2,5-Dihydro-1*H*-imidazole-Based Nitroxides as Prospective Mediators in Living Radical Polymerization

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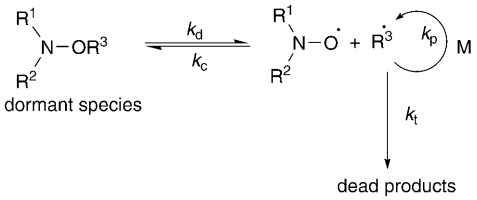
Dedicated to the memory of Professor *Hanns Fischer*

A number of spectroscopic methods were applied to obtain kinetic parameters of reactions modelling the 2,5-dihydro-1*H*-imidazole 1-oxide mediated living polymerization of acrylates. The homolysis rate constants of alkoxyamines based on five nitroxides were measured by EPR spectroscopy at different temperatures. The recombination rate constants k_c between the corresponding alkyl radicals and the nitroxides were measured by means of laser flash photolysis. The time-resolved chemically induced dynamic nuclear polarization (TR-CIDNP) experiments revealed the negligible contribution of disproportionation in the recombination reaction. In addition, the thermodecomposition of alkoxyamines in the NMR probe showed the absence of intramolecular elimination of hydroxylamines from the corresponding alkoxyamines. Analysis of the kinetic parameters showed that the 2,5-dihydro-1*H*-imidazole 1-oxide type radicals are promising mediators for the living polymerization of acrylates and methacrylates.

Introduction. – Nitroxide-mediated polymerization [1][2] (NMP) is a fine synthetic technique, which allows for the design of new types of homo- and copolymers with well-defined architectures and narrow molecular-mass distributions [3]. The principal mechanism of NMP (*Scheme 1*) involves the reversible dissociation of a dormant nitroxide end-capped polymer chain with rate constant k_d, the propagation of C-centered radicals with rate constant k_p, the cross-coupling reaction between the nitroxide and the growing polymer chain with rate constant k_c, and simultaneous irreversible self-termination reactions of the C-centered radicals with rate constant k_t.

Scheme 1



The main contribution to the understanding of the NMP mechanism has been done by *Fischer* [4][5] and *Goto* and *Fukuda* [6]. It has been shown [7][8] that the equilibrium constant $K = k_d/k_c$ should fall in the range from 10^{-7} to 10^{-11} mol l^{-1} for efficient NMP of common monomers. Despite the fact that NMP of monomers based on styrene (=ethenylbenzene) and acrylate (=prop-2-enoate) using a large variety of nitroxides became a routine procedure [3][9], the development of new mediators to be used in the (co)polymerization of methacrylates (=2-methylprop-2-enoates), acrylamides (=2-prop-2-enamides), and dienes [10] still remains a challenging task for many research groups [11–13].

Stable 2,5-dihydro-1*H*-imidazol-1-yloxy radicals with different bulky substituents at the positions 2 and 5 of the imidazole ring (*Fig. 1*) are efficient [14] as pH probes in biological systems, but the overall suitability of these nitroxides for the purposes of NMP has not yet been determined. Aiming at possible applications of this type of nitroxides (*Fig. 1*) as mediators in NMP of acrylate-type monomers, we studied the model reaction occurring during decomposition/reformation of the corresponding alkoxyamines. The present communication deals with the application of a number of experimental spectroscopic techniques to acquire maximum kinetic information on these processes.

Results and Discussion. – *The Coupling Rate Constants* k_{cl}. For the measurements of radical cross-termination rate constants k_c, we applied the same approach as previ-

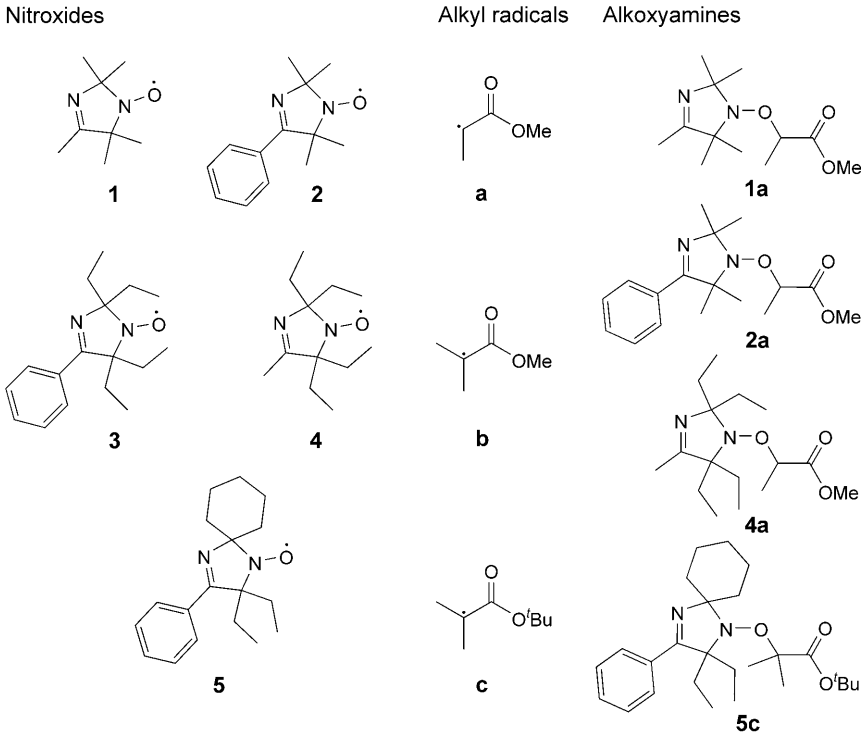


Fig. 1. *Model nitroxides* **1**–**5**, *alkyl radicals* **a**–**c**, *and corresponding alkoxyamines*

