Synthesis and Thermal Stability of *O*-Vinylketoximes

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Abstract: The *O*-vinylketoximes **2** were synthesized from ketoximes **1** and acetylene in superbase systems in good to excellent yields. Their thermal stability was investigated.

Key words: vinylation, *O*-vinylketoximes, ketoximes, acetylene, superbase systems

O-Vinylketoximes, precursors in the synthesis of pyrroles from ketoximes and acetylenes,[1] contain a highly reactive NO-vinyl group and attract much attention as promising monomers and synthons. However, they are potentially explosive and hence for their safe and proper application in organic synthesis and polymer chemistry, the knowledge of their thermal stability is crucial. Meanwhile, no data of such a kind were so far published.

Direct acetylene vinylation of a ketoxime, namely acetoxime **1a**, was first reported 20 years ago.[2] The reaction was carried out under atmospheric pressure at 110 °C, the yield of *O*-vinylacetoxime being 10%. Later, the yield was improved up to 78% by carrying out the reaction in an autoclave (80−90 °C, initial acetylene pressure 15 atmospheres) and by use of fractional vinylation.[3] However, this procedure turned out to be poorly reproducible.

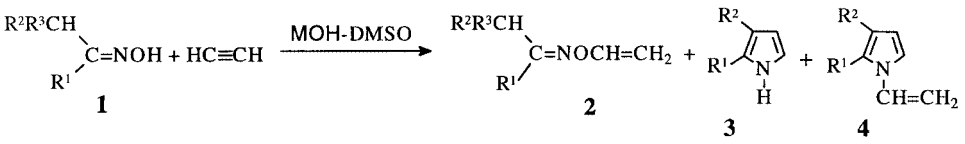
A series of vinylketoximes **2** was unselectively prepared by using superbase systems MOH−DMSO (M = Li, Na, K) under acetylene pressure,[3-12] with the help of indirect methods using halogen derivatives.[13,14] The synthetic conditions and yields of **2** are presented in Table 1.

The goal of the present work was to develop high-performance and reliable synthetic routes to *O*-vinylketoximes of accessible alkyl- and arylmethylketones and to undertake their stability investigation.

Using vinylation of acetoxime **1a** (R^1 = Me, R^2 = R^3 = H) as a model, the effect of the reaction parameters on the yield and purity of *O*-vinylketoximes under both atmospheric and elevated pressure has been examined. The results of acetoxime vinylation under atmospheric pressure are presented in Table 2. The runs were carried out in a flow system; the *O*-vinylacetoxime **2a** formed was brought out with the acetylene flow into a trap cooled to −78 °C. The formation of undesirable (in this case) pyrroles **3** and **4** during *O*-vinylacetoxime synthesis[1] was suppressed by water additives.[2,3] At the same time, it is known that the presence of water in the alkali−DMSO system decreases its basicity[15] and, consequently, the ketoxime-acetylene reaction rate. Indeed, variation of the reaction conditions has shown the yields of *O*-vinylacetoxime **2a** to increase with decreasing the concentration of water and increasing the amount of alkali loading (Table 2).

A significant growth (from 30% to 42%) of the yield of **2a** with increasing the amount of alkali (Table 2, runs 3−5) or with reducing the acetoxime concentration (Table 2, run 6) is observed under anhydrous conditions. The synthesis of oxime **2a** under the conditions of runs 3−5 may be considered as a preparative one, but, though experimentally simple, it suffers from shortcomings. First, a considerable portion of the initial acetoxime transforms to the pyrroles **3a** and **4a**. Second, a loss of *O*-vinylacetoxime **2a** is observed owing to its high volatility in the presence of acetylene; in the trap a solution with a manyfold excess of liquid acetylene over that of the product **2a** is condensed. Therefore, an uptake of the product **2a** with acetylene occurs upon slow heating of the condensate to ambient temperature. Third, by the same reason and due to the formation of large volumes of explosive liquid acetylene the scaling up of the synthesis becomes difficult.

In order to intensify the reaction a series of runs were performed under acetylene pressure (16−17 atmospheres) (Table 3). When the reaction was carried out under milder conditions than those reported,[3] the oxime **2a** was prepared in a yield as low as 29% (Table 3, run 1). Further temperature decrease to 77 °C and shortening the reaction time to 6−10 minutes under anhydrous conditions allow neither selective reaction nor noticeable increase in yield (Table 3, run 2). A more efficient vinylation occurs only with reducing the reagent and catalyst concentrations (Ta-



1 2 3 4

Table 1 Preparative Yields of and Synthetic Routes to all the Known *O*-Vinylketoximes **2**

O-Vinylketoxime			Yield, %		
			Direct Vinylation		Other Methods
R^1	R^2	R^3	Atmospheric pressure	Autoclave	
Me	H	H	10[3]	72[3]	
t-Bu	H	H	16[3]	60[3]	
Ph	H	H	12[6]	46[3]	41[14]
4-ClC_6H_4	H	H		20[3]	
2-Furyl	H	H		38[3]	6[13]
2-Thienyl	H	H		56[3]	43[13]
Ph	Me	Me		37[8]	
2,5-$Me_2C_6H_3$	H	H	10[10]		
4-$H_2NC_6H_4$	H	H	3[11]		
1-Methyl-2-pyrrolyl	H	H	41[12]		
1-Methyl-3-indolyl	H	H		54[9]	
1,2-Dimethyl-3-indolyl	H	H	10[9]		
1,2-Dimethyl-3-indolyl	Me	H	21[9]		
1,2-Dimethyl-3-indolyl	Et	Me	25[9]		

ble 3, run 3). It should be noted that under anhydrous conditions the reaction is difficult to control due to a large exothermal effect.

