity (as compared to vinyl ethers [17]) toward carboxylic acids and alcohols:



VI–**VIII**

VI, R = Ac; **VII**, R = CF_3CO; **VIII**, R = Me.

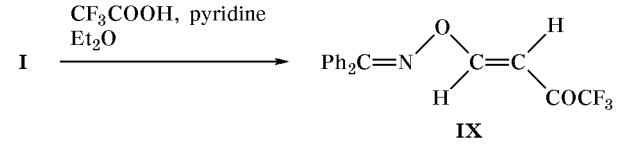
For example, heating of equimolar amounts of compound **I** and acetic acid at 60°C over a period of 0.5 h leads to only 12% conversion of the substrate. Additional heating of the reaction mixture for 3 h at 80°C increases the yield of benzophenone *O*-(1-acetoxyethyl)oxime (**VI**) to ~40%. The rate of addition of a stronger acid (trifluoroacetic) is higher, and almost complete conversion of benzophenone *O*-vinyloxime (**I**) in the reaction with trifluoroacetic acid at 60°C is achieved in 0.5 h. However, the formation of the target product, benzophenone *O*-(1-trifluoroacetoxyethyl)oxime (**VII**), is accompanied by side processes which are likely to involve acid-catalyzed transformations of the *O*-vinyloxime group.

The addition of alcohols to oxime **I** also follows the Markownikoff rule. In the reaction of **I** with boiling methanol (15 min) in the presence of ~1 % of trifluoroacetic acid (with respect to **I**), the substrate conversion was as low as 15%. Raising of the amount of CF_3COOH to 30%, other conditions being equal, leads to complete transformation of **I** into benzophenone *O*-(1-methoxyethyl)oxime (**VIII**). However, owing to side processes with particpation of the *O*-vinyloxime functionality the yield of oxime ether **VIII** does not exceed 26%* (according to the ^{1}H NMR data). A probable reason for the lower reactivity of diaryl ketone *O*-vinyloximes relative to vinyl ethers is partial binding of protons of the acid catalyst by lone electron pair of the oxime group. It should be noted that no disproportionation occurs during the addition of alcohols and carboxylic acids to oxime **I**.

Trifluroacetylation of benzophenone *O*-vinyloxime (**I**) was performed by the procedure reported in [11] for analogous reaction with dialkyl ketone *O*-vinyl-

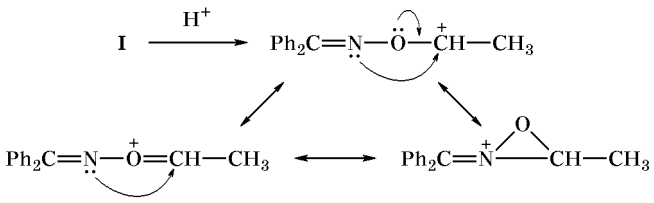
* As in Russian original.—*Publisher.*

oximes (room temperature, reaction time 2.5 h). Since trifluoroacetylation product **IX** cannot be distilled, it was isolated by the procedure used previously [18] in the trifluoroacetylation of vinyl ethers: the target product was separated via dissolution in hexane. However, the isolated material contained only ~25% of **IX** (^{1}H NMR data); protons at the double C=C bond in **IX** give rise to signals at δ 8.30 and 6.27 ppm with a coupling constant ^3J of 12.4 Hz, which indicates *trans* substitution at the β-carbon atom of the vinyl group.



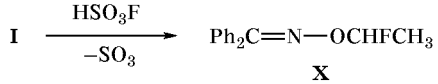
IX

We failed to detect by ^{1}H NMR spectroscopy stable carbocations which could be formed via protonation of the *O*-vinyl gruup by strong acids (CF_3SO_3H, FSO_3H, –70°C), presumably because of positive charge transfer to the heteroatoms:



Also, we observed no intramolecular alkylation of the benzene ring, which could occur in the presence of strong acids. The reason may be the above transfer of the cationic center.

