Photo-Beckmann Rearrangements of Oximes of Androsterone and 13α-Androsterone[1]

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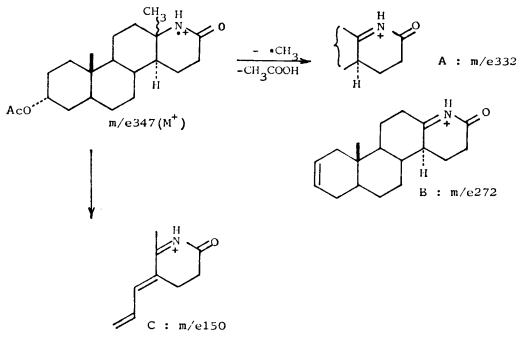
The photolysis of androsterone oxime and 13α-androsterone oxime affords isomeric lactams with and without the original configuration of the C-13 substituent of the starting oxime, although there were poor yields and no products due to photo-Beckmann fission. The formation of an epimeric pair of lactams from an oxime is at variance with our previous results on the photolysis of 5α- and 5β-cholestan-6-one oximes, in which the stereochemical integrity of the terminus of the migrating carbon in the photo-Beckmann rearrangement was observed. The implication of the present results for the migration step of the photo-Beckmann rearrangement is discussed.

In our previous papers it has been shown that in the photo-Beckmann rearrangement of steroidal oximes the bond migration of the oximes to amides proceeds in a stereospecific manner, the migration of carbon α to the oximino group occurring with the retention of the original configuration, and in these unsymmetrically α-substituted oximes the relative amounts of the two isomeric lactams due to the migration of the tri-substituted carbon (C_5) and the disubstituted carbon (C_7) are not significantly different.[2,3] This finding was subsequently confirmed by Just *et al.*[4] They showed that the photo-Beckmann rearrangements of menthone oxime and isomenthone oxime afforded the corresponding lactams with retention of the original configuration at carbon α to the oximino group of the starting oximes.

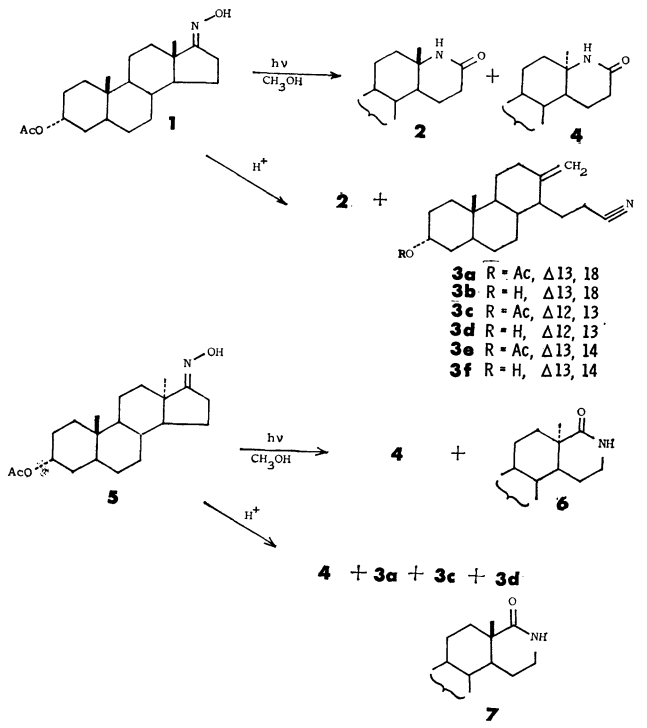
In this paper we wish to report on further results with respect to the stereospecificity of the migration stage in the photo-Beckmann rearrangement. In the present studies we used the title steroidal substrates in which one of the migrating carbons of the oximes is tetra-substituted and therefore, if any radical pair or ion pair is involved in the rearrangement, these species would be more stable and the original configuration of the migrating carbon would be lost more readily in the product lactams.