In order to make the synthesis of *O*-vinyloxime **2a** more controllable we used a second inert liquid phase unmixable with DMSO to dissolve and bring the forming *O*-vinylacetoxime **2a** out of the reaction zone, thus preventing it from further transformation to pyrroles **3a** and **4a**.

Pentane proved to be the most appropriate inert liquid phase (Table 3, run 4, yield of oxime **2a**: 75.6%, purity ~100%). The pentane:DMSO optimal ratio is 0.8 (Figure).

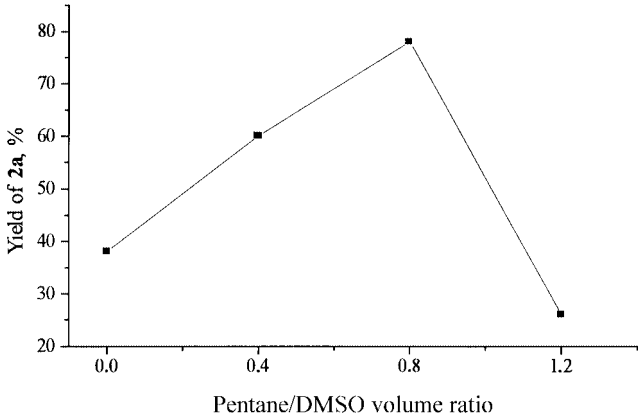


Figure *O*-Vinylacetoxime yield versus pentane:DMSO volume ratio

As *O*-vinylacetoxime boiling point is close to 100 °C (720 mm Hg, depending on the atmospheric pressure), high-boiling hydrocarbons (dodecane and vaseline oil) were also tried as inert phases; but in this case, the acetoxime vinylation was completely suppressed. At the same time, the use of lower-boiling hydrocarbons (such as hexane, petroleum ether, bp: 40−70 °C) makes the purification of *O*-vinylacetoxime difficult because of the low difference between their boiling points. Diethyl ether inhibited the formation of not only pyrroles, but of the target oxime **2a** (Table 3, run 5). The preparation of *O*-vinylacetoxime in the system KOH−DMSO−diethyl ether in a yield of 52.5% requires longer time (1 hour) and higher reaction temperature (77 °C) compared to acetoxime vinylation in the system KOH−DMSO [~0.1 hour and 70 °C (Table 3, run 4)]. As catalysts, RbOH and CsOH were tried in the pentane−DMSO system.

It is known that the nature of cation in MOH exerts significant effect on the catalytic activity of the MOH−DMSO system that, as a rule, increases with increasing the M atomic mass. CsOH formed in situ in the reaction mixture from MOH and CsX was supposed to catalyze the ace-

Table 2 Acetoxime Vinylation under Atmospheric Pressure

Run	Oxime (g)	KOH (g)	DMSO (mL)	H_2O (g)	T (°C)	Time (h)	Yield (%)		
							2a	**3a**	**4a**
1[a]	7.0	2.8	50	2.8	110	6	8–15	52–60	32–33
2	14.0	2.8	50	2.8	92–95	9	4	trace	trace
3	7.0	2.8	50	no	95–97	6	30	15	trace
4	7.0	5.6	50	no	95–97	6	37	50	6
5	7.0	8.4	50	no	92–95	6	42	53	2
6	3.5	2.8	50	no	95–97	3	39	33	12
7	16.8	16.8	250	no	95–97	6	29	trace	trace

[a] Based on the results of a series of runs.

Table 3 Acetoxime Vinylation under Acetylene Pressure

Run	Oxime (g)	KOH (g)	DMSO (pentane), (mL)	T (°C)	Time (h)	Yield (%)		
						2a	**3a**	**4a**
1	12.5	15	250[a]	83	2.0	29.0	5.0	2.3
2	12.5	10	125	77	~0.1	38.2	0.2	12.7
3	6.25	5.0	125	74	0.5	65.9	8.0	trace
4	6.25	5.0	125 (100)	70	~0.1	75.6	no	no
5	6.25	5.0	125 (60)[b]	77	1.0	52.5	no	no
6[c]	12.5	4.1[d]	125 (100)	78	2.0	46.7	3.0	2.0
7[c]	12.5	7.0[e]	125 (100)	73	2.0	56.4	no	no
8[c]	6.25	5.0	125 (100)	69	~0.1	86.9	no	no
9[f]	6.25	5.0	125 (100)	70	~0.1	75.6	no	no
10[g]	6.25	5.0	125 (100)[b]	80	1.0	12.2	trace	trace

[a] 15 g of H_2O is added.
[b] Diethyl ether instead of pentane.
[c] 25.0 g of CsF is added.
[d] LiOH instead of KOH.
[e] NaOH instead of KOH, 12.7 g of CsCl is added.
[f] 11.4 g of CsF is added.

