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COMMUNICATION

Facile dearomatization of nitroaromatic compounds using lithium enolates of unsaturated ketones in conjugate additions and (4+2) formal cycloadditions

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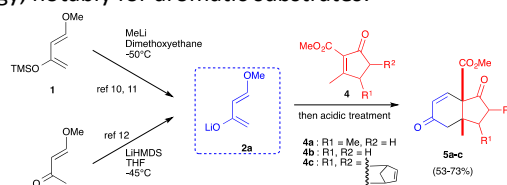
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Dearomatization of conventional nitroarenes by lithiated enolates derived from methyl vinyl ketones easily takes place, following a formal (4+2) cycloaddition process. While nitroindoles react readily with in situ generated conjugated enolates, the deaggregation of these latter species by HMPA extends the reaction scope to the more aromatic nitronaphthalenes and pyridines.

For a long time, drug design has been oriented towards « flat molecules », involving mostly aromatic structures. The last decade has been marked with a strategic turn-around, pharmaceutical industry orienting now its quest for new bioactive molecules through the development of novel 3D scaffolds such as to generate a larger number of differentiated products.¹ At first glance, a straightforward approach to such targets relies on commercially available alicyclic building blocks. A cost-effective alternative consists in dearomatizing arenes.² Cycloadditions or annulations reactions are attractive transformations in this context, generating polycyclic 3D scaffolds in one operation. Because of the electron-richness of most arenes, (4+2) dearomatizing processes rely mainly on their involvement as dienes in normal electron demand (NED) transformations.³ The dienophilic behavior of electron-depleted aromatics is more scarcely described. Nevertheless, provided that the arene is sufficiently electron-poor, substituted C=C aromatic double bonds have been shown to react with electron-rich 1,3-dienes in (4+2) Diels-Alder cycloadditions.⁴ Nitroarenes such as in nitro-indoles, -pyrroles or -naphthalenes have been successfully reacted in this way.⁵ However, efficient transformations are generally observed

under drastic reaction conditions, including extended heating at high temperatures.^{4,5} Such harsh procedures lead to the rearomatization of the cycloadducts most of the time and thus loss of functional groups. Electrophilic activation of the dienophilic partner by acid catalysis (Lewis or Brønsted) usually allows to decrease the reaction temperature by lowering its LUMO energy.⁶ However, the acid sensitivity of the functionalized (silyl)oxydienes, such as Danishefsky diene for instance, prevents their use in many cases.⁷ High pressure activation has been shown to overcome this difficulty, allowing to perform the reactions in a range of temperatures compatible with most substrates/cycloadducts.^{4,5,8} But hyperbaric equipment being seldom available in organic laboratories, a more general alternative method is highly desirable. In this context, the less intuitive activation of the dienic partner, by raising its HOMO energy, appears as an attractive option. This has been considered through (poly)enamine catalysis, an elegant but somewhat limited strategy, notably for aromatic substrates.^{5e-f,9}



Scheme 1. Reaction between activated lithium enolate **2a** and tetrasubstituted cumbersome dienophiles to afford formal (4+2) cycloadducts.

In 1988, Baker *et al.* showed that a nucleophilic activation of Danishefsky diene **1** could overcome the lack of reactivity of inert tetrasubstituted dienophilic substrates, by transforming **1** into lithium enolate **2a** in the presence of methyl lithium in dimethoxyethane (DME) at -50°C (Scheme 1).¹⁰ Reaction with the dienophile **4a** occurred at -90°C in THF to afford the Michael adduct, which was further cyclized under acidic conditions to provide the corresponding formal cycloadduct. Danishefsky *et al.* reported a related transformation, involving **4b**, in the context of the total synthesis of (\pm)-aplikurodinone.¹¹ Recently, Snyder *et al.* performed a similar nucleophilic activation to access Hajos-Parrish ketone isomers

