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Studies on the carbenium-iminium ions derived from *N*-methylmorpholine-*N*-oxide (NMMO)

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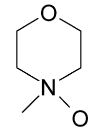
Abstract—Two carbenium-iminium ions, an *exo*-centered species **2** and a ring-centered form **3**, are derived from the widely used oxidant and cellulose solvent *N*-methylmorpholine-*N*-oxide (**1**) by heterolytic degradation. **3** rearranges into **2** in the presence of water, in an endothermic, bimolecular reaction involving a highly organized transition state, which is the first example of a carbenium-iminium ion interconversion. The reaction mechanism was investigated by a combined approach consisting of trapping reactions, isotopic labeling, kinetic studies, and computations on the DFT level.

1. Introduction

N-Methylmorpholine-*N*-oxide (NMMO, **1**) is a frequently applied oxidant in organic synthesis,[1] which is mainly applied in combination with catalytic amounts of transition metal catalysts.[2] It is also used in bulk quantities as a solvent for cellulose in the industrial Lyocell process, which is a new and environmentally benign approach to production of man-made cellulosic fibers.[3] NMMO dissolves cellulose directly without chemical derivatization to give a dope which is spun simply into water. This is in complete contrast to viscose rayon production, which requires intensive use of both derivatization and spinning bath chemicals.

NMMO is a relatively strong oxidant that tends toward uncontrollable decomposition reactions. Both upon usage as oxidant in organic synthesis,[4] as well as upon industrial utilization of NMMO as cellulose solvent[5] there have been reports on the instability of NMMO solutions and on the occurrence of unpredictable thermal runaway reactions. Due to these irregularities great caution must be exercised in all processes involving NMMO. It is evident that the interest in side reactions of NMMO and the NMMO-derived chemical species involved therein originate from very different areas of NMMO utilization.

In previous studies on side reactions of NMMO we have reported on radicals derived from this amine *N*-oxide, i.e., species which are formed by cleavage of the N–O bond with simultaneous transfer of one electron. In these processes NMMO acted as a one-electron oxidant.[6] In the present work, we wish to communicate the peculiar behavior of carbenium-iminium ions (C-I ions, Mannich intermediates) derived from NMMO, the second major class of NMMO-derived intermediates. These rather labile species are generated by breaking the N–O bond of the amine *N*-oxide with concomitant two-electron transfer. In the case of NMMO, two of such species can be expected, the *exo*-centered C-I ion **2** and the ring-centered C-I ion **3**.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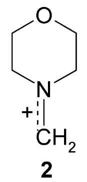
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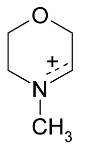
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C-I ions have been shown to be able to cause *O*-alkylation of tertiary amine *N*-oxides. The alkylation step is immediately followed by fragmentation in a concerted mechanism regenerating the C-I ion. The reaction, being an autocatalytic and highly exothermic process,[7] thus easily becomes uncontrollable causing complete degradation of the parent amine *N*-oxide. Also in the case of NMMO reaction mixtures, C-I ion intermediates catalyze its autocatalytic degradation, and are thus mainly responsible for the observed instabilities and exothermicities in NMMO reaction mixtures,[4] which gave the impetus to the present study.

Keywords: Carbenium-iminium ions; *N*-Methylmorpholine-*N*-oxide (NMMO); Mannich intermediates; Trapping; Isotopic labeling; Cellulose solvents.