Results

The oximation of *O*-acetylandrosterone[5] was found to give a single oxime **1** as described previously.[6] The ground state Beckmann rearrangement of **1** has already been described by Regan and Hayes,[6] and later by Barton and his colleagues.[7] Our repetition of this Beckmann rearrangement with thionyl chloride led to a lactam, $C_{21}H_{33}O_3N$, mp 291—292 °C (50% yield), described by the previous investigators, and a mixture of olefins. The structure of the former was confirmed to be 17a-aza-*D*-homo-5α-androsterone **2** both by the NMR spectrum (no signal corresponding to methylene protons adjacent to the nitrogen) and by the mass spectrum in which distinct fragments were observed at *m/e* 347 (M^+), at *m/e* 332, at *m/e* 272, and at *m/e* 150. The respective fragments of the mass spectrum are attributable to the following fragments A, B, and C.[8] The olefins also obtained in a substantial



amount (31%) were amorphous. The elemental analysis and the mass spectrum of this was in accord with the molecular formula $C_{21}H_{31}O_2N$. The infrared spectrum of this revealed the characteristic bands at 2280, 1735, 1643, and 900 cm^{-1} attributable to C≡N stretching, acetoxy C=O stretching, C=C stretching and terminal methylene out-of-plane deformation vibrations. The NMR spectrum of this, however, showed it to be a mixture of 3α-acetoxy-13,17-seco-enoic nitriles, **3a**, **3c**, and **3e** with the double bond at 13, 18, at 12, 13 and at 13, 14. Thus, the NMR spectrum showed a broad singlet at τ 5.00, a couple of singlets of equal intensity at τ 5.23 and 5.54, two singlets at τ 7.96 and 9.29. These signals are safely assignable to the 3β-proton, the exocyclic methylene protons on a cyclohexane ring, the 3-*O*-acetyl group, and the C-10 methyl protons of **3a**. Besides these signals the spectrum showed a doublet at τ 4.38 (J=6.0 Hz) ascribable to the C-12-H of **3c** and a singlet at τ 9.26 ascribable to the 10β-methyl protons of **3c** and **3e**. Based on the peak areas the ratio of **3a**, **3c**, and **3e** were estimated to be 2:2:3. The hydrolysis of this mixture with methanolic KOH at room temperature resulted in the formation of a mixture of the corresponding 3β-ols. In the NMR spectrum two singlets at τ 5.25 and 5.56 and a broad singlet at τ 6.00 were observable and these are attributable to the exocyclic methylene protons and the 3β-proton of **3b**. No signal due to an olefinic proton at C-12 was observed but in the methyl part of the spectrum, in addition to the singlet at τ 9.33 ascribable to 10β-methyl protons of **3b**, another singlet at τ 9.29 and a doublet at τ 7.98 (J=2.4 Hz) were observable. We attribute this to the signal due to 10β-methyl protons and 13-methyl protons of **3f**. Based on the intensities of each signals the ratio of **3b** and



Scheme 1

3f was estimated to be approximately 3:2. The nitriles may be derived either by a second-order Beckmann rearrangement[9] of **1** or by the conversion of the lactam **2** under the reaction condition.[10] But the treatment of **2** in dioxane with $SOCl_2$ did not afford nitriles. Thus, it is certain that these are derived through a second-order Beckmann rearrangement of **1** and is not a secondary reaction product. It is noted that a product due to Beckmann fission of *cis*- and *trans*-8-methyl-1-hydrindanone oximes was a compound with an endocyclic double bond.[11] The obtaining of lactam **2** confirmed that the hydroxyl group is in *anti* position with respect to the C-13 methyl group.

The parallel experiments were then performed with 13α-androsterone oxime. 13α-Androsterone (lumiandrosterone) was first prepared by Butenandt and Poschmann by the photochemical isomerization of androsterone in 1944.[12] In the present study, the irradiation of 3-*O*-acetylandrosterone in dioxane afforded 3-*O*-acetyl-13α-androsterone, mp 122—124 °C, in *ca.* 21% yield. The oximation of this by the usual method afforded a single oxime **5**, mp 186—187 °C, and no isomeric oxime was formed as revealed by tlc. The Beckmann rearrangement of this oxime under the same condition as with androsterone oxime yielded a lactam **4**, mp 193—194 °C* and a mixture of olefins (57 mg) **3a**, **3c**, and **3e** in the ratio of approximately 2:5:3 as was judged by the NMR spectrum. The lactam **4** was isomeric with the lactam **2** and revealed IR bands at 1663 and 3200 cm^{-1} attributable to lactam C=O stretching and lactam NH stretching vibrations. The structure of the lactam **4** should be either 17a-aza-*D*-homo-5α,13α-androsterone or 17-aza-*D*-homo-5α, 13α-androsterone and the former was found to be correct by the NMR and mass spectra. The NMR spectrum of **4** revealed three three-proton singlets at τ 8.74, and at τ 7.96 ascribable to the C-10 methyl, the C-13 methyl and the 3-*O*-acetyl groups, and a three-proton singlet at τ 5.03 and a broad one-proton singlet at τ 3.52 (which vanished on the addition of D_2O), ascribable to the 3β-H and the NH. Since no signals due to methylene protons attached to the lactam nitrogen are found, the structure of the lactam **4** should be 17a-aza-*D*-homo-5α,13α-androsterone. This structure was confirmed by the mass spectrum which showed qualitatively the same major fragmentation patterns with that of the lactam **2**. Therefore, the configuration of the hydroxyl group of **5** should be *anti* with respect to the C-13 methyl group.