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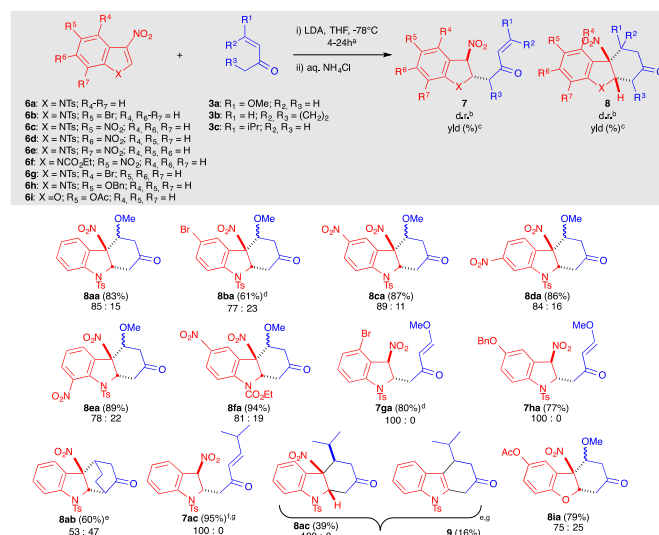
from sterically hindered tetrasubstituted dienophiles **4c** in a three-steps addition/cyclization/retro-Diels-Alder sequence.¹² This successful nucleophilic activation of **conjugated enolate 2a** led to the formal cumbersome cycloadduct **5**, unreachable from **1** under classical conditions. We therefore wondered if this oxydienic nucleophilic activation path could be adapted to more challenging aromatic partners as dienophiles. This low-temperature procedure would give access to formal (4+2) cycloadducts, and would be *compatible with many sensitive substrates/products*, thus extending the scope of dearomatizations and paving the way to novel polycyclic functionalized tridimensional scaffolds useful in the context of natural products or diversity oriented syntheses.

Inspired from Snyder's work, we first tried to generate the lithium **enolate 2a** from butenone **3a** directly, avoiding the use of the more expensive silyloxydiene. **3a** was slowly added to a preformed LDA solution, at -78°C , in THF, in order to prevent the usual condensation of the **conjugated enolate anion** on the butenone precursor, behaving as a Michael acceptor. Reaction of this preformed lithium **enolate** on the model tetrasubstituted ketone **4b**, gratifyingly led to results similar to those reported by Danishefsky from methoxytrimethylsilyloxybutadiene.¹³ This led us to use the methoxybutenone **3a** as **enolate** precursor in standard conditions (THF, at -78°C) for the dearomatization study (see ESI for reaction optimization).

We started this work with 3-nitroindole **6a**, which was reacted with a slight excess of **conjugated enolate 2a**. After 4 hours, the reaction mixture was hydrolyzed and we were pleased to observe the nearly complete conversion of the starting aromatic substrate into the expected cycloadduct **8aa**, obtained as a 85:15 diastereomeric mixture and isolated in a global 83% yield (Scheme 2). This result thus shows the possibility of resorting to a nucleophilic activation of the diene partner in these dearomatizing formal cycloadditions. In the basic conditions of the reaction, rearomatization of the generated indoline by elimination of nitrous acid, could be anticipated but was not observed. In addition, no strong acidic treatment was required after the conjugate addition to trigger the subsequent cyclization step. This reaction compares favourably to the Diels-Alder sequences already reported between **6a** and **1**.⁵ Hence, the reaction is performed at lower temperature, with a slightly higher diastereoselectivity, in conditions preventing the loss of functional groups. Noteworthy, no reaction was observed when interacting **6a** with **3a** in the presence of a catalytic amount of chiral secondary amine to promote the dienamine derived process (see ESI).

We then extended this methodology to other nitroindoles (see ESI for reaction optimization). **6b**, Bearing a bromine substituent in position 5, reacted in an analogous way and led to **8ba** in 61% isolated yield, and in a 77:23 d.r.. With an additional nitro substituent on the 6-membered ring of the indole, **6c** reacted similarly, involving regioselectively the C2=C3 moiety of the 5-membered heteroaromatic part as the Michael acceptor. It furnished **8ca** in 87% yield, as a 89:11 mixture of diastereomers. Dinitroindoles **6d** and **6e** as well as the carbamate **6f** led to cycloadducts **8da**, **8ea** and **8fa** in 86,

89 and 94 % yield respectively in similar diastereoselectivities. The trans relative stereochemistry between the nitro and methoxy group in the major diastereomer could be confirmed by an X-Ray diffraction study on monocrystals of **8fa** (See ESI). The substrate bearing a bromine atom in position 4, **6g**, behaved slightly differently. A larger 2.4 excess of the **conjugated enolate anion** was necessary to get a complete transformation. After hydrolysis, the dearomatized Michael adduct **7ga** was isolated as a single trans diastereomer in 80% yield. An X-ray diffraction study confirmed this relative trans stereochemistry (See ESI). The nitronate intermediate did not spontaneously cyclize in this case and the indoline, which was expected to be unstable and give back the starting materials upon hydrolysis, proved stable and was isolated by chromatography on silica. This outcome suggests that the cyclic adducts obtained before were, as expected, formal cycloadducts, formed through a two-step sequence. The more difficult cyclization step observed in this case might be due to the steric hindrance generated by the bromine atom in position 4, close to the potentially reactive center. More surprisingly, a similar behavior was observed with the 5-benzyloxyindole **6h**, which afforded the *trans* Michael adduct **7ha** in 77% yield.¹⁴