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2. Results and discussion

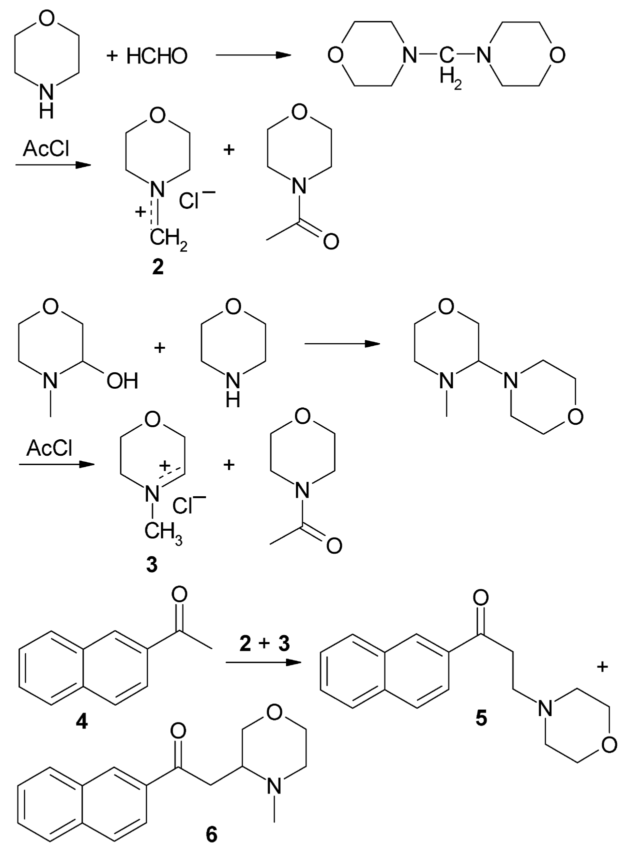
Even though **3** might appear more stable at a first glance, since its ring-centered positive charge seems 'better accommodated' than the one in **2**, it is the latter which occurs predominantly in all different types of side reactions starting from NMMO. In fact, intermediate **2** was produced exclusively in NMMO reaction mixtures containing water,[8] whereas in non-aqueous solutions of NMMO also smaller amounts of **3** were found besides **2**.[9] Thus, both the presence of water and higher temperatures generally seemed to promote the consumption of **3** in favor of **2**.

To study the reactions of these two NMMO-derived *Mannich* intermediates in more detail, the crystalline chloride forms of **2** and **3** were used, which were prepared according to Scheme 1. As reporter method, the trapping with 2-acetonaphthone (**4**) in a Mannich reaction was used. The trapping agent reacts with C-I ions in a fast and neat reaction to give the corresponding Mannich bases **5** and **6**, respectively, which are readily extractable even from very complex mixtures due to their lipophilic naphthalene moiety. Another advantage is the usability of the trap also at elevated temperatures (e.g., in NMMO melts), since the resulting Mannich bases are relatively thermostable and do not undergo elimination to the α,β-unsaturated ketone below 130 °C.

As shown in Table 1, trapping of both **2** and **3** in non-aqueous organic solution at room temperature provided the corresponding Mannich bases **5** and **6**, respectively, quantitatively. The same was true for the reaction of **2** in aqueous dioxane, **3** afforded small amounts of **5** besides the expected trapping product **6**. Refluxing **2** in aqueous dioxane for 24 h before carrying out the trapping reaction had no effect as compared to the room temperature process: only **5** was detected. In the case of **3**, however, **5** and **6** were formed in a 83/17 ratio. Thus, the major part of **3** must have rearranged during the refluxing into **2**.[10] A similar refluxing test carried out in dry dioxane or dry toluene gave no indications of such a reaction: in the case of **2** as the starting material only **5** was produced, and in the case of **3** only **6**. In refluxing wet toluene, in contrast, the rearrangement of **3** into **2** occurred. In general, replacing the refluxing procedure by room-temperature stirring provided essentially the same results in all solvents, but the **3** into **2** conversion proceeded much slower. The results of the experiments are summarized in Table 1. It was evident that higher temperatures and the presence of water favored **2** at the expense of **3**.

Table 1. Different reaction conditions for the conversion of C-I ion **3** into C-I ion **2** followed by trapping