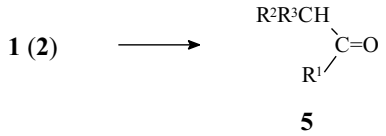
toxime vinylation more actively than KOH. Therefore a series of tests has been carried out to examine the effect of the CsX−MOH systems (M = Li, Na, K; X = F, Cl) on the synthesis of *O*-vinylacetoxime in a two-phase system; DMSO−pentane (Table 3, runs 6−10). The highest activity was observed with the CsF−KOH pair. In this case, the impurity-free oxime **2a** was prepared at a lower temperature in 86.9% yield (Table 3, run 8). This supports CsOH reputation as the strongest base and most active catalyst of the nucleophilic additions to acetylene.[16]

The replacement of DMSO by NMP with water content of approximately 1% did not allow preparation of *O*-vinylacetoxime even in trace amounts, in spite of the fact that the potassium oximate prepared beforehand was used. As shown by potentiometric titration of the reaction mixture, the lactone NMP ring-opening takes place to form the potassium salt of γ-aminobutyric acid. With N-methylpyrrolidones (NMP) (water content < 0.2%) under the conditions of run 3 (Table 3) *O*-vinyloxime **2a** was obtained without impurities, though in low yield (~16%).

Thus, the above investigations have enabled the development of a preparative method for the synthesis of *O*-vinylacetoxime under atmospheric pressure in 42% yield (32% higher than in the known procedure).[2] A two-phase system pentane−DMSO has been first applied for the acetoxime vinylation under pressure. This made it possible to shorten the reaction time (~6 minutes), obtain *O*-vinylacetoxime in 86.9% yield, inhibit pyrrolization of the *O*-vinylacetoxime formed and the side reactions of acetylene with water, which lead to hardly separable vinyloxybutadienes[3] and make the reaction a controllable process. A feasibility of acetoxime vinylation in NMP has been demonstrated.

The optimal conditions found for the acetoxime **1a** vinylation at elevated acetylene pressure in the two-phase system pentane−DMSO were applied to the synthesis of other aliphatic *O*-vinylketoximes. The conditions and results of the syntheses of *O*-vinylpinacolonoxime **2b** (R^1 = *t*-Bu, $R^2 = R^3$ = H) and previously unknown *O*-vinylmethylisopropylketoxime **2c** (R^1 = Me, $R^2 = R^3$ = Me) as well as *O*-vinyldiisopropylketoxime **2d** (R^1 = *i*-Pr, $R^2 = R^3$ = Me) are shown in Table 4.

In runs 2−4, the pyrroles **3** were identified as impurities. Besides, in all the runs the corresponding ketones **5** resulting from deoximation of the initial ketoximes **1** or *O*-vinylketoximes **2** were revealed.



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Thus, close to optimal conditions of the dialkylketoxime vinylation have been found. This enables *O*-vinyldialkylketoximes to be prepared in a yield of up to 88% (the preparation of *O*-vinylpinacolonoxime **2b** in 60% yield in an autoclave was reported).[3]

Table 4 Synthesis of *O*-Vinyldialkylketoximes under Acetylene Pressure (16 atm) [Ketoxime **1b–d** (85.6 mmol), KOH (5.64 g, 85.6 mmol), Pentane (100 mL), DMSO (125 mL), 0.1 h]

Run	Ketoxime	T (°C)	Yield (%)		
			O-Vinyl-ketoxime	Pyrrole	Ketone
1	**1b**	67	**2b**, 59.4	**3b**, none	**5b**, 6.2
2	**1b**	70	**2b,** 74.8	**3b**, 1.9	**5b**, 1.9
3	**1b**	73	**2b,** 73.8	**3b**, 0.6	**5b**, 2.7
4	**1c**	70	**2c,** 51.2	**3c**, trace	**5c**, trace
5	**1d**	70	**2d,** 87.8	none	**5d**, trace

The effect of factors influencing the yields and the selectivity of acetoxime vinylation was investigated in the synthesis of *O*-vinylketoximes having aromatic substituents. The experimental results are presented in Table 5.

The addition of petroleum ether (PE) (Table 5, runs 2−5) with a simultaneous temperature decrease from 75 °C to 58 °C allows selective vinylation to be carried out.

O-Vinylalkylarylketoximes, especially those having electron-withdrawing substituents, are more prone to pyrrolization compared to their aliphatic analogs.[3] Therefore it could be expected that *O*-vinylacetophenonoximes with electron-donating substituents in the benzene ring would be more resistant to pyrrolization than the unsubstituted *O*-vinylacetophenonoxime and this would allow a more selective preparation of the corresponding *O*-vinyloximes. This suggestion has been proven experimentally. Thus, if some amount of 2-phenylpyrrole **3e** is always present in the acetophenonoxime−acetylene reaction mixtures obtained under the conditions of runs 1−5, then the reactions of the methylarylketoximes **1f** and **1g** with acetylene proceed selectively to afford the corresponding *O*-vinylketoximes as the only reaction products (Table 5, runs 6 and 7).

It has been reported[3] that *O*-vinylacetoxime can explode during distillation under normal pressure. In order to assess the thermal stability of selected *O*-vinylketoximes, we have conducted measurements of the heats and temperatures of decomposition using differential scanning calorimetry (DSC) as well as the explosion temperature upon heating the samples in sealed ampoules. Explosion temperature tests for *O*-vinylacetoxime were carried out with the additives supposedly inhibiting the decomposition.

From the data obtained (Table 6) it follows that *O*-vinylketoximes are unstable energetic compounds (for comparison: Enthalpy of explosion of mercury fulminate, a known explosive compound is 1790 J/g[17]) with any correlation of energies of decomposition with molecular mass and radical branching being fuzzy. Considering these data, one should be very careful when working with pure new *O*-vinylketoximes.

As reported earlier,[3] *O*-vinylketoximes can be kept for a long time in a refrigerator without noticeable changes. Comparison of runs 1 and 2 (Table 6) does not show the generation of any explosion-initiating impurities in *O*-vinylacetoxime during its storage for 10 months at room temperature in a sealed vessel.