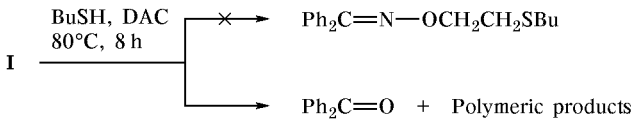
Treatment of oxime **I** with 2–5 equiv of fluorosulfonic acid in methylene chloride at –60°C gives, most probably, the corresponding adduct with HF, benzophenone *O*-(1-fluoroethyl)oxime (**X**). This follows from the appearance in the ^{1}H NMR spectrum of a quartet signal at δ 6.51 ppm and a doublet at δ 1.83 ppm. These signals are similar to those observed in the spectrum of benzophenone *O*-(1-chloroethyl)oxime (**V**). The concentration of compound **X** in the reaction mixture increased as the temperature rose to ambient.



X

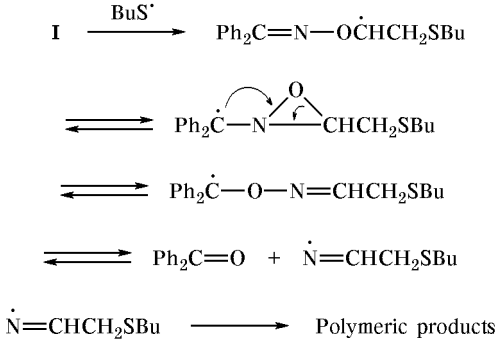
It should be noted that even in the presence of such a strong acid as fluorosulfonic no profound protonation of the oxime nitrogen atom in **I** was observed: The ^{1}H signals from the vinyl group almost did not shift downfield. A weak nucleophilic character of the nitrogen also follows from the lack of its quaternization on mixing of benzophenone *O*-vinyloxime (**I**) with 2 equiv of methyl iodide at room temperature. Even after a month, the mixture contained only the initial compounds.

Our attempt to effect radical addition of 1-butanethiol to oxime **I** was unsuccessful. At 80°C (8 h), the reaction yielded benzophenone (**XI**) and polymeric products which were characterized by broadened signals in the ^{1}H NMR spectrum at δ 7.10–7.35, 2.30–2.70, 1.45–1.70, 1.30–1.45, and 0.80–0.95 ppm.



XI

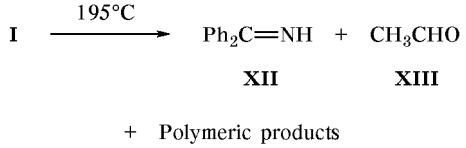
Moreover, benzophenone *O*-vinyloxime (**I**) at 80°C decomposes by 13% in 10 h, while in the presence of DAC (2-methyl-3-butyn-2-ol, dimethylacetylenylcarbinol) without BuSH, by only 5%. This result may be explained by the following DAC-initiated decomposition pathway:



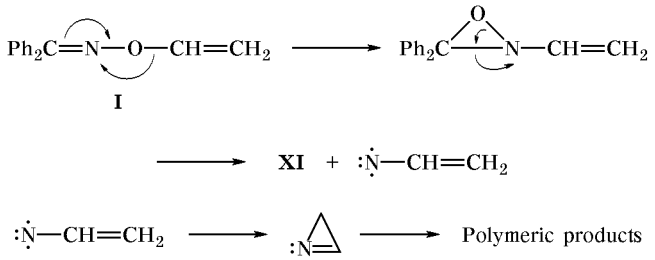
Presumably, in the absence of BuSH, the inhibitory effect of DAC on the decomposition of benzophenone *O*-vinyloxime originates from binding of species which are present in the reaction mixture and catalyze the decomposition process. The decompostion of oxime **I** occurs at a higher rate in the presence of $LiBF_4$ complex with 1,1-dimethoxyethane: under the same conditions (80°C, 10 h) 33% of **I** is converted into benzophenone (**XI**).

The thermal decomposition pattern of pure benzophenone *O*-vinyloxime (**I**) depends on the temperature. At 135–150°C, the reaction was slow, and only benzophenone (**XI**) and a tarry material (a broad

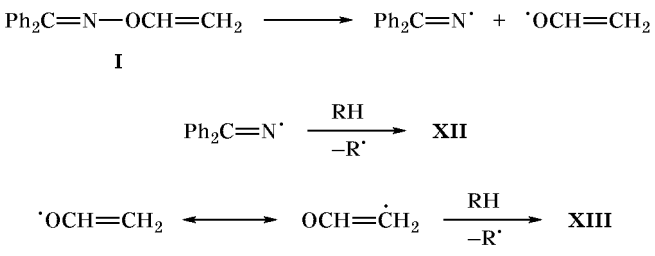
signal at δ 7.0–8.2 ppm in the ^{1}H NMR spectrum) were obtained as nonvolatile products. The formation of benzophenone was also observed in the photolysis of benzophenone *O*-acyloximes [19]. At 195°C, vigorous decomposition of oxime **I** occurred, which resulted in formation of a tarry material containing, apart from polymeric products, benzophenone and probably benzophenone imine (**XII**, δ_C 178.38 ppm). Among volatile products, we succeeded in identifying only acetaldehyde (**XIII**).



