ORGANIC LETTERS

2013
Vol. 15, No. 24
6230–6233

N-Heterocyclic Carbene Catalyzed Reaction of Cinnamils Leading to the Formation of 2,3,8-Triaryl Vinyl Fulvenes: An Uncommon Transformation§

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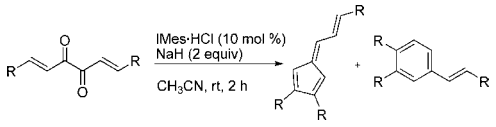
Received October 25, 2013

ABSTRACT



An unexpected transformation of 1,6-diarylhexa-1,5-diene-3,4-diones (cinnamils) to 2,3,8-triaryl vinyl fulvenes via *N*-Heterocyclic Carbene (NHC) catalysis is reported. Mechanistic as well as synthetic novelty is the hallmark of this reaction.

In the general context of organocatalysis,[1] *N*-heterocyclic carbenes (NHCs) occupy a prominent position. NHC catalysis[2] originated as early as 1958 with Breslow's demonstration[3] that thiazolylidene was involved in the thiazolium catalyzed benzoin condensation.[4] However, with the exception of its application in benzoin condensation[5] and the Stetter reaction,[6] NHC catalysis received little attention for a long time. A significant change in this situation occurred in 2004, when Glorius[7] and Bode[8]

§ Dedicated with best wishes to Prof. Gilbert Stork.

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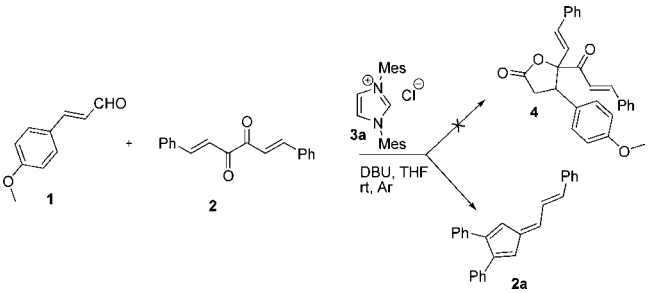
10.1021/ol4030748
Published on Web 12/02/2013

independently showed that NHC can generate homoenolates from enals. Since this discovery, homoenolate annulations to a wide range of carbonyl compounds[9,10] and other electrophiles[11−16] have been reported by several research groups including our own. Other NHC-catalyzed reactions of importance include transesterification[17] and cooperative catalysis;[18] chemistry of α,β-unsaturated acyl azolium ions may also be mentioned in this context.[19] The focal theme of our work has been homoenolate annulation to enones,[9] 1,2-diones, and related compounds.[2g]

The present work has its origin in the observation that homoenolate annulation of cyclic and acyclic 1,2-diones afforded γ-lactones.[12a,20] To explore the scope of this reaction, 1,6-diphenylhexa-1,5-diene-3,4-dione (cinnamil) **2** was exposed to *p*-methoxy cinnamaldehyde in the presence of 1,3-dimesityl imidazole carbene (IMes). A facile reaction occurred; the product isolated, however, was not the expected lactone **4**, but the vinyl fulvene **2a** (Scheme 1).

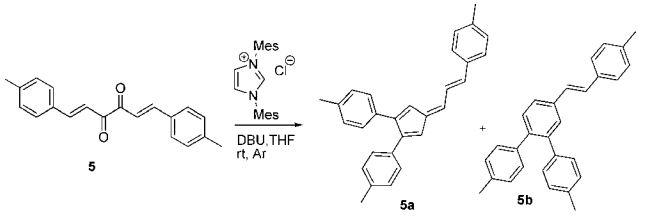
Scheme 1. Background to the Reaction



Evidently, the enal was not a participant in the reaction; the product **2a** was formed by the interaction of two molecules of cinnamil under the influence of NHC. Naturally, the serendipitous formation of a vinyl fulvene and the intriguing mechanistic aspects of the reaction fueled our interest to pursue this uncommon reaction.