The oxime **1** in methanol was photolyzed by a 15 W low pressure Hg arc lamp[13] for 30 hr under argon atmosphere to afford a product in which the presence of major four compounds was evidenced by the tlc analysis. Careful separation of the less polar lactam part by the preparative tlc afforded only two lactams, **2** (3%) and **4** (1%), which were identical with the lactams obtained by the ground state Beckmann rearrangements of **1** and **5**. Apart from these lactams a mixture of 3-*O*-acetylandrosterone and 3-*O*-acetyl-13α-androsterone[14] was obtained in 5% yield, together with the oxime **1** in 6% yield.

The photolysis of 3-*O*-acetyl-13α-androsterone oxime **5** was then studied under the same conditions as **1** and afforded a complex mixture of the products. Tlc analysis of this mixture indicated a similar pattern to that in the photolysis of **1** and disclosed the formation of the four major products. Careful preparative tlc gave the crystalline **4** (1%), a mixture of 3-*O*-acetyl-13α-androsterone and 3-*O*-acetylandrosterone (11%) and a gum **6** (3%), apart from the recovered starting oxime (6%). The product **4** was identical with the lactam obtained by the ground state Beckmann rearrangement of **5**. The NMR and IR spectra of the gum **6**, unobtainable in the pure crystalline form (although the near homogeneity of the material was revealed by the tlc examination), were taken and they revealed that gum **6** might be a 3-*O*-acetyl-17-aza-*D*-homo-5α,13α-androsterone. Thus, the mass spectrum of **6** revealed the M^+ peak at *m/e* 347, corresponding to $C_{21}H_{33}O_3N$, and a significant peak at *m/e* 288 due to the elimination of acetic acid from the parent ion. The IR spectrum of **6** revealed the NH band at around 3400 cm^{-1}, the OAc at 1733 cm^{-1} and the lactam C=O group at 1643 cm^{-1}. The NMR spectrum showed three three-proton singlets at τ 9.32, at τ 8.76, and at τ 7.97, a singlet at τ 5.05 and a multiplet from τ 6.2—7.0. These may be attributable to the C-10 methyl, the C-13 methyl, the 3-*O*-acetyl, the 3β-H and the C-16-methylene protons.

Through the studies of these two photolyses, the lactam parts of the crude products were very carefully examined. However, none of **6** or **7** from the photolysis of **1**, and none of **2** or **7** from the photolysis of **5**, could be detected in the reaction mixture. Moreover, no nitriles stemming from the photo-Beckmann fission

* Described previously[1] as mp 180—182 °C.

were detected in the photolysates of **1** and **5**.

Discussion

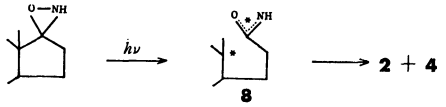
It is notable that while camphor oxime, in which the carbon α to the oximino group is in the bridgehead position and tetra-substituted and is comparable to the present system, gives solely nitriles due to the photo-Beckmann fission,[15] the photolysis of the oximes **1** or **5** does not give any nitriles on photolysis. It is interesting to speculate on the reason for this difference in the modes of photolysis between camphor oxime and steroidal 17-oximes.