Obviously, several thermal decompostion pathways are possible. At low temperature, the main reaction pathway is likely to involve intramolecular rearrangement leading to benzophenone, which is characterized by the least energy of activation among other possible routes:



Heating to a higher temperature (195°C) could induce homolytic dissociation of the N–O bond, which is the most probable site of fragmentation of ketone *O*-vinyloximes under electron impact [20]:



RH is a molecule having a hydrogen atom.

We also examined the possibility for radical (in the presence of DAC) and cationic ($LiBF_4$–1,1-dimethoxyethane complex [21]) polymerization of benzophenone *O*-vinyloxime (**I**) in the bulk. As described above, at 80°C (reaction time 10 h) decomposition of **I** occurred to give benzophenone, and neither oligo- nor poly(benzophenone *O*-vinyloxime) was obtained.

Thus the results of the present study showed that diaryl ketone *O*-vinyloximes can be involved in some reactions typical of conventional vinyl ethers, which are promising from the viewpoint of preparation of previously inaccessible building blocks for organic synthesis. Moreover, chemical properties of the *O*-vinyloxime moiety in diaryl ketone *O*-vinyloximes are more pronounced due to reduced probability for participation of the aryl groups in condensations and heterocyclizations. This is interesting from the viewpoint of theoretical organic chemistry. The examined ways of chemical modification of diaryl ketone *O*-vinyloximes give new prospects in the purposeful synthesis of compounds having an =N–O bond sequence.

EXPERIMENTAL

The ^{1}H and ^{13}C NMR spectra were recorded on a Bruker 400DPX spectrometer operating at 400.13 and 101.61 MHz, respectively; chloroform-*d* was used as solvent, and HMDS, as internal reference. The IR spectra were measured on a Bruker ISF-25 instrument. Initial benzophenone *O*-vinyloxime (**I**) was prepared by the procedure described in [16].

Benzophenone *O*-(1,2-dibromoethyl)oxime (II). A solution of 0.1 g (0.6 mmol) of bromine in 1 ml of dry methylene chloride was added with stirring at room temperature to a solution of 0.13 g (0.6 mmol) of oxime **I** in 1 ml of dry methylene chloride. The solution turned colorless. After 5 min, the solvent was removed under reduced pressure at 40°C. Yield 0.23 g (78%; purity 78%, according to the ^{1}H NMR data), light yellow transparent viscous liquid, n_D^{20} = 1.6195. IR spectrum (film), cm^{-1}: 3085 w, 3058 m, 2983 m, 2924 w, 2852 w, 1657 m, 1597 m, 1578 w, 1492 m, 1445 s, 1420 m, 1367 w, 1341 m, 1327 m, 1306 m, 1278 m, 1220 m, 1205 w, 1169 m, 1146 m, 1110 s, 1075 m, 1038 w, 1026 m, 986 w, 965 s, 914 s, 871, 850 w, 830 w, 775 s, 696 s, 670 m, 650 m, 606 m, 585 s. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 7.52 d (2H, *anti*-*o*-H, $^3J_{o,m}$ = 7.3 Hz), 7.32–7.47 m (8H, H_{arom}), 6.65 d.d (1H, α-H, $^3J_{\alpha,\beta''}$ = 10.2 Hz, $J_{\alpha,\beta'}$ = 2.7 Hz), 4.07 t (1H, β″-H, $^2J_{\beta'',\beta'}$ = 11.1 Hz), 3.89 d.d (1H, β′-H). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 161.97 (C=N); 135.27 (*anti*-C^i); 132.21 (*syn*-C^i); 130.50 (*anti*-C^p); 129.60 (*syn*-C^p); 129.50 (*syn*-C^o); 128.72, 128.43 (*anti*-C^o, *anti*-C^m);

128.14 (*syn*-C^m); 88.38 (C_α); 32.59 (C_β). Found, %: C 48.03; H 3.59; Br 41.58; N 3.66. $C_{15}H_{13}Br_2NO$. Calculated, %: C 47.03; H 3.42; Br 41.72; N 3.66.