Dilution of *O*-vinylacetoxime with toluene (1:1) makes it safe and allows the mixture to be distilled under atmospheric pressure. It should be noted that slightly higher boiling toluene always dominates in the distillation vessel thus bringing up safe concentration in the still. The 1:4 toluene−*O*-vinylacetoxime mixture explodes but at a higher temperature (Table 6, run 4), than it does without toluene. In the presence of CuBr, the explosion of *O*-vinyloxime **2a** occurs even below room temperature (Table 6, run 5).

Solid products from the explosive decomposition of the *O*-vinyloxime **2a** (10−25% yield) were examined. These are dark-brown lustrous polymers, soluble in organic solvents (methanol, acetone, chloroform, DMSO). Their IR spectra (chloroform films) display broad bands and high background, that are characteristic of polymers. The bands of CH_3 and CH_2 groups (ν = 2870−2962, 1435, 1378 cm^{-1}) and bond stretching vibrations (ν = 1177 cm^{-1}) remain in the spectrum. Also, there is a broad intense signal at ν = 1650−1697 cm^{-1} in which a C=N stretching vibration frequency at ν = 1662 cm^{-1} and a C=O signal at ν = 1697 cm^{-1} are distinguished. The C=C double bonds may be present in this region too, whereas the CH_2=CH-O group absorption bands (ν = 3120, 3040, 1620, 1320, 1220, 980, 840 cm^{-1})[18] practically disappear. In addition, a series of new absorption bands appear. These are intense bands at ν = 3290 (NH) and 754 cm^{-1} (O-N=O) and weak bands at ν = 2218 (C≡N) and 1074 (C-O) cm^{-1}.

In the ^1H NMR spectra of the polymers, there are signals of CH= groups (δ = 6.61, 6.08, 5.86 ppm), CH_2-polymer chain (δ = 3.43 ppm) and a broad multiplet of alkyl group

Table 5 The Effect of Reaction Conditions on the Synthesis of *O*-vinylacetophenonoximes **2e–g** (**e**: R^1 = Ph, R^2 = R^3 = H; **f**: R^1 = 4-EtC_6H_4, R^2 = R^3 = H; **g**: R^1 = 4-$MeOC_6H_4$, R^2 = R^3 = H)

Run	Ketoxime	DMSO/PE (mL)	T (°C)	Time (h)	Yield (%)		
					O-Vinylketoxime	Pyrrole	Vinylpyrrole
1	**1e**	100/0	75	2.0	**2e**, 4.5	**3e**, 53.4	**4e**, 0.8
2	**1e**	100/50	75	2.0	**2e**, 14.3	**3e**, 46.4	**4e**, 8.5
3	**1e**	150/100	70	1.0	**2e**, 24.8	**3e**, 32.7	**4e**, 0.2
4	**1e**	150/100	66	~0.1	**2e**, 33.9	**3e**, 3.4	**4e**, no
5	**1e**	75/50	58	2.0	**2e**, 51.0	**3e**, 0.7	**4e**, no
6	**1f**	75/50	60	1.0	**2f**, 41.3	**3f**, no	**4f**, no
7	**1g**	75/50	60	1.0	**2g**, 52.4	**3g**, no	**4g**, no

Table 6 Temperatures and Energies (δQ) of Decomposition of *O*-vinylketoximes **2a–e** (0.4 g, Temperature Rise Rate 4 °C/min, Maximum Heating Temperature: 220 °C)

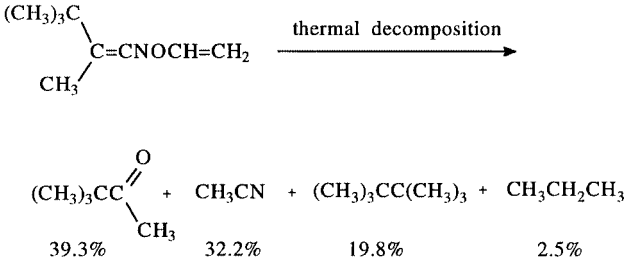
Run	*O*-Vinylketoxime (additive, %)	Decomposition Temperature[a] (°C)	δQ (J/g)	Explosion Temperature[b] (°C)
1	**2a**	102–110	1800	144
2	**2a**[c]			145
3	**2a** (PhMe, 30)			no explosion
4	**2a** (PhMe, 20)			160
5	**2a** (CuBr, 4)			<20
6	**2b**	115–134	1536	no explosion
7	**2c**	114–135	834	143
8	**2d**	110–130	1327	no explosion
9	**2e**	130–150	1267	155

[a] DSC.
[b] In a sealed ampoule.
[c] Sample kept at room temperature over 10 months prior to the test.

signals (δ = 0.83−2.20 ppm). Signals of the CH_2= groups present in the initial monomer (δ = 4.05 and 4.53 ppm) are not observed in the polymers.

Thus, the products obtained are likely to be copolymers containing both *O*-vinylacetoxime units and fragments resulting from *O*-vinylacetoxime thermal decomposition.

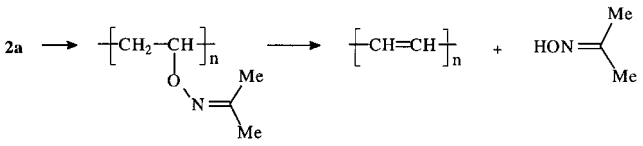
The analysis of liquid and gaseous products of thermal decomposition was carried out with an *O*-vinylpinacolonoxime **2b** sample, that did not explode even at 220 °C. In this case the ratio of the isolated gaseous, liquid and solid products was approximately 4:45:51. The liquid products were examined by GLC, IR, ^{13}C and ^{1}H NMR spectroscopy, and GLC−MS spectrometry. Of eight compounds fixed by the GLC−MS method, four species constituting 93.8 ms% were identified. These are 3,3-dimethyl-2-butanone, 2,2,3,3-tetramethylbutane, acetonitrile and propane dissolved in the liquid (the major propane portion is emitted into air upon opening the ampoules).