Scheme 2. Dearomatization of 3-nitro-indoles and -benzofuran **6** with butenones **3**

a : see ESI for the reaction time. b : determined (det.) by ¹H NMR on the crude mixture. c : isolated overall yield. d : 2.4 equiv of enolate. e : The crude 1,4-adduct cyclized when treated on SiO₂. f. yield of the crude 1,4-adduct, after hydrolysis. g: 1.8 equiv of enolate.

This dearomatizing methodology was next extended to differently substituted **enolate anions of unsaturated ketones**. The use of cyclohexenone (**3b**) as precursor led to the full conversion of the substrate. The resulting 1,4-adduct proved, in this case, unstable on silica and spontaneously cyclized to lead to the formal cycloadduct **8ab**, isolated in an overall 60% yield as a 53:47 mixture of diastereomers. An X-ray diffraction study of the major diastereomer allowed the assignment of the relative stereochemistries (See ESI). Noteworthy, when considering a classical NED cycloaddition process, the corresponding neutral silyloxyhexadiene remained inert

towards nitroindole **6a** (thermal or organocatalyzed conditions). The isopropyl substituted enolate, generated from 5-methylhex-3-en-2-one was an even more challenging case, the hindrance imposed by the *i*Pr group being expected to slow down the cyclization step. A 59% conversion was observed after 3 h at -78°C when 1.2 equiv of **2c** were used; the *trans* Michael adduct **7ac** was expectedly formed. Increasing the reaction time to 24 h and the excess of enolate to 1.8 equiv gratifyingly led to a 95% conversion in the 1,4-Michael adduct, which astonishingly easily cyclized to furnish the corresponding formal cycloadducts. The compound **8ac** featuring a *cis* relationship between the nitro and *i*Pr groups was isolated in a 39% yield, while rearomatized cycloadduct **9**, arising from the *trans* cycloadduct, was obtained in a 16% yield.¹⁵ The structures of **8ac** and **9** could be firmly assigned by X-ray analyses (see ESI).

Noteworthy, a Suzuki coupling was easily performed with the brominated tricyclic compounds **8ba** and phenylboronic acid, under classical conditions, showing the late functionalization potential of this elaborated formal cycloadduct.¹⁶

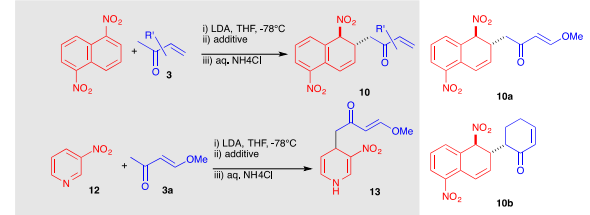
We next considered the involvement of different nitro substituted aromatic rings to enlarge the scope of this reaction. 3-Nitrobenzofuran **6i** reacted like nitroindoles in the presence of enolate anion **2a**, leading to the dearomatized cycloadduct **8ia** directly, obtained as a 75:25 d.r. and isolated in a 79% yield.

We then envisaged these dearomatization reactions with more demanding nitroarenes, such as naphthalenic compounds, renowned for their high stability. When reacted with an excess of enolate **2a** under the reaction conditions used above, 1,5-dinitronaphthalene proved inert. Increasing the reaction time or the excess of enolate did not improve the result (Table 1, entry 1). Performing it at higher reaction temperatures did not facilitate the transformation either while secondary adducts resulting from the self-condensation of the conjugated enolate on its precursor were observed.