One of the rationale for this difference would be the following. In camphor oxime the C_1–C_6 bond may cleave without the intervention of an oxaziridine intermediate since the oxaziridine, if it is formed, should be in the high energy state and would be unstable due to the interaction between the oxaziridine ring and both the C_1-methyl and the extra C_7-methyl. Therefore, the excited camphor oxime would prefer the lower energy reaction pathway, forming an imino radical instead of forming the corresponding oxaziridine ring.

In agreement with this, norcamphor oxime, in which the α-carbon is in bridgehead position but is tri-substituted and there are no C_1- and C_7-methyl groups, affords no cleaved products but the products due solely to normal photo-Beckmann rearrangements.[16]

On the basis of these considerations, we suggest that among several factors which result in the photo-Beckmann fission, the relative stabilities of the intermediate oxaziridine and the N–O bond cleaved species should be the crucial factor together with the strength of the C–C bond to be cleaved.

The formation of an epimeric pair of lactams from an oxime **1** is at variance with the mechanistic pattern on the breakdown of oxaziridine we previously suggested, although we were unable to isolate the lactam **2** from the photolysate of the oxime **5**.[2] The observed non-stereospecificity in the migration from the oxaziridine intermediate to the lactams cannot be due to secondary photolysis of the lactam **2**, which reveals UV absorption maximum at 207 nm (ε: 7300, CH_3OH), as **2** was found to be stable under the condition of the photolysis. The present results would, therefore, require the intervention of a radical or a charged intermediate species, such as **8**, in the rearrangement in liquid phases; in this intermediate[17] the C_{13}–C_{17} bond of the androsterone framework is broken and the C-17 end is released prior to bonding to the nitrogen. The failure in isolating **2** in the photolysis of oxime **5** can either be due to inadequacy of the analysis or due to some complicated origin.



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With regard to the implication of the present results for the migration step of the photo-Beckmann rearrangement, on the basis of our results together with those of others, the following possibilities on the mode of the formation of lactam from oxaziridine may be considered.

The first would be a unifying mechanism for the whole saturated oximes involving the intervention of an intermediate in which the C–C bond between oxaziridine and the migrating α-carbon is released. If this is the case, our previous results on the oximes of cholestane series should be reinterpreted in terms of the involvement of an intermediate with the configurationally stable ion pairs or radical pairs.

Another possibility is dual mechanism for the saturated oximes. Oximes of cholestan-6-ones, menthone, isomenthone and norcamphor bear the tri-substituted migrating carbon whereas in the oximes of androsterone and 13α-androsterone, one of the migrating carbons is tetra-substituted. Thus we might suspect that the dual mechanisms are operative in the saturated oximes, depending on their structural features, particularly the immediate surrounding of the relevant oximino group, and the oxime which can afford stable ionic or radical species by the cleavage would be able to rearrange through an intermediate in which the migrating group becomes free of the migration terminus. In this instance, we cannot exclude the possibility of amide formation without an involvement of the intermediary oxaziridine although this seems less likely.

Between these, a unifying mechanism would have some difficulty in accommodating the fact that the two isomeric lactams are formed in nearly equal amounts in the case of cholestan-6-one oximes,[2] 3α,5-cyclo-5α-cholestan-6-one oxime,[3] unsymmetrically α-substituted cyclohexanone oximes[4] and norcamphor oxime.[16] Results in these oximes, would be better understandable if we assume both the migrating carbons of oxaziridines migrate to lactams without intermediate. Therefore, with reservation, the preference appears to be for the operation of the dual mechanism.

In the present experiments although we obtained only 17a-aza-*D*-homo-androsterones as the product lactam, the photolysis of the oxime **5** afforded 17-aza-*D*-homo-isomer in addition to 17a-aza-*D*-homo-androsterone.

In terms of the dual mechanism these results may be explicable as follows; in the oxime **5**, the C-13 end may rearrange through the open-chain intermediate such as **8** from oxaziridine but the C-16 end may still be able to migrate to lactam **6**, in this case, without intermediate.

This would mean that in the oxime **1** or **5** two mechanistic modes of the breakdown of oxaziridine appear to operate at the same time although we failed to isolate the lactam **7** in the photolysis of the oxime **1**. Further examination of the stereochemistry of the reaction on the various steroidal substrates will obviously be required to clear up the problem.