Methyl isopropyl ketone *O*-(1,2-dibromethyl)-oxime (IV). Following the above procedure, from 0.1 g (0.8 mmol) of compound **III** and 0.12 g (0.8 mmol) of bromine we obtained 0.2 g of a mixture consisting of 0.14 g of a light brown mobile liquid, which contained about ~80% (49%) of dibromo derivative **IV**, and 0.06 g of a brown tarry material. Adduct **IV** was a mixture of *E* and *Z* isomers at a ratio of 6:1. IR spectrum (film), ν, cm^{-1}: 3041 w, 2970 s, 2932 m, 2873 m, 1761 w, 1715 m, 1641 m, 1467 m, 1422 m, 1387 w, 1368 m, 1344 m, 1272 w, 1254 w, 1237 w, 1215 m, 1184 w, 1147 m, 1112 s, 1024 s, 986 m, 916 s, 888 m, 839 m, 772 w, 739 w, 669 m, 588 s. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: *E* isomer: 6.52 d.d (1H, α-H, $^3J_{\alpha,\beta''}$ = 10.0, $J_{\alpha,\beta'}$ = 2.7 Hz), 4.08 d.d (1H, β″-H, $^2J_{\beta'',\beta'}$ = 11.1 Hz), 3.90 d.d (1H, β′-H), 2.57 sept (1H, CH, $^3J_{HH}$ = 6.8 Hz), 1.12 d (6H, CH_3); *Z* isomer: 6.52 d.d (1H, α-H, $^3J_{\alpha,\beta''}$ = 10.2 Hz, $J_{\alpha,\beta'}$ = 2.7 Hz), 4.06 d.d (1H, β″-H, $^2J_{\beta'',\beta'}$ = 11.0 Hz), 3.91 d.d (1H, β′-H), 3.32 sept (1H, CH, $^3J_{HH}$ = 7.0 Hz), 1.06 d (6H, CH_3). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: *E* isomer: 168.09 (C=N), 88.87 (C^α), 34.46 (CH), 32.90 (C^β), 19.63 [$CH(\mathbf{C}H_3)_2$], 12.30 (CH_3); *Z* isomer: 168.09 (C=N), 88.87 (C_α), 32.83 (C_β), 27.58 (CH), 19.05 [$CH(\mathbf{C}H_3)_2$], 15.54 (CH_3). IR spectrum of the tarry material (film), ν, cm^{-1}: 3351 s, br, 3141 s, br, 2975 w, 2936 w, 2875 w, 2751 s, br, 1688 m, 1467 m, 1423 w, 1371 m, 1092 m, 1060 m, 980 w, 939 w, 893 w, 777 w, 596 w.

Benzophenone *O*-(1-chloroethyl)oxime (V). Dry hydrogen chloride prepared by reaction of sodium chloride with sulfuric acid was passed over a period of 10 min through a solution of 0.3 g (1.3 mmol) of oxime **I** in 3 ml of dry methylene chloride. The solvent was distilled off under reduced pressure at 40°C. Yield 0.35 g (87%; purity 87%, according to the ^{1}H NMR data), light yellow transparent viscous liquid, n_D^{20} = 1.5880. IR spectrum (film), ν, cm^{-1}: 3083 w, 3060 m, 3027 w, 2998 w, 2989 w, 2967 w, 2931 m, 2854 w, 1958 w, 1890 w, 1811 w, 1762 w, 1660 w, 1614 w, 1594 w, 1569 w, 1494 m, 1445 s, 1381 m, 1329 m, 1305 m, 1265 m, 1169 m, 1136 s, 1113 s, 1076 w, 1020 m, 1001 w, 980 m, 943 s, 922 w, 869 m, 774 s, 737 w, 696 s, 668 m, 652 m, 629 m, 599 m, 540 w, 492 m. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 7.50 d (2H, *anti*-*o*-H, $^3J_{o,m}$ = 8 Hz), 7.30–7.43 m (8H, H_{arom}), 6.40 q (1H, α-H, $^3J_{\alpha,\beta}$ = 5.8 Hz), 1.78 d (3H, β-H). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 160.59 (C=N); 132.68 (*anti*-C^i); 130.12 (*syn*-C^i; *anti*-C^p); 129.47 (*syn*-C^o); 129.27 (*syn*-C^p); 128.56, 128.35 (*anti*-C^o, *anti*-C^m); 128.09 (*syn*-C^m); 95.42 (CHCl), 24.70 (CH_3). Found, %: C 70.59; H 5.51; N 5.07. $C_{15}H_{14}ClNO$. Calculated, %: C 69.36; H 5.43; N 5.39.

