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On the non-classical course of Polonowski reactions of *N*-benzylmorpholine-*N*-oxide (NBnMO)

Thomas Rosenau,* Peter Schmid and Paul Kosma

Christian-Doppler-Laboratory, Department of Chemistry, University of Natural Resources and Applied Life Sciences, A-1190 Vienna, Austria

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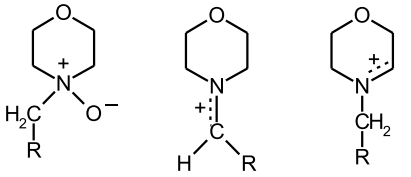
Abstract—The Polonowski reaction of NBnMO (**4**) afforded tropone (**10**) and the novel isoindole **11** besides the expected products benzaldehyde and acetmorpholide, in a temperature-dependent ratio. The reaction proceeded via two primary carbenium–iminium ion intermediates, an *exo*-centered species **5** which underwent a benzylium–tropylium type rearrangement, and a ring-centered species **6**, which reacted further to isoindole **11** by intramolecular electrophilic substitution. The experimental findings were in good agreement with DFT computational data.

1. Introduction

Tertiary amine-*N*-oxide are frequently applied oxidants in organic synthesis,[1] mainly used in combination with catalytic amounts of transition metal catalysts.[2] *N*-Methylmorpholine-*N*-oxide (NMMO, **1**) is moreover used in bulk quantities as a cellulose solvent in the Lyocell process, which is a new and environmentally benign industrial approach to production of man-made cellulosic fibers.[3] NMMO is able to dissolve cellulose directly without chemical derivatization to give a dope which is spun simply into air and water.

In previous studies, we have addressed the chemistry of the Lyocell process[4] and have shown that the NMMO-derived carbenium–iminium ions (**2**, **3**) play a key role in NMMO and Lyocell chemistry. Later we reported on the first example of a carbenium–iminium ion interconversion, which was observed between these two Mannich intermediates. In theory, Polonowski reactions of NMMO would produce the ring-centered, thermodynamically favored **3** as the main product besides small amounts of the *exo*-centered **2**. However, intermediate **3** rearranges into the *exo*-centered **2** via a highly organized transition state involving one molecule of water, the back reaction not being observed,[5] so that the latter intermediate usually predominates. For *N*-benzylmorpholine-*N*-oxide (NBnMO, **4**), which was available from previous NMR studies on conformational equilibria of tertiary amine *N*-oxides,[6] a different behavior was anticipated: first, the corresponding *exo*-cation **5** was supposed to be largely favored from the beginning due to additional charge stabilization at the benzylic position. Second, the rearrangement of ring-centered **6** into **5** would be prevented as the required transition state was strongly disfavored due to steric hindrance imposed by the bulky benzyl group. Even though these expectations proved to be partly true, Polonowski reactions of NBnMO revealed some surprising results, which we wish to report herein, along with related kinetic and computational studies.



1 R = H
4 R = Ph

2 R = H
5 R = Ph

3 R = H
6 R = Ph

2. Results and discussion

Polonowski reactions[7] are intramolecular redox reactions in tertiary aliphatic *N*-oxides. The nitrogen is reduced from the formal oxidation stage −1 to −3, and an α-carbon is oxidized from −2 to ±0. The conversion represents a heterolytic 'self-oxidation' which thus does not require an external oxidant. Polonowski reactions are strictly heterolytic processes.[8] They are induced by *O*-acylation of the

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* Corresponding author. Tel.: +43 1 36006 6071; fax: +43 1 36006 6059; e-mail: thomas.rosenau@boku.ac.at