ously published by *Sobek* and *Fischer* [15], and *Ingold* and co-workers [16–18]. The C-centered radicals **a**–**c** (MP = methyl propionate-2-yl (= 2-methoxy-1-methyl-2-oxoethyl), MiB = methyl isobutyrate-2-yl (= 2-methoxy-1,1-dimethyl-2-oxoethyl), and *t*BiB = '*tert*-butyl isobutyrate-2-yl' (= 2-(*tert*-butoxy)-1,1-dimethyl-2-oxoethyl), respectively) were generated by laser pulse photolysis of the corresponding symmetric ketones R–CO–R. These radicals are the simplest models of propagating radicals formed during the polymerization of methyl or *tert*-butyl methacrylate and methyl acrylate. The photochemistry of the ketones is known [19]. After the excitation of the n–π^* transition and intersystem crossing, the ketones undergo α-cleavage from the triplet state yielding geminate (in-cage) acyl-alkyl radical pairs. The geminate reactions of recombination and disproportionation result in the restoration of the initial ketone R–CO–R and in the formation of aldehyde R–CHO and alkene R(–H). The escaped acyl radicals undergo a fast decarbonylation reaction with the rate constant $k_{CO} = 2 \cdot 10^7$ s^{-1} for MP (**a**) [20] and $k_{CO} = 8 \cdot 10^6$ s^{-1} for MiB (**b**) [21]. The consequent bulk reactions of radical termination k_t rise to the formation of products R–R, RH, and R(–H). In the presence of nitroxide, these reactions are partly or entirely replaced by the formation of alkoxyamine R–Y due to the coupling of C-centered radicals R with the nitroxide Y, and by the formation of the hydroxylamine Y–H and the alkene due to the H-abstraction from the C-centered radicals by the nitroxide [15][22]. In the absence of nitroxides, the C-centered radicals decay in a second-order reaction with $k_t = 1.8 \cdot 10^9$ M^{-1} s^{-1} for MiB and $k_t = 1.2 \cdot 10^9$ M^{-1} s^{-1} for MP. With the nitroxide added, the kinetic curves become first-order decay. The observed pseudo-first-order rate constant k_m was found to be proportional to the nitroxide concentration, $k_m = k_0 + k_c \cdot [Y]$ (k_0 for the processes observed in the absence of nitroxide). The concentration dependencies of k_m are shown in *Fig. 2*, and the calculated values of k_c are listed in *Table 1*. One can see that k_c values decrease with increasing congestion around both the nitroxide moiety and the alkyl-radical centre, in accordance with previously observed trends for other nitroxides [23–25].

Table 1. *Coupling Rate Constants for the Reaction of Nitroxides* **1**–**3** *and* **5** *with Alkyl Radicals* **a**–**c** *in Benzene at Room Temperature*

Nitroxide	Radical	k_c [10^8 M^{-1} s^{-1}]
1	**a**	16.0(2.0)
1	**c**	4.8(1.5)
2	**a**	12.0(2.0)
2	**b**	6.3(1.4)
3	**a**	4.6(1.8)
5	**c**	1.2(0.3)

EPR Measurements of Homolysis Rate Constants k_d. The rate constants of the alkoxyamines decay k_d were obtained by monitoring the appearance of the nitroxide-radical EPR signal during decomposition of the corresponding alkoxyamines [26]. The chlorobenzene solution was used with O_2 as a scavenger for the C-centered radicals. The growth of nitroxide-radical concentration obeyed to the expected first-order kinetic law. The evaluation of the activation energy of homolysis was made by

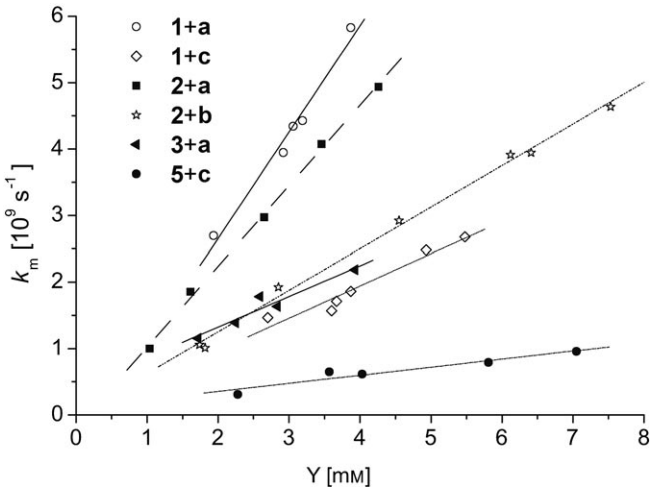


Fig. 2. *Concentration dependencies of the apparent rate constant* k_m *for the cross-coupling of radicals* **a**–**c** *with nitroxides* **1**–**3** *and* **5** *in benzene at room temperature*

using the averaged frequency factor $A = 2.4 \cdot 10^{14}$ s^{-1} [27–29]. The ΔE_a (8.7 kJ/mol, *Table 2*) measured for homolysis of the C–ON bond between **1a** and **4a** is close to the value expected ($\Delta E_a = 11.0$ kJ/mol estimated for the styrene fragment) [23][26][29].

Table 2. *Experimentally Measured Rate Constants of Thermal Decomposition of Alkoxyamines* **1a**, **2a**, **4a**, *and* **5c** *in* C_6H_5Cl

	T [°]	k_d [s^{-1}] [120°][a)]	E_a [kJ/mol]
1a	140	$1.4 \cdot 10^{-5}$	144.8
2a	140	$1.1 \cdot 10^{-5}$	145.5
4a	130	$1.9 \cdot 10^{-4}$	136.1
5c	80–120	$6.8 \cdot 10^{-3}$	124.5

[a)] Estimated with $A = 2.4 \cdot 10^{14}$ s^{-1}, see [23][26][27].

Time-Resolved Chemically Induced Dynamic Nuclear Polarization (TR-CIDNP) *Experiments and Side Reactions.* The photolysis of the ketones in the magnetic field of the NMR spectrometer [24] led to the formation of highly intensive CIDNP (*Fig. 3*). The absorption CIDNP signals are observed for the initial compound R–CO–R (**I** in *Fig. 3*,*a*), and the emission signals for the escape products R–R and RH (**IV** and **III**, resp., in *Fig. 3*,*a*), as predicted by *Kaptein*'s rules [30] ($\Delta g > 0$, $A(\mathrm{Me}) > 0$). The alkene R(–H) (**II** in *Fig. 3*,*a*) can be formed both in geminate reactions and in the bulk. Therefore, immediately after the laser pulse, the signal from the Me group of R(–H) is in emission [24], which then decays on the microsecond timescale due to the compensation by absorptively polarized molecules of R(–H) formed in the bulk (the so-called CIDNP cancellation effect [31]). In the presence of nitroxides, both the CIDNP spectra (*Fig. 3*,*b*) and the kinetics change significantly [24]. Strong