The IR spectrum of the liquid fraction shows no bands corresponding to the initial *O*-vinylketoximes and provides strong evidence for the presence of the above compounds in the condensate. In the spectrum there are also bands of CH_3 and CH_2 group stretching vibrations (ν = 2964, 2873, 2740, 1467, 1370 cm^{-1}), an intense band νC≡N (2243 cm^{-1}) as well as a fundamental intense resolved band $\nu_{C=O}$ at 1705−1719 cm^{-1}. Apart from these, a broadened band appears in the ν = 3612−3432 cm^{-1} region (possibly it is ν_{OH} of water either originated by decomposition or absorbed from air). The structures of the *O*-vinylketoxime decomposition products are supported by the ^{1}H NMR data. The ^{1}H NMR spectra display signals of the methylene (δ = 0.81−1.22 ppm) and CH_3C=O groups (δ = 1.95−1.98 ppm) and a small signal corresponding to the aldehyde function HC=O (δ = 9.80 ppm). Owing to a low concentration of propane in the mixture of volatile decomposition products, there are no signals of the CH_3 and CH_2 groups in the δ = 15−16 ppm region in the ^{13}C NMR spectrum.

All the *O*-vinylketoximes synthesized are relatively stable at room temperature. For example, when *O*-vinylacetoxime **2a** was kept for 10 months (initial purity was 98.7%, impurities were 0.2% of acetone and 1.1% of vinyloxybutadienes[19]), the acetone concentration was only increased to 2.5%. In addition, a brown polymeric product (~2.0% yield) was isolated.

The polymer gives an asymmetrical EPR singlet of free electron (g = 2.0048, ΔH = 8.8 Oe, N = 2.807. 10^{18} sp/g) corresponding to a polyconjugated system, apparently, polyacetylene formed according to the following scheme:

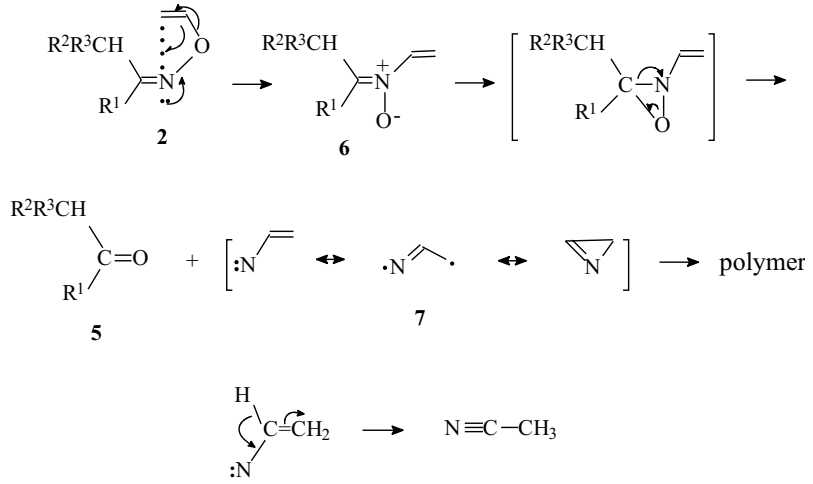


The rearrangement of *O*-vinylketoximes **2** to the parent ketones **5** and acetonitrile upon storage or heating may involve the formation of nitrone **6** followed by the release of vinylnitrene **7** further rearranging to acetonitrile (see decomposition of *O*-vinylpinacoloneoxime), polymerizing or copolimerizing with the *O*-vinylketoxime.[1,20]

Since under normal conditions the decomposition of *O*-vinylketoximes proceeds very slowly, the rate of *O*-vinylacetoxime decomposition at 97 °C was evaluated using a 12.5% *O*-vinylacetoxime solution in octane. The samples of reaction mixtures were taken every 10 minutes and analyzed by GLC (octane as an internal standard). The kinetic curve of *O*-vinylketoxime concentration change corresponds to that described by the first order equation ($k = 1.15 \cdot 10^{-4}$ sec^{-1}):

$-\ln x = kt$,

where *x* is the *O*-vinylacetoxime conversion and t is the reaction time. Taking into account that in the reaction mixture only a brown insoluble polymer is formed and that neither liquid nor gaseous products are discernible, it is suggested that a thermopolymerization is the main di-



rection of the *O*-vinylacetoxime transformation upon heating under the explosion temperature (140−145 °C).

^{1}H and ^{13}C NMR spectra were run on Bruker Avance DPX 250 (250 MHz) and Joel FX-90Q (90 MHz) instruments in $CDCl_3$, HMDS as internal standard. IR spectra were recorded on Bruker IFS 25 and Specord 75 IR spectrometers in microlayer. GLC was performed on an LCM-80 chromatograph: column 3.5 m × 3 mm, liquid phase XE-60 on Chromaton N-AW-HMDS, detector katharometer, gas-carrier He, temperature programming rate 8−12 °C/min.