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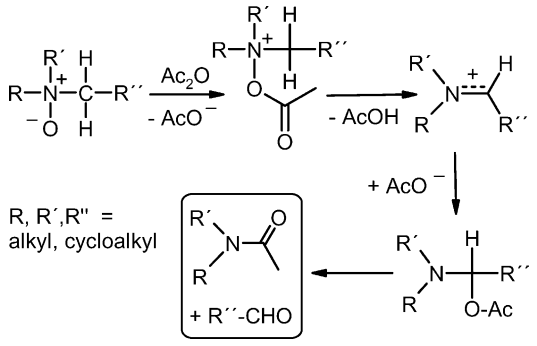
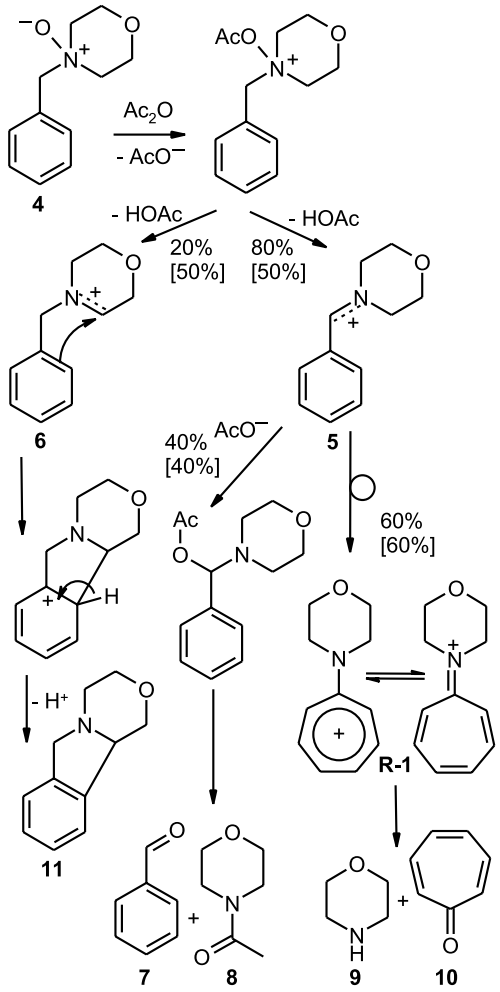
amine *N*-oxide by organic or inorganic acid anhydrides or halides, acetic anhydride being the traditional reagent used. The acylation of the exogenous oxygen lowers the electron density along the N–O bond, and facilitates proton abstraction in α-position to the nitrogen. The classical Polonowski reaction proceeds further with the loss of the respective acid anion, for example, acetate, and simultaneous deprotonation from the α-position in a *trans*-elimination process (Scheme 1). In this step the N–O bond is cleaved, and an iminium ion is generated. Addition of excess acetate in α-position with subsequent N–C bond fission produces the secondary amines in the form of their corresponding acetamides. In the overall process, the amine oxide is dealkylated and acylated, and the α-position of the cleaved alkyl substituent is oxidized to an aldehyde function.[9]



Scheme 1. Classical pathway of the Polonowski reaction.

According to the pathway in Scheme 1, we expected benzaldehyde (**7**) and acetmorpholide (*N*-acetylmorpholine, **8**) to be the main products of the Polonowski reaction between *N*-benzylmorpholine-*N*-oxide (**4**) and acetic anhydride. Indeed, these two compounds were found in equimolar amounts in an approx. 30% yield,[10] but there were three additional main products, however. One of them was morpholine (**9**) in its non-acetylated form in about 50% yield. Surprisingly, it was accompanied by tropone (**10**) in the same amount. In contrast to tropone with its quite simple NMR and mass spectra, identification of the third unexpected product was rather intricate. Finally, the compound was identified as oxazino-isoindole derivative **11**, obtained in 20% yield. Starting from these experimental results we set out to clarify the mechanism of this conversion.