Lithium enolate species are known to form aggregates and their reactivities to be notably influenced by the size of these clusters. Addition of deaggregating agents is known to favour smaller and more reactive nucleophilic species, a phenomenon reported to play a positive role on the reactivity of lithium species.¹⁷ Addition of 1.2 equiv of TMEDA to the reaction mixture proved encouraging, allowing the formation of traces of the expected 1,4-adduct **10a** (entry 2). Even if insufficient, this result suggests that its aggregation state indeed tunes the reactivity of the conjugated enolate anion in these transformations. Switching from TMEDA to DMPU improved the conversion to 28% (entry 3) and the best result was obtained with HMPA which allowed to get nearly complete conversion of the dinitronaphthalene into its dearomatized Michael adduct **10a** (entry 4). The 1,4-adduct **10a** was stable enough to be purified by column chromatography and could be isolated in a 79% yield as a single *trans* diastereomer.¹⁸ Increasing the amount of HMPA led to a full conversion and a slightly increased 82% isolated yield (entry 5). Noteworthy, heating the crude mixture under vacuum to remove the excess

HMPA, led to re-aromatization into naphthalene **11**, after elimination of nitrous acid (Scheme 3).

Table 1. Dearomatization of dinitronaphthalene and nitropyridine

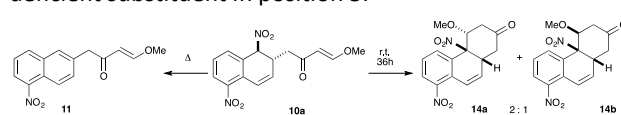


Entry	Additive (equiv)	Adduct	% conv. ^a	Yield (%) ^b
1	none	-	0	-
2	TMEDA (1.2)	10a	traces	-
3	DMPU (1.2)	10a	28	c
4	HMPA (1.2)	10a	97	79
5	HMPA (4.8)	10a	100	82
6	HMPA (4.8)	10b	98	72
7	HMPA (2.4)	13	90	71

a : det. by ^1H NMR on the crude mixture. b : isolated yield. c : not det.

The methodology was next extended to another conjugated enolate partner, using cyclohexenone as precursor. Here again, in the presence of HMPA, the dearomatizing nucleophilic addition occurred at -78°C , furnishing the expected 1,4-adduct **10b** as a single diastereomer in a 72% yield (Table 1, entry 6).

We then envisioned this methodology with the electron-depleted 3-nitropyridine (**12**). Here again, in the absence of HMPA, no reaction took place, while, with HMPA, enolate **2a** added onto the pyridine core, leading to the 1,4-dihydropyridine **13** (71% isolated yield, entry 7). The regiochemistry of this adduct is in line with reported results on nucleophilic additions involving pyridines bearing an electron-deficient substituent in position 3.^{2a,19}



Scheme 3. Transformation of 1,4-adduct **10a**

Interaction of conjugated enolate **2a** with 1,5-dinitronaphthalene furnished the 1,4-adduct **10a**, and no traces of cyclized compound were detected in the crude mixture. However, when the crude was maintained at room temperature for 36h, it fully cyclized into the formal cycloadducts **14a** and **14b** (2:1 ratio). These two diastereomers were separated by column chromatography and isolated in a 53% overall yield (for the two steps sequence). The relative stereochemistries of **14a** and **14b** were assigned by NOESY experiments (See ESI). This methodology thus furnishes the dearomatized (4+2) cycloadducts in smooth conditions. In contrast to classical NED cycloaddition on nitronaphthalenes, rearomatization is not observed. The functional groups are preserved in the products, paving the way to diverse derivatization reactions.

Conclusions

In conclusion, the results described herein show that «conventional» nitroaromatic derivatives can be dearomatized at low temperature in classical conditions using highly nucleophilic lithium enolates derived from simple methyl vinyl ketone derivatives. Trans 1,4-adducts are isolated or go one-step beyond and cyclize to furnish the corresponding formal cycloadducts. This method thus represents an unusual dearomatizing (4+2) formal cycloaddition process promoted by a nucleophilic activation mode, in conditions compatible with many substrates and functionalities. While nitroindoles react with the conjugated enolate anion generated in situ from the corresponding butenones, deaggregation of the nucleophilic species with HMPA enhances its nucleophilic character and extends the scope of the dearomatizing process to more challenging aromatic substrates, such as naphthalenes or pyridines. Nitroaromatics thus behave as Michael acceptors and lead to the formation of 3D (poly)cyclic derivatives advantageously functionalized, that constitute scaffolds prone to potentially interesting derivatizations. Efforts to extend this reactivity to other aromatics and enolates systems are currently under way.

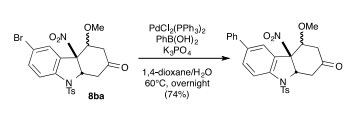
Conflicts of interest

There are no conflicts to declare.

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