A systematic investigation of the reaction was initiated (Scheme 2) by stirring a solution of 1,6-bis(*p*-tolyl)-1,5-hexadiene-3,4-dione **5** and carbene, generated from IMes·HCl and DBU in THF. Conventional workup of the reaction mixture afforded **5a** and a trace of an isomeric product (later identified as the *o*-terphenyl derivative **5b**) along with 4-methylcinnamic acid.

Scheme 2. NHC-Catalyzed Transformation of Cinnamil



The product **5a** was characterized by standard spectroscopic and analytical methods. In the proton NMR spectrum, singlets due to three sets of methyl protons at δ 2.34, 2.35, and 2.37 ppm confirmed the presence of three tolyl groups. The final proof for the structures was obtained from single crystal X-ray determination of **8a** and **5b** (Figure 1).

The reaction was optimized with 1,6-bis(*p*-tolyl)-1,5-hexadiene-3,4-dione **5** by varying the catalyst, base, solvent, and temperature. The results are summarized in Table 1.

The scope of the reaction was examined under the optimized conditions, and the results are summarized in Table 2.

In subsequent experiments it was found that a higher amount of *o*-terphenyl compound could be obtained by varying the reaction conditions from acetonitrile−sodium hydride to toluene−potassium carbonate (Scheme 3).

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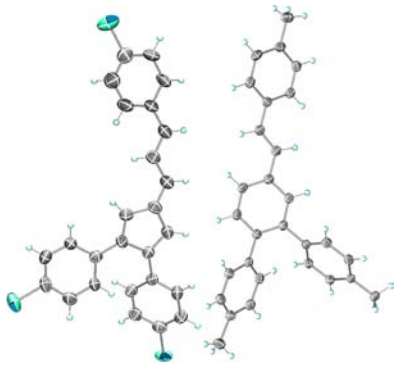


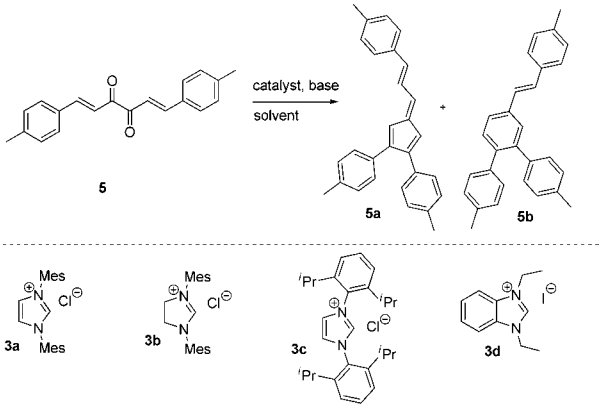
Figure 1. Left: ORTEP diagram of **8a**. Right: ORTEP diagram of **5b**.

Although the mechanistic underpinnings of the uncommon reaction reported herein are not known, a rationalization for the formation of the vinyl fulvene and *o*-terphenyl derivative may be as follows (Scheme 4).