The heats and temperatures of *O*-vinylketoximes decomposition were measured by differential scanning calorimetry on a Universal V2.3C TA instrument. Mass spectra were run on an LKB 2091 CLC-MS spectrometer, ionization energy 60 eV, capillary column 38 m long, SB-5 phase, isothermal conditions, column temperature 40 °C, ion source temperature 200 °C.

Commercial grade DMSO with H_2O content of ~0.4% and NMP (Merck, <0.2% H_2O), LiOH and NaOH (<2% H_2O), KOH (~15% H_2O, in fact 2KOH•H_2O), CsF and CsCl (ABCR, 99+%) were used in experiments.

Synthesis of *O*-Vinylacetoxime 2a under Atmospheric Pressure

Into a three-necked 100 mL flask equipped with a magnetic stirrer, bubbler, thermometer, dropping funnel and a gas outlet connected with a trap cooled to −78 °C, KOH (8.4 g, 128 mmol) and DMSO (50 mL) are placed and heated on a boiling water bath (92−95 °C). Then the reaction mixture is saturated with acetylene for 15 min and acetoxime **1a** (7 g, 96 mmol) in DMSO (20 mL) is added dropwise while bubbling acetylene for 4 h. Then acetylene is bubbled for 2 h more. The *O*-vinylacetoxime formed is condensed in the trap together with dissolved acetylene. The contents of the trap are heated to r.t. (which is accompanied by liberation of the dissolved acetylene) and H_2O (1 mL) is added to the remaining mixture of volatile reaction products. The upper layer is separated, dried ($MgSO_4$), weighed and analyzed (GLC). As a result, *O*-vinylacetoxime (4.45 g, 89% purity) corresponding to 3.96 g (49 mmol) of pure product is obtained. The yield of *O*-vinylacetoxime is 42% (Table 2, run 5).

Vinylation of Acetoxime under Pressure in the KOH−DMSO System

A steel 1 L rotating autoclave is charged with a potassium oximate solution in DMSO prepared by heating of a mixture of acetoxime (6.25 g, 85.5 mmol) and KOH (5.0 g, 75.5 mmol) in DMSO (125 mL) at 110−115 °C for 5 min. The mixture is saturated with acetylene under pressure (16 atm) and subjected to heating for 30 min to the reaction temperature of 74 °C. Once the reaction temperature is reached, the heating is immediately stopped, and the autoclave furnace opened. After cooling to r.t., the reaction mixture is discharged, neutralized with dry ice, and analyzed by GLC. The reaction mixture contains *O*-vinylacetoxime **2a** (5.57 g, 65.9% yield) and 2-methylpyrrole (0.55 g, 8.0% yield) (Table 3, run 3).

Vinylation of Acetoxime under Pressure in the KOH−Pentane−DMSO System

A steel 1 L rotating autoclave is charged with pentane (100 mL) and a potassium oximate solution in DMSO prepared by heating of a mixture of acetoxime (6.25 g, 85.5 mmol) KOH (5.0 g, 75.5 mmol) and CsF (25.0 g, 164.5 mmol) in DMSO (125 mL) at 110−115 °C for 10 min. The mixture is saturated with acetylene and subjected to heating for 30 min at 69 °C and kept at this temperature for 2 h. After this, the autoclave furnace is opened and the reaction mixture cooled to r.t. Excess acetylene is let out to normal pressure through a trap cooled with a mixture of acetone and dry ice (−78 °C). The reaction mixture is discharged, and the pentane layer separated. After vacuum distillation (1−3 mm Hg) of volatile products from DMSO, they are combined with the pentane solution and the trap condensate, washed with H_2O, dried (calcined $MgSO_4$), and analyzed by GLC (*O*-vinylacetoxime content: 7.36 g, yield 86.9%) (Table 3, run 8). No acetoxime is present in the reaction mixture (GLC).

Vinylation of Acetoxime in the KOH−Et_2O−DMSO System

A steel 1 L rotating autoclave is charged with Et_2O (60 mL) and a potassium oximate solution in DMSO prepared by heating of a mixture of acetoxime (6.25 g, 85.5 mmol) and KOH (5 g, 75.5 mmol) in DMSO (125 mL) at 110−115 °C for 10 min. The mixture is saturated with acetylene under pressure (11 atm), heated for 30 min to 77 °C and kept at this temperature for 1 h. Then the autoclave furnace is opened and the reaction mixture cooled to r.t. Excess acetylene is let out to normal pressure through a trap cooled to −78 °C. The reaction mixture is discharged, the Et_2O layer separated. From the DMSO layer, the reaction products are distilled off in vacuum (1−3 mm Hg) and combined with the Et_2O solution and the trap condensate, washed with H_2O, dried (calcined $MgSO_4$), and analyzed by GLC. The yield of *O*-vinylacetoxime is 52.5% (Table 3, run 5).

Vinylation of Acetoxime in the KOH−NMP System

A steel 1 L rotating autoclave is charged with acetoxime (6.25 g, 85.5 mmol), KOH (5.0 g, 75.5 mmol) in NMP (125 mL). The mix-

ture is saturated with acetylene under 14 atm pressure, and heated for 30 min to 75 °C. Then the autoclave furnace is opened and the reaction mixture is cooled to r.t. Excess acetylene is let out to normal pressure through a trap cooled with a mixture of acetone and dry ice (−78 °C). The reaction mixture is discharged, neutralized with dry ice, and analyzed by GLC. The reaction mixture contains *O*-vinylacetoxime (1.35 g, yield: 15.9%).