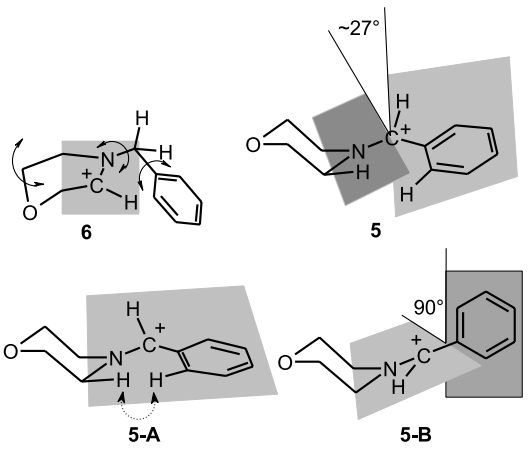
A first valuable clue as to the reaction mechanism was the observed equimolarity between formed benzaldehyde and acetmorpholide on the one hand as well as tropone and morpholine on the other hand, indicating that the first compound couple was formed according to one pathway, and the latter according to a competitive one. Raising the reaction temperature to rt, 35 and 50 °C had no effect on the ratio between the two compound couples, whereas formation of isoindole **11**, was increasingly favored. This indicated that the two compound couples **7/8** and **9/10** originate from one intermediate and **11** from another one which is favored at higher temperatures. From these observations, the overall mechanism as shown in Scheme 2 was developed.



Scheme 2. Non-classical course of the Polonowski reaction of *N*-benzylmorpholine-*N*-oxide (**4**), percentages refer to approx. yields at 0 °C [50 °C].

As the first step in the reaction sequence *N*-benzylmorpholine-*N*-oxide is *O*-acylated by acetic anhydride. Fragmentation of the primary acylation product forms two expected carbenium iminium intermediates, the *exo*-centered (benzyl) cation **5** and the ring-centered **6** (Scheme 2), albeit the latter in surprisingly large amounts. At 0 °C reaction temperature, already about 20% of **6** was produced, and its formation is more and more favored at increasing temperatures. The dependence of the product distribution[11] from the reaction temperature allowed estimating the difference between the free activation energies for formation of either **5** or **6**, which was 12.8 ± 2.3 kJ mol^{-1}, meaning that the activation energy for the formation of **5** was by about 13 kJ mol^{-1} lower than for the formation of **6**.[12]

A possible explanation for these kinetic data was found by means of computational chemistry. In the minimum geometries of both **5** and **6** the positive carbons are sp^2-hybrids with trigonal planar geometry. The morpholinium ring in **6** adopts a twisted chair geometry, as the positively charged carbon has trigonal planar geometry, which anchors the carbenium and the neighboring nitrogen in a rigid structure while the rest of the ring remains flexible (Scheme 3). This flexibility—mainly a flipping of the



Scheme 3. Geometries of the carbenium–iminium ions **5** and **6**. Grey shaded areas indicate in-plane atoms, solid arrows denote conformational flexibility (flipping or bond rotation), dotted arrows sterical hindrance. Hypothetical geometries: **5-A**: phenyl ring in carbenium–iminium plane, maximum benzylic resonance stabilization, but H–H repulsion; **5-B**: phenyl ring perpendicular to carbenium–iminium plane, minimum benzylic resonance stabilization.

conformationally free semi-chair—is increased at increasing temperatures, whereas the rigidity of the carbenium–iminium structure is not influenced. This structural element is the basis of the carbenium–iminium resonance stabilization, which is however only little affected by temperature changes.