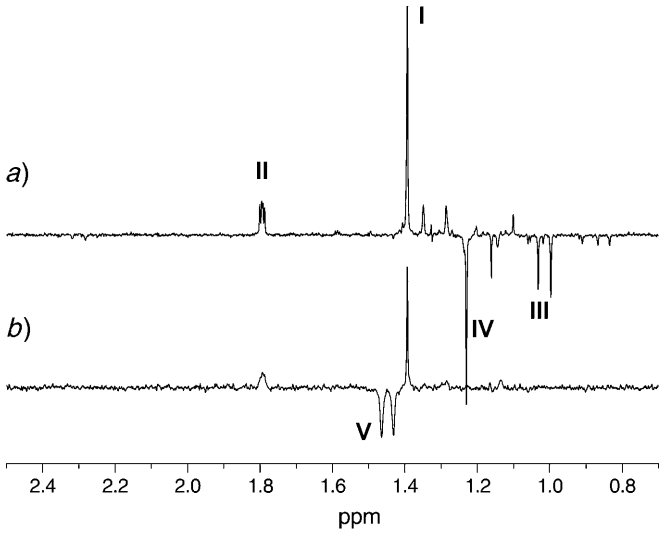


Fig. 3. *CIDNP Spectrum taken 100 microsecond after laser pulse photolysis of ketone* **I** a*) in the absence and* b*) in the presence of nitroxide* **2**. **I** = $MeOOCC(Me)_2COC(Me)_2COOMe$, **II** = $MeOOCC(Me)=CH_2$, **III** = $MeOOCCH(Me)_2$, **IV** = $MeOOCC(Me)_2C(Me)_2COOMe$, and **V** = $MeOOCC(Me)_2Y$ (Y derived from nitroxide **2**)

emissive signals are observed at δ 1.4–1.5, which correspond to the Me group of the coupling product R–Y (**V** in *Fig. 3*, *b*). The polarization shows the fast growth in intensity at short time delays, and then reaches a plateau after *ca.* 1–2 μs. The presence of the nitroxide inhibits the formation of bulk products R–R, RH and R(–H), as indicated by the absence of any emissive bulk polarization on these products. The absence of bulk polarization from the products R(–H) and YH, demonstrates the negligible contribution of H-abstraction in the reaction between R and Y (< 2%). A typical CIDNP spectrum for nitroxide **2** and alkyl radical **b** is shown in *Fig. 3*.

Thermal Decomposition of Alkoxyamines in NMR Probe. The most important process which can interfere with the reactions shown in *Scheme 1* [22][32][33] is the transfer of H–C(β) from the alkyl radical to the nitroxide. This process leads to the formation of a polymeric chain with a terminal C=C bond and a hydroxylamine and can occur due to a radical cross-disproportionation (*vide supra*) or a nonradical hydroxylamine elimination [22]. To check contributions of these reactions, the thermal decomposition of the three alkoxyamines **1a**, **2a**, and **4a** was studied by means of ^{1}H-NMR in degassed solution and in the absence of other scavengers. The analysis of the experimental NMR spectra revealed no formation of methyl acrylate after 10 h of homolysis at 120°[1]), which agrees with the CIDNP experiments and also allows us to neglect the nonradical decomposition of alkoxyamines.

Fischer*'s Diagram Approach.* For the prediction of the NMP result, *Fischer* [8][34][35] developed the phase-diagram approach (*Fig. 4*) based on *Eqns. 1–3*, pro-

[1]) This time corresponds to roughly 50% decomposition under scavenging conditions.

viding both the living fraction ($0 < \Phi \leq 1$ being the percentage of dead chains, *Eqn. 1*), the polydispersity index (*PDI* with $\delta = PDI - 1$ ($PDI > 1.1$), *Eqn. 2*), and the time of polymerization ($t_{90\%}$ being the time for 90% monomer conversion, *Eqn. 3*). For a given monomer (k_p and k_t), the success of the NMP experiments, *i.e.*, high livingness ($\Phi > 80\%$) and high control ($PDI < 1.5$), depends on the k_d and k_c values of the dormant species. Hence, applying *Eqns. 1–3* for given experimental conditions – polymerization temperature, polymerization time, conversion, chain length – it is possible to predict the feasibility of the polymerization or not. Therefore, this approach requires an accurate determination of k_d and k_c. The values of k_p and k_t were given by *Buback* and co-workers [36][37] as averaged values from PLP-SEC experiments, where the monomer conversion did not exceed 3%.

$$\frac{k_d}{k_c} \leq \frac{k_p \cdot [\text{alkoxyamine}]_0}{2\ln 10 \cdot k_t} \cdot \Phi^2 \tag{1}$$

$$k_d \cdot k_c \geq \frac{\pi \cdot k_p^3 \cdot [\text{alkoxyamine}]_0}{k_t} \cdot \frac{1}{\delta^2} \tag{2}$$

$$\frac{k_d}{k_c} \geq \frac{(2\ln 10)^3 \cdot k_t}{9 \cdot k_p^3 \cdot [\text{alkoxyamine}]_0 \cdot t_{90\%}^2} \tag{3}$$

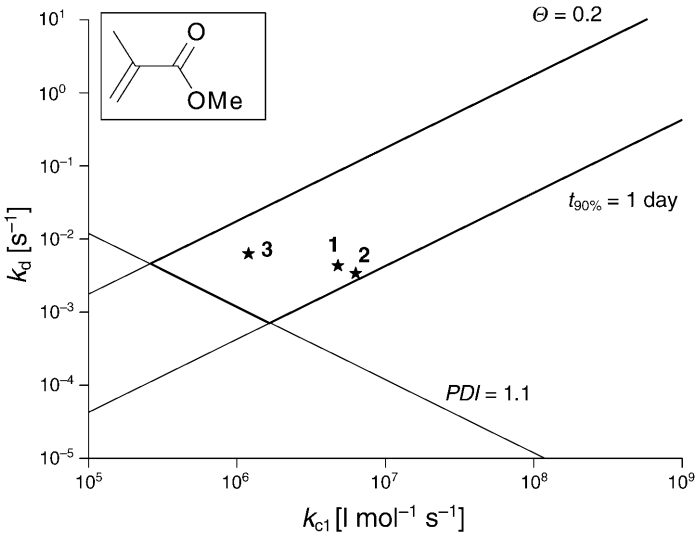


Fig. 4. Fischer*'s phase diagram for NMP of methyl methacrylate.* Parameters for *Eqns. 1–3*: *T* 80°, $[\text{alkoxyamine}]_0 = 5 \cdot 10^{-2}$ mol/l, $k_p = 1298$ l mol^{-1} s^{-1}, $k_t = 3.21 \cdot 10^7$ l mol^{-1} s^{-1} (see [8]), values of k_{c1} and k_d from *Table 3*.