Vinylation of Pinacolonoxime in the KOH−Pentane−DMSO System

A steel 1 L rotating autoclave is charged with pentane (100 mL) and a potassium oximate solution in DMSO prepared by heating of a mixture of pinacolonoxime (9.85 g, 85.6 mmol) and KOH (5.64 g, 85.6 mmol) in DMSO (125 mL) at 110−115 °C for 5 min. The mixture is saturated with acetylene under 16 atm pressure and heated for 30 min to the reaction temperature 70 °C. After this time, heating is ceased immediately and the autoclave furnace is opened, this means about 6 min exposure to 70 °C. After cooling to r.t., the excess acetylene is let through a trap cooled to −78 °C. The reaction mixture is discharged and the pentane layer separated. The DMSO solution is extracted with pentane 5 times. The pentane extracts are combined with the trap condensate, washed with H_2O (3 × 20 mL), and dried (calcined $MgSO_4$). The major pentane portion is removed by distillation. The remaining portion is distilled off in vacuum (50 mm Hg) at 40 °C and analyzed by GLC. As a result, *O*-vinylpinacolonoxime is obtained (6.98 g, 98.9% purity of the extract). The reaction mixture is diluted with H_2O, extracted with Et_2O (4 × 30 mL), the extract is washed with H_2O to remove DMSO and dried ($MgSO_4$). Et_2O is removed in the same manner as pentane. The residue is analyzed by GLC to determine *O*-vinylpinacolonoxime (1.40 g, total yield: 68.8%), pinacolonoxime (1.37 g, conversion 92%) and pinacolone (1.9%). The yield of *O*-vinylpinacolonoxime corrected for the incomplete conversion of initial ketoxime is 74.8% (Table 4, run 2).

O-Vinylpinacolonoxime **2b**: bp 71 °C (60 mm Hg), $[\alpha]_D^{23}$ 1.4400 [Lit.[3] bp 54−55 °C (26 mm Hg), $[\alpha]_D^{20}$ 1.4400].

O-Vinyloximes **2c** and **2d** were prepared analogously.

O-Vinylmethylisopropylketoxime 2c

Bp 75 °C (95 mm Hg), $[\alpha]_D^{20}$ 1.4390.

IR (*E*-isomer): ν = 3050 (ν = CH), 2969 ($\nu_{as}CH_3$), 2933 (νCH_2), 2875 (ν_sCH_3), 1669 (νC = N), 1652 (ν_{trans} C = C), 1623 (ν_{cis} C = C), 1466 ($\delta_{as}CH_3$), 1386 (δ_sCH_3+δCH_2), 1367 (δ_sCH_3), 1246 (ν C-C-C), 1177 (νC-O), 1151 (δCH$_3$, νC-O), 979 (νN-O), 957 (δ_{trans} = CH), 875 (γC-C-C), 803 (γCH$_3$) cm^{-1}.

^{1}H NMR (250 MHz) (*E*-isomer): δ = 6.863 (q, CH =), 4.531 and 4.046 (dd, J_{trans} = 14.3, J_{cis} = 6.7, J_{gem} = 1.5 Hz, CH_2 =), 2.523 m [$CH(CH_3)_2$], 1.846 (s, CH_3), 1.091 [d, $CH(CH_3)_2$].

^{1}H NMR (250 MHz) (*Z*-isomer): δ = 6.846 (q, CH =), 4.508 and 4. 044 (dd, J_{trans} = 14.3, J_{cis} = 6.7, J_{gem} = 1.5 Hz, CH_2 =), 2. 405 [m, $CH(CH_3)_2$], 1.807 (s, CH_3), 1.034 [d, $CH(CH_3)_2$].

^{13}C NMR (62.89 MHz) (*E*:*Z* = 6:1): δ = 164.657 (>C = N), 152.615 (= CH), 86.999 (= CH_2), 34.295 [$CH(CH_3)_2$], 19.625 [$CH(CH_3)_2$], 11.830 (CH_3).

Anal. Calcd for $C_7H_{13}NO$: C, 66.11; H, 10.30; N, 11.01. Found: C, 65.94; H, 10.17; N, 11.09.

O-Vinyldiisopropylketoxime 2d

Bp 59 °C (25 mm Hg), $[\alpha]_D^{24}$ 1.4386.

IR: ν = 3070, 3050 (ν = CH), 2967 ($\nu_{as}CH_3$), 2934 (νCH_2), 2875 (ν_sCH_3), 1667 (νC = N), 1641 (ν_{trans} C = C), 1619 (ν_{cis} C = C), 1486 ($\delta_{as}CH_3$), 1385 (δ_sCH_3+δCH_2), 1366 (δ_sCH_3), 1246 (ν C-C-C), 1181 (νC-O), 1154 (δCH$_3$, νC-O), 1119 (δCH$_3$), 979 (νN-O), 951 (δ_{trans} = CH), 890 (γC-C-C), 829 (γCH$_2$, γCH$_3$) cm^{-1}.

^{1}H NMR (250 MHz): δ = 6.827 (q, CH =), 4.496 and 4.013 (dd, J_{trans} = 14.3, J_{cis} = 6.9, J_{gem} = 1.4 Hz, CH_2 =), 3.023 and 2.544 [m, $2CH(CH_3)_2$], 1.146 and 1.119 [d, $2CH(CH_3)_2$].

^{13}C NMR (62.89 MHz): δ = 171.343 (>C = N), 152.872 (= CH), 86.716 (= CH_2), 31.463, 28.858 [$2CH(CH_3)_2$], 21.064, 19.119 [$2CH(CH_3)_2$].

Anal. Calcd for $C_9H_{17}NO$: C, 69.63; H, 11.04; N, 9.02. Found: C, 69.47; H, 10.98; N, 9.09.