The case of intermediate **5**, which actually is a benzyl cation—carbenium–iminium ion hybrid, is different. Apart from the stabilizing carbenium–iminium resonance effect, there is strong additional stabilization by charge delocalization into the aromatic ring. However, for this resonance stabilization to become effective, the aromatic ring, the benzylic CH and the C–N–C element of the morpholine ring must lie in one plane. Optimum charge delocalization into the phenyl moiety is only possible in periplanar benzyl cations (cf. **5-A** in Scheme 3), whereas the positive charge remains localized at the benzyl position in perpendicular benzyl cations (cf. **5-B** in Scheme 3). At equilibrium geometry of **5**, the dihedral angle Ph-2–Ph-1–C_{benzyl}–N is 27° and thus significantly different from 0°, which would guarantee full resonance stabilization. The steric repulsion of the *ortho*-hydrogen in the phenyl ring and the α-hydrogen in the morpholine ring prevents the latter geometry, the H–H distance still being relatively short with 2.08 Å. Thus, the carbenium–iminium ion in **5** does not experience the full additional benzylic resonance stabilization. Moreover, overcoming the rotational barrier of the benzyl cation (the movement from periplanar into perpendicular conformation and further to another periplanar one) becomes more and more easy at higher temperatures. Hence, the net stabilization of the carbenium–iminium ion **5** is decreased since the phenyl moiety is increasingly adopting conformations other than the fully periplanar one, which explains why **5** becomes less stable at higher temperatures. Assuming also that the thermodynamic stabilities of the products go parallel with the activation energies according to the Hammond principle, it becomes clear why the ratio between **5** and **6** is shifted in favor of the latter with increasing temperature, as was experimentally observed. Computations on the transition states leading to **5** and **6** predict an activation energy difference of 14.5 kJ mol^{-1} between the intermediates **5** and **6**, which is in satisfying agreement with the kinetically determined value. The thermodynamic stability of the two carbenium–iminium ions also was assessed by means of DFT computations, which showed that **5** is by 19.2 kJ mol^{-1} more stable than **6**, which is roughly the sixfold of the difference between the two NMMO-derived carbenium–iminium ions **2** and **3** (2.9 kJ mol^{-1}).[5]

Once intermediate **6** was formed, it immediately underwent intramolecular electrophilic substitution to afford isoindole **11**. Apparently, the intramolecular path was much favored over competitive intermolecular ones, as even in the presence of excess methanol, morpholine or trimethylhydroquinone as competing *O*-, *N*-, or *C*-nucleophiles, respectively, only **11** but no trapping products were found. This must be due to a pre-organizational effect, which holds the attacking positive carbenium ion in optimal position for electrophilic attack on the aromatic.

Two competitive pathways start from intermediate **5**: the first one is the classical Polonowski pathway leading to **7** and **8**, the second one constitutes a benzyl-tropylium conversion, a rearrangement which is well known to occur upon fragmentation of substituted aromatics in mass spectrometry. The temperature independence of the ratio between **7** (or **8**) and **9** (or **10**) indicated that the activation energies for the addition of acetate and rearrangement into the tropylium derivative were nearly equal. To support this mechanistic view, we changed the acylating agent to trifluoroacetic anhydride or sulfuryl chloride, since trifluoroacetate or sulfate as the corresponding weakly nucleophilic anions should disfavor the Polonowski pathway thus promoting the competitive tropylium rearrangement. The effect was even stronger than expected: formation of **7** and **8** was completely prevented, and only **9** and **10** was found besides isoindole **11**. It should be noted that the change of the acylating agent affected only the two pathways extending from carbenium—iminium intermediate **5**, but not the pathways leading to it, that is, the ratio between **5** and **6** is not influenced. This is in full agreement with theory: less basic anions, such as trifluoroacetate or sulfate in comparison to acetate, will less efficiently abstract α-protons from acylated **4**. Since this step is required for both **5** and **6** to form, both pathways are equally affected although different protons are abstracted. Thus, the overall reaction rate is lowered, but the ratio between **5** and **6** remains constant. In contrast, only one pathway extending from **5**—the one leading to **7** and **8**—involves the respective anions, and only that one is influenced by changes of the acylating agent.

The driving force for the rearrangement of **5** into the (1-morpholinyl)tropylium cation (**R-1** in Scheme 2) appears to be the high resonance stabilization of the latter. NRT[13] analysis suggests that there is a 54% participation of the tropylium resonance form and a 46% participation of the enamino-cyclohexatrienone canonical structure, which is nearly the 'ideal' 50/50 partition. The mechanism can be assumed to be that of the well-known benzyl–tropylium rearrangement,[14] from which the present case differs only in

the presence of a morpholine ring as the benzylic substituent which additionally stabilizes the primary intermediate **R-1**.