As it was shown by *Tordo* and co-workers [38], the correct calculation of NMP could be done only by taking account of the k_d and k_c dependence on the length of the polymer chain. Therefore, k_d and k_c values implemented in the phase diagrams

(*Figs. 4* and *5*) were corrected for the account of the penultimate effect on homolysis in cases of methyl methacrylate (MMA) [28][39] and butyl acrylate [40] polymerizations, as well as for the account of the chain-length effect on the recombination [41][42]. The phase-diagram approach (*Fig. 4*) predicts possible successful NMP of MMA lasting one day for nitroxide **1**–**3** at 80°, achieving 90% conversion, and 80% of living chains, and very low *PDI*. In the case of the methyl acrylate (*Fig. 5*), successful NMP is predicted for nitroxides **3** and **4**, reaching 90% conversion in one day, and higher *PDI* (1.4), and 80% living chains. Aiming at slightly higher *PDI*, successful NMP of methyl acrylate would be possible with nitroxides **1** and **2**.

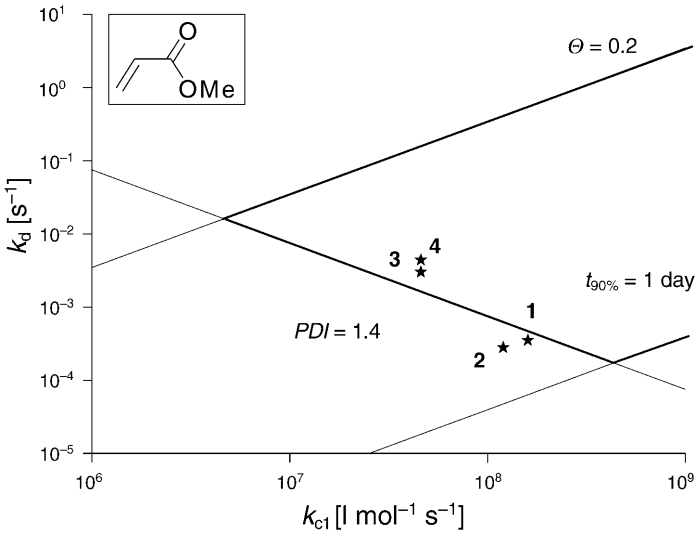


Fig. 5. Fischer's *phase diagram for NMP of methyl acrylate.* Parameters for *Eqns. 1–3*: *T* 140°, $[\text{alkoxyamine}]_0 = 10^{-3}$ mol/l, $k_p = 114.2 \cdot 10^3$ l mol^{-1} s^{-1}, $k_t = 5.05 \cdot 10^7$ l mol^{-1} s^{-1} (see [8]), values of k_{c1} and k_d from *Table 3*.

Conclusions. – We showed, that for the proper ratio of homolysis/reformation rate constants k_d and k_c in the absence of side reactions (hydroxylamine elimination), the nitroxides studied can be promising mediators in polymerization of acrylate and methacrylate monomers. In both cases, the living fraction is expected to be above 80% at 90% conversion at a reasonable reaction time (24 h), and with the *PDI* values in the acceptable range of 1.1–1.4. The polymerization experiments are in progress, and the results will be published in a subsequent report.

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Table 3. *Estimated* k_{c1} *and* k_d *for the Phase Diagrams for the Polymerization of Methyl Methacrylate and Methyl Acrylate*

Reaction	k_{c1}[a]) [10^6 M^{-1} s^{-1}]	E_a[b]) [kJ/mol]	k_d[c]) [s^{-1}]
1+**a**⇌**1a**	160(2)[d])	144.8	$3.5\cdot10^{-4}$ [e])
2+**a**⇌**2a**	120(2)[d])	145.5	$2.8\cdot10^{-4}$ [e])
3+**a**⇌**3a**	46(1.8)[d])	137.4[f])	$3.0\cdot10^{-3}$ [e])
4+**a**⇌**4a**	46(1.8)[d])[g])	136.1	$4.4\cdot10^{-3}$ [e])
1+**b**⇌**1b**	4.8(1.5)[h])[i])	125.7[j])	$4.3\cdot10^{-3}$ [k])
2+**b**⇌**2b**	6.3(1.4)[h])	126.4[l])	$3.4\cdot10^{-3}$ [k])
3+**b**⇌**3b**	1.2(0.3)[h])[m])	124.5[m])	$6.3\cdot10^{-3}$ [k])

[a]) k_c are given at room temperature. It was assumed that no significant changes occur with T, see [15–18][23][24]. [b]) Given in *Table 2* unless otherwise mentioned. [c]) Estimated with $A=2.4\cdot10^{14}$ s^{-1}, see [26][27][29]. [d]) To take into account the chain-length effect, $k_{c1}=k_c/10$ (see [41]). k_c given in *Table 1* unless otherwise mentioned. [e]) Chain-length effect was assumed around a factor three, *i.e.*, $k_d=3\cdot A\exp(-E_a/RT)$, see [40]. [f]) Estimated from E_a(**5c**) + 19.1 kJ/mol (see [28]), assuming the cyclohexyl group as sterically demanding as two Et groups. [g]) A weak polar effect was assumed as exemplified with **1** and **2** (*Table 1*). [h]) To take into account the chain-length effect, $k_{c1}=k_c/100$ (see [42]). k_c given in *Table 1* unless otherwise mentioned. [i]) The influence of the ester-group size on k_c was assumed to be insignificant, see [25]. [j]) Estimated from E_a(**1a**) – 19.1 kJ/mol (see [28]). [k]) Due to the penultimate effect [38], $k_d=70\cdot A\exp(-E_a/RT)$, see [39]. [l]) Estimated from E_a(**2a**) – 19.1 kJ/mol (see [28]). [m]) k_{c1}(**3b**) = k_{c1}(**5c**) and k_d(**3b**) = k_d(**5c**) assuming the same steric effect for two Et groups and the cyclohexyl group, see [29].