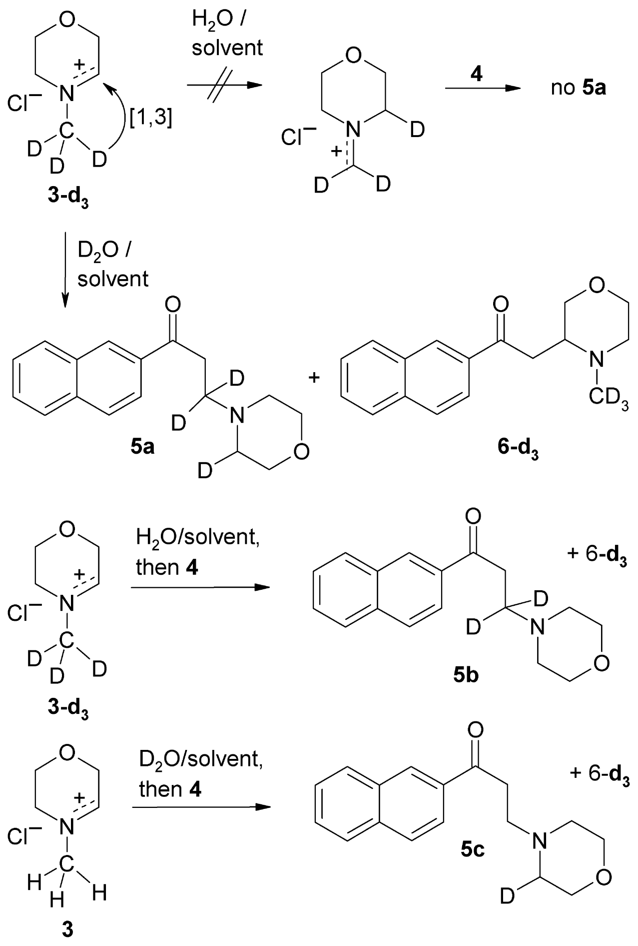
Starting material	Solvent (50 mL), treatment (24 h) before addition of trap	Product ratio
2	Dry toluene, stirring at rt	**5** only
3	Dry toluene, stirring at rt	**6** only
2	Wet toluene (2% H_2O), stirring at rt	**5** only
3	Wet toluene (2% H_2O), stirring at rt	12/88
2	Dry dioxane, stirring at rt	**5** only
3	Dry dioxane, stirring at rt	**6** only
2	Dioxane/water (3/1), stirring at rt	**5** only
3	Dioxane/water (3/1), stirring at rt	8/92
2	Dry toluene, reflux	**5** only
3	Dry toluene, reflux	**6** only
2	Wet toluene (2% H_2O), reflux	**5** only
3	Wet toluene (2% H_2O), reflux	83/17
2	Dry dioxane, reflux	**5** only
3	Dry dioxane, reflux	**6** only
2	Dioxane/water (3/1), reflux	**5** only
3	Dioxane/water (3/1), reflux	79/21
3	Dry DMF, stirring at 120 °C	**5** only
3	DMF/water (9/1), stirring at 120 °C	90/10
3	Dry DMF, stirring at 120 °C	**5** only



Scheme 1. Synthesis of stable carbenium-iminium chlorides **2** and **3** and their trapping with 2-acetonaphthone in a Mannich reaction.

First, we assumed that **3** might undergo a [1,3]-sigmatropic shift to give **2**, meaning that **2** basically would be a more stable tautomeric form of *N*-(alkylene)-morpholinium ions. If this assumption was true, **3-d$_3$** should have rearranged into **2-d$_3$**, which in turn should have produced **5a** upon trapping (see Scheme 2). However, this product was not observed, but only **5b**, the bisdeuterated compound, was found. No incorporation of deuterium into the *N*-methylene group of the morpholine ring—and thus no [1,3]-shift—had occurred. Consequently, the proton entering the morpholine ring must have come from the solvent. Indeed, reaction of **3** in dioxane/D_2O (or toluene/D_2O) provided **5c**, which proved the participation of water as a solvent component in the reaction. Thus, a solvent proton is incorporated into the morpholine ring, while a proton from the *exo*-methyl group is lost into the solvent (Scheme 2).

Kinetic studies have shown the reaction to be of second



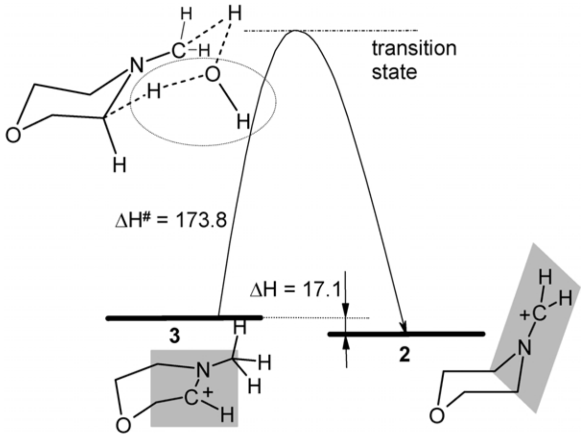
Scheme 2. Use of isotopically labeled material to clarify the reaction mechanism of the C-I ion conversion.