NMMO (**1**) readily undergoes *O*-alkylation by the NMMO-derived carbenium–iminium ions **2** and **3** leading to an autocatalytic degradation cycle.[15] Interestingly, the carbenium–iminium ions derived from NBnMO do not enter a similar path. Evidently, the reaction to the observed products **7**–**11** is energetically favored over *O*-alkylation of NBnMO by either of the carbenium–iminium ions **5** or **6**. The implications of this observation for the stabilization of NMMO solutions will be discussed elsewhere.

3. Conclusions

The Polonowski reaction of *N*-benzylmorpholine-*N*-oxide (**4**) proved to be rather complex. Instead of the expected high yields, only approx. 30% of the two 'traditional' products **7** and **8** were obtained at 0 °C, the majority of the starting material being converted into the novel isoindole **11** and morpholine (**9**)/tropone (**10**). The reaction path and the observed product distribution can be explained by the intermediacy of two competing carbenium–iminium ions **5** and **6**. The differing tolerance of these intermediates towards temperature changes can be utilized to tune the product distribution. The experimental findings agree very well with DFT computational data.

4. Experimental

4.1. 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. ^{1}H NMR spectra were recorded at 300.13 MHz, ^{13}C NMR spectra at 75.47 MHz in $CDCl_3$ as the solvent if not stated otherwise 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.

4.1.1. *N*-Benzylmorpholine-*N*-oxide (4). Benzyl chloride (10 mmol) was added dropwise to a solution of morpholine (20 mmol) in chloroform (100 ml). The mixture was stirred for 30 min at room temperature and refluxed for 2 h. After cooling to 0 °C in ice water and addition of *n*-hexane (50 ml), the white, crystalline precipitate formed (morpholinium chloride) was removed by filtration, and the solvents were evaporated under reduced pressure. The residue, crude *N*-benzylmorpholine, was dissolved in ethanol (50 ml) and hydrogen peroxide (30% in H_2O, 5 ml) was added. The mixture was stirred overnight, excess H_2O_2 was destroyed by slowly adding the reaction mixture to a suspension of MnO_2 (10 mg) in ethanol (5 ml). Removal of MnO_2 by filtration and evaporation of the solvent under reduced pressure provided **7**, which was recrystallized from acetone (24% overall yield, 0.47 g, mp 136 °C). The synthesis was repeated and up-scaled to obtain sufficient material. ^{1}H NMR ($CDCl_3$, 0.1 M): δ 2.94 (dd, 2H, N–CH_{eq}), 3.53 (dt, 2H, N–CH_{ax}), 3.78 (dd, 2H, O–CH_{eq}), 4.16 (dt, 2H, O–CH_{ax}), 4.43 (s, 2H, N–CH_2–Ph), 7.44 (m, 3H, Ph), 7.58 (m, 2H, Ph). ^{13}C NMR ($CDCl_3$, 0.1 M): δ 62.40 (O–CH_2), 64.40 (N–CH_2), 75.96 (N–CH_2–Ph), 129.46 (Ph, d.i., C-3, C-5), 130.26 (Ph, C-1), 130.80 (Ph, C-4), 134.20 (Ph, d.i., C-2, C-6). Anal. calcd for $C_{11}H_{15}NO_2 \cdot H_2O$ (211.27): C 62.54, H 8.11, N 6.63; found C 62.16, H 8.32, N 6.48.

4.2. General experimental procedure for Polonowski reactions of NBnMO

A solution of NBnMO (**4**, 10 mmol) in CH_2Cl_2 (50 ml) was added dropwise to a solution of acetyl chloride or acetic anhydride (10 mmol) in the same solvent (150 ml) under stirring and efficient cooling with an ice/NaCl bath. Also inorganic acid chlorides, such as $POCl_3$ or $SOCl_2$, were used with the same result. (CAUTION! Degradation reactions of amine *N*-oxides are known to easily become uncontrollable![19] Work in an efficient hood and wear appropriate eye protection!). The organic phase was washed thoroughly with a concentrated aqueous sodium hydrogencarbonate solution until evolution of CO_2 ceased, and was dried over $NaSO_4$. Evaporation of the solvent in vacuo yielded a yellow syrup, which was chromatographed on silica gel using *n*-hexane/chloroform (v/v=5:1) to elute the products in the order tropone (**10**), benzaldehyde (**7**), the novel isoindole **11**, acetmorpholide (**8**), and morpholine (**9**). If inorganic acid chlorides were used instead of acetyl chloride or acetic anhydride, no acetmorpholide was found.