Vinylation of Acetophenonoxime 1e in the KOH−Petroleum ether−DMSO System

A steel 1 L rotating autoclave is charged with petroleum ether (50 mL, bp 40−70 °C) and a potassium oximate solution in DMSO prepared by heating of a mixture of acetophenonoxime **1e** (6.75 g, 50 mmol) and KOH (3.0 g, 53.5 mmol) in DMSO (75 mL) at 115−120 °C for 5 min. The mixture is saturated with acetylene under pressure of 14 atm and heated for 30 min to the temperature of 58 °C, after that heating being continued for 2 h. After cooling to r.t., the reaction mixture is discharged and the petroleum ether layer separated. The DMSO solution is extracted with petroleum ether (5 × 20 mL). The extract is washed with H_2O (3 × 20 mL), dried ($MgSO_4$), and petroleum ether is removed by distillation to obtain *O*-vinylacetophenonoxime **2e** (4.11 g, 51.0%, 98.9% purity). The reaction mixture is diluted with H_2O and extracted with Et_2O, the Et_2O extract is washed with H_2O to remove DMSO and dried ($MgSO_4$). After Et_2O removal, the residue containing 2-phenylpyrrole **3e** (0.05 g, yield: 0.7%) and acetophenonoxime **1e** (2.19 g, conversion 67.6%) is obtained (Table 5, run 5). Colorless oil, bp 80 °C (4 mm Hg), $[\alpha]_D^{20}$ 1.5542.

O-Vinylacetophenonoximes **2f** and **2g** were prepared analogously.

O-Vinyl-4-ethylacetophenonoxime 2f

Colorless oil.

IR: ν = 3075 (ν = CH), 2963 ($\nu_{as}CH_3$), 2934 (νCH_2), 2838 (ν_sCH_3), 1639 (ν_{trans}C = C), 1607, 1513 (ν_{cis}C = C benzene ring), 1459 ($\delta_{as}CH_3$), 1385 (δ_sCH_3+δCH_2), 1372 (δ_sCH_3), 1249 (νC-C-C), 1172 (νC-O), 1119 (δCH$_3$), 972 (νN-O), 958 (δ_{trans} = CH), 885 (γC-C-C), 834 (γCH$_2$, γCH$_3$) cm^{-1}.

^{1}H NMR (90 MHz): δ = 7.52−7.10 (m, Ph), 7.00 (q, CH =), 4.64 and 4.10 (dd, CH_2 =), 2.56 (q, CH_2), 2.21 (s, Me), 1.15 (t, $MeCH_2$).

Anal. Calcd for $C_{12}H_{15}NO$: C, 76.19; H, 7.93; N, 7.41. Found: C, 76.37; H, 7.65; N, 7.23.

O-Vinyl-4-methoxyacetophenonoxime 2g

White crystals, mp 53−54 °C.

IR: ν = 3075 (ν = CH), 2963 ($\nu_{as}CH_3$), 2934 (νCH_2), 2838 (ν_sCH_3), 1639 (ν_{trans}C = C), 1607, 1513 (ν_{cis}C = C benzene ring), 1459 ($\delta_{as}CH_3$), 1385 (δ_sCH_3+δCH_2), 1372 (δ_sCH_3), 1249 (νC-C-C), 1172 (νC-O), 1119 (δCH$_3$), 972 (νN-O), 958 (δ_{trans} = CH), 885 (γC-C-C), 834 (γCH$_2$, γCH$_3$) cm^{-1}.

^{1}H NMR (90 MHz): δ = 7.60−6.87 (m, Ph), 7.00 (q, CH =), 4.65 and 4.13 (dd, CH_2 =), 3.77 (s, MeO), 2.24 (s, Me).

Anal. Calcd for $C_{11}H_{13}NO_2$: C, 69.11; H, 6.81; N, 7.33. Found: C; 69.47; H, 7.05; N, 7.09.

A Technique to Determine *O*-Vinylketoxime Explosion Temperature

A sample of *O*-vinylketoxime **2a−e** (400 mg) sealed upon cooling (−78 °C) in a conventional glass ampoule (2.0 mL) was placed into a brass casing with a capillary opening to remove excess pressure and subjected to heating (bath, silicone oil). Explosion was accompanied by emission of volatile products. Immediately after the explosion, the bath temperature was fixed and the casing was cooled

to r.t. A mixture of fine-dispersed fragments of glass and polymers was treated with MeOH. The solution was separated by decantation. After MeOH evaporation, 30−50 mg of a dark-brown powdery product was collected.

Analysis of the *O*-Vinylpinacolonoxime 2b Decomposition Products

A sample of O-vinylpinacolonoxime **2b** (400 mg) was charged into a glass ampoule (1.5 mL), the ampoule was cooled to −78 °C, sealed, placed into a brass casing and heated (bath, silicone oil) to 220 °C, heating time 50 min. After cooling to r.t., the casing with the ampoule was cooled in liquid N_2, the ampoule was taken out and unsealed. Upon elevating the ampoule temperature, a vigorous evolution of gas from the reaction mixture took place. Two syntheses conducted according to this procedure were combined and a colorless liquid was collected on heating to 190 °C into a cooled trap. Four major condensate components: 3,3-dimethyl-2-butanone (39.3%), MeCN (32.2%), 2,2,3,3-tetramethylbutane (19.8%) and propane (2.5%), altogether 93.8% of the mass, were identified (GLC−MS, IR, ^{1}H and ^{13}C NMR).

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