order, i.e., first order with respect to both water and C-I ion **3**. Thus, the reaction was assumed to be a bimolecular process according to rate law d[**2**]/d*t*=*k*[**3**][H_2O]. The kinetic rate constant was determined to be $k=1.40\times10^{-4}$ L mol^{-1} s^{-1}.[11] Evaluation of the temperature dependence of *k* according to the Eyring equation[12] produced the activation parameters of the reaction: a rather large activation enthalpy $\Delta H^{\#}=167.4\pm7.2$ kJ mol^{-1}, the Arrhenius activation energy thus being $E_A=\Delta H^{\#}+RT=169.9\pm7.2$ kJ mol^{-1} at 298 K, and a strongly negative activation entropy $\Delta S^{\#}=-142\pm13.8$ J(mol K)$^{-1}$ indicating a high degree of order in the transition state with limited mobility of the two coreactants as compared to the starting material.

The transmutation of **3** into **2** was prevented by addition of either acids or alkali. In the case of OH^- the C-I ion was evidently quenched to the corresponding *N*-hydroxyalkyl compound, so that neither rearrangement nor reaction with the trapping agent occurred.[13] The presence of strong acids (1 equiv. rel. to **3**) suppressed the transformation of **3** into **2** almost completely, whereas simple trapping proceeded faster than in the neutral case due to acid catalysis effect. This led us to the assumption that the basic oxygen functions in water were required for the C-I ion conversion, which was no longer present due to protonation in acidic media. In summary, the kinetic data indicated that a molecule of **3** and a molecule of water were involved in the rate-determining step of the reaction, having a highly organized transition state.

The stability of the two C-I ions was assessed by means of DFT computations, which showed that **2** is by 2.9 kJ mol^{-1} more stable than **3**.[14] In the minimum geometries of both **2** and **3** the positive carbons are sp^2-hybrids with trigonal planar geometry (Scheme 3). The four atoms of the *N*-(methylene) group in **2** lie in one plane; the morpholine ring is nevertheless able to adopt its typical chair conformation. In contrast, the morpholine ring of C-I-ion **3** is forced into a distorted chair geometry by the trigonal planar geometry of the carbenoid carbon. Thus, the spatial arrangement of the three substituents at the carbenium center can only in **2** be accommodated without additional strain, the resulting twist of the morpholine chair rendering **3** energetically more unfavorable than **2** (Scheme 3). However, this rather small energy difference could neither account for the experimentally observed preference of **2**, nor explain the conversion of **3** into **2**. Thus, in the next step a DFT analysis of the system (**3**+H_2O)[15] was performed, which now produced a plausible picture that agreed with the experimental data (Scheme 3).

According to Scheme 3 the conversion **3**→**2** follows a reaction path that requires a rather high activation energy of $\Delta H^{\#}=173.8$ kJ mol^{-1}, which compares very favorably with the experimental value of $E_A=169.9$ kJ mol^{-1}. Going from **3** to the transition state, the positive charge must be localized at the nitrogen, so that the double bond becomes located and the resonance stabilization of the carbenium-iminium ion is lost. In the transition state, water and the CI-ion **3** arrange in a way that places the reaction centers into a favorable six-membered chair-geometry. One water hydrogen is placed into a distance of 1.26 Å to the ring-carbon, which comes close to the length of a C–H single bond in the *N*–CH_2 groups of *N*-alkylamines with 1.1 Å. The ring carbon reaction center, which is nearly trigonal planar in **3**, already adopts a tetragonal environment in the transition state, which removes the strain from the six-membered ring system. The C–C–N angle (109.83°) almost



Scheme 3. Schematic representation of the computed reactant and transition state geometries as well as reaction energetics for the C-I ion conversion of **3** into **2**. Values are given in kJ mol^{-1}. The trigonal planar environments of the carbenoid carbons are shaded in gray. The participating water molecule is circled by a gray line.