Experimental

All mp's were determined by a Yanagimoto type hot-stage and were uncorrected. Unless stated otherwise, IR was determined in Nujol using a Jasco model IR-E spectrophotometer. All NMR spectra were determined on a

Japan Electron Optics PS-100 high resolution NMR spectrometer in $CDCl_3$ solution using TMS as an internal reference. Wako gel B 5 for the preparative tlc was used. The progress of the reactions was followed by the tlc.

Beckmann Rearrangement of 3-O-Acetylandrosterone Oxime. Oxime **1** (300 mg) and thionyl chloride (0.1 ml) in dioxane were stirred for 10 minutes at room temperature. The reaction mixture was neutralized with aqueous 10% KOH and was extracted with chloroform. The solution was worked up in the usual manner. The residue (305 mg) revealed two spots on tlc and column chromatography (Mallinkrodt, silica gel 100 mesh, 3 g) afforded 88 mg of colorless gum and 154 mg of crystals **2**. The latter was recrystallized from acetone, yielding **2**, mp 291—292 °C. (lit., mp 280—284 °C).[7] IR; 3180 cm^{-1} (NH) 1747 cm^{-1} (OAc). 1678 cm^{-1} (lactam C=O). NMR; τ 5.01 (1H, 3β-H), τ 7.96 (3H, OAc), τ 8.86 (3H, C-13 methyl), τ 9.23 (3H, C-10 methyl). The colorless gum was proved to be a mixture of olefins **3a**, **3c**, and **3e** be the NMR spectrum. (See text.)

The Hydrolysis of 3a, 3c, and 3e. The gum above (88 mg) in 5% methanolic KOH (8 ml) was stirred for 5 hr at room temperature. The usual work-up of this reaction mixture afforded an unsaturated nitrile **3b** and **3f** (84 mg) in the ratio of 3: 2.

Photolysis of 3-O-Acetylandrosterone Oxime. Oxime **1** (960 mg) in dry methanol (400 ml) was irradiated by a 15-W low pressure Hg arc lamp under argon atmosphere at room temperature for 104 hours. The solvent was removed under reduced pressure and the residue showed four major spots on tlc. The reaction mixture was submitted to the preparative tlc. (chloroform–acetone 4: 1). Four fractions A, B, C and D were obtained in the order of their increasing polarity. The fraction A (157 mg) was recrystallized from ether, yielding the lactam **2** (57 mg) identical with the lactam **2** obtained by the ground state Beckmann rearrangement of **1**. The fraction B (84 mg) was recrystallized from ether, yielding the lactam **4**, mp 180—182 °C. The fraction C (157 mg) was recrystallized from acetone to yield the pure starting oxime (57 mg). The fraction D (215 mg) was a gum and the NMR spectrum of this showed it to be a mixture of 3-*O*-acetylandrosterone and 3-*O*-acetyl-13α-androsterone.

3-O-Acetyl-13α-androsterone. 3-*O*-Acetylandrosterone (1.27 g) in dioxane (400 ml) was irradiated for 5 hr by a 100 W high pressure Hg arc lamp. After the evaporation of the solvent, the residue was submitted to the preparative tlc. The separation of 3-*O*-acetylandrosterone and the 13α isomer with the similar R_f values could be achieved by twelve times developments of the thin-layer with a mixed solvent of petroleum ether and benzene with an increasing amount of the latter. The number of developments and the proportions of the volumes of petroleum ether and benzene are as follows; twice with 5 (petroleum ether): 1 (benzene), three times with 3: 1, once with 2: 1, twice with 1: 1, twice with 1: 1, twice with 1: 2 containing a few drops of ethyl acetate. Thus, 3-*O*-acetyl-13α-androsterone (263 mg, 21%) was obtained and showed mp 122—124 °C. Butenandt and Poschmann reported mp 121—122 °C for this compound. NMR τ 9.37 and τ 9.04 (C-10 methyl and C-13 methyl) τ 8.03 (OAc) τ 5.09 (3β-H). IR; 1740 cm^{-1} (OAc, five-membered ring ketone).

