

TRIMETHYLSILYL ENOL ETHERS FORMED BY AN IMINO DIELS-ALDER REACTION: MECHANISTIC IMPLICATIONS

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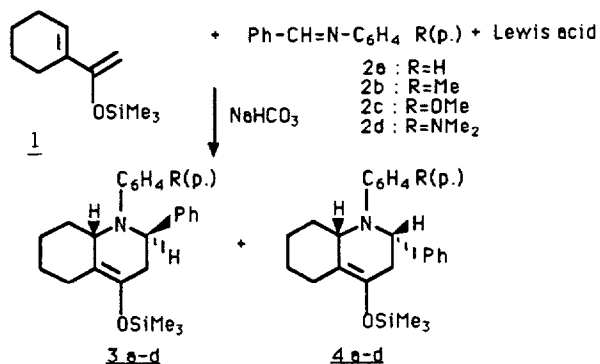
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Summary : Diastereomeric silyl enol ethers **3** and **4a-c** have been isolated starting from **1** and **2a-c** in the presence of AlCl_3 , implying a concerted process. The structures of **3c** and **4c** were assigned by single crystal X-ray crystallography.

The synthetic potentiality of the condensation of silyloxydienes with imines under Lewis acid catalysis has been largely demonstrated ¹⁻⁵. However, the reaction mechanism has given rise to much controversy ⁶⁻⁸. A recent paper relating the X-ray crystal structure of an exo t-butyl dimethylsilyl enol ether adduct obtained by an imino Diels-Alder reaction ⁷⁻⁸ prompts us to publish our results. We reported previously ⁹ the reaction of trimethylsilyloxydiene **1** with benzylideneaniline **2a** ($R = \text{H}$) catalyzed by various Lewis acids and the ¹H NMR characterization of the intermediate cycloadducts **3a** and **4a**. More recently, cyclic intermediates could be isolated starting from 1,3-dimethoxy-1(trimethylsilyloxy)butadiene and various imines but were only characterized by ¹H NMR without assignment of their configuration ⁶. In the present work, we extend our study to imines generated from p-substituted anilines **2b-d**.

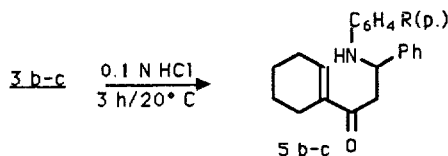


The reactions were run in CH_2Cl_2 by premixing imine and Lewis acid, then adding **1** for various durations and at different temperatures. After aqueous NaHCO_3 treatment, a mixture of cycloadducts **3** and **4b-d** was obtained and analyzed by ¹H NMR. As previously ($R = \text{H}$) ⁹, we observed a **3/4b-c** ratio of 70/30 under kinetic control and 2/98 under thermodynamic control.

When the reaction of **2b**, carried out under kinetically controlled conditions, was followed by treatment with saturated aqueous NH_4Cl or 0.1N HCl for a few minutes, only starting materials and adducts **3b** and **4b** were detected by ¹H NMR.

Subsequent MeOH treatment led to the crystalline **3a-c** and **4a-c** cycloadducts ^{10,11}. To our knowledge, crystalline trimethylsilyloxy cycloadducts had never been isolated. X-ray single crystal structure determination of **3c** and **4c** ¹² indicated that the relative configuration of C-2/H-2 and C-9/H-9 bonds is respectively trans (exo adduct) and cis (endo adduct). In the two diastereomers the C-9/H-9 bond is axial. The geometry of the nitrogen atom is tetrahedral rather than planar, due to the p-methoxy substituent. The ¹H NMR parameters are in good agreement with the dihedral angles so determined.

On the other hand, treatment of **3b-c** by aqueous 0.1N HCl at room temperature for 3 h gave exclusively the α,β -unsaturated monocyclic ketones **5b-c** ^{10,13}. Moreover **5b** did not cyclize in the presence of AlCl₃ and Me₃SiCl in CH₂Cl₂ under conditions in which **3b** and **4b** were formed under kinetic control.



Finally, in all cases, bicyclic ketones were obtained when cycloadducts were treated by Et₃N/MeOH ⁹; they were never detected in the reaction mixtures. Our results differ from previously published ones ^{7,8} as we only characterize cycloadducts in the reaction mixtures, without any α,β -unsaturated or bicyclic ketones. Therefore, in the present study **3** and **4** are the primary products of the reaction, thus implying a Diels-Alder process which is probably a non-synchronous concerted one.

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- 10) All compounds gave correct elemental analysis (C, H, N) and IR, MS, ¹H NMR spectra in agreement with the proposed structures.
- 11) Selected physical constants of cycloadducts : solvent of crystallization ; ¹H NMR : 250 MHz (CDCl₃), δ ppm, ³JHz **3a** : m.p. = 82 °C (EtOH); 4.9 (t) H₂, ³JH₂H₃ = 5 ; ³JH₂H₃' = 5. **4a** : m.p. = 110°C (Et₂O) ; 4.8 (t) H₂, ³JH₂H₃ = 5.5 ; ³JH₂H₃' = 5.5. **3b** : m.p. = 84°C (MeOH) ; 4.7 (t) H₂, ³JH₂H₃ = 5.2 ; ³JH₂H₃' = 5.2. **4b** : m.p. = 127°C (MeOH) ; 4.6 (dd) H₂, ³JH₂H₃ = 8.7 ; ³JH₂H₃' = 4.3. **3c** : m.p. = 85°C (EtOH) ; 4.5 (t) H₂, ³JH₂H₃ = 5.5 ; ³JH₂H₃' = 5.5. **4c** : m.p. = 129°C (EtOH) ; 4.2 (dd) H₂, ³JH₂H₃ = 9 ; ³JH₂H₃' = 3. **3d** : oil ; 4.5 (t) H₂, ³JH₂H₃ = 5.5 ; ³JH₂H₃' = 5.9. **4d** : oil ; 4.2 (dd), H₂, ³JH₂H₃ = 12.8 ; ³JH₂H₃' = 4.4.
- 12) P. Charpin, M. Nierlich, L. Le Coz, L. Wartski, submitted to *Acta Crystallog.*
- 13) Selected physical constants of α,β -unsaturated ketones : ¹H NMR : 250 MHz (CDCl₃) δ ppm, ³JHz. **5b** : m.p. = 118°C.; 4.8 (dd) H₂, ³JH₂H₃ = 5.1 ; ³JH₂H₃' = 10.2. **5c** : m.p. = 123°C.; 4.9 (dd) H₂, ³JH₂H₃ = 7 ; ³JH₂H₃' = 9.

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