equals the normal value of a tetrahedral angle in carbon sp^3 hybrids. Compared to the $N-CH_3$ group in *N*-methylmorpholine having a C–H length of 1.097 Å, the activated C–H bond in the *exo*-CH_3 group is stretched to 1.61 Å, which indicates advanced bond cleavage. The *exo*-carbon almost obtained the trigonal planar geometry of an sp^2-hybrid, with the H–C–H plane standing roughly perpendicular on the C–N–C plane of the morpholine ring. The distances of the three protons bound to the water oxygen are nearly equal (0.99–1.08 Å), close to that in a hydronium ion H_3O^+ (0.98 Å). Thus, the overall geometry of the transition state is rather close to that of the products, **2** and H_2O, indicating a 'late' transition state on the reaction coordinate. The water involved has consequently the effect of a catalyst, which per definitionem is regenerated after the reaction, although the conversion of **3** into **2** is accompanied by a proton exchange in that water molecule: one proton of the *exo*-CH_3 group is taken up, while a proton is donated to the ring carbon. Finally, going from the transition state to the product **2** requires rotation of the *exo*-methylene group, so that the H–C–H plane and the C–N–C plane fall together, re-establishing carbenium-iminium resonance stabilization.

The absence of the reverse reaction **2**→**3** can be explained by the stability of intermediate *N*-hydroxymethyl-morpholine (HMM), which is formed by addition of a hydroxyl ion to **2** (or addition of water with subsequent loss of a proton). HMM subsequently gives morpholine and formaldehyde, from which regeneration of **2** under neutral conditions is very slow. In contrast, 3-hydroxy-*N*-methylmorpholine, formed by formal addition of a hydroxyl ion into 3-position of **3**, is less stable, so that **3** can readily be regenerated by the reversed process. Moreover, formation of 2-(aminomethyl)ethoxy-acetaldehyde—the open-chain form of the cyclic semiaminal 2-hydroxy-*N*-methylmorpholine—is negligible and does not consume **3**, as does the formation of morpholine and HCHO from HMM in the case of C-I ion **2**.

In summary, the NMMO-derived ring-centered carbenium-iminium ion **3** is rearranged into its counterpart, the NMMO-derived *exo*-centered carbenium-iminium ion **2** in the presence of water. The conversion is an endothermic, bimolecular reaction involving **3** and water. The two coreactants pass through a highly organized transition state in which water, acting as a catalyst, is simultaneously accepting and donating a proton. The generated **2** is consumed by formation of the quite stable *N*-hydroxymethylmorpholine, morpholine and formaldehyde, so that the reversed reaction **2**→**3** is largely prevented. These findings agree completely with empirical data from NMMO oxidation chemistry and from the Lyocell fiber-making process. Especially under the rather drastic reaction conditions of the latter—working in a melt of NMMO monohydrate at temperatures around 100 °C—the C-I ion conversion is likely to account for the observed nearly complete absence of **3**.

The described process is the first example of a direct conversion between two Mannich intermediates. Studies on the general synthetic applicability of the reaction with regard to a *N*-demethylation involving a carbenium-iminium ion conversion step are underway.

3. Experimental

3.1. General

All chemicals were commercially available. Thin layer chromatography (TLC) was performed on silica gel 60 plates (5×10 cm, 0.25 mm) with fluorescence detection under UV light at 254 nm. Column chromatography was performed on silica gel G60 (40–63 μm). Melting points, determined on a Kofler-type micro hot stage with Reichert-Biovar microscope, are uncorrected. ^1H NMR spectra were recorded at 300.13 MHz, ^{13}C NMR spectra at 75.47 MHz in $CDCl_3$ as the solvent and TMS as the internal standard. Data are given in ppm. ^{13}C peaks were assigned by means of APT, HMQC and HMBC spectra; 'd.i.' denotes peaks with double intensity.

Computations, as implemented through Spartan Pro 02 by Wavefunction, Inc., Irvine, CA, USA, were carried out on geometries pre-optimized by the semi-empirical PM3 method. For full geometry optimization the widely employed B3LYP hybrid method, which includes a mixture of HF and DFT exchange terms and the gradient-corrected correlation functional of Lee, Yang and Parr[16] parametrized by Becke,[17] was used, along with the double-zeta split valence basis sets 6-31+G*,[18] which includes diffuse functions. Transition states and minima were confirmed by analysis of the calculated vibrational spectrum, and by intrinsic reaction coordinate analysis. For all transition states the number of imaginary frequencies was 1, for all minimum geometries it was 0.