4.2.1. Acetmorpholide (8). ^{1}H NMR (DMSO-d_6, 110 °C): δ 2.04 (s, 3H, CH_3), 3.47 (m, 4H, N–CH_2), 3.68 (t, 4H, O–CH_2). ^{13}C NMR: δ 19.7; 47.4; 67.3; 169.4.

4.2.2. Morpholine (9). ^{1}H NMR: δ 1.73 (s, b, 1H, N*H*), 2.87 (m, 4H, N–CH_2, J=4.7 Hz), 3.68 (m, 4H, O–CH_2, J=4.7 Hz). ^{13}C NMR ($CDCl_3$, 0.1 M): δ 46.4, 64.1.

4.2.3. Tropone (10). ^{1}H NMR: δ 6.97–7.17 (m, 6H, CH). ^{13}C NMR: δ 136.7, 136.1, 142.1, 188.1.

4.2.4. 3,4,6,10b-Tetrahydro-1*H*-[1,4]-oxazino[3,4-*a*]isoindole (11). ^{1}H NMR: δ 2.52 (dd, 1H, ^3J=4.4 Hz, ^2J=11.2 Hz, N–CH_2), 2.66 (ddd, 1H, ^3J=4.4, 6.1 Hz, ^2J=11.2 Hz, N–CH_2), 3.55–3.58 (m, 1H, Ar–CH_2–N, O–CH_2–CH_2), 3.63 (m, 1H, O–CH_2–CH), 3.65–3.72 (m, 2H,

Ar–CH_2–N, O–CH_2–CH_2), 3.76 (m, 1H, O–CH_2–CH), 4.31 (t, 1H, ^3J=6.6 Hz), 6.86 (d, 1H, ^3J=7.8 Hz), 7.13 (t, 1H, ^3J=7.8 Hz), 7.29 (t, 1H, ^3J=7.8 Hz), 7.62 (d, 1H, ^3J=7.8 Hz). ^{13}C NMR: δ 46.7 (N–*C*H_2–CH_2), 56.2 (Ar–CH_2–N), 66.0 (N–CH), 66.2 (O–*C*H_2–CH_2), 72.9 (O–*C*H_2–CH), 121.8, 124.1, 125.8, 128.0, 132.4, 140.1. Anal. calcd for $C_{11}H_{13}NO$ (175.23): C 75.40, H 7.48, N 7.99; found C 75.21, H 7.71, N 8.13. Anal. calcd for $C_{11}H_{14}ClNO$ (211.69, hydrochloride of **11**): C 62.41, H 6.67, Cl 16.75, N 6.62; found C 62.36, H 6.83, Cl 16.34, N 6.32.

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9. Modifications of the Polonowski reaction use competing nucleophiles to yield α-substituted tertiary amines. In the case of water or hydroxyl ions as the nucleophile, these products represent semi-aminals which yield secondary amine and carbonyl compound. Also high-yield variants, so-called Polonowski–Potier reactions are known, which use trifluoroacetic anhydride.
10. As minor byproduct, cinnamic acid was found, evidently produced by a Perkin reaction of **7** with Ac_2O.
11. Estimated by the ^{1}H NMR integrals of the crude reaction mixture.
12. With *R* being the ratio **5** and **6** follows: $R=\exp(-(\Delta E_6^{\#}-\Delta E_5^{\#})/RT)$, so that a plot '$\ln R$ versus $1/T$' gives the slope $-\Delta(\Delta E^{\#})/R$, and thus the difference of activation energies.
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