It is conceivable that the addition of IMes to one of the carbonyls of cinnamil will be followed by the formation of the epoxy derivative **A**[1], by a process analogous to the one reported previously.[21] Clearly **A**[1] is set up for a [3,3] sigmatropic rearrangement to afford the oxepine derivative **C**. Isomerization of **C** followed by intramolecular elimination/displacement of IMes can lead to transient bicyclic β-lactone **E**, and the latter can afford the diaryl cyclopentadiene **F** by a retro [2 + 2] process. Parenthetically it may be added that such a retro [2 + 2] process leading to the formation of cyclopentene is supported experimentally[10b] and by computational studies.[22] The anion of **F** (**G**) presumably can undergo addition to a second molecule of cinnamil and subsequently afford the transient epoxide **I**. Fragmentation of **I** followed by protonation of the intermediate **J** will lead to **K**. The latter is set up to deliver the vinyl fulvene or *o*-terphenyl derivative by a concerted or stepwise process. In the concerted process, a base can eliminate cinnamate from **K** to afford the vinyl fulvene, whereas elimination of cinnamate by anchimeric assistance from the cyclopentadienyl moiety will lead to cyclohexadienyl cation **L** and subsequently the *o*-terphenyl derivative. Alternatively **K** can undergo ionization to deliver a cation (not shown), which on proton loss can afford the fulvene, whereas it can undergo ring expansion to afford the cyclohexadienyl cation **L**. In this context, it is interesting to note that fulvene to benzene rearrangement has been observed previously by irradiation[23] or by gas phase pyrolysis.[24] The reaction has been rationalized by invoking a diradical intermediate.[25] Recently Diederich observed a novel thermal pentafulvene to benzene rearrangement in which an anionic "ring-walk" mechanism has been suggested.[26]

To shed some light on the mechanism of the reaction a crossover experiment was conducted between 1,6-bis(*p*-tolyl)-1,5-hexadiene-3,4-dione and 1,6-bis(p-methoxyphenyl)-1,5-hexadiene-3,4-dione and the formation of hybrid products

Table 1. Optimization of Reaction Conditions



entry	catalyst	conditions[a]	time (h)	yield (%)[b]
1	**3a**	DBU (0.5 equiv), THF, 0 °C−rt	12	16
2	**3a**	DBU (0.5 equiv), DMF, rt	5	64
3	**3a**	K_2CO_3 (1 equiv), CH_3CN, rt	24	50
4	**3b**	K_2CO_3 (1 equiv), CH_3CN, 0 °C−rt	24	–
5	**3c**	K_2CO_3 (1 equiv), CH_3CN, 0 °C−rt	24	35
6	**3d**	K_2CO_3 (1 equiv), CH_3CN, 0 °C−rt	24	19
7	**3a**	K_2CO_3 (1 equiv), DCM, 0 °C−rt	24	40
8	**3a**	K_2CO_3 (1 equiv), toluene, 0 °C−rt	24	44
9	**3a**	DBU (0.5 equiv), DCM, 0 °C−rt	10	56
10	**3a**	KOtBu (1 equiv), CH_3CN, rt	20	25
11	**3a**	NaH (2 equiv), CH_3CN, rt	2	69
12	**3a**	K_2CO_3 (1 equiv), hexane, 0 °C−rt	24	16
13	–	K_2CO_3 (1 equiv), CH_3CN, 0 °C−rt	24	–
14	–	DBU (1 equiv), CH_3CN, 0 °C−rt	24	–

[a] Detailed optimization studies are given in the Supporting Information. [b] Overall yield of **a** and **b**.

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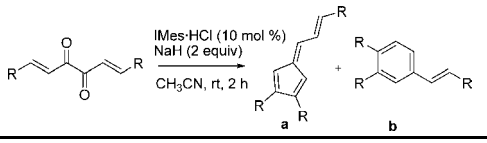
(27) Details of the crossover experiment are given in the Supporting Information.