3.1.1. *N*-(Methylene)morpholinium chloride (2). Formaline (35%, 8.6 mL, 0.1 mol) was cooled to −10 °C (ice/NaCl bath) and morpholine (17.4 g, 0.2 mol) was added under stirring. Within about 30 min the mixture was allowed to reach r.t. Anhydrous solid K_2CO_3 was added until the aqueous phase disappeared. The solids were crushed by a sufficiently powerful magnetic stirrer, removed by filtration, washed with Et_2O, and the combined phases were dried again over K_2CO_3. Et_2O was stripped off and the residue was distilled under reduced pressure to give bis(4-morpholino)methane, $bp_{35}=78$ °C. This product was dissolved in dry Et_2O in an inert atmosphere. Acetyl chloride (7.9 g, 7.1 mL, 0.1 mol) was added at 0 °C under stirring. The resulting precipitate was collected under exclusion of moisture, washed with Et_2O, and dried in vacuo to give *N*-(methylene)morpholinium chloride (**2**) as white crystals (8.05 g, 80.4%). ^1H NMR ($CDCl_3$): δ 3.58 (t, 4H), 4.08 (t, 4H), 8.53 (s, b, 2H). ^{13}C NMR: δ 56.2 (d.i.), 65.5 (d.i.), 167.7. Anal. calcd for $C_5H_{10}NOCl$ (135.59): C 44.29, H 7.43, N 10.33, Cl 26.15. Found: C 44.11, H 7.62, N 10.05, Cl 25.89. Computated thermodynamic data for the cation (without anion): $\Delta H=100.5$ kcal mol^{-1}, $\Delta S=78.05$ cal $(mol\ K)^{-1}$, $\Delta G_{298}=77.2$ kcal mol^{-1}, zero-point vibrational energy 96.6 kcal mol^{-1}.

3.1.2. 4-Methyl-3,6-dihydro-2*H*-[1,4]oxazinium chloride (3). 3-Hydroxy-4-methylmorpholine (11.72 g, 0.1 mol) was cooled to −10 °C (ice/NaCl bath) and morpholine (17.4 g, 0.2 mol) was added under stirring. Within about 30 min the mixture was allowed to reach rt. Anhydrous solid K_2CO_3 was added until the aqueous phase disappeared. The solids were removed by filtration, washed with Et$_2$O, and the combined phases were dried again over K$_2$CO$_3$. Et$_2$O was stripped off and the residue was distilled under reduced pressure to give bis(4-morpholino)methane, bp$_{20}$=112 °C. The product was dissolved in dry Et$_2$O in an inert atmosphere. Acetyl chloride (7.9 g, 7.1 mL, 0.1 mol) was added at 0 °C under stirring. The resulting precipitate was collected under exclusion of moisture, washed with Et$_2$O, and dried in vacuo to give 4-methyl-3,6-dihydro-2*H*-[1,4]oxazinium chloride (**3**) as white crystals (6.25 g, 62.4%). ^{1}H NMR (CDCl$_3$): δ 3.42 (s, 3H), 3.68 (d, b, 2H, ^3J=6.1 Hz), 4.19 (m, 2H), 4.62 (m, 2H), 9.15 (t, b, ^3J=6.1 Hz). ^{13}C NMR: δ 46.9, 55.1, 62.0, 72.4, 147.7. Anal. calcd for $C_5H_{10}NOCl$ (135.59): C 44.29, H 7.43, N 10.33, Cl 26.15. Found: C 44.41, H 7.25, N 10.17, Cl 26.03. Computed thermodynamic data from the cation (without anion): ΔH=100.4 kcal mol^{-1}, ΔS=80.1 cal (mol K)$^{-1}$, ΔG_{298}=76.5 kcal mol^{-1}, zero-point vibrational energy 96.0 kcal mol^{-1}.