Benzophenone *O*-(1-acetoxyethyl)oxime (VI). A mixture of 0.2 g (0.9 mmol) of oxime **I** and 0.06 g (1 mmol) of acetic acid was heated for 0.5 h at 60°C. The mixture turned light brown. Apart from acetic acid, the mixture contained mainly benzophenone *O*-vinyloxime (**I**) and benzophenone *O*-(1-acetoxyethyl)oxime (**VI**) at a ratio of 1:0.1. Heating of the mixture for an additional 3 h at 80°C increased its viscosity, the color changed to dark brown, and the ratio of compounds **I** and **VI** became 1:0.7. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 6.60 q (1H, α-H, $^3J_{\alpha,\beta}$ = 5.5 Hz), 1.44 (3H, β-H).

Benzophenone *O*-(1-trifluoroacetoxyethyl)oxime (VII). A mixture of 0.2 g (0.9 mmol) of oxime **I** and 0.11 g (1 mmol) of trifluoroacetic acid was heated for 0.5 h at 60°C. The mixture turned dark brown; it contained about ~30% of product **VII** (^{1}H NMR data). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 6.76 q (1H, α-H, $^3J_{\alpha,\beta}$ = 5.5 Hz), 1.54 (3H, β-H).

Benzophenone *O*-(1-methoxyethyl)oxime (VIII). Trifluoroacetic acid, 0.03 g (0.3 mmol), was added to a solution of 0.2 g (0.9 mmol) of compound **I** in 2 ml of anhydrous methanol, and the mixture was heated for 15 min under reflux. The solvent was removed under reduced pressure (50°C) to obtain 0.23 g of a light yellow viscous liquid which contained ~40% of product **VIII** (^{1}H NMR data). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 5.26 q (1H, α-H, $^3J_{\alpha,\beta}$ = 5.4 Hz), 1.39 (3H, β-H).

Benzophenone *O*-(2-trifluoroacetylvinyl)oxime (IX). A solution of 1.41 g (6.7 mmol) of trifluoroacetic anhydride in 1.5 ml of dry diethyl ether was added over a period of 3 min under stirring to a solution of 0.5 g (2.2 mmol) of compound **I** and 0.21 g (2.7 mmol) of pyridine in 1.5 ml of dry diethyl ether. The mixture was stirred for 2.5 h, kept for 12 h at 20°C, and poured under stirring into 40 ml of hexane cooled to 0°C. The precipitate was filtered off, and the filtrate was evaporated under reduced pressure (40°C) to obtain 0.87 g of a light red–brown transparent liquid which contained about 25% of product **IX**. Yield ~31%. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 8.30 d (1H, α-H, $^3J_{\alpha,\beta}$ = 12.4 Hz), 6.27 d (1H, β-H).

Reaction of benzophenone *O*-vinyloxime (I) with fluorosulfonic acid. A mixture of 0.07 g (0.7 mmol) of fluorosulfonic acid and CD_2Cl_2 was placed in a 5-mm NMR ampule and cooled to –70°C, and

a solution of 0.03 g (0.13 mmol) of compound **I** in CD_2Cl_2 was added. The ampule was mounted into the probe of NMR spectrometer, maintained at –70°C, and the ^1H NMR spectra were recorded each time as the temperature rose by 5°C. At –60°C, new signal appeared, δ, ppm: 6.51 q and 1.83 d ($^3J_{\alpha,\beta}$ = 5.6 Hz), which were assigned to benzophenone *O*-(1-fluoroethyl)oxime (**X**). The intensity of these signals increased as the temperature rose to 20°C, while the signals from compound **I** decreased in intensity. However, even after 20 h at room temperature, only a half of **I** was converted into product **X**.