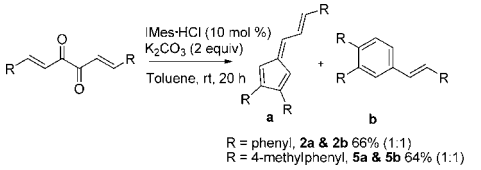
Table 2. Scope of the Reaction



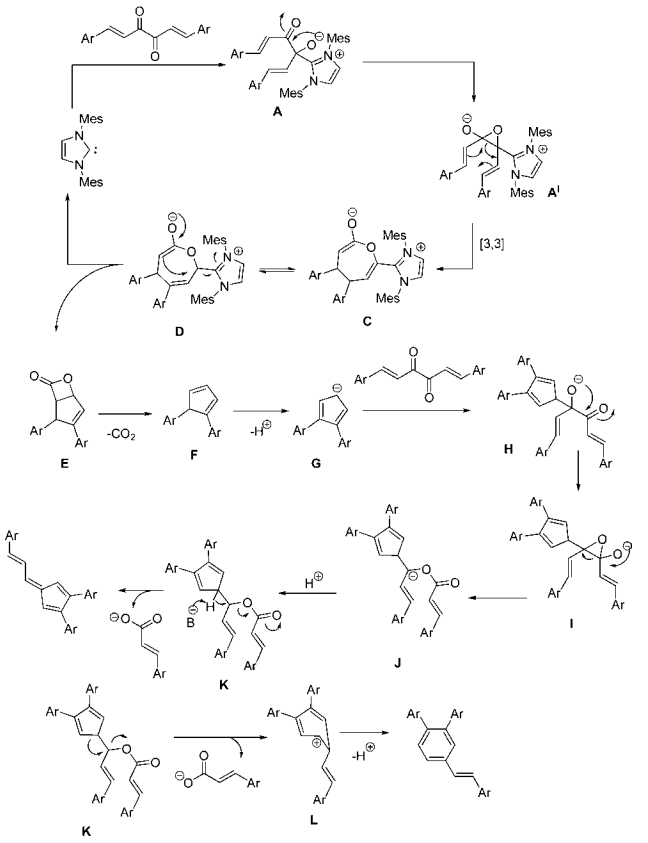
entry	R	products	yield (%)[a,b]
1	phenyl	**2a, 2b**	74(89:11)[c]
2	4-methylphenyl	**5a, 5b**	69(91:09)
3	4-methoxyphenyl	**6a, 6b**	61(87:13)
4	4-bromophenyl	**7a, 7b**	55(91:09)
5	4-chlorophenyl	**8a, 8b**	81(96:04)
6	3-chlorophenyl	**9a, 9b**	40(90:10)
7	4-fluorophenyl	**10a, 10b**	64(94:06)[c]
8	furyl	**11a, 11b**	46(87:13)
9	thienyl	**12a, 12b**	61(90:10)

[a] Isolated yield. [b] Ratio of **a**:**b** is given in brackets. [c] UV−vis spectra are given in the Supporting Information.

Scheme 3. Terphenyl Formation



Scheme 4. Proposed Mechanism



was confirmed by mass spectroscopy.[27] Arguably, these results provide indirect support for the formation of 2,3-diaryl cyclopentadiene and other intermediates invoked in the mechanistic postulate.

As a unique class of trienes, pentafulvenes have evoked great interest from both theoretical and synthetic perspectives.[28,29] In particular, their propensity to undergo multiple modes of cycloadditions has been liberally exploited in synthesis.[30] In contrast, pentafulvenes with multiple substitution and conjugation have not received much attention presumably due to the difficulty in accessing them. It may also be mentioned that *o*-terphenyls are known to have interesting photophysical properties.[31] However, they are obtained by multistep synthesis[32] that cannot be easily adapted to the terphenyl derivatives reported herein.

In conclusion, we have come across an uncommon cascade reaction involving two molecules of 1,2-diones that affords vinyl fulvenes and *o*-terphenyl derivatives. The experimental conditions are simple and the products are obtained in good yields, thus adding preparative value to the reaction. In addition to its synthetic utility, the intriguing mechanistic steps of the process described here are also noteworthy. Further work aimed at exploring the scope and selectivity of the reaction will be undertaken.

Acknowledgment. We thank the Department of Science and Technology (DST) for a Raja Ramanna fellowship for V.N. and the Council of Scientific and Industrial Research (CSIR) and the University Grants Commission (UGC) New Delhi for financial assistance.

Supporting Information Available. General experimental procedure, compound characterization data, and UV−vis spectra of selected compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

The authors declare no competing financial interest.

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