3.2. General experimental procedure for trapping of carbenium-iminium ions

A solution of the carbenium-iminium chloride **2** or **3** (1 mmol) was dissolved in the respective solvent (20 mL), for the solvents used see Table 1. The mixture was stirred for 24 h either under reflux or at room temperature (see Table 1). At room temperature, a solution of 2-acetonaphthone (0.51 g, 7 mmol) in the same solvent (20 mL) and H$_2$SO$_4$ (conc., 0.1 mL) was added at once. The consumption of C-I ions was complete after less than 10 min (DC control). After additional stirring for 30 min, water (100 mL) and chloroform (100 mL) were added and the phases were separated. The organic phase was washed twice with water and dried over Na$_2$SO$_4$. The solvents were carefully removed in vacuo. For determination of the product composition, the remaining waxy solid was re-dissolved in n-hexane (15 mL). Ethereal HCl (3 mL, 2 M) was added, the mixture was left standing for 30 min, and the resulting white, crystalline precipitate was removed by filtration and dried in vacuo. An aliquot of the solid was dissolved in CDCl$_3$ and directly analyzed by NMR using the integrals of the β-methylene group in naphthone **5** (~2.95 ppm) and the β-methine proton in naphthone **6** (~3.10 ppm) for determination of the product ratio. For purification of the products, the above crude solid obtained after drying and solvent evaporation was re-dissolved in 5 mL of toluene and chromatographed on silica gel (toluene/ethyl acetate, v/v=9/1). For better storage, the obtained waxy morpholinonaphthones were converted into their crystalline hydrochlorides by treatment with ethereal HCl.

3.2.1. 3-(Morpholin-4-yl)propionaphthone (5). ^{1}H NMR (CDCl$_3$): δ 2.18 (s, b, 1H), 2.60 (t, 4H, ^3J=5.0 Hz, N–C*H*$_2$–CH$_2$–O), 2.93 (t, 2H, ^3J=7.0 Hz, CH$_2$–C*H*$_2$–CO), 3.46 (t, 2H, ^3J=7.0 Hz, C*H*$_2$–CH$_2$–CO), 3.78 (t, 4H, ^3J=5.0 Hz N–CH$_2$–C*H*$_2$–O), 7.58–7.66 (m, 2H, ^{Ar}C*H*), 7.86–8.08 (m, 4H, ^{Ar}C*H*), 8.45 (s, 1H, ^{Ar}C*H*). ^{13}C NMR: δ 33.7, 53.1, 53.2 (d.i.), 64.7 (d.i.), 124.4, 128.2, 128.8, 129.6, 130.1, 130.8, 131.6, 133.5, 134.2, 136.8, 198.0. Anal. calcd for $C_{17}H_{19}NO_2$ (269.35): C 75.81, H 7.11, N 5.20. Found: C 75.92, H 7.29, N 5.22.

3.2.2. 3,3-Dideutero-3-(3-deutero-morpholin-4-yl)-propio-naphthone (5a). ^{1}H NMR (CDCl$_3$): δ 2.54 (m, 1H, C*H*D), 2.68 (t, 2H, ^3J=5.2 Hz, N–C*H*$_2$–CH$_2$–O), 2.98 (s, b, 1H), 3.12 (s, 2H, C*H*$_2$–CD$_2$–CO), 3.76 (t, 2H, ^3J=5.2 Hz N–CH$_2$–C*H*$_2$–O), 3.78 (dd, 2H, N–CHD–C*H*$_2$–O), 7.58–7.65 (m, 2H, ^{Ar}C*H*), 7.86–8.05 (m, 4H, ^{Ar}C*H*), 8.45 (s, 1H, ^{Ar}C*H*). ^{13}C NMR: δ 30.1, 51.0 (quint), 51.2 (t), 57.7, 63.9, 64.7, 124.4, 128.0, 128.8, 129.5, 130.1, 130.8, 131.5, 133.6, 134.2, 136.6, 197.4. Anal. calcd for $C_{17}H_{16}NO_2D_3$ (272.36): C 74.96, H 7.03, N 5.14. Found: C 75.08, H 6.98, N 5.20.