Experimental Part

General. The solvents benzene, chlorobenzene, and MeCN were distilled prior to use. CC = Column chromatography. UV Spectra: *HP-Agilent-8453* spectrometer; EtOH solns.; in nm (log ε). IR Spectra: *Bruker-Vector-22-FT-IR* spectrometer; KBr pellets (concentration 0.25%; pellet thickness 1 mm). ^{1}H-NMR Spectra: *Bruker-AV300* (300.1 MHz) spectrometer; 5% solns.; with the solvent signal as the standard; δ in ppm, J in Hz. ^{13}C-NMR Spectra: *Bruker-AV300* (75.5 MHz) and *Bruker-AM-400* (100.6 MHz) spectrometers; 5–10% solns. at 300 K, with the solvent signal as the standard; δ in ppm. High-resolution (HR) MS: *Finnigan-8200* spectrometer; in m/z. Element analyses were performed in the Microanalysis Laboratory of NIOCh, Novosibirsk.

Materials. Ketone concentrations were 20 mM in the case of 2,4-dimethyl-3-oxopentanedioic acid dimethyl ester, 2,2,4,4-tetramethyl-3-oxopentanedioic acid dimethyl ester (**I**), and 2,2,4,4-tetramethyl-3-oxopentanedioic acid di(*tert*-butyl) ester. The concentrations of the nitroxides were varied from 2 to 10 mM. The ketones were synthesized according to [43][44] and purified by column chromatography.

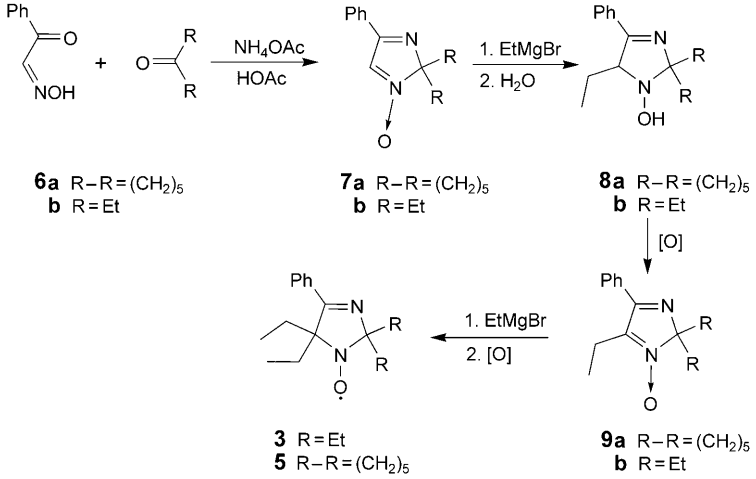
The nitroxides **1** [45], **2** [45] and **4** [14] were prepared by the published procedures. The nitroxides **3** and **5** were synthesized according to *Scheme 2* from **6** *via* **7**–**9** by using two subsequent ethylmagnesium bromide additions to 2*H*-imidazole 1-oxides and oxidation steps. Similar syntheses of 2,5-dihydro-1*H*-imidazole-1-oxy radicals by using organometallic-reagent additions to 2*H*-imidazole 1-oxides have been described earlier [46].

The alkoxyamines **1a**, **2a**, **4a**, and **5c** were prepared by the method developed by *Matyjaszewski* and co-workers [47], see *Scheme 3*.

General Procedure for Alkoxyamine Preparation. A mixture of the nitroxide **1**, **2**, **4**, or **5** (2.2 mmol), 2-bromo-2-methylpropanoic acid *tert*-butyl ester (0.5 g, 2.25 mmol), Cu powder (140 mg, 2.25 mmol), 4,4′-di(*tert*-butyl)-2,2′-bipyridine (24 mg, 0.09 mmol), Cu(OTf)$_2$ (8 mg, 0.023 mmol; TfO = CF_3SO_3), and benzene (5 ml) was placed in a *Schlenk* flask and degassed by three freeze-pump-thaw cycles. The soln. was heated to 75° and stirred for 24 h. The benzene was evaporated and the residue separated by CC (Al_2O_3, hexane/Et_2O 10:1).

2-Phenyl-1,4-diazaspiro[4.5]deca-1,3-diene 4-oxide (**7a**) was prepared according to the method described in [48].

Scheme 2



6a R–R = $(CH_2)_5$
b R = Et

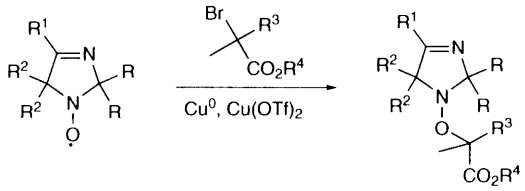
7a R–R = $(CH_2)_5$
b R = Et

8a R–R = $(CH_2)_5$
b R = Et

3 R = Et
5 R–R = $(CH_2)_5$

9a R–R = $(CH_2)_5$
b R = Et

Scheme 3



1 R = R^1 = R^2 = Me

2 R = R^2 = Me, R^1 = Ph

3 R = R^2 = Et, R^1 = Ph

4 R = R^2 = Et, R^1 = Me

5 R–R = $(CH_2)_5$, R^1 = Ph, R^2 = Et

1a R = R^1 = R^2 = R^4 = Me, R^3 = H
b R = R^1 = R^2 = R^3 = R^4 = Me

2a R = R^2 = R^4 = Me, R^1 = Ph, R^3 = H
b R = R^2 = R^3 = R^4 = Me, R^1 = Ph

3a R = R^2 = Et, R^1 = Ph, R^3 = H, R^4 = Me
b R = R^2 = Et, R^1 = Ph, R^3 = R^4 = Me