Decomposition of benzophenone *O*-vinyloxime (I) on slow heating. A glass ampule was charged with 0.1 g of oxime **I** and was heated on an oil bath at a rate of ~5 deg/min. When the temperature reached ~135°C, quiet decomposition of the substrate began, and it turned dark. The ampule was continued to heat up to 150°C and was then cooled. According to the NMR spectra, the main components of the resulting material were benzophenone (**XI**) [^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 196.76 (C=O), 137.66 (C^i), 132.44 (C^p), 130.09 (C^o), 128.33 (C^m)] and polymeric products which showed in the ^1H NMR spectra broad signals in the δ range from 6.9 to 8.1 ppm.

Decomposition of benzophenone *O*-vinyloxime (I) on fast heating. A receiver equipped with a dropping funnel was heated to 195°C, and a small amount of oxime **I** was added dropwise. The substrate boiled up ~1 s after it contacted with the hot surface. The evolved gaseous products were passed through $CDCl_3$ cooled to –70°C. When the entire amount of oxime **I** was added, the heating bath was removed. The ^1H NMR spectrum of the resulting black tarry material contained signals belonging to compounds **I** and **XI** and broad signals in the δ range from 6.5 to 8.2 ppm. In the ^{13}C NMR spectrum, apart from the signals of **I** and **XI**, a signal from a quaternary carbon atom was present at δ_C 178.38 ppm. In the ^1H NMR spectrum of the gaseous decomposition products we identified signals belonging to acetaldehyde, δ, ppm: 9.80 q (1H, CHO, $^3J_{HH}$ = 2.9 Hz), 2.20 d (3H, CH_3).

Thermal polymerization of benzophenone *O*-vinyloxime (I). A 2-ml ampule was charged with 0.35 g (1.6 mmol) of compound **I**. The ampule was purged with argon, sealed, and heated for 10 h at 80°C. The resulting material was analyzed by ^1H NMR spectroscopy. The ratio of compounds **I** and **XI** was 7 : 1.

Radical polymerization of benzophenone *O*-vinyloxime (I). The procedure was the same as above, but 0.007 g (3%) of DAC was added. The ratio of compounds **I** and **XI** was 21 : 1.

Cationic polymerization of benzophenone *O*-vinyloxime (I). The procedure was the same as above, but a solution of 0.003 g (2%) of $LiBF_4$ in 0.05 ml of 1,2-dimethoxyethane was added. The ratio of compounds **I** and **XI** was 2 : 1.

In the above experiments, the contents of the ampule turned brown and became more viscous. After cooling and opening of the ampules, no evoluton of gaseous products was observed, and the initial weight of the material remained unchanged. The resulting materials were readily soluble in most organic solvents, such as acetone, benzene, petroleum ether, and isooctane.

When analogous experiments were carried out under more severe conditions (110°C, 12 h), complete decomposition of substrate **I** occurred. The major products were benzophenone (**XI**) and polymeric compounds which were characterized by very broad signals in the ^1H NMR spectra in the δ range from 6.9 to 8.1 ppm. No upfield signals from the expected oligomers or polymers were observed. The resulting materials were readily soluble in most organic solvents (acetone, benzene, diethyl ether, petroleum ether, isooctane, and methanol) and insoluble in water.

REFERENCES

1. Favorskii, A.E., *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 1940, no. 2, p. 181.
2. Trofimov, B.A., *Geteroatomnye proizvodnye atsetilena. Novye polifunktsional'nye monomery, reagenty i poluprodukty* (Heteroatom Acetylene Derivatives. New Polyfunctional Monomers, Reagents, and Intermediate Products), Moscow: Nauka, 1981.
3. Trofimov, B.A. *Curr. Org. Chem.,* 2002, vol. 6, p. 1121.
4. Mikhaleva, A.I. and Gusarova, N.K., *Atsetilen: reaktsii i proizvodnye. Bibliografiya nauchnykh trudov B.A. Trofimova* (Acetylene and Its Derivatives. Bibliography of Scientific Works of B.A. Trofimov), Novosibirsk: Izd. Sib. Otd. Ross. Akad. Nauk, 1999; Trofimov, B.A. and Nedolya, N.A., *Rev. Heteroatom Chem.*, 1993, vol. 9, p. 205.
5. Sinegovskaya, L.M. and Trofimov, B.A., *Usp. Khim.*, 1996, vol. 65, no. 12, p. 1091; Trofimov, B.A., *Z. Chem.*, 1986, vol. 26, no. 2, p. 41; Sinegovskaya, L.M., Keiko, V.V., and Trofimov, B.A., *Sulfur Rep.*, 1987, vol. 7, no. 5, p. 337; Nedolya, N.A. and Trofimov, B.A., *Sulfur Rep.*, 1994, vol. 15, no. 2, p. 237; Nedolya, N.A. and Trofimov, B.A., *Sulfur Rep.*, 1994, vol. 15, no. 3, p. 339; Nedolya, N.A., Trofimov, B.A., and Senning, A., *Sulfur Rep.*, 1996, vol. 17, no. 2, p. 183.