3.2.3. 3,3-Dideutero-3-(morpholin-4-yl)propio-naphthone (5b). ^{1}H NMR (CDCl$_3$): δ 2.24 (s, b, 1H), 2.65 (t, 4H, ^3J=5.0 Hz, N–C*H*$_2$–CH$_2$–O), 3.36 (s, 2H, C*H*$_2$–CD$_2$–CO), 3.74 (t, 4H, ^3J=5.0 Hz N–CH$_2$–C*H*$_2$–O), 7.58–7.65 (m, 2H, ^{Ar}C*H*), 7.82–8.06 (m, 4H, ^{Ar}C*H*), 8.44 (s, 1H, ^{Ar}C*H*). ^{13}C NMR: δ 30.2, 51.2 (quint), 52.9 (d.i.), 64.6 (d.i.), 124.4, 128.1, 128.8, 129.6, 130.0, 130.7, 131.6, 133.4, 134.3, 136.6, 198.0. Anal. calcd for $C_{17}H_{17}NO_2D_2$ (271.36): C 75.24, H 7.06, N 5.16. Found: C 75.44, H 7.12, N 5.34.

3.2.4. 3-(3-Deutero-morpholin-4-yl)propionaphthone (5c). ^{1}H NMR (CDCl$_3$): δ 2.54 (m, 1H, C*H*D), 2.67 (t, 2H, ^3J=5.1 Hz, N–C*H*$_2$–CH$_2$–O), 2.84 (s, b, 1H), 2.91 (t, 2H, ^3J=7.0 Hz, CH$_2$–C*H*$_2$–CO), 3.44 (t, 2H, ^3J=7.0 Hz, C*H*$_2$–CH$_2$–CO), 3.76 (t, 2H, ^3J=5.1 Hz, N–CH$_2$–C*H*$_2$–O), 3.78 (dd, 2H, N–CHD–C*H*$_2$–O), 7.58–7.65 (m, 2H, ^{Ar}C*H*), 7.86–8.08 (m, 4H, ^{Ar}C*H*), 8.45 (s, 1H, ^{Ar}C*H*). ^{13}C NMR: δ 30.1, 51.4, 51.5 (t), 57.7, 64.0, 64.7, 124.3, 128.0, 128.7, 129.5, 130.1, 130.7, 131.7, 133.6, 134.2, 136.8, 198.0. Anal. calcd for $C_{17}H_{18}NO_2D$ (270.35): C 75.52, H 7.08, N 5.18. Found: C 75.35, H 7.18, N 5.29.

3.2.5. 2-(4-Methyl-morpholin-3-yl)-1-naphthalen-2-yl-ethanone (6). ^{1}H NMR (CDCl$_3$): δ 2.42 (s, 3H, CH$_3$), 2.67 (m, 2H, N–C*H*$_2$), 3.10 (m, 1H, N–CH), 3.18–3.38 (m, 2H, C*H*$_2$–CO), 3.68 (m, 2H, N–CH$_2$–C*H*$_2$–O), 3.89 (m, 2H, N–CH–C*H*$_2$–O), 4.12 (s, b, 1H), 7.54–7.62 (m, 2H, ^{Ar}C*H*), 7.84–8.02 (m, 4H, ^{Ar}C*H*), 8.46 (s, 1H, ^{Ar}C*H*). ^{13}C NMR: δ 39.7, 49.1, 53.8, 61.2, 65.3, 71.4, 124.6, 128.0, 128.8, 129.3, 130.3, 131.0, 131.4, 133.0, 134.4, 136.6, 198.7. Anal. calcd for $C_{17}H_{19}NO_2$ (269.35): C 75.81, H 7.11, N 5.20. Found: C 76.01, H 7.20, N 5.13.

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8. This applies for instance to reaction mixtures containing NMMO monohydrate, or NMMO-cellulose spinning dopes.
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10. It was checked that **6** was stable under the prevailing conditions, and did not transform into **5**. Thus, formation of **5** must be due to the conversion of **3** into **2** rather than a transformation of the trapping products.
11. The overall reaction order was determined using equivalent starting concentrations. Applying a large excess (80 equiv.) of water, the water concentration could be regarded constant over the reaction time, and the reaction became pseudo-first order with regard to the starting material **3**, i.e., $d[2]/dt = k'[3]$, with $k' = k[\mathrm{H2O}]$.
12. Graphical representation of $\ln(k/T)$ versus $1/T$ produced a straight line $y = ax + b$ with the slope $a = -\Delta H^{\#}/R$ in J mol^{-1} und $b = \Delta S^{\#}/R + 23.76$ in J(mol K)$^{-1}$.
13. Trapping after reacidification proved that indeed not only the trapping reaction, but also the rearrangement itself was prevented.
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