4a R = R^2 = Et, R^1 = R^4 = Me, R^3 = H

5c R–R = $(CH_2)_5$, R^1 = Ph, R^2 = Et, R^3 = Me, R^4 = ^{t}Bu

*2,2-Diethyl-4-phenyl-2*H*-imidazole 1-oxide* (**7b**) was prepared similarly to **7a**. A mixture of 2-oxo-2-phenylacetaldehyde oxime (**6**) (3 g, 20 mmol), pentan-3-one (5 ml, 71 mmol), ammonium acetate (9 g, 117 mmol), and AcOH (10 ml) was stirred at 40° for 8 h (TLC (*Silufol UV 254*, Et_2O/hexane 1:2) monitoring of **6**). The mixture was poured into H_2O (200 ml) and extracted with $CHCl_3$. The $CHCl_3$ extract was washed with 5% NaOH soln. and dried ($MgSO_4$), the solvent evaporated, and the residue separated by CC (alumina, CH_2Cl_2): **7b** (2.4 g, 55%). Pinkish crystals. M.p. 45–47° (hexane). UV/VIS (EtOH): 233 (4.27), 277 (4.20). IR (KBr): 3077 (N=C–H), 2974, 2935, 2881 (CH_3, CH_2), 1605, 1590, 1563, 1514 (C=N). ^{1}H-NMR (400 MHz, $CDCl_3$): 0.59 (*t*, *J* = 7.2, 2 *Me*CH_2); 1.92, 2.08 (*AB*(*q*), J_{AB} = 14, ^3J = 7.2, 2 Me*C*H_2); 7.40 (*m*, 2 H_m, H_p); 7.70 (*s*, H–C(5)); 7.82 (*m*, 2 H_o). ^{13}C-NMR (100 MHz, $CDCl_3$): 6.6 (*Me*CH_2); 29.9 (Me*C*H_2); 107.3 (C(2)); 126.5 (C(5)); 127.0 (C_o); 128.8 (C_m); 131.1 (C_{ipso}); 131.4 (C_p); 165.9 (C(4)). Anal. calc. for $C_{13}H_{16}N_2O$: C 72.19, H 7.46, N 12.95; found: C 72.05, H 7.30, N 13.03.

*2,2,5-Triethyl-2,5-dihydro-1-hydroxy-4-phenyl-1*H*-imidazole* (**8b**). A soln. of **7b** (3.25 g, 15 mmol) in dry THF (30 ml) was added to 1M EtMgBr in Et_2O (50 ml). The soln. was stirred for 0.5 h, and then the mixture was quenched with H_2O. The aq. layer was extracted with Et_2O, the combined Et_2O extract dried

($MgSO_4$), the solvent evaporated, and the residue recrystallized from hexane: **8b** (1.67 g, 45%). Colorless crystals. M.p. 137–140°. UV/VIS (EtOH): 237 (4.17). IR (KBr): 3167 (OH), 3032 (=C–H), 2979, 2962, 2922, 2879, 2838 (Me, CH_2), 1631 (C=N). ^{1}H-NMR (200 MHz, $CDCl_3$): 0.74 (*t*, *J* = 7.4, *Me*CH_2–C(5)); 0.87, 0.88 (2*t*, *J* = 7.4, 2 *Me*CH_2–C(2)); 1.85 (*m*, 3 CH_2); 4.47 (*dd*, *J* = 3.6, 6, H–C(5)); 6.79 (br. *s*, OH); 7.34 (*m*, 2 H_m, H_p); 7.54 (*m*, 2 H_o). ^{13}C-NMR (100 MHz, $CDCl_3$): 7.8 (*Me*CH_2–C(5)); 8.6, 8.9 (*Me*CH_2–C(2)); 24.4, 27.3 (Me*C*H_2–C(2)); 31.8 (Me*C*H_2–C(5)); 74.9 (C(5)); 95.2 (C(2)); 127.0 (C_o); 128.2 (C_m), 130.1 (C_p); 133.3 (C_{ipso}); 171.4 (C(4)). Anal. calc. for $C_{15}H_{22}N_2O$: C 73.13, H 9.00, N 11.37; found: C 73.42, H 9.21, N 11.44.

*2,2,4-Triethyl-5-phenyl-2*H-*imidazole 3-Oxide* (**9b**). Lead dioxide 15 g (63 mmol) was added portionwise to a stirred soln. of **8b** (3.2 g, 12.4 mmol) in $CHCl_3$ (30 ml), the mixture was stirred for 2 h, lead oxides were filtered off, $CHCl_3$ was evaporated, and the residue was separated by CC (silica gel *60* (*Merck*), hexane/^{t}BuOMe 4:1): **9b** (2.8 g, 89%). Brownish oil. UV/VIS (EtOH): 231 (4.01), 273 (3.89). IR (neat): 3062 (=C–H, Ph), 2974, 2936, 2880 (CH_3, CH_2), 1515, 1566 (C=N, C=C). ^{1}H-NMR (400 MHz, CD_3OD): 0.64 (*t*, *J* = 7.2, 2 *Me*CH_2C(2)); 1.23 (*t*, *J* = 7.6, *Me*CH_2–C(4)); 2.05, 2.19 (*AB*(*q*), J_{AB} = 14, ^3J = 7.2, 2 MeC*H*$_2$–C(2)); 2.80 (*q*, *J* = 7.6, MeC*H*$_2$–C(4)); 7.58 (*m*, 2 H_m, H_p); 7.80 (*m*, 2 H_o). ^{13}C-NMR (100 MHz, CD_3OD): 7.0 (*Me*CH_2–C(2)); 10.4 (*Me*CH_2–C(4)); 18.0 (MeCH_2–C(4)); 30.4 (Me*C*H_2–C(2)); 104.6 (C(2)); 128.2 (C_o); 129.6 (C_m); 131.7 (C_p); 132.9 (C_{ipso}); 144.4 (C(4)); 168.8 (C(5)). Anal. calc. for $C_{15}H_{20}N_2O$: C 73.74, H 8.25, N 11.47; found: C 73.32, H, 8.01, N 11.14.

*2,2,5,5-Tetraethyl-2,5-dihydro-4-phenyl-1*H-*imidazol-1-yloxy* (**3**). A soln. of **9b** (1.6 g, 6.6 mmol) in dry Et_2O (30 ml) was added dropwise to stirred 1M EtMgBr in Et_2O (34 ml). The mixture was stirred for 0.5 h and quenched with H_2O. The aq. layer was extracted with Et_2O and the combined extract dried ($MgSO_4$). Then MnO_2 (5 g, 57 mmol) was added, and the mixture was stirred for 2 h. The precipitate was filtered off, the solvent evaporated, and the residue separated by CC (silica gel *60* (*Merck*), hexane/Et_2O 4:1): **3** (0.80 g, 50%). Orange oil. UV/VIS (EtOH): 244 (4.11). IR (neat): 3059 (H–C=, Ph), 2972, 2939, 2880 (CH_3, CH_2), 1601, 1572 (C=N, C=C). Anal. calc. for $C_{17}H_{25}N_2O$: C 74.68, H 9.22, N 10.25; found: C 75.48, H 9.16, N, 9.98.