Oxime of 3-O-Acetyl-13α-androsterone. 3-*O*-acetyl-13α-androsterone (165 mg), hydroxylamine hydrochloride (180 mg) and sodium acetate (120 mg) in ethanol (7 ml) were stirred for 6 hours at room temperature and then were warmed for 17 hours at 50—60 °C. The usual work-up of the reaction mixture afforded the crude oxime **5** (129 mg). This was recrystallized from hexane, yielding 111 mg of the oxime **5**, mp 186—187 °C. Found: C, 72.71; H, 9.37; N, 3.88%; Calcd for $C_{21}H_{33}O_3N$: C, 72.58; H, 9.57; N, 4.03%. IR 3440 cm^{-1} (OH), 1710 cm^{-1} (OAc), 1665 cm^{-1} (C=N), Mass *m/e* 347 (M^+). NMR τ 9.34 and τ 8.96 (C-10 methyl and C-13 methyl) τ 7.97 (OAc), τ 4.97 (3β-H).

Beckmann Rearrangement of 3-O-Acetyl-13α-androsterone Oxime. To the solution of **5** (100 mg) in dioxane (1 ml) there was added thionyl chloride (0.5 ml). The solution was stirred for 20 min at room temperature. Work-up as was described in the case of the oxime **1** afforded a crude product (157 mg). This showed to be a mixture of nonpolar and polar substances by the tlc. Purification by the preparative tlc afforded a crude lactam **4** (40 mg) and a mixture of olefins. The former was recrystallized from a mixture of ether and hexane to yield the lactam **4**, mp 193—194 °C (25 mg). Found: C, 72.57; H, 9.62; N, 3.77%. Calcd for $C_{21}H_{33}O_3N$: C, 72.58; H, 9.57; N, 4.03%. IR 3200 cm^{-1} (NH), 1741 cm^{-1} (OAc), 1633 cm^{-1} (lactam C=O). Mass *m/e* 347 (M^+), *m/e* 332, 272, 150. The latter was a colorless gum and it was proved to be a mixture of the three olefinic nitriles **3a**, **3c**, and **3e** in the ratio of 2: 5: 3 as was judged by the NMR spectrum in the same manner as in the case of Beckmann rearrangement of **1**. The hydrolysis of this mixture (43 mg) afforded a mixture of **3b**, **3d**, and **3f** (33 mg) in a ratio of 2: 5: 3 as was judged by the NMR spectrum. The presence of **3d** was apparent by the presence of a broad doublet signal at τ 4.39 (J=4.5 Hz). The 10β-methyl protons of **3d** and **3f** appeared as a coincident singlet at τ 9.29. Moreover, there were two doublets at τ 7.98 (J=2.4 Hz) and at τ 8.05 (J=2.7 Hz), which are attributable to the 13-methyl protons of **3f** and **3d**. The observed small splittings are due to allyl couplings.

Phytolysis of 3-O-Acetyl-13α-androsterone Oxime. Oxime (500 mg) in dry methanol (200 ml) was irradiated by a 15-W low pressure Hg arc lamp under argon atmosphere at room temperature for 30 hr. The solvent was removed under reduced pressure and the residue showed four major spots on tlc. This reaction product was submitted to the preparative tlc. (chloroform–acetone 5: 1). The four fractions A. B, C and D in the order of increasing polarity were obtained. The fraction A (46 mg) was recrystallized from ether to yield 5 mg of the lactam **4** identical with lactam obtained by the ground state Beckmann rearrangement of **5**. The fraction B (30 mg) was purified again by the preparative tlc, yielding 13 mg of gum. It was not in a crystalline state, but the NMR and IR spectra of the gum showed it to be probably a crude lactam **6**. The fraction C (105 mg) was recrystallized from acetone to yield 31 mg of the starting oxime **5**. The fraction D (55 mg) was found to be a mixture of 3-*O*-acetyl-13α-androsterone and 3-*O*-acetylandrosterone from its NMR and IR spectra.

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14) These two isomeric ketones were readily discernible by the difference of the chemical shift of either the C-10 methyl groups or the C-13 methyl groups. (*O*-acetylandrosterone, C-10 methyl at τ 9.18, C-13 methyl at τ 9.14, *O*-acetyl-13α-androsterone, C-10 methyl at τ 9.37, C-13 methyl at τ 9.04) The isomeric *syn* oxime was neither observed on tlc nor isolated. This is understandable by assuming that in steroid 17-oximes the thermal relaxation of photochemically formed *syn* oxime to *anti* is very rapid even at room temperature. (*cf.* G. Wettermark, "The Chemistry of the Carbon-Nitrogen double bond," ed. by S. Patai, Interscience, London (1970), p. 565).

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17) This naturally implies a solvated species.