6. *Khimicheskaya entsiklopediya* (Chemical Encyclopedia), Moscow: Bol'shaya Rossiiskaya Entsiklopediya, 1992, vol. 3, p. 1226.
7. Trofimov, B.A., Mikhaleva, A.I., Vasil'tsov, A.M., Schmidt, E.Yu., Tarasova, O.A., Morozova, L.V., Sobenina, L.N., Preiss, T., and Henkelmann, J., *Synthesis*, 2000, no. 8, p. 1125.
8. Trofimov, B.A., Schmidt, E.Yu., Mikhaleva, A.I., Vasil'tsov, A.M., and Afonin, A.V., *Mendeleev Commun.*, 2000, no. 1, p. 29.
9. Trofimov, B.A., Schmidt, E.Yu., Vasil'tsov, A.M., Mikhaleva, A.I., Zaitsev, A.B., Morozova, L.V., Gorshkov, A.G., Arndt, J.-D., and Henkelmann, J., *Synthesis*, 2001, no. 16, p. 2427.
10. Trofimov, B.A., Schmidt, E.Yu., Mikhaleva, A.I., Vasil'tsov, A.M., Larina, L.I., and Klyba, L.V., *Mendeleev Commun.*, 1999, no. 6, p. 238.
11. Vasil'tsov, A.M., Shmidt, E.Yu., Mikhaleva, A.I., Zaitsev, A.B., Tarasova, O.A., Afonin, A.V., Toryashinova, D.-S.D., Il'icheva, L.N., and Trofimov, B.A., *Russ. J. Org. Chem.*, 2001, vol. 37, p. 334.
12. Trofimov, B.A. and Mikhaleva, A.I., *N-Vinilpirroly* (*N*-Vinylpyrroles), Novosibirsk: Nauka, 1984.
13. Trofimov, B.A., Korostova, S.E., Mikhaleva, A.I., Sobenina, L.N., Vasil'ev, A.N., and Nesterenko, R.N., *Khim. Geterotsikl. Soedin.*, 1983, no. 2, p. 273.
14. *Advances in Heterocyclic Chemistry*, Katritzky, A.R., Ed., San Diego: Academic, 1990, vol. 51, p. 177.
15. Korostova, S.E., Shevchenko, S.G., and Sigalov, M.V., *Khim. Geterotsikl. Soedin.*, 1991, p. 1371.
16. Zaitsev, A.B., Vasil'tsov, A.M., Schmidt, E.Yu., Mikhaleva, A.I., Morozova, L.V., Afonin, A.V., Ushakov, I.A., and Trofimov, B.A., *Tetrahedron*, 2002, vol. 58, p. 10 043.
17. Shostakovskii, M.F., *Prostye vinilovye efiry* (Vinyl Ethers), Moscow: Akad. Nauk SSSR, 1952.
18. Hojo, M., Masuda, R., and Okada, E., *Synthesis*, 1990, no. 4, p. 347.
19. Lalevee, J., Allonas, X., Fouassier, J.P., Tachi, H., Izumitani, A., Shirai, M., and Tsunooka, M., *J. Photochem. Photobiol. A*, 2002, vol. 151, p. 27.
20. Yurovskaya, M.A., Druzhinina, V.V., Tyurekhodzhaeva, M.A., and Bundel', Yu.G., *Khim. Geterotsikl. Soedin.*, 1984, no. 1, p. 69.
21. Trofimov, B.A., Morozova, L.V., Tatarinova, I.V., Khil'ko, M.Ya., Ivanova, N.I., Mikhaleva, A.I., and Scotheim, T., *Vysokomol. Soedin., Ser. B*, 2002, vol. 44, no. 11, p. 2048.