2,2-Diethyl-3-phenyl-1,4-diazaspiro[4.5]dec-3-en-1-yloxy (**5**). A 1M soln. of EtMgBr in Et_2O (20 ml) was added dropwise to a stirred soln. of **7a** (2 g, 8.8 mmol) in dry THF (20 ml). The soln. was stirred for 0.5 h and then poured into the vigorously stirred cold (0°) mixture of Et_2O (65 ml) and AcOH (14 ml). Then H_2O (200 ml) was added to the mixture, the aq. phase extracted with Et_2O, and the combined extract washed with sat. $NaHCO_3$ soln. and dried ($MgSO_4$): crude soln. of *3-ethyl-4-hydroxy-2-phenyl-1,4-diazaspiro[4.5]dec-1-ene* (**8a**). Colorless crystals were obtained from AcOEt. M.p. 184–186.5°. UV/VIS (EtOH): 241 (4.14). IR (KBr): 3175 (OH), 2987, 2962, 2928, 2852 (CH_3, CH_2), 1621 (C=N). ^{1}H-NMR (200 MHz, CD_3OD/$CDCl_3$ 1:10): 0.71 (*t*, *J* = 7.2, *Me*CH_2); 1.23 (*m*, 4 H, MeC*H*$_2$, $(CH_2)_5$); 1.42 (*m*, 7 H, Me*C*H_2, (CH_2)); 1.88 (*m*, 1 H, $(CH_2)_5$); 4.16 (*dd*, *J* = 10, 4, H–C(3)); 7.12 (*m*, 2 H_m, H_p); 7.35 (*m*, 2 H_o). ^{13}C-NMR (50 MHz, CD_3OD/$CDCl_3$ 1:10): 10.4 (*Me*CH_2); 22.7, 22.8, 25.0, 25.2, 31.1, 37.5 (Me*C*H_2, $(CH_2)_5$); 78.4 (C(3)); 92.3 (C(5)); 127.4 (C_o); 128.0 (C_m); 130.0 (C_p); 132.7 (C_{ipso}); 171.1 (C(3)). Anal. calc. for $C_{16}H_{22}N_2O$: C 74.38, H 8.58, N 10.84; found: C 74.11, H 8.58, N 10.70.

The crude soln. of **8a** was stirred with MnO_2 (15 g, 170 mmol) for 1 h. The oxidant was filtered off and the solvent evaporated: crude *2-ethyl-3-phenyl-1,4-diazaspiro[4.5]deca-1,3-diene 1-oxide* (**9a**). A sample was purified by CC (silica gel *60* (*Merck*) hexane/^{t}BuOMe 4:1): brownish oil. UV/VIS (EtOH): 229 (3.90), 269 (3.73). IR (neat): 3062 (=C–H, Ph), 2937, 2858 (CH_3, CH_2), 1564, 1515 (C=N, C=C). ^{1}H-NMR (200 MHz, $CDCl_3$): 1.07 (*t*, *J* = 7.6, *Me*CH_2); 1.83 (*m*, 8 H, $(CH_2)_5$); 2.17 (*m*, 2 H, $(CH_2)_5$); 2.69 (*q*, *J* = 7.6, MeC*H*$_2$); 7.44 (*m*, 2 H_m, H_p); 7.67 (*m*, 2 H_o). ^{13}C-NMR (50 MHz, $CDCl_3$): 9.6 (*Me*CH_2); 17.4, 23.0, 34.8 ($(CH_2)_5$); 24.6 (Me*C*H_2); 101.5 (C(5)); 127.5 (C_o); 128.7 (C_m); 130.6 (C_p); 132.7 (C_{ipso}); 140.8 (C(2)); 166.5 (C(3)). Anal. calc. for $C_{16}H_{20}N_2O$: C 74.97, H 7.86, N 10.93; found: C 74.68, H 8.31, N 10.34.

The crude **9a** was dissolved in dry Et_2O (20 ml), and the soln. was added dropwise to 1M EtMgBr in Et_2O (80 ml). The resulting mixture was stirred for 1 h and quenched with sat. aq. NH_4Cl soln. The aq. phase was extracted with Et_2O and the combined extract dried ($MgSO_4$). Then MnO_2 (10 g, 114 mmol) was added and the mixture stirred for 1 h. The oxidant was filtered off, the solvent evaporated, and the residue separated by CC (silica gel *60* (*Merck*), hexane/$CHCl_3$ 2:1): **5** (1 g, 40%). Yellow crystals. M.p. 97–99°. UV/VIS (EtOH): 245 (4.19). IR (KBr): 3060, 3024 (H–C=, Ph), 2978, 2962, 2933, 2856 (CH_3,

CH_2), 1598, 1571 (C=N, C=C). Anal. calc. for $C_{18}H_{25}N_2O$: C 75.75, H 8.83, N 9.82; found: C 75.36, H 8.61, N 9.68.

*Methyl 2-[(2,5-Dihydro-2,2,4,5,5-pentamethyl-1*H*-imidazol-1-yl)oxy]propanoate* (**1a**). Yield 45%. Colorless oil, a mixture of diastereoisomers. IR (neat): 1754 (C=O), 1656 (C=N). ^{1}H-NMR(200 MHz, $CDCl_3$): 4.28 (*m*, OC*H*Me); 3.67 (*s*, MeO); 1.83 (*s*, Me–C(4)); 1.34, 1.30, 1.28 1.29, 1.25, 1.18, 1.14 (2 Me–C(2)), 2 Me–C(5)). ^{13}C-NMR (50 MHz, $CDCl_3$): 15.2 (*Me*–C(4)); 15.8 (OCH*Me*); 17.05, 17.1, 23.2, 23.5 (*Me*–C(5)); 27.0, 28.2, 30.3, 31.5 (*Me*–C(2)); 51.4 (MeO); 72.9 (C(5)); 79.6, 79.8 (O*C*HMe); 90.8, 90.9 (C(2)); 172.7 (C(4)); 173.8, 174.1 (C=O). HR-MS: 242.16286 ($C_{12}H_{22}N_2O_3^+$; calc. 242.16303).

*Methyl 2-[(2,5-Dihydro-2,2,5,5-tetramethyl-4-phenyl-1*H*-imidazol-1-yl)oxy]propanoate* (**2a**). Yield 30%. Colorless oil, a mixture of diastereoisomers. UV/VIS (EtOH): 237 (3.90). IR (neat): 1755 (C=O), 1617 (C=N). ^{1}H-NMR(200 MHz, $CDCl_3$): 1.55, 1.50, 1.49, 1.48, 1.45, 1.43, 1.41, 1.38, 1.36, 1.35 (10*s*, 2 Me–C(2), 2 Me–C(5), OCH*Me*); 3.71, 3.72 (2*s*, MeO); 4.37 (*m*, OC*H*Me); 7.35 (*m*, 3 arom. H); 7.65 (*m*, 2 arom. H). ^{13}C-NMR (50 MHz, $CDCl_3$): 17.0 (OCH*Me*); 21.1, 21.3, 23.0, 23.3 (*Me*–C(5)); 28.1, 29.2, 30.0, 31.2 (*Me*–C(2)); 51.3 (MeO); 72.55, 72.6 (C(5)); 79.6, 79.9 (O*C*HMe); 90.1, 90.3 (C(2)); 127.4, 127.9, 129.5 (C_o, C_m, C_p); 133.4, 133.5 (C_{ipso}); 172.0, 172.8 (C=N); 173.5, 173.8 (C=O). HR-MS: 304.17939 ($C_{17}H_{24}N_2O_3^+$, calc. 304.17868).

*Methyl 2-[(2,2,5,5-Tetraethyl-2,5-dihydro-4-methyl-1*H*-imidazol-1-yl)oxy]propanoate* (**3a**). Yield 30%. Colorless oil, a mixture of diastereoisomers. IR (neat): 1755 (C=O), 1663 (C=N). ^{1}H-NMR (200 MHz, $CDCl_3$): 0.62–0.72 (*m*, 1 Me); 0.79–0.97 (*m*, 3 Me); 1.23 (*m*, 1 Me); 1.37–1.82 (*m*, 6 H, CH_2); 1.81, 1.78 (*s*, MeC=N); 1.86–1.98 (*m*, 2 H, CH_2); 3.64, 3.63 (*s*, MeO); 4.22 (*m*, OC*H*Me). ^{13}C-NMR (50 MHz, $CDCl_3$): 8.8, 8.9, 9.0, 9.3, 10.2, 10.25, 10.3, 10.35, 16.8, 16.9, 17.0 (*Me*CH_2–C(2), *Me*CH_2–C(5), *Me*–C(4), OCH*Me*); 27.0, 27.2, 27.6, 28.5, 28.6, 29.7, 30.3, 31.4 (Me*C*H_2–C(2), Me*C*H_2–C(5)); 51.2, 51.3 (MeO); 78.3, 78.6 (O*C*HMe); 79.4, 80.0 (C(5)); 95.1, 95.6 (C(2)); 172.0, 172.4 (C=N); 173.7, 174.3 (C=O). HR-MS: 298.22582 ($C_{16}H_{30}N_2O_3^+$, calc. 298.22563).

tert-*Butyl 2-Methyl-2-[(2,2-diethyl-3-phenyl-1,4-diazaspiro[4.5]dec-3-en-1-yl)oxy]propanoate* (**5c**). Yield 84%. Colorless oil. IR (neat): 3058 (=C–H, Ph), 2935, 2858 (CH_3, CH_2), 1732 (C=O), 1630, 1576 (C=N, C=C). ^{1}H-NMR(400 MHz, $CDCl_3$): 0.75 (*t*, *J* = 8, 1 *Me*CH_2); 0.89 (*t*, *J* = 8, 1 *Me*CH_2); 1.40, 1.41 (2*s*, $OC(Me)_2CO$); 1.47 (*s*, ^{t}Bu); 1.69 (*m*, 9 H, Me*C*H_2, $(CH_2)_5$); 1.88 (*m*, 3 H, $(CH_2)_5$); 2.10 (*m*, 1 H, $(CH_2)_5$); 2.27 (*m*, 1 H, MeCH_2); 7.36 (*m*, 2 H_m, H_p); 7.73 (*m*, 2 H_o). ^{13}C-NMR (75 MHz, $CDCl_3$): 9.5, 11.4 (*Me*CH_2); 25.0, 25.1 ($OC(Me)_2CO$); 28.0 (Me_3C); 24.0, 24.6, 26.3, 27.9, 31.1, 33.7, 39.5 (CH_2); 80.8 (C(2)); 81.8 (Me_3C); 93.8 (C(5)); 127.8 (C_o); 128.3 (C_m); 129.5 (C_p); 135.2 (C_{ipso}); 166.8 (C=N); 173.5 (C=O). Anal. calc. for $C_{26}H_{40}N_2O_3$: C 72.86, H 9.41, N 6.54; found: C 72.51, H 8.93, N 6.66.

Time-Resolved(TR)-CIDNP and NMR Experiments. A sample, purged with Ar and sealed in a standard NMR *Pyrex* tube, was irradiated by a *COMPEX-Lambda-Physik* excimer laser (wavelength 308 nm, pulse energy up to 150 mJ) in the probe of an *Avance-200* NMR spectrometer. TR-CIDNP experiments were carried out with the usual pulse sequence: presaturation–laser pulse–evolution time–detection pulse–free induction decay. Because the background signals in CIDNP spectra were suppressed by the presaturation pulses, only signals of the polarized products formed during the variable delay between the laser and NMR radio frequency (rf) pulse appeared in the CIDNP spectra. The rf pulse used had a duration of 3 μs, which corresponds to a flip angle of 30°.

Decomposition of alkoxyamines at 120° were performed in sealed NMR tubes in the probe of the NMR spectrometer. Samples were degassed by three freeze–pump–thaw cycles and sealed in a standard NMR *Pyrex* tube. NMR Spectra were detected during decomposition every 15 min during 10 h.

Laser Flash Photolysis. A detailed description of our laser-flash-photolysis experiments has been published earlier [49]. Solns. in a rectangular cell with inner dimensions 10 mm × 10 mm were irradiated with a *Lambda-Physik-EMG-101* excimer laser 308 nm, pulse energy up to 100 mJ, pulse duration 15–20 ns. The monitoring system included a *DKSh-150* xenon short-arc lamp connected to a high-current pulser, a home-made monochromator, a *9794B* photomultiplier (*Electron Tubes Ltd.*), and a *LeCroy-9310A* digitizer. The monitoring light, concentrated in a rectangular of 3 mm height and 1 mm width, passed through the cell along the front of the laser-irradiated window. Thus, in all experiments, the excitation optical length was 1 mm, and the monitoring optical length was 8 mm. To obtain one kinetic trace, 15–20 signals were averaged. All solns. were bubbled with Ar for 15 min prior to, and all the time during the experiments.

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